

Mono-, di-, and polynuclear 3d transition metal
ion complexes and coordination polymers with
N,O-donor multidentate and compartmental
ligands and their catalytic applications

A Thesis
Submitted for the Degree of
Doctor of Philosophy
By

ANKIT KUMAR SRIVASTAVA



School of Chemistry
University of Hyderabad
Institution of Eminence
Hyderabad- 500 046
Telangana, India

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Dedicated to
Prof. Alfred Werner

CONTENTS

STATEMENT	i
DECLARATION	ii
CERTIFICATE	iii
ACKNOWLEDGEMENT	vi
CHAPTER 1: Introduction	
PART A: Vanadium chemistry	
1.1. Abstract	1
1.2. Overview	1
1.3. Role of vanadium in biology	3
1.4. Vanadium in catalysis	5
1.5. Vanadium in energy storage devices	6
1.6. Coordination chemistry of vanadium	7
PART B: Polynuclear transition metal ion complexes and coordination polymers	
1.7. Overview	18
1.8. Importance of polynuclear complexes	21
1.9. Background of coordination polymers	25
1.10. Synthesis of coordination polymers	28
1.11. Building blocks of coordination polymers	30
1.12. Importance of coordination polymers	32
1.13. Present investigation	39
1.14. References	41
CHAPTER 2: Unusual pentagonal-bipyramidal oxovanadium(V) complexes having five- and six-membered chelate rings: Syntheses, structures and properties	
2.1. Abstract	57
2.2. Introduction	58
2.3. Experimental	59

2.4.	Results and discussion	67
2.5.	Conclusions	84
2.6.	References	85

CHAPTER 3: Ambidentate coordination of oximate in complexes of VO(OMe)²⁺ and VO₂⁺ cores with biacetylmonoxime salicyloylhydraz-one: Structural confirmation, properties and photocatalytic applications

3.1.	Abstract	89
3.2.	Introduction	90
3.3.	Experimental	92
3.4.	Results and discussion	95
3.5.	Photocatalytic activities	111
3.6.	Conclusions	114
3.7.	References	115

CHAPTER 4: Mixed-valent tetracobalt(II/III) cluster as a bifunctional heterogeneous electrocatalyst for water splitting at neutral pH

4.1.	Abstract	120
4.2.	Introduction	121
4.3.	Experimental	123
4.4.	Results and discussion	134
4.5.	Electrocatalytic oxygen evolution	148
4.6.	Electrocatalytic hydrogen evolution	149
4.7.	Catalytic efficiency	151
4.8.	Stability of the catalyst	154
4.9.	Conclusions	170
4.10.	References	171

CHAPTER 5: A cationic one-dimensional Mn(II)Mn(III) coordination polymer with a macrocyclic compartmental ligand: Structure, properties and catecholase like activity

5.1.	Abstract	177
5.2.	Introduction	178
5.3.	Experimental	180
5.4.	Results and discussion	183
5.5.	Catecholase like activity	196
5.6.	Conclusions	197
5.7.	References	198

CHAPTER 6: One-dimensional Mn(III) and Fe(III) coordination polymers based on mixed ligands: Syntheses, structures, and properties

6.1.	Abstract	202
6.2.	Introduction	203
6.3.	Experimental	204
6.4.	Results and discussion	208
6.5.	Conclusions	216
6.6.	References	217

Appendix	220
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List of publications	234
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Participation in conferences and workshops	237
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Plagiarism report	238
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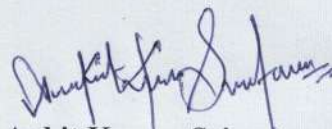
STATEMENT

I hereby declare that the matter embodied in this thesis entitled "*Mono-, di-, and polynuclear 3d transition metal ion complexes and coordination polymers with N,O-donor multidentate and compartmental ligands and their catalytic applications*" is the result of the investigation carried out by me in the School of Chemistry, University of Hyderabad, under the supervision of Prof. Samudranil Pal.

In keeping the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on findings of other's investigations. Any omission which might have occurred by oversight or error is regretted.

University of Hyderabad, India

Date: 28/12/2021



Ankit Kumar Srivastava

DECLARATION

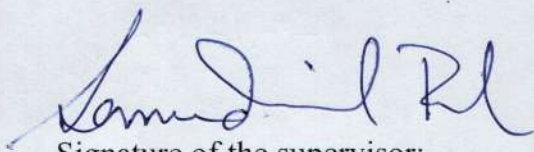
I Ankit kumar Srivastava hereby declare that this thesis entitled "*Mono-, di-, and polynuclear 3d transition metal ion complexes and coordination polymers with N,O-donor multidentate and compartmental ligands and their catalytic applications*" submitted by me under the supervision and guidance of Prof. Samudranil Pal, School of Chemistry, University of Hyderabad is a bonafide research work which is also free from plagiarism. I also declare that it has not been submitted previously in part or full to this University or any other University or Institution for the award of any degree or diploma. I hereby agree that my thesis can be deposited in shodhganga/INFLIBNET.

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CERTIFICATE

This is to certify that the thesis entitled ***“Mono-, di-, and polynuclear 3d transition metal ion complexes and coordination polymers with N,O-donor multidentate and compartmental ligands and their catalytic applications”*** submitted by **Ankit kumar Srivastava** bearing registration number 15CHPH06 in partial fulfillment of the requirements for award of the Doctor of Philosophy (Ph.D.) is a bonafide work carried out by him under my supervision and guidance in the School of Chemistry, University of Hyderabad. This thesis is free from plagiarism and has not been submitted previously in part or in full to this or any other University or Institution for award of any degree or diploma. Further, the student has ten publications before submission of the thesis for adjudication and has produced evidences for the same in the form of reprints.

Parts of this thesis have been published in the following four publications:

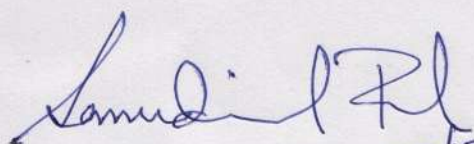
1. [A. K. Srivastava](#), S. Ghosh, S. Jana, S. Pal, *Inorg. Chim. Acta* 483 (2018) 329–336. (Chapter 2)
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He has also made presentations in the following conferences:

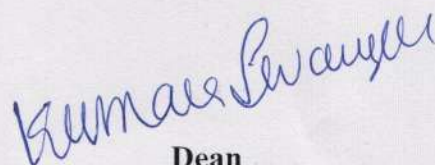
1. Poster presentation in the Symposium on **“Modern Trends in Inorganic Chemistry (MTIC-XVII)”**, 11–14 December, 2017 at IISER Pune.
2. Poster presentation in the **“National Meeting of Synthetic and Theoretical Chemists (NMSTC-2017)”** 13–14 October, 2017 at School of Chemistry, University of Hyderabad,
3. Poster presentation in the **“8th International Collaborative and Cooperative Chemistry Symposium”**, 18–19 December, 2017 at School of Chemistry, University of Hyderabad.
4. Participation and Poster presentation in the **“Indo-French school and conference on the Magnetism of Molecular Systems”** 26–30 November, 2018 at IISC, Bangalore.
5. Poster presentation at **“CHEMFEST-2019”** Annual in-house Symposium of School of Chemistry, University of Hyderabad.
6. Poster presentation in the **“1st International Conference on Crystal Engineering: From Molecule to crystal”**, March 30–31, 2019 at Department of Chemistry, NIT Raipur.
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3.	CY-805	Instrumental Methods-A	3	B/Pass
4.	CY-806	Instrumental Methods-B	3	B ⁺ /Pass


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Part: A

Introduction

1.1. Abstract

Introduction is divided into two parts A and B. In part A, the scope and objectives of the chapters 2 and 3 on vanadium complexes have been discussed in the background of known vanadium chemistry. In part B, the chemistry of polynuclear complexes and coordination polymers of transition metal ions with multidentate and compartmental ligands and the scope and objectives of the chapters 4–6 are discussed.

1.2. Overview

1.2.1. Background of vanadium

There is a very interesting story about the discovery of vanadium. It was not discovered at one time. It was discovered twice. The first time, in 1801 A. M. del Rio, a professor of mineralogy in Mexico city found a specimen of vanadite, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ and sent a sample to Institute de France for inspection and confirmation. However, French chemist H. V. Collet-Descotils refused the new element statement by Del Rio and concluded that the sample was an impure chromium mineral. Del Río agreed with Collet-Descotils' statement and withdrew his claim. After 30 years, it was rediscovered by Swedish chemist N. G. Sefström at Stockholm. He separated it from a sample of cast iron obtained from an ore that had been mined at Småland and named after the Scandinavian goddess of beauty and fertility Vanadis [1].

1.2.2. General properties of vanadium

The element vanadium is a 3d transition metal of atomic no 23 and is assigned with the symbol V which is found in Group V of the Periodic Table. Its ground-state electron configuration is $[\text{Ar}]3d^34s^2$. It is a medium-hard, steel-blue solid having thermally insulating and electrically conductive properties. The elemental form of vanadium hardly exists in nature. It is found in a wide variety of minerals in the earth's crust such as vanadinite, magnetite, patronite, and carnotite. It has a variable oxidation state and forms colorful compounds. Oxidation states of V in its compounds are +5, +4, +3, and +2 having different no of electrons around vanadium atom. Vanadium(II) and vanadium(V) compounds are reducing agents and oxidizing agents, respectively. Vanadium(IV) compounds contain VO^{2+} functional group, which is called as vanadyl or oxovanadium(IV) cation [2].

1.2.3. Importance of vanadium chemistry

Development of the vanadium chemistry began when the value of vanadium for different applications was recognized. The vital roles of vanadium in various biological and chemical systems have motivated the researchers to explore the vanadium chemistry. Recent progress of vanadium chemistry by the vanadium community involves a broad range of topics in the field of synthesis, coordination chemistry, catalysis and biological chemistry. It has versatile chemistry due to its small size and the variability in the oxidation states which support different coordination geometries and spectacular properties. Vanadium is known to participate in a variety of biological processes such as haloperoxidation [3], insulin mimicking [4], and nitrogen fixation [5]. In addition, plenty of vanadium complexes with different ligands have found prominent industrial application as a catalyst for a broad range of organic transformation reactions [6]. Vanadium redox flow batteries (VRFB) are one of the most promising energy storage techniques deemed suitable for effective storage of renewable energy. They have better storage capability compared to Li ion batteries. In addition, with respect to

safety, storage duration and cost, they are expected to be much better than the Li ion batteries [7]. As a result, scientists are very much fascinated to explore the vanadium chemistry for better functional and structural mimics of vanadium based metalloenzymes, much more versatile new catalysts and more effective energy storage devices.

1.3. Role of vanadium in biology

Nature has unfolded a wide range of enzymatic systems involving vanadium, especially in marine environments. They include haloperoxidases, nitrogenases and non-enzymatic amavadin [8] which is a vanadium(IV) complex produced by the mushroom genus *amanita* [9].

1.3.1. Vanadium-based haloperoxidases

Vanadium-based haloperoxidases (V-HPO) are found in fungi, marine macroalgae, lichen and streptomyces bacteria. V-HPO consists of ligated Lewis-acidic V(V) ion as vanadate in their active sites. They utilize the hydrogen peroxide to catalyze the 2-electron oxidation of halide (i.e., chloride, bromide, and iodide) to the corresponding hypohalous acid, HOX (Eqn. 1). Further, HOX combines with a wide range of organic substrates to form different halogenated natural compounds [3d]. Peroxo vanadate complex is the key intermediate for halide oxidation in V-HPO (Fig. 1). In the case of various oxidative reactions, the use of vanadium was primarily inspired by the reactivity of vanadium-dependent natural enzymes, i.e., haloperoxidases (V-HPOs) [3a,b,c,e,f,g].

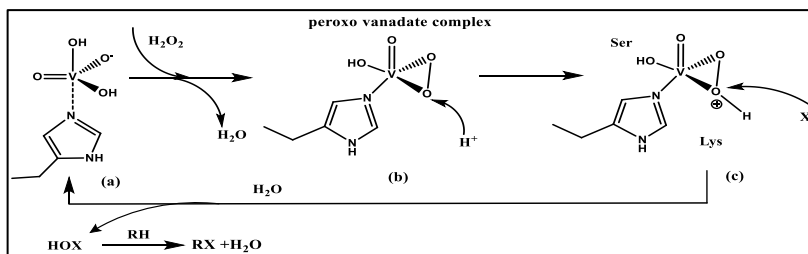
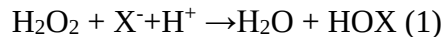


Fig. 1. Proposed catalytic cycle for vanadium-based haloperoxidases.

1.3.2. Vanadium nitrogenase (VNases)

Vanadium nitrogenase (VNases) exists in the nitrogen fixation bacteria of the genus *azotobacter* and in the cyanobacterium *anabaena variabilis*. It catalyzes the atmospheric dinitrogen to ammonia and the overall stoichiometry can be summarized as follows (Eqn. 2).



Binary vanadium(V)-nitrogenase system is comprised of the Fe protein and vanadium iron (VFe) protein. Ferredoxin type $[\text{Fe}_4\text{S}_4]$ clusters are bridged by two Fe protein subunits which serves as an electron donor for the vanadium iron (VFe) protein of vanadium nitrogenase. Additionally, Fe protein holds two binding sites for MgATP. The VFe protein has $\alpha_2\beta_2\delta_4$ subunit structure, and contains two different metal clusters: P-cluster and FeV cofactor. In a possible structure of vanadium site in FeV cofactor, the vanadium is part of a complex iron–sulfur system, attached with the three iron centers and further linked three times by bridging sulfide and also coordinated with a histidine and the vicinal alkoxide along with carboxylate of homocitrate. In the plausible catalytic mechanism, electrons are sequentially transferred from the $[\text{Fe}_4\text{S}_4]$ cluster (of the Fe protein), through the P-cluster, to the catalytic center at the FeV cofactor (of VFe protein), where substrate binding and reduction eventually occur (Fig. 2) [5].

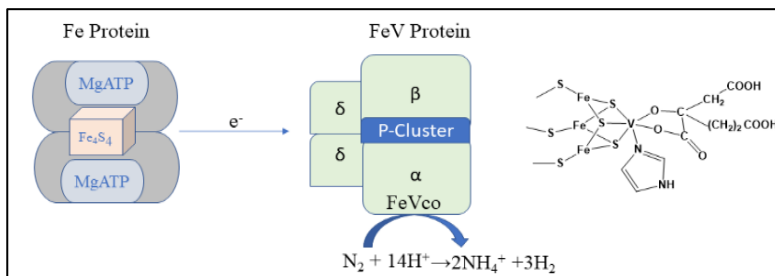


Fig. 2. Schematic representation of the catalytic unit of V-nitrogenase and the possible structure of the V site in the FeV cofactor.

1.3.3. Amavadin

Amavadin is a natural vanadium(IV) complex which is found in 3 species of poisonous amanita mushrooms: *A. regalis*, *A. muscaria*, and *A. velatipes*. In this complex anion $V(S,S\text{-HIDPA})_2]^{2-}$, vanadium(IV) is octa-coordinated and bonded to two fully deprotonated tetradentate N-hydroxyimino-2,2'-dipropionic acid, $H_3(HIDPA)$ (Fig. 3) [8].

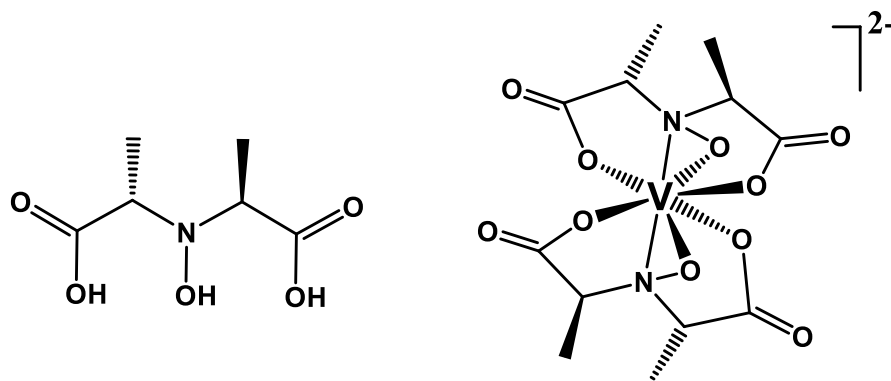


Fig. 3. Ligand precursor found in amavadin (left) and molecular structures of the amavadin complex (right).

1.4. Vanadium in catalysis

Coordination complexes of vanadium with a wide range of ligands have found significant applications as catalysts in a variety of organic transformation reactions [6]. In addition, a large number of oxovanadium(V) (VO^{3+}) and dioxovanadium(V) (VO_2^+) complexes have been also found to be very useful as catalysts in various oxidation reactions of different substrates in presence of peroxides [10]. Vanadium-catalyzed reactions involve a variety of chemical processes such as contact process for the industrial production of sulfuric acid [11], oxidations of alcohols, aldehydes, ketones, alkanes, alkenes, arenes, and sulfur species, as well as oxidative C–O and C–C bond cleavage, olefin epoxidation, carbon-carbon bond formation, cyanation, deoxydehydration,

dehydrogenation, hydrogenation, oxo/imido heterometathesis and ring-opening metathesis polymerization [12], and in the reduction of sulphur and nitrogen oxide emissions resulting from human activities [13]. They are active catalysts under heterogeneous or homogeneous conditions. Numerous VO_x based organic–inorganic nanocomposites have potential photocatalytic properties [14]. Dioxygen activation by biomimetic vanadium complexes and vanadate dependent haloperoxidases, amavadin and vanadium nitrogenase exemplify the significant role of biologically relevant catalytic functions of vanadium compounds [9]. The relevance of vanadate-dependent enzymes in a variety of biological catalytic processes motivated numerous researchers to continue the research on vanadium-based catalysis and develop more efficient catalysts for various organic transformation reactions [15].

1.5. Vanadium in energy storage devices

Energy storage devices such as batteries are gaining increasing importance due to the dramatic increase of personal digital devices such as mobile phones, laptops, iPad, renewable energy technologies and electric vehicles [16]. Vanadium batteries are a type of redox battery also known as vanadium redox batteries, which is cost effective, safer and have longer storage duration compared to lithium-ion batteries. Abundance of vanadium is also more than lithium in the earth crust. Vanadium can form ions of four different valence states (V^{2+} , V^{3+} , V^{4+} , and V^{5+}) which is the prime requirement of an electrolyte in the redox flow batteries. Vanadium redox batteries use the redox couple $\text{V}^{4+}/\text{V}^{5+}$ in the positive half-cell electrolyte, whereas $\text{V}^{2+}/\text{V}^{3+}$ couple is used in the negative half-cell electrolyte. These are stored in a mild sulfuric acid solution. hydrogen-ion permeable polymer membrane allows the exchange of the H^+ ions between two electrolyte tanks during the charge/discharge cycles. The reactions are expressed here in a simple way, $\text{V}^{3+} + \text{e}^- \rightleftharpoons \text{V}^{2+}$ at the negative electrode while at the same

time $V^{4+} \rightleftharpoons V^{5+} + e^-$ at the positive electrode during the charging cycle and energy is stored as chemical energy in the cell. This process is reversed during discharging cycle and stored chemical energy is converted into electrical energy [7]. In the case of lithium-ion batteries where every time lithium charges and discharges, it is plating and deplating lithium metal on the cathode. Their performances decrease due to degradation after few thousand such cycles [17].

1.6. Coordination chemistry of vanadium

Vanadium is a transition metal with a broad range of oxidation state (-1 to +5) and it can adopt a variety of coordination geometries and coordination numbers. In general, bis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2]$ [18] has been used as a common precursor to synthesize vanadium complexes with a variety of organic ligands. Here, $[VO(acac)_2]$ undergoes ligand exchange reaction by replacing one or both $acac^-$ ligands. Generally, oxovanadium(IV) complexes are formed when ligands react with $[VO(acac)_2]$ in inert condition, but under aerobic condition vanadium gets oxidized and vanadium(V) complexes are isolated [19]. In these oxidized complexes, vanadium exists as $[VO]^{3+}$, $[VO_2]^+$ or $[V_2O_3]^{4+}$ cores. Ligand to metal ion precursor ratio, number and strength of donor atoms in the ligand, steric as well as electronic properties of the ligands decide the replacement of one or both $acac^-$ groups leading to the formation of the new complex [20]. The VO^{2+} , is classified as a hard acid and thus the vanadium most effectively binds hard bases like O and N donor organic ligands relative to soft bases such as S donor ligands. For the same reason, very few structurally characterized complexes of oxovanadium(V) moieties (VO^{3+} , VO_2^+ and $V_2O_3^{4+/3+}$) with sulfur coordinating ligands are known [21]. Nature of the final complexes and their stoichiometry are influenced by several factors such as solvents, nature of ligands, pH of the reaction medium etc.

1.6.1. Complexes with bidentate ligands

Generally, monomeric $[V^{IV}OL_2]$ type complexes are produced when a bidentate ligand reacts with $[VO(acac)_2]$ under anaerobic condition. For example, reaction of monobasic bidentate ligand 2-(2'-hydroxyphenyl)benzoxazole (HL) and $[VO(acac)_2]$ leads to the formation of $[V^{IV}OL_2]$ [22]. Another example, where dibasic bidentate ligand 2-(salicylideneamine)-1-hydroxyethane ($H_2sal-EA$) reacted with $[VO(acac)_2]$ in 2:1 molar ratio and formed $[VO(Hsal-EA)_2]$ (Fig. 4) [23]. In the structure of the latter complex azomethine-N and phenolate-O coordinate to the vanadium while alcoholic group remains free. Similarly, 2(α -hydroxyalkyl/aryl)benzimidazole (HL) reacted with $[VO(acac)_2]$ and formed $[VOL_2]$ type complex. But in the presence of KOH under aerobic condition it slowly oxidizes to a dioxovanadium(V) species. Addition of KOH enhances the rate of oxidation and stabilizes the dioxovanadium(V) complexes such as $K[VO_2L_2] \cdot 2H_2O$ (Fig. 4) [24]. 8-Hydroxyquinoline (HL) reacts with $[VO(acac)_2]$ in acetone under aerobic condition to yield the μ -oxo complex $[(VOL_2)_2(\mu-O)]$ [25].

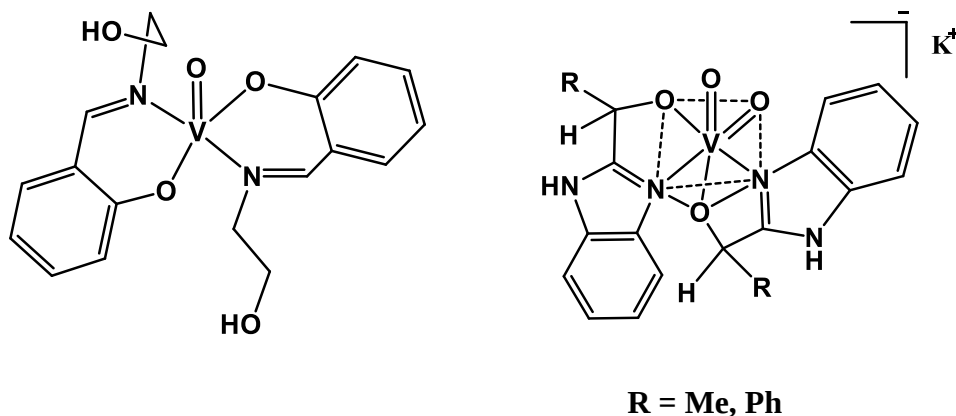


Fig. 4. Molecular structures of $[VO(Hsal-EA)_2]$ (left) and $K[VO_2L_2] \cdot 2H_2O$ (right).

1.6.2. Complexes with tridentate ligands

Under anaerobic condition, [VOL] type of oxovanadium(IV) complexes are produced with various dibasic tridentate ligands (Fig. 5). Generally, these types of complexes of formula $[(V^V OL)_2(\mu-O)]$ stabilize through dimerization where two [VOL] units are bridged through one of the oxygen atoms of each ligand and an oxo group (Fig. 6) [23,26].

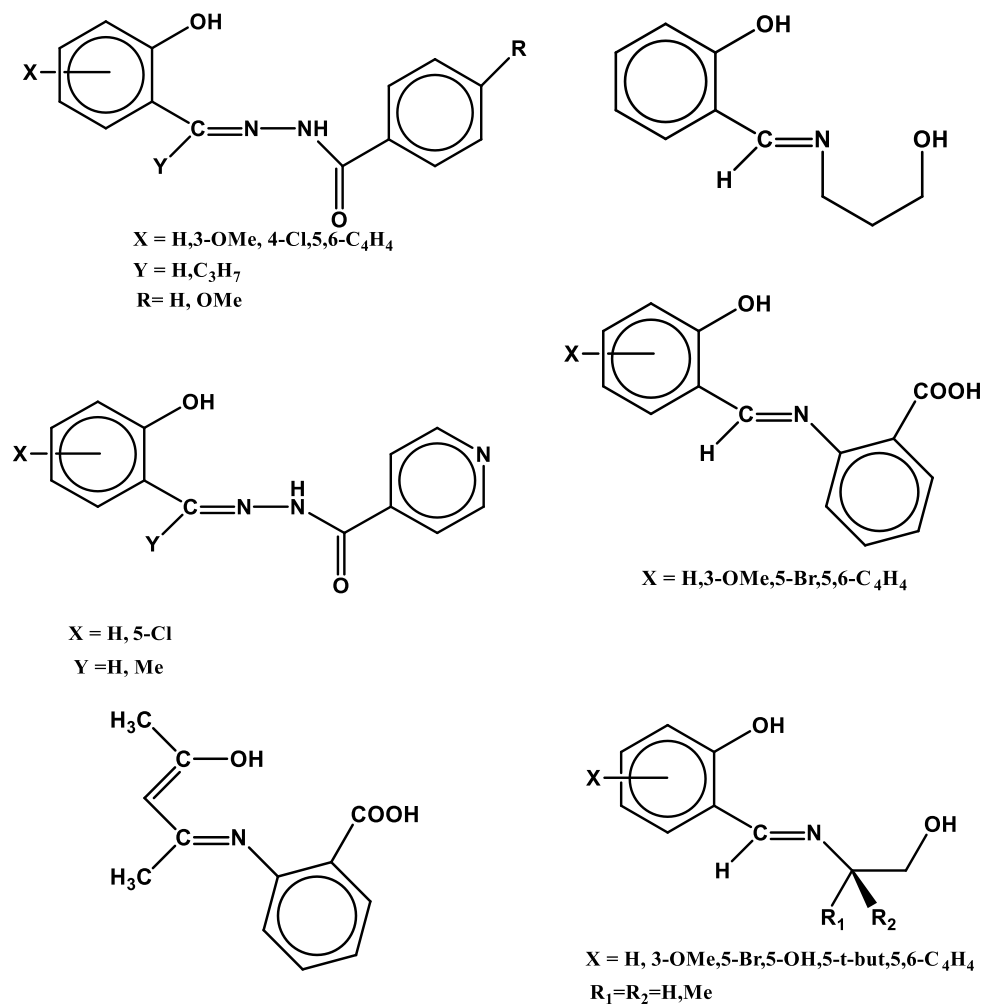


Fig. 5. Examples of tridentate O,N,O-donor ligands.

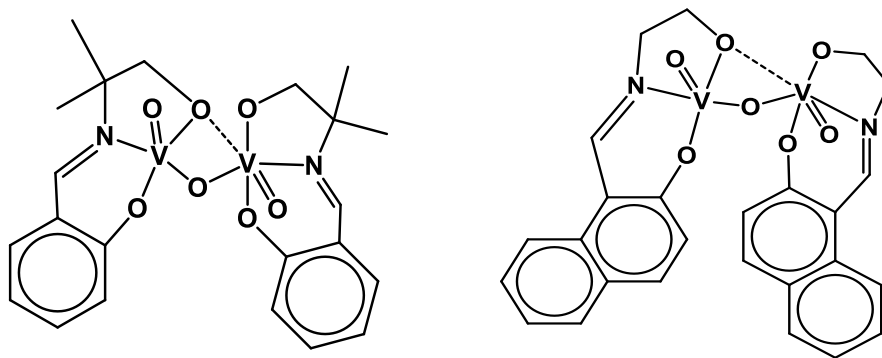


Fig. 6. Molecular structures of $[(VO(\mu-L))_2(\mu-O)]$ type complexes.

Very often oxovanadium(IV) complexes are oxidized to $[(V^V OL)_2(\mu-O)]$ species in solvents under aerobic condition [23,27]. Sometimes, complexes having the $[(VO)_2(\mu-O)]^{4+}$ core have been formed directly from non-protic media. Such kind of complexes are shown in Fig. 7 [28,29].

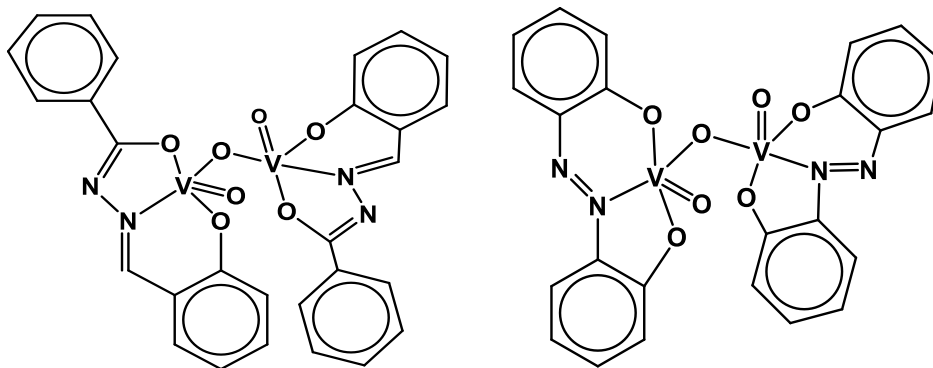


Fig. 7. Examples of $[(V^V OL)_2(\mu-O)]$ type complexes.

In general, oxovanadium complexes containing the $\{VO(OMe)\}^{2+}$ core are synthesized with tridentate ligands in methanolic medium [30]. Selected examples are shown in Fig. 8. In these examples, deprotonated benzoylhydrazones of 2-hydroxy-5-methoxy-benzaldehyde ($H_2bhsOMe$) and 2-hydroxy-5-chloroBenzaldehyde(H_2bhsCl) were used as ligands.

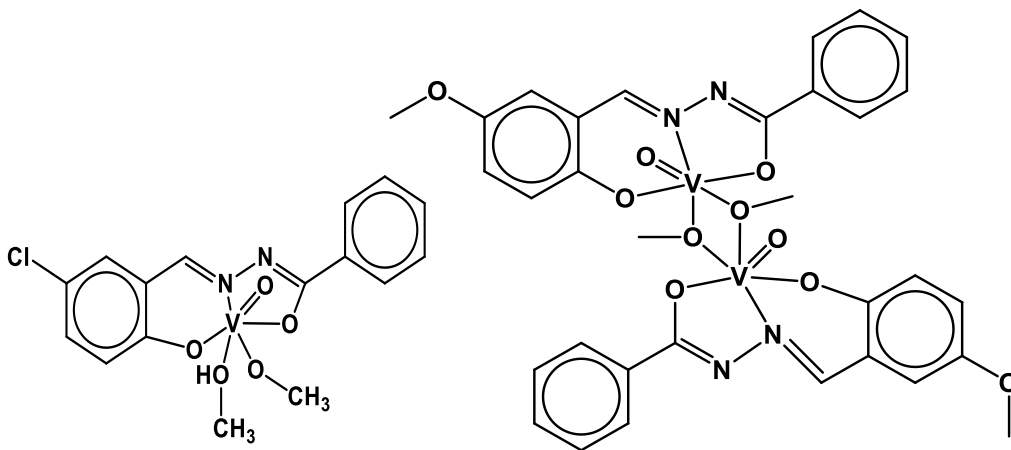


Fig. 8. Mononuclear complex $[\text{VO}(\text{bhsCl})(\text{OMe})(\text{HOMe})]$ (left) and a dinuclear species $[\text{VO}(\text{bhsOMe})(\text{OMe})]_2$ (right).

The N,N,O-donor ligands such as monoanionic deprotonated N-(4-R-aryl)-N'-(picolinylidene)hydrazines (HL) are found to be very efficient in stabilizing the pervanadyl VO_2^+ unit. In this case, under aerobic conditions, in acetonitrile medium, one equivalent of $[\text{VO}(\text{acac})_2]$ reacted with one equivalent of HL and mononuclear pervanadyl (VO_2^+) complexes having the general formula $[\text{VO}_2\text{L}]$ were isolated (Fig. 9)[31].

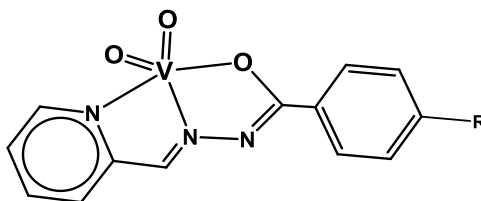


Fig. 9. Molecular structure of $[\text{VO}_2(\text{paph})]$ ($\text{R}=\text{H}$)

Another example where an analogous ligand, N-(anisoyl)-N'-(picolinylidene)-hydrazine (Hpic-anh) combined with $[\text{VO}(\text{acac})_2]$ in acetonitrile under aerobic conditions and formed dimeric pervanadyl (VO_2^+) complex, $[\text{VO}_2(\text{pic-anh})]_2$. There is a distinct tendency towards dimerization which led to $[\text{VO}(\mu\text{-O})\text{L}]_2$ with an octahedral arrangement around each metal center as shown in Fig.10 [32].

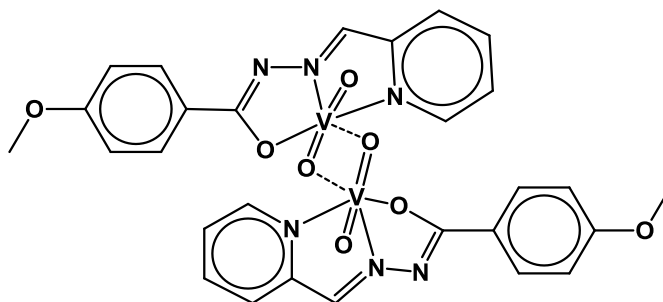


Fig. 10. Example of dimeric complex having monobasic tridentate ligand.

$[\text{VO}(\text{acac})_2]$ and O,N,N-donor ligand such as (Hacpy-inh) in equimolar amounts in dry, refluxing methanol produced oxovanadium(IV) complex $[\text{VO}(\text{acpy-inh})(\text{acac})]$. Aerial oxidation of the complex in presence of a few drops of water in methanol provides the corresponding $[\text{VO}_2\text{L}]$ type mononuclear dioxovanadium(V) complexes $[\text{VO}_2(\text{acpy-inh})]$. Treatment of $[\text{VO}(\text{acpy-inh})(\text{acac})]$ with excess of 30% H_2O_2 yields the peroxo complex $[\text{VO}(\text{O}_2)\text{L}]$ (Fig. 11). [33].

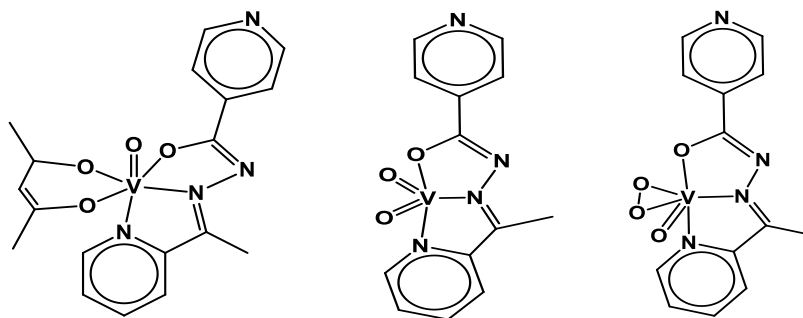


Fig. 11. Structures of $[\text{VOL}]$ (left), $[\text{VO}_2\text{L}]$ (middle) and $[\text{VO}(\text{O}_2)\text{L}]$ (right).

N,N,S donor ligands (HL) are derived from 2-acetylpyridine and S-benzylthiocarbamate (Hacpy-sbdt, I) or S-methylthiocarbamate (Hacpy-smdt, II). When equimolar amount of HL (I or II) and $[\text{VO}(\text{acac})_2]$ are reacted in dry methanolic solution under anaerobic condition oxovanadium(IV) complexes $[\text{VO}(\text{acac})\text{L}]$ are produced. Pentacoordinated dioxovanadium(V) complexes $[\text{VO}_2\text{L}]$ were isolated by reacting ligands HL (I or II) with $[\text{VO}(\text{acac})_2]$ in presence of air and KOH in methanol. $[\text{VO}(\text{O}_2)\text{L}]$, oxo-(peroxo)vanadium(V)

complexes are derived by oxidation of $[\text{VO}(\text{acac})\text{L}]$ in presence of the strong oxidant H_2O_2 . Malonato(oxo)vanadium(V) complex $[\text{VO}(\text{malonate})(\text{acpy-smdt})]$ has been synthesized by addition of a few drops of water to a methanol solution of $[\text{VO}(\text{acac})_2]$, KOH and Hacpy-smdt under aerobic condition [34]. These complexes are shown in the following figure.

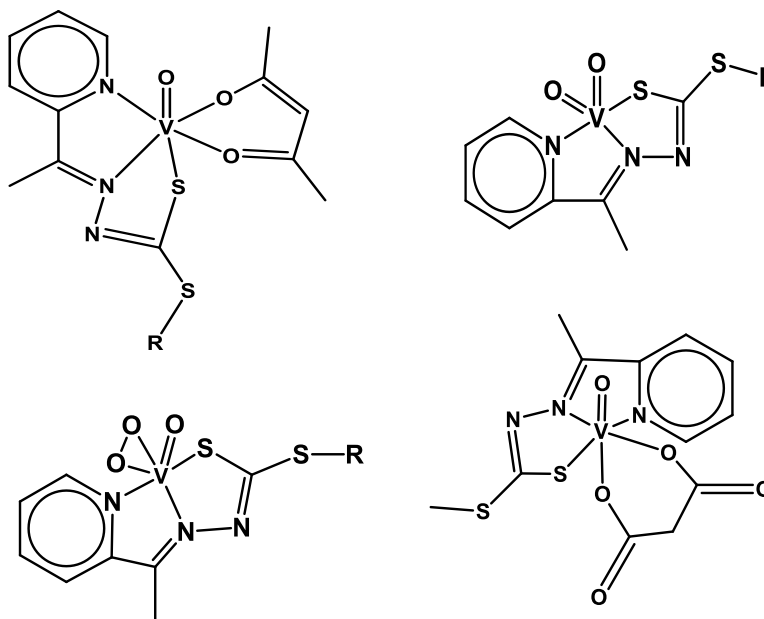


Fig. 12. Oxovanadium(IV), dioxovanadium(V) and oxo-(peroxo)vanadium(V) complexes with N,N,S-donor ligands.

1.6.3. Mixed-valent complexes

A novel mixed-valence (μ -oxo)divanadium(IV,V) complex $(\text{BzimH})[(\text{LVO})_2(\mu\text{-O})]$ was synthesized by using the mononuclear oxovanadium complexes $[\text{V}^{\text{V}}\text{OL}(\text{OEt})]$ and $[\text{V}^{\text{IV}}\text{OL}(\text{Bzim})]$ of the tridentate ONS-donor ligand S-methyl 3-((2-hydroxyphenyl)methyl)dithiocarbazate (H_2L) (Fig. 13). The X-ray crystal structure of the complex reveals an oxo-bridged dinuclear oxovanadium(IV/V) monoanion and protonated benzimidazole (BzimH) as cation [35].

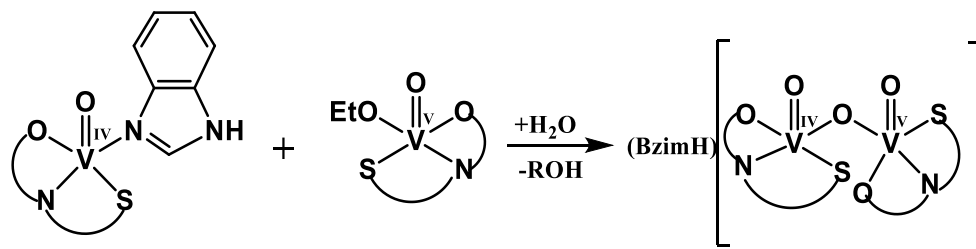


Fig. 13. Reaction scheme for the synthesis of (BzimH)[(LVO)₂(μ-O)] complex.

Nishizawa et. al reported a mixed-valence binuclear oxovanadium(IV/V) complex [VO(nta)-O-VO(nta)]³⁻ (nta = nitrilotriacetate) [36]. The structure of the complex is shown below (Fig. 14).

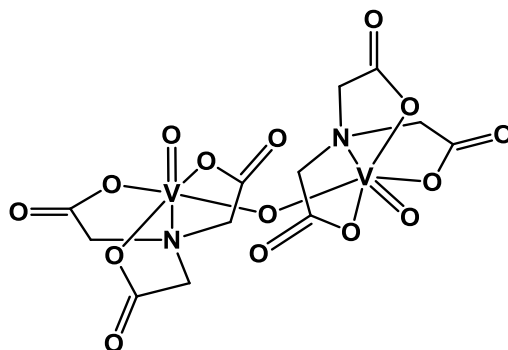


Fig. 14. Molecular structure of [VO(nta)-O-VO(nta)]³⁻.

1.6.4. Complexes with tetradentate ligands

The reaction of [VO(acac)₂] with a tetradentate ligand, N-(2-pyridylmethyl)iminodiacetic acid (H₂pmida) in acetonitrile produced a hexa-coordinated vanadium(IV) complex of formula [VO(pmida)H₂O] (Fig. 15) [37]. Other tetradentate ligands like H₂salen = N,N'-ethylenebis(salicylideneamine) leads to [VO(salen)] and related complexes [38]. A broad range of complexes were obtained depending on the nature of solvent, pH and aerobic/anaerobic reaction conditions [39].

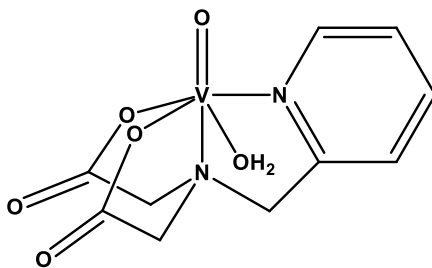


Fig. 15. Molecular structure of $[\text{VO}(\text{pmida})\text{H}_2\text{O}]$.

Few other complexes containing vanadium amide bond are reported with some tetradentate ligands. These amides containing tetradentate ligands are shown in Fig. 16. Reactions of $[\text{VO}(\text{acac})_2]$ with H_2pycac [40], H_4hybeb , H_3hypyb and H_2phepca [41] in presence of base produced these complexes. The base facilitates the deprotonation of the amide nitrogen and its coordination to vanadium [40,41].

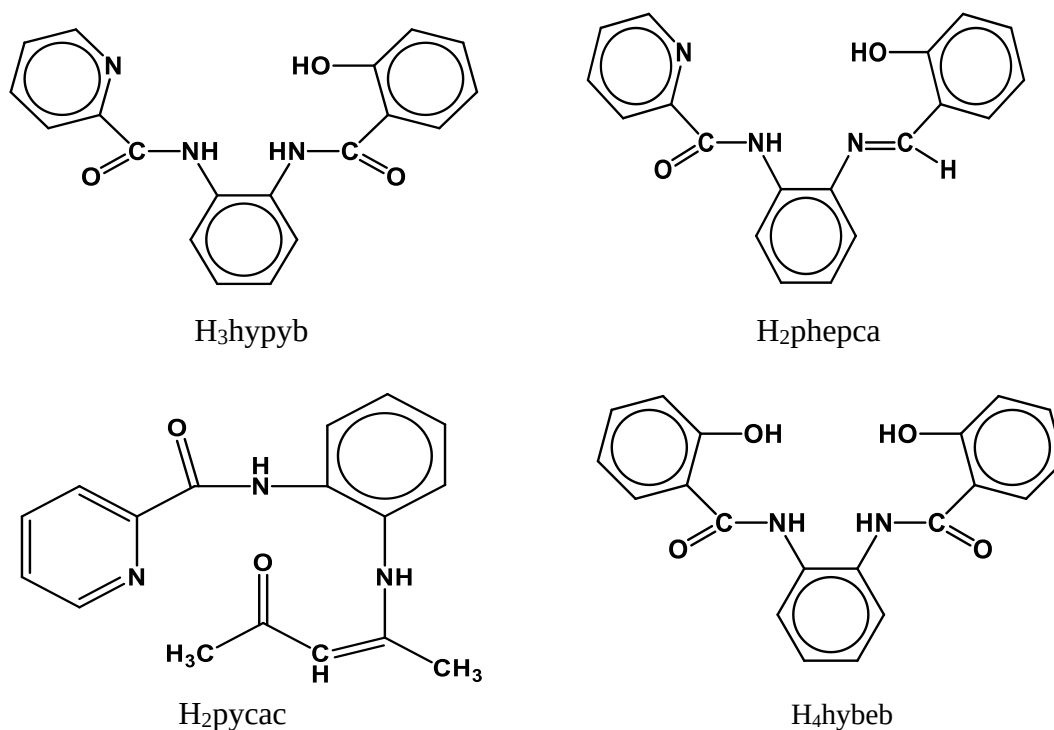


Fig. 16. Amide containing tetradentate ligands.

The tribasic tetradentate ligands (H_4L) generally produce various $[VOL]_2$ type dinuclear oxovanadium(V) complexes under aerobic conditions (Fig. 17) [42]. X-ray structures reveal that one of the CH_2OH groups of each ligand remains uncoordinated in both complexes. In first complex ($X = OMe$), two vanadium atoms are bridged through two alkoxo group of the two ligands and another alkoxo group of each ligand is coordinated to other vanadium and vice versa. In the second complex ($X = H$), the ligand is in reduced form. Here also two alkoxo groups of the two ligands bridge in a similar way as in the first complex but the other alkoxo group of each ligand is coordinated to the same metal.

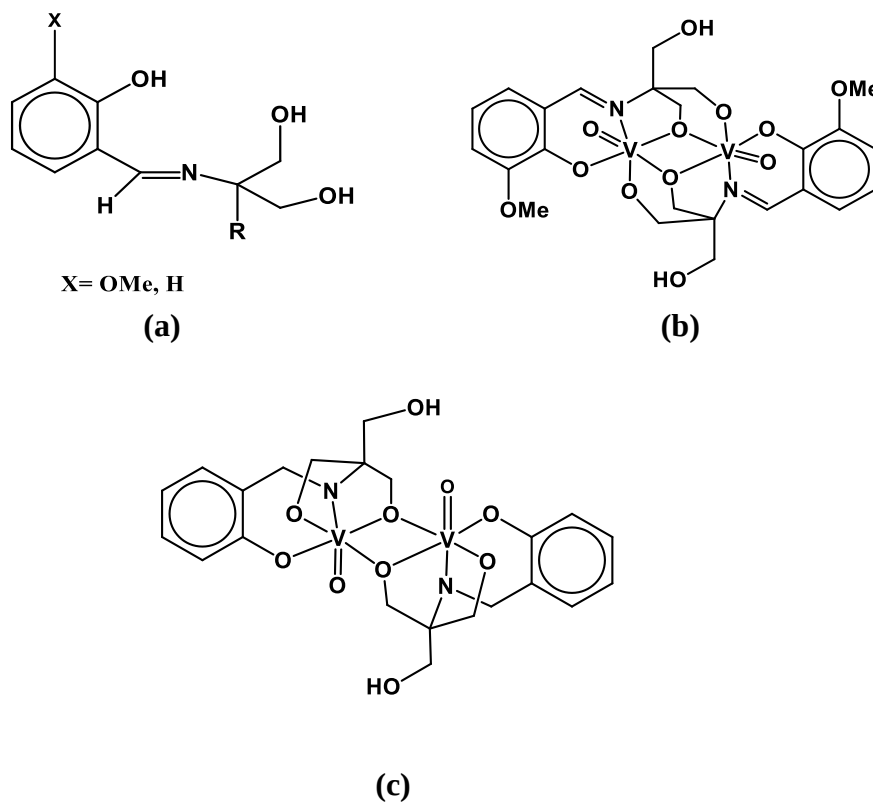


Fig. 17. (a) Tribasic tetradentate ligand system (H_4L) and (b) its oxovanadium(V) complex and (c) the analogous complex with the reduced unsubstituted form of the ligand.

Similar to the $[\text{VO}(\text{salen})]$ type complex, K.S. Murray group have reported a $[\text{V}^{\text{IV}}\text{O}(\text{tsalen})]$ complex with a SNNS-donor ligand where tsalen is N,N'-ethylenebis(thiosalicylideneaminate) (Fig. 18). This complex was synthesized by reacting 2-mercaptobenzaldehyde (tsal), ethylenediamine and $[\text{VO}(\text{acac})_2]$ in 2-methoxyethanol [43].

Anthony W. Addison group synthesized the first oxovanadium(V) thiolate complex, $[\text{VO}\{\text{N}(\text{CH}_2\text{CH}_2\text{S})_3\}]$ (Fig. 18). It was prepared by reacting $[\text{VO}(\text{acac})_2]$ with the thio ligand [44]. X-ray structure reveals a slightly distorted trigonal bipyramidal coordination geometry around the metal center where the three S-atoms occupy the equatorial positions.

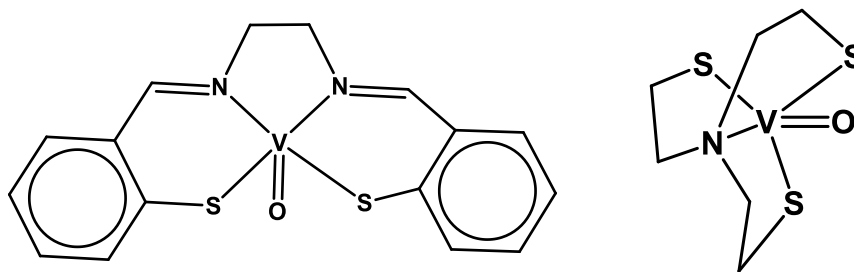


Fig. 18. Mononuclear oxovanadium(IV) complex of NNSS-donor ligand (left) and molecular structure of $[\text{VO}\{\text{N}(\text{CH}_2\text{CH}_2\text{S})_3\}]$ (right).

Part: B

1.7. Overview

1.7.1. Ligands used for polynuclear complexes and coordination clusters

Various types of polydentate ligands have been prepared and successfully used to synthesize polynuclear complexes. These polydentate ligands contain more than two donor atoms and they are excellent hosts of multiple metal ions [45]. A decade ago, Robson started a series of studies concerned with a rational synthetic approach to polynuclear complexes. He initiated the concept of a macrocyclic dinucleating ligand that can bind two metal ions in close proximity [46]. The area of binuclear complexation has seen extensive growth, stimulated by interest with important implications in catalysis, magnetochemistry, and bioinorganic chemistry [47]. Generally, compartmental ligands are used to synthesize these multinuclear complexes. They can bind two or more metal ions in close proximity using two or more identical or different compartments. Similar or different metals inside the compartments are known as homo- and hetero-nuclear, respectively [48]. These ligand systems are generally Schiff bases formed by the condensation of aldehyde or ketone and primary amine precursors under specific conditions. In the recent past, a large variety of macrocyclic [1+1], [2+2], [3+3], [4+4] and acyclic [1+2], [2+1] Schiff bases have been successfully prepared (Fig. 19). Acyclic compartmental systems are classified into two categories: acyclic end off and acyclic side off. Ring sizes can vary based on the shape of the formyl- and the amine precursors and the metal ions during the cyclization reactions [49].

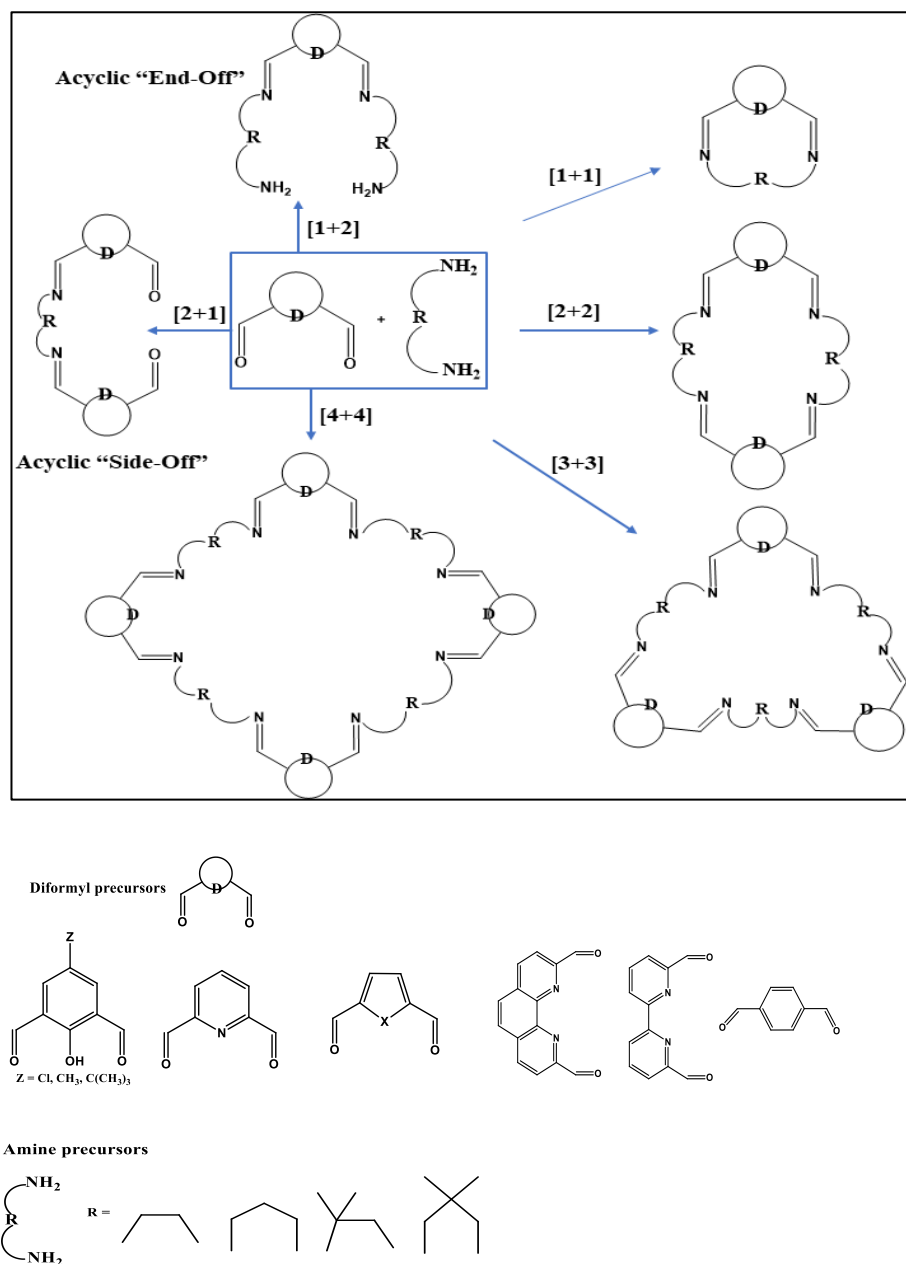


Fig. 19. Various precursors and the macrocyclic [1+1], [2+2], [3+3], [4+4] and acyclic [1+2], [2+1] compartmental ligands.

Among many different polydentate ligands, the phenol-based systems are more popular for synthesizing the polynuclear transition metal complex (Fig. 20). This is due to their multiple electronic and structural characteristics like (i) capability to bind two metal centers in close proximity, (ii) tunability of the phenolate-O basicity by varying the substituents at the para position and (iii) the benzene ring that allows synthetic flexibility via the side arms [50].

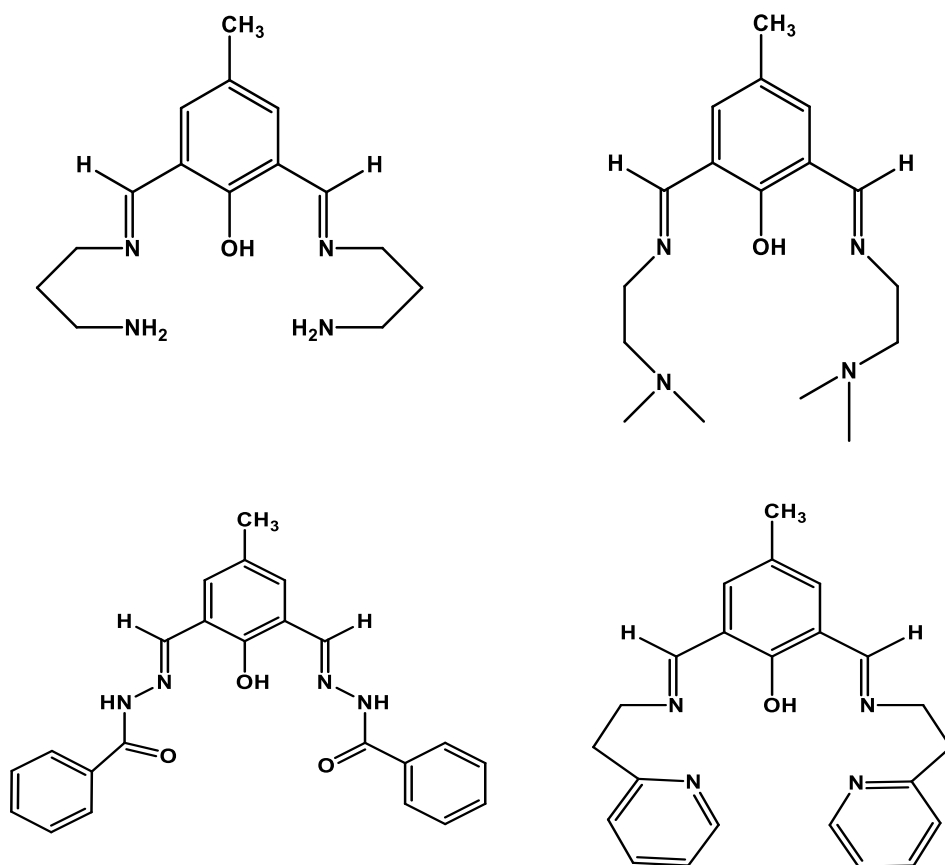


Fig. 20. Common acyclic compartmental ligands used to synthesize polynuclear complexes.

1.8. Importance of polynuclear complexes

The coordination chemistry of polynuclear transition metal complexes assembled from cyclic and acyclic compartmental ligands has received considerable attention due to their potential applications in biological systems, catalysis, magnetism, material science, and photochemistry [51]. Their versatile applications arise from their physical properties which come from their molecular architectures. Synthesis of such clusters is either by serendipity or self-assembly [52]. The nuclearity and topology of the final structure of the coordination clusters depend on the types of polydentate ligands (cyclic or acyclic) and the nature of the ancillary bridging ligands such as hydroxide, oxide, halide, alkoxide, and carboxylate [51a,b].

1.8.1. Polynuclear complexes as a single molecular magnet (SMM)

Single-molecule magnets (SMMs) or molecular nanomagnets are attractive candidates for the application in high-density information storage., quantum computation and spin-based devices (spintronics) [53]. SMMs are discrete polynuclear complexes that contain the magnetic core (exchanged coupled core) surrounded by organic entities, which prevent the core from interacting with the neighbour spins by reducing the intermolecular interactions. The magnetic moment of the molecule primarily depends on the magnetic core. These materials become magnetized upon introducing an external magnetic field and retain their magnetization even after removing the magnetic field for a significant period. These molecules show magnetic hysteresis below a specific temperature known as blocking temperature. Magnetic anisotropy is an important parameter to be understood while studying SMMs. It depends upon zero-field splitting and spin-orbit coupling [54]. Explosive growth in research on molecular magnetic materials in the last two decades has been started with the discovery of a Mn-based coordination cluster having the formula $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]$ (Mn_{12}Ac) in 1980 by Lis [55]. This cluster has been termed as a Single Molecular Magnet

(SMM) in 1993 by Roberta Sessoli and co-workers [56]. This type of molecules comprised of multiple transition metals display slow relaxation of magnetization at low temperatures. After the discovery of $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]$ (Mn_{12}Ac), several efforts have been devoted to synthesize similar coordination clusters with multiple 3d metal ions to acquire maximum energy barriers for slow relaxation of magnetization. $[\text{Fe}_8(\text{tacn})_6\text{O}_2(\text{OH})_{12}]^{8+}$, {where tacn = 1,4,7-triaza cyclononane}, was reported by Wieghardt and co-workers in 1984 [57]. This complex was found to display SMM property. Later, numerous SMMs based on multiple 3d transition metals with polynucleating ligands have been studied extensively [58]. Researchers tried to combine the 3d and 4f metals to improve the performance of SMMs in terms of ground spin states and magnetic anisotropy, responsible for a large energy barrier for slow relaxation of magnetization [59]. In 1996, Jean-Pierre Costes and co-workers reported the first heterometallic 3d-4f coordination cluster having the formula $[\text{LCuGd}(\text{NO}_3)_3]$, {where L is 1,2'-bis((3-methoxysalicylidene)diamino)-2-methylpropane which shows the SMM feature [60]. After this, various heterometallic 3d-4f coordination clusters with different polydentate ligands were synthesized and investigated for SMM property [61]. Despite many efforts, SMMs remain only accessible at a very low (liquid-helium) temperature range. Substantial attempts to synthesize new clusters are still required to increase the blocking temperature and effective energy barrier for practical use [62]. Recently, a new class of nanomagnets named single-chain magnets (SCMs) was reported [63]. The motivation for constructing these nanomagnets is to increase the blocking temperature and effective energy barrier that fulfil the condition for effective application as high-density information storage memory devices. These challenges make this field always active to find new nanomagnets with exceptional magnetic behaviour for practical use.

1.8.2. Polynuclear complexes as catalysts

Application of various polynuclear complexes of transition metals in catalysis and the presence of multimetallic active sites in a variety of enzymes inspired several research groups to develop new and effective bio-mimicking catalysts [64]. Over the past decades, considerable research efforts have been devoted to synthesize homogenous and heterogeneous catalysts to mimic the well-known water oxidation process in photosystem II (PSII) [65]. In natural photosynthesis, the oxygen-evolving complex (OEC) oxidizes water to molecular oxygen on its embedded active site that is a manganese–calcium cluster. Nature's water oxidizing catalyst is a cubane like represents a penta-oxygen tetramanganese–calcium cofactor which is bound in the PS II protein (Fig. 21) [65b,66].

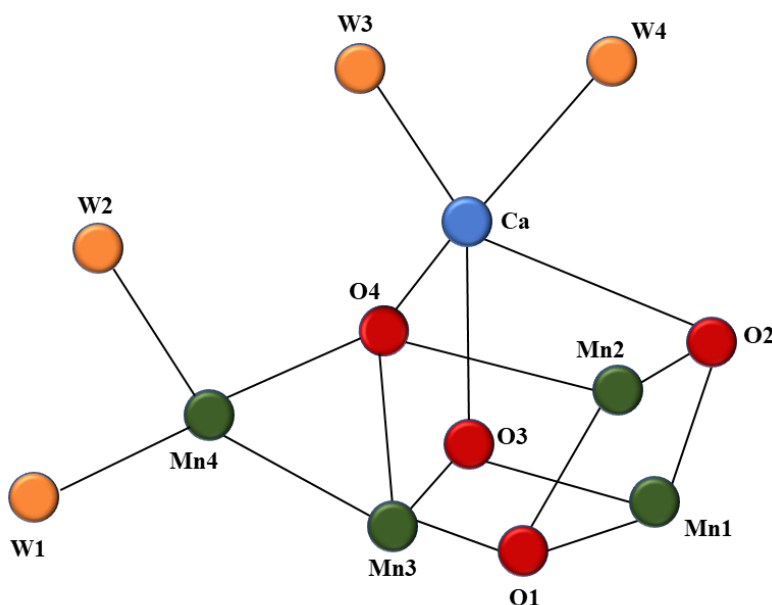


Fig. 21. Oxygen-evolving complex of photosystem II, the site of catalytic water oxidation.

One of the major concerns in the current scenario is having clean and green energy sources. Hydrogen has gained immense attention as an alternative source for fossil fuels with zero emission of carbon dioxide. It is a well-known environment-friendly and renewable source of energy [67]. To achieve this, there are different methods [68]. Among them electrochemical water splitting can be considered the most widely accepted and relatively easy method for producing pure hydrogen gas at a large scale. Water splitting is two half-reactions: water oxidation or oxygen evolution reaction (OER) represented as $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ and hydrogen evolution reaction, i.e., $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (HER). Both OER and HER require high overpotentials due to sluggish reaction kinetics. The tricky part is to design stable, efficient, and cost-effective electrocatalyst for both the half-reactions [69]. A considerable amount of work has been done applying several mono- and polynuclear complexes as molecular catalysts for OER and HER [65,70]. Among these complexes, the Co_4O_4 cubane core containing OER catalysts inspired by the OEC in PS II is of particular interest [71]. O_2 and H_2 evolution via water splitting can occur in acidic, neutral, and alkaline mediums. The corresponding equations are given below:

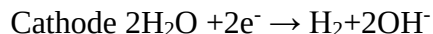
Total reaction



In acidic solution



In alkaline and neutral solutions



1.9. Background of coordination polymers (CPs)

In Greek, the polymer term means ‘many part.’ Polymers are giant molecules or macromolecules composed of a combination of small molecules named ‘monomers’ linked with covalent bonds [72]. In comparison, coordination polymer is a coordination compound having metal cation centers connected by organic ligands with repeating coordination entities extending to one, two, or three dimensions via coordination bonds [73]. In a simple word, it is a polymer whose monomeric units are coordination complexes which are linked to another one by a bridging organic ligand. In 1964, J.C.J. Bailar used the “Coordination Polymer” term for the first time when he compared infinite linear inorganic chain compounds with organic polymers and considered them a polymeric species [74]. Coordination polymers (CPs) which are porous are also known as metal-organic frameworks (MOFs) [75]. In the eighteenth century, German chemists accidentally discovered Prussian blue dye, the first member of CPs [76]. In 1936, crystallographic studies revealed the 3-D polymeric nature of Prussian blue dye, having the formula $\{[\text{Fe}^{\text{III}}_4\text{Fe}^{\text{II}}_3(\text{CN})_{18}] \cdot 11\text{H}_2\text{O}\}_n$. In this polymeric structure, the cyanide ions are bridged by alternating Fe^{3+} and Fe^{2+} [77]. Formation of a CP or MOF from the individual components in solution generally follows the following steps (Fig. 22). The building blocks interact through coordination bonds and weaker forces such as π - π stacking, van der Waals forces or hydrogen bonds giving some small units, followed by self-assembly of these small units to the final CP or MOF [78]. Robson and coworkers had initiated this field by their work in the early 1990s [79]. Later, Kitagawa and coworkers [80] and Yaghi and coworkers [81], demonstrated that it is possible to adapt the idea put forward by Robson to synthesize an extensive library of compounds with specific structural topologies.

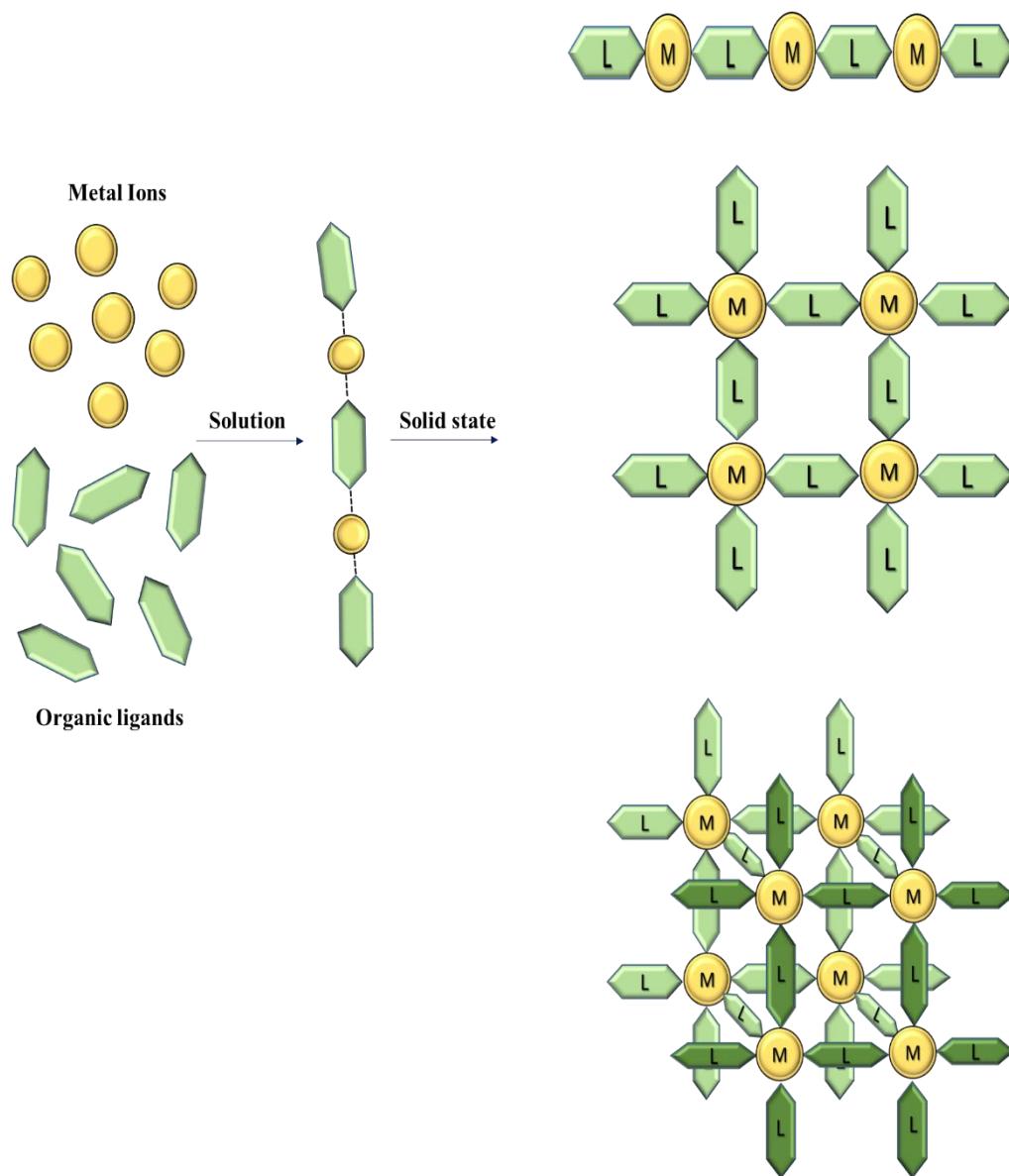


Fig. 22. 1D(top), 2D(middle) and 3D(bottom) coordination polymers.

1.9.1. Coordination polymers (CPs) vs. metal organic frameworks (MOFs)

Coordination polymer and metal-organic framework are two of the most widely investigated areas of material chemistry. Both have lot of similarities in their structures. They are prepared from a combination of metal ions and ligands with bridging features to attach metal centers and create infinite polymeric structures in one, two, and three dimensions. A basic understanding of coordination chemistry is required for the researchers to design both the polymeric framework materials. The similarities create confusion to differentiate between coordination polymers and metal-organic frameworks. Generally, inorganic chemists prefer to use the CP term, while solid-state chemists prefer the term MOF. As a result, there is a confusion and literature searches on them has become difficult. However, a unanimous agreement has eliminated this confusion and frustration regarding this topic among the researchers [82]. In 2009, Jagadese J. Vittal group published an article about the CP vs. MOF. It concluded that the coordination polymers are restricted to 1 or 2 dimensions and it is appropriate to describe them as 1D or 2D extended structures, while MOF term is much more appropriate for only three-dimensional structures [83]. In a recent paper, the Janet L. Scott group has distinguished the definition for CPs and MOFs [84]. Accordingly, coordination polymers are coordination compounds that form 1-D extended chains, 2D sheets, or 3D frameworks. These are classified into two sub-classes: “coordination networks,” which are 2D, 3D, or crosslinked 1D CPs, and “metal-organic frameworks” (MOFs) (also referred to as “porous coordination polymers”), which are coordination networks that contain potential voids [73,84].

1.9.2. Interaction involved in coordination polymers

Coordination bonds mainly govern coordination polymers. Here ligand (Lewis base) donate its lone pair to the metal cation (Lewis acid). In addition, interactions such as van der Waals forces, π - π interactions and hydrogen bonding also affect

the structures and dimensionalities of coordination polymers [85]. Self-assembly based on these interactions between the building blocks leads to network structure [86]. Various types of these interactions are summarized in Table 1 [86b].

Table 1 Strength of different types of intra- and intermolecular forces

S. No.	Type of forces	Strength/kJmol ⁻¹	Reference
1	Van der Waals	1-5	[87]
2	π - π interaction	5-10	[88]
3	Hydrogen bonding	15-40	[89]
4	Hydrophobic/hydrophilic	12-15	[90]
5	Ion-pairing	12-20	[90]
6	Coordinate bond	40-120	[90, 91]
7	Covalent bond	150-1000	[86b,92]

1.10. Synthesis of coordination polymers

Literature survey shows four principle synthetic methodologies for synthesis of coordination polymers [93]. These methodologies are as follows:

1.10.1 Saturation method

A solution of different reagents are kept for crystal formation. Molecular recognition allows the formation of the product following some pre-determined rules. Convenient conditions are essential for this method. The crystal growth may

occur in a saturated solution (ideal concentration) after the slow evaporation of the mother liquor. Temperature rise increases the solubility of the product followed by cooling allows the crystal formation. This process has to be well-controlled as far as final temperature and speed of cooling concerned.

1.10.2. Diffusion method

This method is preferred to get a single crystal for X-ray diffraction analysis. The idea behind this method is to bring into contact the different media slowly. It is possible via liquid-liquid diffusion between the two layers. One layer contains the precipitant solvent and the other one contains the product in a suitable solvent. Crystal growth occurs at the interface when precipitant solvent slowly diffuses into the product containing layer. Another approach very similar to the above is the slow mixing of the reactants, dissolved separately in the two layers. Crystal appears at the junction of the two layers. Sometimes gels are used as crystallization media instead of liquid solvents to slow down the diffusion.

1.10.3. Hydro(solvo)thermal methods

Hydrothermal/solvothermal reactions are generally carried out in a sealed Teflon coated autoclave (steel pressure vessel) with aqueous/organic solvent under autogenous pressure at a range of 100-250 °C. In this condition, at high temperature the reduced viscosity of solvents affects the solubilities of the reactants and facilitates the crystal growth process of the product.

1.10.4. Microwave and ultrasonic methods

As, in hydrothermal process, here also the solubility of the reactants increases and influences the formation of the crystalline product.

1.11. Building blocks of coordination polymers

Coordination polymers are basically derived from four different building blocks namely organic ligands, metal ions, solvents, and counter ions [93d]. We have discussed all the building blocks very briefly below:

1.11.1. Organic ligands

In a coordination polymer, ligands act as bridges between multiple metal centers in neutral or anionic form. It has to be multidentate with at least two donor atoms like N, O, and S. Their shape (rigid or flexible), length, functionalities, and sometimes chirality and symmetry are the deciding factors to determine the structure of the coordination polymer. An example of flexible ligand is 1,2-bis(4-pyridyl)ethane, which can exist in either gauche or anti conformations. Some common neutral and anionic bridging ligands are shown in Fig. 23 [78].

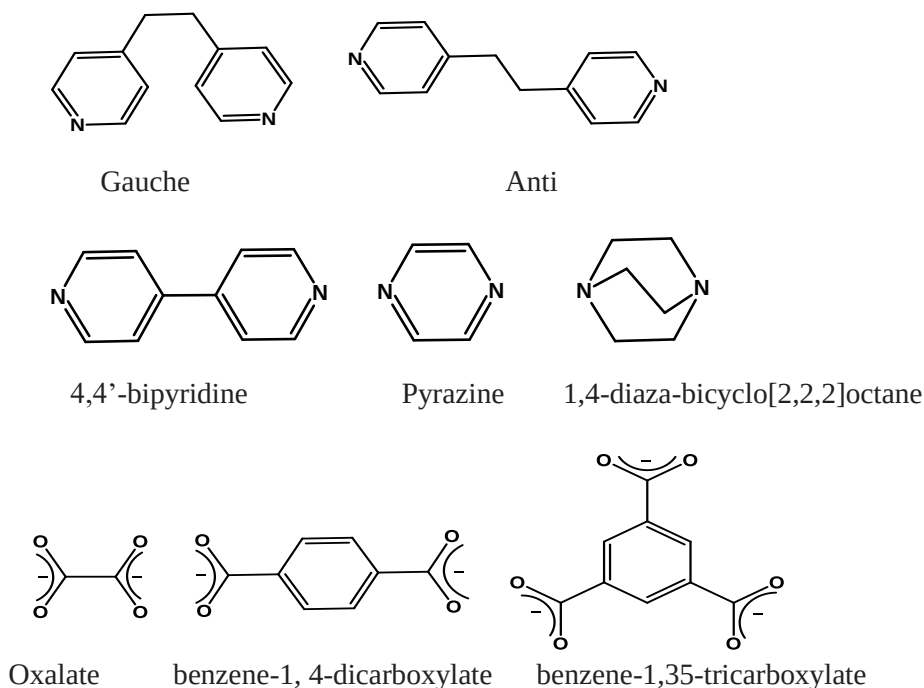


Fig. 23. Few common neutral and anionic ligands as a building block for CPs.

The carboxylate functional group has a versatile coordination behavior. Various mode of its coordination to a single metal ion and two metal ions are shown in Fig. 24. Its ability to shift from one mode to another makes this functional group unique for synthesizing coordination polymers with a variety of network structures [94].

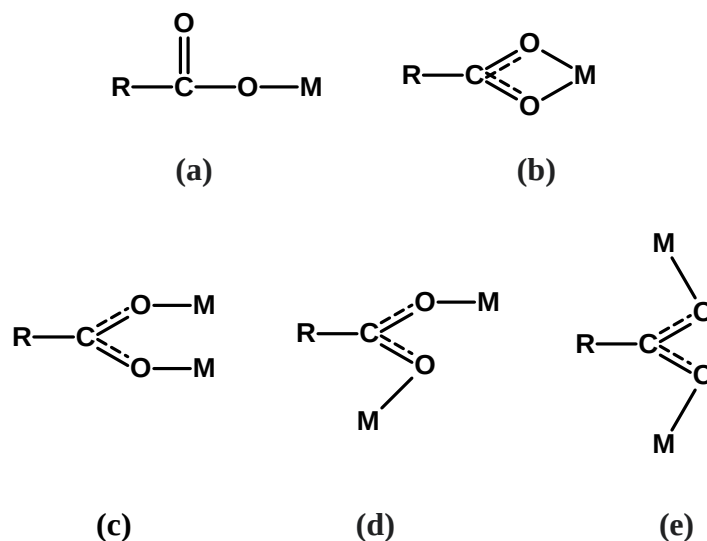


Fig. 24. Common coordinating modes of carboxylate (a) monodentate (b) chelating (c) syn-syn (d) syn-anti (e) anti-anti.

1.11.2. Metal centers

The oxidation state, size, softness/ hardness, ligand field strength, coordination number, and coordination geometry of the metal ions play crucial roles in determining the structural intricacies of a coordination polymer. Additionally, the counter anions of the (nitrate, acetate, perchlorate, sulfates, halides, and so on) metal salts used for the synthesis of a coordination polymer may also participate in the network structure formation. Metal ions with the low coordination number prefer 1- and 2D structures, while metal ions with higher coordination number form 3D structures. According to HSAB, small, non-polarizable, hard metals tend to coordinate with small, non-polarizable, hard ligands, while the larger, more

polarizable soft metals will coordinate with the larger, more polarizable soft ligands [92,93d]. Thus, the hard-soft acid-base (HSAB) characters of the metal ion and ligand can also decide the stability of the final structure.

1.11.3. Counterion

It is present in the structure to balance the overall charge obtained by ligating neutral ligands to metal ions. Generally, counterions are the anions and they are coordinated to metal ions. However, they can influence the overall structure and metal ion environment via some weak interactions or act as a guest molecule in a void spaces in the solid-state structure of the coordination polymers [95].

1.11.4. Solvents

Empty space in the form of pores and channels in the structure of coordination polymers is thermodynamically unfavorable. In general, the solvent molecules act as space fillers in the form of guest molecules. They are held in the pores via a variety of weak interactions with the host molecules [96].

1.12. Importance of coordination polymers (CPs)

Coordination polymers are promising candidates for researchers due to their interesting solid-state assembly patterns and the consequent electronic, optical and magnetic properties [97]. Their crystalline nature, network structures, long-range materials with stiffness, and the physical properties have led to their applications in a wide variety of research areas such as catalysts; molecule-based conductors; and separation and storage, luminescent and nonlinear optical materials [98]. As a result, there is a constant effort to design and synthesize new coordination polymers for various applications.

1.12.1. Catalyst

Coordination polymers as catalysts play a prominent role in various organic reactions [98a]. They have been classified into two categories one is homometallic, and the other one is heterometallic.

1.12.2. Homometallic CPs

In 2008, Karabach and coworkers introduced an inorganic 1D CP having the formula $[\text{Cu}_2(\text{H}_3\text{tea})_2(\mu_4\text{-pma})]_n$. This CP was synthesized through the self-assembly of triethanolamine (H_3tea), Cu(II) nitrate, lithium hydroxide, and pyromellitic acid (H_4pma) in aqueous medium. This 1D CP and the related 2D CP $[\text{Cu}_2(\mu\text{-H}_2\text{tea})_2\{\mu_3\text{-Na}_2(\text{H}_2\text{O})_4\}(\mu_6\text{-pma})]_n \cdot 10\text{H}_2\text{O}$ mimic the alkane partial oxidation activity of the multicopper particulate methane monooxygenase. They act as catalyst precursors for the oxidation of cyclohexane into cyclohexanol and cyclohexanone by hydrogen peroxide in acidic MeCN/ H_2O medium at room temperature (Fig. 25) [99].

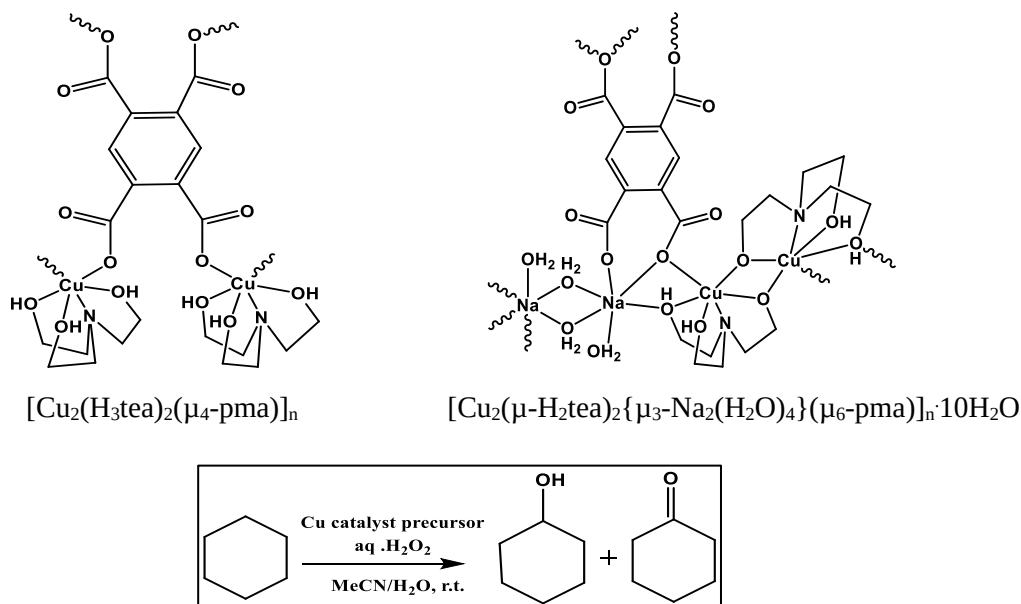


Fig. 25. Oxidation of cyclohexane catalyzed by the CPs shown above.

In 2014, Lympelopoulou and co-workers reported the catalytic activity of a Mn-based 1D CP having the formula $[\text{Mn}(\text{LH})(\text{H}_2\text{O})]_n$ {where LH^{2-} is the dianion of N-(4-carb-oxybenzyl)iminodiacetic acid} in the epoxidation of alkenes (Fig. 26) [100].

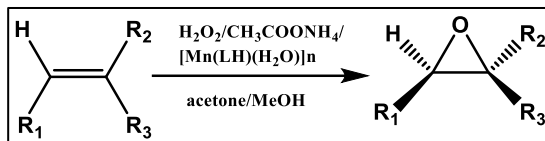


Fig. 26. Olefin epoxidation catalyzed by $[\text{Mn}(\text{LH})(\text{H}_2\text{O})]_n$.

A recent paper by L. Mandal reports a 1D CP $\{[\{\text{Cu}_2^{\text{II}} \text{L}(\mu_{1,1}\text{-N}_3)\}_2(\mu_{1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]\}_n$ formed by a Schiff base ligand (HL; 1:2 condensation product of 3-morpholinopropylamine and 4-ethyl-2,6-diformylphenol). This compound is able to mimic the behavior of catechol oxidase, which catalyzes the oxidation of catechols to quinones (Fig. 27) [101].

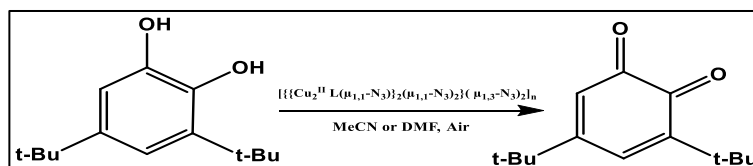


Fig. 27. Catalytic catechol oxidation

The catalytic activity of CPs as catalysts is not limited only to oxidation reactions. In a recent paper, Wani and co-workers reported that a series of three 1D CPs with transition metals (Cd, Zn, and Co) and their catalytic efficiencies in the transesterification reaction (Fig. 28) [102].

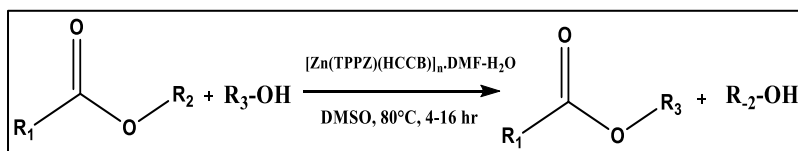


Fig. 28. Transesterification reaction by $[\text{Zn}(\text{TPPZ})(\text{HCCB})]_n \cdot \text{DMF} \cdot \text{H}_2\text{O}$.

Another example reported by C.A. Downes group is a cobalt dithiolene polymer. It was synthesized by reacting cobalt(II) acetate with sulfur based ligand benzene-1,2,4,5-tetrathiol in presence of a base and the generated polymer was immobilized onto glassy carbon electrodes (GCE) to form a stable metal–organic surface (MOS 1|GCE). This surface coated material was stable in acidic aqueous solution and it was able to exhibit efficient hydrogen evolution activity (Fig. 29) [103].

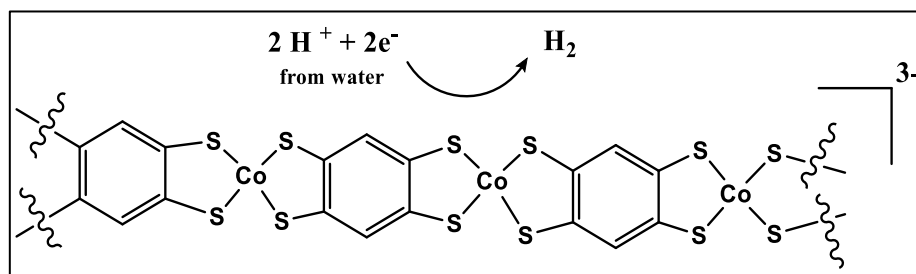


Fig. 29. A schematic representation of the Co-based 1D CP capable of catalysing H_2 evolution reaction.

1.12.3. Heterometallic CPs

The idea behind the heterometallic system by use of two or more different metals was the enhancement of the catalytic performance through synergy and cooperativity effects. Alexander M. Kirillov and co-workers reported the first relevant examples of 1D and 3D $\text{Cu}^{\text{II}}/\text{Na}$ coordination polymers which efficiently promote mild hydrocarboxylation of butane and propane by H_2O and CO to the corresponding carboxylic acids [104]. Another heterometallic 1D lanthanide-based CP has been reported by G. Kumar and co-workers in a recent study. It contains a $\text{Co(III)}/\text{Eu(III)}$ core and shows catalytic activity in various ring-opening reactions of epoxides [105]. A recent paper published by N. Kuwamura and co-workers describes the synthesis of a $\text{Pt(II)}\text{--}\text{Pd(II)}\text{--}\text{Ni(II)}$ heterotrimetallic CP which shows cooperative effect on catalytic activity for hydrogen evolution [106].

1.12.4. Nonlinear optical materials

NLO materials depend on the nonlinear processes resulting from the nonlinear relationship between the electric field of incident light and the dielectric polarization. Nonlinear processes like second harmonic generation (SHG) and third harmonic generation (THG) have a broad range of applications in the laser industry, high-resolution optical microscopy, and optoelectronics technologies in biological and medical applications [107]. Non-centrosymmetric arrangement in the solid-state is required for the construction of nonlinear optical materials. These materials also require organic ligands with large molecular first hyperpolarizability β , ordered structure, and ideal chromophores with a suitable electron donor and acceptor connected through a conjugated bridge. In principle, SHG is limited only to non-centrosymmetric materials, while THG occurs in all materials. There are numerous reports on the 1D CPs of cobalt, zinc, and cadmium that can show either SHG or THG, depending on their crystal symmetry [108]. Several 2D and 3D CPs and MOFs were reported to exhibit SHG, THG, or multiphoton absorption [109]. Huang group in 2008 reported a 3D-diamond-like tetrazole-based Zn(II) CP having the formula $[\text{Zn}(\text{tzf})_2]_n$ (Htzf = 1H-tetrazole-5-formic acid) which shows the nonlinear optical effect and luminescent property [110]. In a recent paper, Min Liu and coworkers have reported a 1D CP that shows multiple nonlinear optical functions concurrently. It can efficiently generate multi-photon-excited photoluminescence (PL), SHG, and THG properties [107].

1.12.5. Luminescence

Luminescence is a phenomenon that involves the spontaneous emission of radiation from an excited state which may be generated in various ways, such as, by applying mechanical forces, photonic excitation, from chemical/electrochemical reactions, etc. [111]. The mechanism involves the

transition of an electron from ground to an excited state by absorption of a photon and then back to the ground state with simultaneous photon emission via various relaxation processes like fluorescence and phosphorescence [112]. Luminescent materials can be classified based on the origin of emission, that is metal-based emission or ligand-based emission. Luminescent materials are widely applied in optoelectronic devices, fluorescent sensors and optical probes [113]. Coordination polymers can be very good luminescent materials due to the tunability of their chemical composition by changing the metal centers or metal clusters and the coordinating organic ligands. Mechanism of luminescence in CPs is based on d-d or f-f transitions, ligand-centered (LC) transitions and various charge transfer including metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), ligand-to-ligand charge transfer (LLCT), and metal-to-metal charge transfer (MMCT) transitions [98f]. There are plenty of reports on transition metal-based CPs showing excellent luminescent properties because of the variation of the coordination numbers and the coordination abilities of the metal ions [114].

1.12.6. Magnetic properties

Magnetic coordination polymers are divided into two classes: one shows long-range ordering, and the other one displays spin cross-over. Long-range ordering comes from the cooperative exchange interaction (coupling) between the spins of the paramagnetic metal centers through the superexchange pathway. The magnetic materials have different categories based on the spin alignment of unpaired electrons. These are ferromagnetic, antiferromagnetic, and ferrimagnetic. Ferromagnetism arises when all magnetic spins are aligned in the same direction, resulting in significant increase in net magnetic moment. On the other hand, in antiferromagnetism, antiparallel alignment of spins displays no net magnetic moment. Ferrimagnetism arises when the magnetic moments of the domains in the substance are aligned in parallel and antiparallel directions in unequal

numbers [98c]. Plenty of reports on transition metal-based CPs showed ferromagnetism, antiferromagnetism, and ferrimagnetism [115]. CPs are ideal for the single-chain magnet (SCM), similar to a single molecular magnet (SMM). To design the SCM the primary requirement is to increase the blocking temperature of SMM. Hence, it can increase their potential applications in recording media or molecular memory devices [116]. Synthetic methodology to construct SCM includes two main aspects: (i) utilization of the bridging ligands as effective magnetic couplers to link uniaxial anisotropic spin carriers like Ni^{2+} , Mn^{3+} , Fe^{2+} , Co^{2+} , and lanthanide ions into 1D chains and (ii) use of appropriate diamagnetic separators to make these chains magnetically well isolated [117]. There are several reports on transition metal-based CPs which display SCM property [118]. Another class of magnetic CPs has spin-crossover (SCO) properties. These magnetic materials are a class of molecules where the spin state can switch reversibly between a diamagnetic low spin (LS) state and paramagnetic high spin (HS) state upon physical stimuli such as light irradiation, temperature, or pressure change. Vibrational, electronic, and structural properties of the compound will change after spin transition (ST). As a result, there is a constant effort to synthesize SCO materials due to their potential applications in sensors or memory devices [119]. In 1996, Takafumi Kitazawa and coworkers reported a transition metal-based coordination polymer $\text{Fe}^{\text{II}}(\text{C}_5\text{H}_5\text{N})_2\text{Ni}(\text{CN})_4$ which displays SCO behavior [120]. A recent report published in 2018, where Charles Lochenie and coworkers synthesized a spin-crossover CP having a formula of $[\text{Fe}(\text{L})(\text{bipy})]_n$ ($\text{L}^{2-} = \text{N}_2\text{O}_2^-$ donor Schiff base like ligand which contains a phenazine fluorophore and bipy = 4,4'-bipyridine) [121].

1.12.7. Conductivity

Electrically conductive coordination polymers have received immense attention worldwide due to its versatile potential in material science. These polymers are hybrid multifunctional materials consisting of organic ligands linked with metal ions or clusters. Designing and synthesizing highly conductive CPs require a basic understanding of their electronic structures and charge transport mechanisms [122]. 1D CPs constructed from stacked macrocyclic metal complexes of the type $[M(L)(\mu-L')]_n$ {M = Fe, Ru, Os; L = octaethylporphyrinato (oep), phthalocyaninato (pc); and L' = pyz, 4,4'-bipy, dabco} have been evaluated for their conductivity. Their conductivity abruptly increased after iodine doping. The conductivity of CPs depends on the interaction between the π^* level of the bridging ligand and metal d-orbitals. Conductivity is more remarkable for the more π -acidic bridging ligand $\text{pyz} > \text{bpy} \gg \text{dabco}$ and through better π -bonding metals $\text{Os} > \text{Ru} > \text{Fe}$ [123]. Another example where Daofeng Sun and coworkers have synthesized a 3D CP having the formula $[\{\text{Ag}(\text{H}_2\text{btc})_2\}\{\text{Ag}_2(\text{Hbtc})\}]$ which shows increase of conductivity with temperature [124].

1.13. Present investigation

In part A, the coordination chemistry of vanadium(IV/V) was explored with some hydrazine-based ligands. We have successfully synthesized six novel ternary oxovanadium(V) complexes of formula $[\text{VO}(\text{acac})(\text{L}^n)]$ by using α -diketone bis(4-R-benzoylhydrazones) (H_2L^n ($n = 1-6$)). In another work of part A, we were able to synthesize one dimeric oxomethoxovanadium(V) complex $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ and a pervanadyl complex $\text{K}[\text{VO}_2(\text{HL})] \cdot \text{MeOH}$ by using biacetylmonoxime salicyloylhydrazone (H_3L). The photocatalytic activities of the latter two complexes in degradation of the organic dye rhodamine B (RhB) have been also evaluated. Molecular structures of all these complexes have been confirmed by X-ray crystallography. All the complexes have been characterized

by mass spectrometric, elemental analysis, various spectroscopic (IR, UV–Vis, and ^1H NMR), solution electrical conductivity and cyclic voltammetric measurements. The ligands and their corresponding complexes are presented in Fig. 30.

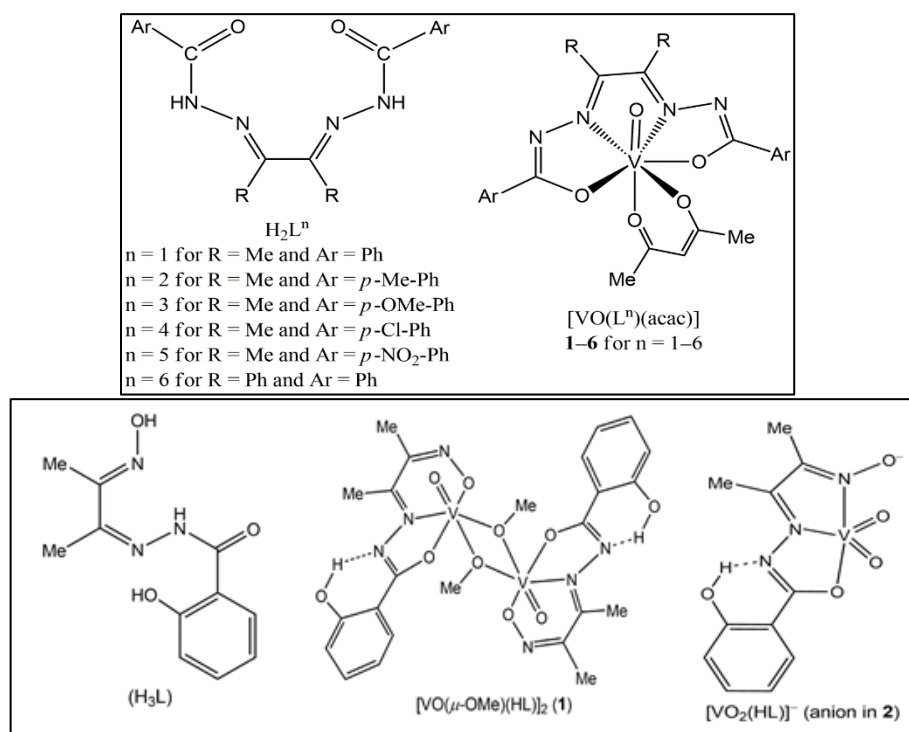


Fig. 30. Oxovanadium and pervanadyl complexes discussed in the present study.

In part B, we have synthesized and characterized a tetranuclear mixed-valent complex of molecular formula $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, 1D $\text{Mn}(\text{II})\text{Mn}(\text{III})$, $\text{Fe}(\text{III})$ and $\text{Mn}(\text{III})$ based coordination polymers having formulas $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$, $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ and $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$, respectively (Fig. 31). X-ray crystallographic studies confirmed their molecular and polymeric structures. The physical properties and catalytic applications of the tetranuclear complex and the mixed-valent coordination polymer are discussed.

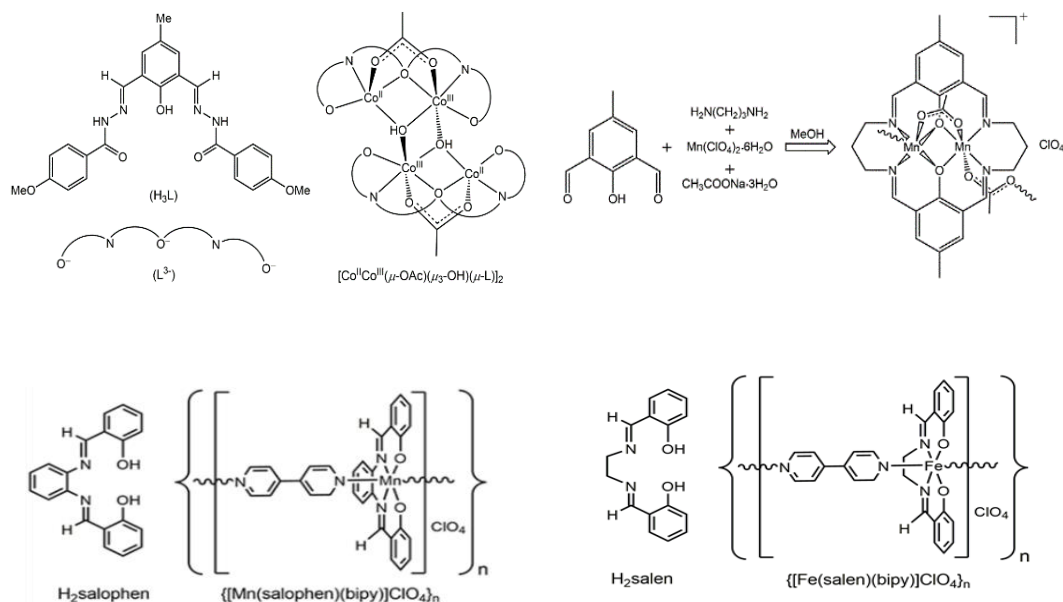


Fig. 31. Chemical structure diagrams of Co cluster and Mn and Fe based one dimensional CPs.

1.14. References

- [1] (a) D.G. Barceloux, *Clin. Toxicol.* 37 (1999) 265-278. (b) R.R. Moskalyk, A. M. Alfantazi, *Miner. Eng.* 16 (2003) 793-805. (c) D. Rehder, *Adv. Chem. Res.* 2 (2020) 1-17.
- [2] N.D. Chasteen (Ed.), *Vanadium in Biological Systems*, Kluwer, Dordrecht, (1990).
- [3] (a) A. Butler, *Curr. Opin. Chem. Biol.* 2 (1998) 279-285. (b) S. Raugei, P. Carloni, *J. Phys. Chem. B* 110 (2006) 3747-3758. (c) C. Kimblin, X. Bu, A. Butler, *Inorg. Chem.* 41 (2002) 161-163. (d) A. Butler, J.N. Carter-Franklin, *Nat. Prod. Rep.* 21 (2004) 180-188. (e) R. Wever, M.A. van der Horst, *Dalton Trans.* 42 (2013) 11778-11786. (f) C. Leblanc, H. Vilter, J.-B. Fournier, L. Delagea, P. Potina, E. Rebuffet, G. Michel, P.L. Solari, M.C. Feiters, M. Czjzek, *Coord.*

Chem. Rev. 301–302 (2015) 134–146. (g) M.R. Maurya, *Asian J. Chem.* 24 (2012) 5441-5446.

[4] (a) C. Orvig, K.H. Thompson, M. Battell, J H McNeill, *Met. Ion. Biol. Syst.* 31 (1995) 575. (b) K.H. Thompson, John H. McNeill, Chris Orvig, *Chem. Rev.* 99 (1999) 2561-2571.

[5] (a) B.M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D.R. Dean, L.C. Seefeldt, *Chem. Rev.* 114 (2014) 4041-4062. (b) D. Rehder, *J. Inorg. Biochem.* 80 (2000) 133-136. (c) R.R. Eady, *Polyhedron* 8 (1989) 1695-1700. (d) Y. Hu, C.C. Lee, M. W. Ribbe, *Dalton Trans.* 41 (2012) 1118-1127. (e) C.C. Lee, Y. Hu, M. W. Ribbe, *Science* 329 (2010) 642. (f) M. Rohde, K. Grunau, I. Djurdjevic, C. Trncik, F. Schneider, J. Gies-Elterlein, O. Einsle, *Encyclopedia of Inorganic and Bioinorganic Chemistry* (2019) 1-10.

[6] (a) A.G.J. Ligtenbarg, R. Hage, B.L. Feringa, *Coord. Chem. Rev.* 237 (2003) 89-101. (b) M. Sutradhar, L.M.D.R.S. Martins, M. Fátima C. G. D. Silvaa, A.J. L. Pombeiro, *Coord. Chem. Rev.* 301–302 (2015) 200–239.

[7] (a) A. Parasuramana, T.M. Lima, C. Menictas, M. Skyllas-Kazacos, *Electrochim Acta* 101 (2013) 27-40. (b) C. Minkea, T. Turek, *J. Power Sources* 376 (2018) 66–81. (c) I. Aramendia, U. Fernandez-Gamiz, A. Martinez-San-Vicente, E. Zulueta, J. M. Lopez-Guede, *Energies* 14 (2021) 176-196. (d) K. Lourenszen, J. Williams, F. Ahmadpour, R. Clemmer, S. Tasnim, *J. Energy Storage* 25 (2019) 100844-100861.

[8] (a) J.A.L. da Silva, João J.R. Fraústo da Silva, A.J.L. Pombeiro, *Coord. Chem. Rev.* 257 (2013) 2388-2400. (b) M. Domarus, M.L. Kuznetsov, J. MarÅalo, A.J.L. Pombeiro, J.A.L. da Silva, *Angew. Chem.* 128 (2016) 1511-1514. (c) R.E. Berry, E.M. Armstrong, R.L. Beddoes, D. Collison, S. Nigar Ertok, M. Helliwell, C.D. Garner, *Angew. Chem. Int. Ed.* 38 (1999) 795-797. (d) E.M. Armstrong, R.L.

Beddoes, L.J. Calviou, J.M. Charnock, D. Collison, N. Ertok, J. H. Naismith, C.D. Garner, *J. Am. Chem. Soc.* 115 (1993) 807-808.

[9] (a) D. Rehder, *Metallomics* 7 (2015) 730-742. (b) A. Butler, C.J. Carrano, *Coord. Chem. Rev.* 109 (1991) 61-105. (c) S.R. Akabayov, B. Akabayov, *Inorg. Chim. Acta* 420 (2014) 16-23.

[10] A. Butler, M.J. Clague, G.E. Meister, *Chem. Rev.* 94 (1994) 625-638.

[11] J.P. Dunna, H.G. Stenger Jr., Israel E. Wachs, *Catal. Today* 51 (1999) 301-318.

[12] R.R. Langeslay, D.M. Kaphan, C.L. Marshall, P.C. Stair, A.P. Sattelberger, M. Delferro, *Chem. Rev.* 119 (2019) 2128-2191.

[13] M.O. Guerrero-Pérez, *Catalysts* 8 (2018) 564-578.

[14] (a) P. Ahuja, S.K. Ujjain, R. Kanojia, P. Attri, *J. Compos. Sci.* 5 (2021) 82-109. (b) M. Rafique, M. Hamza, M. Shakil, M. Irshad, M.B. Tahir, M.R. Kabli, *Appl. Nanosci.* 10 (2020) 2365. (c) M.M. Sajida, N.A. Shadb, Y. Javedf, S.B. Khanc, Z. Zhange, N. Aminb, H. Zhai, *Surf. Interfaces* 19 (2020) 100502-100511. (d) W.A. Jr, V.R. de Mendonça, O.F. Lopesbc, C. Ribeiroc, *RSC Adv.* 5 (2015) 12000-12006. (e) H. Letifi, Y. Litaïem, D. Dridi, S. Ammar, R. Chtourou, *Adv. Condens. Matter Phys.* (2019) 1-11.

[15] (a) D. Rehder, *Dalton Trans.* 42 (2013) 11749-11761. (b) D.C. Crans, Dinorah Gambino, S.B. Etcheverry, *New J. Chem.* 43 (2019) 17535-17537.

[16] (a) O. Krishan, S. Suhag, *Int J Energy Res.* 43 (2019) 6171-6210. (b) H. Chen, T.N. Cong, W. Yang, C. Tan, Y. Li, Y. Ding, *Prog. Nat. Sci.* 19 (2009) 291-312.

- [17] (a) M.J. Lain, E. Kendrick, *J. Power Sources* 493 (2021) 229690-229699. (b) D. Deng, *Energy Sci. Eng.* 3 (2015) 385-418. (c) N. Nitta, F. Wu, J.T. Lee, G. Yushin, *Mater. Today* 18 (2015) 252-264.
- [18] (a) R.A. Rowe, M.M. Jones, *Inorg. Synth.* 5 (1957) 113-116. (b) M. Bhattacharjee, *J. Chem. Res.* (1992) 415.
- [19] M.R. Maurya, *Coord. Chem. Rev.* 237 (2003) 163-181.
- [20] R.L. Richards, *Encyclopedia of Inorganic Chemistry* (2011) 1-17.
- [21] (a) S. Samanta, D. Ghosh, S. Mukhopadhyay, A. Endo, T.J.R. Weakley, M. Chaudhury, *Inorg. Chem.* 42 (2003) 1508-1517. (b) S. Samanta, S. Mukhopadhyay, D. Mandal, R.J. Butcher, M. Chaudhury, *Inorg. Chem.* 42 (2003) 6284-6293. (c) M.R. Maurya, A. Kumar, A.R. Bhat, A. Azam, C. Bader, D. Rehder, *Inorg. Chem.* 45 (2006) 1260-1269. (d) S.K. Dutta, S. Samanta, D. Ghosh, R.J. Butcher, M. Chaudhury, *Inorg. Chem.* 41 (2002) 5555-5560. (e) S.K. Dutta, S.B. Kumar, S. Bhattacharyya, E.R.T. Tiekink, M. Chaudhury, *Inorg. Chem.* 36 (1997) 4954-4960. (f) S.K. Dutta, S. Samanta, S.B. Kumar, O.H. Han, P. Burckel, A.A. Pinkerton, M. Chaudhury, *Inorg. Chem.* 38 (1999) 1982-1988.
- [22] L.J. Calviou, D. Collison, C.D. Garner, F.E. Mabbs, M.A. Passand, M. Pearson, *Polyhedron* 8 (1989) 1835-1837.
- [23] (a) C.J. Carrano, C.M. Nunn, R. Quan, J.A. Bonadies, V.L. Pecoraro, *Inorg. Chem.* 29 (1990) 944-951. (b) G. Asgedom, A. Sreedhara, J. Kivikoski, C.P. Rao, *Polyhedron* 16 (1997) 643-651.
- [24] M.R. Maurya, S. Khurana, *J. Chem. Res. (S)* (2002) 260-261.
- [25] A. Giacomelli, C. Floriani, A. O. de Souza Duarte, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* 21 (1982) 3310-3316.

- [26] H. Schmidt, M. Bashirpoor, D. Rehder, *J. Chem. Soc. Dalton Trans.* (1996) 3865-3870.
- [27] M.R. Maurya, S. Khurana, C. Schulzke, D. Rehder, *Eur. J. Inorg. Chem.* (2001) 779-788.
- [28] N.R. Sangeetha, S. Pal, *Bull. Chem. Soc. Jpn.* 73 (2000) 357-363.
- [29] S. Dutta, P. Basu, A. Chakravorty, *Inorg. Chem.* 32 (1993) 5343-5348.
- [30] N.R. Sangeetha, V. Kavita, S. Wocadlo, A.K. Powell, S. Pal, *J. Coord. Chem.* 51 (2000) 55-66.
- [31] S.N. Pal, K.R. Radhika, S. Pal, *Z. Anorg. Allg. Chem.* 627 (2001) 1631-1637.
- [32] S.N. Pal, S. Pal, *J. Chem. Crystallogr.* 30 (2000) 329-333.
- [33] M.R. Maurya, S. Khurana, W. Zhang, D. Rehder, *J. Chem. Soc. Dalton Trans.* (2002) 3015-3023.
- [34] M.R. Maurya, S. Khurana, W. Zhang, D. Rehde, *Eur. J. Inorg. Chem.* (2002) 1749-1760.
- [35] S.K. Dutta, S.B. Kumar, S. Bhattacharyya, E.R.T. Tiekink, M. Chaudhury, *Inorg. Chem.* 36 (1997) 4954-4960.
- [36] N.M. Hirotsu, K. Ooi, S. Saito, K. Saito, *J. Chem. Soc. Chem. Commun.* (1979) 707-708.
- [37] S. Ooi, M. Nishizawa, K. Matsumoto, H. Kuroya, K. Saito, *Bull. Chem. Soc. Jpn.* 52 (1979) 452-457.
- [38] J.A. Bonadies, C. J. Carrano, *J. Am. Chem. Soc.* 108 (1986) 4088-4095.
- [39] (a) D.L. Hughes, U. Kleinkes, G.J. Leigh, M. Maiwald, J.R. Sanders, C. Sudbrake, J. Weisner, *J. Chem. Soc. Dalton Trans.* (1993) 3093-3096. (b) N.F.

Choudhary, D.L. Hughes, U. Kleinkes, L.F. Larkworthy, G.J. Leigh, M. Maiwald, C. J. Marmion, J.R. Sanders, G.W. Smith, C. Sudbrake, *Polyhedron* 16 (1997) 1517-1528. (c) N.F. Choudhary, N.G. Connelly, P.B. Hitchcock, G.J. Leigh, *J. Chem. Soc. Dalton Trans.* (1999) 4437-4446.

[40] (a) T.A. Kabanos, A.D. Keramidas, D. Mentzafos, A. Terzis, *J. Chem. Soc. Chem. Commun.* (1990) 1664-1665. (b) G.R. Hanson, T.A. Kabanos, A. D. Keramidas, D. Mentzafos, A. Terzis, *Inorg. Chem.* 31 (1992) 2587-2594.

[41] (a) T.A. Kabanos, A.D. Keramidas, A.B. Papaioannou, A. Terzis, *J. Chem. Soc. Chem. Commun.* (1993) 643-645. (b) A.D. Keramidas, A.B. Papaioannou, A. Vlahos, T.A. Kabanos, G. Bonas, A. Makriyannis, C.P. Raptopoulou, A. Terzis, *Inorg. Chem.* 35 (1996) 357-367. (c) C.R. Cornman, E.P. Zovinka, Y.D. Boyajian, K.M. Geiser-Bush, P.D. Boyle, P. Singh, *Inorg. Chem.* 34 (1995) 4213-4219.

[42] (a) G. Asgedom, A. Sreedhara, J. Kivikoski, J. Valkonen, E. Kolehmainen, C.P. Rao, *Inorg. Chem.* 35 (1996) 5674-5683. (b) G. Asgedom, A. Sreedhara, C.P. Rao, *Polyhedron* 14 (1995) 1873-1879. (c) C.P. Rao, A. Sreedhara, P. V. Rao, M. B. Verghese, K. Rissanen, E. Kolehmainen, N.K. Lokanath, M.A. Sridhar, J. S. Prasad, *J. Chem. Soc. Dalton Trans.* (1998) 2383-2293.

[43] J.C. Dutton, G.D. Fallon, K.S. Murray, *Inorg. Chem.* 27 (1988) 34-38.

[44] K.K. Nanda, E. Sinn, A.W. Addison, *Inorg. Chem.* 35 (1996) 1-2.

[45] F. Mautner, R. Fischer, M. Spell, A. Acevedo, D. Tran, S. Massoud, *Crystals* 6 (2016) 91.

[46] (a) R. Robson, *Aust. J. Chem.* 23 (1970) 2217-2224. (b) N. Pilkington, R. Robson, *Aust. J. Chem.* 23 (1970) 2225-2236.

[47] (a) S. Mameri, D. Specklin, R. Welter, *C. R. Chim.* 18 (2015) 1370–1384. (b) G. Li, D. Zhu, X. Wang, Z. Su, M.R. Bryce, *Chem. Soc. Rev.* 49 (2020) 765–838.

- [48] (a) D.E. Fenton, S.E. Gayda, *J. Chem. Soc., Dalton Trans.* (1977) 2095-2101. (b) U. casellato, P.A. Vigato, D.E. Fenton, M. Vidali *Compartmental Ligands: Routes to Homo- and Hetero-dinuclear Complexes* 8 (1979) 199-220. (c) D.E. Fenton, S.E. Gayda, C.M. Regan, M.A. Cushing, S.D. Ittel, *Inorg. Synth.*, John Wiley & Sons (1980) 90–96. (d) M. Andruh, *Chem. Commun.* 47 (2011) 3025-3042.
- [49] (a) U. Casellato, S. Tamburini, P. Tomasin, P.A. Vigato, *Inorg. Chim. Acta.* 357 (2004) 4191–4207. (b) P. Vigato, S. Tamburini, L. Bertolo, *Coord. Chem. Rev.* 251 (2007) 1311–1492. (c) P.A. Vigato, V. Peruzzo, S. Tamburini, *Coord. Chem. Rev.* 256 (2012) 953–1114.
- [50] G. Ambrosi, M. Formica, V. Fusi, L. Giorgi, M. Micheloni, *Coord. Chem. Rev.* 252 (2008) 1121–1152.
- [51] (a) S.I. Sampani, E. Loukopoulos, M. Azam, K. Griffiths, A. Abdul-Sada, G. Tizzard, S. Coles, A. Escuer, A. Tsipis, G.E. Kostakis, *CrystEngComm.* 20 (2018) 1411–1421. (b) S. Maloth, S.K. Kurapati, S. Pal, *J. Coord. Chem.* 68 (2015) 1402–1411. (c) C. Zhang, C. Chen, H. Dong, J.-R. Shen, H. Dau, J. Zhao, *Science* 348 (2015) 690–693. (d) S. Anbu, R. Ravishankaran, M.F.C. Guedes da Silva, A.A. Karande, A.J.L. Pombeiro, *Inorg. Chem.* 53 (2014) 6655–6664. (e) R.D. Adams, F. A. Cotton, Wiley-VCH, New York, 1998, ISBN 0-471-23930-5. (f) G.E. Kostakis, S.P. Perlepes, V.A. Blatov, D.M. Proserpio, A.K. Powell, *Coord. Chem. Rev.* 256 (2012) 1246–1278. (g) J.R. Anaconda, J. Calvo, O.A. Almanza, *Int. J. Inorg. Chem.* 2013 (2013) 1–7. (h) K. Das, T.K. Mondal, E. Garribba, M. Fondo, C. Sinha, A. Datta, *Inorg. Chim. Acta.* 413 (2014) 194–202. (i) Y.-Z. Zheng, G.-J. Zhou, Z. Zheng, R.E.P. Winpenny, *Chem Soc Rev.* 43 (2014) 1462–1475. (j) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* 96 (1996) 759–833. (k) M.W. Cooke, G.S. Hanan, *Chem. Soc. Rev.* 36 (2007) 1466-1476.

- [52] R.E.P. Winpenny, *J. Chem. Soc. Dalton Trans.* (2002) 1–10.
- [53](a) G. Christou, D. Gatteschi, D.N. Hendrickson, R. Sessoli, *MRS Bull.* 25 (2000) 66–71. (b) M.N. Leuenberger, D. Loss, *Nature* 410 (2001) 789–793. (c) L. Bogani, W. Wernsdorfer, *Nat. Mater.* 7 (2008) 179–185.
- [54](a) D. Gatteschi, *J. Alloys Compd.* 317–318 (2001) 8–12. (b) N.T. Madhu, J.-K. Tang, I.J. Hewitt, R. Clérac, W. Wernsdorfer, J. van Slageren, C.E. Anson, A.K. Powell, *Polyhedron* 24 (2005) 2864–2869.
- [55] T. LIs, *Acta Cryst.* B36 (1980) 2042–2046.
- [56](a) R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, *Nature* 365 (1993) 141–143. (b) R. Sessoli, H.-L. Tsai, A.R. Schake, S.Wang, J.B.Vincent, K.folting, D.gatteschi, G. christou, D.N. Hendrickson. *J.A.C.S.*115 (1993) 1804–1816.
- [57] K. Weighardt, K. Pohl, I. Jibril, G. Huttner, *Angew. Chem. Int. Ed. Engl.* 23 (1984) 77–78.
- [58](a) E.-C. Yang, D.N. Hendrickson, W. Wernsdorfer, M. Nakano, L.N. Zakharov, R.D. Sommer, A.L. Rheingold, M. Ledezma-Gairaud, G. Christou, *J. Appl. Phys.* 91 (2002) 7382. (b) M. Murrie, *Chem. Soc. Rev.* 39 (2010) 1986–1995. (c) C. Cadiou, M. Murrie, C. Paulsen, V. Villar, W. Wernsdorfer, R.E.P. Winpenny, *Chem. Commun.* (2001) 2666–2667. (d) E.-C. Yang, W. Wernsdorfer, S. Hill, R.S. Edwards, M. Nakano, S. Maccagnano, L.N. Zakharov, A.L. Rheingold, G. Christou, D.N. Hendrickson, *Polyhedron* 22 (2003) 1727–1733.
- [59] S.K. Langley, C. Le, L. Ungur, B. Moubaraki, B.F. Abrahams, L.F. Chibotaru, K.S. Murray, *Inorg. Chem.* 54 (2015) 3631–3642.
- [60] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* 35 (1996) 2400–2402.

- [61] (a) C. Zhang, Y. Chen, H. Ma, T. Yu, B. Liu, H. Pang, *N. J. Chem.* 37 (2013) 1364–1370. (b) S. Goswami, A.K. Mondal, S. Konar, *Inorg. Chem. Front.* 2 (2015) 687–712. (c) L. Rosado Piquer, E.C. Sañudo, *Dalton Trans.* 44 (2015) 8771–8780. (d) H.-R. Wen, P.-P. Dong, S.-J. Liu, J.-S. Liao, F.-Y. Liang, C.-M. Liu, *Dalton Trans.* 46 (2017) 1153–1162. (e) A. Dey, J. Acharya, V. Chandrasekhar, *Asian J. Chem.* 14 (2019) 4433–4453.
- [62] (a) E. Coronado, D. Gatteschi, *J. Mater. Chem.* 16 (2006) 2513–2515. (b) D. Shao, X. Wang, *Chin. J. Chem.* 38 (2020) 1005–1018.
- [63] (a) L. Bogani, A. Vindigni, R. Sessoli, D. Gatteschi, *J. Mater. Chem.* 18 (2008) 4750–4758. (b) K.S. Pedersen, A. Vindigni, R. Sessoli, C. Coulon, R. Clérac, *Mol. Magn. Mater.* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, (2016) 131–159.
- [64] D.S. Nesterov, O.V. Nesterova, A.J.L. Pombeiro, *Coord. Chem. Rev.* 355 (2018) 199–222.
- [65] (a) A. Singh, L. Spiccia, *Coord. Chem. Rev.* 257 (2013) 2607–2622. (b) J.D. Blakemore, R.H. Crabtree, G.W. Brudvig, *Chem. Rev.* 115 (2015) 12974–13005. (c) M. Tahir, L. Pan, F. Idrees, X. Zhang, L. Wang, J.-J. Zou, Z.L. Wang, *Nano Energy.* 37 (2017) 136–157.
- [66] (a) M.M. Najafpour, *J. Photochem. Photobiol. B.* 104 (2011) 111–117. (b) S. Mukherjee, J.A. Stull, J. Yano, T.C. Stamatatos, K. Pringouri, T.A. Stich, K.A. Abboud, R.D. Britt, V.K. Yachandra, G. Christou, *Proc. Natl. Acad. Sci.* 109 (2012) 2257–2262. (c) M.M. Najafpour, A.N. Moghaddam, S.I. Allakhverdiev, Govindjee, *Biochim. Biophys. Acta Bioenerg.* 1817 (2012) 1110–1121. (d) S. Paul, F. Neese, D.A. Pantazis, *Green Chem.* 19 (2017) 2309–2325.
- [67] W. Lubitz, B. Tumas, *Chem. Rev.* 107 (2007) 3900–3903.

- [68] S. Dutta, *J. Ind. Eng. Chem.* 20 (2014) 1148–1156.
- [69] (a) S. Anantharaj, S.R. Ede, K. Sakthikumar, K. Karthick, S. Mishra, S. Kundu, *ACS Catal.* 6 (2016) 8069–8097. (b) Electrochemical Water Splitting, 1st ed., *Materials Research Forum LLC*, 2019. (c) X. Li, L. Zhao, J. Yu, X. Liu, X. Zhang, H. Liu, W. Zhou, *Nano-Micro Lett.* 12 (2020) 131.
- [70] (a) M. Yagi, M. Kaneko, *Chem. Rev.* 101 (2001) 21–35. (b) M. Yagi, A. Syouji, S. Yamada, M. Komi, H. Yamazaki, S. Tajima, *Photochem Photobiol Sci.* 8 (2009) 139–147. (c) J.L. Dempsey, B.S. Brunschwig, J.R. Winkler, H.B. Gray, *Acc. Chem. Res.* 42 (2009) 1995–2004. (d) N. Queyriaux, R.T. Jane, J. Massin, V. Artero, M. Chavarot-Kerlidou, *Coord. Chem. Rev.* 304–305 (2015) 3–19. (e) J. Wang, K. Yamauchi, H. Huang, J. Sun, Z. Luo, D. Zhong, T. Lu, K. Sakai, *Angew. Chem. Int. Ed.* 58 (2019) 10923–10927. (f) S. Ghosh, A.K. Srivastava, R. Govu, U. Pal, S. Pal, *Inorg. Chem.* 58 (2019) 14410–14419.
- [71] (a) N.S. McCool, D.M. Robinson, J.E. Sheats, G.C. Dismukes, *J. Am. Chem. Soc.* 133 (2011) 11446–11449. (b) A.M. Ullman, Y. Liu, M. Huynh, D.K. Bediako, H. Wang, B.L. Anderson, D.C. Powers, J.J. Breen, H.D. Abruña, D.G. Nocera, *J. Am. Chem. Soc.* 136 (2014) 17681–17688. (c) A. Genoni, G. La Ganga, A. Volpe, F. Puntoriero, M. Di Valentin, M. Bonchio, M. Natali, A. Sartorel, *Faraday Discuss.* 185 (2015) 121–141. (d) F. Song, R. Moré, M. Schilling, G. Smolentsev, N. Azzaroli, T. Fox, S. Lubner, G.R. Patzke, *J. Am. Chem. Soc.* 139 (2017) 14198–14208. (e) A.I. Nguyen, K.M. Van Allsburg, M.W. Terban, M. Bajdich, J. Oktawiec, J. Amtawong, M.S. Ziegler, J.P. Dombrowski, K.V. Lakshmi, W.S. Drisdell, J. Yano, S.J.L. Billinge, T.D. Tilley, *Proc. Natl. Acad. Sci.* 116 (2019) 11630–11639.
- [72] F.W. Harris, *J. Chem. Educ.* 58 (1981) 7.

- [73] S.R. Batten, N.R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O’Keeffe, M. Paik Suh, J. Reedijk, *Pure Appl. Chem.* 85 (2013) 1715–1724.
- [74] (a) J.C.J. Bailar, 1 (1964) 1–27. (b) S.R. Batten, N.R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O’Keeffe, M.P. Suh, J. Reedijk, *CrystEngComm*. 14 (2012) 3001.
- [75] J.-C.G. Bünzli, *J. Coord. Chem.* 67 (2014) 3706–3733.
- [76] A. Kraft, G. Gmbh, *Berlin Bull. Hist. Chem.* 33 (2008) 7.
- [77] (a) F.D.M. J.F. Keggin, *Nature* 137 (1936) 577–578. (b) F. Grandjean, L. Samain, G.J. Long, *Dalton Trans.* 45 (2016) .
- [78] C. Janiak, *Dalton Trans.* 24 (2003) 2781-2804.
- [79] B.F. Hoskins, R. Robson, *J. Am. Chem. Soc.* 112 (1990) 1546–1554. (b) R. Robson, B.F. Abrahams, S.R. Batten, R.W. Gable, B.F. Hoskins, J. Liu (1992) 256-273.
- [80] M. Kondo, T. Yoshitomi, H. Matsuzaka, S. Kitagawa, K. Seki, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1725–1727.
- [81] H. Li, M. Eddaoudi, M. O’Keeffe, O.M. Yaghi, *Nature* 402 (1999) 276–279.
- [82] R. Robson, *Dalton Trans.* (2008) 5113–5131.
- [83] K. Biradha, A. Ramanan, J.J. Vittal, *Cryst. Growth Des.* 9 (2009) 2969–2970.
- [84] E.R. Engel, J.L. Scott, *Green Chem.* 22 (2020) 3693–3715.
- [85] (a) A.M. Maharramov, K.T. Mahmudov, M.N. Kopylovich, A.J.L. Pombeiro, eds., John Wiley & Sons, Inc, Hoboken, NJ, 2016. (b) K.T. Mahmudov, M.N.

Kopylovich, M.F.C. Guedes da Silva, A.J.L. Pombeiro, *Coord. Chem. Rev.* 345 (2017) 54–72.

[86](a) B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629–1658. (b) V.A. Friese, D.G. Kurth, *Curr. Opin. Colloid Interface Sci.* 14 (2009) 81–93.

[87] J.N. Israelachvili, *Contemp. Phys.* 15 (1974) 159–178.

[88] R.E. Gillard, F.M. Raymo, J.F. Stoddart, *Chem.-Eur. J.* 3 (1997) 1933–1940.

[89] T. Steiner, *Angew. Chem. Int. Ed.* 41 (2002) 48–76. (b) A. Nangia, *CrystEngComm.* 4 (2002) 93. (c) L. Applegarth, A.E. Goeta, J.W. Steed, *Chem. Commun.* (2005) 2405.

[90] G.F. Swiegers, T.J. Malefetse, *J. Incl. Phenom. Macrocycl. Chem.* 40 (2001) 253–264.

[91] S. Leininger, B. Olenyuk, P.J. Stang, *Chem. Rev.* 100 (2000) 853–908.

[92] Lutz H. Gade, *Coordination Chemistry*, John Wiley & Sons, 2012.

[93] (a) M. Sánchez-Serratos, J. Raziel Álvarez, E. González-Zamora, I.A. Ibarra, *J. Mex. Chem. Soc.* 60 (2017). (b) M.-L. Tong, X.-M. Chen, in: *Mod. Inorg. Synth. Chem.* (2017) 189–217. (c) K.M. Fromm, J.L. Sagué, L. Mirolo, *Macromol. Symp.* 291–292 (2010) 75–83. (d) A.Y. Robin, K.M. Fromm, *Coord. Chem. Rev.* 250 (2006) 2127–2157.

[94] (a) D.A. Dickie, P.T.K. Lee, O.A. Labeodan, G. Schatte, N. Weinberg, A.R. Lewis, G.M. Bernard, R.E. Wasylishen, J.A.C. Clyburne, *Dalton Trans.* (2007) 2862. (b) P. Uznanski, J. Zakrzewska, F. Favier, S. Kazmierski, E. Bryszewska, *J. Nanoparticle Res.* 19 (2017) 121.

[95] (a) J.L. Sague, M. Meuwly, K.M. Fromm, *CrystEngComm.* 10 (2008) 1542. (b) A. Beheshti, V. Nobakht, L. Carlucci, D.M. Proserpio, C. Abrahams, *J. Mol.*

Struct. 1037 (2013) 236–241. (c) X.-W. Wu, F. Pan, D. Zhang, G.-X. Jin, J.-P. Ma, *CrystEngComm*. 19 (2017) 5864–5872.

[96] (a) X. Wang, C. Gong, N. Chen, G. Liu, H. Lin, J. Luan, *J. Coord. Chem.* 67 (2014) 3473–3483. (b) B. Notash, B. Rezaei Kheirkhah, *New J. Chem.* 42 (2018) 15014–15021. (c) M. Rancan, A. Carlotto, G. Bottaro, L. Armelao, *Inorganics* 7 (2019) 103. (d) N. Contreras-Pereda, P. Hayati, S. Suárez-García, L. Esrafil, P. Retailleau, S. Benmansour, F. Novio, A. Morsali, D. Ruiz-Molina, *Ultrason. Sonochem.* 55 (2019) 186–195.

[97] Stuart R. Batten, Suzanne M. Neville, David R. Turner. *Angew. Chem. Int. Ed.* 48 (2009) 4890–4891.

[98] (a) E. Loukopoulos, G.E. Kostakis, *J. Coord. Chem.* 71 (2018) 371–410. (b) C.-T. Chen, K.S. Suslick, *Coord. Chem. Rev.* 128 (1993) 293–322. (c) A. Morsali, L. Hashemi, John Wiley and sons (2017). (d) R. Mas-Ballesté, J. Gómez-Herrero, F. Zamora, *Chem. Soc. Rev.* 39 (2010) 4220. (e) W.L. Leong, J.J. Vittal *Chem. Rev.* 111 (2011) 688–764. (f) J.-Q. Liu, Z.-D. Luo, Y. Pan, A. Kumar Singh, M. Trivedi, A. Kumar, *Coord. Chem. Rev.* 406 (2020) 213145.

[99] Y.Y. Karabach, A.M. Kirillov, M. Haukka, M.N. Kopylovich, A.J.L. Pombeiro, *J. Inorg. Biochem.* 102 (2008) 1190–1194.

[100] S. Lympelopoulou, M. Papastergiou, M. Louloudi, C.P. Raptopoulou, V. Psycharis, C.J. Milios, J.C. Plakatouras, *Eur. J. Inorg. Chem.* (2014) 3638–3644.

[101] L. Mandal, S. Mandal, S. Mohanta, *New J. Chem.* 41 (2017) 4689–4701.

[102] M.A. Wani, A. Kumar, M.D. Pandey, R. Pandey, *Polyhedron* 126 (2017) 142–149.

[103] C.A. Downes, S.C. Marinescu, *J. Am. Chem. Soc.* 137 (2015) 13740–13743.

- [104] A.M. Kirillov, J.A.S. Coelho, M.V. Kirillova, M.F.C.G. da Silva, D.S. Nesterov, K.R. Gruenwald, M. Haukka, A.J.L. Pombeiro, *Inorg. Chem.* 49 (2010) 6390–6392.
- [105] G. Kumar, G. Kumar, R. Gupta, *RSC Adv.* 6 (2016) 21352–21361.
- [106] Y.K.N. Kuwamura, Takumi Konno, *Chem Commun.* 53 (2017) 846.
- [107] M. Liu, H.S. Quah, S. Wen, J. Wang, P.S. Kumar, G. Eda, J.J. Vittal, W. Ji, *J. Mater. Chem. C* 5 (2017) 2936–2941.
- [108] (a) Y.-B. Chen, J. Zhang, J.-K. Cheng, Y. Kang, Z.-J. Li, Y.-G. Yao, *Inorg. Chem. Commun.* 7 (2004) 1139–1141. (b) W.-W. Zhou, W. Zhao, B. Wei, F.-W. Wang, Y.-H. Chen, W.-Y. Fang, X. Zhao, *Inorg. Chim. Acta.* 386 (2012) 17–21. (c) N. Zhao, P. Liu, C.-X. An, T.-X. Wang, Z.-X. Lian, *Inorg. Chem. Commun.* 50 (2014) 97–100. (d) H. Zhao, D. Jia, J. Li, G.J. Moxey, C. Zhang, *Inorg. Chim. Acta.* 432 (2015) 1–12.
- [109] O.R. Evans, W. Lin, *Acc. Chem. Res.* 35 (2002) 511–522.
- [110] Q.-Y. Chen, Y. Li, F.-K. Zheng, W.-Q. Zou, M.-F. Wu, G.-C. Guo, A.-Q. Wu, J.-S. Huang, *Inorg. Chem. Commun.* 11 (2008) 969–971.
- [111] M. Nazarov, *Research and Reviews in Materials Science and Chemistry* 6 (2016) 41–74.
- [112] T. Jüstel, S. Möller, H. Winkler, W. Adam, *Luminescent Materials* (2012) 1–75.
- [113] C. Feldmann, T. Jüstel, C.R. Ronda, P.J. Schmidt, *Adv. Funct. Mater.* 13 (2003) 511–516.
- [114] (a) Y. Wu, G.-P. Yang, Y. Zhao, W.-P. Wu, B. Liu, Y.-Y. Wang, *Dalton Trans.* 44 (2015) 3271–3277. (b) J.-A. Hua, Y. Zhao, Y.-S. Kang, Y. Lu, W.-Y.

Sun, *Dalton Trans.* 44 (2015) 11524–11532. (c) S.-L. Li, X.-M. Zhang, *Inorg. Chem.* 53 (2014) 8376–8383.

[115] (a) J.-Q. Liu, B. Liu, Y.-Y. Wang, P. Liu, G.-P. Yang, R.-T. Liu, Q.-Z. Shi, S.R. Batten, *Inorg. Chem.* 49 (2010) 10422–10426. (b) W.-W. Sun, X.-B. Qian, C.-Y. Tian, E.-Q. Gao, *Inorg. Chim. Acta.* 362 (2009) 2744–2748. (c) Y.-Z. Tang, X.-S. Wang, T. Zhou, R.-G. Xiong, *Cryst. Growth Des.* 6 (2006) 11–13. (d) M. Ahmad, R. Das, J. Mrozinski, A. Bienko, P. Poddar, P.K. Bharadwaj, *CrystEngComm.* 16 (2014) 8523. (e) B. Ding, L. Yi, P. Cheng, D.-Z. Liao, S.-P. Yan, *Inorg. Chem.* 45 (2006) 5799–5803. (f) H.-J. Chen, Z.-W. Mao, S. Gao, X.-M. Chen, *Chem. Commun.* (2001) 2320–2321. [g] J.-T. Li, J. Tao, R.-B. Huang, L.-S. Zheng, T. Yuen, C.L. Lin, P. Varughese, J. Li, *Inorg. Chem.* 44 (2005) 4448–4450.

[116] L. Bogani, A. Vindigni, R. Sessoli, D. Gatteschi, *J. Mater. Chem.* 18 (2008) 4750.

[117] H.-L. Sun, Z.-M. Wang, S. Gao, *Coord. Chem. Rev.* 254 (2010) 1081–1100.

[118] (a) Y.-Z. Zheng, M.-L. Tong, W.-X. Zhang, X.-M. Chen, *Angew. Chem. Int. Ed.* 45 (2006) 6310–6314. (b) C. Papatriantafyllopoulou, S. Zartilas, M.J. Manos, C. Pichon, R. Clérac, A.J. Tasiopoulos, *Chem Commun.* 50 (2014) 14873–14876. (c) L. Chatelain, F. Tuna, J. Pécaut, M. Mazzanti, *Chem. Commun.* 51 (2015) 11309–11312. (d) M. Chen, H. Zhao, E.C. Sañudo, C.-S. Liu, M. Du, *Inorg. Chem.* 55 (2016) 3715–3717.

[119] M.A. Halcrow, ed., John Wiley & Sons Ltd, Oxford, UK, (2013).

[120] Y. Gomi, M. Takahashi, M. Takeda, M. Enomoto, T. Enoki, *J. Mater. Chem.* 1996 6(1) 119–121.

[121] C. Lochenie, K. Schötz, F. Panzer, H. Kurz, B. Maier, F. Puchtler, S. Agarwal, A. Köhler, B. Weber, *J. Am. Chem. Soc.* 140 (2018) 700–709.

[122] (a) G. Givaja, P. Amo-Ochoa, C.J. Gómez-García, F. Zamora, *Chem. Soc. Rev.* 41 (2012) 115–147. (b) H. Liu, Y. Wang, Z. Qin, D. Liu, H. Xu, H. Dong, W. Hu, *J. Phys. Chem. Lett.* 12 (2021) 1612–1630.

[123] (a) J.P. Collman, J.T. McDEVITT, G.T. Yee, M.B. Zisk, *Synth. met.* 15 (1986) 129–140. (b) J.P. Collman, J.T. McDevitt, G.T. Yee, C.R. Leidner, L.G. McCullough, W.A. Little, J.B. Torrance, *Proc. Natl. Acad. Sci.* 83 (1986) 4581–4585. (c) J.P. Collman, J.T. McDevitt, C.R. Leidner, G.T. Yee, J.B. Torrance, W.A. Little, *J. Am. Chem. Soc.* 109 (1987) 4606–4614. (d) M. Hanack, S. Deger, A. Lange, *Coord. Chem. Rev.* 83 (1988) 115–136.

[124] D. Sun, R. Cao, J. Weng, M. Hong, Y. Liang, *J. Chem. Soc. Dalton Trans.* (2002) 291.

Chapter 2

Unusual pentagonal-bipyramidal oxovanadium(V) complexes having five- and six-membered chelate rings: Syntheses, structures and properties[§]

2.1. Abstract

Reactions of bis(acetylacetonato)oxovanadium(IV) [VO(acac)₂] with isolated or in-situ generated α -diketone bis(*para*-R-benzoylhydrazones) (H₂Lⁿ (n = 1–6), where 2 H represent the two dissociable amide protons) in methanol or chloroform-methanol (1:3) mixture afford six novel oxovanadium(V) complexes of formula [VO(acac)(Lⁿ)] (**1–6**) in 51–64% yields. All the complexes have been characterized by elemental analysis, mass spectrometric, solution electrical conductivity, various spectroscopic (IR, UV–Vis, and ¹H NMR) and cyclic voltammetric measurements. They are diamagnetic and non-electrolytes. Molecular structures of all six complexes have been determined by single crystal X-ray crystallography. The metal center in each complex is in a distorted pentagonal-bipyramidal N₂O₅ coordination sphere. The fused 5,5,5-membered chelate rings forming ON₂O-donor (Lⁿ)^{2–} and one of the acetylacetonate-O form a N₂O₃ pentagonal plane around the vanadium atom, while the second acetylacetonate-O and the oxo atom occupy the two axial positions. In the crystal lattice, the complexes form one-dimensional chain-, ladder- and ribbon-like supramolecular structures via various types of intermolecular non-covalent interactions such as trifurcated O–H $\cdots$ (O,O,O), bifurcated C–H $\cdots$ O $\cdots$ H–C and C–H $\cdots$ (O,O), simple C–H $\cdots$ O, π – π , C–H $\cdots$ π and O $\cdots$ O interactions. All the complexes are redox active and display a quasi-reversible vanadium(V) to vanadium(IV) reduction in the potential range –0.80 to –0.92 V (vs. Ag/AgCl).

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2.2. Introduction

Generally, the ionic radius of a metal ion and the nature of the coordinating ligands play crucial roles in deciding the coordination number of the metal ion in its complex [1–5]. Coordination number more than six is very uncommon in complexes of 3d transition metal ions, particularly of 3d higher-valent transition metal ions. The primary reason for the scarcity of such 3d metal ion complexes is the small ionic radius of the metal center and hence its inability to accommodate more than six coordinating atoms due to steric congestion. Examples of higher coordinated species are mostly with only small monoatomic ligands and sometimes with one or two chelating ligands and remaining small monoatomic ligands. Discrete mononuclear heptacoordinated complexes with specially designed pentadentate macrocyclic [1,6] or hexadentate ethylenediamine tetraacetic acid type primary ligands [2,7,8] and monodentate ancillary ligands are also reported. Pentavalent vanadium, one of the early 3d metal ions, has an ionic radius of 0.54 Å [9]. There are several reports on structurally characterized heptacoordinated pentagonal-bipyramidal multi-ligand complexes of oxovanadium(V) [10–21]. However, essentially all these complexes contain at least one sterically less hindering three-membered chelate ring forming N,O-donor hydroxyamido/oximato ligand [10–14] or bidentate peroxo group [15–20]. Tris(*N,N*-diethyldithiocarbamato) oxovanadium(V) is the rare example which does not have any three-membered chelate ring [21]. It has three four-membered chelate rings formed by the three S,S-coordinating *N,N*-diethyldithiocarbamates. To the best of our knowledge, there is no report on pentagonal-bipyramidal oxovanadium(V) complexes with five- and six-membered chelate ring forming ligands. Herein, we report a series of six such ternary oxovanadium(V) complexes of general molecular formula $[\text{VO}(\text{acac})(\text{L}^n)]$ where $(\text{acac})^-$ and $(\text{L}^n)^{2-}$ represent the 6-membered chelate ring forming acetylacetonate and the fused 5,5,5-membered chelate rings forming α -diketone bis(*para*-*R*-benzoylhydrazonates), respectively (Chart 1). Molecular structures of all the complexes have been confirmed by

single crystal X-crystallographic studies. Synthesis, characterization, physical properties and structures of these complexes have been described in the following sections.

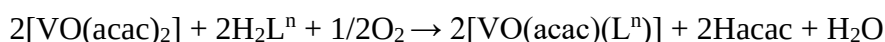
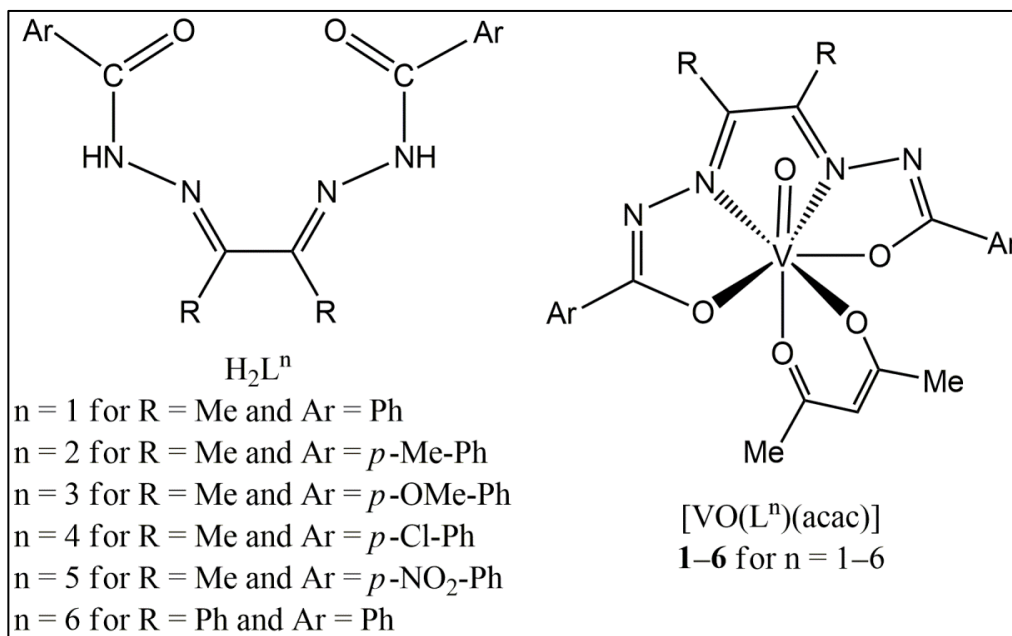


Chart 1. Chemical structure diagrams of α -diketone bis(*p*-R-benzoylhydrazones) (H_2L^n) and the complexes $[VO(acac)(L^n)]$ derived therefrom.

2.3. Experimental

2.3.1. Materials

The Schiff bases H_2L^1 and H_2L^6 were prepared in 70–80% yields by condensation reactions of two mole equivalents of benzoylhydrazine with one mole equivalent of the corresponding α -diketones (diacetyl for H_2L^1 and benzil for H_2L^6) by following reported methods [22,23]. The remaining Schiff bases H_2L^{2-5} were generated in-situ from diacetyl and the appropriate *para*-R-benzoylhydrazines. Bis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2]$, was synthesized by using a literature procedure [24].

2.3.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used for the microanalytical (CHN) measurements. High resolution mass spectra were recorded with a Bruker Maxis (ESI-TOF analyzer) spectrometer. A Sherwood Scientific balance was used for room temperature magnetic susceptibility measurements. The solution electrical conductivities were measured with the help of a Digisun DI-909 conductivity meter. The infrared spectra were recorded on a Bruker TENSOR II FT-IR spectrophotometer. A Jasco-V-770 UV-Vis spectrophotometer was employed to collect the electronic spectra. The ^1H -NMR (400 MHz) spectra were recorded on a Bruker NMR spectrometer. Cyclic voltammetric measurements were performed with the help of a CH Instruments model 620A electrochemical analyzer.

2.3.3. Synthesis of $[\text{VO}(\text{acac})(\text{L}^1)]$ (1)

A methanol solution (8 ml) of $[\text{VO}(\text{acac})_2]$ (100 mg, 0.38 mmol) was added to a suspension of H_2L^1 (122 mg, 0.38 mmol) in methanol (7 ml) and the mixture was boiled under reflux for 6 h. It was then cooled to room temperature (298 K). The complex precipitated as a brown solid was collected by filtration and dried in air. Yield: 110 mg (60%). Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{N}_4\text{O}_5\text{V}$ (%): C, 56.79; H, 4.77; N, 11.52. Found: C, 56.68; H, 4.73; N, 11.62. HRMS in CH_2Cl_2 m/z found (calcd) for $[\text{M}+\text{H}]^+$: 487.1186 (487.1186). Selected IR bands: $\nu(\text{cm}^{-1}) = 1589 (\text{C}=\text{N}), 988 (\text{V}=\text{O})$. UV-Vis in CH_3CN : λ_{max} (nm) (ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$)) = 515^{sh} (3.1), 436 (5.4), 296 (18.1), 231 (23.5). ^1H NMR in CDCl_3 : δ (ppm) (J (Hz)) = 8.12 (8, 2) (dd, 4H, *ortho* Hs of benzoyl Ph groups), 7.52 (8, 2) (tt, 2H, *para* Hs of benzoyl Ph groups), 7.44 (8) (dd $\rightarrow$ t, 4H, *meta* Hs of benzoyl Ph groups), 5.42 (s, 1H, methine H), 2.60 (s, 6H, protons of the two Me groups of the α -diketimine moiety), 2.32 (s, 3H, protons of MeC(O) of $(\text{acac})^-$ at *cis* to the oxo atom), 1.73 (s, 3H, protons of MeC(O) of $(\text{acac})^-$ at *trans* to the oxo atom). CV in CH_3CN : $E_{1/2}$ (V) (ΔE_p (mV)) = -0.88 (120).

2.3.4. Synthesis of [VO(acac)(L²)] (2)

A methanol solution (10 ml) of [VO(acac)₂] (53 mg, 0.2 mmol) was added to a solution of diacetyl (17 mg, 0.2 mmol) and *para*-methylbenzoylhydrazine (60 mg, 0.4 mmol) in methanol (10 ml) and the mixture was boiled under reflux for 4 h. The reaction mixture was then kept at low temperature (5 °C). The dark brown crystalline material separated in about one week was collected by filtration and dried in air. Yield: 60 mg (58%). Anal. Calcd for C₂₅H₂₇N₄O₅V (%): C, 58.37; H, 5.29; N, 10.89. Found C, 58.26; H, 5.23; N, 10.82. HRMS in CH₂Cl₂ *m/z* found (calcd) for [M+H]⁺, [M+Na]⁺, [M+K]⁺: 515.1479 (515.1499), 537.1319 (537.1319) and 553.1045 (553.1058). Selected IR bands: ν (cm⁻¹) = 1583 (C=N), 949 (V=O). UV–Vis in CH₃CN: $\lambda_{\max}$ (nm) (ϵ (10³ M⁻¹ cm⁻¹)) = 525^{sh} (3.1), 440 (6.0), 297 (17.1), 233 (23.6). ¹H NMR in CDCl₃: δ (ppm) (*J* (Hz)) = 8.01 (8) (d, 4H, *ortho* Hs of *para*-methylbenzoyl groups), 7.23 (8) (d, 4H, *meta* Hs of *para*-methylbenzoyl groups), 5.39 (s, 1H, s, methine H), 2.58 (s, 6H, protons of the 2 Me groups of the α -diketimine moiety), 2.43 (s, 6H, protons of the two Me groups at *para* positions of the benzoyl moieties), 2.31 (s, 3H, protons of MeC(O) of (acac)⁻ at *cis* to the oxo atom), 1.71 (s, 3H, protons of MeC(O) of (acac)⁻ at *trans* to the oxo atom). CV in CH₃CN: *E*_{1/2} (V) (ΔE_p (mV)) = -0.89 (120 mV).

2.3.5. Synthesis of [VO(acac)(L³)] (3)

This complex has been synthesized in methanolic medium in 62% yield by following the same procedure as described above for **2** using [VO(acac)₂], diacetyl and *para*-methoxybenzoylhydrazine in 1:1:2 mole ratio. Anal. Calcd for C₂₅H₂₇N₄O₇V (%): C, 54.95; H, 4.98; N, 10.25. Found C, 54.85; H, 5.06; N, 10.18. HRMS in CH₂Cl₂ *m/z* found (calcd) for [M+H]⁺, [M+Na]⁺, [M+K]⁺: 547.1386 (547.1398), 569.1215 (569.1217), 585.0944 (585.0956). Selected IR bands: ν (cm⁻¹) = 1602 (C=N), 948 (V=O). UV–Vis in CH₃CN: $\lambda_{\max}$ (nm) (ϵ (10³ M⁻¹ cm⁻¹)) = 530^{sh} (1.2), 447 (2.5), 293^{sh} (10.3), 242 (22.3). ¹H NMR in CDCl₃: δ (ppm) (*J* (Hz)) = 8.07 (9) (d, 4H, *ortho* Hs of *para*-methoxybenzoyl

groups), 6.94 (9) (d, 4H, *meta* Hs of *para*-methoxybenzoyl-benzoyl groups), 5.39 (s, 1H, s, methine H), 3.88 (s, 6H, protons of the 2 OMe groups at *para* positions of the benzoyl moieties), 2.56 (s, 6H, protons of the two Me groups of the α -diketimine moiety), 2.30 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.72 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH₃CN: $E_{1/2}$ (V) (ΔE_p (mV)) = −0.92 (120).

2.3.6. Synthesis of [VO(acac)(L⁴)] (4)

The same procedure described for **2** has been used to synthesize **4** in methanolic medium in 64% yield using [VO(acac)₂], diacetyl and *para*-chlorobenzoylhydrazine in 1:1:2 mole ratio. Anal. Calcd for C₂₃H₂₁Cl₂N₄O₅V (%): C, 49.75; H, 3.81; N, 10.09. Found: C, 49.68; H, 3.76; N, 10.16. HRMS in CH₂Cl₂ m/z found (calcd) for [M+H]⁺, [M+Na]⁺, [M+K]⁺: 555.0383 (555.0407), 577.0227 (577.0226), 592.9956 (592.9966). Selected IR bands: ν (cm^{−1}) = 1582 (C=N), 949 (V=O). UV–Vis in CH₃CN: $\lambda_{\max}$ (nm) (ϵ (10³ M^{−1} cm^{−1})) = 515^{sh} (3.5), 434 (6.6), 295 (17.5), 231 (21.3). ¹H NMR in CDCl₃: δ (ppm) (J (Hz)) = 8.05 (9) (d, 4H, *ortho* Hs of *para*-chlorobenzoyl groups), 7.41 (9) (d, 4H, *meta* Hs of *para*-chlorobenzoyl groups), 5.42 (s, 1H, s, methine H), 2.59 (s, 6H, protons of the two Me groups of the α -diketimine moiety), 2.31 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.74 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH₃CN: $E_{1/2}$ (V) (ΔE_p (mV)) = −0.85 (110).

2.3.7. Synthesis of [VO(acac)(L⁵)] (5)

This complex has also been synthesized in methanolic medium in 60% yield from [VO(acac)₂], diacetyl and *para*-nitrobenzoylhydrazine taken in 1:1:2 mole ratio by following the same procedure used for **2**. Anal. Calcd for C₂₃H₂₁N₆O₉V (%): C, 47.93; H, 3.67; N, 14.58. Found C, 47.85; H, 3.62; N, 14.65. HRMS in CH₂Cl₂ m/z found (calcd) for [M+H]⁺, [M+Na]⁺: 577.0889 (577.0888), 599.0708 (599.0707). Selected IR bands: ν (cm^{−1}) = 1589 (C=N), 952 (V=O), 1520 and 1342 (NO₂). UV–Vis in CH₃CN: $\lambda_{\max}$ (nm) (ϵ (10³ M^{−1} cm^{−1})) = 515^{sh} (3.5), 434 (6.6), 295 (17.5), 231 (21.3).

$\text{cm}^{-1}) = 515^{\text{sh}}$ (2.0), 440 (3.2), 294 (16.0), 252 (16.0). ^1H NMR in CDCl_3 : δ (ppm) (J (Hz)) = 8.34–8.23 (AA'BB' m, 8H, *ortho* and *meta* Hs of *para*-nitrobenzoyl groups), 5.47 (s, 1H, s, methine H), 2.66 (s, 6H, protons of the two Me groups of the α -diketimine moiety), 2.34 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.76 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH_3CN : E_{pc} (V) = −0.87.

2.3.8. Synthesis of $[\text{VO}(\text{acac})(\text{L}^6)]$ (6)

A solution of H_2L^6 (100 mg, 0.22 mmol) in chloroform (5 ml) was added to a solution of $[\text{VO}(\text{acac})_2]$ (60 mg, 0.23 mmol) in methanol (15 ml) and the mixture was boiled under reflux for 10 h. After reducing the volume to 10 ml the reaction mixture was kept at low temperature (5 °C). The complex separated as a brown solid was collected by filtration and dried in air. Yield: 70 mg (51%). Anal. Calcd for $\text{C}_{33}\text{H}_{27}\text{N}_4\text{O}_5\text{V}$ (%): C, 64.92; H, 4.46; N, 9.18. Found: C; 64.85 H; 4.41, N; 9.23. HRMS in CH_2Cl_2 m/z found (calcd) for $[\text{M}+\text{H}]^+$, $[\text{M}+\text{Na}]^+$, $[\text{M}+\text{K}]^+$; 611.1499 (611.1499), 633.1320 (633.1319), 649.1041 (649.1058). Selected IR bands: ν (cm^{-1}) = 1583 (C=N), 950 (V=O). UV–Vis in MeCN: λ_{max} (nm) (ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$)) = 495 (3.2), 375 (6.3), 287 (18.0), 232 (20.2). ^1H NMR in CDCl_3 : δ (ppm) (J (Hz)) = 8.02 (8, 3) (dd, 4H, *ortho* Hs of benzoyl Ph groups), 7.50–7.45 (m, 6H, Hs of Ph groups), 7.42–7.33 (m, 10H, Hs of Ph groups), 5.47 (s, 1H, methine H), 2.36 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.81 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH_3CN : $E_{1/2}$ (V) (ΔE_{p} (mV)) = −0.80 (140).

2.3.9. X-ray crystallography

Single crystals of [VO(acac)(L¹)] (**1**) and [VO(acac)(L⁶)] (**6**) were grown by slow evaporation of the corresponding methanol solutions. Single crystals of [VO(acac)(L²⁻⁵)] (**2-5**) were collected from the crystalline products obtained from their synthetic reaction mixtures. The first complex crystallizes as 1·0.25MeOH, while each of **2-6** crystallizes as it is without any solvent molecule. A BRUKER D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite monochromated Mo $K\alpha$ Radiation ($\lambda = 0.71073 \text{ \AA}$) was used for unit cell determination and intensity data collection at 298 K for each of 1·0.25MeOH and **2-6**. Data collection, integration, reduction and absorption correction were performed using the APEX3 software package [25]. The structures were solved by direct method and refined on F^2 by full matrix least-squares procedures. In the case of 1·0.25MeOH, the methanol C and O atoms having partial occupancies were refined isotropically with geometric restraint. The remaining non-hydrogen atoms of 1·0.25MeOH and all the non-hydrogen atoms of **2-6** were refined with anisotropic thermal parameters. The hydrogen atoms were included at idealized positions using a riding model. The SHELX-97 programs [26] provided in the WinGX software suite [27] were used for structure solution and refinement. The Mercury package [28] was used to search for intermolecular non-covalent interactions and molecular graphics. Selected crystallographic data for 1·0.25MeOH and **2-6** is summarized in tables 1 and 2. Detailed X-ray crystallographic data for 1·0.25MeOH, **2-5** and **6** have been deposited with the Cambridge crystallographic data center under the deposition numbers 1836523, 1842288–1842291 and 1836524 respectively.

Table 1 Selected crystallographic data

Complex	1·0.25MeOH	2	3
Chemical formula	C _{23.25} H ₂₄ N ₄ O _{5.25} V	C ₂₅ H ₂₇ N ₄ O ₅ V	C ₂₅ H ₂₇ N ₄ O ₇ V
Formula weight	494.40	514.45	546.45
Crystal system	Triclinic	Triclinic	Triclinic
Space Group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.2071(8)	7.9483(3)	7.8843(4)
<i>b</i> (Å)	14.6476(15)	12.3434(4)	12.5167(7)
<i>c</i> (Å)	20.201(2)	13.6255(4)	13.5651(7)
α (°)	89.902(4)	103.713(1)	99.478(2)
β (°)	84.279(4)	96.219(1)	94.723(2)
γ (°)	84.278(4)	96.823(1)	95.263(2)
<i>V</i> (Å ³)	2404.3(4)	1276.51(7)	1308.35(12)
<i>Z</i>	4	2	2
ρ (g cm ⁻³)	1.366	1.338	1.387
μ (mm ⁻¹)	0.454	0.430	0.430
Reflns collected	86415	47625	46719
Reflns unique	8443	5235	5330
Reflns [<i>I</i> ≥ 2σ(<i>I</i>)]	6130	4343	4526
Data / restr. / param.	8443 / 1 / 612	5235 / 0 / 322	5330 / 0 / 340
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0629, 0.1566	0.0391, 0.0997	0.0380, 0.0978
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0926, 0.1702	0.0518, 0.1057	0.0492, 0.1040
GOF on <i>F</i> ²	1.071	1.049	1.083
Largest diff. peak / hole (e Å ⁻³)	1.035 / -0.407	0.255 / -0.247	0.401 / -0.324

Table 2 Selected crystallographic data

Complex	4	5	6
Chemical formula	C ₂₃ H ₂₁ N ₄ O ₅ Cl ₂ V	C ₂₃ H ₂₁ N ₆ O ₉ V	C ₃₃ H ₂₇ N ₄ OV
Formula weight	555.28	576.40	610.53
Crystal system	Triclinic	Monoclinic	Triclinic
Space Group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	7.1920(4)	11.6717(10)	11.1240(4)
<i>b</i> (Å)	11.0218(6)	7.0841(5)	12.3131(4)
<i>c</i> (Å)	16.3414(9)	30.637(3)	13.4539(5)
α (°)	81.987(2)	90	113.527(1)
β (°)	78.321(2)	94.814(3)	108.436(1)
γ (°)	84.245(2)	90	98.184(2)
<i>V</i> (Å ³)	1252.69(12)	2524.2(3)	1524.56(9)
<i>Z</i>	2	4	2
ρ (g cm ⁻³)	1.472	1.517	1.330
μ (mm ⁻¹)	0.651	0.458	0.372
Reflns collected	33840	40278	49430
Reflns unique	5098	5208	5347
Reflns [<i>I</i> ≥ 2σ(<i>I</i>)]	4387		4741
Data / restr. / param.	5098 / 0 / 320	5208 / 0 / 356	5347 / 0 / 388
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0409, 0.1073	0.0504, 0.1270	0.0475, 0.1298
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0490, 0.1129	0.0852, 0.1457	0.0542, 0.1351
GOF on <i>F</i> ²	1.052	1.074	1.092
Largest diff. peak / hole (e Å ⁻³)	0.583 / -0.410	0.504 / -0.349	1.191 / -0.385

2.4. Results and discussion

2.4.1. Synthesis and characterization

Six oxovanadium(V) complexes (**1–6**) having the general molecular formula $[\text{VO}(\text{acac})(\text{L}^n)]$ were synthesized in moderate to good yields (51–64%) by reacting equimolar amounts of $[\text{VO}(\text{acac})_2]$ with the corresponding isolated or in-situ generated tetradentate α -diketone bis(*para*-R-benzoylhydrazones) (H_2L^n , where $n = 1–6$) (Chart 1). The reactions were carried out aerobically under reflux conditions in methanol for **1–5** and in chloroform-methanol (1:3) mixture for **6**. The elemental (CHN) analysis data of all the complexes are in good agreement with their molecular formulas. The ESI mass spectra of **1–6** recorded in dichloromethane confirms their molecular formulas. The spectrum of **1** shows $[\text{M}+\text{H}]^+$ as the only major peak. On the other hand, the spectra of **2–4** and **6** display three prominent peaks corresponding to $[\text{M}+\text{H}]^+$, $[\text{M}+\text{Na}]^+$ and $[\text{M}+\text{K}]^+$. The spectrum of **6** is depicted in Fig. 1. In contrast, **5** displays two major peaks due to the $[\text{M}+\text{H}]^+$ and $[\text{M}+\text{Na}]^+$ ions. The complexes are dark brown in color. The oxygen in air is the most likely oxidant for the oxidation of vanadium(IV) to vanadium(V) during their synthesis from $[\text{VO}(\text{acac})_2]$.

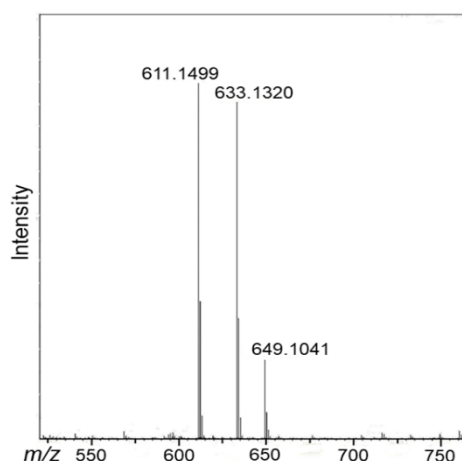


Fig. 1. ESI mass spectrum of $[\text{VO}(\text{acac})(\text{L}^6)]$.

2.4.2. Description of X-ray molecular structures

Each of $[\text{VO}(\text{acac})(\text{L}^1) \cdot 0.25\text{MeOH}]$ (**1**·0.25MeOH), $[\text{VO}(\text{acac})(\text{L}^{2-4})]$ (**2–4**) and $[\text{VO}(\text{acac})(\text{L}^6)]$ (**6**) crystallize in the triclinic space group $P\bar{1}$, while $[\text{VO}(\text{acac})(\text{L}^5)]$ (**5**) crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of **1**·0.25MeOH contains two independent complex molecules and a methanol molecule with half occupancy. On the other hand, the asymmetric unit of each of **2–6** contains one complete molecule of the corresponding complex. The perspective views of the asymmetric unit of **1**·0.25MeOH is illustrated in Fig.2 and $[\text{VO}(\text{acac})(\text{L}^{2-6})]$ six structures are illustrated in Figs. 3, 4 and 5.

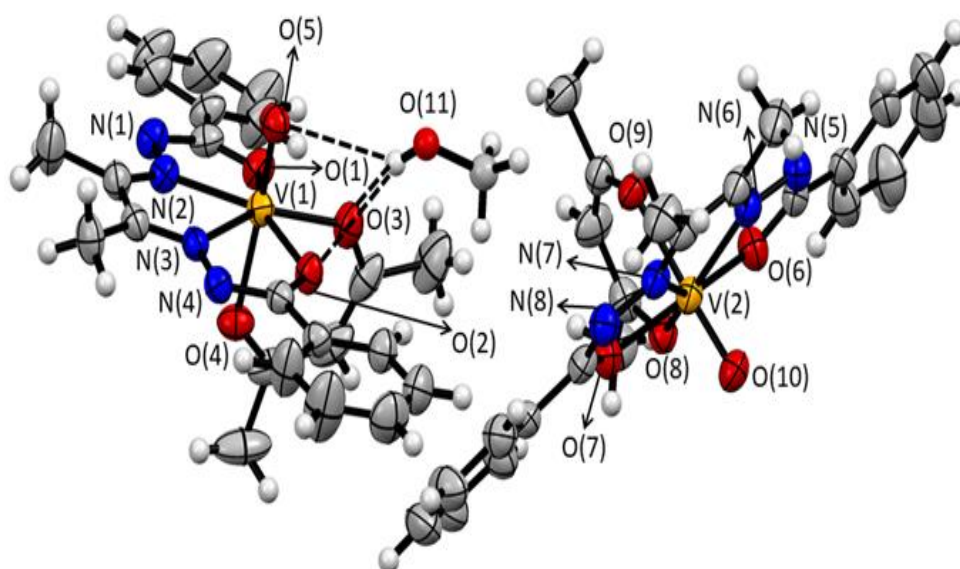


Fig. 2. The asymmetric unit of $[\text{VO}(\text{acac})(\text{L}^1)] \cdot 0.25\text{MeOH}$ (**1**·0.25MeOH). The non-hydrogen atoms are shown by their 40% probability thermal ellipsoids and the carbon atoms are not labeled for clarity.

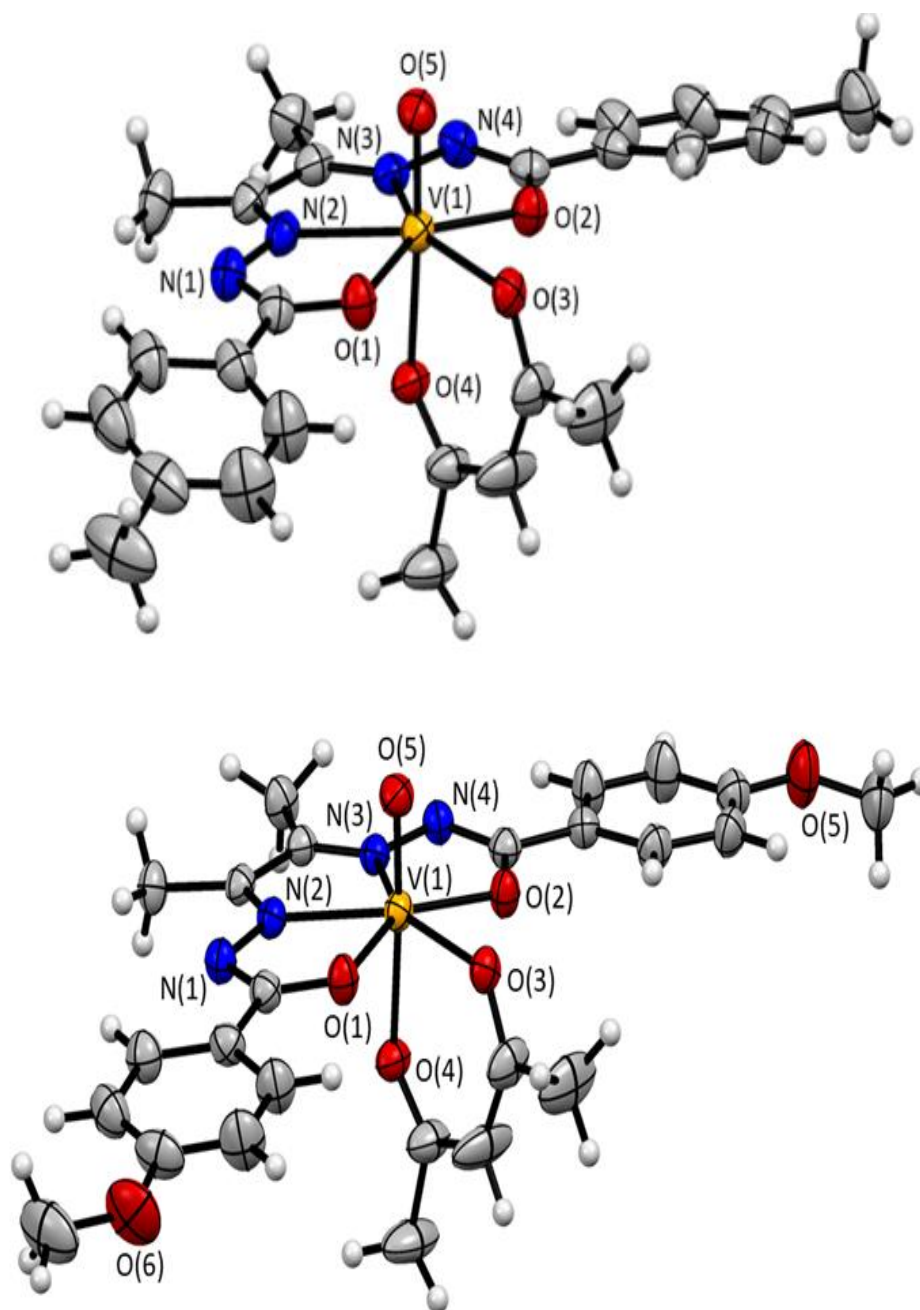


Fig. 3. Perspective views of the molecular structures of $[\text{VO}(\text{acac})(\text{L}^2)]$ (**2**) (top) and $[\text{VO}(\text{acac})(\text{L}^3)]$ (**3**) (bottom). For all structures, thermal ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level and only the non-carbon atoms are labeled for clarity.

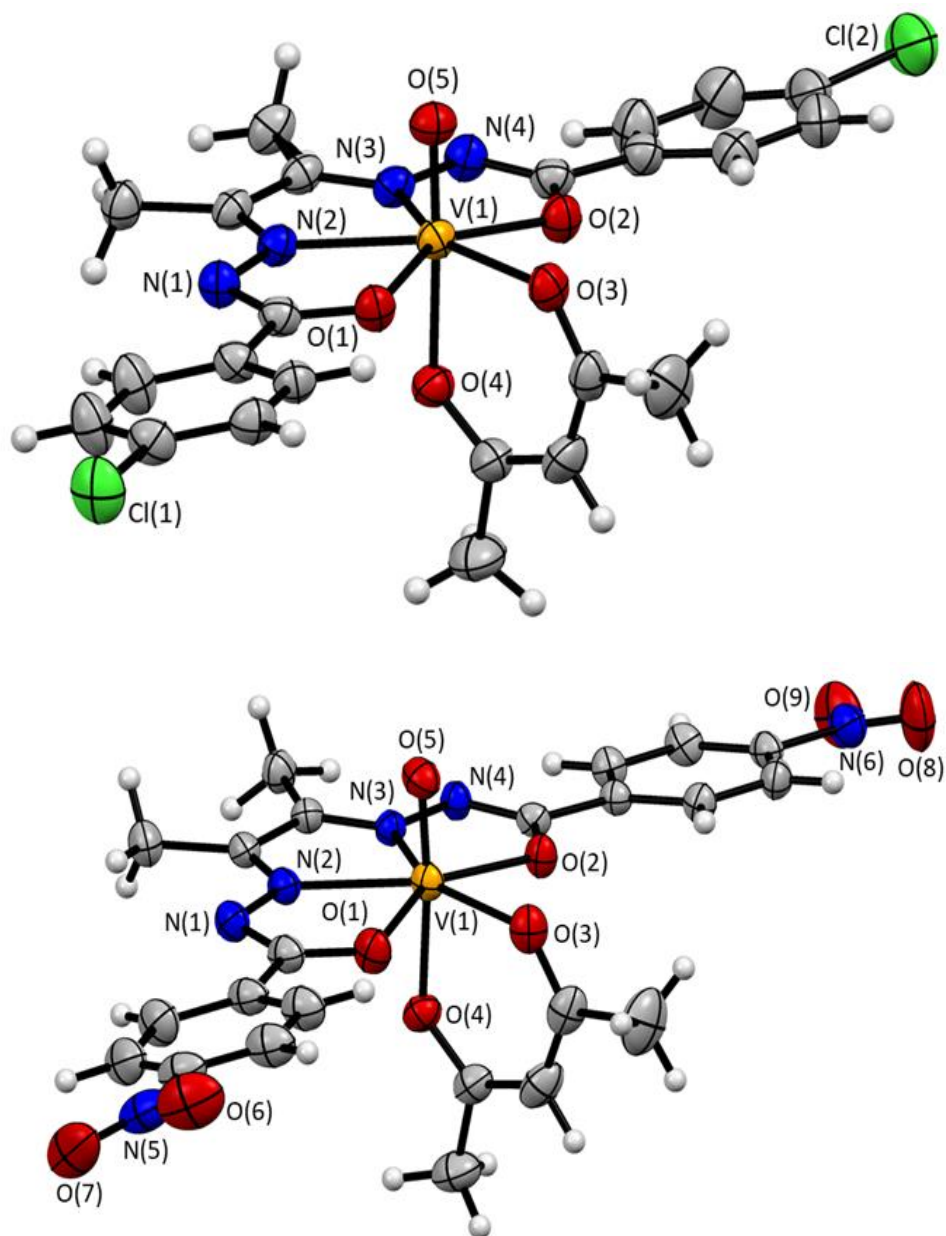


Fig. 4. Perspective views of the molecular structures of $[\text{VO}(\text{acac})(\text{L}^4)]$ (**4**) (top) and $[\text{VO}(\text{acac})(\text{L}^5)]$ (**5**) (bottom). Thermal ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level for **4** and non-hydrogen atoms are drawn at the 30% probability level for **5** and only the non-carbon atoms are labeled for clarity.

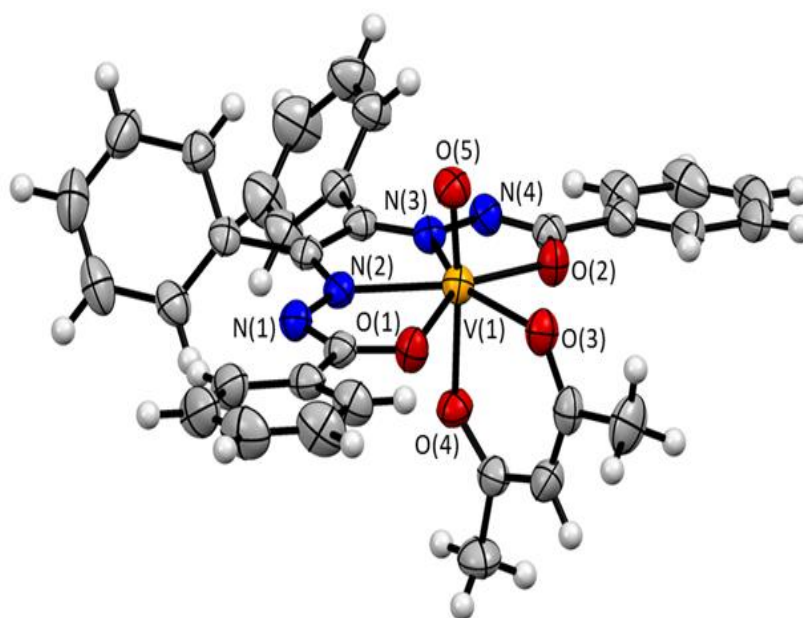


Fig. 5. Molecular structures of and $[\text{VO}(\text{acac})(\text{L}^6)](\mathbf{6})$. The thermal ellipsoids are at 40% probability level. Only the non-carbon atoms are labeled for clarity.

The bond lengths and angles associated with the metal center in $\mathbf{1} \cdot 0.25\text{MeOH}$ are listed in Table 3, while those for $\mathbf{2}$ – $\mathbf{6}$ are given in Table 4. Very similar geometric parameters of the two complex molecules (Table 3) present in the asymmetric unit of $\mathbf{1} \cdot 0.25\text{MeOH}$ indicate that structurally they are essentially identical. In each of $\mathbf{1}$ – $\mathbf{6}$, the metal center is in pentagonal-bipyramidal coordination environment. The tetradentate ligand $(\text{L}^n)^{2-}$ coordinates the metal center through the two amidate-O and two azomethine-N atoms and forms fused 5,5,5-membered chelate rings. The ON_2O -donor $(\text{L}^n)^{2-}$ and one of the two O-atoms of the 6-membered chelate ring forming $(\text{acac})^-$ assemble a N_2O_3 pentagonal plane (rms deviations: 0.003–0.035 Å) around the metal atom. The second O-atom of $(\text{acac})^-$ and the oxo atom satisfy the two axial positions and complete the N_2O_5 pentagonal-bipyramidal coordination sphere of the vanadium center. In each of the six complex molecules, the metal atom is slightly shifted (by ~ 0.17 Å) from the pentagonal plane towards the axial oxo atom. The whole of $(\text{L}^n)^{2-}$ moiety in $\mathbf{1}$ – $\mathbf{5}$ is reasonably planar (rms deviations: 0.10–0.23 Å). However, in $\mathbf{6}$, excluding the C-atoms of the two phenyl groups

of the α -diketimine fragment, the remaining atoms including the two benzoyl phenyl rings of $(L^6)^{2-}$ are only satisfactorily planar (rms deviation: 0.11 Å). The dihedral angles between this plane and the α -diketimine phenyl ring planes are 52.79(9) and 48.17(9)°. The dihedral angle between the α -diketimine phenyl ring planes is 58.29(12)°. In all of **1–6**, the *trans* O=V–O(acetate) bond angle (172.83(9)–175.94(13)°) (Tables 3 and 4) is somewhat shorter than the ideal value of 180°. The chelate bite angles formed by $(L^n)^{2-}$ and $(acac)^-$ are unexceptional. The C–O and the C–N bond lengths of the two amidate ($-N=C(O^-)-$) fragments of $(L^n)^{2-}$ in **1–6** are in the ranges 1.278(5)–1.294(2) and 1.295(5)–1.313(3) Å, respectively. These values are comparable with the corresponding values reported for amidate-O coordinated complexes [22,23,29–34]. The remaining intraligand bond parameters for $(L^n)^{2-}$ are unexceptional [22,23,29]. The V=O bond length (Tables 3 and 4) in each of **1–6** is comparable with that found in oxovanadium(V) complexes reported earlier [30–37]. In all six structures, the axial V–O bond is noticeably longer than the three equatorial V–O bonds due to the *trans* effect of the oxo atom (Tables 3 and 4). Between the two O-atoms of $(acac)^-$, O(3) and O(4), O(4) is at *trans* to the oxo atom, while O(3) is at *cis* to the oxo atom. The V–O(3) bond length is ~0.1 Å shorter than the V–O(4) bond length. In the O(3)CC(H)CO(4) fragment, at the O(3) side the O–C and C–C(H) bond lengths are ~0.01 longer and shorter than the corresponding bond lengths at the O(4) side. These intra-acetylacetonate bonds lengths and the short V–O(3) bond indicate that the negative charge is somewhat localized at the O(3) atom. In general, all the V–O and the V–N bond lengths in **1–6** are within the ranges observed for oxovanadium(V) complexes with ligands having similar coordinating atoms [30–37].

Table 3 Selected bond parameters (Å and °) for [VO(acac)(L¹)]·0.25MeOH

Molecule 1			
V(1)–O(1)	2.004(3)	V(1)–O(2)	2.024(3)
V(1)–O(3)	1.988(3)	V(1)–O(4)	2.073(3)
V(1)–O(5)	1.578(3)	V(1)–N(2)	2.136(3)
V(1)–N(3)	2.137(3)		
O(1)–V(1)–O(2)	146.23(11)	O(1)–V(1)–O(3)	73.24(11)
O(1)–V(1)–O(4)	85.98(11)	O(1)–V(1)–O(5)	96.56(13)
O(1)–V(1)–N(2)	70.84(12)	O(1)–V(1)–N(3)	139.92(12)
O(2)–V(1)–O(3)	73.94(11)	O(2)–V(1)–O(4)	85.25(11)
O(2)–V(1)–O(5)	94.30(14)	O(2)–V(1)–N(2)	140.47(11)
O(2)–V(1)–N(3)	70.86(11)	O(3)–V(1)–O(4)	88.15(13)
O(3)–V(1)–O(5)	95.61(14)	O(3)–V(1)–N(2)	143.83(12)
O(3)–V(1)–N(3)	144.26(12)	O(4)–V(1)–O(5)	175.94(13)
O(4)–V(1)–N(2)	85.32(12)	O(4)–V(1)–N(3)	83.02(11)
O(5)–V(1)–N(2)	92.50(14)	O(5)–V(1)–N(3)	93.01(13)
N(2)–V(1)–N(3)	69.92(12)		
Molecule 2			
V(2)–O(6)	2.018(3)	V(2)–O(7)	1.994(3)
V(2)–O(8)	2.003(3)	V(2)–O(9)	2.094(3)
V(2)–O(10)	1.590(3)	V(2)–N(6)	2.137(4)
V(2)–N(7)	2.143(3)		
O(6)–V(2)–O(7)	145.81(12)	O(6)–V(2)–O(8)	72.74(11)
O(6)–V(2)–O(9)	87.10(12)	O(6)–V(2)–O(10)	94.46(14)
O(6)–V(2)–N(6)	71.34(13)	O(6)–V(2)–N(7)	141.19(13)
O(7)–V(2)–O(8)	73.35(11)	O(7)–V(2)–O(9)	87.30(12)
O(7)–V(2)–O(10)	94.56(14)	O(7)–V(2)–N(6)	140.51(13)
O(7)–V(2)–N(7)	71.02(12)	O(8)–V(2)–O(9)	87.64(11)
O(8)–V(2)–O(10)	98.29(14)	O(8)–V(2)–N(6)	142.72(13)
O(8)–V(2)–N(7)	143.37(12)	O(9)–V(2)–O(10)	174.06(14)
O(9)–V(2)–N(6)	80.93(12)	O(9)–V(2)–N(7)	82.48(12)
O(10)–V(2)–N(6)	94.12(14)	O(10)–V(2)–N(7)	92.78(14)
N(6)–V(2)–N(7)	70.13(14)		

Table 4 Selected bond parameters (Å and °) for [VO(acac)(L²⁻⁶)] (2–6)

Complex	2	3	4	5	6
V(1)–O(1)	2.0085(15)	2.0045(14)	2.0297(16)	2.0369(19)	2.0165(18)
V(1)–O(2)	2.0162(14)	2.0142(14)	2.0310(16)	2.022(2)	2.0072(18)
V(1)–O(3)	2.0013(13)	2.0051(13)	1.9862(15)	1.971(2)	1.9895(18)
V(1)–O(4)	2.0953(13)	2.1026(14)	2.0861(16)	2.078(2)	2.0983(18)
V(1)–O(5)	1.5921(14)	1.5909(14)	1.5897(16)	1.590(2)	1.5880(19)
V(1)–N(2)	2.1396(16)	2.1389(16)	2.1513(18)	2.138(2)	2.146(2)
V(1)–N(3)	2.1354(16)	2.1376(16)	2.1415(18)	2.150(3)	2.147(2)
O(1)–V(1)–O(2)	145.53(6)	145.27(6)	146.30(7)	146.14(9)	145.20(8)
O(1)–V(1)–O(3)	72.78(6)	72.78(6)	73.41(6)	73.30(8)	72.90(8)
O(1)–V(1)–O(4)	86.57(6)	86.10(6)	86.19(7)	86.40(9)	86.46(8)
O(1)–V(1)–O(5)	96.13(7)	95.68(7)	96.63(8)	96.43(10)	95.44(9)
O(1)–V(1)–N(2)	71.04(6)	71.14(6)	70.67(6)	71.14(8)	71.33(8)
O(1)–V(1)–N(3)	140.67(6)	140.95(6)	139.67(7)	140.17(9)	140.51(8)
O(2)–V(1)–O(3)	73.27(6)	73.16(6)	74.05(6)	73.70(9)	73.08(8)
O(2)–V(1)–O(4)	86.48(6)	86.04(6)	84.37(7)	85.86(9)	85.68(8)
O(2)–V(1)–O(5)	94.11(7)	95.31(7)	95.42(8)	94.75(10)	96.53(9)
O(2)–V(1)–N(2)	140.81(6)	140.23(6)	139.87(7)	140.04(10)	140.67(8)
O(2)–V(1)–N(3)	71.28(6)	71.31(6)	71.11(7)	71.18(9)	71.40(8)
O(3)–V(1)–O(4)	88.04(5)	87.73(6)	88.35(6)	89.32(10)	88.73(8)
O(3)–V(1)–O(5)	97.70(7)	97.71(7)	96.41(8)	96.81(11)	98.43(9)
O(3)–V(1)–N(2)	142.89(6)	142.72(6)	143.69(7)	143.98(9)	143.63(8)
O(3)–V(1)–N(3)	143.68(6)	143.89(6)	144.85(7)	144.51(9)	143.82(8)
O(4)–V(1)–O(5)	174.17(7)	174.56(7)	175.00(7)	173.77(11)	172.83(9)
O(4)–V(1)–N(2)	81.91(6)	80.83(6)	84.21(7)	82.96(9)	82.77(7)
O(4)–V(1)–N(3)	82.21(6)	83.69(6)	83.88(7)	83.25(9)	82.03(7)
O(5)–V(1)–N(2)	94.05(7)	94.86(7)	92.81(8)	92.68(11)	91.28(9)
O(5)–V(1)–N(3)	92.47(7)	91.73(7)	91.32(8)	91.07(11)	92.19(9)
N(2)–V(1)–N(3)	70.12(6)	70.05(6)	69.49(7)	69.47(9)	69.82(8)

2.4.3. Self-assembly and supramolecular structures

All of **1**·0.25MeOH and **2–6** contain classical and non-classical hydrogen bond donors and acceptors as well as aromatic fragments. Therefore, all the structures were scrutinized for intermolecular non-covalent interactions and the resulting self-assembled supramolecular structures. The interactions found and the self-assembly guided by them are described below.

In the case of **1**·0.25MeOH, two types of furcated hydrogen bonding interactions have been found. These are trifurcated O–H $\cdots$ (O,O,O) interaction [38–40] and bifurcated C–H $\cdots$ O $\cdots$ H–C interaction [41,42]. The trifurcated interaction involves the methanol O–H as the single donor and the metal bound facially oriented oxo, amidate-O and enolate-O atoms as the three acceptors. The O $\cdots$ O distances and the O–H $\cdots$ O angles are in the ranges 3.124(12)–3.291(12) Å and 138–153°, respectively. This interaction only connects the methanol molecule to one of the two complex molecules present in the asymmetric unit and plays no further role in the self-assembly process (Fig. 2). The bifurcated C–H $\cdots$ O $\cdots$ H–C interaction involves *ortho* C–H of one benzoyl phenyl ring and the *meta* C–H of another benzoyl phenyl ring as the two donors and a metal bound oxo atom as the single acceptor. The C $\cdots$ O distances are 3.410(6) and 3.501(6) Å, the C–H $\cdots$ O angles are 174 and 149° and the H $\cdots$ O $\cdots$ H angle is 63°. This bifurcated interaction is responsible for the formation of discrete tetranuclear **1**₄·MeOH units in the crystal lattice (Fig. 6, top). Each of these tetranuclear units is connected to its two adjacent neighbors by a pair of reciprocal C–H $\cdots$ O interactions on either side involving one of the α -diketimine methyl-CH as the donor and an equatorially coordinated acetylacetonate-O as the acceptor. The C $\cdots$ O distance and the C–H $\cdots$ O angle are 3.454(6) Å and 162°, respectively. As a result of this inter-tetranuclear C–H $\cdots$ O interaction a one-dimensional assembly of **1**₄·MeOH is formed (Fig. 6, bottom).

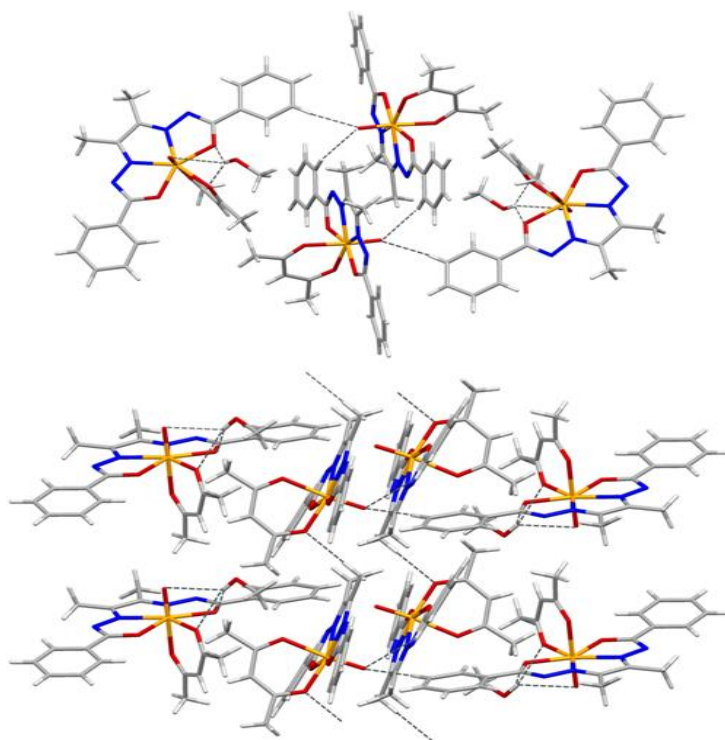


Fig. 6. The tetranuclear $[\text{VO}(\text{acac})(\text{L}^1)]_4 \cdot \text{MeOH}$ ($\mathbf{1}_4 \cdot \text{MeOH}$) unit assembled via trifurcated $\text{O}-\text{H} \cdots (\text{O}, \text{O}, \text{O})$ and bifurcated $\text{C}-\text{H} \cdots \text{O} \cdots \text{H}-\text{C}$ interactions (top) and the one-dimensional ordering of $\mathbf{1}_4 \cdot \text{MeOH}$ via reciprocal $\text{C}-\text{H} \cdots \text{O}$ interactions (bottom).

A bifurcated $\text{C}-\text{H} \cdots \text{O} \cdots \text{H}-\text{C}$ [41,42] and a simple $\text{C}-\text{H} \cdots \text{O}$ intermolecular interactions have been found in the case of **2**. Both methyl groups of the α -diketimine fragment participate as donors in these interactions. One of the two methyl groups utilizes one H-atom for the bifurcated interaction and another H-atom for the $\text{C}-\text{H} \cdots \text{O}$ interaction, while the other methyl group is involved only in the bifurcated interaction. In the $\text{C}-\text{H} \cdots \text{O} \cdots \text{H}-\text{C}$ interaction, the acetylacetonate-O coordinated to the metal atom at the equatorial position acts as the acceptor. Here, the $\text{C} \cdots \text{O}$ distances are 3.500(3) and 3.375(3) Å, the $\text{C}-\text{H} \cdots \text{O}$ angles are 157 and 163° and the $\text{H} \cdots \text{O} \cdots \text{H}$ angle is 62°. In the simple $\text{C}-\text{H} \cdots \text{O}$ interaction, the metal bound oxo atom acts as the acceptor.

The C $\cdots$ O distance and the C–H $\cdots$ O angle are 3.292(3) Å and 129°, respectively. The bifurcated C–H $\cdots$ O $\cdots$ H–C interaction helps to form a one-dimensional chain of **2**. Two such inversion symmetry related parallel chains are connected by the C–H $\cdots$ O interaction in a reciprocal manner and a ribbon-like supramolecular structure is formed (Fig. 7, top).

The molecules of **3** form discrete dimeric units via a pair of reciprocal C–H $\cdots$ O interactions involving the C–H of a methyl group of the α -diketimine fragment as the donor and the metal bound oxo atom as the acceptor (Fig. 7, middle). In this C–H $\cdots$ O interaction, the C $\cdots$ O distance and the C–H $\cdots$ O angle are 3.498(3) Å and 154°, respectively. The two *para*-methoxybenzoyl rings on either side of each dimer participate in two π – π interactions with the corresponding rings of the two neighboring dimers. In this π – π interaction, the C_g $\cdots$ C_g distance and the slip angle (angle between the C_g–C_g vector and the normal to the ring planes) [43] are 3.761(1) Å and 21.3°, respectively. This inter-dimer π – π interaction leads to a one-dimensional chain-like arrangement of the hydrogen bonded dimers of **3** in the crystal lattice (Fig. 7, middle).

A bifurcated C–H $\cdots$ (O,O) and a C–H $\cdots\pi$ [44] intermolecular interactions direct the self-assembly of the molecules of **4** in the crystal lattice. The bifurcated interaction involves the C–H of a methyl group of the α -diketimine fragment as the single donor and the metal coordinated amidate-O of (L⁴)^{2–} and the oxo atom as the two acceptors. The C $\cdots$ O(amidate) and the C $\cdots$ O(oxo) distances are 3.516(3) and 3.337(3) Å and the corresponding C–H $\cdots$ O angles are 141 and 152°, respectively. In the C–H $\cdots\pi$ interaction, the C–H of the second methyl group of the α -diketimine fragment acts as donor and a *para*-chlorobenzoyl ring acts as the acceptor. The C $\cdots$ C_g and H $\cdots$ C_g distances are 3.509 and 2.994 Å, respectively and the C–H $\cdots$ C_g angle is 115°. In the crystal lattice, both interactions assist in the formation of a one-dimensional ordering of **4** (Fig. 7, bottom).

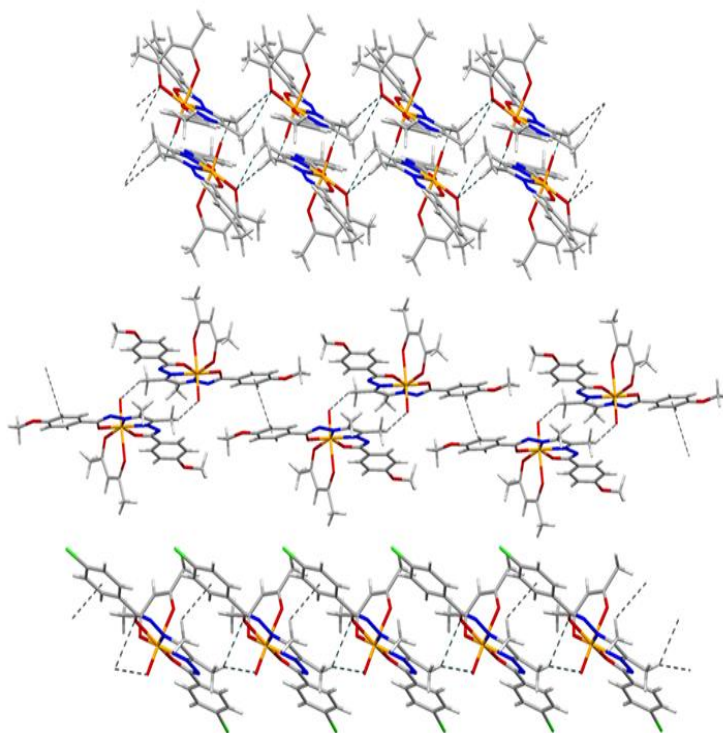


Fig. 7. One-dimensional supramolecular assemblies of [VO(acac)(L²)] (**2**) via C–H $\cdots$ O $\cdots$ H–C and C–H $\cdots$ O interactions (top), [VO(acac)(L³)] (**3**) via C–H $\cdots$ O and π – π interactions (middle) and [VO(acac)(L⁴)] (**4**) via C–H $\cdots$ (O,O) and C–H $\cdots$ π interactions (bottom).

A one-dimensional chain-like ordering of the molecules of **5** occurs through an intermolecular C–H $\cdots$ O interaction involving the C–H of a methyl group of the α -diketimine fragment as the donor and the metal coordinated oxo atom as the acceptor. The C $\cdots$ O distance and the C–H $\cdots$ O angle are 3.147(4) Å and 116°, respectively. The *para*-nitrobenzoyl rings on one side of each chain are involved in π – π interactions (C_g $\cdots$ C_g distance = 3.989(2) Å and the slip angle = 24.5° [43]) with the *para*-nitrobenzoyl rings of the inversion symmetry related parallel chain. In addition, an oxygen-oxygen interaction (O $\cdots$ O distance = 2.856(7) Å) [45–48] involving an O-atom of the nitro substituent of the same *para*-nitrobenzoyl ring that participates in the π – π interaction provides a second type of connection between the two-inversion symmetry

related parallel chains. These two inter-chain interactions form a one-dimensional ribbon-like supramolecular assembly of **5** (Fig. 8, top).

Two types of intermolecular interactions namely π - π and C-H $\cdots$ π have been detected for **6** [44]. The π - π interactions between the benzoyl phenyl rings lead to a one-dimensional chain-like assembly of **6**. In this π - π interaction, the C_g $\cdots$ C_g distance is 3.959(3) Å and the slip angle is $\sim 31.3^\circ$ [43]. Two such inversion symmetry related parallel chains are connected by C-H $\cdots$ π interactions in a reciprocal way involving the *ortho* C-H of one of the two phenyl groups of the α -diketimine fragment as the donor and one benzoyl phenyl ring C-atom as the acceptor. The C $\cdots$ C and H $\cdots$ C distances are 3.463(4) and 2.862 Å, respectively and the C-H $\cdots$ C angle is 123° . The resulting overall supramolecular assembly appears to be somewhat ladder-like (Fig. 8, bottom).

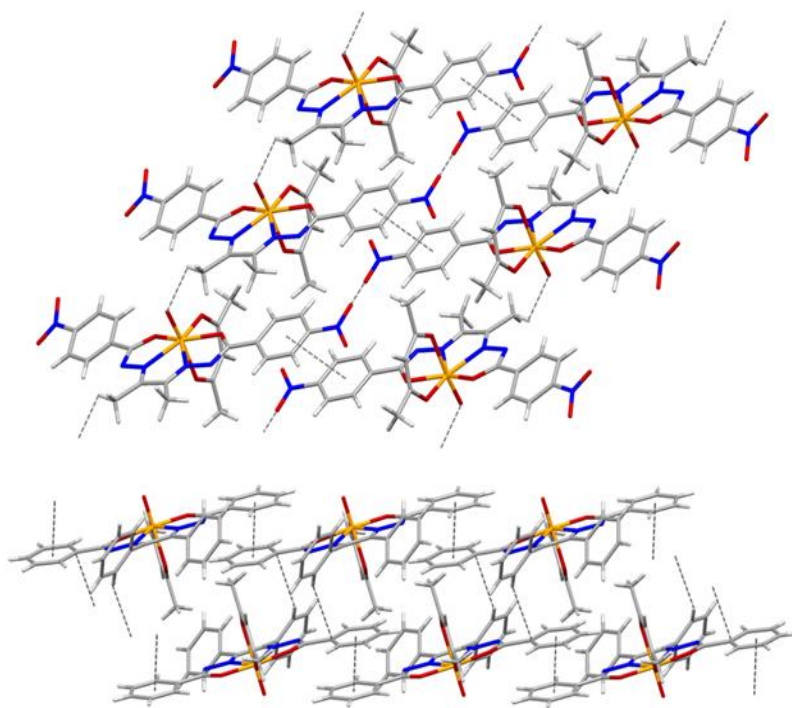


Fig. 8. One-dimensional ribbon-like array of [VO(acac)(L⁵)] (**5**) via C-H $\cdots$ O, π - π and O $\cdots$ O interactions (top), and π - π and C-H $\cdots$ π interactions assisted ladder-like ordering of [VO(acac)(L⁶)] (**6**) (bottom).

2.4.4. Spectroscopic characteristics

The infrared spectra of **1–6** were recorded by using KBR pellets in the range 4000–400 cm^{-1} . Each spectrum displays a large number of bands with various intensities. No attempt has been made to assign all the bands except for the following few. The Schiff bases of the type H_2L^n are known to display the typical amide N–H and C=O stretching bands at ~ 3200 and ~ 1650 cm^{-1} , respectively [22,23,29,30,32,33]. The spectra of **1–6** are devoid of these two characteristic amide bands. Thus, the amide functionalities of the Schiff bases are deprotonated in their corresponding complexes. All the complexes display a medium to strong band in the range 1582–1602 cm^{-1} . This band is attributed to the $-\text{C}=\text{N}-\text{N}=\text{C}-$ fragments of the $(\text{L}^n)^{2-}$ [22,23,29–34,36]. The spectrum of **5** shows two strong bands at 1520 and 1342 cm^{-1} . These two bands are most likely due to the asymmetric and symmetric stretches of the nitro substituent on the aroyl moiety. The V=O stretching vibration appears as a strong band at 988 for **1** and at ~ 950 cm^{-1} for **2–6** [11–14,16,17,20,30–37].

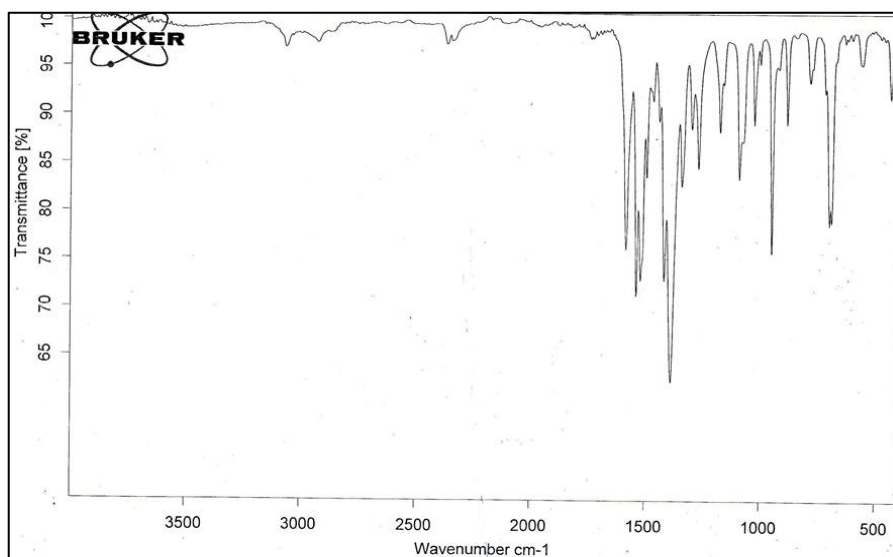


Fig. 9. Infrared spectrum of $[\text{VO}(\text{acac})(\text{L}^6)]$ (**6**).

The electronic spectra of **1–6** were recorded using their acetonitrile solutions. The spectroscopic profiles of all the complexes are quite comparable. The spectra of **1** and **6** are represented in Fig. 10. In the visible region, the complexes display two moderately intense absorptions, a shoulder in the range 515–530 nm and a band within 434–447 nm for **1–5** and at 375 nm for **6**. In the ultraviolet region, two strong absorption bands in the ranges 293–297 nm and 231–252 nm are observed. The free Schiff bases (H_2L^1 and H_2L^6) display only a strong band at ~ 310 nm. Thus, the two visible region absorptions are assigned to ligand-to-metal charge transfer transitions, while the two strong absorptions below 300 nm are attributed to ligand centered transitions [30–36].

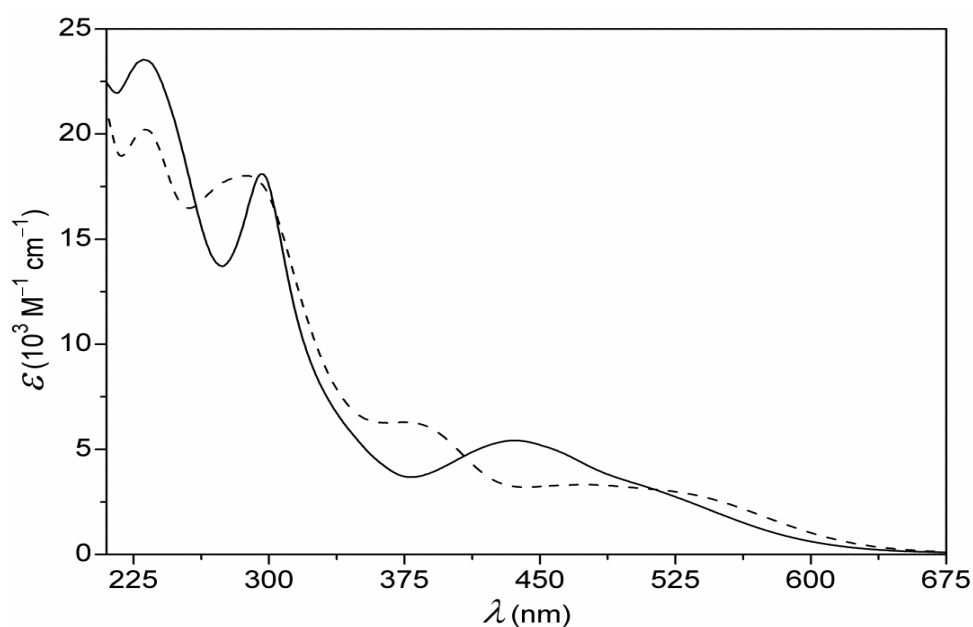


Fig. 10. Electronic spectra of $[VO(acac)(L^1)]$ (**1**) (—) and $[VO(acac)(L^6)]$ (**6**) (----) in acetonitrile.

The 1H NMR spectra of **1–6** were recorded in the $CDCl_3$ solvent using tetramethylsilane as internal standard. The chemical shifts with tentative assignments have been listed in the experimental section under the respective complexes. None of the six complexes display any signal assignable to the

amide-NH of the free Schiff bases [22,23]. Absence of this signal is consistent with the deprotonation of both amide functionalities and the dianionic (L^n)²⁻ form of the ligands in the complexes. The spectra also indicate that the two halves of (L^n)²⁻ in each complex are equivalent. The four *ortho* protons of the two benzoyl phenyl rings resonate as a doublet of doublet at δ 8.12 and 8.02 ppm for **1** and **6**, respectively. The remaining sixteen aromatic protons of **6** are observed as two multiplets of six and ten protons in the ranges δ 7.50–7.45 ppm and δ 7.42–7.33 ppm, respectively. In contrast, the two *para* protons and the four *meta* protons of the benzoyl phenyl rings in **1** are observed as two well resolved signals. The *para* protons resonate as a triplet of triplet at δ 7.52 ppm, while the *meta* protons are observed as a triplet at δ 7.44 ppm. On the other hand, both *ortho* and *meta* protons of the two *para*-substituted benzoyl rings in **2–4** resonate as doublets each of four protons in the ranges δ 8.01–8.07 and 6.94–7.41 ppm, respectively. In the case of **5**, these eight protons of the two *para*-nitrobenzoyl rings appear as an AA'BB' type.

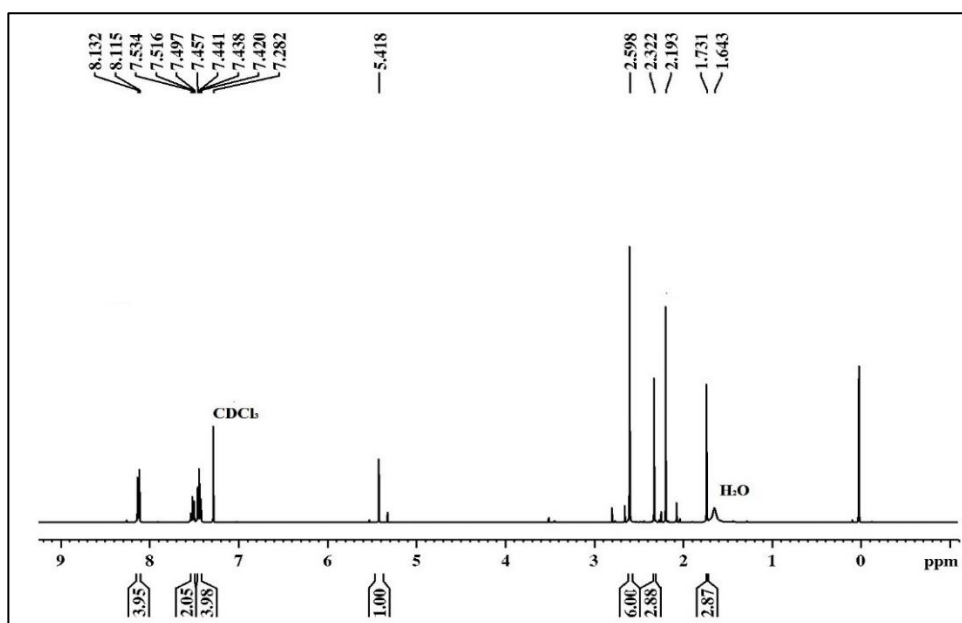


Fig. 11. ¹H-NMR spectrum of [VO(acac)(L¹)] (**1**).

2.4.5. Redox properties

Electron transfer behaviors of **1–6** were investigated by cyclic voltammetry. The measurements were carried out at room temperature (298 K) using about 1×10^{-3} M solutions of the complexes in acetonitrile containing tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte under nitrogen atmosphere using a glassy carbon disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Under identical condition the $E_{1/2}$ and ΔE_p values of the ferrocenium/ferrocene (Fc^+/Fc) couple were found as 0.19 V and 170 mV, respectively. All six complexes display a reduction response at potentials cathodic to the reference electrode. The reduction is quasi-reversible for all the complexes except for **5**, where it is irreversible. The cyclic voltammograms of **1** and **6** are shown in Fig. 12. The $E_{1/2}$ values for **1–4** are in the range -0.85 to -0.92 V and the ΔE_p values are 110 or 120 mV. For **6**, the $E_{1/2}$ is -0.80 V and the ΔE_p is 140 mV. The E_{pc} value for the irreversible reduction of **5** is -0.87 V. The peak currents for all six complexes are comparable with those observed for Fc^+/Fc couple and other known one-electron redox couples under similar conditions [49,50]. The free Schiff bases (H_2L^1 and H_2L^6) do not show any such reduction in the above potential range. Thus, the single electron reduction response observed for **1–6** is assigned to a metal centered process. The E_{pc} values of **1–5** show a cathodic shift with the increase in the electron donating ability of the substituent R at the *para* position of the benzoyl fragment of $(\text{L}^{1-5})^{2-}$. A satisfactory linear fit has been obtained (Fig. 12, inset) when the E_{pc} values are plotted against the Hammett substituent constants [51]. The cathodic shift of reduction potential indicates that the pentavalent state of the metal center becomes more stable with the increase in the electron donating ability of the substituent.

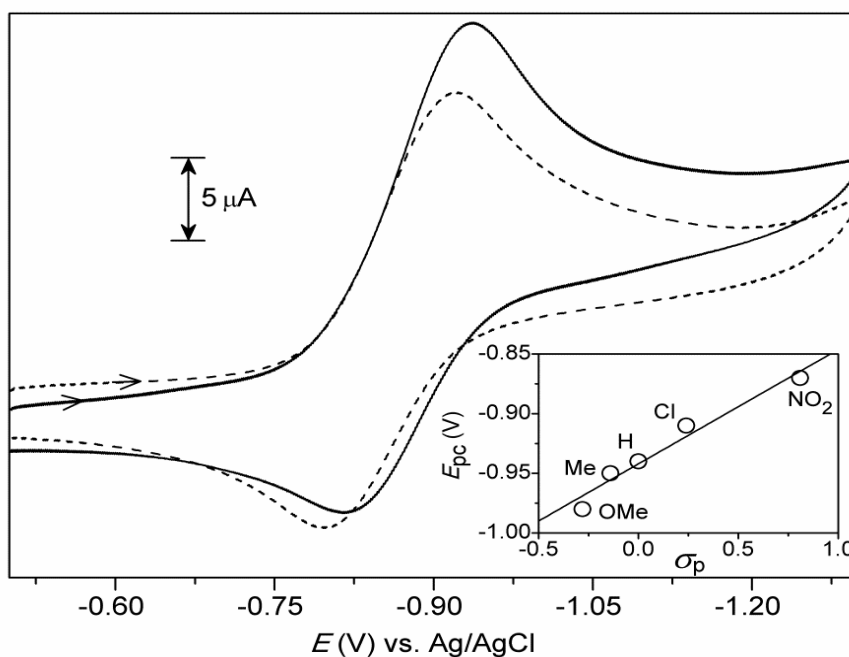


Fig. 12. Cyclic voltammograms of $[\text{VO}(\text{acac})(\text{L}^1)]$ (**1**) (—) and $[\text{VO}(\text{acac})(\text{L}^6)]$ (**6**) (----) in acetonitrile (0.1 M TBAP) using the experimental conditions described in the text. Inset: Correlation between the E_{pc} values of the reduction responses of **1–5** and the Hammett substituent constants. The straight line represents a linear least-squares fit.

2.5. Conclusions

A series of six ternary oxovanadium(V) complexes with the bidentate six-membered chelate ring forming acetylacetone (Hacac) and the tetradentate fused 5,5,5-membered chelate rings forming Schiff base system α -diketone bis(*para*-R-benzoylhydrazones) (H_2L^n) have been synthesized. The pentavalent character of the metal center in these complexes and the $[\text{VO}(\text{acac})(\text{L}^n)]$ as their general molecular formula have been established by elemental analysis, mass spectrometric, magnetic susceptibility and solution electrical conductivity measurements. The molecular structures of all six complexes determined by X-ray crystallographic studies revealed the hepta-coordination of the vanadium(V) atom and a distorted pentagonal-bipyramidal

N₂O₅ coordination geometry assembled by the fused 5,5,5-membered chelate rings forming ON₂O-donor (Lⁿ)²⁻, 6-membered chelate ring forming O₂-donor (acac)⁻ and the oxo atom. There is no other example of structurally characterized pentagonal-bipyramidal complex of oxovanadium(V) with more than four-membered chelate ring forming ligands. Several intermolecular non-covalent interactions such as trifurcated O–H⋯(O,O,O), bifurcated C–H⋯O⋯H–C and C–H⋯(O,O), simple C–H⋯O, π – π , C–H⋯ π and O⋯O interactions are detected in the crystal lattices of these complexes. Self-assembly of them via these interactions lead to one-dimensional chain-, ladder- and ribbon-like supramolecular structures in the corresponding crystal lattices. The spectroscopic characteristics of the six complexes corroborate their similar molecular structures. The electrochemically active complexes display a quasi-reversible metal centered one-electron reduction which is sensitive to the electronic nature of the substituent on the tetradentate (Lⁿ)²⁻. Currently we are engaged in synthesizing analogous high coordinated (>6) vanadium(V) complexes with various Schiff base ligands.

2.6. References

- [1] R.K. Bogges, W.D. Wiegele, *J. Chem. Educ.* 55 (1978) 156–158.
- [2] S.R. Trifunović, Z.D. Matović, V. Milovanović, H. Kawaguchi, M. Yamasaki, *Transition Met. Chem.* 25 (2000) 680–685.
- [3] K. Dehnicke, A. Greiner, *Angew. Chem. Int. Ed.* 42 (2003) 1340–1354.
- [4] R.–F. Jin, S.–Y. Yang, H.–M. Li, L.–S. Long, R.–B. Huang, L.–S. Zheng, *CrystEngComm.* 14 (2012) 1301–1316.
- [5] J.–C.G. Bünzli, *J. Coord. Chem.* 67 (2014) 3706–3733.
- [6] B. Drahoš, R. Herchel, Z. Trávníček, *RSC Adv.* 6 (2016) 34674–34684.
- [7] J. Sanchiz, S. Dominguez, A. Mederos, F. Brito, J.M. Arrieta, *Inorg. Chem.* 36 (1997) 4108–4114.
- [8] R. Meier, F.W. Heinemann, *Inorg. Chim. Acta* 337 (2002) 317–327.
- [9] R.D. Shannon, *Acta Crystallogr. Sect. A* 32 (1976) 751–767.

- [10] P.C. Paul, S.J. Angus-Dunne, R.J. Batchelor, F.W.B. Einstein, A.S. Tracey, *Can. J. Chem.* 75 (1997) 183–191.
- [11] K.J. Ooms, S.E. Bolte, J.J. Smee, B. Baruah, D.C. Crans, T. Polenova, *Inorg. Chem.* 46 (2007) 9285–9293.
- [12] V. Sharma, V. Sharma, R. Bohra, J.E. Drake, M.B. Hursthouse, M.E. Light, A.L. Bingham, *Transition Met. Chem.* 32 (2007) 442–448.
- [13] Q.–Y. Zhang, H.–Q. Zhang, A.–G. Kong, Q. Yang, Y.–K. Shan, Z. *Naturforsch.* B65 (2010) 157–162.
- [14] S.A. Elsayed, A.M. El-Hendawy, M.I. El-Mahdy, *ISRN Inorg. Chem.* (2014) doi:10.1155/2014/709258.
- [15] K. Kanamori, K. Nishida, N. Miyata, K. Okamoto, *Chem. Lett.* (1998) 1267–1268;
- [16] K. Kanamori, K. Nishida, N. Miyata, K. Okamoto, Y. Miyoshi, A. Tamura, H. Sakurai, *J. Inorg. Biochem.* 86 (2001) 649–656.
- [17] K. Kanamori, K. Nishida, N. Miyata, T. Shimoyama, K. Hata, C. Mihara, K. Okamoto, Y. Abe, S. Hayakawa, S. Matsugo, *Inorg. Chem.* 43 (2004) 7127–7140.
- [18] X.–Y. Yu, L. Deng, B. Zheng, B.–R. Zeng, P. Yi, X. Xu, *Dalton Trans.* 43 (2014) 1524–1533.
- [19] S. Zhang, W. Xia, Y. Yang, X. Yu, X. Li, *J. Coord. Chem.* 70 (2017) 2958–2968.
- [20] A.–C. Schmidt, M. Hermesen, F. Rominger, R. Dehn, J.H. Teles, A. Schäfer, O. Trapp, T. Schaub, *Inorg. Chem.* 56 (2017) 1319–1332.
- [21] J.C. Dewan, D.L. Kepert, C.L. Raston, D. Taylor, A.H. White, E.N. Maslen, *J. Chem. Soc. Dalton Trans.* (1973) 2082–2086.
- [22] T. Ghosh, A. Mukhopadhyay, K.S.C. Dargaiah, S. Pal, *Struct. Chem.* 21 (2010) 147–152.
- [23] E. López-Torres, M.A. Mendiola, *Dalton Trans.* (2009) 7639–7647.
- [24] R.A. Rowe, M.M. Jones, *Inorg. Synth.* 5 (1957) 113–116.

- [25] Bruker (2016). APEX3, SAINT-Plus and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- [26] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 64 (2008) 112–122.
- [27] L.J. Farrugia, *J. Appl. Crystallogr.* 45 (2012) 849–854.
- [28] F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P.M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Crystallogr.* 41 (2008) 466–470.
- [29] T. Ghosh, S. Pal, *J. Chem. Sci.* 127 (2015) 1201–1209.
- [30] N.R. Sangeetha, S. Pal, *Bull. Chem. Soc. Jpn.* 73 (2000) 357–363.
- [31] N.R. Sangeetha, V. Kavita, S. Wocadlo, A.K. Powell, S. Pal, *J. Coord. Chem.* 51 (2000) 55–66.
- [32] S.N. Pal, K.R. Radhika, S. Pal, *Z. Anorg. Allg. Chem.* 627 (2001) 1631–1637.
- [33] A. Sarkar, S. Pal, *Inorg. Chim. Acta* 362 (2009) 3807–3812.
- [34] A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* (2009) 5391–5398.
- [35] A. Sarkar, S. Pal, *Polyhedron* 26 (2007) 1205–1210.
- [36] A. Sarkar, S. Pal, *Inorg. Chim. Acta* 361 (2008) 2296–2304.
- [37] A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* (2009) 622–627.
- [38] S.K. Panigrahi, G.R. Desiraju, *J. Biosci.* 32 (2007) 677–691.
- [39] C.S. Neupane, S.K. Awasthi, *Tetrahedron Lett.* 53 (2012) 6067–6070.
- [40] K. Nieszporek, P. Podkościelny, J. Nieszporek, *Phys. Chem. Chem. Phys.* 18 (2016) 5957–5963.
- [41] I. Rozas, I. Alkorta, J. Elguero, *J. Phys. Chem. A* 102 (1998) 9925–9932.
- [42] E.S. Feldblum, I.T. Arkin, *Proc. Natl. Acad. Sci. USA* 111 (2014) 4085–4090.
- [43] N.R. Sangeetha, S.N. Pal, C.E. Anson, A.K. Powell, S. Pal, *Inorg. Chem. Commun.* 3 (2000) 415–419.
- [44] M. Nishio, *CrystEngComm* 6 (2004) 130–158.

- [45] M. Das, B.N. Ghosh, A. Bauzá, K. Rissanen, A. Frontera, S. Chattopadhyay, *RSC Advances* 5 (2015) 73028–73039.
- [46] K. Remya, C.H. Suresh, *Phys. Chem. Chem. Phys.* 17 (2015) 18380–18392.
- [47] S. Chen, Z. Xu, J. Li, *New J. Phys.* 18 (2016) 023052.
- [48] N. Chaudhri, N. Grover, M. Sankar, *Inorg. Chem.* 56 (2017) 11532–11545.
- [49] S.G. Sreerama, S. Pal, *Inorg. Chem.* 41 (2002) 4843–4845.
- [50] S.G. Sreerama, D. Shyamraj, S.N. Pal, S. Pal, *Indian J. Chem.* 42A (2003) 2352–2358.
- [51] J. March, in: *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; Fourth Edition, Wiley, New York, 1992, p. 280.

Chapter 3

Ambidentate coordination of oximate in complexes of $\text{VO}(\text{OMe})^{2+}$ and VO_2^+ cores with biacetylmonoxime salicyloylhydrazone: Structural confirmation, properties and photocatalytic applications[§]

3.1. Abstract

Reaction of equimolar amounts of bis(acetylacetonato)oxovanadium(IV) $[\text{VO}(\text{acac})_2]$ with biacetylmonoxime salicyloylhydrazone (H_3L , where three dissociable protons represent the oxime, the amide and the phenol protons) in methanol produced the dimeric oxomethoxovanadium(V) complex $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) in 55% yield, while the same reaction in presence of two mole equivalents of KOH afforded a pervanadyl complex $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2**·MeOH) in 60% yield. Both complexes were characterized by elemental analysis, mass spectrometry, magnetic susceptibility and electrical conductivity measurements, differential scanning calorimetry, various spectroscopy (IR, UV-Vis and ^1H NMR) and cyclic voltammetry. In solution, **1** is non-electrolytic, while **2**·MeOH behaves as 1:1 electrolyte. X-ray crystal structures of both **1** and **2**·MeOH were determined. In the centrosymmetric edge-shared bioctahedral **1**, $(\text{HL})^{2-}$ acts as fused 5,6-membered chelate rings forming amidate-O, imine-N and oximate-O donor. In contrast, $(\text{HL})^{2-}$ acts as fused 5,5-membered chelate rings forming amidate-O, imine-N and oximate-N donor in trigonal-bipyramidal $[\text{VO}_2(\text{HL})]^-$. Cyclic voltammograms of the complexes and H_3L in acetonitrile solutions show irreversible reduction responses with the E_{pc} values in the potential range -0.9 to -1.5 V (vs. Ag/AgCl). Both complexes show decent catalytic activity for photodegradation of rhodamine B (RhB) under visible light irradiation.

[§] This work has been published in *Inorg. Chim. Acta* 502 (2020) 119344.

3.2. Introduction

Coordination complexes of vanadium are of continued interest because of their relevance to several biological processes such as haloperoxidation [1–4], nitrogen fixation [5–7], insulin mimicking [8–10] and anticancer activity [11,12]. In addition, a large number of vanadium complexes with a variety of ligands have found significant applications as catalysts in a wide range of organic transformation reactions [13,14]. As a consequence, synthesis of new coordination complexes of vanadium is receiving considerable attention to develop better functional and structural mimics of vanadium containing metalloenzymes and more efficient catalysts [15–18]. We have been working on oxovanadium(IV/V) complexes with tri- and tetradentate Schiff bases derived by condensation reactions of acid hydrazides with *ortho*-hydroxy-aryl-aldehydes, pyridine-2-aldehyde and α - and β -diketones during the past couple of decades [19–23]. This type of hydrazine-based Schiff base ligands are known to exhibit non-innocent character [24,25]. These ligands being amide-O coordinating also provide the scope to study the effect of amide protonation state on the geometric and redox features of their complexes [26,27]. The ambidentate oxime containing ligands are well known to provide high-valent highly reactive metal ion complexes as well as oximate bridged polynuclear complexes [28–33]. The Schiff base 2-hydroxy-*N'*-(3-(hydroxyimino)butan-2-ylidene)benzohydrazide (IUPAC name) or biacetylmonoxime salicyloylhydrazone (H₃L) contains both the O-coordinating amide and the oxime functionalities (Chart 1). Several structurally characterized transition metal ion (V(V), Fe(III), Ni(II), Zn(II) and Ru(II)) [34–41] and one rare earth metal ion (Dy(III)) [42] complexes have been reported with this Schiff base. The tridentate ligand coordinates the metal center via the amidate-O, imine-N and oxime- or oximate-N and forms fused 5,5-membered chelate rings in all these complexes [36–42] except for the vanadium(V) complexes [34,35]. In

the vanadium(V) complexes, it acts as fused 5,6-membered chelate ring forming amidate-O, imine-N and oximate-O donor. It may be noted that vanadium(V) has the smallest effective ionic radius when compared with that of the other five metal ions [43]. It is generally observed that the large metal ions prefer to form 5-membered chelate ring, while 6-membered chelate ring is more stable with small metal ions [44,45]. Thus, the oximate-O coordination and formation of the fused 5,6-membered chelate ring only in the vanadium(V) complexes is not inexplicable. In this work, we report a dimeric oxomethoxodovanadium(V) complex $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) and a solvated dioxovanadium(V) complex $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2**·MeOH) with H_3L (Chart 1). In these two complexes, the oxime functionality of the tridentate ligand $(\text{HL})^{2-}$ exhibits the rare ambidentate behavior for the same metal ion. In the following sections, synthesis, X-ray crystal structures and physical properties of **1** and **2**·MeOH are described. The photocatalytic activities of the two complexes in degradation of the organic dye rhodamine B (RhB) have been also evaluated.

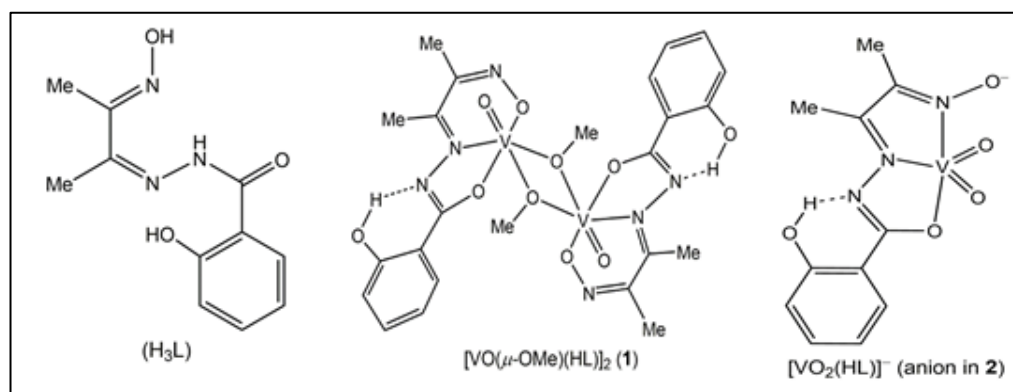


Chart 1. Chemical structure diagrams of biacetylmonoxime salicyloylhydrazone (H_3L) and the complexes $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) and $[\text{VO}_2(\text{HL})]^-$ (**2**) derived from it.

3.3. Experimental

3.3.1. Materials

As reported in literature, biacetylmonoxime salicyloylhydrazine (H_3L) was prepared in ~70% yield by condensation reaction of equimolar amounts of biacetyl monoxime and salicyloylhydrazine in methanol [37]. Bis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2]$, was synthesized by following a literature procedure [46]. All other reagents and solvents used in this work were of analytical grade available commercially and were used as received without further purification.

3.3.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used for the microanalytical (CHN) measurements. High resolution mass spectra were recorded with a Bruker Maxis (ESI-TOF analyzer) spectrometer. A Sherwood Scientific balance was used for the measurement of magnetic susceptibilities. The solution electrical conductivities were measured using a Digisun DI-909 conductivity meter. Powder X-ray diffraction experiments were performed using a Bruker D8 Advance X-ray diffractometer. A TA Instruments Discovery DSC 250 was used for differential scanning calorimetric (DSC) measurements. The infrared spectra were collected on a Bruker TENSOR II FT-IR spectrophotometer. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used for electronic spectroscopic measurements. The 1H -NMR (400 MHz) spectra were collected on a Bruker NMR spectrometer. A CH Instruments model 620A electrochemical analyzer was used for the cyclic voltammetric experiments.

3.3.3. Synthesis of $[VO(\mu-OMe)(HL)]_2$ (1)

A methanol solution (10 ml) of $[VO(acac)_2]$ (80 mg, 0.3 mmol) was added to a methanol solution (10 ml) of H_3L (70 mg, 0.3 mmol) and the mixture was stirred at room temperature under aerobic conditions for 6 h. The resulting brown solution was allowed to evaporate slowly at room temperature (298 K) in air. The dark brown crystalline material separated in about 4–5 days was

collected by filtration, washed with cold methanol and dried in air. Yield: 55 mg (55%). Anal. Calcd for $C_{24}H_{28}N_6O_{10}V_2$ (%): C, 43.52; H, 4.26; N, 12.69. Found: C, 43.58; H, 4.29; N, 12.61. HRMS in MeCN m/z found (calcd) for $C_{24}H_{29}N_6O_{10}V_2$ ($[M+H]^+$): 663.4496 (663.0824). Selected IR bands: ν (cm^{-1}) = 3225 (O–H), 1623 & 1589 (C=N), 1254 (N–O), 974 (V=O). UV-Vis in MeCN: λ_{max} (nm) (ϵ ($10^4 M^{-1} cm^{-1}$)) = 375^{sh} (1.05), 270 (2.85), 207 (2.97). 1H NMR in $CDCl_3$: δ (ppm) (J (Hz)) = 10.02 (s, 1H, phenolic-OH), 7.34 (6) (dd→t, 1H, H at *para* to amide), 7.33 (6) (d, 1H, H at *ortho* to amide), 6.92 (6) (d, 1H, H at *ortho* to phenolic-OH), 6.65 (6) (dd→t, 1H, H at *para* to phenolic-OH), 3.42 (s, 3H, OCH_3), 2.56 (s, 3H, $H_3CC=NO$), 1.94 (s, 3H, $H_3CC=N$). CV in MeCN: E_{pc} (V) = –1.34.

3.3.4. Synthesis of $K[VO_2(HL)] \cdot MeOH$ (2·MeOH)

A methanol solution (5 ml) of KOH (34 mg, 0.6 mmol) was added dropwise to a methanol solution (5 ml) of H_3L (70 mg, 0.3 mmol) with stirring. To the resulting light yellow solution, $[VO(acac)_2]$ (80 mg, 0.3 mmol) was added and the mixture was stirred at room temperature (298 K) under aerobic conditions for 6 h. The brown reaction mixture was then kept at room temperature (298 K) in air for slow evaporation. The brown crystalline material precipitated in about 4–5 days was collected by filtration, washed with cold methanol and dried in air. Yield: 70 mg (60%). Anal. Calcd for $C_{12}H_{15}N_3O_6KV$ (%): C, 37.21; H, 3.90; N, 10.85. Found C, 37.28; H, 3.86; N, 10.92. HRMS in MeOH m/z found (calcd) for $C_{11}H_{11}N_3O_5V$ ($[M]^-$): 316.0138 (316.0138). Selected IR bands: ν (cm^{-1}) = 3260 (O–H), 1621 & 1590 (C=N), 1253 (N–O), 939 & 915 (VO_2). UV-Vis in MeCN: λ_{max} (nm) (ϵ ($10^3 M^{-1} cm^{-1}$)) = 452 (5.8), 320 (7.8), 252 (10.4, 207 (23.3). 1H NMR in $(CD_3)_2SO$: δ (ppm) (J (Hz)) = 11.78 (s, 1H, phenolic-OH), 7.72 (6, 2) (dd, 1H, H at *ortho* to amide), 7.37 (6, 2), (td, 1H, H at *para* to amide), 6.94 (6) (d, 1H, H at *ortho* to phenolic-OH), 6.90 (6, 2) (td, 1H, H at *para* to phenolic-OH), 2.43 (s, 3H, $H_3CC=NO$), 1.84 (s, 3H, $H_3CC=N$). CV in MeCN: E_{pc} (V) = –0.9.

3.3.5. X-ray crystallography

Single crystals of both $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2**·MeOH) were collected from the crystalline materials obtained during their syntheses. Unit cell determination and intensity data collection for both **1** and **2**·MeOH were performed using a BRUKER D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite monochromated Mo $K\alpha$ Radiation ($\lambda = 0.71073 \text{ \AA}$). The APEX3 software package [47] was used for data collection, integration, reduction and absorption correction. Each structure was solved by direct method and refined on F^2 by full matrix least-squares procedures. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the phenolic hydroxyl group in each of **1** and **2**·MeOH and the hydrogen atom of the methanolic hydroxyl group in **2**·MeOH were found in the corresponding difference maps and refined with $U_{\text{iso}} = 1.5 \times U_{\text{eq}}$ of the oxygen atoms to which they are attached. All other hydrogen atoms in both structures were included at idealized positions using a riding model. The SHELX-97 programs [48] accessed via the WinGX software suite [49] were used for structure solution and refinement. Structural illustrations were prepared using the Mercury package [50]. Selected crystallographic data are listed in Table 2.

Detailed X-ray crystallographic data for **1** and **2**·MeOH have been deposited with the Cambridge crystallographic data center under the deposition numbers 1943839 and 1943840 respectively.

3.3.6. Photocatalysis

Organic dye rhodamine B (RhB) was chosen for the heterogeneous photodegradation experiment. The powdered complex catalyst (10 mg) was suspended in a $1 \mu\text{M}$ aqueous solution of the dye (20 ml) and the suspension was magnetically stirred under aerobic conditions for $\frac{1}{2}$ h in dark to establish the adsorption/desorption equilibrium between the dye and the surface of the catalyst. The mixture was then irradiated with visible light with continuous

stirring. After every 15 min of interval about 1 ml of the suspension was collected and centrifuged to remove the catalyst particulates and the clear solution obtained was used for spectrophotometric analysis. The degradation of RhB with the increase of irradiation time was monitored by measuring the change in the absorbance of its characteristic absorption band at 554 nm.

3.4. Results and discussion

3.4.1. Synthesis and characterization

The reaction of biacetylmonoxime salicyloylhydrazone (H_3L) and $[VO(acac)_2]$ in 1:1 mole ratio in methanol in presence of air produced $[VO(\mu\text{-OMe})(HL)]_2$ (**1**) in decent yield. On the other hand, if two mole equivalents of KOH was added in the above reaction mixture the product formed was $K[VO_2(HL)] \cdot MeOH$ (**2**·MeOH) in similar yield. The elemental (CHN) analysis data of both complexes are in good agreement with their molecular formulas. The high-resolution electrospray ionization mass spectra of both species further confirm their molecular formulas (Fig. 1). The base peak appeared at $m/z = 663.4496$ in the spectrum of **1** recorded in the positive ionization mode. This value is consistent with the protonated species $[1+H]^+$. The spectrum of **2**·MeOH collected in negative ionization mode displayed the base peak at $m/z = 316.0138$ corresponding to the complex anion $[VO_2(HL)]^-$. Room temperature (298 K) magnetic susceptibility measurements with the powdered samples of the two complexes showed their diamagnetic character. Both complexes are brown in color and highly soluble in methanol, acetonitrile, dimethylformamide and dimethylsulfoxide. In acetonitrile solution, **1** is electrically non-conducting, whereas the molar conductivity ($\Lambda_M = 130 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) of **2**·MeOH indicates 1:1 electrolytic behavior [51]. The molecular formulas, diamagnetic character and the solution electrical conductivity behaviors suggest the +5 oxidation state of the vanadium centers in both **1** and **2**·MeOH. As the complexes were synthesized under aerobic conditions, oxygen in air is the most likely oxidizing agent for the oxidation of the

tetravalent vanadium of the starting material to the pentavalent state in the products. In this context, it may be noted that although no base was used for the synthesis of **1**, but in all likelihood, the initial neutral synthesis reaction mixture became basic with the progress of the reaction due to complete reduction of oxygen and generation of the weak base $(\text{acac})^-$ from the dissociation of the starting material $[\text{VO}(\text{acac})_2]$. This basicity appears to be strong enough for the deprotonation of both H_3L and the bridging methanol leading to the formation of the methoxo bridged dinuclear **1**.

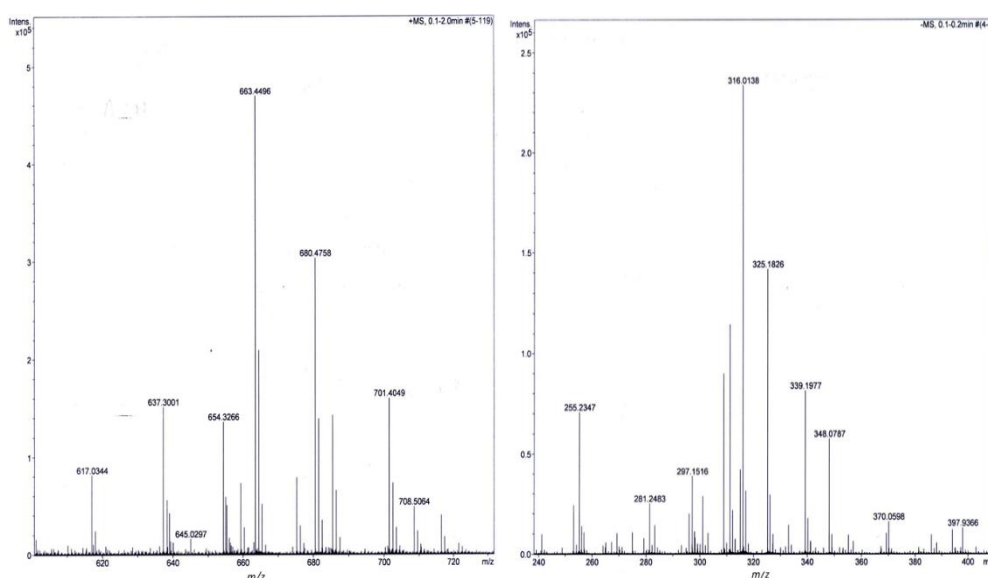


Fig. 1. ESI mass spectra of $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) (left) and $\text{K}[\text{VO}_2(\text{HL})] \cdot \text{MeOH}$ (**2**·MeOH) (right).

3.4.2. Description of X-ray molecular structures

The dimeric complex $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) crystallizes in the monoclinic $P2_1/c$ space group with one half of the molecule in the asymmetric unit. On the other hand, the solvated mononuclear ionic complex $\text{K}[\text{VO}_2(\text{HL})] \cdot \text{MeOH}$ (**2**·MeOH) crystallizes in the triclinic $P\bar{1}$ space group and here the asymmetric unit contains the complete formula unit and one methanol molecule. The thermal ellipsoid plots of **1** and **2**·MeOH are illustrated in Figs. 2 and 3(a), respectively. The metal centered bond parameters of **1** and **2**·MeOH are listed

in Tables 3 and 4, respectively. In general, the V=O and the vanadium to other coordinating atom bond lengths in both complexes are comparable with the corresponding bond lengths in the vanadium(V) complexes with analogous ligands [19–23,34,35]. For further support of the pentavalent state of vanadium in each of **1** and **2**·MeOH, the bond valence sum calculations were performed using the EXPO2014 software [52]. The values for the oxidation state of vanadium in **1** and **2** were found to be 5.12 and 5.04, respectively.

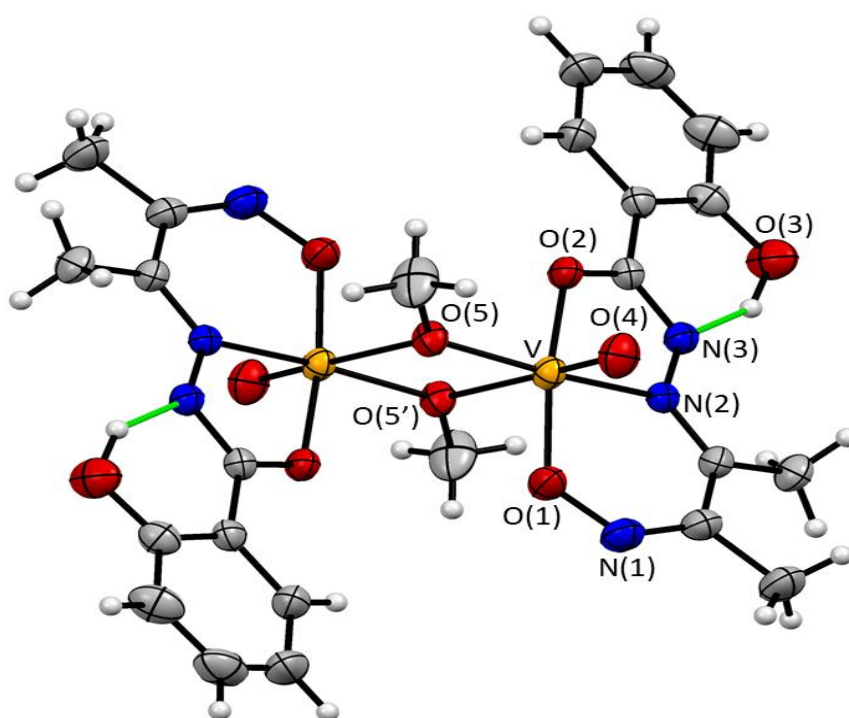


Fig. 2. The molecular structure of $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**). Thermal ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level and the carbon atoms are not labeled for clarity.

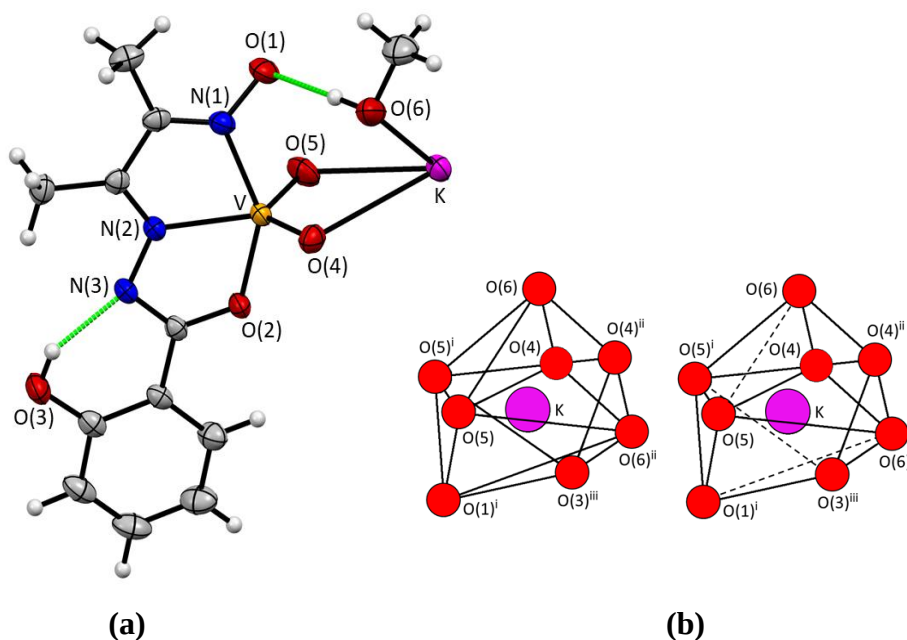


Fig. 3. (a) The asymmetric unit of $K[VO_2(HL)] \cdot MeOH (2 \cdot MeOH)$. Thermal ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level and the carbon atoms are not labeled for clarity. (b) The coordination polyhedron observed (left) and the calculated gyrobifastigium geometry shown by solid lines (right) around K in $K[VO_2(HL)] \cdot MeOH (2 \cdot MeOH)$. Symmetry transformations used to generate the equivalent atoms: $^i -x, -y, -z + 1$; $^{ii} -x + 1, -y, -z + 1$ and $^{iii} x, y-1, z$.

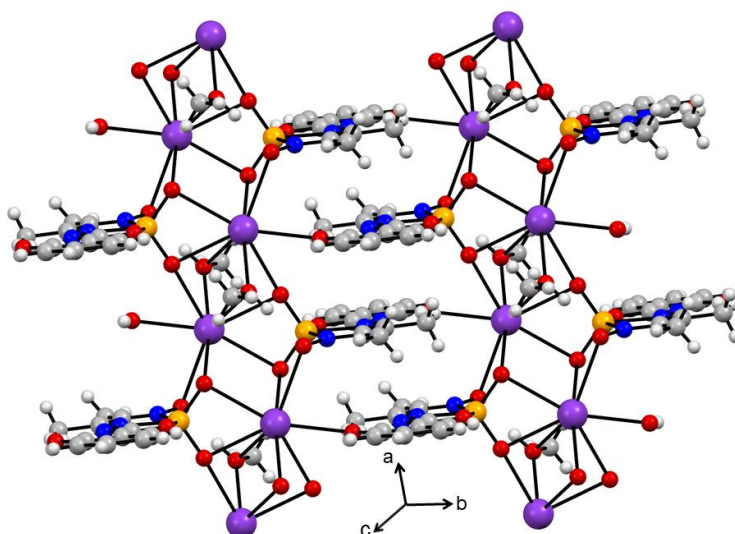


Fig. 4. Two-dimensional network structure of $K[VO_2(HL)] \cdot MeOH (2 \cdot MeOH)$.

The two halves of the dimeric molecule of **1** are related by an inversion center (Fig. 2). In the asymmetric unit, the meridionally spanning $(\text{HL})^{2-}$ coordinates to the metal center via the amidate-O, the imine-N and the oximate-O atoms (O(2), N(2) and O(1)) and forms fused 5,6-membered chelate rings. The methoxo-O (O(5)) occupies the fourth equatorial position of a NO_3 square-plane (rms deviation = 0.03 Å) and the oxo group (O(4)) occupies the apical position to complete a square-pyramidal NO_5 coordination environment around the metal center. As generally observed in square-pyramidal geometry, here also the vanadium atom is shifted towards the apical oxo group by 0.33 Å. Two such inversion symmetry related square-pyramidal units form the dimeric molecule where the sixth coordination sites *trans* to the oxo groups of the metal centers are occupied by the methoxo-O atoms in a reciprocal manner (Fig. 2). As a result, a divanadium(V) core, $\{\text{OV}(\mu\text{-OMe})_2\text{VO}\}^{4+}$, is formed at the center of **1** and each metal center in it resides in a distorted octahedral NO_5 coordination sphere. On the whole, two $(\text{HL})^{2-}$, two methoxo groups and the two oxo O-atoms constitute an edge-shared bioctahedral coordination geometry ($\text{NO}_3\text{VO}_2\text{VO}_3\text{N}$). The central $\text{V}_2(\mu\text{-OMe})_2$ moiety has a pair of short (1.8307(11) Å) and a pair of long (2.3256(11) Å) V–O bond lengths. The longer ones are *trans* to the corresponding oxo groups. The V...V distance is 3.3422(5) Å. The uncoordinated phenolic-OH groups of the two $(\text{HL})^{2-}$ are involved in intramolecular strong hydrogen bonds with the uncoordinated amidate-N atoms. In this O–H...N hydrogen bond, the O...N distance and the O–H...N angle are 2.5653(18) Å and 146(3)°, respectively.

The perspective view of the asymmetric unit of **2**·MeOH is depicted in Fig. 3(a). In contrast to **1**, here the vanadium atom of the anion $[\text{VO}_2(\text{HL})]^-$ is penta-coordinated and the $(\text{HL})^{2-}$ coordinates to the metal center through the amidate-O, the imine-N and the oximate-N atoms (O(2), N(2) and N(1)) and creates fused 5,5-membered chelate rings. The two oxo groups (O(4) and O(5)) occupy the other two coordination sites. Based on the value of τ (0.61)

[53], the N_2O_3 coordination geometry around vanadium center is best described as trigonal bipyramidal, where N(2), O(4) and O(5) create the trigonal equatorial-plane and N(1) and O(2) occupy the axial positions. In the asymmetric unit, the counter cation K^+ is coordinated by the two oxo groups and a methanol oxygen (O(6)). In addition to these three O-atoms, five more symmetry related O-atoms coordinate to the potassium atom. These are one oximate-O (O(1)), one phenol-O (O(3)), one more methanol-O and two more oxo groups. The K–O distances are in the range 2.7203(17)–3.0740(18) Å. The KO_8 polyhedron is shown in Fig. 3(b). It has one tetragonal plane and ten trigonal planes. Continuous shape measures (CShM) calculations were performed to classify the observed polyhedron using the SHAPE 2.1 software [54]. The best description of the geometry around potassium is found to be distorted gyrobifastigium or Johnson solid J26 (Fig. 3(b)) and Table 1, [55]. As observed in **1**, here also an intramolecular $\text{O}\cdots\text{H}\cdots\text{N}$ hydrogen bond involving the phenolic-OH and the amidate-N atom is present (Fig. 3(a)). The $\text{O}\cdots\text{N}$ distance and the $\text{O}\cdots\text{H}\cdots\text{N}$ angle are 2.590(2) Å and $145(3)^\circ$, respectively. The methanol-OH is also involved in hydrogen bonding with the uncoordinated oximate-O atom. Here the $\text{O}\cdots\text{O}$ distance and the $\text{O}\cdots\text{H}\cdots\text{O}$ angle are 2.745(2) Å and $174(3)^\circ$, respectively.

The crystal packing of **2**·MeOH reveals a two-dimensional coordination network structure (Fig. 4). The KO_8 polyhedra are interconnected in a linear fashion. In this chain structure, the $\text{K}\cdots\text{K}$ distance is alternating between 3.8104(10) and 4.2245(10) Å due to alternating four and two bridging atoms. In the first case, the bridging atoms are two vanadium-bound oxo and two methanol-O atoms, while, in the second case, these are two vanadium-bound oxo atoms. The complex anions are in a one-dimensional stacked columnar structure in between the $(\text{KO}_8)_n$ chains. As a result, alternating interconnected $(\text{KO}_8)_n$ and $\{[\text{VO}_2(\text{HL})]^- \}_n$ chains assemble a two-dimensional network structure.

Table 1Continuous shape measurement for K in $K[VO_2(HL)] \cdot MeOH (2 \cdot MeOH)$.

S.No.	Geometry	Symmetry	CShM value
1	Octagon	D_{8h}	29.030
2	Heptagonal pyramid	C_{7v}	18.356
3	Hexagonal bipyramid	D_{6h}	8.728
4	Cube	O_h	13.127
5	Square antiprism	D_{4d}	8.965
6	Triangular dodecahedro	D_{2d}	9.747
7	Johnson gyrobifastigium J26	D_{2d}	6.351
8	Johnson elongated triangular bipyramid J14	D_{3h}	22.088
9	Biaugmented trigonal prism J50	C_{2v}	9.515
10	Biaugmented trigonal prism	C_{2v}	8.948
11	Snub diphennoid J84	D_{2d}	10.231
12	Triakis tetrahedron	T_d	13.767
13	Elongated trigonal bipyramid	D_{3h}	19.063

Table 2 Selected crystallographic data for **1** and **2·MeOH**.

Complex	1	2·MeOH
Chemical formula	C ₂₄ H ₂₈ N ₆ O ₁₀ V ₂	C ₁₂ H ₁₅ N ₃ O ₆ KV
Formula weight	662.40	387.31
Crystal system	Monoclinic	Triclinic
Space Group	<i>P</i> 2 ₁ /c	<i>P</i> $\bar{1}$
<i>a</i> (Å)	7.4157(4)	7.0018(11)
<i>b</i> (Å)	18.5212(10)	11.234(2)
<i>c</i> (Å)	10.5562(5)	11.442(2)
α (°)	90	106.503(5)
β (°)	101.830(2)	106.104(5)
γ (°)	90	96.228(5)
<i>V</i> (Å ³)	1419.07(13)	811.7(3)
<i>Z</i>	2	2
ρ (g cm ⁻³)	1.550	1.585
μ (mm ⁻¹)	0.724	0.900
Reflns collected	36866	26078
Reflns unique	2882	3338
Reflns [<i>I</i> ≥ 2σ(<i>I</i>)]	2752	3058
Data / parameters	2882 / 196	3338 / 217
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0291, 0.0834	0.0298, 0.0801
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0305, 0.0845	0.0330, 0.0823
GOF on <i>F</i> ²	1.078	1.056
Largest diff. peak / hole (e Å ⁻³)	0.388 / -0.325	0.410 / -0.348

Table 3 Selected bond parameters (Å and °) for **1**.

V–O(1)	1.8217(12)	V–O(2)	1.9652(11)
V–O(4)	1.5818(13)	V–O(5)	1.8307(11)
V–O(5') ^a	2.3256(11)	V–N(2)	2.1054(13)
O(1)–V–O(2)	148.82(5)	O(1)–V–O(4)	99.90(7)
O(1)–V–O(5)	106.81(5)	O(1)–V–O(5') ^a	79.89(5)
O(1)–V–N(2)	80.42(5)	O(2)–V–O(4)	100.64(6)
O(2)–V–O(5)	90.98(5)	O(2)–V–O(5') ^a	80.99(4)
O(2)–V–N(2)	74.70(5)	O(4)–V–O(5)	103.21(6)
O(4)–V–O(5') ^a	176.47(6)	O(4)–V–N(2)	94.86(6)
O(5)–V–O(5') ^a	73.56(5)	O(5)–V–N(2)	158.81(5)
O(5') ^a –V–N(2)	88.59(4)		

^a Symmetry transformation used: 1– x, 1– y, 1– z.**Table 4** Selected bond parameters (Å and °) for **2·MeOH**.

V–O(2)	1.9647(13)	V–O(4)	1.6202(13)
V–O(5)	1.6242(14)	V–N(1)	2.0846(16)
V–N(2)	2.0844(14)		
O(2)–V–O(4)	103.03(6)	O(2)–V–O(5)	102.01(7)
O(2)–V–N(1)	146.74(6)	O(2)–V–N(2)	73.94(5)
O(4)–V–O(5)	110.38(8)	O(4)–V–N(1)	96.89(6)
O(4)–V–N(2)	120.45(7)	O(5)–V–N(1)	95.52(7)
O(5)–V–N(2)	128.71(7)	N(1)–V–N(2)	73.02(6)

To examine whether the bulk material is composed of only the X-ray structurally characterized complex or a mixture of more than one complex, room temperature powder X-ray diffraction patterns of the bulk samples of both **1** and **2**·MeOH were recorded using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and the experimental patterns were compared with the corresponding simulated patterns generated from the single crystal X-ray structures (Fig. 5). Essentially, in each case, there is a one-to-one correspondence between the peaks in the calculated pattern and those in the experimental pattern. This similarity clearly indicates the phase purity of the bulk materials for both **1** and **2**·MeOH.

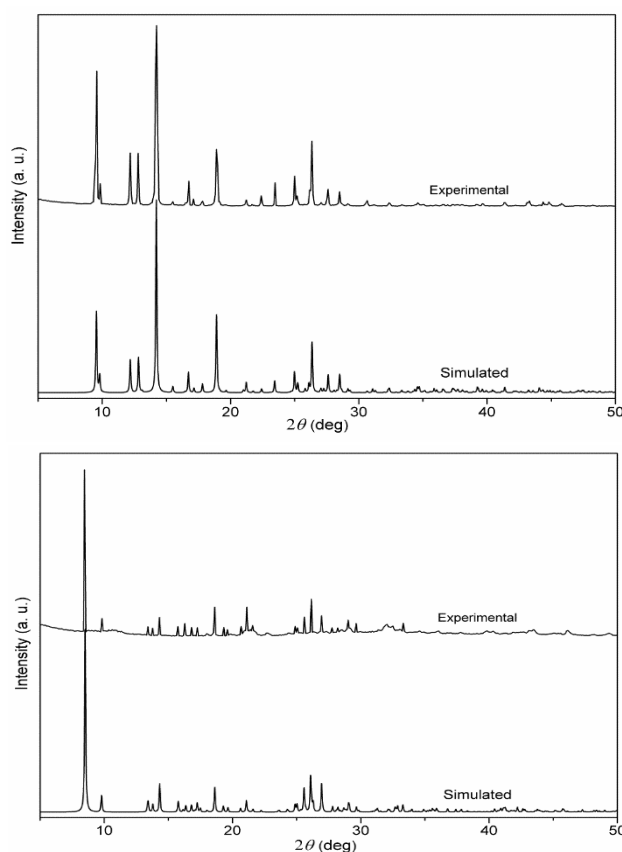


Fig. 5. Experimental and simulated powder X-ray ($\lambda = 1.5406 \text{ \AA}$) diffractograms of $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) (top) and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2**·MeOH) (bottom).

3.4.3. Thermal studies

Thermal stability of both complexes has been investigated by differential scanning calorimetry under nitrogen over the temperature range of 30 to 400 °C at a scan rate of 5°C min⁻¹. The thermograms of **1** and **2**·MeOH are depicted in Fig. 6. Complex **1** shows an exothermic peak at 169°C preceded by a shoulder at ~158°C, a relatively much less intense peak at 215°C, a broad peak centered at ~280°C and another small peak at 325°C. On the other hand, **2**·MeOH displays a sharp exothermic peak at 271°C followed by a very weak shoulder like peak at ~280°C. In each case, the first major peak is likely to be associated with the thermal decomposition process of the complex. Thus, the ionic **2**·MeOH is thermally much more stable than the neutral **1**.

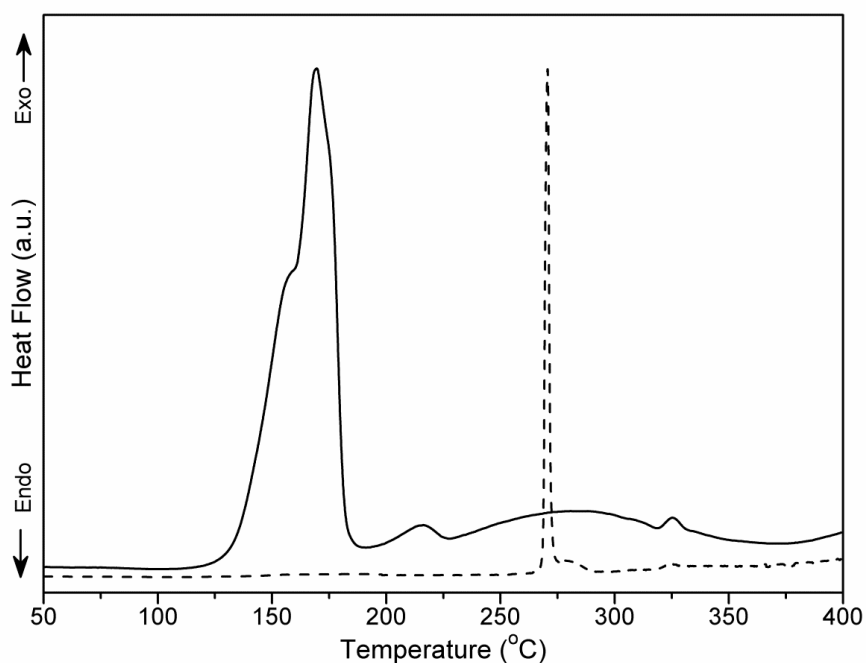


Fig. 6. DSC thermograms of $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) (—) and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2**·MeOH) (----).

3.4.4. Spectroscopic characteristics

Infrared spectra of **1** and **2**·MeOH were recorded in the ATR mode (Fig. 7). Both spectra show a broad band at $\sim 3240\text{ cm}^{-1}$ due to the hydrogen bonded hydroxyl groups. Two medium intensity bands are observed at ~ 1620 and $\sim 1590\text{ cm}^{-1}$. Similar bands are assigned to the C=N(imine) and C=N(oxime) stretches, respectively [38,41]. A strong band observed at $\sim 1254\text{ cm}^{-1}$ is most likely associated with the oxime N–O stretching [28]. A strong band at 974 cm^{-1} displayed by **1** is attributed to the V=O stretching [19,22,23,34,35]. The asymmetric and symmetric stretching bands of VO_2^+ unit in **2**·MeOH appear as two strong bands at 939 and 915 cm^{-1} [20,21].

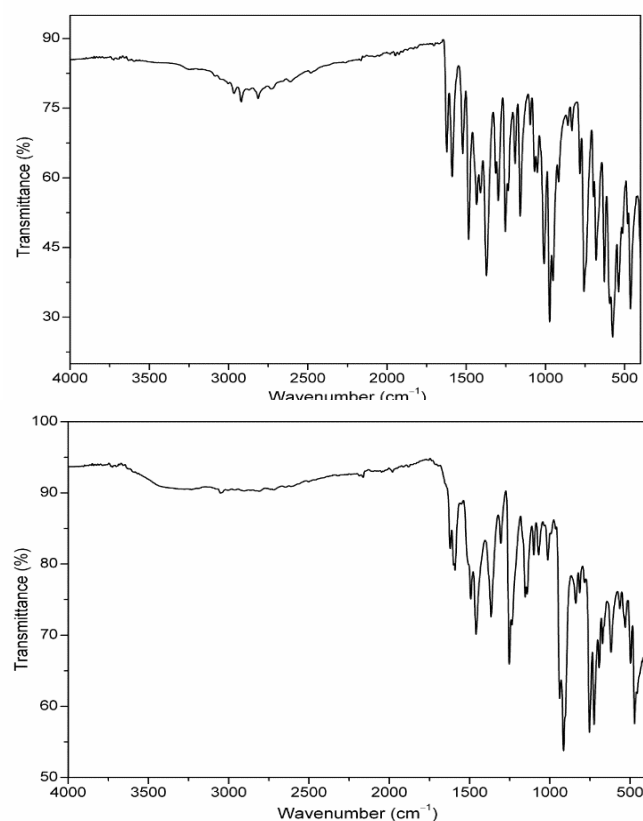


Fig. 7. Infrared spectra of $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) (top) and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2**·MeOH) (bottom).

Electronic spectra of both complexes collected using their corresponding acetonitrile solutions are illustrated in Fig. 8. The spectrum of **1** displays a strong absorption shoulder at 375 nm with a long tail extending into the visible region and two very strong bands at 270 and 207 nm. In contrast, **2**·MeOH shows three strong bands at 452, 320 and 262 nm and a very strong band at 207 nm. The absorptions observed above 300 nm are attributed to ligand-to-metal charge transfer bands and the two higher energy bands observed below 300 nm are assigned to ligand-centered transitions [19–23,34,35].

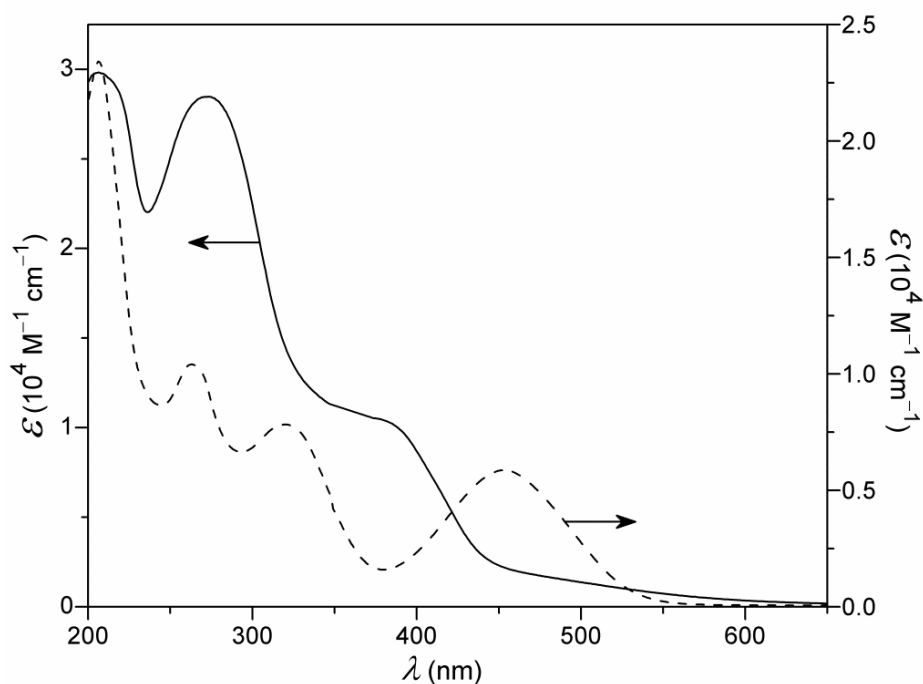


Fig. 8. Electronic spectra of $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) (—) and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2**·MeOH) (---) in acetonitrile.

The ^1H NMR spectra of **1** and **2**·MeOH were recorded in CDCl_3 and $(\text{CD}_3)_2\text{SO}$, respectively (Fig. 9). The chemical shift data with the tentative assignments are listed in the experimental section with the respective complexes. The spectrum of **1** is consistent with its centrosymmetric dimeric structure. The free Schiff base (H_3L) is known to display three singlets each of one-proton at δ 11.33, 11.62 and 11.72 ppm for the amide-NH, oxime-OH and phenolic-OH protons, respectively [42]. In contrast, both **1** and **2**·MeOH show only one sharp singlet at δ 10.02 and 11.78 ppm, respectively. Appearance of a single peak is consistent with the deprotonation of the amide-NH and oxime-OH and the protonated state of the phenol functionality of the tridentate ligand (HL) $^{2-}$ in both complexes. Two three-proton singlets observed at δ 1.94 and 2.56 ppm for **1** and δ 1.84 and 2.43 ppm for **2**·MeOH are attributed to the protons of the methyl groups at the imine and the oxime ends, respectively. The protons of the metal coordinated methoxo group of **1** are observed as a three-proton singlet at δ 3.42 ppm. The four aromatic ring protons of **1** and **2**·MeOH appear with the expected splitting patterns in the chemical shift ranges δ 6.65–7.34 and 6.90–7.72 ppm, respectively. No signal assignable to the methanol methyl protons is observed in the spectrum of **2**·MeOH. Perhaps it is masked by the intense water signal at δ 3.33 ppm. Overall, the spectra of the two complexes are consistent with their corresponding molecular structures.

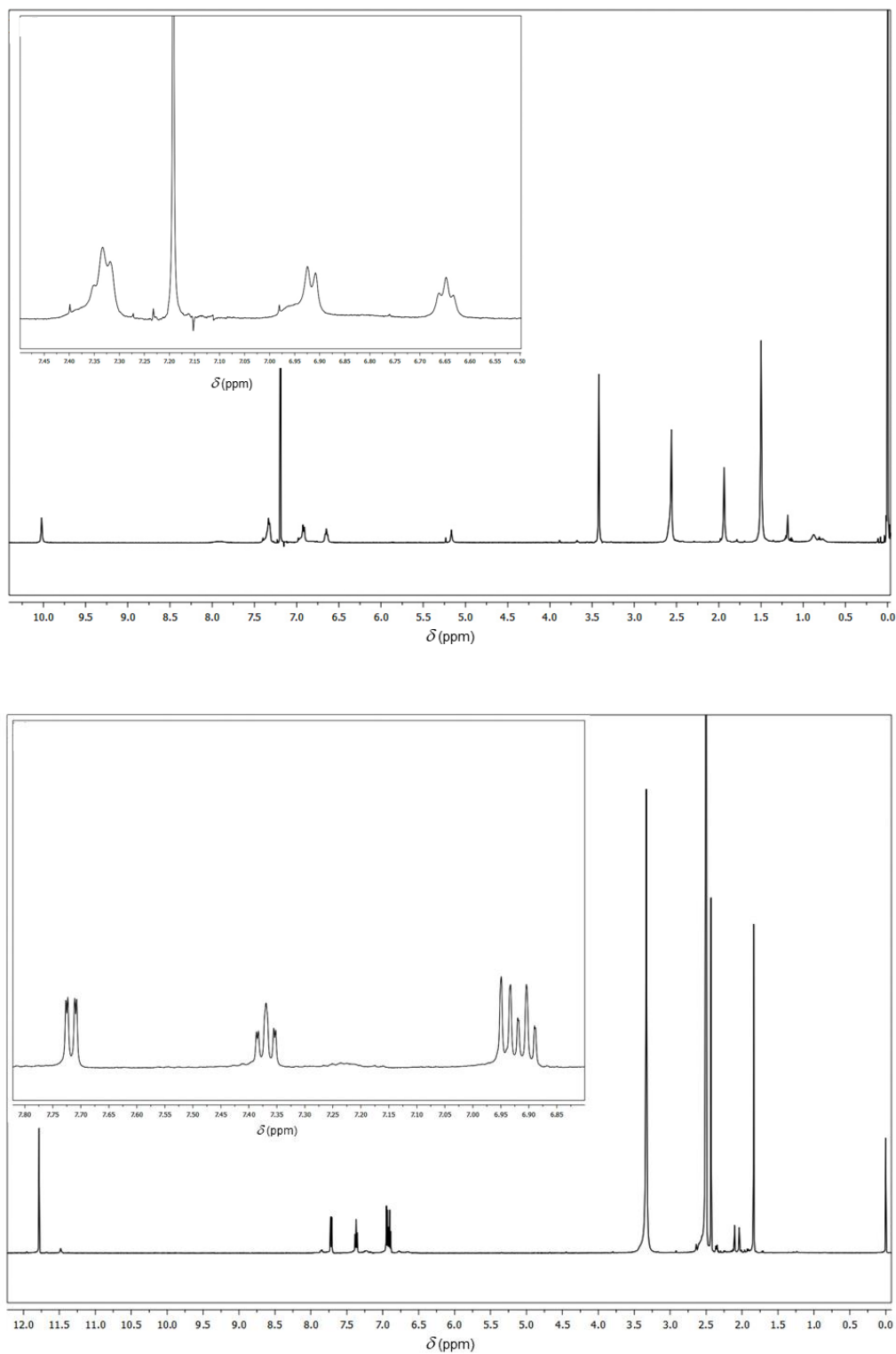


Fig. 9. ^1H NMR spectra of $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (1) in CDCl_3 and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (2·MeOH) in $(\text{CD}_3)_2\text{SO}$ (bottom).

3.4.5. Redox properties

Electron transfer characteristics of **1**, **2**·MeOH and the Schiff base H₃L were examined by cyclic voltammetry. Each three-electrode measurement was carried out at room temperature (298 K) with 1×10^{-3} M acetonitrile solution of the compound containing Bu₄NClO₄ (0.1 M) as the supporting electrolyte using a glassy carbon working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode at a scan rate of 100 mV s⁻¹. Under identical conditions, the ferrocenium/ferrocene (Fc⁺/Fc) couple was observed at $E_{1/2} = 0.58$ V ($\Delta E_p = 150$ mV). The cyclic voltammograms of **1**, **2**·MeOH and the Schiff base H₃L are illustrated in Fig. 10. Complex **1** displays an irreversible reduction at $E_{pc} = -1.34$ V. However, **2**·MeOH shows a broad reduction peak near -0.9 V followed by a continuous increase of current. The free Schiff base H₃L also displays two irreversible broad reduction responses at -0.9 and -1.5 V. Thus, the reductions observed for the complexes are very likely to be ligand centered rather than metal centered.

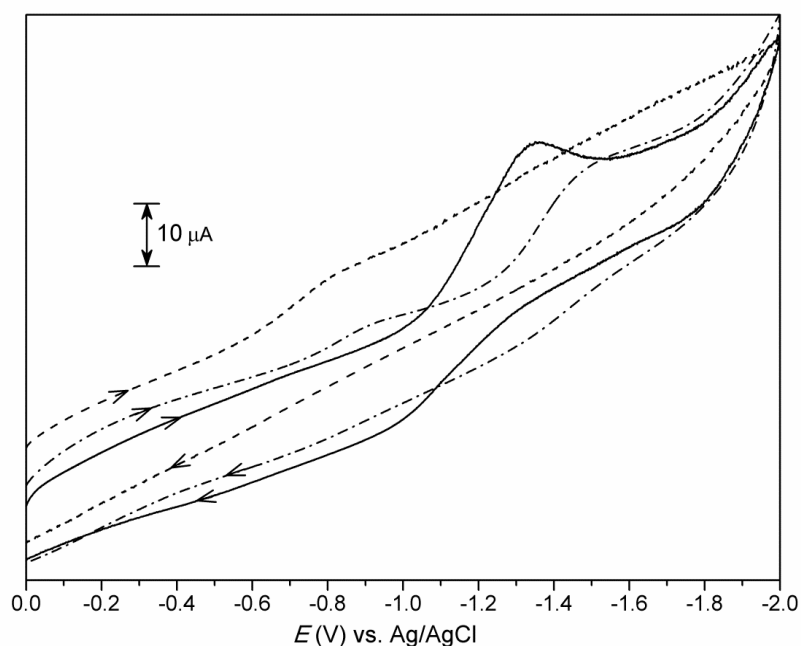


Fig. 10. Cyclic voltammograms of H₃L (---), [VO(μ - OMe)(HL)]₂ (**1**) (—) and K[VO₂(HL)]·MeOH (**2**·MeOH) (- - -) in acetonitrile.

3.5. Photocatalytic activities

Photocatalysts are of immense contemporary interest because of their applications in effective handling of environmental pollution problems. They can be used for removal of various toxic pollutants by their degradation, generation of bio-fuels and valuable chemicals by degradation of plant biomass and for water splitting to produce clean fuel hydrogen [56–65]. In recent times, oxovanadium(V) complexes and divanadium(V) pentoxide have found visible light driven photocatalytic applications in degradation of lignin like molecules and organic dyes [59–65]. A shoulder band at 375 nm with the tail extending up to ~450 nm is the lowest energy optical absorption for **1**, while that for **2**·MeOH is at 452 nm (*vide supra*). Because of these absorptions, both complexes have been examined for their photocatalytic activities in degradation of the organic dye rhodamine B (RhB) under visible light irradiation. The degradation reactions performed were heterogeneous in nature. The water insoluble powdered catalyst (**1** or **2**·MeOH) was added to the aqueous solution of RhB solution and the suspension was stirred and irradiated with visible light. The dye degradation was monitored spectrophotometrically. The variation of the spectroscopic profile of RhB with time in presence of the catalyst **1** is depicted in Fig. 11, while that for **2**·MeOH as catalyst is shown in Fig. 12. In 2 h, the extents of degradation of RhB are 84% and 91% for **1** and **2**·MeOH, respectively. In the control experiment without catalyst, the decrease in the concentration of RhB solution in 2 h of exposure to light is significantly smaller (13%). The changes in the dye concentrations with the increase of irradiation time in absence and in presence of catalysts are shown in Fig. 13. Assuming pseudo-first-order degradation of RhB, the degradation rate constants (k) for the two catalysts have been calculated using the equation $-\ln(C/C_i) = kt$ (C_i = initial concentration and C = concentration at time t). The k values obtained are 0.012(2) and 0.016(2) min^{-1} for **1** and **2**·MeOH, respectively. These rates are comparable with the rates reported for vanadium-doped nanomaterials catalyzed RhB degradation reactions under visible light

irradiation [62–65]. The first absorption maxima (452 nm) of **2**·MeOH is in the visible region, while that (375 nm) of **1** is in the violet end of the visible light. The band gap energies for these ligand-to-metal charge transfer bands calculated using the Tauc plot method are 2.87 and 2.42 eV for **1** and **2**·MeOH, respectively. Slightly better photocatalytic activity of **2**·MeOH than **1** is likely to be due to the difference in their absorption maxima, and hence the corresponding band gap energies [66].

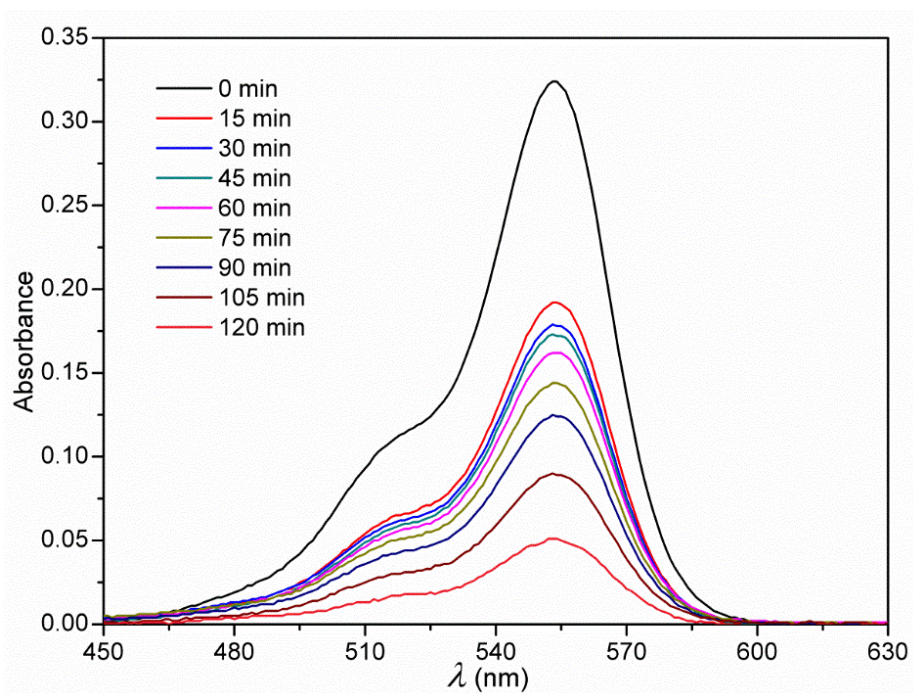


Fig. 11. Visible light driven catalytic degradation of rhodamine B (RhB) in presence of $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) as catalyst using the experimental conditions described in the text.

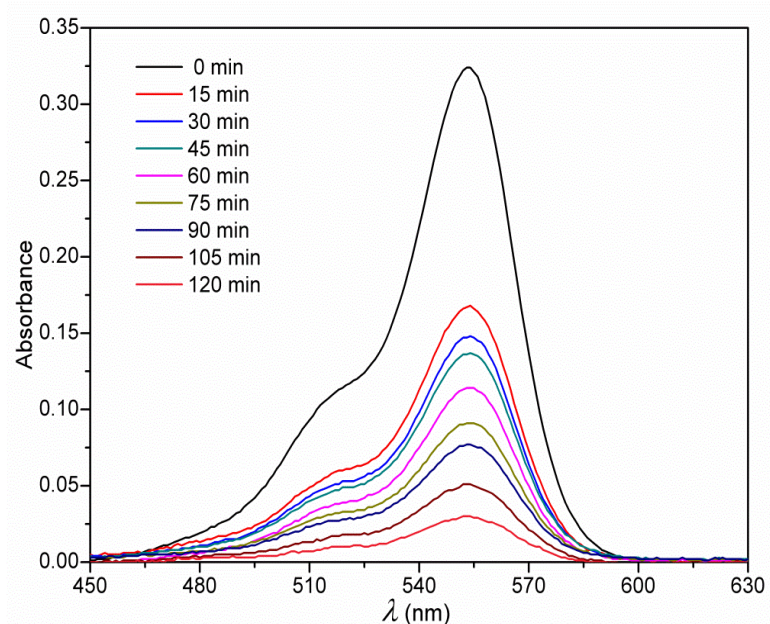


Fig. 12. Visible light driven catalytic degradation of rhodamine B (RhB) in presence of $K[VO_2(HL)] \cdot MeOH (2 \cdot MeOH)$ as catalyst using the experimental conditions described in the text.

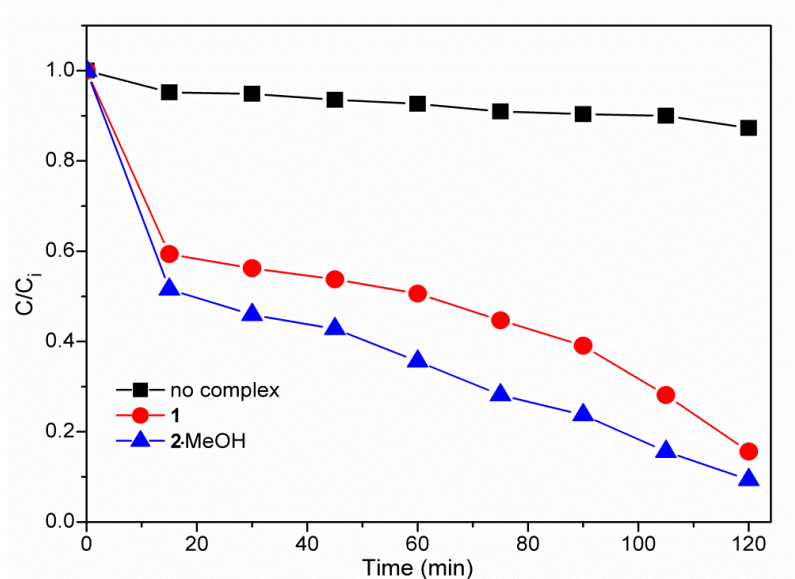


Fig. 13. Change of rhodamine B (RhB) concentration in absence and in presence of catalysts (**1** and **2·MeOH**) as a function of irradiation time. C and C_i represent the dye concentrations after and before irradiation, respectively.

Close to 90% of each of the two complex catalysts was collected after the catalytic reaction by filtration. The infrared and ^1H NMR spectra of the recovered samples showed no significant variation when compared with the corresponding spectra of the complexes before the reactions. Therefore, both complexes are recyclable and they can be reused for further catalytic cycles. Each of the two recovered catalysts was used for second time in the degradation reaction of RhB. In this second cycle, the degradation percentages of the dye were found to be 2–3% lower (82 and 88% for **1** and **2**·MeOH, respectively) than those observed in the first cycle.

It has been proposed that in photocatalytic dye degradation using oxovanadium(V) species as catalyst, the first step is an electron transfer from the photoexcited dye (RhB^*) to the oxovanadium(V) species and hydrogen abstraction leading to the formation of oxovanadium(IV) species, dye radical cation and water [61]. In the present system, it is very likely that the degradation of the dye begins in a similar fashion. Here, the catalytic reactions were performed under aerobic conditions and therefore the dissolved oxygen can regenerate the catalyst by oxidizing the reduced complex (**1** or **2**) and itself getting reduced to reactive oxygen species such as superoxide or peroxide. These reactive species can complete the oxidative degradation of the dye radical cation. In the control experiment using either of the two catalysts under nitrogen atmosphere in presence of light, there is no significant variation of the absorption spectrum of the dye. Thus, aerobic conditions are crucial for effective degradation of the dye.

3.6. Conclusions

Two complexes having the formulas $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2**·MeOH) with the Schiff base biacetylmonoxime salicyloylhydrazone (H_3L) have been reported. The X-ray molecular structures of **1** and **2**·MeOH revealed the ambidentate coordination behavior of the oximate group (O and N) of $(\text{HL})^{2-}$. The centrosymmetric dimeric **1** is an

edge-shared bioctahedral complex. Here $(\text{HL})^{2-}$ has a fused 5,6-membered chelate rings forming amidate-O, imine-N and oximate-O coordination mode. On the other hand, in $2\cdot\text{MeOH}$, the distorted trigonal bipyramidal monoanionic complex $[\text{VO}_2(\text{HL})]^-$ contains the fused 5,5-membered chelate rings forming amidate-O, imine-N and oximate-N donor $(\text{HL})^{2-}$. The counter cation K^+ in $2\cdot\text{MeOH}$ is in distorted gyrobifastigium O_8 coordination sphere. In the crystal lattice, $2\cdot\text{MeOH}$ forms two-dimensional coordination polymeric network structure. Physical and spectroscopic characteristics of the two complexes are in good agreement with their molecular formulas and structures. Both complexes are photocatalytically active and visible light induced photodegradation of rhodamine B up to 84 and 91% has been achieved in 2 h using **1** and $2\cdot\text{MeOH}$, respectively as catalysts.

3.7. References

- [1] D. Rehder, *Bioinorganic Vanadium Chemistry*, Willey, Chichester, 2008.
- [2] M.R. Maurya, *J. Chem. Sci.* 123 (2011) 215–228.
- [3] C. Leblanc, H. Vilter, J.-B. Fournier, L. Delage, P. Potin, E. Rebuffet, G. Michel, P.L. Solari, M.C. Feiters, M. Czjzek, *Coord. Chem. Rev.* 301–302 (2015) 134–146.
- [4] C.C. McLauchlan, H.A. Murakami, C.A. Wallace, D.C. Crans, *J. Inorg. Biochem.* 186 (2018) 267–279.
- [5] B.J. Hales, Vanadium Nitrogenase. In: B.E. Smith, R.L. Richards, W.E. Newton, (Eds.), *Catalysts for Nitrogen Fixation*. Nitrogen Fixation: Origins, Applications, and Research Progress, Vol. 1, *Springer, Dordrecht*, 2004, pp 255–279.
- [6] Y. Hu, C.C. Lee, M.W. Ribbe, *Dalton Trans.* 41 (2012) 1118–1127.
- [7] Y. Tanabe, Y. Nishibayashi, *Coord. Chem. Rev.* 381 (2019) 135–150.
- [8] Y. Shechter, I. Goldwasser, M. Mironchik, M. Fridkin, D. Gefel, *Coord. Chem. Rev.* 237 (2003) 3–11.

- [9] T. Scior, J.A. Guevara-Garcia, Q.-T. Do, P. Bernard, S. Laufer, *Curr. Med. Chem.* 23 (2016) 2874-2891.
- [10] T. Jakusch, T. Kiss, *Coord. Chem. Rev.* 351 (2017) 118–126.
- [11] I. Kostova, *Anti-Cancer Agents Med. Chem.* 9 (2009) 827–842.
- [12] E. Kioseoglou, S. Petanidis, C. Gabriel, A. Salifoglou, *Coord. Chem. Rev.* 301–302 (2015) 87–105.
- [13] H. Pellissier, *Coord. Chem. Rev.* 284 (2015) 93–110.
- [14] R.R. Langeslay, D.M. Kaphan, C.L. Marshall, P.C. Stair, A.P. Sattelberger, M. Delferro, *Chem. Rev.* 119 (2019) 2128–2191.
- [15] D.C. Crans, J.J. Smee, Vanadium, In: J.A. McCleverty, T.J. Meyer, (Eds.) *Comprehensive Coordination Chemistry II, Vol. 4, Elsevier*, 2003.
- [16] R.L. Richards, *Vanadium: Inorganic & Coordination Chemistry*. In: *Encyclopedia of Inorganic Chemistry*, John Wiley & Sons, Ltd: Brighton, UK, 2006.
- [17] P. Galloni, V. Conte, B. Floris, *Coord. Chem. Rev.* 301–302 (2015) 240–299.
- [18] M.R. Maurya, *Coord. Chem. Rev.* 383 (2019) 43–81.
- [19] N.R. Sangeetha, S. Pal, *Bull. Chem. Soc. Jpn.* 73 (2000) 357–363.
- [20] S.N. Pal, K.R. Radhika, S. Pal, *Z. Anorg. Allg. Chem.* 627 (2001) 1631–1637.
- [21] A. Sarkar, S. Pal, *Polyhedron* 26 (2007) 1205–1210.
- [22] A. Sarkar, S. Pal, *Inorg. Chim. Acta* 362 (2009) 3807–3812.
- [23] A.K. Srivastava, S. Ghosh, S. Jana, S. Pal, *Inorg. Chim. Acta* 483 (2018) 329–336.
- [24] A. Mukhopadhyay, S. Pal, *Eur. J. Inorg. Chem.* (2009) 4141–4148.
- [25] W. Kaim, *Dalton Trans.* 48 (2019) 8521–8529.
- [26] N.R. Sangeetha, C.K. Pal, P. Ghosh, S. Pal, *J. Chem. Soc., Dalton Trans.* (1996) 3293–5296.
- [27] S.N. Pal, S. Pal, *J. Chem. Soc., Dalton Trans.* (2002) 2102–2108.
- [28] A. Chakravorty, *Coord. Chem. Rev.* 13 (1974) 1–46.

- [29] V.Y. Kukushkin, A.J.L. Pomberio, *Coord. Chem. Rev.* 181 (1999) 147–175.
- [30] P. Chaudhuri, *Coord. Chem. Rev.* 243 (2003) 143–190.
- [31] C.J. Milios, T.C. Stamatatos, S.P. Perlepes, *Polyhedron* 25 (2006) 134–194.
- [32] S.G. Sreerama, S. Pal, *Inorg. Chem.* 41 (2002) 4843–4845.
- [33] S.G. Sreerama, S. Pal, *Eur. J. Inorg. Chem.* (2004) 4718–4723.
- [34] S.P. Dash, S. Pasayat, Saswati, H.R. Dash, S. Das, R.J. Butcher, R. Dinda, *Polyhedron* 31 (2012) 524–529.
- [35] M. Sutradhar, T.R. Barman, S. Ghosh, M.G.B. Drew, *J. Mol. Struct.* 1037 (2013) 276–282.
- [36] Z.-J. Xiao, S.-X. Liu, C.C. Lin, *Chinese J. Inorg. Chem.* 20 (2004) 513–518.
- [37] S. Naskar, D. Mishra, R.J. Butcher, S.K. Chattopadhyay, *Polyhedron* 26 (2007) 3703–3714.
- [38] N. Chitrapriya, V. Mahalingam, M. Zeller, K. Natarajan, *Inorg. Chim. Acta* 363 (2010) 3685–3693.
- [39] M. Sutradhar, L.M. Carrella, E. Rentschler, *Eur. J. Inorg. Chem.* (2012) 4273–4278.
- [40] S. Martínez, F. Igoa, I. Carrera, G. Seoane, N. Veiga, A.S.S. De Camargo, C. Kremer, J. Torres, *J. Coord. Chem.* 71 (2018) 874–889.
- [41] N. Chitrapriya, V. Mahalingam, L.C. Channels, M. Zeller, F.R. Fronczek, K. Natarajan, *Inorg. Chim. Acta* 361 (2008) 2841–2850.
- [42] J.-P. Costes, C. Duhayon, *Eur. J. Inorg. Chem.* (2014) 4745–4749.
- [43] R.D. Shannon, *Acta Crystallogr. Sect. A* 32 (1976) 751–767.
- [44] R.D. Hancock, *Pure Appl. Chem.* 58 (1986) 1445–1452.
- [45] R.D. Hancock, *Chem. Soc. Rev.* 42 (2013) 1500–1524.
- [46] R.A. Rowe, M.M. Jones, *Inorg. Synth.* 5 (1957) 113–116.
- [47] APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2016.

- [48] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 64 (2008) 112–122.
- [49] L.J. Farrugia, *J. Appl. Crystallogr.* 45 (2012) 849–854.
- [50] F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Crystallogr.* 41 (2008) 466–470.
- [51] W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81–122.
- [52] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, *J. Appl. Cryst.* 46 (2013) 1231–1235.
- [53] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, *J. Chem. Soc., Dalton Trans.* (1984) 1349–1356.
- [54] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, SHAPE, version 2.1, Universitat de Barcelona, Barcelona, Spain, 2013.
- [55] D. Casanova, M. Llunell, P. Alemany, S. Alvarez, *Chem. Eur. J.* 11 (2005) 1479–1494.
- [56] Q.-Q. Xiao, D. Liu, Y.-L. Wei, G.-H. Cui, *Polyhedron* 158 (2019) 342–351.
- [57] X.-J. Wei, D. Liu, Y.-H. Li, G.-H. Cui, *J. Solid State Chem.* 272 (2019) 138–147.
- [58] S. Ghosh, A.K. Srivastava, S. Pal, *New J. Chem.* 43 (2019) 970–978.
- [59] S. Gazi, W.K.H. Ng, R. Ganguly, A.M.P. Moeljadi, H. Hirao, H.S. Soo, *Chem. Sci.* 6 (2015) 7130–7142.
- [60] S. Gazi, M. Dokić, A.M.P. Moeljadi, R. Ganguly, H. Hirao, H.S. Soo, *ACS Catal.* 7 (2017) 4682–4691.
- [61] Y. Li, J.-L. Kuang, Y. Lu, W.-B. Cao, *Acta Metall. Sin. (Engl. Lett.)* 30 (2017) 1017–1026.
- [62] X. Hu, T. Mohamood, W. Ma, C. Chen, J. Zhao, *J. Phys. Chem. B* 110 (2006) 26012–26018.
- [63] A.A. Taha, A.A. Hriez, Y.-N. Wu, H. Wang, F. Li, *J. Colloid Interface Sci.* 417 (2014) 199–205.

- [64] D. Lu, B. Zhao, P. Fang, S. Zhai, D. Li, Z. Chen, W. Wu, W. Chai, Y. Wu, N. Qi, *Appl. Surf. Sci.* 359 (2015) 435–448
- [65] M. Epifani, S. Kaciulis, A. Mezzi, D. Altamura, C. Giannini, R. Díaz, C. Force, A. Genç, J. Arbiol, P. Siciliano, E. Comini, I. Concina, *Sci. Rep.* 7 (2017) 44763.
- [66] A. Hassan, T. Iqbal, M.B. Tahir, S. Afsheen, *Int. J. Energy Res.* 43 (2019)9–28.

Chapter 4

Mixed-valent tetracobalt(II/III) cluster as a bifunctional heterogeneous electrocatalyst for water splitting at neutral pH

4.1. Abstract

The reaction of 2,6-diformyl-4-methylphenol, 4-methoxybenzoyl-hydrazine and cobalt(II) acetate tetrahydrate in 1:2:2 mole ratio in methanol under aerobic conditions produced in 61% yield a tetranuclear complex having the molecular formula $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ where OAc^- and L^{3-} represent acetate and N',N'' -(5-methyl-2-oxido-1,3-phenylene)bis(methan-1-yl-1-ylidene)bis(4-methoxybenzoylhydrazonate), respectively. The X-ray structure shows that each cobalt(II) center has a square-pyramidal NO_4 coordination sphere, while each cobalt(III) center is in octahedral NO_5 environment. The four metal atoms and the four bridging O-atoms form an open cubane type Co_4O_4 motif. The infrared and electronic spectroscopic features of the complex are consistent with its molecular structure. Cryomagnetic measurements together with theoretical calculations suggest presence of easy-axis anisotropy for the square-pyramidal cobalt(II) centers. The complex is redox-active and displays metal centered oxidation and reduction responses on the anodic and cathodic sides, respectively, of Ag/AgCl electrode. Bifunctional heterogeneous electrocatalytic activities of the complex in H_2 and O_2 evolution reactions (HER and OER) in neutral aqueous medium have been explored in detail.

4.2. Introduction

The growing concerns about the global warming caused by the continuously increasing air pollution and the impending energy crisis are due to the excessive dependence on fossil-based fuels and hence their rapid depletion. As a consequence, there is a worldwide effort to find a clean combustible alternative to fossil fuel. Hydrogen is well known as an environment friendly energy source because of the zero-emission of greenhouse gases [1]. Electrochemical water splitting is the most widely accepted and relatively simple strategy for the production of pure hydrogen gas at a large scale compared to various other methods [2–5]. The challenging part in electrochemical water splitting is to develop efficient, stable and cost-effective electrocatalyst for its two half-reactions: oxidation of water or oxygen evolution reaction (OER), i.e., $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ and reduction of water or hydrogen evolution reaction (HER), i.e., $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$. Both processes have sluggish reaction kinetics and therefore they require high overpotentials. As a result, large scale production of either of the two gases becomes difficult. Electrocatalysts are expected to reduce the overpotential for efficient water splitting. Till now, low overpotential Pt-group metal [6] based catalysts are well known for efficient HER, while RuO_2 and IrO_2 are most effective catalysts for OER [7]. However, these metals are of very low abundance and hence very expensive. Thus, there is a continuous quest for exploration of earth abundant low-cost transition metal based electrocatalysts capable of showing HER and OER with low overpotential, low Tafel slope, and high turnover frequency. In this effort, various earth abundant transition metal carbides, borides, nitrides, phosphides and chalcogenides have been successfully used as efficient heterogeneous electrocatalysts for HER [2–4], while the above-mentioned materials as well as transition metal oxides, hydroxides, phosphates, and perovskites have been shown to exhibit excellent electrocatalytic OER

[3,4,7]. Some of these materials are bifunctional as they are able to electrocatalyze both HER and OER [3,4]. Recently, there has been considerable interest in cobalt analogs of the above-mentioned materials as heterogeneous electrocatalysts [4] for water splitting because of its high abundance and hence low cost and the very high aqueous cobalt(III)/cobalt(II) reduction potential (1.83 V vs. RHE) [8]. A significant amount of work has also been reported on the application of various mono- and polynuclear coordination complexes of cobalt as molecular catalysts for both HER and OER [9]. Among these complexes, the Co_4O_4 cubane core containing OER catalysts are of particular interest with regard to the oxygen evolving center of the photosystem II [9h-m]. In comparison, very few cobalt complexes attached to an electrode surface have been employed as heterogeneous electrocatalyst for HER or OER [10]. Herein, we report a tetranuclear mixed-valent complex of formula $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ (HOAc = acetic acid and H_3L = N',N'' -(2-hydroxy-5-methyl-1,3-phenylene)bis(methan-1-yl-1-ylidene)bis(4-methoxybenzoylhydrazone), where 3 Hs denote the dissociable phenol and two secondary amide protons) having an open cubane Co_4O_4 core (Chart 1) and its heterogeneous electrocatalytic activities in both O_2 and H_2 evolution reactions (OER and HER) in neutral aqueous buffer medium.

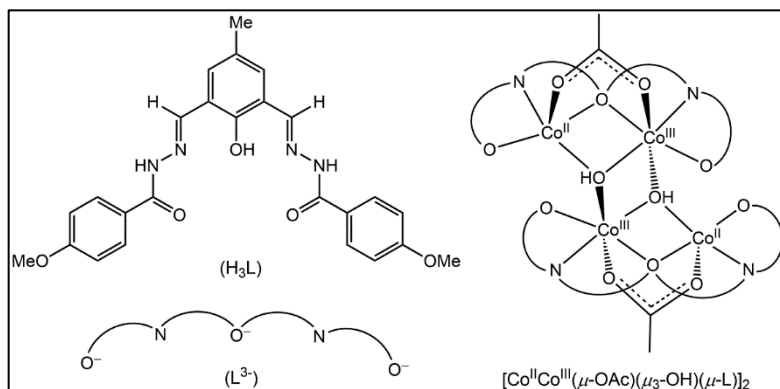


Chart 1. Chemical diagrams of H_3L and the mixed-valent tetracobalt complex.

4.3. Experimental section

4.3.1. Materials

2,6-diformyl-4-methylphenol was synthesized by following a reported procedure.¹¹ All other chemicals and solvents used in this work were of analytical grade available commercially and were used as received without further purification.

4.3.2. Physical measurements

Elemental analysis (CHN) data were obtained with a Thermo Finnigan Flash EA1112 series elemental analyzer. Mass spectrum was recorded using a Bruker Maxis (ESI-TOF analyzer) spectrometer. A Digisun DI-909 conductivity meter was used to measure the solution electrical conductivity. The infrared spectrum was recorded in ATR mode on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used to collect the electronic spectrum. Cyclic and differential pulse voltammetric measurements with *N,N*-dimethylformamide (DMF) solution of the complex were performed with a CH Instruments model 620A electrochemical analyzer. Variable temperature magnetic susceptibility measurements were performed using a Quantum Design SQUID-VSM magnetometer. Varian 720-ES and Perkin Elmer Sciex ELAN DRC spectrometers were used for ICP-OES and ICP-MS measurements, respectively. Gas chromatographic experiments were performed with a Shimadzu Nexis GC-2030 gas chromatograph equipped with a thermal conductivity detector and a molecular sieve 5 Å column. Field emission scanning electron microscopy (FESEM) was carried out with a Carl Zeiss Ultra 55 microscope. Energy dispersive X-ray (EDX) spectra and elemental mappings were recorded using Oxford Instruments X-Max^N SDD (50 mm²) system and INCA analysis software.

4.3.3. Synthesis of $[Co^{II}Co^{III}(\mu-OAc)(\mu_3-OH)(\mu-L)]_2$

A methanol solution (5 mL) of 4-methoxybenzoylhydrazine (66 mg, 0.4 mmol) was added dropwise to a methanol solution (15 mL) of 2,6-diformyl-4-methyl phenol (33 mg, 0.2 mmol) and the mixture was stirred at room temperature (298 K) for ½ h. To the resulting yellow solution, solid $Co(OAc)_2 \cdot 4H_2O$ (100 mg, 0.4 mmol) was added and stirring continued at 298 K under aerobic conditions for 6 h. The brown solid separated was collected by filtration, washed with cold methanol, and finally dried in air. Yield: 80 mg (61%). Anal. Calcd (%) for $C_{54}H_{50}N_8O_{16}Co_4$ (1302.77): C, 49.79; H, 3.87; N 8.60. Found: C, 49.61; H, 3.78; N, 8.54. ESI-MS in DMF (m/z) Calcd. for $C_{54}H_{51}N_8O_{16}Co_4^+$ ($M + H$)⁺: 1303.0751. Found: 1303.0750. Selected IR bands (ν (cm⁻¹)): 3360 (O–H), 1606 (C=N), 1563 and 1410 (COO⁻). UV-Vis in DMF (λ_{max} (nm) (ϵ (M⁻¹cm⁻¹))): 600^{sh} (68), 415^{sh} (3.7×10^3), 345 (10.5×10^3). CV in DMF (V): $E_{pa} = 0.48$ and 0.82 , $E_{pc} = -0.96$. DPV in DMF (V): $E_p = 0.42$, 0.77 and -0.78 , -0.88 .

4.3.4. Electrocatalytic studies

All the electrochemical hydrogen and oxygen evolution experiments were performed using a Zahner Zanium electrochemical workstation operated with Thales software using a $[Co^{II}Co^{III}(\mu-OAc)(\mu_3-OH)(\mu-L)]_2$, carbon-black (CB), and Nafion coated fluorine-doped tin oxide (FTO) glass plate as the working electrode, Ag/AgCl reference electrode, and a Pt wire as the counter electrode in 0.1 M aqueous sodium phosphate buffer of neutral pH at ambient temperature (298 K). Method for the coating on FTO glass plates was as follows: Nafion solution (5 wt%, 10 μ L) was added to a mixture of $[Co^{II}Co^{III}(\mu-OAc)(\mu_3-OH)(\mu-L)]_2$ (4 mg) and CB (1 mg) in 1 mL of a mixture of ethanol-water (3:2, v/v) and the whole mixture was sonicated for 2 h. A 30 μ L portion of this mixture was spread over the surface of a FTO glass plate of area 0.2 cm² by drop casting method and then the surface was dried by heating with an IR lamp. The open

circuit potential was used as the initial potential for all cyclic voltammetric measurements. All the electrode potentials obtained were converted to the normal hydrogen electrode (NHE) scale by using the relation $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.2 \text{ V}$. Constant current electrolysis (CCE) experiments were performed using a locally designed and constructed electrolysis cell (Fig. 1) [12].

4.3.5. Quantitative estimation of electrocatalytically produced hydrogen/oxygen

The quantitative estimation of the evolved gas was performed by constant current electrolysis (CCE) with a locally designed and constructed electrolysis cell, where the working electrode and the counter electrode were placed in two separate chambers (Fig. 1). Bulk electrolysis at a constant current of $-500 \mu\text{A}$ (for HER) or $500 \mu\text{A}$ (for OER) was carried out for 6 h using the two-electrode system and 0.1 M sodium phosphate buffer of pH 7 as the



electrolyte. Surface coated (with $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, carbon-black and Nafion) FTO electrode with surface area of 0.5 cm^2 was used as the working electrode (cathode for HER/anode for OER) and a spiral platinum wire was used as the counter electrode (anode for HER/cathode for OER). The loading of the catalyst on FTO was maintained at 0.6 mg/cm^2 . During electrolysis gas bubbles were formed at the surface coated FTO electrode which steadily accumulated in the graduated tube by displacing the electrolyte solution. The cell was designed in such a way that the gas bubbles formed at the counter electrode could no way interfere with those formed at the working electrode.

Fig. 1. Locally designed and constructed electrolysis cell. Samar K. Das et al, *Angew. Chem. Int. Ed.* 2018, 57, 1918 –1923.

4.3.5.1. Calculations of faradaic efficiency and turnover frequencies for OER using complex, CB, and Nafion mixture coated FTO electrode

Faradaic efficiency (OER)

In the CCE experiment for OER, 0.53 mL of oxygen was evolved at ambient temperature and pressure in 6 h. Therefore, the number of moles of oxygen evolved in 1 h = $0.53/(6 \times 22400)$ mol = 3.94×10^{-6} mol.

In the controlled experiment performed using carbon-black and Nafion coated FTO electrode keeping all other experimental conditions identical the amount of oxygen evolved in 6 h was ~0.04 mL. Hence, the number of moles oxygen evolved in 1 h = $0.04/(6 \times 22400)$ mol = 0.3×10^{-6} mol.

Hence, the amount of oxygen actually evolved = $(3.94 - 0.3) \times 10^{-6}$ mol
= 3.64×10^{-6} mol.

The ideal number of moles of oxygen expected to be evolved is Q/nF , where Q is the total charge employed, n is the number of electrons involved for O₂ production and F is the Faraday constant. The value of n for OER is 4 as it is a four-electron process and since we employed 500 μ A current, Q/nF in 1 h = $(0.5 \times 10^{-3} \times 3600)/(4 \times 96500)$ = 4.66×10^{-6} mol.

The expression used for the calculation of the Faradaic Efficiency is as follows:

$$\text{Faradaic Efficiency} = \frac{\text{Moles of oxygen evolved experimentally in 1 h}}{\text{Moles of oxygen ideally expected in 1 h}} \times 100$$

$$= \{(3.64 \times 10^{-6})/(4.66 \times 10^{-6})\} \times 100 = 78\%$$

Turnover frequency (OER)

Here, the equation used for the calculation of TOF was $\text{TOF} = I/4mF$, where, I (= 2.4×10^{-5} A) is the steady state current in the constant potential (1.05 V) electrolysis (CPE) plot for OER (Fig. 15), F is the Faraday constant (in C mol⁻¹), m is the number of active sites (in mol), and 4 is the number of electrons required

to form one oxygen molecule from two water molecules. The number of active sites m was calculated using the equation, $m = Q/2F$, where, Q (3.97×10^{-5} C) is the charge calculated by integrating the current vs time plot (within the potential range 0.5 to 1.1 V) generated from the cyclic voltammogram trace (in Fig. 10) recorded using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, carbon-black, and nafion coated FTO as the working electrode under non-catalytic conditions (THF medium rather than the neutral sodium phosphate buffer medium) and the factor $\frac{1}{2}$ is for the 2 electron oxidation of the catalyst $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$. Now, replacing m by $Q/2F$ in the equation for TOF (in h^{-1}) we get:

$$\begin{aligned}\text{TOF (in h}^{-1}\text{)} &= (I/4mF) \times 3600 = (I/2Q) \times 3600 \\ &= \{(2.4 \times 10^{-5})/(2 \times 3.97 \times 10^{-5})\} \times 3600 \\ &= 1088 = 1.1 \times 10^3\end{aligned}$$

4.3.5.2. Calculations of the faradaic efficiencies and turn over frequency for HER using complex, CB, and Nafion mixture coated FTO electrode

Faradaic efficiency (HER)

In the CCE experiment for HER, it was found that 1.4 mL of hydrogen was evolved at ambient temperature and pressure in 6 h. Therefore, the number of moles of hydrogen evolved in 1 h = $1.4/(6 \times 22400)$ mol = 10.41×10^{-6} mol.

The controlled experiment was performed using carbon-black and nafion coated FTO electrode keeping all other experimental conditions identical. The total amount of hydrogen evolved in 6 h was ~0.22 mL. Therefore, in terms of number of moles, the amount of hydrogen evolved in 1 h = $0.22/(6 \times 22400)$ mol = 1.63×10^{-6} mol.

Thus, the amount of hydrogen actually evolved in 1 h = $(10.41 - 1.63) \times 10^{-6}$ mol = 8.78×10^{-6} mol.

The ideal number of moles of hydrogen expected to be evolved is Q/nF , where Q is the total charge employed, n is the number of electrons involved for H_2

production and F is the Faraday constant. The value of n for HER is 2 as it is a two-electron process and since we employed $-500 \mu\text{A}$ current, Q/nF in 1 h = $(0.5 \times 10^{-3} \times 3600)/(2 \times 96500) = 9.33 \times 10^{-6} \text{ mol}$.

The expression used for the calculation of faradaic efficiency is as follows:

$$\text{Faradaic Efficiency} = \frac{\text{Moles of hydrogen evolved experimentally in 1 h}}{\text{Moles of hydrogen ideally expected in 1 h}} \times 100$$

$$= \{(8.78 \times 10^{-6})/(9.33 \times 10^{-6})\} \times 100 = 94\%$$

Turnover frequency (HER)

The TOF was calculated using the following equation: $\text{TOF} = I/2mF$, where, I ($= 2.55 \times 10^{-4} \text{ A}$) is the steady state current in the constant potential (-1.05 V) electrolysis (CPE) plot for HER (Fig. 15), F is the Faraday constant (in C mol^{-1}), m is the number of active sites (in mol), and 2 is the number of electrons required to form one hydrogen molecule from two protons.

The number of active sites m can be calculated using the equation, $m = Q/2F$, where, Q ($1.96 \times 10^{-4} \text{ C}$) is the charge calculated by integrating the current vs time plot (within the potential range -0.8 to -1.2 V) generated from the cyclic voltammogram trace (in Fig. 11) recorded using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$, carbon-black, and Nafion coated FTO as the working electrode under non-catalytic conditions (THF medium rather than the neutral sodium phosphate buffer medium) and the factor $\frac{1}{2}$ is for the 2 electron reduction of the catalyst $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$. Now, replacing m by $Q/2F$ in the equation for TOF (in h^{-1}) we get:

$$\begin{aligned} \text{TOF (in h}^{-1}\text{)} &= (I/2mF) \times 3600 = (I/Q) \times 3600 \\ &= \{(2.55 \times 10^{-4})/(1.96 \times 10^{-4})\} \times 3600 \\ &= 4683 = 4.6 \times 10^3 \end{aligned}$$

4.3.5.3. Calculations of the faradaic efficiency and turnover frequency for OER using pure complex coated FTO electrode

Faradaic efficiency (OER)

In the CCE experiment for OER, 0.51 mL of oxygen was evolved at ambient temperature and pressure in 6 h. Therefore, the number of moles of oxygen evolved in 1 h = $0.51/(6 \times 22400)$ mol = 3.8×10^{-6} mol.

In the controlled experiment performed using pristine FTO electrode keeping all other experimental conditions identical, the amount of oxygen evolved in 6 h was ~0.05 mL. Hence, the number of moles oxygen evolved in 1 h = $0.05/(6 \times 22400)$ mol = 0.4×10^{-6} mol.

Hence, the amount of oxygen actually evolved = $(3.8 - 0.4) \times 10^{-6}$ mol
= 3.4×10^{-6} mol.

The ideal number of moles of oxygen expected to be evolved is Q/nF , where Q is the total charge employed, n is the number of electrons involved for O₂ production and F is the Faraday constant. The value of n for OER is 4 as it is a four-electron process and since we employed 500 μ A current, Q/nF in 1 h = $(0.5 \times 10^{-3} \times 3600)/(4 \times 96500)$ = 4.66×10^{-6} mol.

The expression used for the calculation of Faradaic Efficiency is as follows:

$$\text{Faradaic Efficiency} = \frac{\text{Moles of oxygen evolved experimentally in 1 h}}{\text{Moles of oxygen ideally expected in 1 h}} \times 100$$

$$= \{(3.4 \times 10^{-6})/(4.66 \times 10^{-6})\} \times 100 = 73\%$$

Turnover frequency (OER)

Here, the equation used for the calculation of TOF was $\text{TOF} = I/4mF$, where, I (= 6.8×10^{-5} A) is the steady state current in the constant potential (1.28 V) electrolysis (CPE) plot for OER (Fig. 21), F is the Faraday constant (in C mol⁻¹),

m is the number of active sites (in mol), and 4 is the number of electrons required to form one oxygen molecule from two water molecules.

The number of active sites m was calculated using the equation, $m = Q/2F$, where, Q (3.6×10^{-5} C) is the charge calculated by integrating the current vs time plot (within the potential range 0.5 to 1.1 V) generated from the cyclic voltammogram trace recorded using only $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$ coated FTO as the working electrode under non-catalytic conditions (THF medium rather than the neutral sodium phosphate buffer medium) and the factor $\frac{1}{2}$ is for the 2 electron oxidation of the catalyst $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$. Now, replacing m by $Q/2F$ for m in the equation for TOF (in h^{-1}) we get:

$$\begin{aligned}\text{TOF (in h}^{-1}\text{)} &= (I/4mF) \times 3600 = (I/2Q) \times 3600 \\ &= \{(6.8 \times 10^{-5})/(2 \times 3.6 \times 10^{-5})\} \times 3600 \\ &= 3400 = 3.4 \times 10^3\end{aligned}$$

4.3.5.4. Calculations of the faradaic efficiency and turnover frequency for HER using pure complex coated FTO electrode

Faradaic efficiency (HER)

In the CCE experiment for HER, it was found that 1.33 mL of hydrogen was evolved at ambient temperature and pressure in 6 h. Therefore, the number of moles of hydrogen evolved in 1 h = $1.33/(6 \times 22400)$ mol = 9.89×10^{-6} mol.

The controlled experiment was performed using pristine FTO electrode keeping all other experimental conditions identical. The total amount of hydrogen evolved in 6 h was ~0.20 mL. Therefore, in terms of number of moles, the amount of hydrogen evolved in 1 h = $0.20/(6 \times 22400)$ mol = 1.48×10^{-6} mol.

Thus, the amount of hydrogen actually evolved in 1 h = $(9.89 - 1.48) \times 10^{-6}$ mol = 8.41×10^{-6} mol.

The ideal number of moles of hydrogen expected to be evolved is Q/nF , where Q is the total charge employed, n is the number of electrons involved for H_2

production and F is the Faraday constant. The value of n for HER is 2 as it is a two-electron process and since we employed $-500 \mu\text{A}$ current, Q/nF in 1 h = $(0.5 \times 10^{-3} \times 3600)/(2 \times 96500) = 9.33 \times 10^{-6} \text{ mol}$.

The expression used for the calculation of Faradaic Efficiency is as follows:

$$\begin{aligned} \text{Faradaic Efficiency} &= \frac{\text{Moles of hydrogen evolved experimentally in 1 h}}{\text{Moles of hydrogen ideally expected in 1 h}} \times 100 \\ &= \{(8.41 \times 10^{-6})/(9.33 \times 10^{-6})\} \times 100 = 90\% \end{aligned}$$

Turnover frequency (HER)

The TOF was calculated using the following equation: $\text{TOF} = I/2mF$, where, I ($= 7.57 \times 10^{-4} \text{ A}$) is the steady state current in the constant potential (-1.28 V) electrolysis (CPE) plot for HER (Fig. 21), F is the Faraday constant (in C mol^{-1}), m is the number of active sites (in mol), and 2 is the number of electrons required to form one hydrogen molecule from two protons. The number of active sites m can be calculated using the equation, $m = Q/2F$, where, Q ($1.77 \times 10^{-4} \text{ C}$) is the charge calculated by integrating the current vs time plot (within the potential range -0.8 to -1.2 V) generated from the cyclic voltammogram trace recorded using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ coated FTO as the working electrode under non-catalytic conditions (THF medium rather than the neutral sodium phosphate buffer medium) and the factor $\frac{1}{2}$ is for the 2 electron reduction of the catalyst $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$. Now, replacing m by $Q/2F$ in the equation for TOF (in h^{-1}) we get:

$$\begin{aligned} \text{TOF (in h}^{-1}\text{)} &= (I/2mF) \times 3600 = (I/Q) \times 3600 \\ &= \{(7.57 \times 10^{-4})/(1.77 \times 10^{-4})\} \times 3600 \\ &= 15396 = 1.53 \times 10^4 \end{aligned}$$

4.3.6. X-ray crystallography

X-ray quality single crystals of the complex were grown by slow evaporation of its acetonitrile solution. The complex crystallizes as a solvated species $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2 \cdot 1.5\text{MeCN}$. A Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source for graphite monochromated Mo $K\alpha$ Radiation ($\lambda = 0.71073 \text{ \AA}$) was used for the X-ray crystallographic measurements. The APEX3 software package [13] was used for data collection, integration and reduction. The data were corrected for absorption effects using the empirical multi-scan method implemented in the SADABS program [14]. The structure was solved by the direct method and refined on F^2 using full-matrix least-squares procedures. The full occupancy as well as the half occupancy acetonitrile molecules were refined with geometric restraints. All the non-hydrogen atoms were refined anisotropically, except for those of the half occupancy acetonitrile, which were refined isotropically. All the hydrogen atoms were placed at idealized positions and were refined as riding atoms. Structure solution and refinement were performed using the SHELX-97 programs [15] as contained in the WinGX software suite [16]. Structural illustrations were prepared with the help of the Mercury package [17] and EXPO2014 software [18]. Significant crystal and refinement data for $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2 \cdot 1.5\text{MeCN}$ are summarized in Table 1. Detailed X-ray crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center under the deposition number 2035075.

Table 1 Selected Crystallographic Data

Chemical formula	C ₅₇ H _{54.5} N _{9.5} O ₁₆ Co ₄
Formula weight	1364.32
Crystal system	Monoclinic
Space Group	<i>P</i> 2 ₁ /n
<i>a</i> (Å)	14.5982(6)
<i>b</i> (Å)	23.6769(10)
<i>c</i> (Å)	17.7661(8)
β (°)	101.349(2)
<i>V</i> (Å ³)	6020.6(4)
<i>Z</i>	4
ρ (g cm ⁻³)	1.505
μ (mm ⁻¹)	1.158
Reflections collected	95043
Reflections unique	10532
Reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	8885
Data / restraints / parameters	10532 / 6 / 788
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0540, 0.1431
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0659, 0.1542
GOF on <i>F</i> ²	1.050
Largest diff. peak / hole (e Å ⁻³)	0.912 / -0.416

4.4. Results and discussions

4.4.1. Synthesis and some properties

The complex $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ was synthesized in good yield (61%) through an in-situ method by reacting 2,6-diformyl-4-methylphenol, 4-methoxybenzoylhydrazine and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in 1:2:2 mole ratio in methanol under aerobic conditions. The complex is brown in color and highly soluble in *N,N*-dimethylformamide and Dimethyl sulfoxide, sparsely soluble in methanol and acetonitrile, and insoluble in chloroform, dichloromethane, and hexane. In solution, it behaves as non-electrolyte. The molecular formula of the bulk sample was confirmed by elemental analysis and high-resolution electrospray ionization mass spectrometry. The mass spectrum displays the molecular ion as the base peak with the expected isotopic pattern at an m/z value of 1303.0750 (Fig. 2). In consistence with the presence of two high-spin cobalt(II) centers known for large orbital contribution, the effective magnetic moment ($6.93 \mu_{\text{B}}$) at room temperature (300 K) of the complex in powder phase is considerably higher than the spin only value ($5.48 \mu_{\text{B}}$) (*vide infra*).

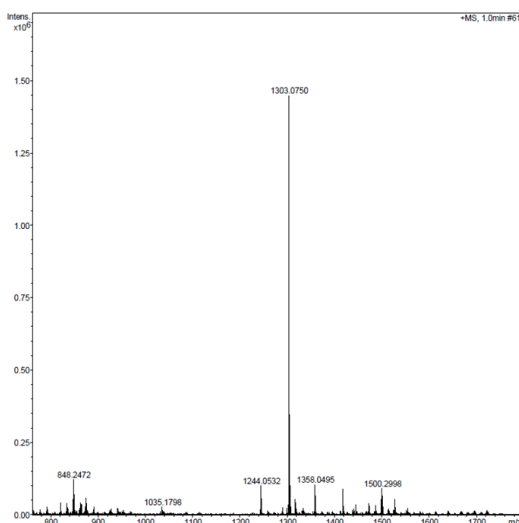


Fig. 2. ESI mass spectrum of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ in DMF.

4.4.2. X-ray structure

The structure of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2 \cdot 1.5\text{MeCN}$ was solved in the monoclinic $P2_1/n$ space group. The asymmetric unit comprises of one complete tetranuclear complex, one full occupancy acetonitrile and another half occupancy acetonitrile molecules. The acetonitrile N-atoms are somewhat close to the metal coordinated polarized azomethine-C–H groups indicating weak intermolecular hydrogen bonding interactions [19]. The $\text{C}\cdots\text{N}$ distance and the $\text{C-H}\cdots\text{N}$ angle are 3.761(17) Å and 153° for the full occupancy acetonitrile, while they are 4.149(19) Å and 143° for the half occupancy acetonitrile. The structure of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ is illustrated in Fig. 3 and the bond lengths and angles associated with the metal centers are listed in Table 2. Each of the two compartmental L^{3-} is bridging two metal centers via the phenolate-O atom and satisfies two more coordination sites of each bridged metal center via the azomethine-N and the amidate-O atoms. In addition to the phenolate-O atom of L^{3-} an acetate group is also bridging the metal centers. Thus L^{3-} and acetate satisfy four coordination sites of each metal center and form a dinuclear $\{\text{Co}_2(\mu\text{-OAc})(\mu\text{-L})\}$ unit. Two such dinuclear units are linked by two triply bridging hydroxo groups and the tetranuclear complex molecule is formed (Chart 1 and Fig. 3). In this tetranuclear molecule, two Co-centers (Co1 and Co3) are in distorted octahedral NO_5 coordination spheres, while the other two Co-centers (Co2 and Co4) are in square-pyramidal NO_4 coordination spheres. For each octahedral metal center, the bridging acetate-O and one of the two triply bridging hydroxo-O atoms occupy the axial sites, while the equatorial sites are satisfied by the bridging phenolate-O and one NO-donor arm of L^{3-} and the second triply bridging hydroxo-O atom. This second triply bridging hydroxo-O and the bridging phenolate-O and the other NO-donor arm of L^{3-} constitute the basal plane and the bridging acetate-O atom occupies the apical position of the square-pyramidal metal center. Interestingly, the

bridging phenolate-O atoms O2 and O7 are near the vacant coordination sites of the square-pyramidal metal centers Co4 and Co2, respectively (Fig. 3). However, they are too far away ($\text{Co2}\cdots\text{O7}$ 2.603(3) Å and $\text{Co4}\cdots\text{O2}$ 2.579(3) Å) for any kind of interaction. Thus, the four metal centers, the doubly bridging phenolate-O atoms (O2 and O7), and the triply bridging hydroxo-O atoms (O11 and O12) constitute an open cubane type Co_4O_4 motif (Fig. 3, inset). The large variation of the metal $\cdots$ metal distances (2.9244(7)–3.7008(8) Å) reflects the irregularity of the open cubane structure of this Co_4O_4 core. For the phenoxo-hydroxo bridged metal pairs the Co $\cdots$ Co distances are shortest ($\text{Co1}\cdots\text{Co2}$, 2.9244(7) Å and $\text{Co3}\cdots\text{Co4}$, 2.9386(7) Å), while that for the dihydroxo bridged metal pair is slightly longer ($\text{Co1}\cdots\text{Co3}$, 2.9798(7) Å). Compared to these distances in the di-atom bridged dicobalt fragments the Co $\cdots$ Co distances in the mono-hydroxo bridged fragments are ~ 0.4 Å longer ($\text{Co1}\cdots\text{Co4}$, 3.2972(8) Å and $\text{Co2}\cdots\text{Co3}$, 3.3231(8) Å) and the distance between the unbridged metals Co2 and Co4 is the longest (3.7008(8) Å). The bond lengths associated with the octahedral metal centers (Co1 and Co3) are significantly smaller than those associated with the square-pyramidal metal centers (Co2 and Co4) (Table 2). This difference is consistent with the trivalent state of Co1 and Co3 and the bivalent state of Co2 and Co4. Bond valence sum calculations were carried out with EXPO2014 [18] software for further confirmation of the oxidation states. The values obtained are 3.04 and 2.85 for Co1 and Co3, respectively, while those are 1.78 and 1.77 for Co2 and Co4, respectively. Continuous shape measurement (CShM) calculations were also performed to scrutinize the polyhedron around each metal center using the SHAPE 2.1 software [20]. The calculations clearly show that Co1 and Co3 are in distorted octahedral geometry, while Co2 and Co4 are in distorted square-pyramidal coordination sphere (Table 3).

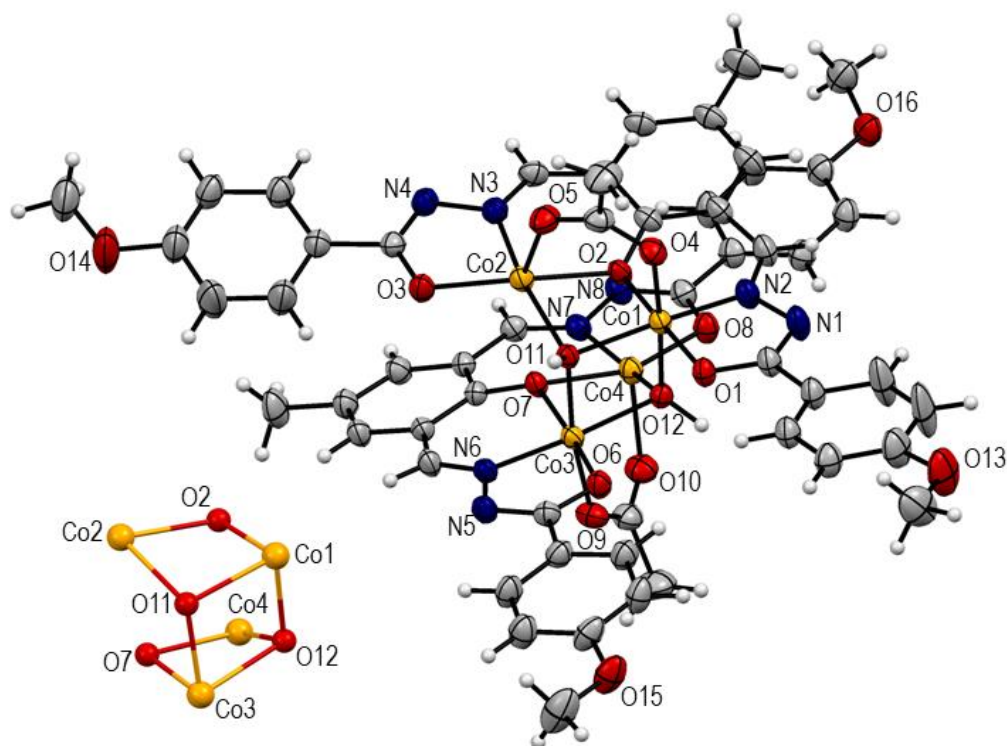


Fig. 3. The molecular structure of $[\text{Co}^{\text{II}} \text{Co}^{\text{III}} (\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$. All non-hydrogen atoms are represented by their 30% probability ellipsoids. Only the non-carbon atoms are labelled for clarity. Inset: Open cubane arrangement of Co_4O_4 core.

Table 2 Selected bond parameters (Å and °) for $\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2 \cdot 1.5\text{MeCN}$.

Co(1)–O(1)	1.878(3)	Co(1)–O(2)	1.918(3)
Co(1)–O(4)	1.896(3)	Co(1)–O(11)	1.965(2)
Co(1)–O(12)	1.905(3)	Co(1)–N(2)	1.844(3)
Co(2)–O(2)	2.071(3)	Co(2)–O(3)	1.967(3)
Co(2)–O(5)	2.051(3)	Co(2)–O(11)	2.050(3)
Co(2)–N(3)	2.020(3)	Co(3)–O(6)	1.885(3)
Co(3)–O(7)	1.934(3)	Co(3)–O(9)	1.914(3)
Co(3)–O(11)	1.939(3)	Co(3)–O(12)	1.984(3)
Co(3)–N(6)	1.886(3)	Co(4)–O(7)	2.076(3)

Co(4)–O(8)	1.983(3)	Co(4)–O(10)	2.039(3)
Co(4)–O(12)	2.057(3)	Co(4)–N(7)	2.018(3)
O(1)–Co(1)–O(2)	175.85(12)	O(1)–Co(1)–O(4)	87.91(13)
O(1)–Co(1)–O(11)	96.87(11)	O(1)–Co(1)–O(12)	90.81(12)
N(2)–Co(1)–O(1)	83.90(14)	O(2)–Co(1)–O(4)	95.18(13)
O(2)–Co(1)–O(11)	85.64(11)	O(2)–Co(1)–O(12)	86.34(11)
O(2)–Co(1)–N(2)	93.34(14)	O(4)–Co(1)–O(11)	94.95(12)
O(4)–Co(1)–O(12)	175.14(12)	O(4)–Co(1)–N(2)	89.67(15)
O(11)–Co(1)–O(12)	80.55(11)	O(11)–Co(1)–N(2)	175.34(15)
O(12)–Co(1)–N(2)	94.85(15)	O(2)–Co(2)–O(3)	159.34(12)
O(2)–Co(2)–O(5)	92.50(13)	O(2)–Co(2)–O(11)	79.65(10)
O(2)–Co(2)–N(3)	86.99(12)	O(3)–Co(2)–O(5)	105.13(14)
O(3)–Co(2)–O(11)	111.23(11)	O(3)–Co(2)–N(3)	79.14(13)
O(5)–Co(2)–O(11)	87.60(12)	O(5)–Co(2)–N(3)	101.44(14)
O(11)–Co(2)–N(3)	164.22(12)	O(6)–Co(3)–O(7)	172.96(12)
O(6)–Co(3)–O(9)	88.70(14)	O(6)–Co(3)–O(11)	89.43(12)
O(6)–Co(3)–O(12)	98.97(11)	O(6)–Co(3)–N(6)	82.78(13)
O(7)–Co(3)–O(9)	96.69(13)	O(7)–Co(3)–O(11)	85.92(11)
O(7)–Co(3)–O(12)	85.36(10)	O(7)–Co(3)–N(6)	92.55(12)
O(9)–Co(3)–O(11)	171.11(13)	O(9)–Co(3)–O(12)	92.44(13)
N(6)–Co(3)–O(9)	91.22(15)	O(11)–Co(3)–O(12)	79.27(10)
O(11)–Co(3)–N(6)	97.17(13)	O(12)–Co(3)–N(6)	175.98(13)
O(7)–Co(4)–O(8)	160.23(12)	O(7)–Co(4)–O(10)	93.93(12)
O(7)–Co(4)–O(12)	79.96(10)	O(7)–Co(4)–N(7)	85.87(12)
O(8)–Co(4)–O(10)	102.75(14)	O(8)–Co(4)–O(12)	110.95(11)
O(8)–Co(4)–N(7)	79.30(12)	O(10)–Co(4)–O(12)	87.53(12)
O(10)–Co(4)–N(7)	106.63(14)	N(7)–Co(4)–O(12)	160.66(12)

Metal atom	S. No.	Geometry	Symmetry	CShM value
Co1	1	Hexagon	D _{6h}	30.776
	2	Pentagonal pyramid	C _{5v}	27.439
	3	Octahedron	Oh	0.426
	4	Trigonal prism	D _{3h}	14.389
	5	Johnson pentagonal pyramid J2	C _{5v}	31.198
Co2	1	Pentagon	D _{5h}	26.788
	2	Vacant octahedron (Johnson square pyramid J1)	C_{4v}	1.791
	3	Trigonal bipyramid	D _{3h}	6.025
	4	Spherical square pyramid	C _{4v}	1.831
	5	Johnson trigonal bipyramid J12	D _{3h}	8.109
Co3	1	Hexagon	D _{6h}	30.679
	2	Pentagonal pyramid	C _{5v}	25.914
	3	Octahedron	Oh	0.626
	4	Trigonal prism	D _{3h}	12.916
	5	Johnson pentagonal pyramid J2	C _{5v}	29.769
Co4	1	Pentagon	D _{5h}	25.170
	2	Vacant octahedron (Johnson square pyramid J1)	C _{4v}	1.971
	3	Trigonal bipyramid	D _{3h}	7.114
	4	Spherical square pyramid	C_{4v}	1.864
	5	Johnson trigonal bipyramid J12	D _{3h}	9.215

Table 3 Continuous shape measurement for Co-centers in [Co^{II}Co^{III}(μ-OAc)(μ₃-OH)(μ-L)]₂.

The extent of distortion of the square-pyramidal geometry around each of Co2 and Co4 toward a trigonal-bipyramidal geometry has been measured by calculating the parameter τ which is defined as $(\beta - \alpha)/60$, where β is the larger and α is the smaller *trans* bond angles in the basal plane [21]. The value of τ will be 0 or 1 for an ideal square-pyramid or trigonal-bipyramid, respectively. The τ has been found to be 0.08 for Co2 and 0.01 for Co4. Thus, there is very little distortion for Co2 and essentially no distortion for Co4. As generally observed for square-pyramidal complexes, here also Co2 and Co4 are shifted by 0.234(2) and 0.262(2) Å, respectively from the basal plane toward the corresponding apical acetate-O atoms. The spherical square-pyramid shape of the polyhedron around Co4 found in CShM calculations (Table 3) is consistent with the less distortion and slightly larger shift of Co4 toward the apical atom. One edge of the basal plane of each CoNO₄ square-pyramid is shared with the CoNO₅ octahedron and a di-polyhedral motif is formed. The octahedral sides of two such di-polyhedral motifs share one edge and form the discrete tetra-polyhedral aggregate (Fig. 4).

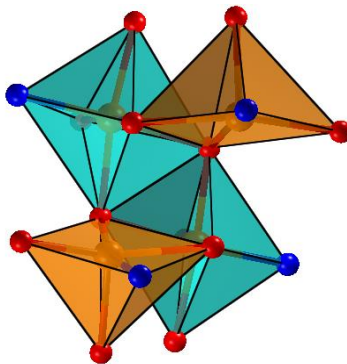


Fig. 4. The edge-shared tetra-polyhedral aggregate.

The structure of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2 \cdot 1.5\text{MeCN}$ was scrutinized for intermolecular hydrogen bonding interactions and the resulting self-assembly pattern. As mentioned before the acetonitrile molecules are connected to the

azomethine-CH fragments of the complex molecule via non-classical C–H $\cdots$ N interactions. There is no other involvement of the solvent molecules in any other interaction and hence in the self-assembly process. On the other hand, both μ_3 -OH groups (O11 and O12) of the complex molecule are involved in strong intermolecular classical hydrogen bonds with the O-atoms (O15 and O16) of the methoxy substituents of one of the two L^{3-} . The O $\cdots$ O distance and the O–H $\cdots$ O angle are 2.735(4) Å and 170°, respectively for O11–H $\cdots$ O16 interaction and those are 2.744(4) Å and 168°, respectively for O12–H $\cdots$ O15 interaction. Two tetranuclear complex molecules form a dimeric unit via a pair of reciprocal O12–H $\cdots$ O15 interactions (Fig. 5, top). Each of these dimeric units are connected to four more dimeric units via the O11–H $\cdots$ O16 interactions and a two-dimensional network structure is formed in the crystal lattice (Fig. 5, bottom).

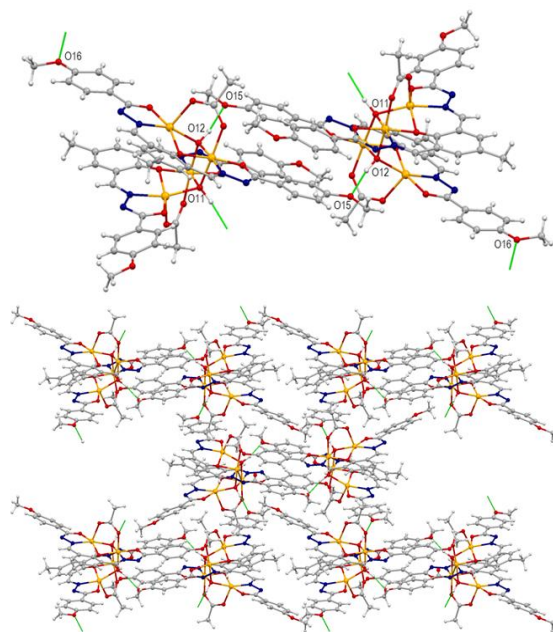


Fig. 5. Hydrogen bonded dimer of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ (top) and the two-dimensional assembly of these dimeric units viewed along the a -axis (bottom).

4.4.3. Infrared and electronic spectra

The infrared spectrum of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ was collected within the range $4000\text{--}500\text{ cm}^{-1}$. The spectrum shows a large number of bands with various intensities (Fig. 6). No attempt has been made to assign all the bands except for the following few. The broad band centered at $\sim 3360\text{ cm}^{-1}$ is attributed to the $\mu_3\text{-OH}$ groups [22]. The lower wavenumber and the broadness of the band are very likely due to the participation of these OH groups in strong intermolecular hydrogen bonding interactions (*vide supra*) [23]. The metal coordinated azomethine (--HC=N--) group appears as a sharp and medium intensity band at $\sim 1606\text{ cm}^{-1}$ [24]. The strong bands at 1563 and 1486 cm^{-1} are ascribed to the asymmetric and symmetric stretching vibrations of the bridging carboxylate [25,26].

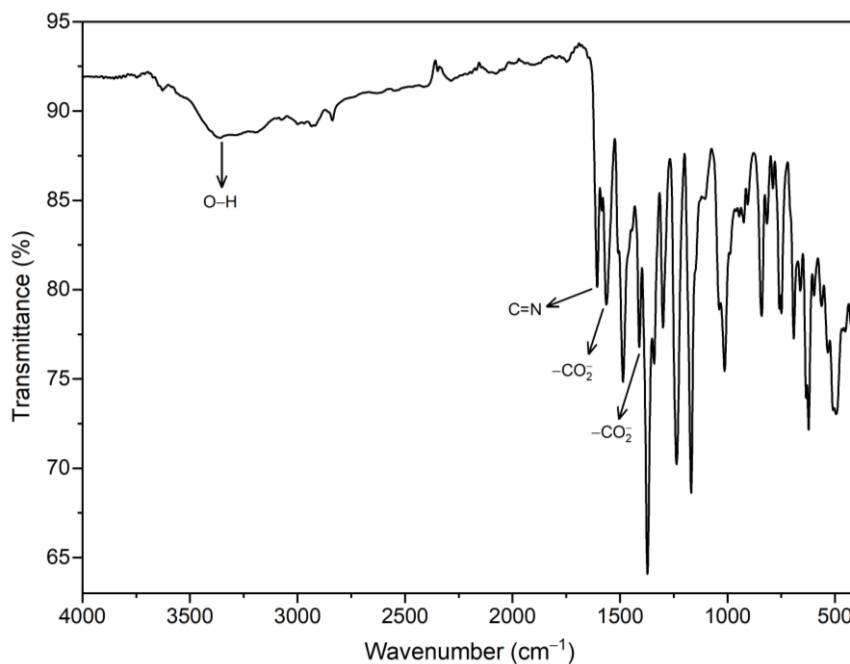


Fig. 6. Infrared spectrum of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ in powder phase.

A DMF solution of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ was used to record the electronic absorption spectrum (Fig. 7). In the visible region, the complex displays a very weak shoulder at ~600 nm followed by another shoulder of moderate intensity at ~415 nm. In the ultraviolet region, it shows a very strong and somewhat broad band at 345 nm. The weak shoulder is assigned to a d-d transition [26]. The second moderately intense shoulder and the strong and broad absorption in the ultraviolet region are attributed primarily to ligand-to-metal charge transfer (LMCT) and ligand centered transitions, respectively [24b,26,27].

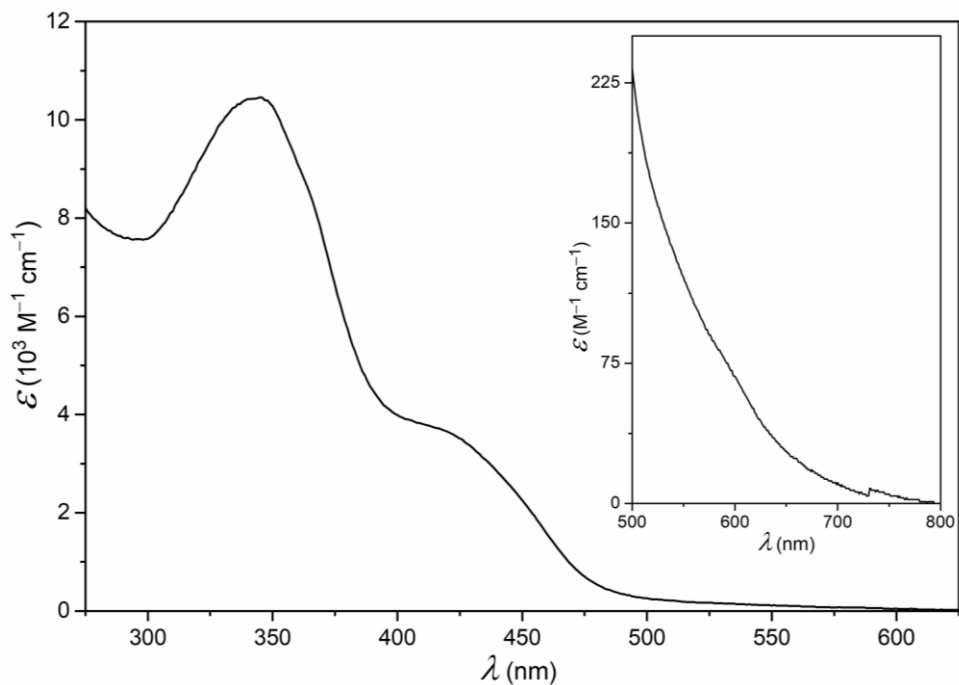


Fig. 7. Electronic spectrum of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ in *N,N*-dimethylformamide. Inset: Enlarged low-energy portion.

4.4.4. Magnetic properties

The magnetic susceptibility of a polycrystalline sample of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$ was measured in the temperature range of 2–300 K under an external magnetic field of 0.1 T. The room temperature (300 K) $\chi_M T$ value (χ_M = molar magnetic susceptibility) was found to be $6.00 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (Fig. 8) which is higher than the spin only value ($3.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) for two cobalt centers. The higher value indicates considerable contribution from the orbital angular momentum as expected for cobalt(II) high spin system. Upon cooling, the $\chi_M T$ remained almost constant ($5.82 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) down to 80 K indicating no exchange interaction between the paramagnetic cobalt(II) centers which are not directly bridged and $3.7008(8) \text{ \AA}$ apart from each other as discussed in the structural analysis (*vide supra*). On further lowering of the temperature, it decreased very quickly and reached to the minimum value of $3.61 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This sudden decrease at low temperature is attributed mainly to the anisotropy of the cobalt(II) centers due to zero-field splitting (ZFS). The spin Hamiltonian used for quantification of the ZFS parameters is given in equation 1, where the axial and the rhombic anisotropic components are represented by D and E , respectively. The fitting of the $\chi_M T$ vs. T plot (Fig. 8) keeping the g tensor as isotropic was performed using the PHI software [28]. The best fit

$$H = g\mu_B S \cdot B + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \quad (1)$$

gives $D = -23.59 \text{ cm}^{-1}$, $|E| = 0.03 \text{ cm}^{-1}$ and $g = 2.52$. The negative sign of D indicates the presence of easy-axis anisotropy in the studied complex. In recent times, the *ab initio* theoretical calculations have been found to be a very useful tool in evaluating the magnetic anisotropy for transition metal complexes [29]. Thus, the *ab initio* calculation with ORCA 4.0 software package [30] was carried out to check the nature of the magnetic anisotropy in the present complex. The

calculation shows negative sign of the anisotropic parameter D which signifies the presence of easy-axis anisotropy.

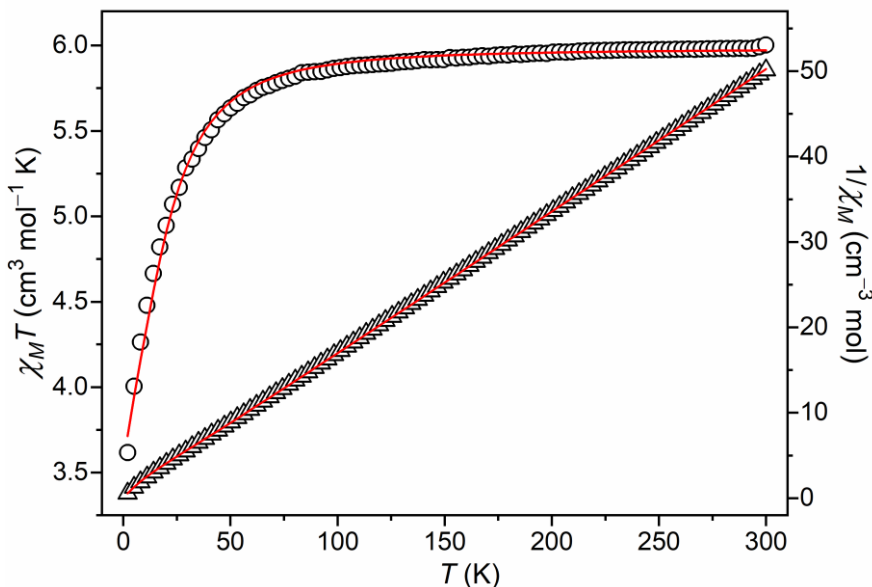


Fig. 8. $\chi_M T$ (O) and $1/\chi_M$ (Δ) as functions of temperature for $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$. Solid lines represent the best fits.

4.4.5. Theoretical calculations to determine the magnetic anisotropy

The ab initio calculations were performed using the coordinates obtained from X-ray crystal structure without optimization. The diamagnetic Co(III) atoms were replaced by Ga(III) atoms in all the calculations. In these calculations, ZORA (zeroth-order regular approximation) was employed for both first principles and ZFS calculations. The basis sets def2-TZVPP for Co, def2-TZVP for Ga, def2-TZVP for N and O, and def2-SV(P) for C and H with the auxiliary basis set def2/JK for all the atoms were used for all calculations. Using the configuration interaction (CI) procedure, 10 quartet and 40 doublet spin states with the active space containing 7 electrons distributed over 5 d-orbitals (CAS 7, 5) were computed. In addition, to introduce the effect of dynamic correlation N-electron

valence perturbation theory (NEVPT2) was employed on top of the CASSCF wave function. Further, the spin-orbit coupling was included by using quasi-degenerate perturbation theory (QDPT) approach. Both second-order perturbation theory and an effective Hamiltonian approach (EHA) were used to calculate the ZFS parameters D and E .

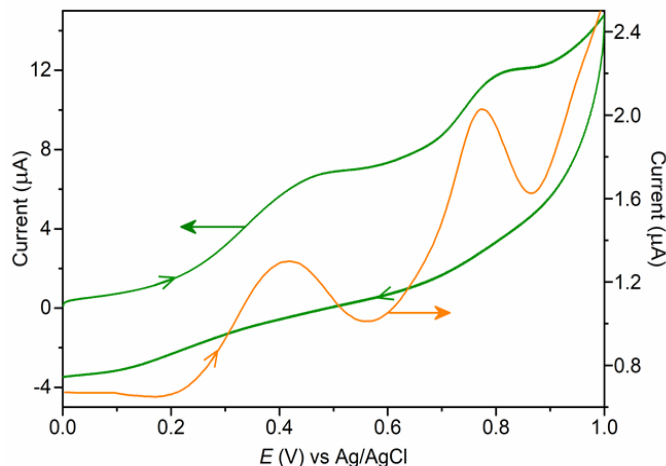
Table 4 The SH parameters obtained from fitting of experimental data and ab initio calculations

Complex	D_{exp} (cm^{-1})	$ E _{\text{exp}}$ (cm^{-1})	g_{exp}	D_{theo} (cm^{-1})	$ E _{\text{theo}}$ (cm^{-1})	g_{theo}
$[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$	-23.59	0.03	2.52	-67.34	0.30	2.47

4.4.6. Redox properties

The electron transfer behavior of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ was studied by cyclic and differential pulse voltammetry at scan rates of 100 and 10 mVs^{-1} , respectively. The experiments were performed with a DMF solution (~ 1 mM) of the complex containing $n\text{-Bu}_4\text{NClO}_4$ (TBAP) (0.1 M) as the supporting electrolyte using a glassy-carbon working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode at room temperature (298 K) under a nitrogen atmosphere. Under identical conditions, the cyclic voltammogram (CV) of a DMF solution (~ 1 mM) of ferrocene (Fc) displayed the Fc^+/Fc couple at $E_{1/2} = 0.58$ V ($\Delta E_p = 130$ mV). The voltammograms of the complex are illustrated in Fig. 9. On the anodic side, the CV displays two irreversible oxidation responses at 0.48 and 0.82 V. Corresponding peak potentials are 0.42 and 0.77 V in the differential pulse voltammogram (DPV). Metal centered oxidation potentials for X-ray structurally characterized square-pyramidal cobalt(II) complexes are very rarely reported. Thus, it is very difficult to compare the potentials observed for the

present complex with those for complexes having comparable coordinating atoms. Extensive literature search provided only one report on the redox properties of a series of X-ray structurally characterized high spin square-pyramidal ternary cobalt(II) complexes with tridentate facial N₃-coordinating tris(pyrazolyl)borates and bidentate N₂-coordinating bis(imidazolyl)borates [31]. These complexes show an irreversible cobalt(II) to cobalt(III) oxidation response. Depending on the electronic nature of the substituent on the tridentate ligand the E_{pa} value varies from 0.07 to 0.52 V (vs. Ag⁺/Ag). The coordinating atoms in this system are much better binder and hence cobalt(II) to cobalt(III) oxidation should be easier than that for the NO₄-coordinated cobalt(II) centers in the present complex. Thus, the observed peaks having the E_{pa} values at the higher end of the above range indicate that these are due to successive oxidations of the two cobalt(II) centers to two cobalt(III) centers. In contrast to the anodic side of the reference electrode, the CV on the cathodic side shows an irreversible and somewhat broad reduction peak with a very high current at -0.96 V (Fig. 9). In the DPV, this reduction peak resolves into two closely spaced peaks at -0.78 and -0.88 V. These values are within the potential range observed for octahedral cobalt(III) complexes with N,O-donor Schiff bases known to display metal centered reductions [32]. Therefore, the two closely spaced reduction responses displayed by the present complex are assigned to the successive reductions of its two cobalt(III) centers to two cobalt(II) centers.



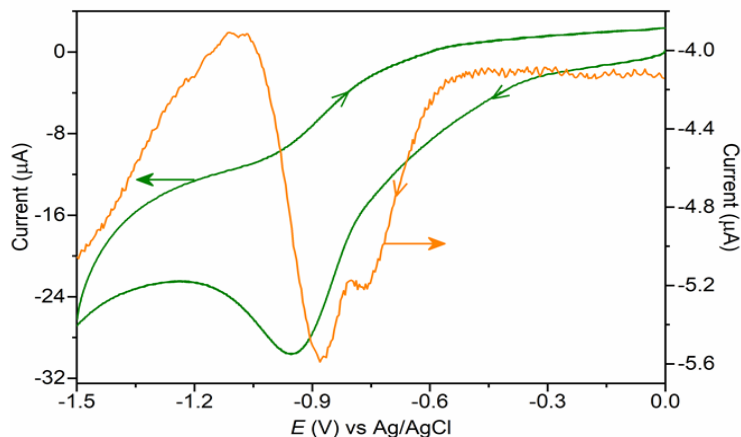


Fig. 9. CVs (—) and DPVs (—) of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ on the anodic side (top) and the cathodic side (bottom) under the experimental conditions described in the text.

4.5. Electrocatalytic oxygen evolution

The oxygen evolution experiment was also carried out in 0.1 M sodium phosphate buffer of pH 7 using the $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, CB, and Nafion mixture coated FTO working electrode. On anodic scan, the CV displays a broad oxidation response centered at ~ 0.9 V followed by a sharp increase in the current (Fig. 10). This increase indicates catalytic OER on the electrode surface. Comparing with the electron transfer behavior of the complex in homogeneous non-aqueous medium on the anodic side of the reference electrode, the broad oxidation response is assigned to the cobalt(II) centers of the complex coated on the electrode surface. No catalytic current was observed with the same working electrode when dry THF containing TBAP as the supporting electrolyte was used as medium instead of the neutral phosphate buffer (Fig. 10). As observed on the cathodic side, the CV recorded on the anodic side using CB and Nafion coated FTO electrode in aqueous phosphate buffer (pH 7) also displays flat curves with very low currents during both forward and reverse scans (Fig. 10). This observation clearly indicates that $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ is only responsible for the electrocatalytic OER.

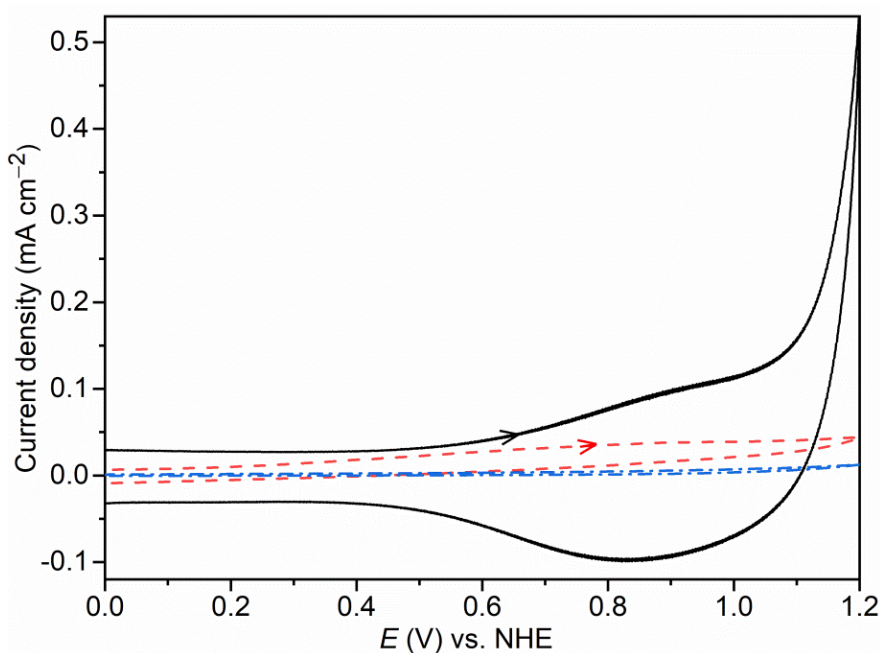


Fig. 10. CVs at the anodic side (at a scan rate of 100 mV s^{-1}) using: complex/CB/Nafion coated FTO working electrode in sodium phosphate buffer of pH 7 (—) and in THF (0.1 M TBAP) (- - -) and CB/Nafion coated FTO working electrode in the neutral phosphate buffer (- . - .).

4.6. Electrocatalytic hydrogen evolution

The CV recorded using a $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$, CB, and Nafion mixture coated FTO working electrode within the potential range 0 to -1.0 V in 0.1 M aqueous sodium phosphate buffer of pH 7 shows a reduction response at $E_{\text{pc}} = -0.91 \text{ V}$ with the corresponding oxidation peak at $E_{\text{pa}} = -0.61 \text{ V}$ (vs. NHE) (Fig. 11, Inset). This reduction response is very similar to that observed for the complex in homogeneous non-aqueous medium except for the anodic peak on reverse scan (*vide supra*). Thus, in all likelihood this response is due to the reduction of the cobalt(III) centers of the complex coated on the electrode surface. On further cathodic scan up to -1.3 V there is a sharp increase in the current indicating initiation of the HER on the electrode surface (Fig. 11). The CV

recorded using the same working electrode but in dry tetrahydrofuran (THF) (0.1 M TBAP) shows a broad irreversible reduction peak at around -1.0 V but no increase in the current after this reduction response (Fig. 11). To verify whether the complex, $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, is the electrocatalyst or not, another CV was recorded in the same neutral buffer medium using only CB and Nafion coated FTO electrode. It displays essentially very low currents curves with during the forward and the reverse scans and confirms that HER activity takes place in the presence of the complex only (Fig. 11).

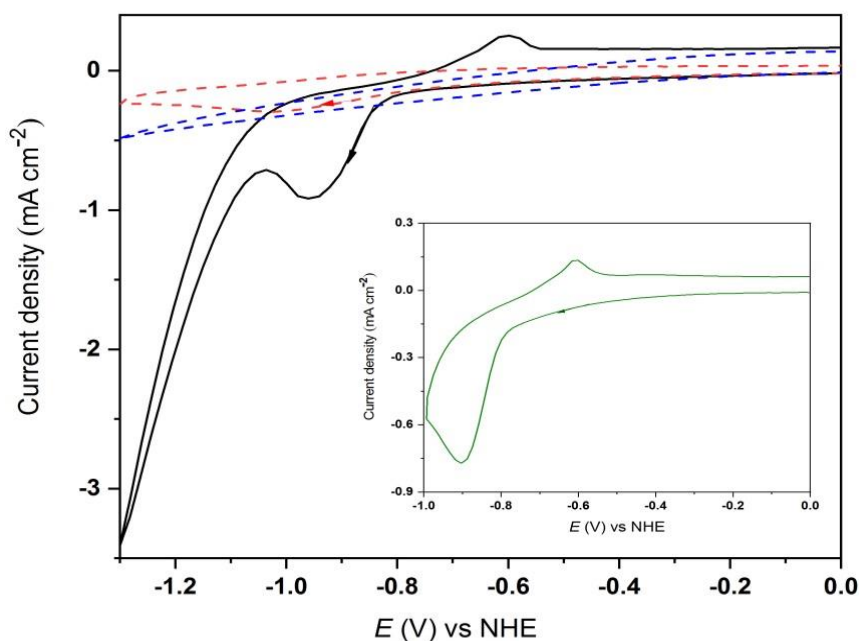


Fig. 11. CVs at the cathodic side using: complex/CB/Nafion coated FTO working electrode in sodium phosphate buffer of pH 7 (—) and in THF (0.1 M TBAP) (-----) and CB/Nafion coated FTO working electrode in phosphate buffer of pH 7 (-.-.-). Inset: CV using CB/Nafion/complex coated FTO working electrode in phosphate buffer of pH 7 in the potential window of 0 to -1.0 V (—). All CVs were recorded at a scan rate of 100 mV s^{-1} .

4.7. Catalytic efficiency

The efficiency of an electrocatalyst is generally evaluated by measuring the overpotential (η), exchange current density (i_0 , current density at $\eta = 0$) and the Tafel slope (b) from the Tafel plot generated using the equation $\eta = a + b \log(i)$, where i is the measured current density. A large i_0 and low η and b indicate a promising electrocatalyst for HER/OER [2,33]. The Tafel plots for the electrocatalytic HER as well as OER using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$ as catalyst are shown in Fig. 12. The values of η (corresponding to a current density of 1 mA cm^{-2}), i_0 , and b obtained are 690 mV, $2.8 \text{ } \mu\text{A cm}^{-2}$, and 270 mV dec^{-1} , respectively for HER and 768 mV, $4.0 \text{ } \mu\text{A cm}^{-2}$, and 320 mV dec^{-1} , respectively for OER. These values indicate rather slow charge transfer through the electrocatalytic interface presumably due to poor conductivity of the coating material despite the use of better conducting carbon black in the mixture.

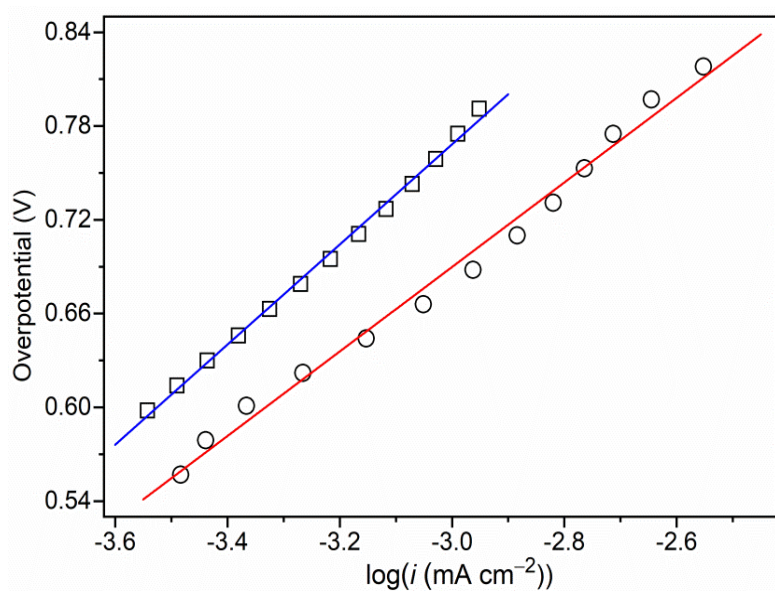


Fig. 12. Tafel plots for HER (O) and OER (□). The solid lines represent the best linear least-squares fits.

Another measure for the effectiveness of an electrocatalyst is the measurement of the Faradaic efficiency and the TOF value [2,33]. CCE experiments with the complex, CB, and Nafion mixture coated FTO working electrode in 0.1 M sodium phosphate buffer of pH 7 were performed to determine the Faradaic efficiencies of the complex catalyst in OER and HER. The Faradaic efficiencies have been found to be 78% for OER and 94% for HER. The turnover frequencies (TOF) were calculated using the equations $\text{TOF} = I/2Q$ for OER and $\text{TOF} = I/Q$ for HER [34], where I is the steady state current (in A) in the constant potential electrolysis (CPE at 1.05 V for OER and at -1.05 V for HER) plots (*vide infra*) and Q is the charge (in C) calculated from the reduction (for HER) or oxidation (for OER) response in the corresponding CV recorded in non-catalytic THF medium with the complex, CB, and Nafion mixture coated FTO working electrode. The values of TOF obtained are $1.1 \times 10^3 \text{ h}^{-1}$ and $4.6 \times 10^3 \text{ h}^{-1}$ for OER and HER, respectively (Experimental section, 4.3.5.1 and 4.3.5.2). Chromatographic analyses of the gases evolved in these electrolysis experiments confirmed both OER and HER (Fig. 13 and Fig. 14).

The Faradaic efficiency and the TOF values of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ for both OER and HER are comparable to or better than the corresponding values of the previously reported cobalt complex catalysts immobilized on an electrode surface [10].

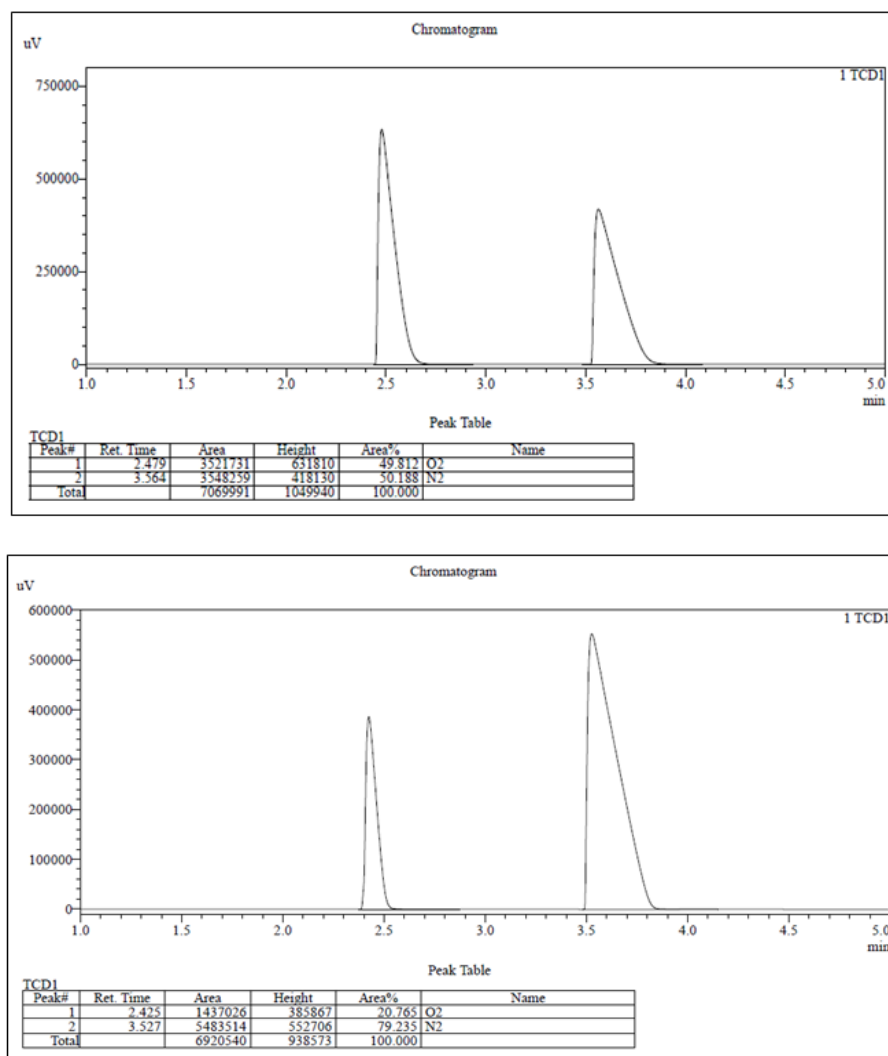


Fig. 13. Chromatograms of the gas evolved in the oxidative electrolysis (top) and air (bottom). The nitrogen peak in the first chromatogram is due to contamination by air during sample collection.

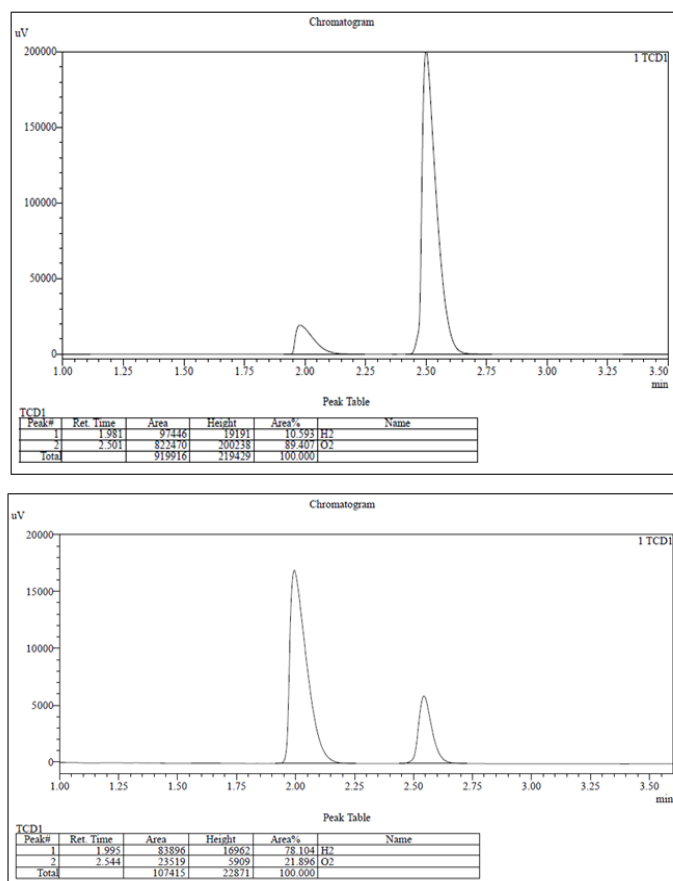


Fig. 14. Chromatograms of the gas evolved in the reductive electrolysis (top) and hydrogen (bottom). The oxygen peaks are due to contamination by air during sample collection.

4.8. Stability of the catalyst

A good and effective electrocatalyst should be stable and have a long-term durability. To assess the stability and performance of the present catalyst over a long period of time CPE experiments were performed in 0.1 M sodium phosphate buffer of pH 7 with the complex, CB, and Nafion mixture coated FTO working electrode. For HER, electrolysis was conducted at the onset potential of -1.05 V (vs. NHE), while for OER, it was conducted at the onset potential of 1.05 V (vs. NHE). Electrolysis was performed for a period of 10 h for each of HER and OER.

In both cases, essentially constant currents were observed throughout the duration of 10 h (Fig. 15). The CVs were recorded with the coated FTO electrode before and after its use in the above mentioned reductive and oxidative CPE experiments. In case of OER, very similar CVs are obtained except for a slight decrease of current density after the oxidative electrolysis (Fig. 16). However, for HER a completely different CV was obtained after the reductive electrolysis (Fig. 17). ICP-OES analyses of the electrolyte solutions after 10 h of reductive as well as oxidative electrolysis were performed. No cobalt content was detected in either case. We have also performed ICP-MS analyses of both electrolyte solutions mentioned above. In the latter analyses, the cobalt content was found to be 4.5 and 7.2 ppb after reductive and the oxidative electrolysis, respectively. These concentrations indicate insignificant (approximately 0.2 and 0.3%, respectively) leaching of the complex from the electrode surface for HER and OER.

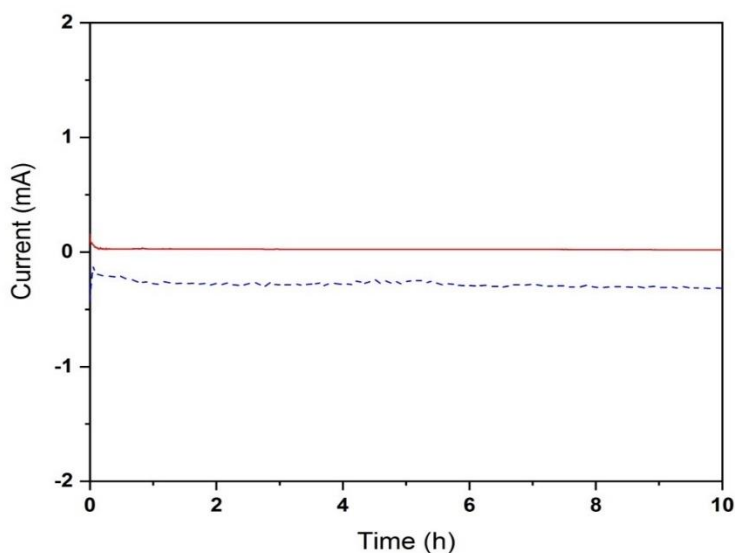


Fig. 15. Constant potential electrolysis (CPE) plots for HER (-----) and OER (—) using the $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu\text{-OH})(\mu\text{-L})]_2$, CB, and Nafion mixture coated FTO electrode in 0.1 M sodium phosphate buffer of pH 7.

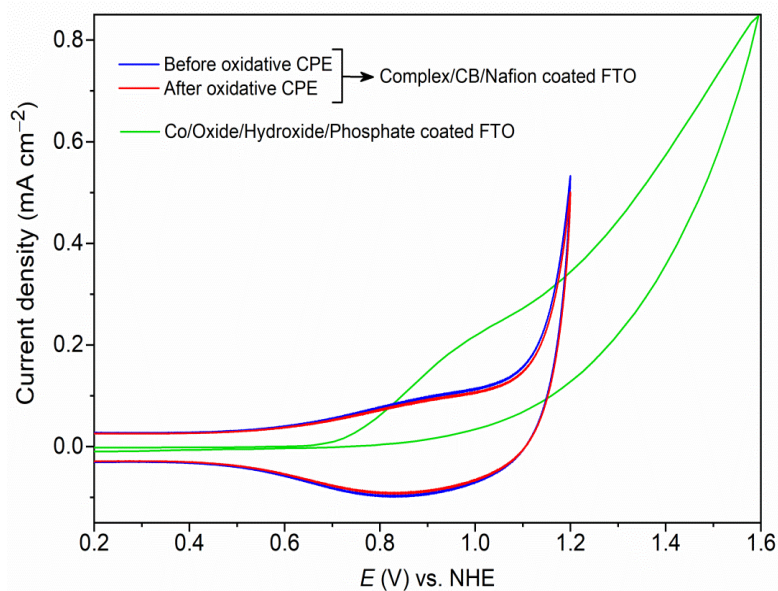


Fig. 16. CVs using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$, CB, and Nafion mixture coated FTO as working electrode before and after its use in CPE experiments and the CV using cobalt oxide/hydroxide/phosphate coated FTO as working electrode.

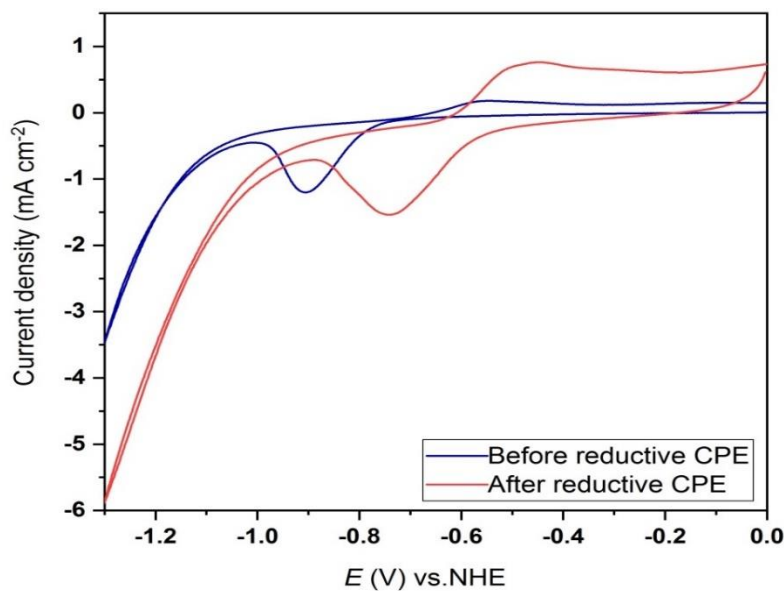


Fig. 17. CVs using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$, CB, and Nafion mixture coated FTO as working electrode before and after reductive CPE experiment.

Cobalt complexes with N,N'-bis(salicylidene)ethylenediamine (H_2salen) and analogous Schiff bases [10f,35] and also with porphyrins [10h] used for electrocatalytic OER from aqueous alkaline medium ($pH = 9.2$) have been shown to be not the actual catalysts but precatalysts for formation of the active cobalt oxide coating on the electrode surface due to decomposition of the complex. It is well known that electrolysis of cobaltous salt solution in aqueous phosphate buffer of neutral pH causes the formation of a film of an amorphous material composed of cobalt oxide/hydroxide and phosphate which is very active in electrocatalytic OER [36]. To examine whether there is any change in the complex, CB, and Nafion mixture coating on the FTO surface due to the formation of such amorphous material after 10 h of oxidative CPE in neutral sodium phosphate buffer or not, the FESEM images of the coated FTO electrode surface before and after CPE were recorded and compared with the FESEM image of the cobalt oxide/hydroxide/phosphate coated FTO electrode surface prepared in neutral sodium phosphate buffer by following the reported method [36]. There is no noticeable difference in the morphologies of the present electrode coating before and after CPE and they are completely dissimilar to that of the cobalt oxide/hydroxide/phosphate coating (Fig. 18). EDX analyses were also done to determine the elemental compositions of the coatings (Fig. 19). As observed for the morphologies, the elemental compositions of the present electrode coating before and after CPE are also similar and entirely different than that of the cobalt oxide/hydroxide/phosphate coating. In this context, it may be noted that in the present work sodium phosphate buffer was used instead of the reported potassium phosphate buffer as electrolysis medium to prepare the cobalt oxide/hydroxide/phosphate coating. However, both the morphology and the approximate Co:P:Na ratio of 2:1:1 observed for the present coating are comparable with the morphology and the Co:P:K ratio of the reported coating indicating formation of analogous material [36a,b].

In addition to the above, the CV using the cobalt oxide/hydroxide/phosphate coated FTO electrode in neutral sodium phosphate buffer was recorded and compared with the almost identical CVs recorded in the same medium with the complex, CB, and Nafion mixture coated FTO electrode before and after its use in the oxidative CPE (Fig. 16). There is no similarity between the first CV profile and the two identical CV profiles.

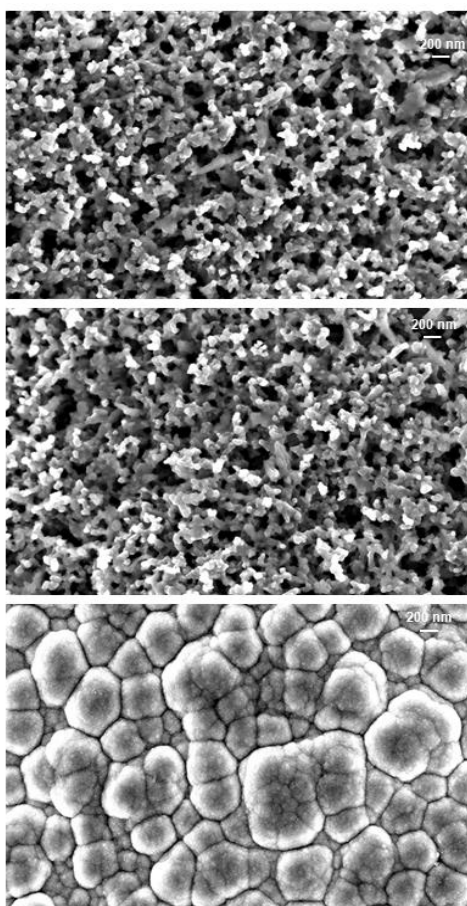


Fig. 18. FESEM images of FTO electrode coatings: CB/Nafion/complex before (top) and after (middle) CPE and electrodeposited cobalt oxide/hydroxide/phosphate material (bottom).

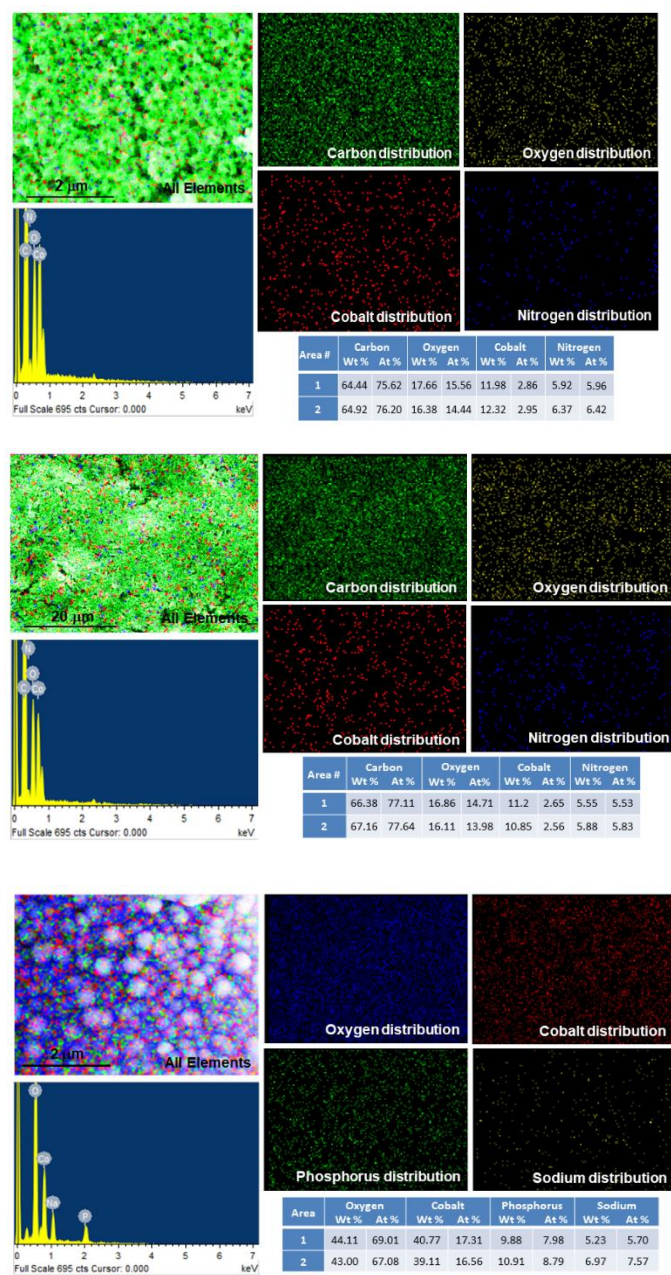


Fig. 19. EDX spectra and elemental compositions of FTO electrode coatings: complex/CB/Nafion before CPE (top) and after CPE (middle) and the electrodeposited cobalt oxide/hydroxide/phosphate material (bottom).

The above-described experiments indicate that the complex remains unchanged after its use as an electrocatalyst in OER. However, considering that the FTO surface coating also had Nafion and CB with the complex, the difference in morphology due to any small change/decomposition of the complex catalyst after electrolysis may not be reflected clearly in the FESEM image. Therefore, as reported earlier for cobalt salen and porphyrin complexes [10f,h], the FTO electrode surface was coated with only the complex catalyst without Nafion and CB by the following procedure. A 30 μL portion of a 1 mL DMF solution of the complex (4 mg) was spread over the surface of the FTO glass plate of area 0.2 cm^2 by drop casting method and the solvent was evaporated by heating with an IR lamp. The loading of the catalyst on FTO was 0.6 mg/cm^2 . The CV recorded with this complex coated FTO electrode in 0.1 M aqueous sodium phosphate buffer of pH 7 displays a broad oxidation response centered ~ 0.95 V followed by a sharp rise in the current due to the catalytic OER (Fig. 20). Using this FTO electrode coated with the pure complex, 10 h of oxidative CPE was performed at 1.28 V (Fig. 21) and the FESEM images of the electrode surface before and after CPE were recorded. Using a 0.5 cm^2 FTO working electrode coated with pure complex (0.6 mg/cm^2) oxidative CCE using 500 μA current for 6 h was also performed and the FESEM image after CCE was collected. These FESEM images have been compared with the FESEM image of the electrodeposited cobalt oxide/hydroxide/phosphate material [36] coated FTO electrode surface (Fig. 22). The morphologies of the unused complex coated FTO electrode surface and after its use in CPE and CCE are identical and completely dissimilar to that of the cobalt oxide/hydroxide/phosphate coated electrode surface. In addition, the EDX spectra and the elemental compositions of the complex coated FTO electrode surface before its use in any electrolysis experiment and after its use in the above-mentioned CPE (Fig. 23) are also very similar and different from that of the cobalt oxide/hydroxide/phosphate coat (Fig. 19). Thus, these FESEM and EDX

experiments with pure complex coating do not indicate any decomposition of the complex after its use as heterogenous electrocatalyst for OER in neutral phosphate buffer.

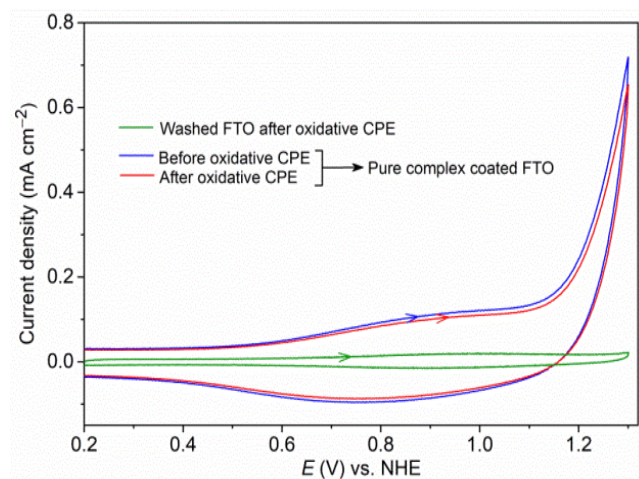


Fig. 20. CVs with complex coated FTO as working electrode: before and after its use in CPE (at 1.28 V) and water and DMF washed FTO working electrode.

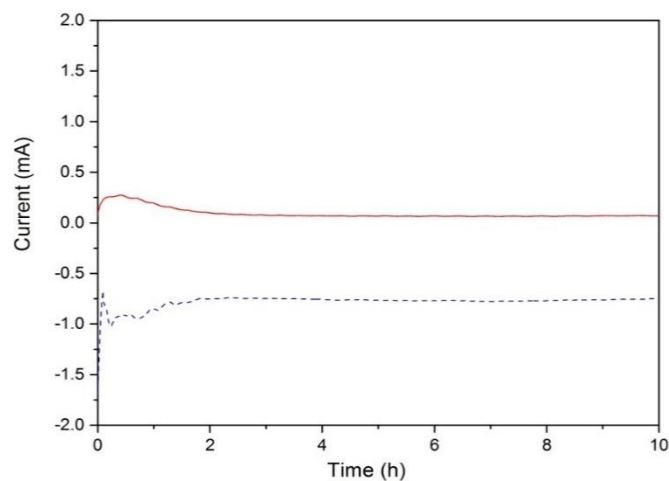


Fig. 21. Constant potential electrolysis (CPE at 1.28 V for OER and at -1.28V for HER) plots for OER (—) and HER (----) using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$ coated FTO electrode in 0.1 M sodium phosphate buffer of pH 7 (top).

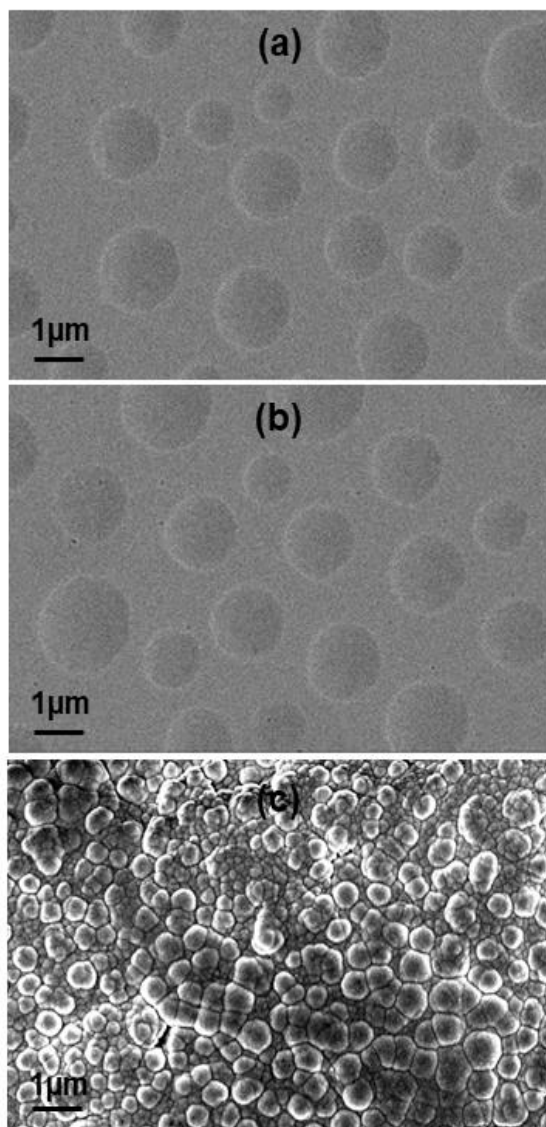


Fig. 22. FESEM images of pure complex coated FTO electrode surface: (a) unused, (b) after oxidative CPE at 1.28 V (c) electrodeposited cobalt oxide/hydroxide/phosphate material coating.

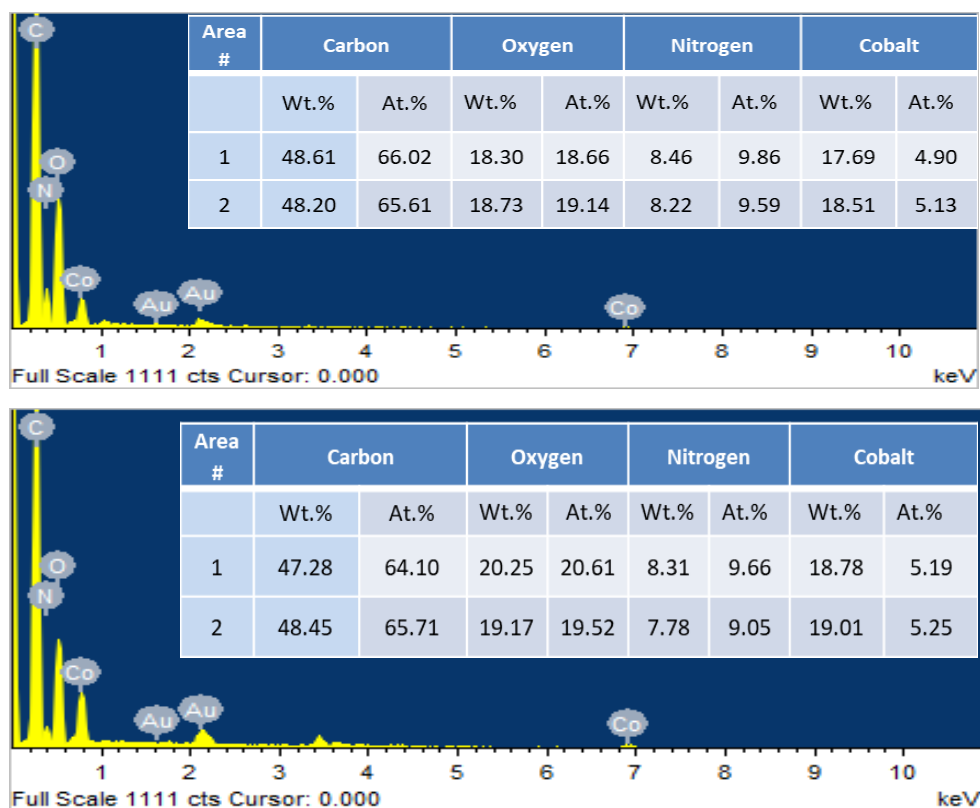


Fig. 23. EDX spectra and elemental compositions of the pure complex coated FTO electrode surface: (a) unused (b) after oxidative CPE at 1.28 V.

Earlier it has been demonstrated through cyclic voltammetry that the activity of the FTO electrodes coated with complexes of cobalt with salen and porphyrin increases with time during electrocatalytic OER in alkaline medium due to decomposition of the complex and deposition of the active cobalt oxide catalyst on the electrode surface [10f,h]. In contrast, in the present case, instead of an increase in the catalytic current an overall decrease in the current density was observed in the CV recorded using the complex coated FTO electrode after 10 h of oxidative CPE (Fig. 20) in neutral aqueous medium than that in the CV recorded before it uses in the CPE. This decrease in current density and hence the catalytic activity is very likely due to leaching of the complex from the electrode surface as detected earlier by ICP-MS measurements for the complex, CB, and Nafion coated electrode (*vide supra*). After using the complex coated electrode for oxidative CPE, it was thoroughly washed with water to remove the electrolyte and then with DMF to remove the complex. The CV recorded with this washed electrode displays essentially flat curves with very low current density throughout the scanned potential window without any trace of catalytic current indicating no deposition of catalytically active cobalt oxide/hydroxide/phosphate material due to decomposition of the complex (Fig. 20).

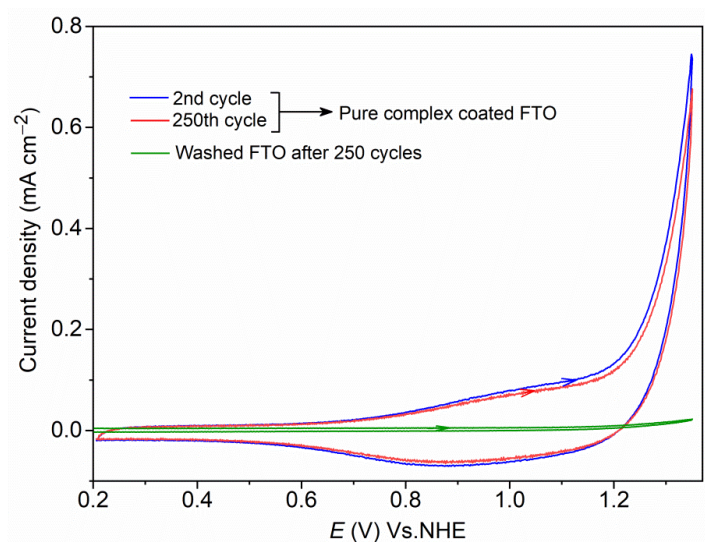


Fig. 24. CVs using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ coated FTO as working electrode: 2nd and 250th cycles in 250 consecutive CV cycles and water and DMF washed FTO electrode. All CVs were recorded at a scan rate of 100 mV s^{-1} .

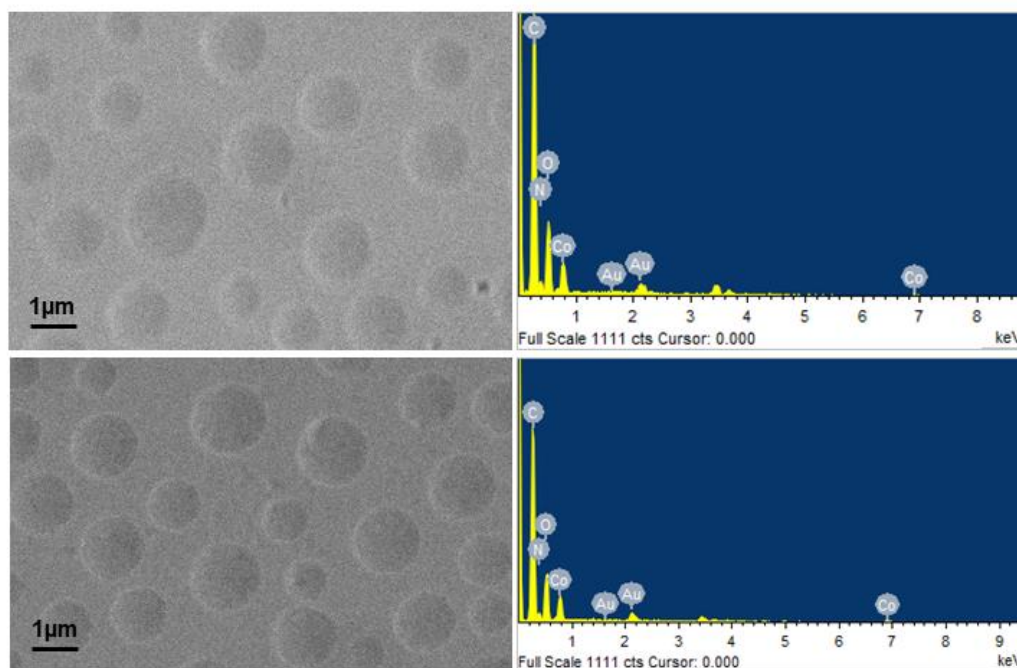


Fig. 25. FESEM images and EDX spectra of pure complex coated FTO electrode before (top) and after (bottom) its use in 250 consecutive CV cycles.

In order to further check the stability of the catalyst, 250 consecutive CV scans using the complex coated FTO electrode in 0.1 M aqueous sodium phosphate buffer of pH 7 were performed. The 2nd and the 250th cycles are illustrated in Fig. 24. As observed in the CVs with the complex coated electrode before and after its use in oxidative CPE, here also the 250th CV scan shows no increase of the catalytic current but an overall slight decrease of the current density throughout the scanned potential range compared to that of the 2nd CV scan. The FESEM images and the EDX spectra of the complex coated FTO electrode before and after its use in 250 consecutive CV scans are illustrated in Fig. 25. No difference is visible between the images and the spectra. The used electrode was then washed with water followed by DMF to remove the electrolyte and the complex, respectively and then a CV was recorded with this washed electrode in neutral phosphate buffer. This CV shows essentially flat current responses for both forward and reverse scans indicating no redox active material on the electrode surface (Fig. 24).

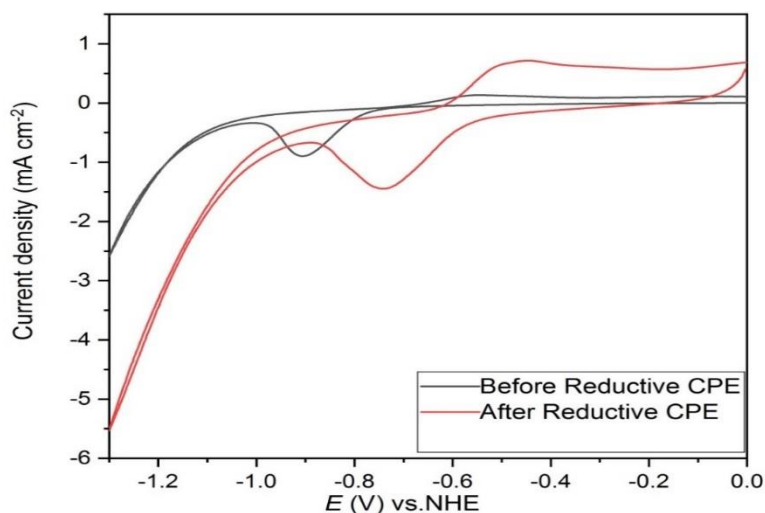


Fig. 26. CVs using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ coated FTO as working electrode: before and after its use in reductive CPE (at -1.28 V). Both CVs were recorded at a scan rate of 100 mV s^{-1} .

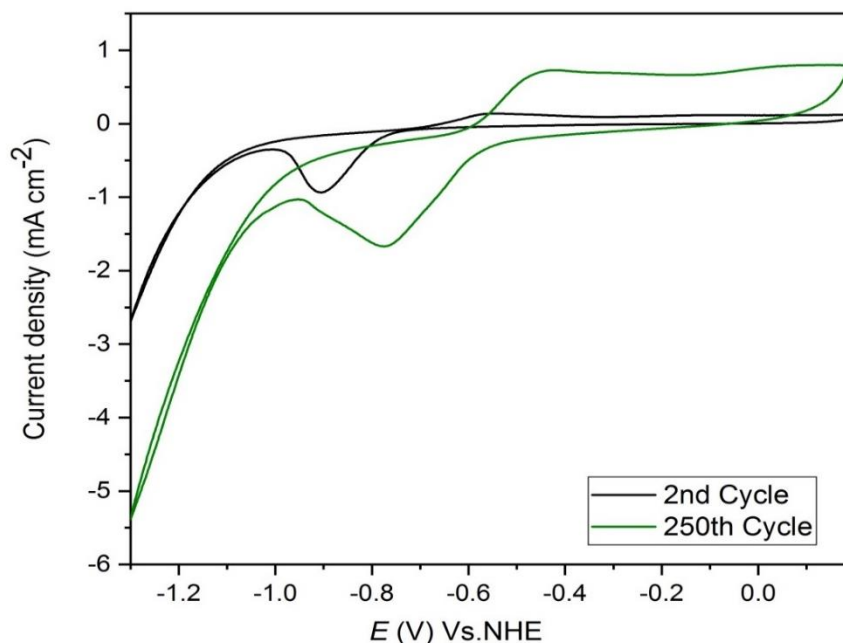


Fig. 27. CVs using $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})_2]$ coated FTO as working electrode: 2nd and 250th cycles in 250 consecutive CV cycles. Both CVs were recorded at a scan rate of 100 mV s^{-1} .

The Faradaic efficiency and the TOF for OER were determined by using the pure complex coated FTO electrode in oxidative electrolysis experiments (CCE using $500 \mu\text{A}$ current and CPE at 1.28 V , respectively) in 0.1 M neutral sodium phosphate buffer (Experimental section, 4.3.5.3). The values of the Faradaic efficiency and the TOF are found to be 73% and $3.4 \times 10^3 \text{ h}^{-1}$, respectively. The Faradaic efficiency is slightly lower than that (78%) obtained with the complex, CB, and Nafion mixture coated FTO working electrode; however, here the TOF was determined at a higher potential (1.28 V) and hence it is 3 times higher than that ($1.1 \times 10^3 \text{ h}^{-1}$) determined at a lower potential (1.05 V) with the complex, CB, and Nafion mixture coated FTO working electrode (vide supra).

Unlike in oxidative CPE, the CVs recorded with the complex coated FTO electrode before and after its use in reductive CPE are dissimilar. After electrolysis, there are anodic shifts of the reduction peak and the onset potentials with a significant increase in the catalytic current (Fig. 26). Thus, the complex catalyst is not stable and it is transformed to a more stable and active species during HER. Instability of the catalyst during HER was further confirmed by using the complex coated FTO electrode in 250 consecutive CV scans in 0.1 M aqueous sodium phosphate buffer of pH 7. As observed in the CVs with complex coated FTO electrode before and after its use in reductive CPE, here also the initial scan and the 250th scan are completely different (Fig. 27). Compared to the 2nd scan the 250th scan shows anodic shifts of the reduction peak and the onset potentials and an increased catalytic current.

The Faradaic efficiency and the TOF for HER were also determined by using the pure complex coated FTO electrode in reductive electrolysis experiments (CCE using $-500\ \mu\text{A}$ current and CPE at $-1.28\ \text{V}$, respectively) in 0.1 M neutral sodium phosphate buffer (Experimental section, 4.3.5.4). The Faradaic efficiency has been found to be 90 % which is somewhat lower than that (94%) found with the complex, CB, and Nafion mixture coated FTO working electrode. However, as observed for the TOF values for OER using the pure complex coated FTO electrode and complex, CB, and Nafion mixture coated FTO electrode, here also the TOF value ($1.53 \times 10^4\ \text{h}^{-1}$) determined at ($-1.28\ \text{V}$) is much higher than that ($4.6 \times 10^3\ \text{h}^{-1}$) determined at a relatively higher potential ($-1.05\ \text{V}$) with the complex, CB, and Nafion mixture coated FTO working electrode (vide supra).

The above-described CPE, CCE, FESEM, EDX, and CV experiments with the complex coated FTO electrode, the used and washed electrodes, and the pristine FTO electrode indicate that the catalyst $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ does not decompose during OER in neutral phosphate buffer medium to form any redox active inorganic material or the well-known OER catalyst the cobalt oxide/hydroxide/phosphate material [36]. In the previously reported examples of electrocatalytic OER using cobalt complex coated electrodes, the complexes acted as precatalysts and the catalytically active cobalt oxide material [36] was formed due to decomposition of the complexes [10f,h]. These complexes were mononuclear and the electrolysis experiments were performed in aqueous medium of pH = 9.2. It is well known that cobalt(II) is very labile [37]. Thus, it is very likely that the lability of the metal ion and the harsh alkaline aqueous environment together result into the formation of the cobalt oxide in these cases. In contrast, the present complex is a mixed-valent tetracobalt(II/III) species having a tightly congregated open cubane Co_4O_4 core and the electrolysis was performed in relatively milder aqueous medium of pH = 7. It has been demonstrated earlier that as one moves from mononuclear cobalt(II) complex to triple helical dicobalt(II) complex lability decreases due the rigidity of the triple helix structure [37b]. It appears that here also the rigidity of the tetranuclear structure assembled by the two each of the doubly bridging L^{3-} and OAc^- , and two triply bridging OH^- makes the cobalt(II) centers of the open cubane Co_4O_4 core inert. In addition, the neutral aqueous buffer medium is also not very conducive for the cobalt oxide formation. Therefore, unlike the previous mononuclear complexes [10f,h], $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ does not decompose to form the cobalt oxide material during the electrocatalytic OER. However, as observed for the $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, CB and Nafion coated FTO electrode, here also the long-term reductive CPE and consecutive multiple CV scans with pure

complex coated FTO electrode revealed the transformation of the complex to some active species responsible for the catalytic HER and hence its pre-electrocatalyst character. Similar pre-electrocatalytic behavior of cobalt(III) complexes, cobalt containing metallopolymers and chalcogenides in HER has been reported earlier [38].

4.9. Conclusion

A tetranuclear mixed-valent complex of molecular formula $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ was synthesized and characterized. X-ray crystallography confirmed a dimer of dinuclear $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$ structure where the cobalt(II) centers and the cobalt(III) centers are in square-pyramidal NO_4 and octahedral NO_5 coordination spheres, respectively. The structure shows an open cubane Co_4O_4 motif assembled by the four metal atoms, two doubly bridging phenolate-O atoms from two L^{3-} , and the two triply bridging hydroxo-O atoms. Microanalytical, mass spectrometric, and spectroscopic data are in good agreement with the molecular formula and the structure of the complex. The magnetic studies revealed an easy-axis anisotropy for the cobalt(II) centers. In non-aqueous solvent, the complex displayed two oxidation and two reduction responses, both being metal centered. In electrocatalytic water splitting in neutral aqueous medium, it exhibited decent Faradaic efficiencies in the range 73–78% (OER) and 90–94% (HER) and turnover frequencies in the order of 10^3 h^{-1} (OER) and $10^3\text{--}10^4 \text{ h}^{-1}$ (HER) depending upon the composition of the electrode surface coating. Various control and long-term electrolysis experiments followed by FESEM, EDX and electrochemical characterization indicated no sign of degradation and hence implied the true electrocatalytic nature of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ in OER condition. In contrast, long-term CV and reductive electrolysis experiments revealed the pre-electrocatalyst character of the complex in HER.

4.10. References

- [1] (a) W. Lubitz, W. Tumas, *Chem. Rev.* 107 (2007) 3900–3903. (b) S. Dutta, *J. Ind. Eng. Chem.* 20 (2014) 1148–1156. (c) I. Staffell, D. Scamman, A.V. Abad, P. Balcombe, P.E. Dodds, P. Ekins, N. Shah, K.R. Ward, *Energy and Environ. Sci.* 12 (2019) 463–491.
- [2] (a) V.S. Thoi, Y. Sun, J.R. Long, C.J. Chang, *Chem. Soc. Rev.* 42 (2013) 2388–2400. (b) M. Zeng, Y. Li, *J. Mater. Chem. A* 3 (2015) 14942–14962. (c) X. Zou, Y. Zhang, *Chem. Soc. Rev.* 44 (2015) 5148–5180; (d) T. Karchiyappan, *Energy Sources, Part A* 41 (2019) 902–909. (e) S. Gupta, M.K. Patel, A. Miotello, N. Patel, *Adv. Funct. Mater.* 30 (2020) 1906481.
- [3] (a) S. Anantharaj, S.R. Ede, K. Sakthikumar, K. Karthick, S. Mishra, S. Kundu, *ACS Catal.* 6 (2016) 8069–8097. (b) Y. Yan, B.Y. Xia, B. Zhao, X. Wang, *J. Mater. Chem. A* 4 (2016) 17587–17603. (c) B. You, Y. Sun, *Acc. Chem. Res.* 51 (2018) 1571–1580. (d) H. Jin, J. Joo, N.K. Chaudhari, S. Choi, K. Lee, *ChemElectroChem* 6 (2019) 3244–3253. (e) M.A. Younis, S. Lyu, Q. Zhao, C. Lei, P. Zhang, B. Yang, Z. Li, L. Lei, Y. Hou, X. Feng, *BMC Mat.* 1 (2019) 6 (f) J. Wang, X. Yue, Y. Yang, S. Sirisomboonchai, P. Wang, X. Ma, A. Abudula, G. Guan, *J. Alloy. Comp.* 819 (2020) 153346. (g) J. Yu, T.A. Le, N.Q. Tran, H. Lee, *Chem. Eur. J.* 26 (2020) 6423–6436. (h) L. Xia, H. Song, X. Li, X. Zhang, B. Gao, Y. Zheng, K. Huo, P.K. Chu, *Front. Chem.* 8 (2020) 382.
- [4] (a) J. Wang, W. Cui, Q. Liu, Z. Xing, A.M. Asiri, X. Sun, *Adv. Mater.* 28 (2016) 215–230. (a) H. Zhong, C.A. Campos-Roldán, Y. Zhao, S. Zhang, Y. Feng, N. Alonso-Vante, *Catalysts* 8 (2018) 559. (b) G. Huang, Z. Xiao, R. Chen, S. Wang, *ACS Sustainable Chem. Eng.* 6 (2018) 15954–15969. (c) O. Basu, S. Mukhopadhyay, S.K. Das *J. Chem. Sci.* 130 (2018) 93; (d) S. Li, X. Hao, A. Abudula, G. Guan, *J. Mater. Chem. A* 7 (2019) 18674–18707. (e) W. Zhang, L. Cui, J. Liu, *J. Alloy. Comp.* 821 (2020) 153542.

- [5] (a) Y. Lang, R.R. Arnepalli, A. Tiwari, *J. Nanosci. Nanotechnol.* 11 (2011) 3719–3739. (b) C.L. Muhich, B.D. Ehrhart, I. Al-Shankiti, B.J. Ward, C.B. Musgrave, A.W. Weimer, *WIREs Energy Environ.* 5 (2016) 261–287. (c) C. Acar, I. Dincer, *J. Cleaner Prod.* 218 (2019) 835–849.
- [6] K. Kunitatsu, T. Senzaki, M. Tsushima, M. Osawa, *Chem. Phys. Lett.* 401 (2005) 451–454.
- [7] (a) A. Singh, L. Spiccia, *Coord. Chem. Rev.* 257 (2013) 2607–2622. (b) B.M. Hunter, H.B. Gray, A.M. Müller, *Chem. Rev.* 116 (2016) 14120–14136. (c) N.–T. Suen, S.–F. Hung, Q. Quan, N. Zhang, Yi.–J. Xu, H.M. Chen, *Chem. Soc. Rev.* 46 (2017) 337–365. (d) F. Song, L. Bai, A. Moysiadou, S. Lee, C. Hu, L. Liardet, X. Hu, *J. Am. Chem. Soc.* 140 (2018) 7748–7759. (e) M.–I. Jamesh, X. Sun, *J. Power Sources* 400 (2018) 31–68. (f) T. Zhang, Y. Zhu, J.Y. Lee, *J. Mater. Chem. A* 6 (2018) 8147–8158. (g) Q. Shi, C. Zhu, D. Du, Y. Lin, *Chem. Soc. Rev.* 48 (2019) 3181–3192. (h) L. Wu, L. Yu, X. Xiao, F. Zhang, S. Song, S. Chen, Z. Ren, *Research* (2020) Article ID 3976278. (i) N. Yuan, Q. Jiang, J. Li, J. Tang, *Arabian J. Chem.* 13 (2020) 4294–4309.
- [8] (a) A.A. Noyes, T.J. Deahl, *J. Am. Chem. Soc.* 59 (1937) 1337–1344. (b) *CRC Handbook of Chemistry and Physics*, 70th ed.; R.C. West, D.R. Lide, M.J. Astle, W.H. Beyer, Eds.; CRC Press: Boca Raton, FL, (1989) D-152.
- [9] (a) J.L. Dempsey, B.S. Brunschwig, J.R. Winkler, H.B. Gray, *Acc. Chem. Res.* 42 (2009) 1995–2004. (b) S. Losse, J.G. Vos, S. Rau, *Coord. Chem. Rev.* 254 (2010) 2492–2504. (c) V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem. Int. Ed.* 50 (2011) 7238–7266. (d) W.T. Eckenhoff, W.R. McNamara, P. Du, R. Eisenberg, *Biochim. Biophys. Acta* 1827 (2013) 958–973. (e) N. Kaeffer, M. Chavarot-Kerlidou, V. Artero, *Acc. Chem. Res.* 48 (2015) 1286–1295. (f) N. Queyriaux, R.T. Jane, J. Massin, V. Artero, M. Chavarot-Kerlidou, *Coord. Chem. Rev.* 304–305 (2015) 3–19. (g) D.S. Nesterov, O.V. Nesterova, *Catalysts* 8 (2018) 602. (h) M.D. Symes, Y. Surendranath, D.A. Lutterman, D.G. Nocera, *J. Am.*

- Chem. Soc.* 133 (2011) 5174–5177. (i) N.S. McCool, D.M. Robinson, J.E. Sheats, G.C. Dismukes, *J. Am. Chem. Soc.* 133 (2011) 11446–11449. (j) A.M. Ullman, Y. Liu, M. Huynh, D.K. Bediako, H. Wang, B.L. Anderson, D.C. Powers, J.J. Breen, H.D. Abruña, D.G. Nocera, *J. Am. Chem. Soc.* 136 (2014) 17681–17688. (k) A. Genoni, G.L. Ganga, A. Volpe, F. Puntoriero, M.D. Valentin, M. Bonchio, M. Natali, A. Sartorel, *Faraday Discuss.* 185 (2015) 121–141. (l) F. Song, R. Moré, M. Schilling, G. Smolentsev, N. Azzaroli, T. Fox, S. Lubner, G.R. Patzke, *J. Am. Chem. Soc.* 139 (2017) 14198–14208. (m) A.I. Nguyen, K.M. V. Allsburg, M.W. Terban, M. Bajdich, J. Oktawiec, J. Amtawong, M.S. Ziegler, J.P. Dombrowski, K.V. Lakshmi, W.S. Drisdell, J. Yano, S.J.L. Billinge, T.D. Tilley, *Proc. Natl. Acad. Sci.* 116 (2019) 11630–11639.
- [10] (a) R.M. Kellett, T.G. Spiro, *Inorg. Chem.* 24 (1985) 2378–2382. (b) T. Abe, F. Taguchi, H. Imai, F. Zhao, J. Zhang, M. Kaneko, *Polym. Adv. Technol.* 9 (1998) 559–562. (c) F. Zhao, J. Zhang, T. Abe, D. Wöhrle, M. Kaneko, *J. Mol. Catal. A: Chem.* 145 (1999) 245–256. (d) O. Pantani, E. Anxolabéhère-Mallart, A. Aukauloo, P. Millet, *Electrochem. Commun.* (2007) 9 54–58. (e) L.A. Berben, J. C. Peters, *Chem. Commun.* 46 (2010) 398–400. (f) H. Chen, Z. Sun, X. Liu, A. Han, P. Du, *J. Phys. Chem. C* 119 (2015) 8998–9004. (g) H.A. Younus, N. Ahmad, A.H. Chughtai, M. Vandichel, M. Busch, K.V. Hecke, M. Yusubov, S. Song, F. Verpoort, *ChemSusChem*. 10 (2017) 862–875. (h) Q. Daniel, R.B. Ambre, B. Zhang, B. Philippe, H. Chen, F. Li, K. Fan, S. Ahmadi, H. Rensmo, L. Sun, *ACS Catal.* 7 (2017) 1143–1149.
- [11] R.R. Gagné, C.L. Spiro, T.J. Smith, C.A. Hamann, W.R. Thies, A.K. Shiemke, *J. Am. Chem. Soc.* 103 (1981) 4073–4081.
- [12] (a) S. Mukhopadhyay, J. Debgupta, C. Singh, A. Kar, S.K. Das, *Angew. Chem. Int. Ed.* 57 (2018) 1918–1923 (b) C. Singh, S. Mukhopadhyay, S.K. Das, *Inorg. Chem.* 57 (2018) 6479–6490.

- [13] *APEX3: Program for Data Collection on Area Detectors*, Bruker AXS Inc., Madison, Wisconsin, USA, (2016).
- [14] G.M. Sheldrick, *SADABS: Program for Area Detector Absorption Correction*, University of Göttingen, Göttingen, Germany, (1997).
- [15] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 64 (2008) 112–122.
- [16] L.J. Farrugia, *J. Appl. Crystallogr.* 45 (2012) 849–854.
- [17] F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P.M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Crystallogr.* 41 (2008) 466–470.
- [18] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, *J. Appl. Crystallogr.* 46 (2013) 1231–1235.
- [19] (a) J.-Y. Le Questel, M. Berthelot, C. Laurence, *J. Phys. Org. Chem.* 13 (2000) 347–358. (b) D.R. Turner, A.J. Edwards, R.O. Piltz, *CrystEngComm*. 14 (2012) 6447–6451.
- [20] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, *SHAPE v2.1: Continuous Shape Measures Calculation*, Universitat de Barcelona, Barcelona, Spain, (2013).
- [21] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, *J. Chem. Soc. Dalton Trans.* (1984) 1349–1356.
- [22] (a) D. Lee, L. Sorace, A. Caneschi, S.J. Lippard, *Inorg. Chem.* 40 (2001) 6774–6781. (b) Z.A. Siddiqi, A. Siddique, M. Shahid, M. Khalid, P.K. Sharma, Anjuli, M. Ahmad, S. Kumar, Y. Lan, A.K. Powell, *Dalton Trans.* 42 (2013) 9513–9522.
- [23] (a) C.M. Lee, J.D. Kubicki, B. Fan, L. Zhong, M.C. Jarvis, S.H. Kim, *J. Phys. Chem. B* 119 (2015) 15138–15149. (b) D. Ngo, H. Liu, Z. Chen, H. Kaya, T. J. Zimudzi, S. Gin, T. Mahadevan, J. Du, S. H. Kim, *NPJ Mater. Degrad.* 4 (2020) 1.

- [24] (a) S.N. Pal, K.R. Radhika, S. Pal, *Z. Anorg. Allg. Chem.* 627 (2001) 1631–1637 (b) S.G. Sreerama, D. Shyamraj, S. Pal, S. Pal, *Indian J. Chem.* 42A (2003) 2352–2358. (c) S.G. Sreerama, S. Pal, *Inorg. Chem.* 44 (2005) 6299–6307.
- [25] F.E.Ö. Özbek, *J. Chem. Sci.* 132 (2020) 61.
- [26] (a) J. Luo, N.P. Rath, L.M. Mirica, *Inorg. Chem.* 50 (2011) 6152–6157; (b) S. Majumder, S. Mondal, P. Lemoine, S. Mohanta, *Dalton Trans.* 42 (2013) 4561–4569.
- [27] S. Maloth, S.K. Kurapati, S. Pal, *J. Coord. Chem.* 68 (2015) 1402–1411.
- [28] N.F. Chilton, R.P. Anderson, L.D. Turner, A. Soncini, K.S. Murray, *J. Comput. Chem.* 34 (2013) 1164–1175.
- [29] (a) A.K. Mondal, A. Mondal, B. Dey, S. Konar, *Inorg. Chem.* 57 (2018) 9999–10008. (b) A. Mondal, A.K. Kharwar, S. Konar, *Inorg. Chem.* 58 (2019) 10686–10693. (c) A. Mondal, S.–Q. Wu, O. Sato, S. Konar, *Chem. Eur. J.* 26 (2020) 4780–4789.
- [30] F. Neese, *WIREs Comput. Mol. Sci.* 2 (2012) 73–78.
- [31] T. Nishiura, Y. Chiba, J. Nakazawa, S. Hikichi, *Inorg. Chem.* 57 (2018) 14218–14229.
- [32] (a) A. Böttcher, T. Takeuchi, K.I. Hardcastle, T.J. Meade, H.B. Gray, *Inorg. Chem.* 36 (1997) 2498–2504. (b) S. Thakurta, R.J. Butcher, G. Pilet, S. Mitra, *J. Mol. Struct.* 929 (2009) 112–119. (c) L.–Q. Chai, J.–J. Huang, H.–S. Zhang, Y.–L. Zhang, J.–Y. Zhang, Y.–X. Li, *Spectrochim. Acta Part A* 131 (2014) 526–533. (d) L. Pogány, J. Moncol; M. Gál; I. Šalitroš, R. Boča, *Inorg. Chim. Acta* 462 (2017) 23–29. (e) K. Ghosh, A. Banerjee, A. Bauzá, A. Frontera, S. Chattopadhyay, *RSC Adv.* 8 (2018) 28216–28237. (f) S. Ambika, Y. Manojkumar, S. Arunachalam, B. Gowdhami, K.K. M. Sundaram, R.V. Solomon, P. Venuvanalingam, M.A. Akbarsha, M. Sundararaman, *Sci. Rep.* 9 (2019) 2721.
- [33] (a) Y.–H. Fang, Z.–P. Liu, *ACS Catal.* 4 (2014) 4364–4376. (b) T. Shinagawa, A. T. Garcia-Esparza, K. Takanabe, *Sci. Rep.* 5 (2015) 13801. (c) S.

Anantharaj, S.R. Ede, K. Karthick, S.S. Sankar, K. Sangeetha, P.E. Karthik, S. Kundu, *Energy Environ. Sci.* 11 (2018) 744–771.

[34] (a) R. Liu, S. Gu, H. Du, C.M. Li, *J. Mater. Chem. A* 2 (2014) 17263–17267.

(b) J. Mahmood, F. Li, S.M. Jung, M. S. Okay, I. Ahmad, S.J. Kim, N. Park, Y. H. Jeong, J.B. Baek, *Nature Nanotech.* 12 (2017) 441–447. (c) S. Ghosh, A.K. Srivastava, R. Govu, U. Pal, S. Pal, *Inorg. Chem.* 58 (2019) 14410–14419.

[35] M.M. Najafpour, H. Feizi, *Catal. Sci. Technol.* 8 (2018) 1840–1848.

[36] (a) M.W. Kanan, D.G. Nocera, *Science* 321 (2008) 1072–1075. (b) M. W. Kanan, Y. Surendranath, D.G. Nocera, *Chem. Soc. Rev.* 38 (2009) 109–114. (c) M.W. Kanan, J. Yano, Y. Surendranath, M. Dincă, V.K. Yachandra, D. G. Nocera, *J. Am. Chem. Soc.* 132 (2010) 13692–13701. (d) Y. Surendranath, M. W. Kanan, D.G. Nocera, *J. Am. Chem. Soc.* 132 (2010) 16501–16509.

[37] (a) J. Lilie, N. Shinohara, M.G. Simic, *J. Am. Chem. Soc.* 98 (1976) 6516–6520. (b) L.J. Charbonnière, A.F. Williams, U. Frey, A.E. Merbach, P. Kamalaprija, O. Schaad, *J. Am. Chem. Soc.* 119 (1997) 2488–2496. (c) A.P. King, H.A. Gellineau, S.N. MacMillan, J. J. Wilson, *Dalton Trans.* 48 (2019) 5987–6002.

[38] (a) E. Anxolabéhère-Mallart, C. Costentin, M. Fournier, S. Nowak, M. Robert and J.–M. Savéant, *J. Am. Chem. Soc.* 2012 134 6104–6107; (b) Z. Kap, E. Ülker, S. V.K. Nune and F. Karadas, *J. Appl. Electrochem.* 2018 48 201–209; (c) J. Dai, D. Zhao, W. Sun, X. Zhu, L.–J. Ma, Z. Wu, C. Yang, Z. Cui, L. Li and S. Chen, *ACS Catal.*, 2019 9 10761–10772.

Chapter 5

A cationic one-dimensional Mn(II)Mn(III) coordination polymer with a macrocyclic compartmental ligand: Structure, properties and catecholase like activity[§]

5.1. Abstract

Reaction of 2,6-diformyl-4-methylphenol, 1,3-diaminopropane, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in 1:1:1:1 mole ratio in methanol afford a linear coordination polymer of formula $\{[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (L^{2-} represents the Robson-type ligand) in 64% yield. The complex has been characterized by elemental (CHN) analysis, magnetic susceptibility, spectroscopic (IR and UV–Vis) and solution electrical conductivity measurements. The linear polymeric structure and the mixed-valent character of the complex have been confirmed by single crystal X-ray crystallography. In the repetitive dinuclear unit, both metal centers are in N_2O_4 coordination spheres assembled by the compartmental macrocyclic $\text{N}_2\text{O}_2\text{N}_2$ -donor L^{2-} , an intra-dinuclear bridging acetate and an inter-dinuclear bridging acetate. Variable temperature magnetic susceptibility measurements indicate a weak intra-dinuclear ferromagnetic ($J = 1.12(3) \text{ cm}^{-1}$) interaction as well as a weak inter-molecular antiferromagnetic ($zJ' = -0.679(3) \text{ cm}^{-1}$) interaction. CV of the complex displays a metal centered quasi-reversible reduction at -0.03 V and an irreversible ligand centered reduction at -1.16 V (vs Ag/AgCl). The complex efficiently catalyzes the aerobic oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butylbenzoquinone with a turnover number (k_{cat}) $1.2 \times 10^4 \text{ h}^{-1}$.

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5.2. Introduction

The sustained interest in dinuclear complexes stems from their diverse physicochemical properties such as metal-metal interaction, redox characteristics and cooperative bimetallic reactivities, which enable them for applications in a large variety of research areas ranging from bioinorganic modelling to medicinal chemistry to materials science to catalysis [1–10]. Since the first report on the dinuclear transition metal ion complexes with the compartmental macrocyclic tetraiminodiphenolate ligand formed through metal ion assisted template $2 + 2$ cyclocondensation of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol [11], a vast literature is now available on this and analogous macrocyclic Schiff base ligands and their dinuclear complexes [12–19]. Generally, in a discrete dinuclear complex of this type, the dianionic macrocyclic $N_2O_2N_2$ -donor compartmental ligand satisfies four equatorial positions of each of the two proximate di-phenoxo bridged metal ions and the remaining apical/axial sites of them are occupied by various ancillary monodentate ligands or bidentate bridging ligands such as mono-carboxylates [14–23]. Thus, the bare Robson-type dinuclear unit $\{N_2MO_2MN_2\}$ with unoccupied apical/axial sites can be used as the building block for the formation of one-dimensional coordination polymers via self-assembly process in presence of polynucleating bridging ligands. The polynucleating ligands are expected to occupy the apical/axial positions of the metal ions of the building blocks and propagate the polymeric chain. There are a few reports on such one-dimensional coordination polymers with the following polynucleating bridging ligands: 1,3-diaminopropane [24], 4,4'-bipyridine [25,26], terephthalic acid [26], acetylene-dicarboxylate [27], isonicotinonitrile [28] and perchlorate [29]. All these polymeric complexes are of nickel(II), copper(II) and zinc(II).

Although several X-ray structurally characterized discrete dimanganese complexes with various macrocyclic Robson-type ligands have been reported so far [20,21,30–35], but to the best of our knowledge there is only one report on a polymeric dimanganese(II) complex with a $\text{N}_2\text{O}_2\text{N}_2$ -donor ligand where acetate acts as the polynucleating bridging ligand [36]. In this one-dimensional polymer, each metal center is in N_2O_3 square-pyramidal environment constituted by the compartmental ligand and the inter-dinuclear bridging acetate. In most of the dinuclear manganese complexes, the macrocyclic ligands are derived from triamines and they are $\text{N}_3\text{O}_2\text{N}_3$ -donor [20]. About nine dinuclear manganese complexes are known where the macrocyclic ligands are $\text{N}_2\text{O}_2\text{N}_2$ -donors [21,30–35]. Out of these nine complexes, six are dimanganese(II) species, while the other three are mixed-valent manganese(II)-manganese(III) complexes. In the dimanganese(II) complexes, two bidentate or bridging acetates complete the distorted hexacoordination of the manganese centers in three of them [31–33,35] and the metal atoms are square-pyramidal with chloride or thiocyanate at the apical positions in the other two [30,34]. In contrast, the metal centers in all three mixed-valent complexes are hexacoordinated. In one of these three complexes, one chloride and one bromide both being monodentate and a bridging chloride complete the hexacoordination of the metal centers [30]. On the other hand, a bridging mono-carboxylate satisfies the fifth coordination site of each metal center and monodentate O-coordinating water, methanol or perchlorate occupy the sixth coordination sites of both metal centers in the remaining two mixed-valent complexes [21]. In our attempt to synthesize a Robson-type dimanganese complex, we have isolated a one-dimensional mixed-valent manganese(II)-manganese(III) coordination polymer, $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**), where the Robson dinuclear units are interconnected by the acetates (Chart 1). Herein, we describe its synthesis, X-ray structure, physicochemical properties and its application as catalyst in catechol oxidation reaction.

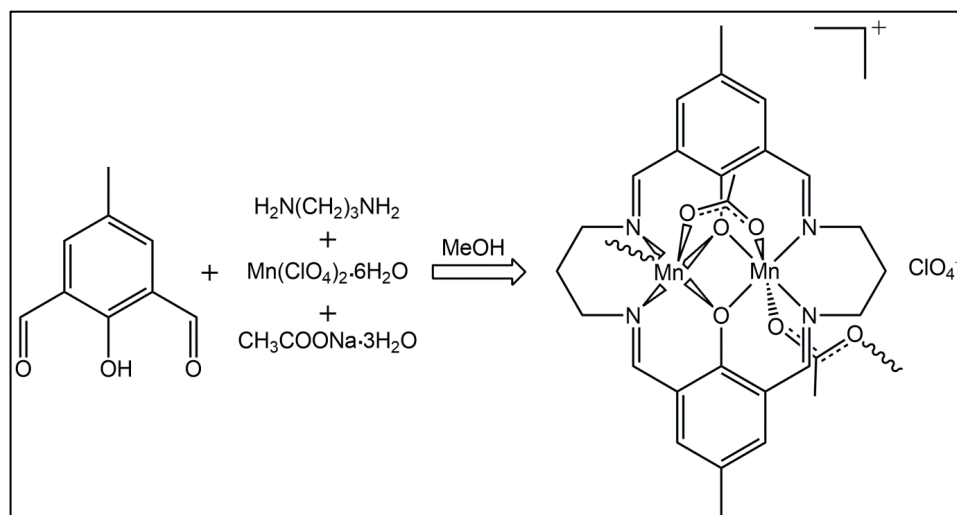


Chart 1. Synthesis of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**).

5.3. Experimental

5.3.1. Materials

All the chemicals and the solvents used in this work were of analytical grade available commercially and were used as received without further purification.

5.3.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used for elemental (CHN) analysis. Powder X-ray diffraction pattern was recorded on a Bruker D8 Advance X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) generated at 40 kV and 30 mA. Solid state variable temperature magnetic susceptibility measurements were carried out with a Quantum Design PPMS-VSM instrument at 10 kG. The solution electrical conductivity was measured using a Digisun DI-909 conductivity meter. The infrared spectrum was recorded in ATR mode on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used to collect the electronic spectrum. A Jeol JES-FA200 spectrometer was used to record the EPR spectrum. Cyclic voltammetric measurements were performed with the help of a CH Instruments model 620A electrochemical analyzer. In all the measurements with solutions of **1**, the molar concentration was calculated using the formula weight of the repetitive dinuclear unit.

5.3.3. Synthesis of $\{[Mn_2L(OAc)_2]ClO_4\}_n$ (**1**)

A solution of 2,6-diformyl-4-methylphenol (100 mg, 0.6 mmol) in methanol (15 ml) was added dropwise over a period of 10 min to a solution of 1,3-diaminopropane (45 mg, 0.6 mmol) in methanol (15 ml) and the mixture was stirred in presence of air at room temperature for $\frac{1}{2}$ h. To the above mixture, solid $Mn(ClO_4)_2 \cdot 6H_2O$ (217 mg, 0.6 mmol) was added and stirred for another $\frac{1}{2}$ h under aerobic conditions. The reaction mixture turned from yellow to brown. Solid $CH_3COONa \cdot 3H_2O$ (82 mg, 0.6 mmol) was added to this brown reaction mixture and stirring was continued for 24 h. The complex precipitated as a microcrystalline solid was collected by filtration, washed with cold methanol and dried under vacuum. The volume of the brown filtrate was reduced to about 10 ml on a steam bath and then it was kept at low temperature (278 K) for slow evaporation. The complex separated as a dark brown crystalline material was filtered off and dried in air. The combined yield was 140 mg (64%). Anal. Calcd for $C_{28}H_{32}N_4O_{10}ClMn_2$: C, 46.07; H, 4.42; N, 7.68. Found: C, 46.15; H, 4.38; N, 7.76. Selected IR data (ν (cm^{-1})): 1635 (C=N), 1542 and 1412 (COO^-), 1084 and 621 (ClO_4^-). UV-Vis data ($\lambda_{max}(nm)$ (ϵ ($10^4 M^{-1} cm^{-1}$))): 373 (1.20), 260 (2.15).

5.3.4. X-ray crystallography

An X-ray quality single crystal of $\{[Mn_2L(OAc)_2]ClO_4\}_n$ (**1**) was collected from the crystalline material obtained by slow evaporation of the synthetic reaction mixture filtrate. Unit cell determination and intensity data collection at 298 K were performed on a BRUKER D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite monochromated Mo $K\alpha$ Radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection, integration, reduction and absorption correction were performed using the APEX3 software package [37]. The structure was solved by direct method and refined on F^2 by full matrix least-squares procedures. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included at idealized positions using a riding model. The

SHELX-97 programs [38] accessible in the WinGX software suite [39] were used for structure solution and refinement. The Mercury package [40] was used to search for intermolecular non-covalent interactions and make graphical representations. Selected crystal and refinement data are listed in Table 1. Detailed X-ray crystallographic data for $\{[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ **1** have been deposited with the Cambridge crystallographic data center under the deposition numbers 1890524 respectively.

Table 1 Selected crystal and refinement data

Complex	$\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (1)
Chemical formula	$\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_{10}\text{ClMn}_2$
Formula weight	729.91
Crystal system	Monoclinic
Space Group	$P2_1/c$
a (Å)	12.6528(6)
b (Å)	15.6463(6)
c (Å)	15.6504(7)
β (°)	93.388(2)
V (Å ³)	3092.9(2)
Z	4
ρ (g cm ⁻³)	1.568
μ (mm ⁻¹)	0.965
Reflns collected	25030
Reflns unique	5471
Reflns [$I \geq 2\sigma(I)$]	4427
Data / restraints / parameters	5471 / 0 / 410
$R1, wR2$ [$I \geq 2\sigma(I)$]	0.0430, 0.1076
$R1, wR2$ [all data]	0.0577, $wR2 = 0.1163$
GOF on F^2	1.050
Largest diff. peak / hole (e Å ⁻³)	0.751 / -0.627

5.4. Results and discussion

5.4.1. Synthesis and characterization

The brown polymeric complex $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**) was synthesized in 64% yield by reacting equimolar amounts of 2,6-diformyl-4-methylphenol, 1,3-diaminopropane, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in methanol under aerobic conditions (Chart 1). About 85–90% of the yield was precipitated as a microcrystalline solid during the stirring of the reaction mixture. The remaining yield was obtained as X-ray quality single crystalline material by reducing the volume of the filtrate followed by its slow evaporation at low temperature. The elemental (CHN) analysis data of the complex are in good agreement with its formula. The magnetic moment of the repetitive dinuclear unit at 300 K is $7.64 \mu_{\text{B}}$. This value is very close to the calculated spin-only magnetic moment ($7.69 \mu_{\text{B}}$) of a dinuclear complex having metal centers with $S = 5/2$ and $S = 2$ spin states. The complex is moderately soluble in methanol, dimethylformamide and dimethylsulfoxide; sparingly soluble in acetonitrile and insoluble in chloroform, dichloromethane and hexane. In solution, the complex is electrically conducting. Using the formula weight of the repetitive dinuclear unit, the molar conductivity (Λ_{M}) value in methanol has been obtained as $110 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. This value falls within the range expected for a 1:1 electrolyte [41]. Thus the Λ_{M} value indicates that the one-dimensional polymeric structure of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]^+\}_n$ found in the solid state (*vide infra*) breaks down in solution and discrete dinuclear monocationic species are formed. In solution, the vacant coordination site available due to the breakage of the polymeric structure (Chart 1) may be occupied by a solvent molecule as observed before [21] or both acetates may act as bidentate bridging ligands to form the dinuclear monocationic species.

The magnetic moment at 300 K and the molar conductivity together with the elemental analysis data of **1** are consistent with its mixed-valent (II-III) state and the dinuclear formula of the repetitive unit. The aerial oxygen is the most likely oxidant for the oxidation of one of the metal center from bivalent to trivalent state during the synthesis of **1** using the manganese(II) starting material.

5.4.2. Description of X-ray structure

The structure of the monocationic dinuclear repetitive unit of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**) has been illustrated in Fig. 1. The bond lengths and the bond angles associated with the two metal centers are listed in Table 2. The complex crystallizes in the $P2_1/c$ space group and the asymmetric unit contains one monocationic dinuclear unit $[\text{Mn}_2\text{L}(\text{OAc})_2]^+$ and a perchlorate counter anion. In the dinuclear unit, the compartmental macrocyclic ligand L^{2-} coordinates the two metal centers through the four azomethine-N atoms and the two bridging phenoxo-O atoms and forms two N_2O_2 square-planes around the two manganese atoms. Around Mn(1), an almost perfect N_2O_2 square-plane (rms deviation 0.01 Å) is formed and there is essentially no deviation (0.04 Å) of Mn(1) from this plane. On the other hand, the N_2O_2 square-plane (rms deviation 0.19 Å) around Mn(2) has a slight tetrahedral distortion and the metal center is significantly shifted (by 1.08 Å) from the mean plane. The average Mn–O(phenoxo) and Mn–N(azomethine) bond lengths involving Mn(1) are shorter by ~ 0.37 and ~ 0.23 Å, respectively, when compared with the corresponding bond lengths involving Mn(2). These differences in the bond lengths and no shift of Mn(1) and a large shift of the Mn(2) from the corresponding N_2O_2 square-planar environment clearly indicate that the Mn(1) is smaller than Mn(2) and their oxidation states are +3 and +2, respectively.

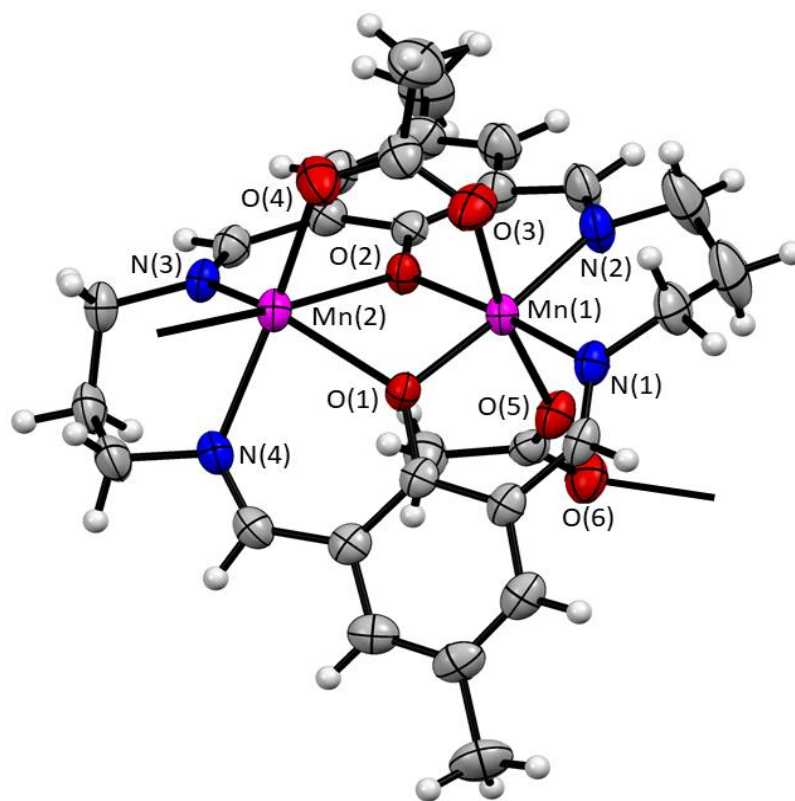


Fig. 1. Perspective view of the dinuclear $[\text{Mn}_2\text{L}(\text{OAc})_2]^+$ repetitive unit. Thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level and only the non-carbon atoms are labeled for clarity.

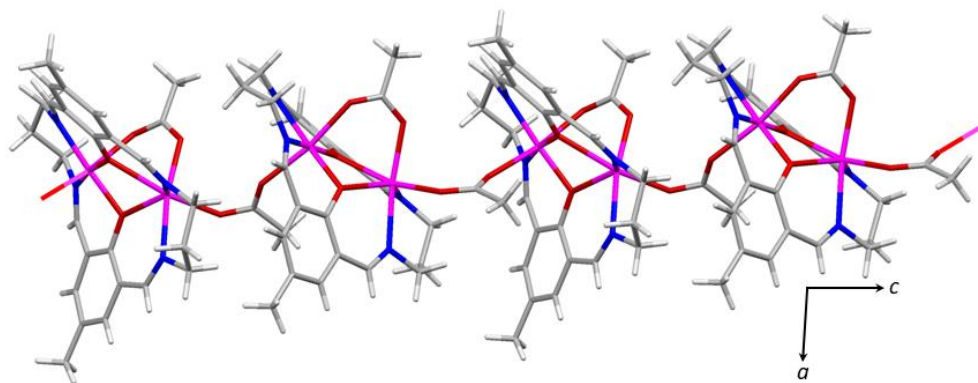


Fig. 2. The linear polymeric structure of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]^+\}_n$.

Table 2Selected bond parameters (Å and °) for {[Mn₂L(OAc)₂]ClO₄}_n (**1**)

Mn(1)–O(1)	1.939(2)	Mn(2)–O(1)	2.217(2)
Mn(1)–O(2)	1.909(2)	Mn(2)–O(2)	2.366(2)
Mn(1)–O(3)	2.142(2)	Mn(2)–O(4)	2.153(3)
Mn(1)–O(5)	2.154(2)	Mn(2)–O(6) ^a	2.104(2)
Mn(1)–N(1)	2.015(3)	Mn(2)–N(3)	2.204(3)
Mn(1)–N(2)	2.023(3)	Mn(2)–N(4)	2.301(3)
O(1)–Mn(1)–O(2)	83.92(9)	O(1)–Mn(2)–O(2)	68.22(7)
O(1)–Mn(1)–O(3)	93.77(10)	O(1)–Mn(2)–O(4)	100.60(10)
O(1)–Mn(1)–O(5)	94.22(9)	O(1)–Mn(2)–O(6) ^a	106.19(9)
O(1)–Mn(1)–N(1)	88.69(10)	O(1)–Mn(2)–N(3)	131.04(9)
O(1)–Mn(1)–N(2)	175.22(10)	O(1)–Mn(2)–N(4)	79.53(9)
O(2)–Mn(1)–O(3)	90.06(10)	O(2)–Mn(2)–O(4)	77.17(9)
O(2)–Mn(1)–O(5)	95.13(9)	O(2)–Mn(2)–O(6) ^a	162.29(9)
O(2)–Mn(1)–N(1)	171.97(10)	O(2)–Mn(2)–N(3)	77.21(8)
O(2)–Mn(1)–N(2)	91.49(11)	O(2)–Mn(2)–N(4)	113.79(9)
O(3)–Mn(1)–O(5)	170.88(10)	O(4)–Mn(2)–O(6) ^a	87.77(11)
O(3)–Mn(1)–N(1)	87.29(11)	O(4)–Mn(2)–N(3)	104.37(11)
O(3)–Mn(1)–N(2)	84.87(12)	O(4)–Mn(2)–N(4)	167.72(11)
O(5)–Mn(1)–N(1)	88.52(10)	O(6) ^a –Mn(2)–N(3)	116.13(10)
O(5)–Mn(1)–N(2)	87.50(12)	O(6) ^a –Mn(2)–N(4)	80.46(10)
N(1)–Mn(1)–N(2)	95.82(12)	N(3)–Mn(2)–N(4)	84.15(10)
Mn(1)–O(1)–Mn(2)	100.71(9)	Mn(1)–O(2)–Mn(2)	96.56(9)

^a Symmetry transformation used to generate the equivalent atom: x, –y + 1/2, z – 1/2.

The dihedral angle ($55.2(1)^\circ$) between the two mean planes (rms deviations $0.05 \text{ \AA}$) constituted by the two 2,6-dimethine-4-methylphenolate moieties indicate the non-planarity of the macrocyclic ligand L^{2-} . The coordination of the larger manganese(II) is likely to be the reason for this distortion from planarity. A bridging acetate occupies the fifth coordination site of each metal center in the dinuclear unit (Fig. 1). The O-atoms of a second acetate satisfies the sixth coordination sites of Mn(1) and Mn(2) of another repetitive dinuclear unit. As a result of this inter-dinuclear bridging acetates, the one-dimensional polymeric structure of $\{[Mn_2L(OAc)_2]^+\}_n$ propagates along the *c*-axis (Fig. 2) and in each dinuclear unit, both metal centers have hexacoordinated N_2O_4 coordination environment. The manganese(III) center, Mn(1), has a tetragonally elongated coordination geometry where the macrocycle provides the N_2O_2 square-plane and the O-atoms (O(3) and O(5)) of the two acetates are at the tetragonally elongated axial sites (Fig. 3 and Table 2). In each of the previously reported analogous dimanganese(II/III) complexes, the trivalent metal center has similar tetragonally elongated octahedral geometry [21,30]. However, the coordination geometry around the manganese(II) center in the present complex (**1**) is not distorted trigonal prismatic as reported before [21,30]. Here, the coordination geometry around the manganese(II) atom, Mn(2), is closer to distorted octahedron rather than trigonal prism (Fig. 3). One azomethine-N and one phenoxo-O (N(4) and O(2)) atoms from the macrocycle and the acetate-O atoms (O(4) and O(6)) from the two acetates constitute a satisfactory NO_3 square-plane (rms deviation $0.05 \text{ \AA}$) around Mn(2) and the remaining two mutually *trans* sites are occupied by another azomethine-N and the second phenoxo-O (N(3) and O(1)) atoms of the macrocycle (Fig. 3). The metal center is shifted from the NO_3 square-plane towards N(3) by a very small amount ($0.14 \text{ \AA}$).

The distortion from the octahedral geometry is primarily due to a very large deviation (by $\sim 49^\circ$) of the *trans* N(3)–Mn(2)–O(1) angle from the ideal value of 180° (Fig. 3). The intra-dinuclear bis(phenoxo)-acetato bridged Mn(1)⋯Mn(2) distance (3.2057(7) Å) in $[\text{Mn}_2\text{L}(\text{OAc})_2]^+$ is slightly longer than that (3.168(3)–3.187(1) Å) reported for previously reported mixed-valent complexes with $\text{N}_2\text{O}_2\text{N}_2$ -donor macrocyclic Robson-type ligands [21,30]. The inter-dinuclear acetato-bridged Mn(1)⋯Mn(2) distance is 5.3006(7) Å. Thus, the one-dimensional chain-like structure of **1** has alternating short and long metal⋯metal distances (Fig. 2). The bond parameters associated with the central $\{\text{Mn}_2(\mu\text{-O}(\text{phenoxo}))_2(\mu\text{-OAc})\}^{2+}$ core in **1** are comparable with those observed for the same core stabilized by a $\text{N}_2\text{O}_2\text{N}_2$ -donor macrocycle that is analogous to the present macrocycle L^{2-} [21]. Overall, the Mn(II/III)–N and Mn(II/III)–O bond lengths and the bond parameters of L^{2-} in **1** are within the ranges reported for dimanganese (II/II and II/III) complexes with $\text{N}_2\text{O}_2\text{N}_2$ -donor Robson-type macrocycles [21,30–36]. The bond parameters associated with the two acetates and the perchlorate are unexceptional [36,42–45].

The crystal packing of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ is shown in Fig. 4. The perchlorate counter anions are located in between the $\{[\text{Mn}_2\text{L}(\text{OAc})_2]^+\}_n$ chains and they are involved in several C–H⋯O hydrogen bonding interactions with various types of C–H groups of the macrocyclic ligand L^{2-} and the acetate moieties (Table 3). These C–H groups are phenolate ring *meta* C–H, azomethine C–H, methylene C–H and acetate methyl C–H. In these interactions, the C⋯O distances are in the range 3.376–3.589 Å and the C–H⋯O angles are within $148\text{--}163^\circ$. The parallel chains of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]^+\}_n$ are inter-connected by the perchlorates through these C–H⋯O interactions and as a result a three-dimensional network is formed (Fig. 4).

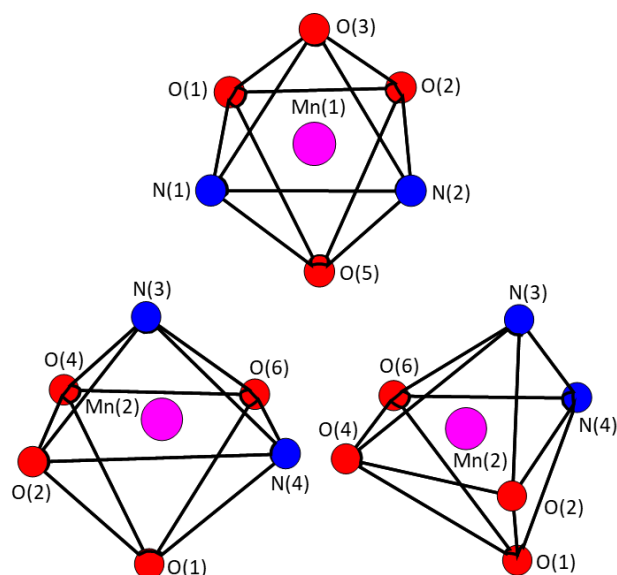


Fig. 3. The coordination spheres around the manganese(III) (top) and manganese(II) (bottom) in $[\text{Mn}_2\text{L}(\text{OAc})_2]^+$.

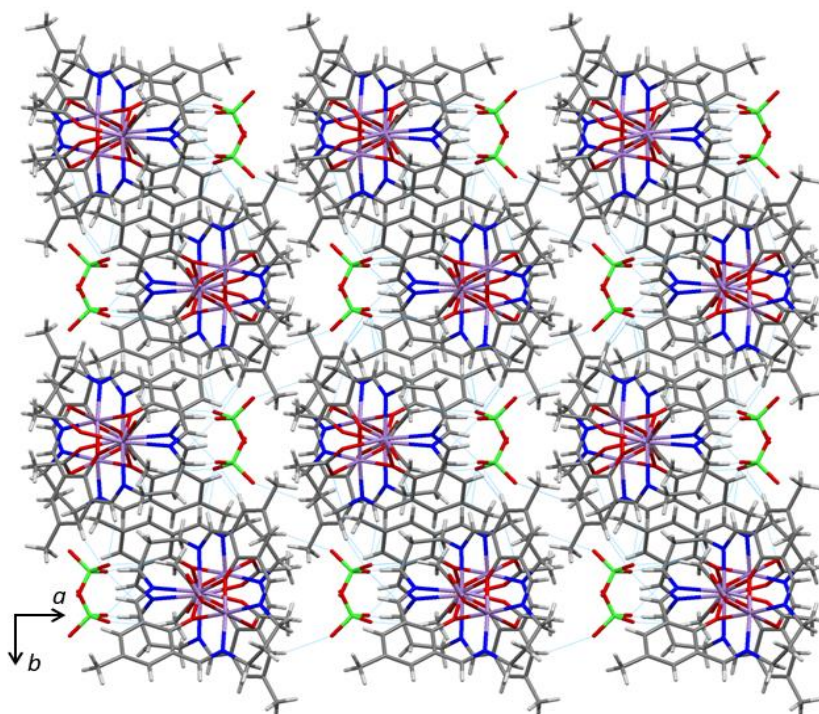


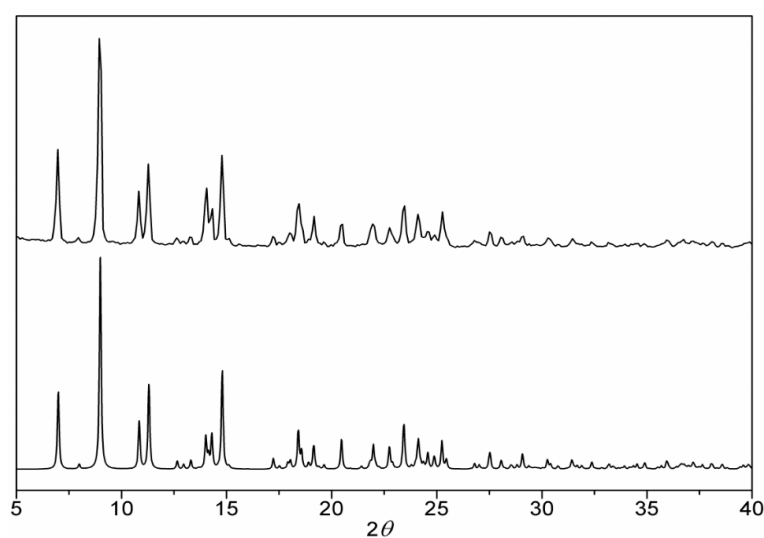
Fig. 4. The three-dimensional network structure of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ viewed along the c -axis.

Table 3 Intermolecular C–H...O interactions in {[Mn₂L(OAc)₂]ClO₄}_n (**1**)^a

Type of C–H	Interaction	D–A (Å)	∠D–H...O	Symm. Transf. used to generate the C–H
Phenolate <i>meta</i> -CH	C(15)–H(15)...O7	3.564	159	1 – x, 1 – y, 1 – z
–N=CH–	C(18)–H(18)...O(7)	3.580	158	1 – x, 1 – y, 1 – z
–CH ₂ –	C(8)–H(8A)...O(8)	3.580	161	1 – x, ½ + y, ½ – z
–N=CH–	C(7)–H(7)...O(8)	3.553	155	1 – x, ½ + y, ½ – z
Acetate-CH ₃	C(28)–H(28A)...O(8)	3.589	163	x, y, z
Phenolate <i>meta</i> -CH	C(13)–H(13)...O(10)	3.376	148	1 + x, y, z

^a Interactions having D–A distances < 3.6 Å and D–H...O angle > 140°, are only considered.

Powder X-ray diffraction pattern of the microcrystalline solid was collected and compared with the powder diffraction pattern simulated from the single crystal X-ray structure (*vide infra*). The essentially one-to-one correspondence between the experimental and the simulated patterns confirms that both materials are of the same complex (Fig. 5).

**Fig. 5.** Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of {[Mn₂L(OAc)₂]ClO₄}_n(**1**).

5.4.3. Magnetic properties

Magnetic susceptibility (χ_M) measurements in the temperature range 300–3 K were performed with a powdered sample of **1**. The $\chi_M T$ values for the dinuclear repetitive unit $[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4$ vs T plot is shown in Fig. 6. The $\chi_M T$ at 300 K is $7.294 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. This value is very close to the calculated spin only value of $7.38 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. The $\chi_M T$ increases gradually with the decrease of temperature. It reaches a maximum value of $8.506 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 100 K. After this increase, there is a gradual decrease and at 55 K it becomes $8.304 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Below 55 K there is a sharp decrease and the final value of $\chi_M T$ at 3 K is $2.26 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. The data were fitted using an isotropic dinuclear model ($H = -2JS_1S_2$, where $S_1 = 2$ and $S_2 = 5/2$) with a molecular field correction (zJ') to account for the intra-chain and inter-chain interactions [46,47]. The least-squares fitting of the data provides $J = 1.12(3) \text{ cm}^{-1}$, $zJ' = -0.679(3) \text{ cm}^{-1}$ and $g = 2.155(5)$ with a least-square error of 2.2×10^{-4} . Using this simple model a reasonable fit has been obtained in the low temperature range but not in the high temperature range (Fig. 6). For a better understanding of the magnetic characteristics of **1**, an improved theoretical model including the zero-field splitting effects on the manganese(II) and manganese(III) centers and variable field measurements will be carried out in future. Nevertheless, the weak intra-dinuclear ferromagnetic and inter-molecular antiferromagnetic interactions are consistent with the observed $\chi_M T$ vs T curve profile. Similar weak interaction is also reported for complexes of the same mixed-valent $\{\text{Mn}_2(\mu\text{-O(phenoxo)})_2(\mu\text{-carboxylate})\}^{2+}$ core with analogous $\text{N}_2\text{O}_2\text{N}_2$ -donor Robson macrocycle [21] where the geometric parameters of the tribridged dimetal core are very similar to those of **1**.

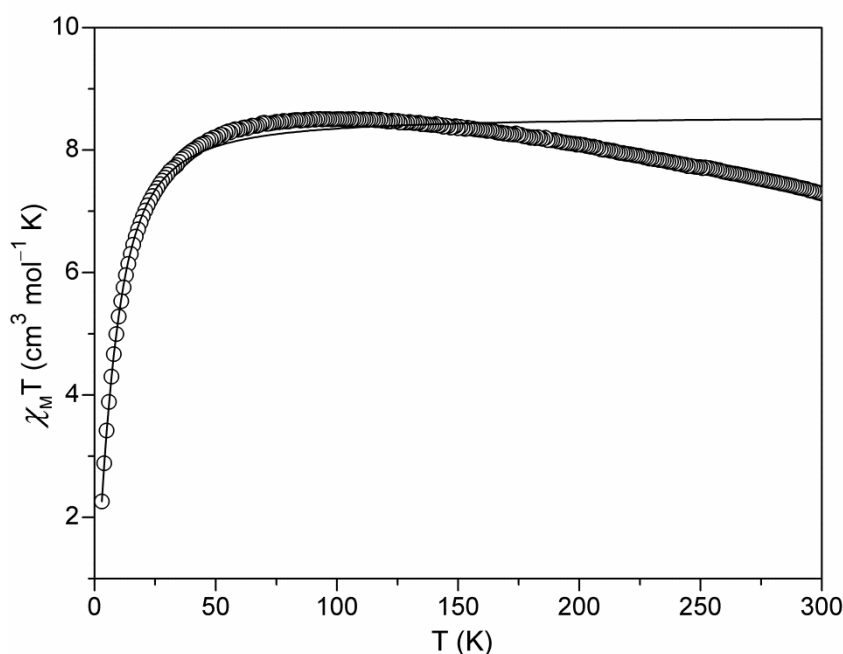


Fig. 6. The product of molar paramagnetic susceptibility and temperature vs temperature plot for $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$. The solid line was generated from the best fit parameters given in the text.

5.4.4. Spectroscopic characteristics

The infrared spectrum of **1** was collected within the range 4000–500 cm^{-1} (Fig. 7). Absence of any band assignable to the phenolic-OH is consistent with the deprotonated state of the two phenol functionalities of the macrocyclic ligand. A large number of bands having various intensities have been observed between 1650–500 cm^{-1} . Except for the following few, no attempt has been made to assign the remaining bands. A strong band observed at 1635 cm^{-1} is attributed to the azomethine ($\text{HC}=\text{N}$) double bond [20,21,31,34,35]. Two more strong bands appeared at 1543 and 1412 cm^{-1} are assigned to the acetate asymmetric and symmetric stretches, respectively [21,35,42,43]. The presence of the uncoordinated perchlorate counter anion is indicated by a very strong band and a sharp medium intensity band at 1084 cm^{-1} and at 621 cm^{-1} , respectively [21,35,36,44,45].

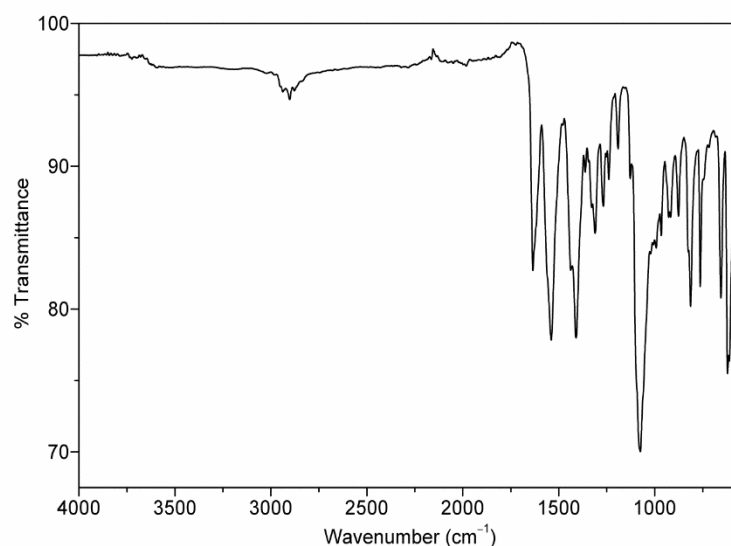


Fig. 7. Infrared spectrum of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**).

The electronic spectrum of **1** was recorded in methanol. The spectrum displays two strong and bands centered at 370 and 260 nm (Fig. 8). The lower energy strong band is likely to be primarily due to ligand-to-metal charge transfer transition with some contribution from the manganese(III) ($S = 2$) centered d–d transition in its long tail in the visible region [21,31,33,48]. The higher energy very strong broad band is attributed to the macrocyclic ligand centered π to π^* transition [20,21,31,34].

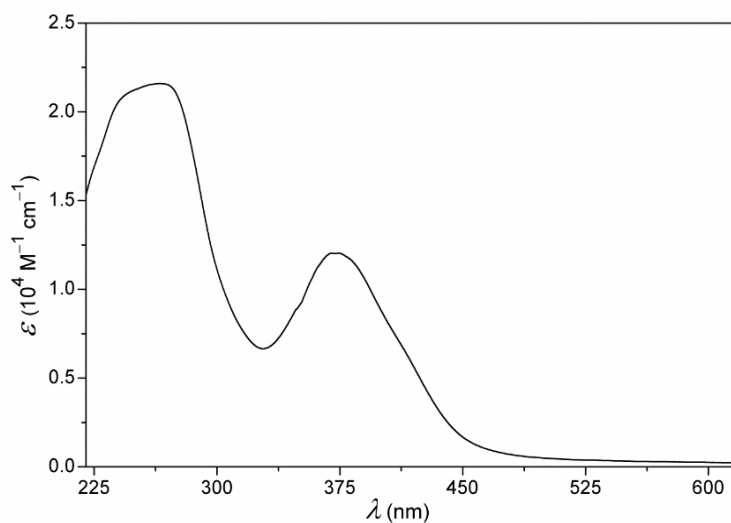


Fig. 8. Electronic spectrum of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**) in methanol.

X-band EPR spectrum of **1** was recorded in frozen methanol solution at 77 K. The spectrum is typical for a complex of high-spin manganese(II) (Fig. 9). It shows a strong six-line hyperfine structure at $g \approx 2.0$ due to the allowed $\Delta M_I = 0$ transitions. In between the six lines there are some weak fine structures. The forbidden $\Delta M_I = 1$ transitions are expected to appear as weak ten-line structure together with the six-line pattern [30,32]. The spectrum clearly indicates that there is essentially no or very weak spin-coupling between the manganese(II) and manganese(III) centers in **1**. Thus, the spectrum is consistent with the very small spin-coupling constants obtained from the variable temperature magnetic susceptibility data of **1** (*vide supra*). It may be noted that analogous weakly coupled mixed-valent manganese(II)-manganese(III) complexes in frozen solution display very similar EPR spectra [30,32,48].

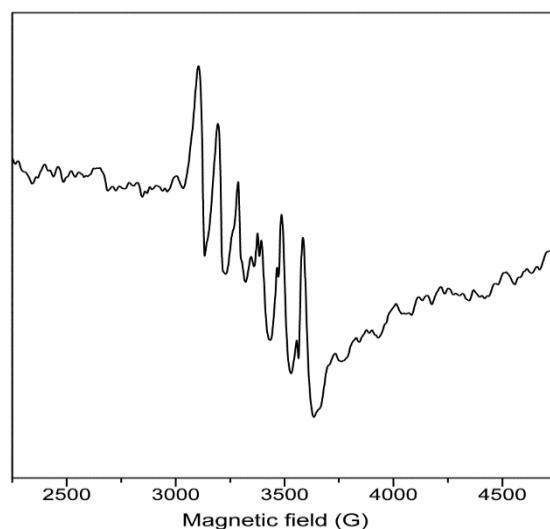


Fig. 9. EPR spectrum of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**) in frozen (77 K) methanol.

5.4.5. Redox properties

Cyclic voltammetric measurements were performed at room temperature (298 K) with a methanol solution of **1** (1×10^{-3} M) containing Bu_4NClO_4 (0.1 M) as the supporting electrolyte using a glassy-carbon working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1} . Under identical condition the ferrocenium/ferrocene (Fc^+/Fc) couple was observed at $E_{1/2} = 0.19 \text{ V}$ ($\Delta E_p = 190 \text{ mV}$). There is no oxidation response

for the complex on the anodic side of the reference electrode. However, on the cathodic side, it displays a quasi-reversible reduction at $E_{1/2} = -0.03$ V ($\Delta E_p = 230$ mV) and an irreversible reduction at -1.16 V (Fig. 10). The peak currents of the quasi-reversible response are comparable with those of the Fc^+/Fc couple and other known one-electron redox processes under comparable conditions [49–51]. In contrast, the irreversible response has relatively much larger cathodic peak current. There is no report of any ligand reduction near 0.0 V for dimanganese complexes with analogous macrocyclic Schiff base ligands [20,30–32]. On the other hand, metal centered one-electron redox response having an $E_{1/2}$ value at a little higher potential range (0.03 V vs Fc^+/Fc , 0.08 V vs Ag^+/Ag , 0.6 V vs NHE and 0.11–0.29 V vs SCE) has been reported for analogous Robson-type dimanganese(II,II) complexes [20,30–32,48]. Thus, the first quasi-reversible reduction of **1** is assigned to a metal centered Mn(II)Mn(III)/Mn(II)Mn(II) redox couple. The second irreversible reduction at -1.16 V with high peak current is attributed to the reduction of the azomethine fragments of L^{2-} [48].

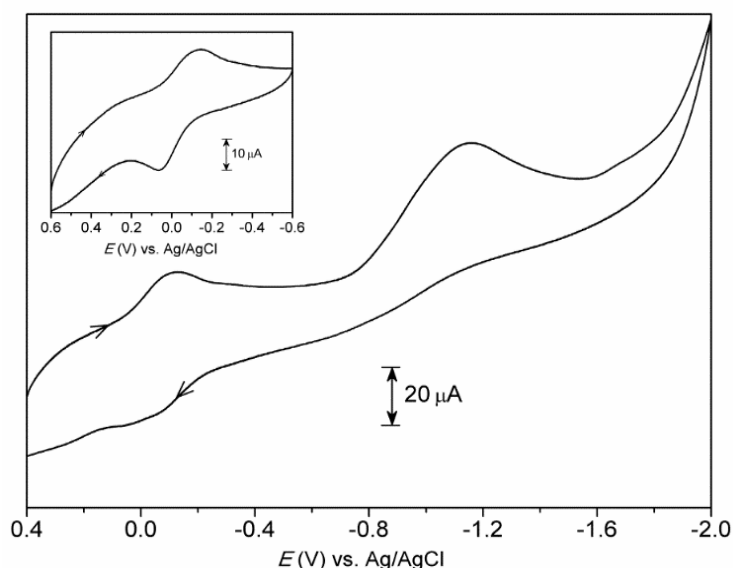


Fig. 10. CV of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ using the experimental conditions described in the text. Inset: The quasi-reversible metal centered reduction.

5.5. Catecholase like activity

The catecholase mimicking activity of **1** was investigated using 3,5-di-tert-butylcatechol (3,5-DTBC) as the model substrate. The reactions were carried out by adding 3,5-DTBC to 1×10^{-4} M solutions of the complex in methanol at 298 K under aerobic conditions. The formation of the 3,5-di-tert-butyl-1,2-benzoquinone (3,5-DTBQ) was followed spectrophotometrically over a period of 1 h (Fig. 11). Dependence of the reaction rate and the various kinetic parameters on the substrate concentration has been determined by treating the catalyst with 25, 50, 100, 200 and 300 molar equivalents of 3,5-DTBC. The rates of the reactions were calculated from the change in absorbance (at 382 nm) against time plots. Using Michaelis–Menten equation and the Lineweaver–Burk plot (Fig. 12), the kinetic parameters Michaelis–Menten constant (K_M), maximum velocity (V_{max}) and the turnover number (k_{cat}) were calculated as 33.6×10^{-3} M, 20.3×10^{-3} M min^{-1} and 1.2×10^4 h^{-1} , respectively. Till now a large number of manganese(II/III/IV) complexes having a variety of nuclearities and two mixed-valent manganese(II/III) polymeric complexes have been reported to exhibit low to high catecholase activities with turnover numbers (k_{cat}) in the range 1.7 to 1.32×10^6 h^{-1} [21,52–55]. The k_{cat} value of **1** displays its catalytic efficiency in oxidation of catechol to quinone is the fifth best amongst the above-mentioned complexes [54].

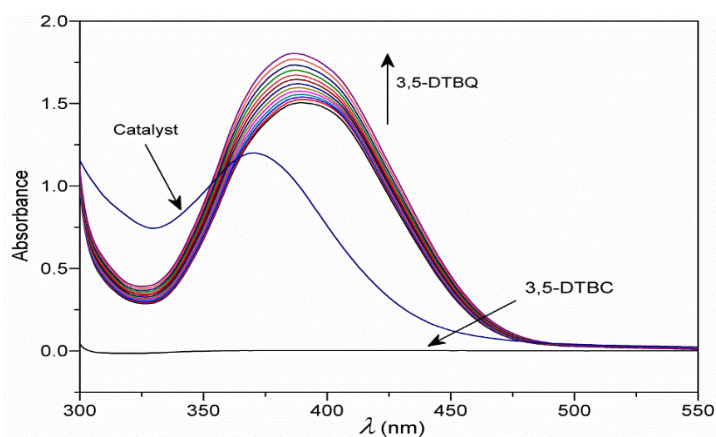


Fig. 11. Change of absorbance of 3,5-DTBQ band around 390 nm. The spectra were recorded at time intervals of 5 min.

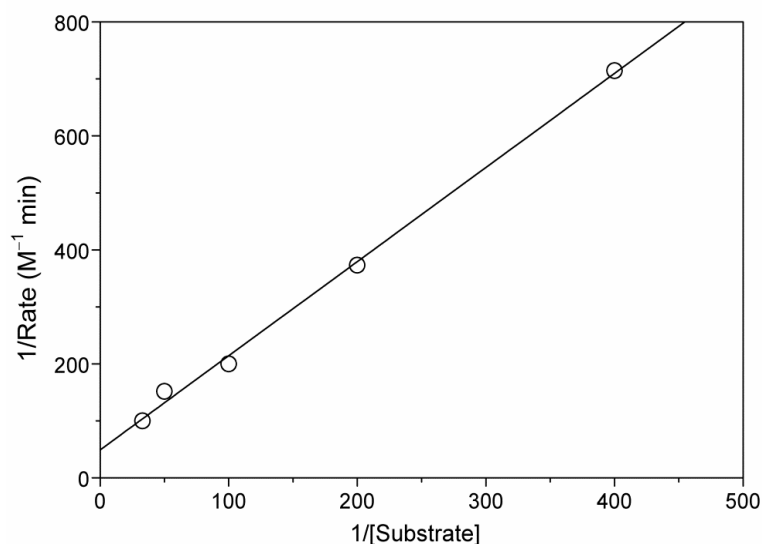


Fig. 12. Lineweaver–Burk plot. The straight line represents a linear least-squares fit.

5.6. Conclusions

A one-dimensional coordination polymer of a monocationic bis(phenoxo)-acetato bridged dimanganese(II/III) complex with a Robson-type macrocyclic L^{2-} as the principal ligand, acetate as coligand and perchlorate as counter anion was synthesized and structurally characterized. In this polymeric complex, $\{[Mn^{II}Mn^{III}L(OAc)_2]ClO_4\}_n$, half of the acetates act as intra-dinuclear bridges, while the other half provide the inter-dinuclear bridges. In the chain-like structure, the Mn...Mn distance alternates between long and short values. The microanalytical data and the spectroscopic features are consistent with the formula of the complex. Magnetic susceptibility measurements reveal that the bis(phenoxo)-acetato bridged metal centers in the repetitive dinuclear unit of the polymeric chain are weakly ferromagnetically coupled, while a weak antiferromagnetic interaction is operative in and between the polymeric chains. The complex is redox active and shows a metal centered and a ligand centered reduction responses. It exhibits an excellent catalytic activity in aerobic oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-1,2-benzoquinone.

5.7. References

- [1] A.E. Martell, J. Perutka, D. Kong, *Coord. Chem. Rev.* 216–217 (2001) 55–63.
- [2] K.D. Demadis, C.M. Hartshorn, T.J. Meyer, *Chem. Rev.* 101 (2001) 2655–2685.
- [3] W.R. Browne, R. Hage, J.G. Vos, *Coord. Chem. Rev.* 250 (2006) 1653–1668.
- [4] M. Shibasaki, S. Matsunaga, *J. Synth. Org. Chem. Jpn*, 68 (2010) 1142–1149.
- [5] F. Habib, M. Murugesu, *Chem. Soc. Rev.* 42 (2013) 3278–3288.
- [6] L.J. Daumann, G. Schenk, D.L. Ollis, L.R. Gahan, *Dalton Trans.* 43 (2014) 910–928.
- [7] S. Mameria, D. Specklin, R. Welter, *C.R. Chimie* 18 (2015) 1370–1384.
- [8] T. Inatomi, Y. Koga, K. Matsubara, *Molecules* 23 (2018) 140.
- [9] L. Habala, F. Devínsky, A.E. Egger, *J. Coord. Chem.* 71 (2018) 907–940.
- [10] S. Rej, H. Tsurugi, K. Mashima, *Coord. Chem. Rev.* 355 (2018) 223–239.
- [11] N.H. Pilkington, R. Robson, *Aust. J. Chem.* 23 (1970) 2225–2236.
- [12] B. Dutta, P. Bag, B. Adhikary, U. Flörke, K. Nag, *J. Org. Chem.* 69 (2004) 5419–5427.
- [13] N.E. Borisova, M.D. Reshetova, Y.A. Ustynyuk, *Chem. Rev.* 107 (2007) 46–79.
- [14] K.K. Nanda, R. Das, K. Venkatsubramanian, K. Nag, *Proc. Indian Acad. Sci. Chem. Sci.* (106) 1994 673–680.
- [15] A.J. Atkins, D. Black, A.J. Blake, A. Marin-Becerra, S. Parsons, I. ena kuiz-Ramirez, M. Schröder, *Chem. Commun.* (1996) 457–464.
- [16] H. Ōkawa, H. Furutachi, D.E. Fenton, *Coord. Chem. Rev.* 174 (1998) 51–75.
- [17] W. Huang, H.–B. Zhu, S.–H. Gou, *Coord. Chem. Rev.* 250 (2006) 414–423.

- [18] V. Lozan, C. Loose, J. Kortus, B. Kersting, *Coord. Chem. Rev.* 253 (2009) 2244–2260.
- [19] D. Venegas-Yazigi, D. Aravena, E. Spodine, E. Ruiz, S. Alvarez, *Coord. Chem. Rev.* 254 (2010) 2086–2095.
- [20] S. Kal, A.S. Filatov, P.H. Dinolfo, *Inorg. Chem.* 52 (2013) 13963–13973 and references therein.
- [21] A. Jana, N. Aliaga-Alcalde, E. Ruiz, S. Mohanta, *Inorg. Chem.* 52 (2013) 7732–7746.
- [22] L. Mandal, S. Mohanta, *Dalton Trans.* 43 (2014) 15737–15751.
- [23] S. Sasmal, S. Roy, L. Carrella, A. Jana, E. Rentschler, S. Mohanta, *Eur. J. Inorg. Chem.* (2015) 680–689.
- [24] A. Asokan, B. Varghese, A. Caneschi, P.T. Manoharan, *Inorg. Chem.* 37 (1998) 228–232.
- [25] W. Huang, S. Gou, D. Hu, S. Chantrapromma, H.-K. Fun, Q. Meng, *Inorg. Chem.* 40 (2001) 1712–1715.
- [26] Q.R. Cheng, H. Zhou, Z.Q. Pan, G.Y. Liao, Z.G. Xu, *Polyhedron* 81 (2014) 668–674.
- [27] M. Pascu, M. Andruh, A. Müller, M. Schmidtman, *Polyhedron* 23 (2004) 673–678.
- [28] W. Huang, Z. Chu, S. Gou, T. Ogawa, *Polyhedron* 26 (2007) 1483–1492.
- [29] J. Pan, L. Cheng, H. Zhou, Z.-Q. Pan, Q.-M. Huang, X.-L. Hu, *Polyhedron* 29 (2010) 1588–1592.
- [30] H.-R. Chang, S.K. Larsen, P.D.W. Boyd, C.G. Pierpont, D.N. Hendrickson, *J. Am. Chem. Soc.* 110 (1988) 4565–4576.
- [31] A.J. Downard, V. McKee, S. Tandon, *Inorg. Chim. Acta* 173 (1990) 181–190.
- [32] H. Wada, K. Motoda, M. Ohba, H. Sakiyama, N. Matsumoto, H. Ōkawa, *Bull. Chem. Soc. Jpn.* 68 (1995) 1105–1114.

- [33] T. Aono, H. Wada, M. Yonemura, M. Ohba, H. Ōkawa, D.E. Fenton, *J. Chem. Soc., Dalton Trans.* (1997) 1527–1531.
- [34] J.-C. Jiang, Z.-L. Chu, W. Huang, G. Wang, X.-Z. You, *Inorg. Chem.* 49 (2010) 5897–5911.
- [35] Y.-F. Chen, L. Wei, J.-L. Bai, H. Zhou, Q.-M. Huang, J.-B. Li, Z.-Q. Pan, *J. Coord. Chem.* 64 (2011) 1153–1164.
- [36] D. Luneau, J.-M. Savariault, P. Cassoux, J.-P. Tuchagues, *J. Chem. Soc. Dalton Trans.* (1988) 1225–1235.
- [37] APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2016.
- [38] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 64 (2008) 112–122.
- [39] L.J. Farrugia, *J. Appl. Crystallogr.* 45 (2012) 849–854.
- [40] F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Crystallogr.* 41 (2008) 466–470.
- [41] W.J. Geary, *Coord. Chem Rev.* 7 (1971) 81–122.
- [42] S. Pal, M.M. Olmstead, W.H. Armstrong, *Inorg. Chem.* 34 (1995) 4708–4715.
- [43] A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* (2009) 622–627.
- [44] S.G. Sreerama, S. Pal, *Eur. J. Inorg. Chem.* 2004, 4718–4723.
- [45] S. Maloth, S.K. Kurapati, S. Pal, *J. Coord. Chem.* 68 (2015) 1402–1411.
- [46] G.V.R. Chandramouli, C. Balagopalakrishna, M.V. Rajasekharan, P.T. Manoharan, *Computers Chem.* 20 (1996) 353–358.
- [47] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Comput. Chem.* 20 (1999) 1391–1400.
- [48] J.C. da Rocha, G. Poneti, J.G. Ferreira, R.R. Ribeiro, F.S. Nunes, *J. Braz. Chem. Soc.* 25 (2014) 1528–1535.
- [49] S.G. Sreerama, S. Pal, *Inorg. Chem.* 41 (2002) 4843–4845.
- [50] A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* (2009) 5391–5398.

- [51] A.K. Srivastava, S. Ghosh, S. Jana, S. Pal, *Inorg. Chim. Acta* 483 (2018) 329–336.
- [52] P. Chakraborty, S. Majumder, A. Jana, S. Mohanta, *Inorg. Chim. Acta* 410 (2014) 65–75.
- [53] P. Chakraborty, I. Majumder, K.S. Banu, B. Ghosh, H. Kara, E. Zangrando, D. Das, *Dalton Trans.* 45 (2016) 742–752.
- [54] S.K. Dey, A. Mukherjee, *Coord. Chem. Rev.* 310 (2016) 80–115.
- [55] S. Ganguly, P. Kar, M. Chakraborty, A. Ghosh, *New J. Chem.* 42 (2018) 9517–9529.

Chapter 6

One-dimensional Mn(III) and Fe(III) coordination polymers based on mixed ligands: Syntheses, structures and properties[†]

6.1. Abstract

Reactions of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ with the tetradentate N_2O_2 -donor Schiff bases *N,N'*-bis(salicylidine)-*ortho*-phenylenediamine and *N,N'*-bis(salicylidine)ethylenediamine ($\text{H}_2\text{salophen}$ and H_2salen , where 2 Hs represent the two dissociable phenolic protons) and the bridging ligand 4,4'-bipyridine (bipy) in presence of triethyl amine in methanol under ambient conditions produce one dimensional coordination polymers $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) in ~60% yields. Both complexes have been characterized by elemental analysis and spectroscopic (IR and DR) measurements. The linear polymeric structures of **1** and **2** have been confirmed by single crystal X-ray crystallography. The metal centres in these polymers are in distorted octahedral N_4O_2 coordination spheres. Each of the two dibasic tetradentate ligands (salophen^{2-} and salen^{2-}) forms an ONNO square-plane around the metal centre, while the two axial coordination sites are occupied by N-atoms of the two bridging bipy ligands. Variable temperature magnetic susceptibility measurements reveal the high-spin configuration of manganese(III) and iron(III) and Curie paramagnetic behaviour of each of the two coordination polymers.

[†] This work has been published in *J. Chem. Sci.* 133 (2021) 73.

6.2. Introduction

Since the first classification of infinite linear inorganic chain compounds as coordination polymers in 1964[1] the design and synthesis of polymeric coordination compounds have attracted immense attention due to their interesting solid state assembly patterns and the consequent electronic, optical and magnetic properties [2–11]. The network structures and the physical properties of these compounds have led to their applications in a wide variety of research areas such as gas absorption, separation and storage; molecule-based conductors, magnets and sensors; nonlinear optical materials and catalysis [6–11]. As a result, there is a constant effort for new coordination polymers having potential for use as functional materials and efficient catalysts. We have been working on structural aspects and catalytic applications of coordination polymers involving some 3d metal ions for quite some time [12–14]. Herein, we report two analogous one-dimensional coordination polymers of manganese(III) and iron(III) having the formulas $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) assembled from square-planar N_2O_2 coordination geometry forming Schiff bases *N,N'*-bis(salicylidine)-*ortho*-phenylenediamine ($\text{H}_2\text{salophen}$) and *N,N'*-bis(salicylidine)ethylene-diamine (H_2salen), respectively and the bridging ligand 4,4'-bipyridine (bipy) (Chart 1). In the following account, syntheses, single crystal X-ray structures and the physical properties of **1** and **2** have been described.

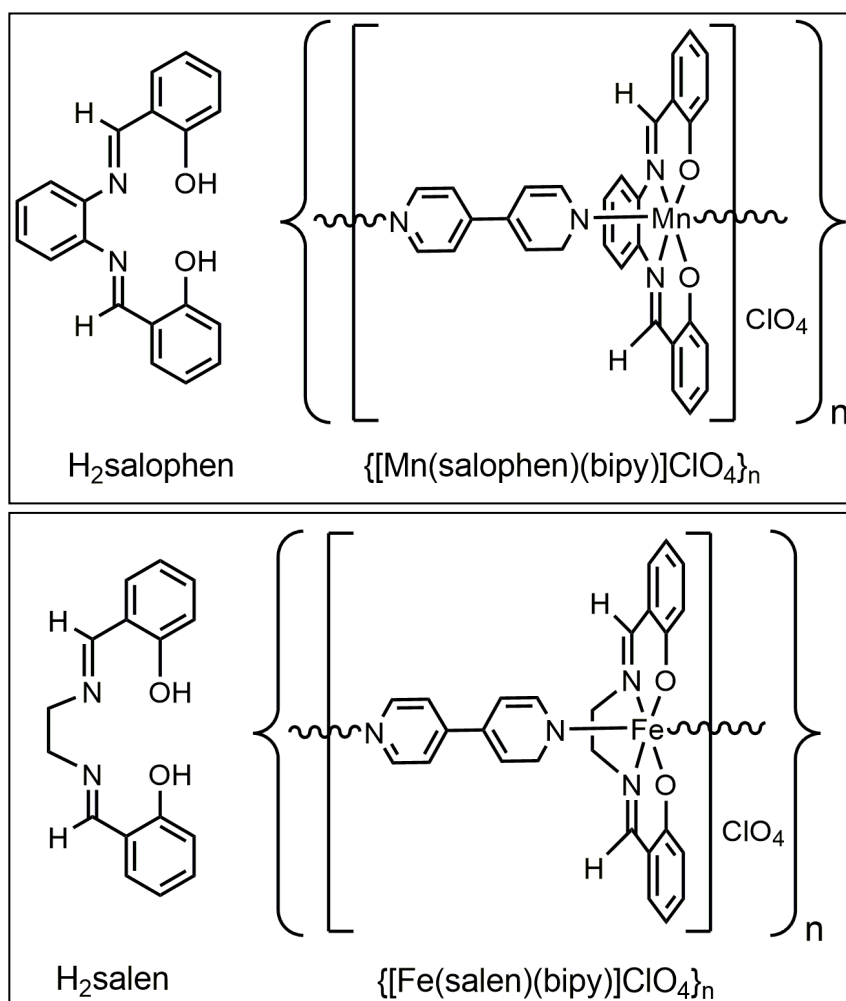


Chart 1. Chemical structure diagrams of the teradentate Schiff bases and the corresponding one-dimensional manganese(III) and iron(III) coordination polymers.

6.3. Experimental

6.3.1 Materials

The Schiff bases H_2salen and $H_2salophen$ were prepared from two mole equivalents of salicylaldehyde and one mole equivalent of ethylene diamine and *ortho*-phenylenediamine, respectively in methanol by following a reported procedure [15]. All other chemicals used in this work were of analytical grade available commercially and were used as received without any further purification. Solvents used were purified by standard methods [16].

6.3.2 Physical measurements

Elemental (CHN) analyses were performed with the help of a Thermo Finnigan Flash EA1112 series elemental analyser. A Quantum Design SQUID-VSM instrument was used for solid state variable temperature magnetic susceptibility measurements. The infrared spectra were recorded in ATR mode on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer. The electronic spectra were recorded in the solid-state diffuse-reflectance spectroscopy (DRS) mode with the help of a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere.

6.3.3. Synthesis of {[Mn(salophen)(μ -bipy)]ClO₄}_n (1)

To a suspension of H₂salophen (95 mg, 0.3 mmol) in 10 mL of methanol NEt₃ (60 mg, 0.6 mmol) and 4,4'-bipyridine (bipy) (47 mg, 0.3 mmol) were added and stirred for 10 min. To the resulting mixture a methanol solution (10 mL) of Mn(ClO₄)₂·6H₂O (110 mg, 0.3 mmol) was added and stirred in air at room temperature (298 K) for 2 h. The brown solution obtained was filtered and the filtrate was kept for slow evaporation. The dark crystalline material separated in about 7–10 days was collected by filtration and dried in vacuum. Yield: 120 mg (64%). Anal. Calcd for C₃₀H₂₂N₄O₆ClMn: C, 57.66; H, 3.55; N, 8.97. Found: C, 57.62; H, 3.56; N, 8.91. Selected IR bands: ν (cm⁻¹) = 1599 (azomethine-CN), 1064 and 621 (ClO₄⁻). UV-Vis (diffuse reflectance) bands: $\lambda_{\max}$ (nm) = 570^{sh}, 450^{sh}, 350, 252.

6.3.4. Synthesis of {[Fe(salen)(μ -bipy)]ClO₄}_n (2)

The iron(III) coordination polymer was also synthesized in methanolic medium by using H₂salen, NEt₃, 4,4'-bipyridine (bipy) and Fe(ClO₄)₃·6H₂O in the same mole ratio and the same procedure as described for **1**. Yield: 105 mg (60%). Anal. Calcd for C₂₆H₂₂N₄O₆ClFe: C, 54.05; H, 3.84; N, 9.70. Found: C, 54.15; H, 3.86; N, 9.62. Selected IR bands: ν (cm⁻¹) = 1617 (azomethine-CN), 1083 and 618 (ClO₄⁻). UV-Vis (diffuse reflectance) bands: $\lambda_{\max}$ (nm) = 580^{sh}, 442, 345, 248.

6.3.5. X-ray crystallography

A single crystal of $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) suitable for X-ray data collection was collected from the crystalline material obtained from its synthesis reaction mixture. On the other hand, X-ray quality crystals of $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) were grown by slow evaporation of its solution in acetonitrile. Complex **1** crystallized as it is without any solvent molecule, while complex **2** formed an acetonitrile solvate $2 \cdot \text{CH}_3\text{CN}$. X-ray intensity data for both crystals were collected at 298 K on a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection and reduction were performed with the help of APEX3 package [17]. Absorption corrections were applied using the SADABS program [18]. Each of the two structures was solved by direct method and refined on F^2 by full-matrix least-squares procedures. All non-hydrogen atoms of **1** and except for the isotropically refined non-hydrogen atoms of the two half-occupancy CH_3CN molecules the remaining non-hydrogen atoms of $2 \cdot \text{CH}_3\text{CN}$ were refined with anisotropic thermal parameters. All hydrogen atoms of both structures were included in the structure factor calculations at idealized positions by using a riding model. The SHELX-97 programs [19] available in the WinGX package [20] were used for structure solution and refinement. The structural illustrations were prepared using the Mercury package [21]. Selected crystal data and refinement summary for both structures are listed in Table 1. Detailed X-ray crystallographic data for **1** and $2 \cdot \text{CH}_3\text{CN}$ have been deposited with the Cambridge crystallographic data center under the deposition numbers 2077457 and 2077458 respectively.

Table 1 Selected crystal data and structure refinement summary

Complex	1	2·CH₃CN
Chemical formula	C ₃₀ H ₂₂ N ₄ O ₆ ClMn	C ₂₈ H ₂₅ N ₅ O ₆ ClFe
Formula weight	624.91	618.83
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ /c	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.7703(5)	9.6938(18)
<i>b</i> (Å)	30.1432(16)	11.533(3)
<i>c</i> (Å)	16.4637(8)	15.084(3)
α (°)	90	102.352(13)
β (°)	99.697(2)	102.883(12)
γ (°)	90	105.925(13)
Volume (Å ³)	5757.8(5)	1511.2(5)
Z	8	2
ρ (g cm ⁻³)	1.442	1.360
μ (mm ⁻¹)	0.602	0.635
Reflections collected	208861	49255
Reflections unique	10099	5285
Reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	8068	3800
Data / restr. / param.	10099 / 0 / 757	5285 / 0 / 369
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0648, 0.1945	0.0950, 0.2421
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0813, 0.2063	0.1283, 0.2594
GoF on <i>F</i> ²	1.062	1.095
Max. / Min. Δρ (e Å ⁻³)	1.698 / -0.688	1.222 / -0.586

6.4. Results and discussion

6.4.1. Synthesis and characterization

$\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) were synthesized in decent yields (64 and 60%, respectively) by reacting hexahydrated manganese(II) and iron(III) perchlorates, the corresponding Schiff bases $\text{H}_2\text{salophen}$ and H_2salen , 4,4'-bipyridine and triethylamine in 1:1:1:2 mole ratio in methanol at room temperature (300 K) under aerobic conditions. The elemental (CHN) analysis data of the two compounds are in good agreement with their molecular formulas. In the solid state, room temperature (300 K) magnetic moments of the repetitive mononuclear units are 4.61 and 6.02 μ_{B} for **1** and **2**, respectively. These values are close to the spin-only magnetic moments of 4.89 and 5.92 μ_{B} calculated for $S = 2$ and $S = 5/2$ spin states for the manganese(III) and iron(III) centres in **1** and **2**, respectively. In the case of **1**, it is very likely that the oxygen in air oxidized the manganese centre from bivalent state to the trivalent state during its synthesis from manganese(II) perchlorate under aerobic conditions.

6.4.2. X-ray structures

The structures of **1** and **2**·CH₃CN were solved in the space groups $P2_1/c$ and $P\bar{1}$, respectively. The asymmetric unit of **1** contains two repetitive units of the polymer, while that of **2**·CH₃CN contains one repetitive unit of the polymer and two half occupancy acetonitrile molecules. In both coordination polymers, the perchlorate ions are somewhat close to the metal coordinated polarized azomethine C–H groups indicating hydrogen bonding interactions. The shortest C···O distances and the corresponding C–H···O angles are in the ranges 3.360(14)–3.618(16) Å and 123–163°, respectively. However, no significant close contact could be detected for the two half-occupancy acetonitrile molecules with the complex cation or perchlorate ion in **2**·CH₃CN. The structures of the asymmetric units of **1** and **2**·CH₃CN are illustrated in t. 1 and 2, respectively. Metal centred geometric parameters of both are listed in

Table 2 and 3. In the asymmetric unit of **1**, the bond lengths and angles associated with the manganese centres of the two repetitive cations are very similar. In each of $[\text{Mn}(\text{salophen})(\mu\text{-bipy})]^+$ and $[\text{Fe}(\text{salen})(\mu\text{-bipy})]^+$, the metal ion is in a distorted octahedral N_4O_2 coordination sphere assembled by the N_2O_2 -donor Schiff base ligand and two N-atoms of the two bridging 4,4'-bipyridine molecules. The tetradentate Schiff base forms an ONNO square-plane around the metal centre. There is no deviation of the metal ion from this square-plane. The rms deviations from the mean plane constituted by the metal centre and the four coordinating atoms are about 0.03 and 0.07 Å for **1** and **2**, respectively. The N-atoms of two symmetry related 4,4'-bipyridine molecules satisfy the two axial positions of the metal centre in each of the planar $\{\text{Mn}(\text{salophen})\}^+$ and $\{\text{Fe}(\text{salen})\}^+$ units. As a result infinite linear chains of $[\text{Mn}(\text{salophen})(\mu\text{-bipy})]^+$ and $[\text{Fe}(\text{salen})(\mu\text{-bipy})]^+$ are formed in the crystal lattices of **1** and **2**·CH₃CN, respectively (Fig. 3). The bridging 4,4'-bipyridine moieties are twisted in both complexes. The twisting is relatively more in **1** than in **2**. In the asymmetric unit of **1**, the dihedral angles between the two pyridine rings are 49.7(2)° and 37.8(2)° in the first and the second $[\text{Mn}(\text{salophen})(\mu\text{-bipy})]^+$ units, respectively, whereas, in $[\text{Fe}(\text{salen})(\mu\text{-bipy})]^+$, the dihedral angle is 28.2(4)°. The metal to coordinating atom distances observed for $[\text{Mn}(\text{salophen})(\mu\text{-bipy})]^+$ and $[\text{Fe}(\text{salen})(\mu\text{-bipy})]^+$ are comparable with bond lengths reported for manganese(III) and iron(III) complexes, respectively, having similar coordinating atoms [22–25]. Bond valence sum calculations were also carried out using the EXPO2014 [26] software for further confirmation of the oxidation states. The values obtained are 3.21 and 3.19 for the two metal centres of the two $[\text{Mn}(\text{salophen})(\mu\text{-bipy})]^+$ units present in the asymmetric unit of **1**, whereas that is 2.99 for iron in $[\text{Fe}(\text{salen})(\mu\text{-bipy})]^+$ present in the asymmetric unit of **2**·CH₃CN.

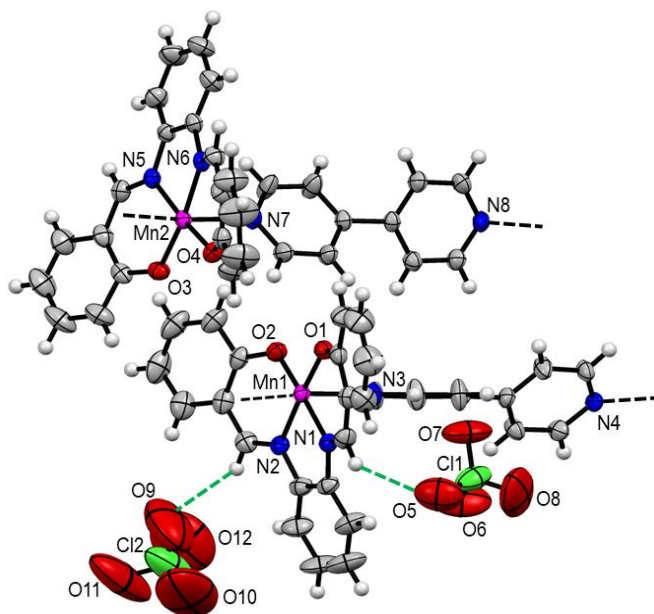


Fig. 1. The asymmetric unit of **1** with the atom labelling scheme. Thermal ellipsoids of all non-hydrogen atoms are drawn at the 50% probability level. For clarity only the non-carbon atoms are labelled.

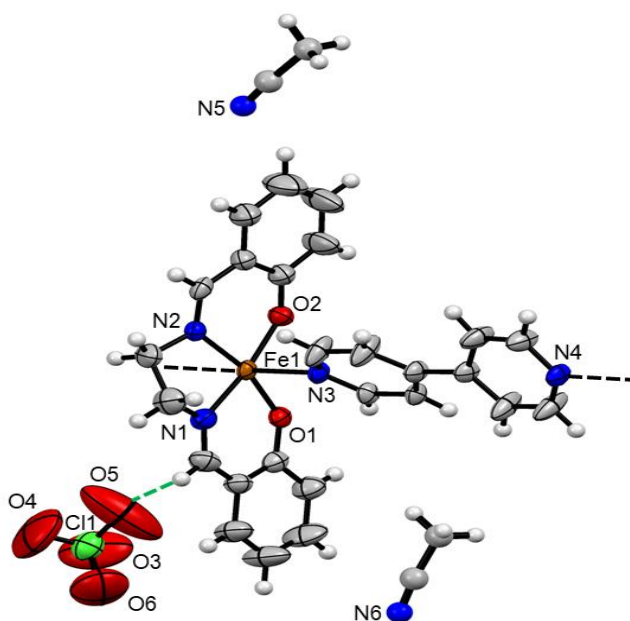


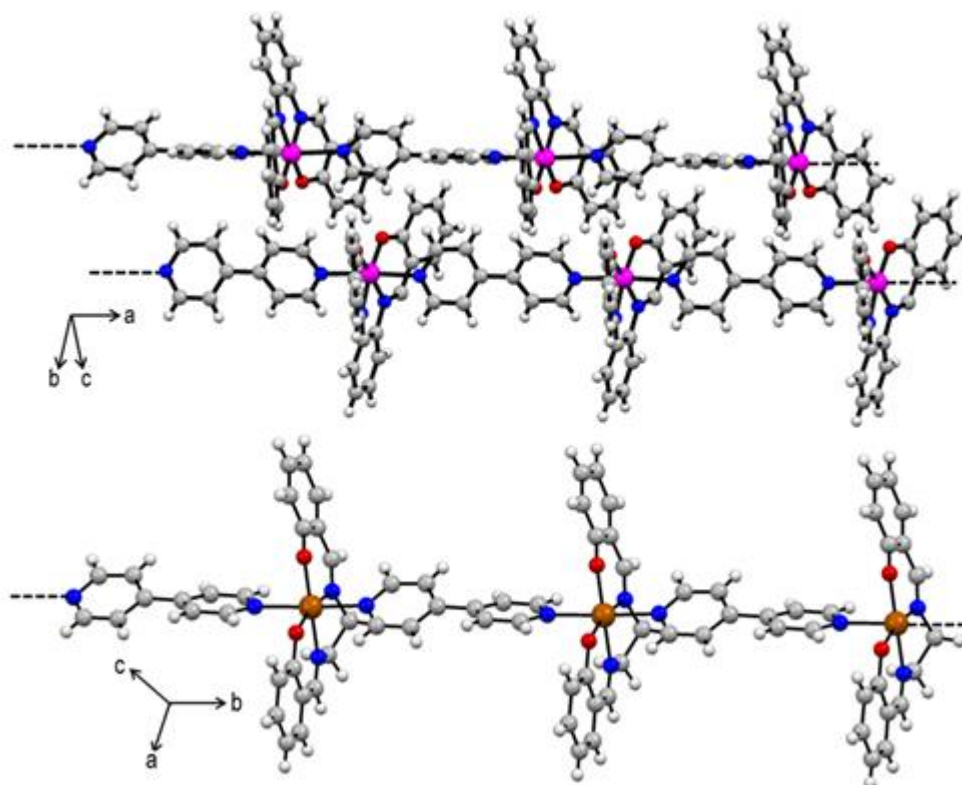
Fig. 2. The asymmetric unit of **2**·CH₃CN with the atom labelling scheme. Thermal ellipsoids of all non-hydrogen atoms except for those of the two half-occupancy CH₃CN molecules are drawn at the 50% probability level. For clarity the carbon atoms are not labelled.

Table 2 Selected bond parameters for {[Mn(salophen)(μ -bipy)]ClO₄}_n (**1**)

Mn(1)–O(1)	1.871(3)	Mn(2)–O(3)	1.886(3)
Mn(1)–O(2)	1.879(3)	Mn(2)–O(4)	1.865(3)
Mn(1)–N(1)	1.984(3)	Mn(2)–N(5)	1.977(3)
Mn(1)–N(2)	1.983(3)	Mn(2)–N(6)	1.994(3)
Mn(1)–N(3)	2.315(3)	Mn(2)–N(7)	2.334(3)
Mn(1)–N(4') ^a	2.396(3)	Mn(2)–N(8') ^a	2.390(3)
O(1)–Mn(1)–O(2)	95.05(13)	O(3)–Mn(2)–O(4)	94.10(12)
O(1)–Mn(1)–N(1)	91.91(13)	O(3)–Mn(2)–N(5)	91.80(13)
O(1)–Mn(1)–N(2)	173.09(14)	O(3)–Mn(2)–N(6)	172.84(13)
O(1)–Mn(1)–N(3)	90.74(13)	O(3)–Mn(2)–N(7)	91.72(12)
O(1)–Mn(1)–N(4') ^a	89.19(12)	O(3)–Mn(2)–N(8') ^a	89.32(12)
O(2)–Mn(1)–N(1)	172.87(13)	O(4)–Mn(2)–N(5)	172.81(13)
O(2)–Mn(1)–N(2)	91.41(13)	O(4)–Mn(2)–N(6)	92.69(13)
O(2)–Mn(1)–N(3)	92.10(12)	O(4)–Mn(2)–N(7)	94.21(12)
O(2)–Mn(1)–N(4') ^a	91.52(12)	O(4)–Mn(2)–N(8') ^a	88.72(12)
N(1)–Mn(1)–N(2)	81.70(14)	N(5)–Mn(2)–N(6)	81.27(13)
N(1)–Mn(1)–N(3)	89.32(12)	N(5)–Mn(2)–N(7)	89.73(12)
N(1)–Mn(1)–N(4') ^a	87.06(12)	N(5)–Mn(2)–N(8') ^a	87.23(12)
N(2)–Mn(1)–N(3)	86.57(13)	N(6)–Mn(2)–N(7)	90.02(12)
N(2)–Mn(1)–N(4') ^a	93.09(12)	N(6)–Mn(2)–N(8') ^a	88.59(12)
N(3)–Mn(1)–N(4') ^a	176.38(12)	N(7)–Mn(2)–N(8') ^a	176.82(12)

Table 3 Selected bond parameters for (2·CH₃CN)

Fe(1)–O(1)	1.871(4)	Fe(1)–O(2)	1.906(4)
Fe(1)–N(1)	2.123(6)	Fe(1)–N(2)	2.097(5)
Fe(1)–N(3)	2.231(5)	Fe(1)–N(4') ^b	2.232(5)
O(1)–Fe(1)–O(2)	105.9(2)	O(1)–Fe(1)–N(1)	88.7(2)
O(1)–Fe(1)–N(2)	165.0(2)	O(1)–Fe(1)–N(3)	90.24(19)
O(1)–Fe(1)–N(4') ^b	88.80(19)	O(2)–Fe(1)–N(1)	164.5(2)
O(2)–Fe(1)–N(2)	89.0(2)	O(2)–Fe(1)–N(3)	86.6(2)
O(2)–Fe(1)–N(4') ^b	90.8(2)	N(1)–Fe(1)–N(2)	76.8(2)
N(1)–Fe(1)–N(3)	88.1(2)	N(1)–Fe(1)–N(4') ^b	94.8(2)
N(2)–Fe(1)–N(3)	92.9(2)	N(2)–Fe(1)–N(4') ^b	88.8(2)

**Fig. 3.** One-dimensional linear structures of {[Mn(salophen)(μ-bipy)]⁺}_n (top) and {[Fe(salen)(μ-bipy)]⁺}_n (bottom).

6.4.3. Spectroscopic properties

Infrared spectra of **1** and **2** were recorded in the range 4000–400 cm^{-1} . Both spectra display a large number of bands of various intensities (Fig. 4). No attempt was made to assign all the bands except for a selected few. The free Schiff bases $\text{H}_2\text{salophen}$ and H_2salen are reported to show the phenolic-OH stretches as a broad band centred at 3450 and 3318 cm^{-1} , respectively [27,28]. As expected no such band is present in the spectra of **1** and **2** due to the deprotonation of the phenolic-OH groups in both compounds. A sharp and strong band observed at 1599 cm^{-1} for **1** is assigned to the azomethine C=N group. This C=N stretching band in **1** is about 11 cm^{-1} lower than that in the free $\text{H}_2\text{salophen}$ [27]. Similarly, **2** displays a sharp and strong band at 1617 cm^{-1} , which is about 15 cm^{-1} lower than that in the corresponding free Schiff base [28]. The shift of the C=N stretch to lower energy in each of the two polymers is consistent with the coordination of the azomethine-N atom to the metal centre. The presence of the perchlorate ion in **1** and **2** is indicated by a very strong and broad band centred at $\sim 1070 \text{ cm}^{-1}$ and a sharp strong band at $\sim 620 \text{ cm}^{-1}$.

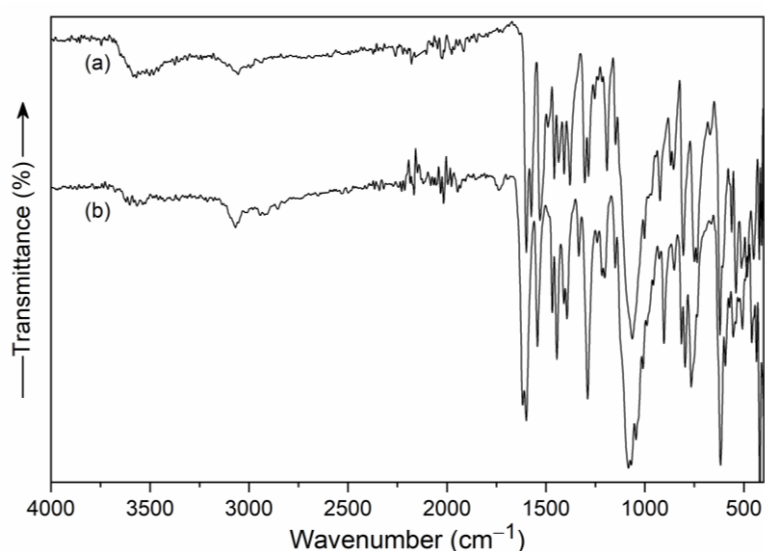


Fig. 4. Infrared spectra of (a) $[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4_n$ (**1**) and (b) $[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4_n$ (**2**).

The optical features of **1** and **2** were determined by UV–Vis diffuse reflectance spectroscopy using BaSO₄ as the reference. The spectral profiles are very similar except for some shift in the band positions and variations in their relative intensities (Fig. 5). Both compounds display a weak shoulder at ~575 nm, followed by another relatively strong absorption at ~455 nm and two very strong absorptions at ~348 and ~250 nm. The electronic spectra of H₂salophen and H₂salen are known to show three strong absorptions in the range 368–214 nm [27,29]. A ligand centred absorption band of the 4,4'-bipyridine has been reported to be observed at 363 nm [30]. Thus, for **1** and **2**, the two bands in the ultraviolet region (~348 and ~250 nm) are assigned to ligand centred transitions and the two visible region absorptions (~575 and ~455 nm) are attributed to ligand-to-metal charge transfer (LMCT) transitions. Previously reported manganese(III) and iron(III) complexes with salen type ligands display LMCT bands in the comparable wavelength range [24,25,31].

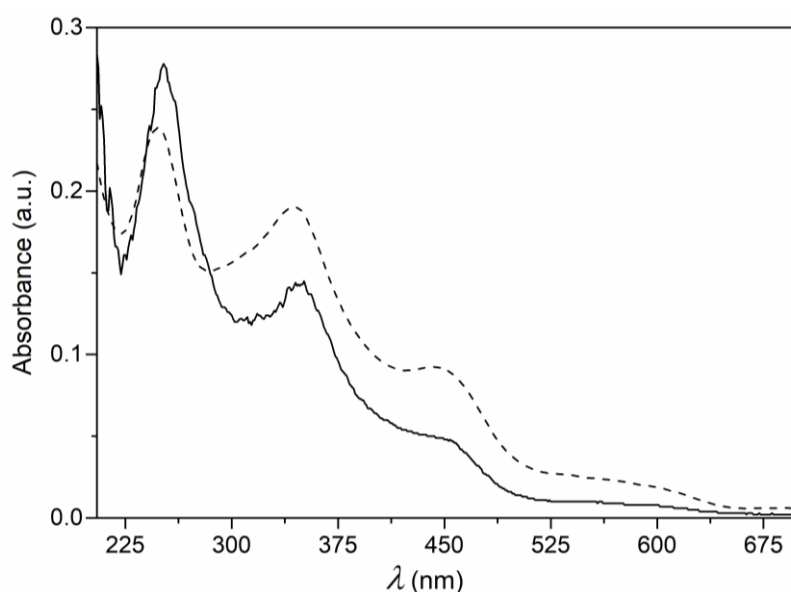


Fig. 5. Diffuse reflectance spectra of {[Mn(salophen)(μ-bipy)]ClO₄}_n (**1**) (solid trace) and {[Fe(salen)(μ-bipy)]ClO₄}_n (**2**) (dashed trace).

6.4.4. Magnetic properties

The magnetic properties of **1** and **2** were investigated by variable temperature magnetic susceptibility measurements with their powdered samples in the temperature range 5–300 K at a constant magnetic field of 1000 Oe. The effective magnetic moment (μ_{eff}) of the repetitive unit of **1** is found to be 4.61 μ_{B} at 300 K, which is somewhat lower than the calculated spin-only value (4.89 μ_{B}) of high-spin manganese(III) ($S = 2$). There is essentially no change in the magnetic moment with lowering of temperature down to 65 K, where μ_{eff} is 4.59 μ_{B} (Figure 6). On further lowering the temperature it increases slightly and becomes 4.65 μ_{B} at 20 K and then decreases rapidly to a value of 4.34 μ_{B} . In case of the repetitive unit of **2**, the μ_{eff} is 6.02 μ_{B} at 300 K, which is very close to the spin-only value (5.92 μ_{B}) of high-spin iron(III) ($S = 5/2$). With lowering of temperature, the μ_{eff} decreases and reaches the value of 5.91 μ_{B} at 50 K and then increases slightly to 5.94 μ_{B} at 20 K (Fig. 6). Below 20 K the μ_{eff} decreases rather sharply to a value of 5.68 μ_{B} at 5 K. The extents of overall decrease of the μ_{eff} values due to lowering of temperature from 300 to 5 K are 0.27 and 0.34 μ_{B} for **1** and **2**, respectively. Thus, it appears that there is no significant spin-spin interaction in either of the two coordination polymers. The inverse molar magnetic susceptibility values of the repetitive units of **1** and **2** are plotted against temperature (Figure 6). A near perfect linear plot has been obtained for each of **1** and **2**. In both cases, the data were fitted using the expression for the Curie–Weiss law. The Curie (C in $\text{cm}^3 \text{K mol}^{-1}$) and Weiss (θ in K) constants obtained are 2.65 and -0.40 for **1** and 4.55 and -1.87 for **2**. The linear plots and the intercepts very close to the origin indicate the Curie paramagnetic behaviour of both coordination polymers. The μ_{eff} calculated from the above-mentioned values of C are 4.60 and 6.03 μ_{B} for **1** and **2**, respectively. Generally, very weak or no spin-spin interactions are reported for 4,4'-bipyridine bridged complexes [23,32]. A possible explanation proposed for such magnetic behaviour is as follows [32]. The single bond character of

the C–C bond (1.477(5) and 1.491(5) Å in **1** and 1.482(9) Å in **2**) between the two pyridine rings of the bridging 4,4'-bipyridine allows unhindered twisting of the two pyridine rings around this C–C bond (*vide supra*) and therefore prevents the super-exchange pathway via the pyridine ring π -electrons for effective spin-spin interaction between the bridged metal ions.

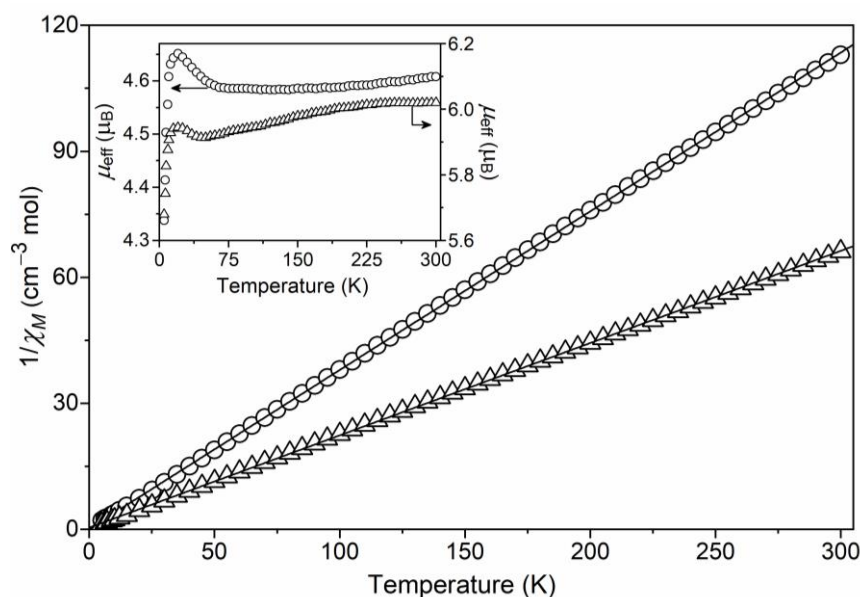


Fig. 6. Inverse molar magnetic susceptibility as a function of temperature for $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) (O) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) (Δ). The straight lines represent linear least-squares fits. Inset: Variation of effective magnetic moments with temperature for $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) (O) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) (Δ).

6.5. Conclusions

Syntheses and characterization of two one-dimensional coordination polymers of formulas $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) with N₂O₂-donor Schiff base ligands (salophen²⁻ and salen²⁻) and 4,4'-bipyridine (bipy) are reported. Structures of both coordination polymers were determined by single crystal X-ray crystallography. In each structure, the twisted 4,4'-bipyridine molecules act as bridges by occupying

the axial coordination sites of the metal ions of the planar $\{M(\text{salophen/salen})\}^+$ units and assemble the one-dimensional linear structures of $\{[M(\text{salophen/salen})(\mu\text{-bipy})]^+\}_n$. Microanalytical and the solid state infrared and electronic spectroscopic characteristics of both polymeric compounds are consistent with their structures. Variable temperature magnetic susceptibility studies revealed the $S = 2$ and $5/2$ spin states of the metal ions in **1** and **2**, respectively and their Curie paramagnetic character due to twisting of the bridging 4,4'-bipyridine, which does not allow any super-exchange induced spin-spin interaction between the metal ions.

6.6. References

- [1] J.C. Bailar Jr. in W.L. Jolly (Ed) 1964 *Preparative Inorganic Reactions*, Vol 1 pp 1–25 (Interscience: New York)
- [2] R Murugavel, G Anantharaman, D Krishnamurthy, M Sathiyendiran, M G Walawalkar, *Proc. Indian Acad. Sci. (Chem. Sci.)* 112 (2000) 273-290.
- [3] L. Rajput, M. Sarkar, K. Biradha, *J. Chem. Sci.* 122 (2010) 707-720.
- [4] G.I. Dzhardimalieva, I. E. Uflyand, *RSC Adv.* 7 (2017) 42242-42288.
- [5] E.R. Engel, J.L. Scott, *Green Chem.* 22 (2020) 3693-3715.
- [6] C.-T. Chen, K.S. Suslick, *Coord. Chem. Rev.* 128 (1993) 293-322.
- [7] S.R. Batten, S.M. Neville, D. R. Turner, *Coordination Polymers: Design, Analysis and Application* (RSC Publishing: Cambridge) (2009).
- [8] R.M.-B., J. G.-H., F Zamora, *Chem. Soc. Rev.* 39 (2010) 4220-4233.
- [9] W.L. Leong, J. J. Vittal, *Chem. Rev.* 111 (2011) 688-764.
- [10] E. Loukopoulos, G.E. Kostakis, *J. Coord. Chem.* 71 (2018) 371-410.
- [11] J.-Q. Liu, Z.-D. Luo, Y. Pan, A.K. Singh, M. Trivedi, A. Kumar, *Coord. Chem. Rev.* (2020) 406 213145-213191.
- [12] N.R. Sangeetha, S. Pal, *Polyhedron* 19 (2000) 1593-1600.
- [13] S. Das, S. Maloth, S. Pal, *Eur. J. Inorg. Chem.* (2011) 4270-4276.
- [14] A.K. Srivastava, S. Ghosh, S. Pal, *Polyhedron* 172 (2019) 112-119.
- [15] L. Zhou, Y. Feng, J. Cheng, N. Sun, X. Zhou, H. Xiang, *RSC Advances* 2 (2012) 10529-10536.

- [16] D.D. Perrin, W.L.F. Armarego and D.P. Perrin, *Purification of Laboratory Chemicals* (Pergamon: Oxford) (1983).
- [17] APEX3: Program for Data Collection on Area Detectors, Bruker Analytical X-ray Systems Inc., Madison Wisconsin, USA (2014).
- [18] G.M. Sheldrick, SADABS, Program for Area Detector Absorption Correction University of Göttingen, Göttingen, Germany (1997).
- [19] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 64 (2008) 112.
- [20] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837-838.
- [21] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Crystallogr.* 41 (2008) 466-470.
- [22] Y.-X. Zhou, X.-F. Zheng, D. Han, H.-Y. Zhang, X.-Q. Shen, C.-Y. Niu, P.-K. Chen, H.-W. Hou, Y. Zhu, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* 36 (2006) 693-699.
- [23] Y. Deawati, D. Onggo, I. Mulyani, I. Hastiawan, D. Kurnia, P. Lönnecke, S. Schmorl, B. Kersting, E. Hey-Hawkins, *Inorg. Chim. Acta* 482 (2018) 353-357.
- [24] S. Shova, A. Vlad, M. Cazacu, J. Krzystek, L. Bucinsky, M. Breza, D. Darvasiová, P. Raptá, J. Cano, J. Telser, V.B. Arion, *Dalton Trans.* 46 (2017) 11817-11829.
- [25] M. Cozzolino, V. Leo, C. Tedesco, M. Mazzeo, M. Lamberti, *Dalton Trans.* 47 (2018) 13229-13238.
- [26] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, *J. Appl. Crystallogr.* 46 (2013) 1231-1235.
- [27] M.K. Koley, S.C. Sivasubramanian, B. Varghese, P.T. Manoharan, A.P. Koley, *J. Coord. Chem.* 65 (2012) 3623-3640.
- [28] X.-M. Hu, L.-W. Xue, G.-Q. Zhao, W.-C. Yang, *Bull. Chem. Soc. Ethiop.* 29 (2015) 407-413.
- [29] T. Gao, Y. Yang, W.-B. Sun, G.-M. Li, G.-F. Hou, P.F. Yan, J.-T. Lia, D.-D. Ding, *CrystEngComm* 15 (2013) 6213-6220.

- [30] S. Xiu-min, W. Hai-yan, L. Yan-bing, Y. Jing-xiu, C. Lei, H. Ge, X. Wei-qing, Z. Bing, *Chem. Res. Chin. Univ.* 26 (2010) 1011.
- [31] T. Kurahashi, H. Fujii, *Bull. Chem. Soc. Jpn.* 85 (2012) 940-947.
- [32] M.-X. Li, G.-Y. Xie, Y.-D. Gu, J. Chen, Zheng P.-J, *Polyhedron* 14 (1995) 1235-1239.

Appendix

Tables for atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table A.1. [VO(acac)(L¹)] (Chapter 2)

Atom	x	y	z	U(eq)
V(1)	10056(1)	2350(1)	9052(1)	45(1)
O(1)	8667(3)	3555(2)	9060(1)	57(1)
O(2)	10767(3)	1150(2)	8562(1)	52(1)
O(3)	9339(4)	2518(2)	8145(1)	61(1)
O(4)	7878(3)	1781(2)	9327(2)	59(1)
O(5)	11768(3)	2746(2)	8886(1)	57(1)
N(1)	8962(4)	3768(2)	10151(2)	57(1)
N(2)	9756(4)	2910(2)	10037(2)	49(1)
N(3)	11019(4)	1364(2)	9731(2)	44(1)
N(4)	11657(4)	510(2)	9503(2)	49(1)
C(1)	8399(5)	4044(3)	9591(2)	51(1)
C(2)	7389(5)	4928(3)	9572(2)	59(1)
C(3)	6610(7)	5166(3)	9027(3)	85(2)
C(4)	5562(8)	5971(4)	9022(3)	107(2)
C(5)	5323(8)	6531(4)	9571(3)	102(2)
C(6)	6114(7)	6307(3)	10115(3)	85(2)
C(7)	7141(6)	5509(3)	10120(3)	69(1)
C(8)	10401(5)	2485(3)	10525(2)	55(1)
C(9)	10412(8)	2903(4)	11200(2)	91(2)
C(10)	11132(5)	1570(3)	10348(2)	52(1)
C(11)	11946(6)	932(3)	10819(2)	72(1)
C(12)	11454(4)	476(3)	8870(2)	45(1)
C(13)	12068(5)	-372(3)	8493(2)	50(1)
C(14)	12791(8)	-1128(3)	8810(3)	91(2)
C(15)	13338(10)	-1903(4)	8437(3)	125(3)
C(16)	13201(8)	-1946(4)	7770(3)	90(2)
C(17)	12498(7)	-1212(4)	7465(2)	78(1)
C(18)	11923(5)	-423(3)	7824(2)	61(1)
C(19)	7707(9)	2835(4)	7282(3)	113(2)
C(20)	7901(7)	2479(3)	7966(3)	71(1)
C(21)	6637(7)	2128(4)	8339(3)	86(2)
C(22)	6677(5)	1755(3)	8976(3)	68(1)
C(23)	5269(6)	1289(4)	9281(4)	106(2)
V(2)	8225(1)	2296(1)	4638(1)	48(1)
O(6)	7638(4)	3270(2)	3971(1)	62(1)

O(7)	7528(3)	1713(2)	5500(1)	59(1)
O(8)	5916(3)	2831(2)	4915(1)	54(1)
O(9)	9025(3)	3337(2)	5197(1)	57(1)
O(10)	7814(4)	1471(2)	4193(1)	60(1)
N(5)	10280(5)	3140(3)	3501(2)	62(1)
N(6)	10405(4)	2535(2)	4018(2)	56(1)
N(7)	10314(4)	1512(2)	4985(2)	53(1)
N(8)	10074(4)	960(2)	5523(2)	59(1)
C(24)	8751(6)	3492(3)	3524(2)	55(1)
C(25)	8234(6)	4176(3)	3031(2)	60(1)
C(26)	6600(8)	4465(3)	3016(2)	80(2)
C(27)	6065(9)	5117(4)	2565(3)	100(2)
C(28)	7216(11)	5486(4)	2130(3)	108(2)
C(29)	8835(10)	5215(4)	2138(3)	97(2)
C(30)	9369(8)	4544(4)	2578(2)	81(2)
C(31)	11843(5)	2145(3)	4123(2)	60(1)
C(32)	13419(6)	2305(4)	3719(3)	87(2)
C(33)	11779(5)	1526(3)	4684(2)	59(1)
C(34)	13274(6)	975(4)	4903(3)	78(1)
C(35)	8542(5)	1116(3)	5755(2)	53(1)
C(36)	7898(5)	613(3)	6344(2)	54(1)
C(37)	6308(6)	828(3)	6622(2)	73(1)
C(38)	5690(8)	376(4)	7170(3)	92(2)
C(39)	6637(8)	-316(4)	7430(3)	91(2)
C(40)	8221(8)	-551(4)	7168(3)	89(2)
C(41)	8865(6)	-90(3)	6624(2)	69(1)
C(42)	3601(6)	3721(4)	5407(3)	90(2)
C(43)	5444(5)	3507(3)	5299(2)	60(1)
C(44)	6463(6)	4038(3)	5609(3)	74(1)
C(45)	8155(6)	3944(3)	5539(2)	57(1)
C(46)	9048(6)	4609(4)	5901(3)	82(2)
O(11)	12770(14)	2084(8)	7330(5)	144(4)
C(47)	12008(19)	2091(11)	6739(6)	133(5)

Table A.2. [VO(acac)(L²)] (Chapter 2)

Atom	x	y	z	U(eq)
V(1)	2745(1)	-475(1)	7647(1)	37(1)
O(1)	2534(2)	1036(1)	8543(1)	49(1)
O(2)	1761(2)	-1667(1)	6358(1)	46(1)
O(3)	509(2)	-63(1)	7143(1)	43(1)
O(4)	3900(2)	417(1)	6704(1)	44(1)
O(5)	2048(2)	-1200(1)	8381(1)	48(1)
N(1)	5260(2)	1203(2)	9333(1)	49(1)
N(2)	5119(2)	196(1)	8623(1)	41(1)
N(3)	4623(2)	-1537(1)	7235(1)	40(1)
N(4)	4190(2)	-2475(1)	6436(1)	46(1)

C(1)	3810(3)	1585(2)	9218(2)	45(1)
C(2)	3619(3)	2707(2)	9840(2)	52(1)
C(3)	2292(4)	3239(2)	9554(2)	77(1)
C(4)	2164(4)	4320(3)	10090(3)	91(1)
C(5)	3328(4)	4893(2)	10928(2)	79(1)
C(6)	4619(4)	4343(3)	11221(2)	81(1)
C(7)	4796(3)	3269(2)	10688(2)	66(1)
C(8)	6458(2)	-305(2)	8541(2)	44(1)
C(9)	8150(3)	135(2)	9187(2)	62(1)
C(10)	6159(3)	-1330(2)	7730(2)	44(1)
C(11)	7504(3)	-2058(2)	7490(2)	62(1)
C(12)	2633(3)	-2457(2)	6011(2)	43(1)
C(13)	1849(3)	-3351(2)	5102(2)	45(1)
C(14)	2813(3)	-4081(2)	4550(2)	57(1)
C(15)	2050(3)	-4882(2)	3683(2)	65(1)
C(16)	326(3)	-5000(2)	3338(2)	59(1)
C(17)	-636(3)	-4280(2)	3908(2)	61(1)
C(18)	111(3)	-3470(2)	4775(2)	53(1)
C(19)	3163(6)	6083(3)	11488(3)	113(1)
C(20)	-508(4)	-5882(2)	2393(2)	82(1)
C(21)	-1543(3)	862(3)	6470(3)	93(1)
C(22)	265(3)	614(2)	6603(2)	57(1)
C(23)	1482(3)	1131(3)	6149(3)	89(1)
C(24)	3206(3)	1010(2)	6205(2)	55(1)
C(25)	4334(4)	1622(3)	5629(3)	83(1)

Table A.3. [VO(acac)(L³)] (Chapter 2)

Atom	x	y	z	U(eq)
V(1)	7875(1)	4394(1)	12658(1)	34(1)
O(1)	7518(2)	5823(1)	13486(1)	43(1)
O(2)	7036(2)	3297(1)	11415(1)	43(1)
O(3)	5612(2)	4802(1)	12138(1)	41(1)
O(4)	9020(2)	5324(1)	11685(1)	42(1)
O(5)	7185(2)	3662(1)	13424(1)	44(1)
O(6)	7444(3)	10458(2)	16082(2)	95(1)
O(7)	5394(3)	-687(2)	7815(1)	74(1)
N(1)	10256(2)	6009(1)	14218(1)	41(1)
N(2)	10196(2)	5035(1)	13579(1)	35(1)
N(3)	9845(2)	3370(1)	12308(1)	35(1)
N(4)	9479(2)	2467(1)	11573(1)	39(1)
C(1)	8753(3)	6359(2)	14104(2)	39(1)
C(2)	8440(3)	7418(2)	14681(2)	44(1)
C(3)	6901(3)	7835(2)	14489(2)	60(1)
C(4)	6610(4)	8840(2)	14976(2)	74(1)
C(5)	7853(4)	9453(2)	15663(2)	65(1)

C(6)	9379(4)	9042(2)	15885(2)	62(1)
C(7)	9665(3)	8029(2)	15391(2)	53(1)
C(8)	11576(2)	4547(2)	13537(1)	35(1)
C(9)	13215(3)	4960(2)	14158(2)	47(1)
C(10)	11359(2)	3552(2)	12796(2)	36(1)
C(11)	12747(3)	2837(2)	12607(2)	49(1)
C(12)	7949(3)	2518(2)	11134(2)	38(1)
C(13)	7249(3)	1671(2)	10273(2)	40(1)
C(14)	8223(3)	870(2)	9867(2)	54(1)
C(15)	7563(3)	98(2)	9052(2)	62(1)
C(16)	5917(3)	114(2)	8619(2)	52(1)
C(17)	4934(3)	903(2)	9010(2)	53(1)
C(18)	5608(3)	1670(2)	9841(2)	49(1)
C(19)	8656(6)	11141(3)	16785(3)	103(1)
C(20)	3780(4)	-690(3)	7290(2)	76(1)
C(21)	3493(3)	5696(3)	11431(3)	99(1)
C(22)	5331(3)	5484(2)	11579(2)	59(1)
C(23)	6552(3)	6035(3)	11124(3)	94(1)
C(24)	8295(3)	5930(2)	11181(2)	57(1)
C(25)	9416(4)	6583(3)	10598(3)	89(1)

Table A.4. [VO(acac)(L⁴)] (Chapter 2)

Atom	x	y	z	U(eq)
V(1)	13948(1)	400(1)	7794(1)	37(1)
Cl(1)	4545(1)	6017(1)	8455(1)	74(1)
Cl(2)	21893(2)	-5559(1)	5999(1)	94(1)
O(1)	11724(2)	1686(1)	7782(1)	44(1)
O(2)	15713(2)	-850(2)	7151(1)	46(1)
O(3)	12726(2)	141(2)	6852(1)	45(1)
O(4)	15564(2)	1688(1)	6968(1)	45(1)
O(5)	12849(2)	-588(2)	8475(1)	46(1)
N(1)	12541(3)	2523(2)	8845(1)	44(1)
N(2)	13969(3)	1618(2)	8712(1)	38(1)
N(3)	16460(3)	4(2)	8327(1)	39(1)
N(4)	17769(3)	-900(2)	8052(1)	45(1)
C(1)	11428(3)	2481(2)	8307(1)	40(1)
C(2)	9749(3)	3372(2)	8325(1)	42(1)
C(3)	8366(3)	3245(2)	7867(1)	44(1)
C(4)	6762(3)	4053(2)	7904(2)	48(1)
C(5)	6561(4)	5000(2)	8395(2)	51(1)
C(6)	7929(4)	5156(3)	8844(2)	63(1)
C(7)	9517(4)	4340(2)	8809(2)	59(1)
C(8)	15262(3)	1493(2)	9176(1)	39(1)
C(9)	15239(4)	2260(2)	9862(2)	50(1)
C(10)	16726(3)	535(2)	8950(1)	39(1)

C(11)	18375(3)	191(2)	9376(2)	49(1)
C(12)	17237(3)	-1287(2)	7417(1)	42(1)
C(13)	18457(4)	-2277(2)	7007(2)	46(1)
C(14)	20266(4)	-2608(3)	7183(2)	64(1)
C(15)	21340(5)	-3601(3)	6853(2)	73(1)
C(16)	20597(5)	-4253(3)	6356(2)	63(1)
C(17)	18857(5)	-3913(3)	6143(2)	65(1)
C(18)	17783(4)	-2917(2)	6471(2)	54(1)
C(19)	11713(5)	303(3)	5579(2)	80(1)
C(20)	12994(4)	667(2)	6108(2)	49(1)
C(21)	14313(5)	1524(3)	5770(2)	62(1)
C(22)	15533(4)	1974(2)	6194(2)	49(1)
C(23)	16926(5)	2879(3)	5725(2)	78(1)

Table A.5. [VO(acac)(L⁵)] (Chapter 2)

Atom	x	y	z	U(eq)
V(1)	2894(1)	288(1)	8595(1)	44(1)
O(1)	2259(2)	2287(3)	8987(1)	49(1)
O(2)	2801(2)	-881(3)	7991(1)	61(1)
O(3)	1966(2)	2026(3)	8207(1)	59(1)
O(4)	1416(2)	-1248(3)	8687(1)	53(1)
O(5)	4101(2)	1279(3)	8551(1)	58(1)
O(6)	3432(3)	-3841(7)	5893(1)	121(1)
O(7)	3475(3)	-6721(6)	6121(1)	123(2)
O(8)	719(3)	9393(5)	10374(1)	112(1)
O(9)	919(3)	7459(5)	10910(1)	105(1)
N(1)	3053(2)	732(3)	9589(1)	45(1)
N(2)	3336(2)	-459(3)	9264(1)	42(1)
N(3)	3696(2)	-2445(3)	8638(1)	48(1)
N(4)	3837(2)	-3415(4)	8258(1)	55(1)
N(5)	3433(3)	-5048(8)	6180(1)	88(1)
N(6)	960(3)	7868(5)	10524(1)	68(1)
C(1)	2471(2)	2137(4)	9403(1)	41(1)
C(2)	2053(2)	3620(4)	9691(1)	40(1)
C(3)	1582(3)	5279(4)	9513(1)	47(1)
C(4)	1224(3)	6689(4)	9782(1)	52(1)
C(5)	1348(3)	6389(4)	10231(1)	49(1)
C(6)	1813(3)	4760(4)	10415(1)	51(1)
C(7)	2167(3)	3382(4)	10145(1)	48(1)
C(8)	3916(2)	-1973(4)	9377(1)	45(1)
C(9)	4316(3)	-2459(5)	9833(1)	56(1)
C(10)	4131(2)	-3142(4)	9004(1)	45(1)
C(11)	4785(3)	-4940(5)	9046(1)	63(1)
C(12)	3323(3)	-2454(5)	7937(1)	53(1)
C(13)	3344(3)	-3174(5)	7482(1)	58(1)

C(14)	3643(3)	-5024(6)	7404(1)	75(1)
C(15)	3661(3)	-5635(6)	6971(2)	81(1)
C(16)	3398(3)	-4378(7)	6639(1)	71(1)
C(17)	3102(3)	-2547(6)	6707(1)	75(1)
C(18)	3070(3)	-1956(6)	7135(1)	69(1)
C(19)	460(5)	3558(7)	7815(2)	111(2)
C(20)	886(3)	1988(6)	8108(1)	62(1)
C(21)	146(3)	633(6)	8241(1)	70(1)
C(22)	413(3)	-880(5)	8517(1)	56(1)
C(23)	-514(3)	-2194(6)	8633(1)	80(1)

Table A.6. [VO(acac)(L⁶)] (Chapter 2)

Atom	x	y	z	U(eq)
V(1)	3889(1)	3278(1)	6817(1)	43(1)
O(1)	2670(2)	2806(2)	7513(2)	53(1)
O(2)	5790(2)	3793(2)	7040(2)	53(1)
O(3)	5026(2)	3721(2)	8484(2)	53(1)
O(4)	4049(2)	1474(2)	6282(2)	50(1)
O(5)	3652(2)	4584(2)	7053(2)	54(1)
N(1)	897(2)	2044(2)	5744(2)	48(1)
N(2)	1917(2)	2301(2)	5433(2)	43(1)
N(3)	3915(2)	2924(2)	5128(2)	42(1)
N(4)	5114(2)	3205(2)	5069(2)	47(1)
C(1)	1407(3)	2367(2)	6876(2)	45(1)
C(2)	497(3)	2250(3)	7451(3)	51(1)
C(3)	1005(3)	2718(3)	8671(3)	64(1)
C(4)	146(4)	2659(4)	9214(4)	83(1)
C(5)	-1192(4)	2156(4)	8559(4)	85(1)
C(6)	-1698(4)	1689(4)	7352(4)	84(1)
C(7)	-866(3)	1724(3)	6787(3)	65(1)
C(8)	1633(2)	2118(2)	4348(2)	42(1)
C(9)	260(3)	1718(2)	3448(2)	45(1)
C(10)	-728(3)	718(3)	3238(3)	57(1)
C(11)	-2006(3)	397(3)	2423(3)	74(1)
C(12)	-2325(3)	1083(4)	1841(3)	83(1)
C(13)	-1353(4)	2074(3)	2044(3)	76(1)
C(14)	-68(3)	2381(3)	2828(3)	57(1)
C(15)	2830(3)	2440(2)	4156(2)	42(1)
C(16)	2807(3)	2198(2)	2981(2)	47(1)
C(17)	2048(3)	1056(3)	1996(3)	61(1)
C(18)	2046(4)	810(3)	901(3)	82(1)
C(19)	2773(4)	1712(4)	773(3)	88(1)
C(20)	3522(4)	2865(3)	1752(3)	76(1)
C(21)	3543(3)	3100(3)	2842(3)	57(1)
C(22)	6049(3)	3660(2)	6140(2)	46(1)

C(23)	7459(3)	4024(2)	6321(3)	50(1)
C(24)	7800(3)	3796(3)	5367(3)	63(1)
C(25)	9127(4)	4109(3)	5563(4)	76(1)
C(26)	10104(3)	4651(3)	6695(4)	77(1)
C(27)	9776(3)	4892(3)	7643(4)	70(1)
C(28)	8454(3)	4572(3)	7459(3)	58(1)
C(33)	4570(4)	-281(3)	6359(3)	74(1)
C(32)	4623(3)	1063(3)	6960(3)	50(1)
C(31)	5277(3)	1761(3)	8201(3)	60(1)
C(30)	5451(3)	3012(3)	8879(2)	54(1)
C(29)	6198(4)	3651(4)	10210(3)	84(1)

Table A.7. [VO(μ -OMe)(HL)]₂ (Chapter 3)

Atom	x	y	z	U(eq)
V	6429(1)	5606(1)	5845(1)	35(1)
O(1)	4612(2)	6282(1)	5686(1)	47(1)
O(2)	7655(2)	4756(1)	6749(1)	40(1)
O(3)	8213(2)	4532(1)	10759(1)	62(1)
O(4)	8145(2)	6113(1)	5841(1)	55(1)
O(5)	6126(2)	5139(1)	4287(1)	38(1)
N(1)	4683(2)	6952(1)	6240(2)	51(1)
N(2)	6405(2)	5775(1)	7814(1)	34(1)
N(3)	7039(2)	5210(1)	8630(1)	37(1)
C(1)	5287(3)	7719(1)	8065(2)	67(1)
C(2)	5270(2)	6977(1)	7477(2)	45(1)
C(3)	5861(2)	6353(1)	8319(2)	38(1)
C(4)	5872(3)	6394(1)	9736(2)	49(1)
C(5)	7717(2)	4705(1)	7977(1)	34(1)
C(6)	8518(2)	4061(1)	8684(2)	37(1)
C(7)	8680(2)	4000(1)	10027(2)	44(1)
C(8)	9312(3)	3360(1)	10648(2)	62(1)
C(9)	9793(3)	2791(1)	9950(2)	66(1)
C(10)	9724(3)	2852(1)	8642(2)	65(1)
C(11)	9087(3)	3481(1)	8007(2)	51(1)
C(12)	7518(3)	5049(2)	3549(2)	74(1)

Table A.8. K[VO₂(HL)]·MeOH (2·MeOH) (Chapter 3)

Atom	x	y	z	U(eq)
V	2489(1)	2679(1)	5438(1)	28(1)
K	2911(1)	-391(1)	5681(1)	41(1)
O(1)	113(2)	820(1)	2905(2)	49(1)
O(2)	3763(2)	4154(1)	7005(1)	34(1)
O(3)	4275(2)	7882(1)	6902(2)	45(1)

O(4)	4340(2)	1952(1)	5326(1)	41(1)
O(5)	867(2)	1887(1)	5857(2)	49(1)
O(6)	3065(3)	-602(2)	3077(2)	61(1)
N(1)	829(2)	2030(1)	3480(2)	35(1)
N(2)	2254(2)	4272(1)	4859(1)	28(1)
N(3)	3125(2)	5451(1)	5779(1)	30(1)
C(1)	-456(3)	2423(2)	1421(2)	44(1)
C(2)	570(3)	2832(2)	2839(2)	33(1)
C(3)	1406(2)	4148(2)	3656(2)	29(1)
C(4)	1292(3)	5225(2)	3149(2)	40(1)
C(5)	3884(2)	5279(2)	6892(2)	27(1)
C(6)	4876(3)	6387(2)	8052(2)	30(1)
C(7)	5023(3)	7628(2)	8007(2)	34(1)
C(8)	5960(3)	8647(2)	9139(2)	45(1)
C(9)	6698(3)	8448(2)	10293(2)	52(1)
C(10)	6535(4)	7231(2)	10358(2)	52(1)
C(11)	5650(3)	6212(2)	9243(2)	41(1)
C(12)	2254(4)	-1803(2)	2139(2)	61(1)

Table A.9. [Co^{II}Co^{III}(μ-OAc)(μ₃-OH)(μ-L)]₂ (Chapter 4)

Atom	x	y	z	U(eq)
Co(1)	2372(1)	1754(1)	4368(1)	42(1)
Co(2)	3007(1)	2819(1)	3815(1)	47(1)
Co(3)	4403(1)	1940(1)	4969(1)	42(1)
Co(4)	3228(1)	2525(1)	5889(1)	47(1)
O(1)	2569(2)	976(1)	4267(2)	49(1)
O(2)	2161(2)	2538(1)	4546(2)	45(1)
O(3)	3907(2)	3294(1)	3412(2)	58(1)
O(4)	1607(2)	1737(1)	3373(2)	57(1)
O(5)	2116(2)	2515(1)	2864(2)	66(1)
O(6)	4696(2)	1208(1)	4674(2)	55(1)
O(7)	4118(2)	2720(1)	5148(2)	44(1)
O(8)	2159(2)	2572(1)	6423(2)	56(1)
O(9)	5153(2)	1800(2)	5962(2)	64(1)
O(10)	4269(2)	2208(2)	6717(2)	67(1)
O(11)	3497(2)	2011(1)	4016(2)	41(1)
O(12)	3229(2)	1766(1)	5326(2)	43(1)
O(13)	1719(4)	-1659(2)	4217(4)	115(2)
O(14)	6014(4)	5291(2)	2154(4)	144(2)
O(15)	6670(3)	-912(1)	3616(2)	84(1)
O(16)	-1301(2)	3535(2)	7702(2)	74(1)
N(1)	1279(3)	937(2)	4824(3)	68(1)
N(2)	1368(2)	1521(2)	4778(2)	55(1)
N(3)	2470(2)	3596(1)	3916(2)	50(1)
N(4)	2935(3)	4027(2)	3617(2)	56(1)

N(5)	5891(2)	1680(1)	4277(2)	54(1)
N(6)	5468(2)	2137(1)	4574(2)	45(1)
N(7)	3186(2)	3364(1)	6076(2)	48(1)
N(8)	2454(2)	3534(2)	6426(2)	53(1)
C(1)	2546(3)	-210(2)	4122(3)	60(1)
C(2)	2518(4)	-789(2)	4029(3)	67(1)
C(3)	1835(4)	-1087(2)	4267(4)	87(2)
C(4)	1206(6)	-807(3)	4618(6)	141(4)
C(5)	1233(5)	-228(3)	4700(5)	118(3)
C(6)	1920(3)	78(2)	4446(3)	60(1)
C(7)	1931(3)	695(2)	4519(3)	54(1)
C(8)	754(3)	1835(2)	4997(3)	60(1)
C(9)	671(3)	2435(2)	4908(3)	52(1)
C(10)	1346(3)	2766(2)	4639(2)	48(1)
C(11)	1169(3)	3346(2)	4514(2)	50(1)
C(12)	359(3)	3575(2)	4712(3)	61(1)
C(13)	-279(3)	3260(2)	5010(3)	62(1)
C(14)	-111(3)	2686(2)	5089(3)	61(1)
C(15)	1760(3)	3737(2)	4203(3)	55(1)
C(16)	3656(3)	3819(2)	3375(2)	48(1)
C(17)	4250(3)	4221(2)	3046(3)	58(1)
C(18)	3970(4)	4761(2)	2826(3)	68(1)
C(19)	4530(4)	5128(2)	2515(3)	76(2)
C(20)	5390(5)	4965(3)	2440(4)	94(2)
C(21)	5713(5)	4438(3)	2714(6)	132(3)
C(22)	5133(5)	4065(3)	2991(4)	100(2)
C(23)	2288(5)	-1963(3)	3793(5)	109(2)
C(24)	-1125(4)	3534(3)	5234(4)	88(2)
C(25)	5760(6)	5834(3)	1892(5)	119(3)
C(26)	1665(3)	2064(2)	2817(3)	58(1)
C(27)	1129(5)	1886(3)	2048(3)	91(2)
C(28)	5248(4)	191(2)	4172(3)	64(1)
C(29)	5566(4)	-328(2)	3991(3)	71(1)
C(30)	6392(4)	-369(2)	3745(3)	71(1)
C(31)	6905(4)	106(2)	3648(3)	74(1)
C(32)	6584(4)	628(2)	3848(3)	66(1)
C(33)	5766(3)	671(2)	4114(3)	57(1)
C(34)	5434(3)	1217(2)	4373(3)	51(1)
C(35)	5840(3)	2624(2)	4562(3)	54(1)
C(36)	5535(3)	3128(2)	4900(2)	47(1)
C(37)	4716(3)	3158(2)	5205(2)	42(1)
C(38)	4510(3)	3671(2)	5547(2)	44(1)
C(39)	5110(3)	4131(2)	5543(3)	54(1)
C(40)	5901(3)	4111(2)	5229(3)	59(1)
C(41)	6098(3)	3605(2)	4915(3)	56(1)
C(42)	3718(3)	3760(2)	5911(2)	49(1)
C(43)	1971(3)	3087(2)	6568(2)	51(1)

C(44)	1140(3)	3208(2)	6904(2)	53(1)
C(45)	851(4)	3751(2)	6971(3)	70(1)
C(46)	44(4)	3879(2)	7234(3)	72(1)
C(47)	-479(3)	3449(2)	7440(3)	61(1)
C(48)	-194(4)	2892(2)	7395(3)	63(1)
C(49)	604(3)	2777(2)	7124(3)	58(1)
C(50)	-1695(4)	4081(3)	7621(4)	88(2)
C(51)	6524(4)	4622(2)	5221(4)	86(2)
C(52)	7465(6)	-986(3)	3285(4)	114(3)
C(53)	4910(3)	1889(2)	6601(3)	65(1)
C(54)	5468(5)	1578(3)	7291(4)	98(2)
N(9)	7480(11)	3260(6)	3406(8)	212(6)
C(55)	7903(10)	2837(5)	3379(7)	181(7)
C(56)	8308(12)	2282(6)	3362(8)	275(12)
N(10)	1803(12)	5028(8)	6067(11)	166(6)
C(57)	1073(14)	5148(11)	6220(14)	179(9)
C(58)	105(13)	5155(10)	6290(14)	181(9)

Table A.10. {[Mn₂L(OAc)₂]ClO₄]_n (Chapter 5)

Atom	x	y	z	U(eq)
Mn(1)	2560(1)	1851(1)	5643(1)	30(1)
Mn(2)	3528(1)	2555(1)	3931(1)	34(1)
Cl(1)	7726(1)	3226(1)	6945(1)	56(1)
O(1)	3820(2)	1663(1)	5021(1)	32(1)
O(2)	2578(2)	2956(1)	5126(1)	34(1)
O(3)	1509(2)	1402(2)	4617(2)	52(1)
O(4)	1922(2)	2225(2)	3532(2)	57(1)
O(5)	3429(2)	2233(1)	6806(1)	41(1)
O(6)	4006(2)	3092(2)	7840(2)	48(1)
O(7)	7108(4)	3214(2)	6152(3)	100(1)
O(8)	7024(4)	3430(3)	7600(3)	122(2)
O(9)	8178(4)	2439(3)	7132(3)	122(2)
O(10)	8495(3)	3882(2)	6927(2)	82(1)
N(1)	2662(2)	632(2)	6053(2)	36(1)
N(2)	1220(2)	2133(2)	6228(2)	44(1)
N(3)	3562(2)	3962(2)	3875(2)	34(1)
N(4)	5335(2)	2682(2)	4155(2)	37(1)
C(1)	4672(3)	1277(2)	5384(2)	31(1)
C(2)	5703(3)	1552(2)	5223(2)	34(1)
C(3)	6564(3)	1145(2)	5659(2)	41(1)
C(4)	6470(3)	469(2)	6212(2)	43(1)
C(5)	5468(3)	167(2)	6314(2)	40(1)
C(6)	4564(3)	573(2)	5934(2)	33(1)
C(7)	3545(3)	236(2)	6130(2)	36(1)
C(8)	1695(3)	175(2)	6281(3)	49(1)

C(9)	1094(4)	699(3)	6904(4)	77(2)
C(10)	526(4)	1449(3)	6544(4)	79(2)
C(11)	880(3)	2898(2)	6300(2)	48(1)
C(12)	1306(3)	3671(2)	5941(2)	39(1)
C(13)	831(3)	4447(2)	6155(2)	47(1)
C(14)	1107(3)	5219(2)	5814(2)	46(1)
C(15)	1854(3)	5199(2)	5201(2)	43(1)
C(16)	2339(3)	4450(2)	4943(2)	35(1)
C(17)	2088(2)	3666(2)	5336(2)	31(1)
C(18)	3083(3)	4542(2)	4275(2)	37(1)
C(19)	4301(3)	4281(2)	3254(2)	40(1)
C(20)	5445(3)	4169(2)	3581(2)	46(1)
C(21)	5858(3)	3259(2)	3561(2)	47(1)
C(22)	5966(3)	2228(2)	4627(2)	39(1)
C(23)	7434(3)	96(3)	6696(3)	64(1)
C(24)	597(4)	6049(3)	6062(3)	66(1)
C(25)	1285(3)	1777(2)	3924(2)	45(1)
C(26)	202(4)	1665(3)	3552(3)	76(1)
C(27)	3919(3)	2881(2)	7070(2)	33(1)
C(28)	4478(3)	3432(3)	6460(2)	51(1)

Table A.11. {[Mn(salophen)(μ -bipy)]ClO₄]_n (Chapter 6)

Atom	x	y	z	U(eq)
Mn(1)	4622(1)	3094(1)	5611(1)	28(1)
O(1)	4928(2)	3191(1)	6749(2)	39(1)
O(2)	4606(2)	3699(1)	5329(2)	35(1)
N(1)	4643(3)	2441(1)	5761(2)	33(1)
N(2)	4226(3)	2920(1)	4435(2)	33(1)
N(3)	2659(3)	3093(1)	5627(2)	36(1)
N(4)	-3346(3)	3047(1)	5610(2)	34(1)
C(1)	5516(3)	2923(2)	7308(3)	38(1)
C(2)	6031(4)	3106(2)	8061(3)	52(1)
C(3)	6646(5)	2841(2)	8671(3)	66(2)
C(4)	6790(5)	2394(2)	8541(3)	69(2)
C(5)	6280(4)	2202(2)	7796(3)	58(1)
C(6)	5630(4)	2462(2)	7179(3)	42(1)
C(7)	5130(4)	2244(2)	6438(3)	41(1)
C(8)	4165(4)	2205(2)	5040(3)	41(1)
C(9)	3930(5)	1756(2)	5008(4)	60(1)
C(10)	3467(7)	1573(2)	4242(4)	80(2)
C(11)	3229(7)	1823(2)	3568(4)	81(2)
C(12)	3447(5)	2271(2)	3590(3)	60(1)
C(13)	3927(4)	2465(1)	4322(3)	38(1)
C(14)	4237(4)	3190(2)	3805(3)	41(1)
C(15)	4486(4)	3646(2)	3859(3)	39(1)

C(16)	4549(5)	3873(2)	3125(3)	57(1)
C(17)	4770(6)	4323(2)	3114(4)	70(2)
C(18)	4912(6)	4549(2)	3839(4)	71(2)
C(19)	4844(5)	4342(2)	4576(3)	55(1)
C(20)	4648(3)	3886(1)	4608(3)	37(1)
C(21)	2220(4)	2882(2)	6209(3)	43(1)
C(22)	1064(3)	2865(2)	6241(3)	42(1)
C(23)	295(3)	3082(1)	5639(3)	34(1)
C(24)	753(4)	3301(2)	5030(3)	52(1)
C(25)	1921(4)	3293(2)	5041(3)	50(1)
C(26)	-959(3)	3070(1)	5642(3)	34(1)
C(27)	-1528(4)	2675(1)	5740(3)	41(1)
C(28)	-2703(3)	2678(2)	5705(3)	39(1)
C(29)	-2786(3)	3425(1)	5554(3)	42(1)
C(30)	-1611(3)	3450(2)	5551(3)	46(1)
Mn(2)	8103(1)	4431(1)	7584(1)	27(1)
O(3)	7755(2)	4446(1)	6423(2)	36(1)
O(4)	8263(2)	3815(1)	7633(2)	37(1)
N(5)	8091(3)	5085(1)	7653(2)	30(1)
N(6)	8516(3)	4495(1)	8803(2)	30(1)
N(7)	6152(3)	4418(1)	7693(2)	34(1)
N(8)	106(3)	4485(1)	7501(2)	34(1)
C(31)	7967(3)	4775(1)	5941(2)	36(1)
C(32)	7950(5)	4688(2)	5100(3)	55(1)
C(33)	8198(6)	5017(2)	4586(3)	76(2)
C(34)	8469(7)	5442(2)	4869(4)	84(2)
C(35)	8440(6)	5542(2)	5671(3)	66(2)
C(36)	8203(4)	5214(1)	6223(3)	40(1)
C(37)	8189(4)	5350(1)	7048(3)	38(1)
C(38)	8109(3)	5252(1)	8468(2)	33(1)
C(39)	7892(4)	5683(2)	8663(3)	46(1)
C(40)	7951(5)	5808(2)	9467(3)	55(1)
C(41)	8216(5)	5495(2)	10086(3)	57(1)
C(42)	8401(4)	5059(2)	9905(3)	45(1)
C(43)	8355(3)	4931(1)	9088(2)	31(1)
C(44)	8910(3)	4174(1)	9299(3)	38(1)
C(45)	9149(4)	3734(1)	9048(3)	40(1)
C(46)	9761(5)	3454(2)	9669(3)	58(1)
C(47)	10077(6)	3037(2)	9471(4)	69(2)
C(48)	9789(6)	2883(2)	8677(4)	70(2)
C(49)	9167(5)	3146(2)	8071(3)	54(1)
C(50)	8844(3)	3576(1)	8240(3)	35(1)
C(51)	5665(4)	4587(2)	8285(3)	51(1)
C(52)	4485(4)	4615(2)	8262(3)	51(1)
C(53)	3764(3)	4441(1)	7598(2)	32(1)
C(54)	4268(3)	4247(2)	6987(3)	41(1)
C(55)	5448(3)	4245(2)	7056(3)	41(1)

C(56)	2486(3)	4459(1)	7535(2)	31(1)
C(57)	1964(3)	4829(2)	7824(3)	40(1)
C(58)	785(4)	4828(2)	7789(3)	40(1)
C(59)	619(3)	4137(1)	7210(3)	37(1)
C(60)	1787(3)	4114(1)	7210(3)	35(1)
Cl(1)	1362(2)	3230(1)	2360(1)	83(1)
O(5)	2387(7)	3164(2)	1985(4)	139(2)
O(6)	1249(9)	2839(2)	2777(5)	173(4)
O(7)	1591(6)	3580(2)	2917(4)	126(2)
O(8)	497(8)	3292(4)	1718(5)	201(4)
Cl(2)	6540(4)	1018(1)	5792(2)	158(1)
O(9)	6846(11)	1461(4)	5839(12)	294(8)
O(10)	6300(17)	965(6)	5021(8)	364(12)
O(11)	7540(14)	773(4)	6067(6)	271(7)
O(12)	5988(14)	1106(5)	6366(8)	273(7)

Table A.12. {[Fe(salen)(μ -bipy)]ClO₄]_n (Chapter 6)

Atom	x	y	z	U(eq)
Fe(1)	4365(1)	6610(1)	3158(1)	31(1)
Cl(1)	-557(3)	-2367(2)	416(2)	67(1)
O(1)	6113(5)	7298(4)	4196(3)	38(1)
O(2)	2734(5)	6249(4)	3682(3)	40(1)
O(3)	-222(12)	-1467(12)	1217(8)	180(6)
O(4)	-1113(16)	-2154(16)	-374(8)	211(7)
O(6)	729(12)	-2670(13)	320(10)	173(5)
N(1)	5738(7)	6653(6)	2241(4)	46(1)
N(2)	2803(6)	5987(5)	1800(4)	36(1)
N(3)	4382(6)	4671(5)	3125(4)	38(1)
N(4)	4311(6)	-1444(5)	3263(4)	43(1)
C(1)	7569(8)	7670(6)	4268(5)	42(2)
C(2)	8615(9)	8091(8)	5167(6)	61(2)
C(3)	10149(10)	8497(11)	5276(8)	88(3)
C(4)	10667(10)	8484(12)	4473(8)	90(3)
C(5)	9667(9)	8067(9)	3595(7)	70(3)
C(6)	8098(8)	7620(7)	3465(5)	45(2)
C(7)	7158(8)	7126(7)	2508(6)	52(2)
C(8)	4932(10)	6080(10)	1216(6)	67(2)
C(9)	3439(9)	6251(9)	1034(5)	58(2)
C(10)	1387(8)	5430(6)	1611(5)	41(2)
C(11)	606(8)	5154(7)	2288(5)	45(2)
C(12)	-930(9)	4472(9)	1931(7)	65(2)
C(13)	-1779(11)	4162(13)	2546(9)	104(4)
C(14)	-1067(12)	4493(14)	3475(8)	117(5)
C(15)	417(10)	5186(12)	3852(7)	88(4)
C(16)	1306(8)	5550(7)	3281(5)	47(2)

C(17)	3525(10)	3647(7)	2420(6)	62(2)
C(18)	3473(10)	2437(7)	2434(6)	68(3)
C(19)	4303(8)	2260(6)	3240(5)	43(2)
C(20)	5211(7)	3324(6)	3967(5)	37(2)
C(21)	5209(7)	4496(6)	3892(5)	37(2)
C(22)	4280(7)	982(6)	3281(5)	40(2)
C(23)	3045(9)	-81(7)	2782(7)	63(2)
C(24)	3102(8)	-1254(7)	2785(6)	56(2)
C(25)	5454(10)	-428(7)	3780(7)	73(3)
C(26)	5488(10)	776(7)	3808(7)	70(3)
N(5)	-4770(30)	2330(20)	579(17)	125(8)
C(27)	-5600(30)	1460(30)	490(19)	104(8)
C(28)	-6700(30)	170(20)	383(19)	110(8)
N(6)	13260(30)	10000(30)	8023(19)	138(9)
C(29)	12140(30)	9410(20)	7952(18)	97(7)
C(30)	10760(30)	8630(30)	7960(20)	139(11)

List of Publications

Publications from thesis work:

1. Ternary pentagonal-bipyramidal oxovanadium(V) complexes containing five- and six- membered chelate rings: Syntheses, structures and properties
[Ankit Kumar Srivastava](#), Sabari Ghosh, Subhendu Jana, Samudranil Pal
Inorg. Chim. Acta 483 (2018) 329–336.
2. Coordination mode variation of oximate in complexes of $\text{VO}(\text{OMe})^{2+}$ and VO_2^+ with biacetylmonoxime salicyloylhydrazone: structural confirmation, properties and photocatalytic applications
[Ankit Kumar Srivastava](#), Sabari Ghosh, Samudranil Pal
Inorg. Chim. Acta 502 (2020) 119344.
3. A one-dimensional polymeric mixed-valent Mn(II)Mn(III) complex with a Macrocyclic compartmental ligand: structure, properties and catecholase like activity
[Ankit Kumar Srivastava](#), Sabari Ghosh, Samudranil Pal
Polyhedron 172 (2019) 112–119.
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J. Chem. Sci. 133 (2021) 73(1–9).

Other publications:

5. Di- μ -acetato Diuranyl(VI) Complexes with N-(2-pyridyl)-N'-(5-R-salicylidene)hydrazines: Syntheses, Structures, Properties and Extraction Studies
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Chemistry Select 3 (2018) 4865–4872.
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Appl Organomet Chem. 35 (2021) e6261.
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CrystEngComm 23 (2021) 1859-1869.
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Solid State Sci. 114 (2021) 106577.
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Manuscripts under preparation

1. Tetracobalt(II/III) Complex with an Open Cubane Co₄O₄ Core and Square-pyramidal Cobalt(II) and Octahedral Cobalt(III) centers: Application as a Bifunctional Heterogeneous Electrocatalyst for Water Splitting at Neutral pH
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To be submitted.
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 3. Winter school on **“Computational Chemistry and Biology”** held at UGC-NRC, School of Chemistry, University of Hyderabad during 12–28 December, 2018.
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Mono-, di-, and polynuclear 3d transition metal ion complexes and coordination polymers with N,O-donor multidentate and compartmental ligands and their catalytic applications

by Ankit Kumar Srivastava

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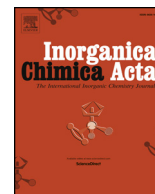
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Ternary pentagonal-bipyramidal oxovanadium(V) complexes containing five- and six-membered chelate rings: Syntheses, structures and properties

Ankit Kumar Srivastava, Sabari Ghosh, Subhendu Jana, Samudranil Pal*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

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ABSTRACT

Reactions of bis(acetylacetonato)oxovanadium(IV) $[\text{VO}(\text{acac})_2]$ with isolated or in-situ generated α -diketone bis(*para*-R-benzoylhydrazones) (H_2L^n) ($n = 1-6$), where 2H represent the two dissociable amide protons) in methanol or chloroform–methanol (1:3) mixture afford six novel oxovanadium(V) complexes of formula $[\text{VO}(\text{acac})(\text{L}^n)]$ (1–6) in 51–64% yields. All the complexes have been characterized by elemental analysis, mass spectrometric, solution electrical conductivity, various spectroscopic (IR, UV–Vis, and ^1H NMR) and cyclic voltammetric measurements. The complexes are brown in color. They are diamagnetic and non-electrolytes. Molecular structures of all six complexes have been determined by single crystal X-ray crystallography. The metal center in each complex is in a distorted pentagonal-bipyramidal N_2O_5 coordination sphere. The fused 5,5,5-membered chelate rings forming ON_2O -donor $(\text{L}^n)^{2-}$ and one of the acetylacetonate-O form a N_2O_3 pentagonal plane around the vanadium atom, while the second acetylacetonate-O and the oxo atom occupy the two axial positions. In the crystal lattice, the complexes form one-dimensional chain-, ladder- and ribbon-like supramolecular structures via various types of intermolecular non-covalent interactions such as trifurcated $\text{O} \cdots \text{H} \cdots (\text{O}, \text{O}, \text{O})$, bifurcated $\text{C} \cdots \text{H} \cdots \text{O} \cdots \text{H} \cdots \text{C}$ and $\text{C} \cdots \text{H} \cdots (\text{O}, \text{O})$, simple $\text{C} \cdots \text{H} \cdots \text{O}$, $\pi \cdots \pi$, $\text{C} \cdots \text{H} \cdots \pi$ and $\text{O} \cdots \text{O}$ interactions. The spectroscopic features of 1–6 are consistent with their molecular structures. All the complexes are redox active and display a quasi-reversible to irreversible vanadium(V) to vanadium(IV) reduction in the potential range -0.80 to -0.92 V (vs. Ag/AgCl).

1. Introduction

Generally, the coordination number of a metal ion in its complex is determined by its ionic radius and the nature of the coordinating ligands [1–5]. Coordination number more than six is very uncommon in complexes of 3d transition metal ions, particularly of early 3d higher valent transition metal ions. The primary reason for the scarcity of such 3d metal ion complexes is the small ionic radius of the metal center and hence its inability to accommodate more than six coordinating atoms due to steric congestion. Examples of higher coordinated species are mostly with small monoatomic ligands and sometimes with one or two chelating ligands and remaining small monoatomic ligands. Discrete mononuclear heptacoordinated complexes with specially designed pentadentate macrocyclic [1,6] or hexadentate ethylenediamine tetraacetic acid type primary ligands [2,7,8] and monodentate ancillary ligands are also reported. Penta-valent vanadium, one of the early 3d metal ions, has an ionic radius of $0.54 \text{ \AA}$ [9]. There are several reports on structurally characterized heptacoordinated pentagonal-bipyramidal multi-ligand complexes of

oxovanadium(V) [10–21]. However, essentially all these complexes contain at least one sterically less hindering 3-membered chelate ring forming N,O-donor hydroxyamido/oximate ligand [10–14] or bidentate peroxo group [15–20]. Tris(*N,N*-diethyldithiocarbamate)oxovanadium(V) is the rare example which does not have any 3-membered chelate ring [21]. It has three 4-membered chelate rings formed by the three S,S-coordinating *N,N*-diethyldithiocarbamates. To the best of our knowledge, there is no report on pentagonal-bipyramidal oxovanadium(V) complexes with only 5- and/or 6-membered chelate ring forming ligands. Herein, we report a series of six such ternary oxovanadium(V) complexes of general molecular formula $[\text{VO}(\text{acac})(\text{L}^n)]$ where $(\text{acac})^-$ and $(\text{L}^n)^{2-}$ represent the 6-membered chelate ring forming acetylacetonate and the fused 5,5,5-membered chelate rings forming α -diketone bis(*para*-R-benzoylhydrazones), respectively (Chart 1). Molecular structures of all the complexes have been confirmed by single crystal X-ray crystallographic studies. Synthesis, characterization, physical properties and structures of these complexes have been described in the following sections.

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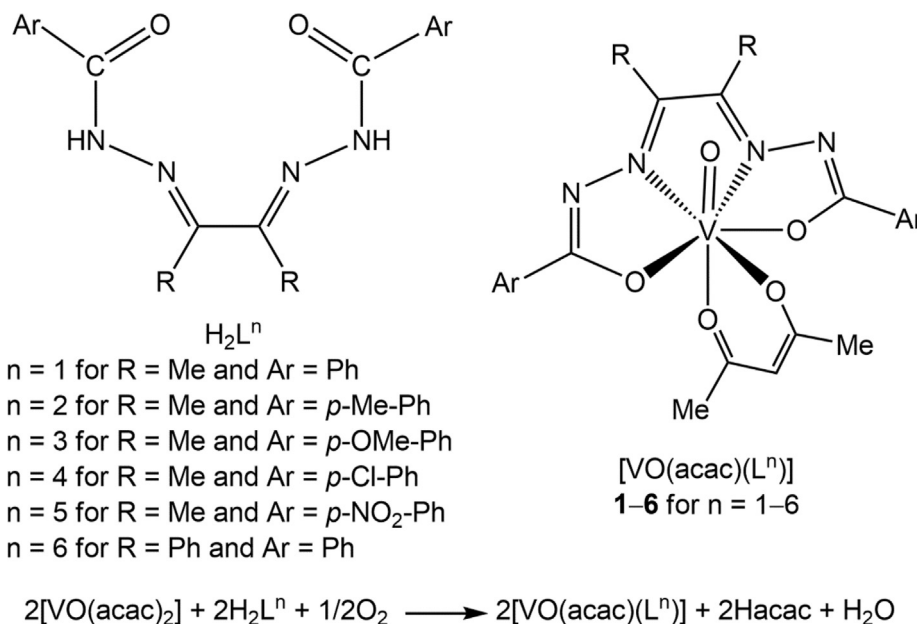


Chart 1. Chemical structure diagrams of α -diketone bis(*para*-*R*-benzoylhydrazones) (H_2L^n) and the complexes $[\text{VO}(\text{acac})(\text{L}^n)]$ derived therefrom.

2. Experimental

2.1. Materials

The Schiff bases H_2L^1 and H_2L^6 were prepared in 70–80% yields by condensation reactions of two mole equivalents of benzoylhydrazine with one mole equivalent of the corresponding α -diketones (diacetyl for H_2L^1 and benzil for H_2L^6) by following reported methods [22,23]. The remaining Schiff bases H_2L^{2-5} were generated in-situ from diacetyl and the appropriate *para*-*R*-benzoylhydrazines. Bis(acetylacetonato)oxovanadium(IV), $[\text{VO}(\text{acac})_2]$, was synthesized by using a literature procedure [24]. All other chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification.

2.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used for the microanalytical (CHN) measurements. High resolution mass spectra were recorded with a Bruker Maxis (ESI-TOF analyzer) spectrometer. A Sherwood Scientific balance was used for room temperature magnetic susceptibility measurements. The solution electrical conductivities were measured with the help of a Digisun DI-909 conductivity meter. The infrared spectra were recorded on a Bruker TENSOR II FT-IR spectrophotometer. A Jasco-V-770 UV-Vis spectrophotometer was employed to collect the electronic spectra. The ^1H NMR (400 MHz) spectra were recorded on a Bruker NMR spectrometer. Cyclic voltammetric measurements were performed with the help of a CH Instruments model 620A electrochemical analyzer.

2.3. Synthesis of $[\text{VO}(\text{acac})(\text{L}^1)]$ (**1**)

A methanol solution (8 ml) of $[\text{VO}(\text{acac})_2]$ (100 mg, 0.38 mmol) was added to a suspension of H_2L^1 (122 mg, 0.38 mmol) in methanol (7 ml) and the mixture was boiled under reflux for 6 h. It was then cooled to room temperature (298 K). The complex precipitated as a brown solid was collected by filtration and dried in air. Yield: 110 mg (60%). Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{N}_4\text{O}_5\text{V}$ (%): C, 56.79; H, 4.77; N, 11.52. Found: C, 56.68; H, 4.73; N, 11.62. HRMS in CH_2Cl_2 m/z found (calcd) for $[\text{M} + \text{H}]^+$: 487.1186 (487.1186). Selected IR bands: ν (cm^{-1}) = 1589 (C=N), 988 (V=O). UV-Vis in CH_3CN : λ_{max} (nm) (ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$)) = 515^{sh} (3.1), 436 (5.4), 296 (18.1), 231 (23.5).

^1H NMR in CDCl_3 : δ (ppm) (J (Hz)) = 8.12 (8, 2) (dd, 4H, *ortho* Hs of benzoyl Ph groups), 7.52 (8, 2) (tt, 2H, *para* Hs of benzoyl Ph groups), 7.44 (8) (dd $\rightarrow$ t, 4H, *meta* Hs of benzoyl Ph groups), 5.42 (s, 1H, methine H), 2.60 (s, 6H, protons of the two Me groups of the α -diketimine moiety), 2.32 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.73 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH_3CN : $E_{1/2}$ (V) (ΔE_p (mV)) = -0.88 (120).

2.4. Synthesis of $[\text{VO}(\text{acac})(\text{L}^2)]$ (**2**)

A methanol solution (10 ml) of $[\text{VO}(\text{acac})_2]$ (53 mg, 0.2 mmol) was added to a solution of diacetyl (17 mg, 0.2 mmol) and *para*-methylbenzoylhydrazine (60 mg, 0.4 mmol) in methanol (10 ml) and the mixture was boiled under reflux for 4 h. The reaction mixture was then kept at low temperature (5 °C). The dark brown crystalline material separated in about one week was collected by filtration and dried in air. Yield: 60 mg (58%). Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{N}_4\text{O}_5\text{V}$ (%): C, 58.37; H, 5.29; N, 10.89. Found C, 58.26; H, 5.23; N, 10.82. HRMS in CH_2Cl_2 m/z found (calcd) for $[\text{M} + \text{H}]^+$, $[\text{M} + \text{Na}]^+$, $[\text{M} + \text{K}]^+$: 515.1479 (515.1499), 537.1319 (537.1319), 553.1045 (553.1058). Selected IR bands: ν (cm^{-1}) = 1583 (C=N), 949 (V=O). UV-Vis in CH_3CN : λ_{max} (nm) (ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$)) = 525^{sh} (3.1), 440 (6.0), 297 (17.1), 233 (23.6). ^1H NMR in CDCl_3 : δ (ppm) (J (Hz)) = 8.01 (8) (d, 4H, *ortho* Hs of *para*-methylbenzoyl groups), 7.23 (8) (d, 4H, *meta* Hs of *para*-methylbenzoyl groups), 5.39 (s, 1H, s, methine H), 2.58 (s, 6H, protons of the 2 Me groups of the α -diketimine moiety), 2.43 (s, 6H, protons of the two Me groups at *para* positions of the benzoyl moieties), 2.31 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.71 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH_3CN : $E_{1/2}$ (V) (ΔE_p (mV)) = -0.89 (120).

2.5. Synthesis of $[\text{VO}(\text{acac})(\text{L}^3)]$ (**3**)

This complex has been synthesized in methanolic medium in 62% yield by following the same procedure as described above for **2** using $[\text{VO}(\text{acac})_2]$, diacetyl and *para*-methoxybenzoylhydrazine in 1:1:2 mol ratio. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{N}_4\text{O}_7\text{V}$ (%): C, 54.95; H, 4.98; N, 10.25. Found C, 54.85; H, 5.06; N, 10.18. HRMS in CH_2Cl_2 m/z found (calcd) for $[\text{M} + \text{H}]^+$, $[\text{M} + \text{Na}]^+$, $[\text{M} + \text{K}]^+$: 547.1386 (547.1398), 569.1215 (569.1217), 585.0944 (585.0956). Selected IR bands: ν (cm^{-1}) = 1602

(C=N), 948 (V=O). UV–Vis in CH₃CN: $\lambda_{\max}$ (nm) (ϵ (10³ M^{−1} cm^{−1})) = 530^{sh} (1.2), 447 (2.5), 293^{sh} (10.3), 242 (22.3). ¹H NMR in CDCl₃: δ (ppm) (J (Hz)) = 8.07 (9) (d, 4H, *ortho* Hs of *para*-methoxybenzoyl groups), 6.94 (9) (d, 4H, *meta* Hs of *para*-methoxybenzoyl groups), 5.39 (s, 1H, s, methine H), 3.88 (s, 6H, protons of the 2 OMe groups at *para* positions of the benzoyl moieties), 2.56 (s, 6H, protons of the two Me groups of the α -diketimine moiety), 2.30 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.72 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH₃CN: $E_{1/2}$ (V) (ΔE_p (mV)) = −0.92 (120).

2.6. Synthesis of [VO(acac)(L⁴)] (4)

The same procedure described for **2** has been used to synthesize **4** in methanolic medium in 64% yield using [VO(acac)₂], diacetyl and *para*-chlorobenzoylhydrazine in 1:1:2 mol ratio. Anal. Calcd for C₂₃H₂₁Cl₂N₄O₅V (%): C, 49.75; H, 3.81; N, 10.09. Found: C, 49.68; H, 3.76; N, 10.16. HRMS in CH₂Cl₂ m/z found (calcd) for [M + H]⁺, [M + Na]⁺, [M + K]⁺: 555.0383 (555.0407), 577.0227 (577.0226), 592.9956 (592.9966). Selected IR bands: ν (cm^{−1}) = 1582 (C=N), 949 (V=O). UV–Vis in CH₃CN: $\lambda_{\max}$ (nm) (ϵ (10³ M^{−1} cm^{−1})) = 515^{sh} (3.5), 434 (6.6), 295 (17.5), 231 (21.3). ¹H NMR in CDCl₃: δ (ppm) (J (Hz)) = 8.05 (9) (d, 4H, *ortho* Hs of *para*-chlorobenzoyl groups), 7.41 (9) (d, 4H, *meta* Hs of *para*-chlorobenzoyl groups), 5.42 (s, 1H, s, methine H), 2.59 (s, 6H, protons of the two Me groups of the α -diketimine moiety), 2.31 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.74 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH₃CN: $E_{1/2}$ (V) (ΔE_p (mV)) = −0.85 (110).

2.7. Synthesis of [VO(acac)(L⁵)] (5)

This complex has also been synthesized in methanolic medium in 60% yield from [VO(acac)₂], diacetyl and *para*-nitrobenzoylhydrazine taken in 1:1:2 mol ratio by following the same procedure used for **2**. Anal. Calcd for C₂₃H₂₁N₆O₅V (%): C, 47.93; H, 3.67; N, 14.58. Found: C, 47.85; H, 3.62; N, 14.65. HRMS in CH₂Cl₂ m/z found (calcd) for [M + H]⁺, [M + Na]⁺: 577.0889 (577.0888), 599.0708 (599.0707). Selected IR bands: ν (cm^{−1}) = 1589 (C=N), 952 (V=O), 1520 and 1342 (NO₂). UV–Vis in CH₃CN: $\lambda_{\max}$ (nm) (ϵ (10³ M^{−1} cm^{−1})) = 515^{sh} (2.0), 440 (3.2), 294 (16.0), 252 (16.0). ¹H NMR in CDCl₃: δ (ppm) (J (Hz)) = 8.34–8.23 (AA'BB', 8H, *ortho* and *meta* Hs of *para*-nitrobenzoyl groups), 5.47 (s, 1H, s, methine H), 2.66 (s, 6H, protons of the two Me groups of the α -diketimine moiety), 2.34 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.76 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH₃CN: E_{pc} (V) = −0.87.

2.8. Synthesis of [VO(acac)(L⁶)] (6)

A solution of H₂L⁶ (100 mg, 0.22 mmol) in chloroform (5 ml) was added to a solution of [VO(acac)₂] (60 mg, 0.23 mmol) in methanol (15 ml) and the mixture was boiled under reflux for 10 h. After reducing the volume to 10 ml the reaction mixture was kept at low temperature (5 °C). The complex separated as a brown solid was collected by filtration and dried in air. Yield: 70 mg (51%). Anal. Calcd for C₃₃H₂₇N₄O₅V (%): C, 64.92; H, 4.46; N, 9.18. Found: C, 64.85; H, 4.41; N, 9.23. HRMS in CH₂Cl₂ m/z found (calcd) for [M + H]⁺, [M + Na]⁺, [M + K]⁺: 611.1499 (611.1499), 633.1320 (633.1319), 649.1041 (649.1058). Selected IR bands: ν (cm^{−1}) = 1583 (C=N), 950 (V=O). UV–Vis in CH₃CN: $\lambda_{\max}$ (nm) (ϵ (10³ M^{−1} cm^{−1})) = 495 (3.2), 375 (6.3), 287 (18.0), 232 (20.2). ¹H NMR in CDCl₃: δ (ppm) (J (Hz)) = 8.02 (8, 3) (dd, 4H, *ortho* Hs of benzoyl Ph groups), 7.50–7.45 (m, 6H, Hs of Ph groups), 7.42–7.33 (m, 10H, Hs of Ph groups), 5.47 (s, 1H, methine H), 2.36 (s, 3H, protons of MeC(O) of (acac)[−] at *cis* to the oxo atom), 1.81 (s, 3H, protons of MeC(O) of (acac)[−] at *trans* to the oxo atom). CV in CH₃CN: $E_{1/2}$ (V) (ΔE_p (mV)) = −0.80 (140).

2.9. X-ray crystallography

Single crystals of [VO(acac)(L¹)] (**1**) and [VO(acac)(L⁶)] (**6**) were grown by slow evaporation of the corresponding methanol solutions. Single crystals of [VO(acac)(L^{2–5})] (**2–5**) were collected from the crystalline products obtained from their synthetic reaction mixtures. The first complex crystallizes as 1·0.25MeOH, while each of **2–6** crystallizes as it is without any solvent molecule. A BRUKER D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite monochromated Mo K α Radiation (λ = 0.71073 Å) was used for unit cell determination and intensity data collection at 298 K for each of 1·0.25MeOH and **2–6**. Data collection, integration, reduction and absorption correction were performed using the APEX3 software package [25]. The structures were solved by direct method and refined on F^2 by full matrix least-squares procedures. In the case of 1·0.25MeOH, the methanol C and O atoms having partial occupancies were refined isotropically with geometric restraint. The remaining non-hydrogen atoms of 1·0.25MeOH and all the non-hydrogen atoms of **2–6** were refined with anisotropic thermal parameters. The hydrogen atoms were included at idealized positions using a riding model. The SHELX-97 programs [26] provided in the WinGX software suite [27] were used for structure solution and refinement. The Mercury package [28] was used to search for intermolecular non-covalent interactions and molecular graphics. Selected crystallographic data are summarized in Table S1 (supplementary material).

3. Results and discussion

3.1. Synthesis and characterization

Six oxovanadium(V) complexes (**1–6**) having the general molecular formula [VO(acac)(L^{*n*})] were synthesized in moderate to good yields (51–64%) by reacting equimolar amounts of [VO(acac)₂] with the corresponding isolated or in-situ generated tetradentate α -diketone bis(*para*-R-benzoylhydrazones) (H₂L^{*n*}, where *n* = 1–6) (Chart 1). The reactions were carried out aerobically under reflux conditions in methanol for **1–5** and in chloroform–methanol (1:3) mixture for **6**. The elemental (CHN) analysis data of all the complexes are in good agreement with their molecular formulas. The ESI mass spectra of **1–6** recorded in dichloromethane confirm their molecular formulas. The spectrum of **1** shows [M + H]⁺ as the only major peak. On the other hand, the spectra of **2–4** and **6** display three prominent peaks corresponding to [M + H]⁺, [M + Na]⁺ and [M + K]⁺. The spectrum of **6** is provided in Fig. S1 (supplementary material). In contrast, **5** displays two major peaks due to the [M + H]⁺ and [M + Na]⁺ ions. Magnetic susceptibility measurements at 298 K with powdered samples of **1–6** indicate their diamagnetic character. The complexes are dark brown in color. They are soluble in methanol, ethanol, acetonitrile, chloroform, dichloromethane, dimethylformamide and dimethylsulfoxide, and insoluble in benzene, toluene and *n*-hexane. Consistent with their neutral molecular formulas, all of **1–6** are electrically non-conducting in solution. The molecular formula, diamagnetic character and the non-electrolytic behavior suggest that the metal center in each of the six complexes is in pentavalent state. In all probability, the oxygen in air is the oxidant for the oxidation of the metal center from tetravalent to pentavalent state during their synthesis from [VO(acac)₂] (Chart 1).

3.2. Description of X-ray molecular structures

Each of [VO(acac)(L¹)]·0.25MeOH (1·0.25MeOH), [VO(acac)(L^{2–4})] (**2–4**) and [VO(acac)(L⁶)] (**6**) crystallize in the triclinic space group *P*1, while [VO(acac)(L⁵)] (**5**) crystallizes in the monoclinic space group *P*2₁/c. The asymmetric unit of 1·0.25MeOH contains two independent complex molecules and a methanol molecule with half occupancy. On the other hand, the asymmetric unit of each of **2–6** contains one complete

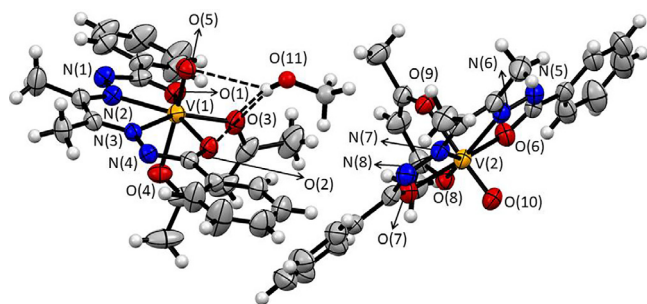


Fig. 1. The asymmetric unit of [VO(acac)(L¹)]·0.25MeOH (1·0.25MeOH). The non-hydrogen atoms are shown by their 40% probability thermal ellipsoids and the carbon atoms are not labeled for clarity.

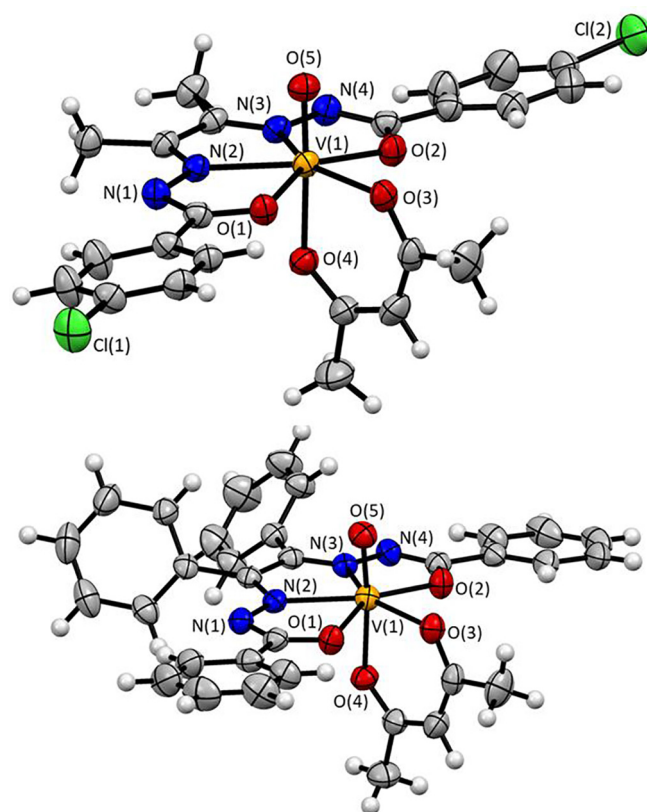


Fig. 2. Perspective views of the molecular structures of [VO(acac)(L⁴)] (4) (top) and [VO(acac)(L⁶)] (6) (bottom). For both structures, thermal ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level and only the non-carbon atoms are labeled for clarity.

molecule of the corresponding complex. The perspective view of the asymmetric unit of 1·0.25MeOH is illustrated in Fig. 1. The molecular structures of 4 and 6 are depicted in Fig. 2, whilst those of 2, 3 and 5 are provided in Fig. S2 (supplementary material). The bond lengths and angles associated with the metal center in 1·0.25MeOH are listed in Table 1 and those for 2–6 are given in Table 2. Very similar geometric parameters of the two complex molecules (Table 1) present in the asymmetric unit of 1·0.25MeOH indicate that structurally they are essentially identical. In each of 1–6, the metal center is in pentagonal-bipyramidal coordination environment. The tetradentate ligand (Lⁿ)^{2−} coordinates the metal center through the two amidate-O and two azomethine-N atoms and forms fused 5,5,5-membered chelate rings. The ON₂O-donor (Lⁿ)^{2−} and one of the two O-atoms of the 6-membered chelate ring forming (acac)[−] assemble a N₂O₃ pentagonal plane (rms deviations: 0.003–0.035 Å) around the metal atom. The second O-atom

Table 1
Selected bond parameters (Å and °) for [VO(acac)(L¹)]·0.25MeOH (1·0.25MeOH).

Molecule 1			
V(1)–O(1)	2.004(3)	V(1)–O(2)	2.024(3)
V(1)–O(3)	1.988(3)	V(1)–O(4)	2.073(3)
V(1)–O(5)	1.578(3)	V(1)–N(2)	2.136(3)
V(1)–N(3)	2.137(3)		
O(1)–V(1)–O(2)	146.23(11)	O(1)–V(1)–O(3)	73.24(11)
O(1)–V(1)–O(4)	85.98(11)	O(1)–V(1)–O(5)	96.56(13)
O(1)–V(1)–N(2)	70.84(12)	O(1)–V(1)–N(3)	139.92(12)
O(2)–V(1)–O(3)	73.94(11)	O(2)–V(1)–O(4)	85.25(11)
O(2)–V(1)–O(5)	94.30(14)	O(2)–V(1)–N(2)	140.47(11)
O(2)–V(1)–N(3)	70.86(11)	O(3)–V(1)–O(4)	88.15(13)
O(3)–V(1)–O(5)	95.61(14)	O(3)–V(1)–N(2)	143.83(12)
O(3)–V(1)–N(3)	144.26(12)	O(4)–V(1)–O(5)	175.94(13)
O(4)–V(1)–N(2)	85.32(12)	O(4)–V(1)–N(3)	83.02(11)
O(5)–V(1)–N(2)	92.50(14)	O(5)–V(1)–N(3)	93.01(13)
N(2)–V(1)–N(3)	69.92(12)		
Molecule 2			
V(2)–O(6)	2.018(3)	V(2)–O(7)	1.994(3)
V(2)–O(8)	2.003(3)	V(2)–O(9)	2.094(3)
V(2)–O(10)	1.590(3)	V(2)–N(6)	2.137(4)
V(2)–N(7)	2.143(3)		
O(6)–V(2)–O(7)	145.81(12)	O(6)–V(2)–O(8)	72.74(11)
O(6)–V(2)–O(9)	87.10(12)	O(6)–V(2)–O(10)	94.46(14)
O(6)–V(2)–N(6)	71.34(13)	O(6)–V(2)–N(7)	141.19(13)
O(7)–V(2)–O(8)	73.35(11)	O(7)–V(2)–O(9)	87.30(12)
O(7)–V(2)–O(10)	94.56(14)	O(7)–V(2)–N(6)	140.51(13)
O(7)–V(2)–N(7)	71.02(12)	O(8)–V(2)–O(9)	87.64(11)
O(8)–V(2)–O(10)	98.29(14)	O(8)–V(2)–N(6)	142.72(13)
O(8)–V(2)–N(7)	143.37(12)	O(9)–V(2)–O(10)	174.06(14)
O(9)–V(2)–N(6)	80.93(12)	O(9)–V(2)–N(7)	82.48(12)
O(10)–V(2)–N(6)	94.12(14)	O(10)–V(2)–N(7)	92.78(14)
N(6)–V(2)–N(7)	70.13(14)		

of (acac)[−] and the oxo atom satisfy the two axial positions and complete the N₂O₅ pentagonal-bipyramidal coordination sphere of the vanadium center. In each of the six complex molecules, the metal atom is slightly shifted (by ~0.17 Å) from the pentagonal plane towards the axial oxo atom. The whole of (Lⁿ)^{2−} moiety in 1–5 is reasonably planar (rms deviations: 0.10–0.23 Å). However, in 6, excluding the C-atoms of the two phenyl groups of the α -diketimine fragment, the remaining atoms including the two benzoyl phenyl rings of (L⁶)^{2−} are satisfactorily planar (rms deviation: 0.11 Å). The dihedral angles between this plane and the α -diketimine phenyl ring planes are 52.79(9) and 48.17(9)°. The dihedral angle between the α -diketimine phenyl ring planes is 58.29(12)°. In all of 1–6, the *trans* O=V–O(acetate) bond angle (172.83(9)–175.94(13)°) (Tables 1 and 2) is somewhat shorter than the ideal value of 180°. The chelate bite angles formed by (Lⁿ)^{2−} and (acac)[−] are unexceptional. The C–O and the C–N bond lengths of the two amidate (–N=C(O[−])) fragments of (Lⁿ)^{2−} in 1–6 are in the ranges 1.278(5)–1.294(2) and 1.295(5)–1.313(3) Å, respectively. These values are comparable with the corresponding values reported for amidate-O coordinated complexes [22,23,29–34]. The remaining intraligand bond parameters for (Lⁿ)^{2−} are unexceptional [22,23,29]. The V=O bond length (Tables 1 and 2) in each of 1–6 is comparable with that found in oxovanadium(V) complexes reported earlier [30–37]. In all six structures, the axial V–O bond is noticeably longer than the three equatorial V–O bonds due to the *trans* effect of the oxo atom (Tables 1 and 2). Between the two O-atoms of (acac)[−], O(3) and O(4), O(4) is at *trans* to the oxo atom, while O(3) is at *cis* to the oxo atom (Fig. 2–4). The V–O(3) bond length is ~0.1 Å shorter than the V–O(4) bond length. In the O(3)CC(H)CO(4) fragment, at the O(3) side the O–C and C–C(H) bond lengths are ~0.01 longer and shorter than the corresponding bond lengths at the O(4) side. These intra-acetylacetonate bonds lengths and the short V–O(3) bond indicate that the negative charge is somewhat localized at the O(3) atom. In general, all the V–O and the V–N bond lengths in 1–6 are within the ranges observed for oxovanadium(V) complexes with ligands having similar coordinating atoms [30–37].

Table 2
Selected bond parameters (Å and °) for [VO(acac)(L²⁻⁵)] (2–5).

Complex	2	3	4	5	6
V(1)–O(1)	2.0085(15)	2.0045(14)	2.0297(16)	2.0369(19)	2.0165(18)
V(1)–O(2)	2.0162(14)	2.0142(14)	2.0310(16)	2.022(2)	2.0072(18)
V(1)–O(3)	2.0013(13)	2.0051(13)	1.9862(15)	1.971(2)	1.9895(18)
V(1)–O(4)	2.0953(13)	2.1026(14)	2.0861(16)	2.078(2)	2.0983(18)
V(1)–O(5)	1.5921(14)	1.5909(14)	1.5897(16)	1.590(2)	1.5880(19)
V(1)–N(2)	2.1396(16)	2.1389(16)	2.1513(18)	2.138(2)	2.146(2)
V(1)–N(3)	2.1354(16)	2.1376(16)	2.1415(18)	2.150(3)	2.147(2)
O(1)–V(1)–O(2)	145.53(6)	145.27(6)	146.30(7)	146.14(9)	145.20(8)
O(1)–V(1)–O(3)	72.78(6)	72.78(6)	73.41(6)	73.30(8)	72.90(8)
O(1)–V(1)–O(4)	86.57(6)	86.10(6)	86.19(7)	86.40(9)	86.46(8)
O(1)–V(1)–O(5)	96.13(7)	95.68(7)	96.63(8)	96.43(10)	95.44(9)
O(1)–V(1)–N(2)	71.04(6)	71.14(6)	70.67(6)	71.14(8)	71.33(8)
O(1)–V(1)–N(3)	140.67(6)	140.95(6)	139.67(7)	140.17(9)	140.51(8)
O(2)–V(1)–O(3)	73.27(6)	73.16(6)	74.05(6)	73.70(9)	73.08(8)
O(2)–V(1)–O(4)	86.48(6)	86.04(6)	84.37(7)	85.86(9)	85.68(8)
O(2)–V(1)–O(5)	94.11(7)	95.31(7)	95.42(8)	94.75(10)	96.53(9)
O(2)–V(1)–N(2)	140.81(6)	140.23(6)	139.87(7)	140.04(10)	140.67(8)
O(2)–V(1)–N(3)	71.28(6)	71.31(6)	71.11(7)	71.18(9)	71.40(8)
O(3)–V(1)–O(4)	88.04(5)	87.73(6)	88.35(6)	89.32(10)	88.73(8)
O(3)–V(1)–O(5)	97.70(7)	97.71(7)	96.41(8)	96.81(11)	98.43(9)
O(3)–V(1)–N(2)	142.89(6)	142.72(6)	143.69(7)	143.98(9)	143.63(8)
O(3)–V(1)–N(3)	143.68(6)	143.89(6)	144.85(7)	144.51(9)	143.82(8)
O(4)–V(1)–O(5)	174.17(7)	174.56(7)	175.00(7)	173.77(11)	172.83(9)
O(4)–V(1)–N(2)	81.91(6)	80.83(6)	84.21(7)	82.96(9)	82.77(7)
O(4)–V(1)–N(3)	82.21(6)	83.69(6)	83.88(7)	83.25(9)	82.03(7)
O(5)–V(1)–N(2)	94.05(7)	94.86(7)	92.81(8)	92.68(11)	91.28(9)
O(5)–V(1)–N(3)	92.47(7)	91.73(7)	91.32(8)	91.07(11)	92.19(9)
N(2)–V(1)–N(3)	70.12(6)	70.05(6)	69.49(7)	69.47(9)	69.82(8)

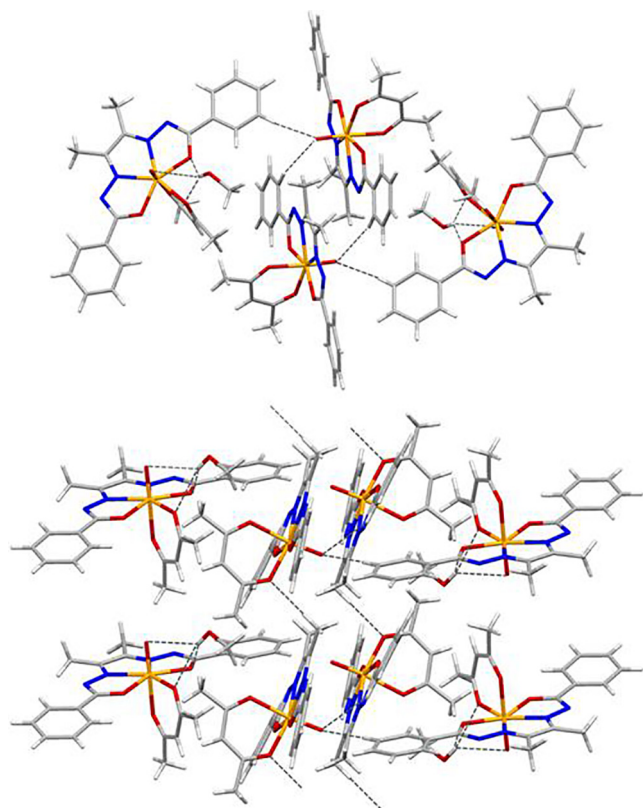


Fig. 3. The tetranuclear [VO(acac)(L¹)]₄MeOH (1₄MeOH) unit assembled via trifurcated O–H···(O,O,O) and bifurcated C–H···O–H–C interactions (top) and the one-dimensional ordering of 1₄MeOH via reciprocal C–H···O interactions (bottom).

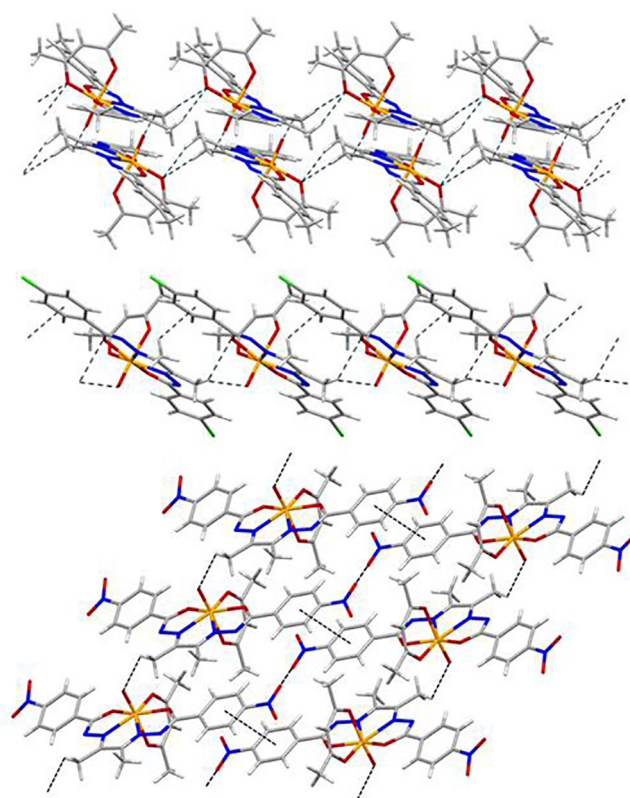


Fig. 4. One-dimensional supramolecular assemblies of [VO(acac)(L²)] (2) via C–H···O–H–C and C–H···O interactions (top), [VO(acac)(L⁴)] (4) via C–H···(O,O) and C–H···π interactions (middle) and [VO(acac)(L⁵)] (5) via C–H···O, π–π and O···O interactions (bottom).

3.3. Self-assembly and supramolecular structures

All of 1-0.25MeOH and 2-6 contain classical and non-classical hydrogen bond donors and acceptors as well as aromatic fragments. Therefore, all the structures were scrutinized for intermolecular non-covalent interactions and the resulting self-assembled supramolecular structures. The interactions found and the self-assembly guided by them are described below.

In the case of 1-0.25MeOH, two types of furcated hydrogen bonding interactions have been found. These are trifurcated O–H···(O,O,O) interaction [38–40] and bifurcated C–H···O–H–C interaction [41,42]. The trifurcated interaction involves the methanol O–H as the single donor and the metal bound facially oriented oxo, amidate-O and enolate-O atoms as the three acceptors. The O···O distances and the O–H···O angles are in the ranges 3.124(12)–3.291(12) Å and 138–153°, respectively. This interaction only connects the methanol molecule to one of the two complex molecules present in the asymmetric unit and plays no further role in the self-assembly process (Fig. 1). The bifurcated C–H···O–H–C interaction involves *ortho* C–H of one benzoyl phenyl ring and the *meta* C–H of another benzoyl phenyl ring as the two donors and a metal bound oxo atom as the single acceptor. The C···O distances are 3.410(6) and 3.501(6) Å, the C–H···O angles are 174 and 149° and the H···O–H angle is 63°. This bifurcated interaction is responsible for the formation of discrete tetranuclear 1₄MeOH units in the crystal lattice (Fig. 3, top). Each of these tetranuclear units is connected to its two adjacent neighbors by a pair of reciprocal C–H···O interactions on either side involving one of the α -diketimine methyl-CH as the donor and an equatorially coordinated acetylacetonate-O as the acceptor. The C···O distance and the C–H···O angle are 3.454(6) Å and 162°, respectively. As a result of this inter-tetranuclear C–H···O interaction a one-dimensional assembly of 1₄MeOH is formed (Fig. 3, bottom).

A bifurcated C–H···O–H–C [41,42] and a simple C–H···O intermolecular interactions have been found in the case of 2. Both methyl groups of the α -diketimine fragment participate as donors in these interactions. One of the two methyl groups utilizes one H-atom for the bifurcated interaction and another H-atom for the C–H···O interaction, while the other methyl group is involved only in the bifurcated interaction. In the C–H···O–H–C interaction, the acetylacetonate-O coordinated to the metal atom at the equatorial position acts as the acceptor. Here, the C···O distances are 3.500(3) and 3.375(3) Å, the C–H···O angles are 157 and 163° and the H···O–H angle is 62°. In the simple C–H···O interaction, the metal bound oxo atom acts as the acceptor. The C···O distance and the C–H···O angle are 3.292(3) Å and 129°, respectively. The bifurcated C–H···O–H–C interaction helps to form a one-dimensional chain of 2. Two such inversion symmetry related parallel chains are connected by the C–H···O interaction in a reciprocal manner and a ribbon-like supramolecular structure is formed (Fig. 4, top).

The molecules of 3 form discrete dimeric units via a pair of reciprocal C–H···O interactions involving the C–H of a methyl group of the α -diketimine fragment as the donor and the metal bound oxo atom as the acceptor (Fig. S3, supplementary material). In this C–H···O interaction, the C···O distance and the C–H···O angle are 3.498(3) Å and 154°, respectively. The two *para*-methoxybenzoyl rings on either side of each dimer participate in two π – π interactions with the corresponding rings of the two neighboring dimers. In this π – π interaction, the C_g–C_g distance and the slip angle (angle between the C_g–C_g vector and the normal to the ring planes) [43] are 3.761(1) Å and 21.3°, respectively. This inter-dimer π – π interaction leads to a one-dimensional chain-like arrangement of the hydrogen bonded dimers of 3 in the crystal lattice (Fig. S3).

A bifurcated C–H···(O,O) and a C–H··· π [44] intermolecular interactions direct the self-assembly of the molecules of 4 in the crystal lattice. The bifurcated interaction involves the C–H of a methyl group of the α -diketimine fragment as the single donor and the metal coordinated amidate-O of (L⁴)^{2–} and the oxo atom as the two acceptors.

The C···O(amidate) and the C···O(oxo) distances are 3.516(3) and 3.337(3) Å and the corresponding C–H···O angles are 141 and 152°, respectively. In the C–H··· π interaction, the C–H of the second methyl group of the α -diketimine fragment acts as donor and a *para*-chlorobenzoyl ring acts as the acceptor. The C···C_g and H···C_g distances are 3.509 and 2.994 Å, respectively and the C–H···C_g angle is 115°. In the crystal lattice, both interactions assist in the formation of a one-dimensional ordering of 4 (Fig. 4, middle).

A one-dimensional chain-like ordering of the molecules of 5 occurs through an intermolecular C–H···O interaction involving the C–H of a methyl group of the α -diketimine fragment as the donor and the metal coordinated oxo atom as the acceptor. The C···O distance and the C–H···O angle are 3.147(4) Å and 116°, respectively. The *para*-nitrobenzoyl rings on one side of each chain are involved in π – π interactions (C_g–C_g distance = 3.989(2) Å and the slip angle = 24.5° [43]) with the *para*-nitrobenzoyl rings of the inversion symmetry related parallel chain. In addition, an oxygen–oxygen interaction (O···O distance = 2.856(7) Å) [45–48] involving an O-atom of the nitro substituent of the same *para*-nitrobenzoyl ring that participates in the π – π interaction provides a second type of connection between the two inversion symmetry related parallel chains. These two inter-chain interactions form a one-dimensional ribbon-like supramolecular assembly of 5 (Fig. 4, bottom).

Two types of intermolecular interactions namely π – π and C–H··· π have been detected for 6 [44]. The π – π interactions between the benzoyl phenyl rings lead to a one-dimensional chain-like assembly of 6 (Fig. S3, supplementary material). In this π – π interaction, the C_g–C_g distance is 3.959(3) Å and the slip angle is ~31.3° [43]. Two such inversion symmetry related parallel chains are connected by C–H··· π interactions in a reciprocal way involving the *ortho* C–H of one of the two phenyl groups of the α -diketimine fragment as the donor and one benzoyl phenyl ring C-atom as the acceptor. The C···C and H···C distances are 3.463(4) and 2.862 Å, respectively and the C–H···C angle is 123°. The resulting overall supramolecular assembly appears to be somewhat ladder-like (Fig. S3).

3.4. Spectroscopic characteristics

The infrared spectra of 1–6 were recorded by using KBR pellets in the range 4000–400 cm^{–1}. Each spectrum displays a large number of bands with various intensities. No attempt has been made to assign all the bands except for the following few. The Schiff bases of the type H₂Lⁿ are known to display the typical amide N–H and C=O stretching bands at ~3200 and ~1650 cm^{–1}, respectively [22,23,29,30,32,33]. The spectra of 1–6 are devoid of these two characteristic amide bands. Thus the amide functionalities of the Schiff bases are deprotonated in their corresponding complexes. All the complexes display a medium to strong band in the range 1582–1602 cm^{–1}. This band is attributed to the C=N–N=C–fragments of the (Lⁿ)^{2–} [22,23,29–34,36]. The spectrum of 5 shows two strong bands at 1520 and 1342 cm^{–1}. These two bands are most likely due to the asymmetric and symmetric stretches of the nitro substituent on the aroyl moiety. The V=O stretching vibration appears as a strong band at 988 for 1 and at ~950 cm^{–1} for 2–6 [11–14,16,17,20,30–37].

The electronic spectra of 1–6 were recorded using their acetonitrile solutions. The spectroscopic profiles of all the complexes are quite comparable. The spectra of 1 and 6 are represented in Fig. 5. In the visible region, the complexes display two moderately intense absorptions, a shoulder in the range 515–530 nm and a band within 434–447 nm for 1–5 and at 375 nm for 6. In the ultraviolet region, two strong absorption bands in the ranges 293–297 nm and 231–252 nm are observed. The free Schiff bases (H₂L¹ and H₂L⁶) display only a strong band at ~310 nm. Thus, the two visible region absorptions are assigned to ligand-to-metal charge transfer transitions, while the two strong absorptions below 300 nm are attributed to ligand centered transitions [30–36].

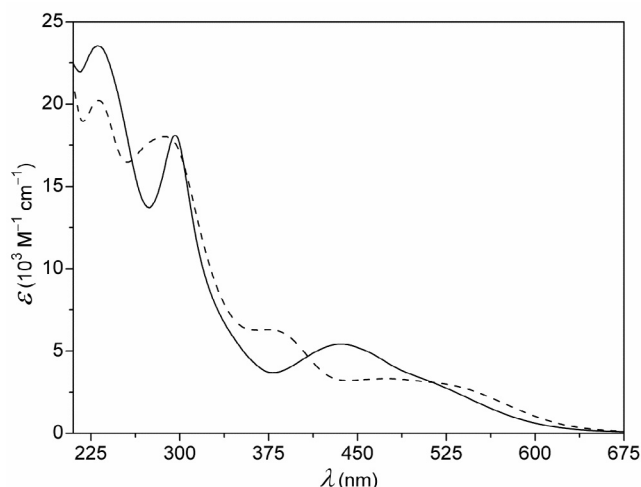


Fig. 5. Electronic spectra of [VO(acac)(L¹)] (**1**) (—) and [VO(acac)(L⁶)] (**6**) (---) in acetonitrile.

The ¹H NMR spectra of **1–6** were recorded in the CDCl₃ solvent using tetramethylsilane as internal standard. The chemical shifts with tentative assignments have been listed in the experimental section under the respective complexes. None of the six complexes display any signal assignable to the amide-NH of the free Schiff bases [22,23]. Absence of this signal is consistent with the deprotonation of both amide functionalities and the dianionic (Lⁿ)²⁻ form of the ligands in the complexes. The spectra also indicate that the two halves of (Lⁿ)²⁻ in each complex are equivalent. The four *ortho* protons of the two benzoyl phenyl rings resonate as a doublet of doublet at δ 8.12 and 8.02 ppm for **1** and **6**, respectively. The remaining sixteen aromatic protons of **6** are observed as two multiplets of six and ten protons in the ranges δ 7.50–7.45 ppm and δ 7.42–7.33 ppm, respectively. In contrast, the two *para* protons and the four *meta* protons of the benzoyl phenyl rings in **1** are observed as two well resolved signals. The *para* protons resonate as a triplet of triplet at δ 7.52 ppm, while the *meta* protons are observed as a triplet at δ 7.44 ppm. On the other hand, both *ortho* and *meta* protons of the two *para*-substituted benzoyl rings in **2–4** resonate as doublets each of four protons in the ranges δ 8.01–8.07 and 6.94–7.41 ppm, respectively. In the case of **5**, these eight protons of the two *para*-nitrobenzoyl rings appear as an AA'BB' type multiplet centred at δ ~8.29 ppm. The six protons of the two methyl groups of the α -diketimine fragment of (Lⁿ)²⁻ in each of **1–5** resonate as a singlet within δ 2.36–2.66 ppm. Two singlets each of three protons are observed in the ranges δ 2.31–2.66 and 1.71–1.81 ppm in all six spectra. Most likely the downfield and the upfield signals are due to the two MeC(O) groups of the (acac)⁻ that are *cis* and *trans*, respectively to the metal bound oxo atom. The methyl protons of the *para*-methylbenzoyl groups in **2** and of the *para*-methoxybenzoyl groups in **3** appear as six-proton singlets at δ 2.43 and 3.88 ppm, respectively. Overall, all the spectra are consistent with pentagonal bipyramidal molecular structure of **1–6**.

3.5. Redox properties

Electron transfer behaviors of **1–6** were probed by cyclic voltammetric measurements at 298 K under nitrogen atmosphere with their acetonitrile solutions (~1 × 10⁻³ M) containing tetra-*n*-butylammonium perchlorate as the supporting electrolyte using a glassy carbon disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Under identical condition the E_{1/2} and ΔE_p values of the ferrocenium/ferrocene (Fc⁺/Fc) couple were found as 0.19 V and 170 mV, respectively. Each complex displays a reduction response at potential cathodic to the reference electrode. The reduction is quasi-reversible for all of **1–6** except for **5**, where it is irreversible.

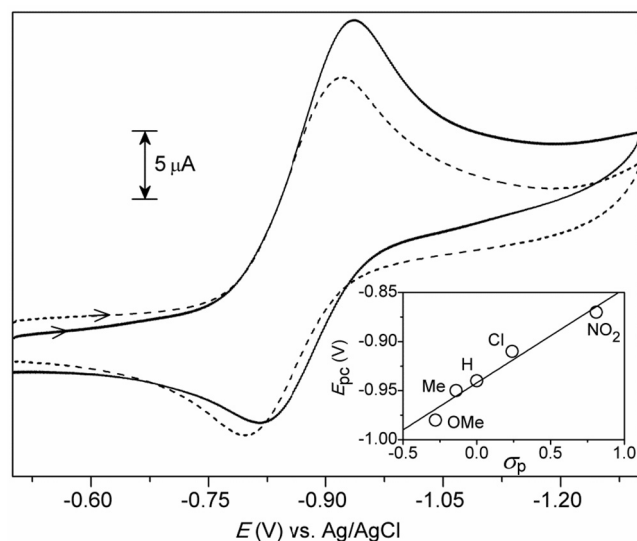


Fig. 6. Cyclic voltammograms of [VO(acac)(L¹)] (**1**) (—) and [VO(acac)(L⁶)] (**6**) (---) in acetonitrile using the experimental conditions described in the text. Inset: Correlation between the E_{pc} values of the reduction responses of **1–5** and the Hammett substituent constants. The straight line represents a linear least-squares fit.

The cyclic voltammograms of **1** and **6** are shown in Fig. 6. The E_{1/2} and the ΔE_p values for **1–4** and **6** are in the ranges -0.80 to -0.92 V and 110–140 mV, respectively. The E_{pc} value for the irreversible reduction of **5** is -0.87 V. The peak currents for all six complexes are comparable with those observed for Fc⁺/Fc couple and other known one-electron redox couples under similar conditions [49,50]. The free Schiff bases (H₂L¹ and H₂L⁶) are redox inactive in the above potential range. Thus, the reduction observed for **1–6** is assigned to vanadium(V) to vanadium(IV) process. The E_{pc} values of **1–5** show a continuous cathodic shift with the change of the substituent R on the benzoyl fragment of (Lⁿ)²⁻ from -NO₂ to -Cl to -H to -Me to -OMe. A satisfactory linear fit has been obtained (Fig. 6, inset) when the E_{pc} values are plotted against the Hammett substituent constants [51]. Thus the pentavalent state of the metal center becomes more stable with the increase in the electron donating ability of the substituent R.

4. Conclusions

A series of six ternary oxovanadium(V) complexes with acetylacetone (Hacac) and the Schiff base system α -diketone bis(*para*-R-benzoylhydrazones) (H₂Lⁿ) are reported. Their general molecular formula as [VO(acac)(Lⁿ)] and the pentavalent state of the metal center in them have been established by various physical measurements. The X-ray molecular structures of all six complexes revealed the hepta-coordination of the vanadium(V) atom and a distorted pentagonal-bipyramidal N₂O₅ coordination geometry assembled by the fused 5,5,5-membered chelate rings forming (Lⁿ)²⁻, 6-membered chelate ring forming (acac)⁻ and the oxo atom. There is no other example of a structurally characterized pentagonal-bipyramidal complex of oxovanadium(V) without at least one less than 5-membered chelate ring forming ligand. Supramolecular self-assembly of these complexes via a variety of intermolecular non-covalent interactions leads to one-dimensional chain-, ladder- and ribbon-like structures in the corresponding crystal lattices. The spectroscopic characteristics of these six analogous complexes validate their similar molecular structures. The electrochemically active complexes display a metal centered one-electron reduction, which is sensitive to the electronic nature of the substituent on the tetradentate (Lⁿ)²⁻. Currently we are engaged in the synthesis of similar higher coordinated (greater than 6) vanadium(V) complexes with various Schiff base ligands.

Acknowledgements

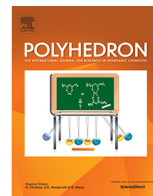
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Appendix A. Supplementary data

CCDC 1836523, 1842288–1842291 and 1836524 contain the supplementary crystallographic data for 1-0.25MeOH, 2-5 and 6, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing to data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033. Additional supplementary data (Table S1 and Figs. S1, S2 and S3) associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jica.2018.08.036>.

References

- [1] R.K. Bogges, W.D. Wiegele, *J. Chem. Educ.* 55 (1978) 156–158.
- [2] S.R. Trifunović, Z.D. Matović, V. Milovanović, H. Kawaguchi, M. Yamasaki, *Transition Met. Chem.* 25 (2000) 680–685.
- [3] K. Dehnicke, A. Greiner, *Angew. Chem. Int. Ed.* 42 (2003) 1340–1354.
- [4] R.-F. Jin, S.-Y. Yang, H.-M. Li, L.-S. Long, R.-B. Huang, L.-S. Zheng, *CrystEngComm* 14 (2012) 1301–1316.
- [5] J.-C.G. Bünzli, *J. Coord. Chem.* 67 (2014) 3706–3733.
- [6] B. Drahoš, R. Herchel, Z. Trávníček, *RSC Adv.* 6 (2016) 34674–34684.
- [7] J. Sanchiz, S. Dominguez, A. Mederos, F. Brito, J.M. Arrieta, *Inorg. Chem.* 36 (1997) 4108–4114.
- [8] R. Meier, F.W. Heinemann, *Inorg. Chim. Acta* 337 (2002) 317–327.
- [9] R.D. Shannon, *Acta Crystallogr., Sect. A* 32 (1976) 751–767.
- [10] P.C. Paul, S.J. Angus-Dunne, R.J. Batchelor, F.W.B. Einstein, A.S. Tracey, *Can. J. Chem.* 75 (1997) 183–191.
- [11] K.J. Ooms, S.E. Bolte, J.J. Smee, B. Baruah, D.C. Crans, T. Polenova, *Inorg. Chem.* 46 (2007) 9285–9293.
- [12] V. Sharma, V. Sharma, R. Bohra, J.E. Drake, M.B. Hursthouse, M.E. Light, A.L. Bingham, *Transition Met. Chem.* 32 (2007) 442–448.
- [13] Q.-Y. Zhang, H.-Q. Zhang, A.-G. Kong, Q. Yang, Y.-K. Shan, *Z. Naturforsch. B* 65 (2010) 157–162.
- [14] S.A. Elsayed, A.M. El-Hendawy, M.I. El-Mahdy, I.S.R.N. *Inorg. Chem.* (2014), <https://doi.org/10.1155/2014/709258>.
- [15] K. Kanamori, K. Nishida, N. Miyata, K. Okamoto, *Chem. Lett.* (1998) 1267–1268.
- [16] K. Kanamori, K. Nishida, N. Miyata, K. Okamoto, Y. Miyoshi, A. Tamura, H. Sakurai, *J. Inorg. Biochem.* 86 (2001) 649–656.
- [17] K. Kanamori, K. Nishida, N. Miyata, T. Shimoyama, K. Hata, C. Mihara, K. Okamoto, Y. Abe, S. Hayakawa, S. Matsugo, *Inorg. Chem.* 43 (2004) 7127–7140.
- [18] X.-Y. Yu, L. Deng, B. Zheng, B.-R. Zeng, P. Yi, X. Xu, *Dalton Trans.* 43 (2014) 1524–1533.
- [19] S. Zhang, W. Xia, Y. Yang, X. Yu, X. Li, *J. Coord. Chem.* 70 (2017) 2958–2968.
- [20] A.-C. Schmidt, M. Hermesen, F. Rominger, R. Dehn, J.H. Teles, A. Schäfer, O. Trapp, T. Schaub, *Inorg. Chem.* 56 (2017) 1319–1332.
- [21] J.C. Dewan, D.L. Kepert, C.L. Raston, D. Taylor, A.H. White, E.N. Maslen, *J. Chem. Soc. Dalton Trans.* (1973) 2082–2086.
- [22] T. Ghosh, A. Mukhopadhyay, K.S.C. Dargaiyah, S. Pal, *Struct. Chem.* 21 (2010) 147–152.
- [23] E. López-Torres, M.A. Mendiola, *Dalton Trans.* (2009) 7639–7647.
- [24] R.A. Rowe, M.M. Jones, *Inorg. Synth.* 5 (1957) 113–116.
- [25] APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2016.
- [26] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 64 (2008) 112–122.
- [27] L.J. Farrugia, *J. Appl. Crystallogr.* 45 (2012) 849–854.
- [28] F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P.M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Crystallogr.* 41 (2008) 466–470.
- [29] T. Ghosh, S. Pal, *J. Chem. Sci.* 127 (2015) 1201–1209.
- [30] N.R. Sangeetha, S. Pal, *Bull. Chem. Soc. Jpn.* 73 (2000) 357–363.
- [31] N.R. Sangeetha, V. Kavita, S. Wocadlo, A.K. Powell, S. Pal, *J. Coord. Chem.* 51 (2000) 55–66.
- [32] S.N. Pal, K.R. Radhika, S. Pal, *Z. Anorg. Allg. Chem.* 627 (2001) 1631–1637.
- [33] A. Sarkar, S. Pal, *Inorg. Chim. Acta* 362 (2009) 3807–3812.
- [34] A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* (2009) 5391–5398.
- [35] A. Sarkar, S. Pal, *Polyhedron* 26 (2007) 1205–1210.
- [36] A. Sarkar, S. Pal, *Inorg. Chim. Acta* 361 (2008) 2296–2304.
- [37] A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* (2009) 622–627.
- [38] S.K. Panigrahi, G.R. Desiraju, *J. Biosci.* 32 (2007) 677–691.
- [39] C.S. Neupane, S.K. Awasthi, *Tetrahedron Lett.* 53 (2012) 6067–6070.
- [40] K. Nieszporek, P. Podkościelny, J. Nieszporek, *Phys. Chem. Chem. Phys.* 18 (2016) 5957–5963.
- [41] I. Rozas, I. Alkorta, J. Elguero, *J. Phys. Chem. A* 102 (1998) 9925–9932.
- [42] E.S. Feldblum, I.T. Arkin, *Proc. Natl. Acad. Sci. USA* 111 (2014) 4085–4090.
- [43] N.R. Sangeetha, S.N. Pal, C.E. Anson, A.K. Powell, S. Pal, *Inorg. Chem. Commun.* 3 (2000) 415–419.
- [44] M. Nishio, *CrystEngComm* 6 (2004) 130–158.
- [45] M. Das, B.N. Ghosh, A. Bauzá, K. Rissanen, A. Frontera, S. Chattopadhyay, *RSC Advances* 5 (2015) 73028–73039.
- [46] K. Remya, C.H. Suresh, *Phys. Chem. Chem. Phys.* 17 (2015) 18380–18392.
- [47] S. Chen, Z. Xu, J. Li, *New J. Phys.* 18 (2016) 023052.
- [48] N. Chaudhri, N. Grover, M. Sankar, *Inorg. Chem.* 56 (2017) 11532–11545.
- [49] S.G. Sreerama, S. Pal, *Inorg. Chem.* 41 (2002) 4843–4845.
- [50] S.G. Sreerama, D. Shyamraj, S.N. Pal, S. Pal, *Indian J. Chem.* 42A (2003) 2352–2358.
- [51] J. March, in: *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, Fourth Edition, Wiley, New York, 1992, p. 280.



A one-dimensional polymeric mixed-valent Mn(II)Mn(III) complex with a macrocyclic compartmental ligand: Structure, properties and catecholase like activity

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ABSTRACT

Reaction of 2,6-diformyl-4-methylphenol, 1,3-diaminopropane, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in 1:1:1:1 mole ratio in methanol afford a linear coordination polymer of formula $\{[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (L^{2-} represents the Robson-type ligand) in 64% yield. The complex has been characterized by elemental (CHN) analysis, magnetic susceptibility, spectroscopic (IR, UV-Vis and EPR) and solution electrical conductivity measurements. The linear polymeric structure and the mixed-valent character of the complex have been confirmed by single crystal X-ray crystallography. In the repetitive dinuclear unit, both metal centers are in N_2O_4 coordination spheres assembled by the compartmental macrocyclic $\text{N}_2\text{O}_2\text{N}_2$ -donor L^{2-} , an intra-dinuclear bridging acetate and an inter-dinuclear bridging acetate. The coordination geometry around the manganese(II) center ($S = 5/2$) is severely distorted octahedral, while that around the manganese(III) center ($S = 2$) is tetragonally elongated octahedral. Variable temperature magnetic susceptibility measurements indicate a weak intra-dinuclear ferromagnetic ($J = 1.12(3) \text{ cm}^{-1}$) interaction as well as a weak inter-molecular antiferromagnetic ($zJ' = -0.679(3) \text{ cm}^{-1}$) interaction. Cyclic voltammogram of the complex displays a metal centered quasi-reversible reduction at -0.03 V and an irreversible ligand centered reduction at -1.16 V (vs Ag/AgCl). The complex efficiently catalyzes the aerobic oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylbenzoquinone with a turnover number (k_{cat}) $1.2 \times 10^4 \text{ h}^{-1}$.

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1. Introduction

The sustained interest in dinuclear complexes stems from their diverse physicochemical properties such as metal–metal interaction, redox characteristics and cooperative bimetallic reactivities, which enable them for applications in a large variety of research areas ranging from bioinorganic modelling to medicinal chemistry to materials science to catalysis [1–10]. Since the first report on the dinuclear transition metal ion complexes with the compartmental macrocyclic tetraaminodiphenolate ligand formed through metal ion assisted template 2 + 2 cyclocondensation of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol [11], a vast literature is now available on this and analogous macrocyclic Schiff base ligands and their dinuclear complexes [12–19]. Generally, in a discrete dinuclear complex of this type, the dianionic macrocyclic $\text{N}_2\text{O}_2\text{N}_2$ -donor compartmental ligand satisfies four equatorial positions of each of the two proximate di-phenoxo bridged metal ions and the remaining apical/axial sites of them are occupied by vari-

ous ancillary monodentate ligands or bidentate bridging ligands such as mono-carboxylates [14–23]. Thus the bare Robson-type dinuclear unit $\{\text{N}_2\text{MO}_2\text{MN}_2\}$ with unoccupied apical/axial sites can be used as the building block for the formation of one-dimensional coordination polymers via self-assembly process in presence of polynucleating bridging ligands. The polynucleating ligands are expected to occupy the apical/axial positions of the metal ions of the building blocks and propagate the polymeric chain. There are a few reports on such one-dimensional coordination polymers with the following polynucleating bridging ligands: 1,3-diaminopropane [24], 4,4'-bipyridine [25,26], terephthalic acid [26], acetylene-dicarboxylate [27], isonicotinonitrile [28] and perchlorate [29]. All these polymeric complexes are of nickel(II), copper(II) and zinc(II). Although several X-ray structurally characterized discrete dimanganese complexes with various macrocyclic Robson-type ligands have been reported so far [20,21,30–35], but to the best of our knowledge there is only one report on a polymeric dimanganese(II) complex with a $\text{N}_2\text{O}_2\text{N}_2$ -donor ligand where acetate acts as the polynucleating bridging ligand [36]. In this one-dimensional polymer, each metal center is in N_2O_3 square-pyramidal environment constituted by the compartmental

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ligand and the inter-dinuclear bridging acetate. In most of the dinuclear manganese complexes, the macrocyclic ligands are derived from triamines and they are $N_3O_2N_3$ -donor [20]. About ten dinuclear manganese complexes are known where the macrocyclic ligands are $N_2O_2N_2$ -donors [21,30–35]. Out of these ten complexes, seven are dimanganese(II) species, while the other three are mixed-valent manganese(II)-manganese(III) complexes. In the seven dimanganese(II) complexes, two bidentate or bridging acetates complete the hexacoordination of the manganese centers in four [31–33,35] and the metal atoms are square-pyramidal with chloride or thiocyanate at the apical positions in the other three [30,34]. In contrast, the metal centers in all three mixed-valent complexes are hexacoordinated. In one of these three complexes, one chloride and one bromide both being monodentate and a bridging chloride complete the hexacoordination of the metal centers [30]. On the other hand, a bridging mono-carboxylate satisfies the fifth coordination site of each metal center and monodentate O-coordinating water, methanol or perchlorate occupy the sixth coordination sites of both metal centers in the remaining two mixed-valent complexes [21]. In our attempt to synthesize a Robson-type dimanganese complex, we have isolated a one-dimensional mixed-valent manganese(II)-manganese(III) coordination polymer, $\{[Mn_2L(OAc)_2]ClO_4\}_n$ (**1**), where the Robson dinuclear units are interconnected by the acetates (Chart 1). Herein, we describe its synthesis, X-ray structure, physicochemical properties and its application as catalyst in catechol oxidation reaction.

2. Experimental

2.1. Materials

All the chemicals and the solvents used in this work were of analytical grade available commercially and were used as received without further purification.

2.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used for elemental (CHN) analysis. Powder X-ray diffraction pattern was recorded on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) generated at 40 kV and 30 mA. Solid state variable temperature magnetic susceptibility measurements were carried out with a Quantum Design PPMS-VSM instrument at 10 kG. The solution electrical conductivity was measured using a Digisun DI-909 conductivity meter. The

infrared spectrum was recorded in ATR mode on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used to collect the electronic spectrum. A Jeol JES-FA200 spectrometer was used to record the EPR spectrum. Cyclic voltammetric measurements were performed with the help of a CH Instruments model 620A electrochemical analyzer. In all the measurements with solutions of **1**, the molar concentration was calculated using the formula weight of the repetitive dinuclear unit.

2.3. Synthesis of $\{[Mn_2L(OAc)_2]ClO_4\}_n$ (**1**)

A solution of 2,6-diformyl-4-methylphenol (100 mg, 0.6 mmol) in methanol (15 ml) was added dropwise over a period of 10 min to a solution of 1,3-diaminopropane (45 mg, 0.6 mmol) in methanol (15 ml) and the mixture was stirred in presence of air at room temperature for $\frac{1}{2}$ h. To the above mixture, solid $Mn(ClO_4)_2 \cdot 6H_2O$ (217 mg, 0.6 mmol) was added and stirred for another $\frac{1}{2}$ h under aerobic conditions. The reaction mixture turned from yellow to brown. Solid $CH_3COONa \cdot 3H_2O$ (82 mg, 0.6 mmol) was added to this brown reaction mixture and stirring was continued for 24 h. The complex precipitated as a microcrystalline solid was collected by filtration, washed with cold methanol and dried under vacuum. The volume of the brown filtrate was reduced to about 10 ml on a steam bath and then it was kept at low temperature (278 K) for slow evaporation. The complex separated as a dark brown crystalline material was filtered off and dried in air. The combined yield was 140 mg (64%). *Anal.* Calc. for $C_{28}H_{32}N_4O_{10}ClMn_2$: C, 46.07; H, 4.42; N, 7.68. Found: C, 46.15; H, 4.38; N, 7.76. Selected IR data (ν (cm^{-1})): 1635 (C=N), 1542 and 1412 (COO^-), 1084 and 621 (ClO_4^-). UV-Vis data ($\lambda_{max}(nm)$ (ϵ ($10^4 M^{-1} cm^{-1}$))): 373 (1.20), 260 (2.15).

2.4. X-ray crystallography

An X-ray quality single crystal of $\{[Mn_2L(OAc)_2]ClO_4\}_n$ (**1**) was collected from the crystalline material obtained by slow evaporation of the synthetic reaction mixture filtrate. Unit cell determination and intensity data collection at 298 K were performed on a BRUKER D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite monochromated Mo K α Radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection, integration, reduction and absorption correction were performed using the APEX3 software package [37]. The structure was solved by direct method and refined on F^2 by full matrix

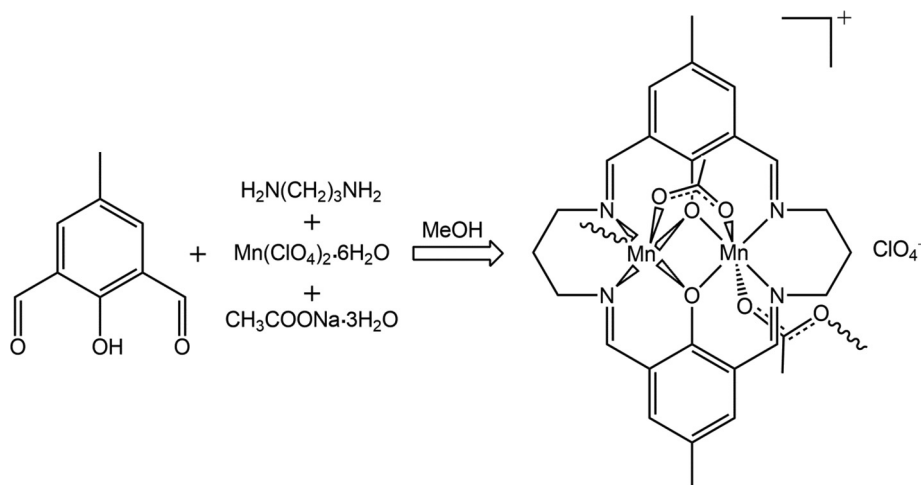


Chart 1. Synthesis of $\{[Mn_2L(OAc)_2]ClO_4\}_n$ (**1**).

least-squares procedures. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included at idealized positions using a riding model. The SHELX-97 programs [38] accessible in the WinGX software suite [39] were used for structure solution and refinement. The Mercury package [40] was used to search for intermolecular non-covalent interactions and make graphical representations. Selected crystal and refinement data are listed in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

The brown polymeric complex $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**) was synthesized in 64% yield by reacting equimolar amounts of 2,6-diformyl-4-methylphenol, 1,3-diaminopropane, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in methanol under aerobic conditions (Chart 1). About 85–90% of the yield was precipitated as a microcrystalline solid during the stirring of the reaction mixture. The remaining yield was obtained as X-ray quality single crystalline material by reducing the volume of the filtrate followed by its slow evaporation at low temperature. Powder X-ray diffraction pattern of the microcrystalline solid was collected and compared with the powder diffraction pattern simulated from the single crystal X-ray structure (*vide infra*). The essentially one-to-one correspondence between the experimental and the simulated patterns confirms that both materials are of the same complex (Fig. 1). The elemental (CHN) analysis data of the complex are in good agreement with its formula. The magnetic moment of the repetitive dinuclear unit at 300 K is $7.64 \mu_B$. This value is very close to the calculated spin-only magnetic moment ($7.69 \mu_B$) of a dinuclear complex having metal centers with $S = 5/2$ and $S = 2$ spin states. The complex is moderately soluble in methanol, dimethylformamide and dimethylsulfoxide; sparingly soluble in acetonitrile and insoluble in chloroform, dichloromethane and hexane. In solution, the complex is electrically conducting. Using the formula weight of the repetitive dinuclear unit, the molar conductivity (Λ_M) value in methanol has been obtained as $110 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. This value falls within the range expected for a 1:1 electrolyte [41]. Thus the Λ_M value indicates that the one-dimensional polymeric structure of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]^+\}_n$ found in the solid state (*vide infra*) breaks down in solution and discrete dinuclear monocationic species are formed. In solution, the vacant coordination site avail-

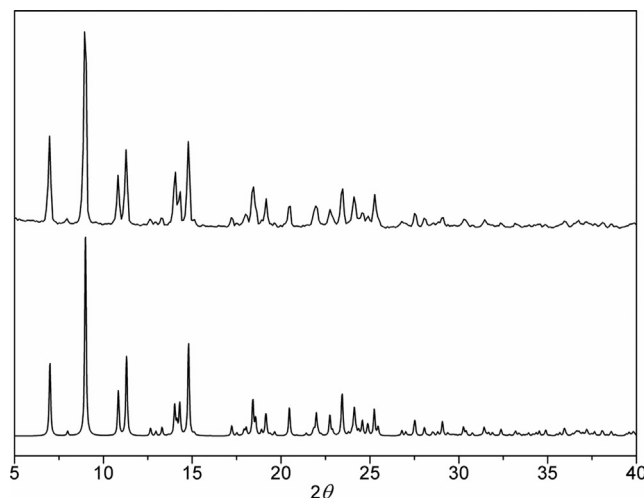


Fig. 1. Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**).

able due to the breakage of the polymeric structure (Chart 1) may be occupied by a solvent molecule as observed before [21] or both acetates may act as bidentate bridging ligands to form the dinuclear monocationic species. The magnetic moment at 300 K and the molar conductivity together with the elemental analysis data of **1** are consistent with its mixed-valent (II–III) state and the dinuclear formula of the repetitive unit. The aerial oxygen is the most likely oxidant for the oxidation of one of the metal center from bivalent to trivalent state during the synthesis of **1** using the manganese(II) starting material.

3.2. Description of X-ray structure

The structure of the monocationic dinuclear repetitive unit of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (**1**) has been illustrated in Fig. 2. The bond

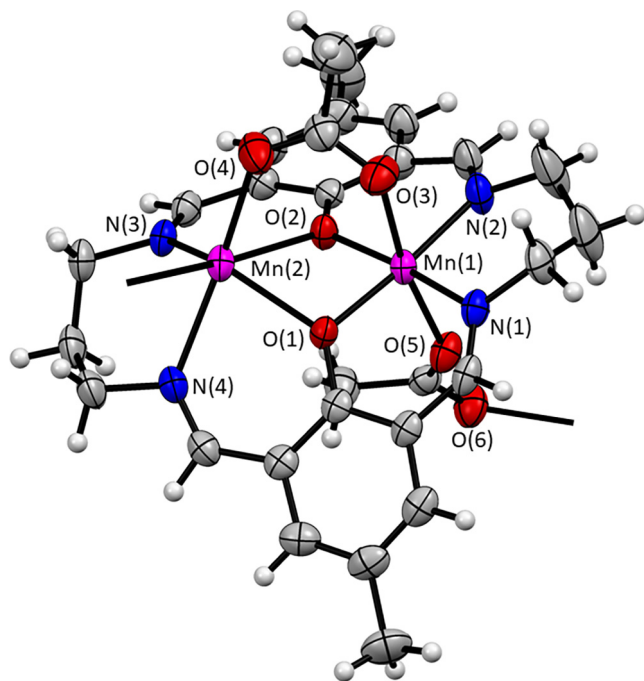


Fig. 2. Perspective view of the dinuclear $[\text{Mn}_2\text{L}(\text{OAc})_2]^+$ repetitive unit. Thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level and only the non-carbon atoms are labeled for clarity.

Table 1
Selected crystal and refinement data.

Complex	$\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (1)
Chemical formula	$\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_{10}\text{ClMn}_2$
Formula weight	729.91
Crystal system	monoclinic
Space Group	$P2_1/c$
a (Å)	12.6528(6)
b (Å)	15.6463(6)
c (Å)	15.6504(7)
β (°)	93.388(2)
V (Å ³)	3092.9(2)
Z	4
ρ (g cm ^{−3})	1.568
μ (mm ^{−1})	0.965
Reflections collected	25 030
Reflections unique	5471
Reflections $[I \geq 2\sigma(I)]$	4427
Data/restraints/parameters	5471/0/410
R_1, wR_2 $[I \geq 2\sigma(I)]$	0.0430, 0.1076
R_1, wR_2 [all data]	0.0577, 0.1163
Goodness-of-fit (GOF) on F^2	1.050
Largest difference in peak/hole (e Å ^{−3})	0.751/−0.627

lengths and the bond angles associated with the two metal centers are listed in Table 2. The complex crystallizes in the $P2_1/c$ space group and the asymmetric unit contains one monocationic dinuclear unit $[\text{Mn}_2\text{L}(\text{OAc})_2]^+$ and a perchlorate counter anion. In the dinuclear unit, the compartmental macrocyclic ligand L^{2-} coordinates the two metal centers through the four azomethine-N atoms and the two bridging phenoxo-O atoms and forms two N_2O_2 square-planes around the two manganese atoms. Around Mn(1), an almost perfect N_2O_2 square-plane (rms deviation 0.01 Å) is formed and there is essentially no deviation (0.04 Å) of Mn(1) from this plane. On the other hand, the N_2O_2 square-plane (rms deviation 0.19 Å) around Mn(2) has a slight tetrahedral distortion and the metal center is significantly shifted (by 1.08 Å) from the mean plane. The average Mn–O(phenoxo) and Mn–N(azomethine) bond lengths involving Mn(1) are shorter by ~ 0.37 and ~ 0.23 Å, respectively, when compared with the corresponding bond lengths involving Mn(2). These differences in the bond lengths and no shift of Mn(1) and a large shift of the Mn(2) from the corresponding N_2O_2 square-planar environment clearly indicate that the Mn(1) is smaller than Mn(2) and their oxidation states are +3 and +2, respectively. The dihedral angle ($55.2(1)^\circ$) between the two mean planes (rms deviations 0.05 Å) constituted by the two 2,6-dimethine-4-methylphenolate moieties indicate the non-planarity of the macrocyclic ligand L^{2-} . The coordination of the larger manganese(II) is likely to be the reason for this distortion from planarity. A bridging acetate occupies the fifth coordination site of each metal center in the dinuclear unit (Fig. 2). The O-atoms of a second acetate satisfies the sixth coordination sites of Mn(1) and Mn(2) of another repetitive dinuclear unit. As a result of this inter-dinuclear bridging acetates, the one-dimensional polymeric structure of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]^+\}_n$ propagates along the c -axis (Fig. 3) and in each dinuclear unit, both metal centers have hexacoordinated N_2O_4 coordination environment. The manganese(III) center, Mn(1), has a tetragonally elongated coordination geometry where the macrocycle provides the N_2O_2 square-plane and the O-atoms (O(3) and O(5)) of the two acetates are at the tetragonally elongated axial sites (Fig. 4 and Table 2). In each of the previously reported analogous dimanganese(II/III) complexes, the trivalent metal center has similar tetragonally elongated octahedral geometry [21,30]. However, the coordination geometry around the manganese(II) center in the present complex (1) is not distorted

trigonal prismatic as reported before [21,30]. Here, the coordination geometry around the manganese(II) atom, Mn(2), is closer to distorted octahedron rather than trigonal prism (Fig. 4). One azomethine-N and one phenoxo-O (N(4) and O(2)) atoms from the macrocycle and the acetate-O atoms (O(4) and O(6)) from the two acetates constitute a satisfactory NO_3 square-plane (rms deviation 0.05 Å) around Mn(2) and the remaining two mutually *trans* sites are occupied by another azomethine-N and the second phenoxo-O (N(3) and O(1)) atoms of the macrocycle (Fig. 4). The metal center is shifted from the NO_3 square-plane towards N(3) by a very small amount (0.14 Å). The distortion from the octahedral geometry is primarily due to a very large deviation (by $\sim 49^\circ$) of the *trans* N(3)–Mn(2)–O(1) angle from the ideal value of 180° (Fig. 4). The intra-dinuclear bis(phenoxo)-acetato bridged Mn(1)–Mn(2) distance (3.2057(7) Å) in $[\text{Mn}_2\text{L}(\text{OAc})_2]^+$ is slightly longer than that (3.168(3)–3.187(1) Å) reported for previously reported mixed-valent complexes with $\text{N}_2\text{O}_2\text{N}_2$ -donor macrocyclic Robson-type ligands [21,30]. The inter-dinuclear acetato-bridged Mn(1)–Mn(2) distance is 5.3006(7) Å. Thus, the one-dimensional chain-like structure of 1 has alternating short and long metal–metal distances (Fig. 3). The bond parameters associated with the central $\{\text{Mn}_2(\mu\text{-O}(\text{phenoxo}))_2(\mu\text{-OAc})\}^{2+}$ core in 1 are comparable with those observed for the same core stabilized by a $\text{N}_2\text{O}_2\text{N}_2$ -donor macrocycle that is analogous to the present macrocycle L^{2-} [21]. Overall, the Mn(II/III)–N and Mn(II/III)–O bond lengths and the bond parameters of L^{2-} in 1 are within the ranges reported for dimanganese (II/II and II/III) complexes with $\text{N}_2\text{O}_2\text{N}_2$ -donor Robson-type macrocycles [21,30–36]. The bond parameters associated with the two acetates and the perchlorate are unexceptional [36,42–45].

The crystal packing of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ is shown in Fig. 5. The perchlorate counter anions are located in between the $\{[\text{Mn}_2\text{L}(\text{OAc})_2]^+\}_n$ chains and they are involved in several C–H $\cdots$ O hydrogen bonding interactions with various types of C–H groups of the macrocyclic ligand L^{2-} and the acetate moieties (Table S1). These C–H groups are phenolate ring *meta* C–H, azomethine C–H, methylene C–H and acetate methyl C–H. In these interactions, the C $\cdots$ O distances are in the range 3.376–3.589 Å and the C–H $\cdots$ O angles are within 148 – 163° . The parallel chains of $\{[\text{Mn}_2\text{L}(\text{OAc})_2]^+\}_n$ are inter-connected by the perchlorates through these C–H $\cdots$ O interactions and as a result a three-dimensional network is formed (Fig. 5).

3.3. Magnetic properties

Magnetic susceptibility (χ_M) measurements in the temperature range 300–3 K were performed with a powdered sample of 1. The $\chi_M T$ values for the dinuclear repetitive unit $[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4$ vs T plot is shown in Fig. 6. The $\chi_M T$ at 300 K is $7.294 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. This value is very close to the calculated spin only value of $7.38 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. The $\chi_M T$ increases gradually with the decrease of temperature. It reaches a maximum value of $8.506 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 100 K. After this increase, there is a gradual decrease and at 55 K it becomes $8.304 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Below 55 K there is a sharp decrease and the final value of $\chi_M T$ at 3 K is $2.26 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. The data were fitted using an isotropic dinuclear model ($H = -2JS_1S_2$, where $S_1 = 2$ and $S_2 = 5/2$) with a molecular field correction (zJ') to account for the intra-chain and inter-chain interactions [46,47]. The least-squares fitting of the data provides $J = 1.12 (3) \text{ cm}^{-1}$, $zJ' = -0.679(3) \text{ cm}^{-1}$ and $g = 2.155(5)$ with a least-square error of 2.2×10^{-4} . Using this simple model a reasonable fit has been obtained in the low temperature range but not in the high temperature range (Fig. 6). For a better understanding of the magnetic characteristics of 1, an improved theoretical model including the zero-field splitting effects on the manganese(II) and manganese(III) centers and variable field measurements will be carried

Table 2
Selected bond parameters (Å and $^\circ$) for $\{[\text{Mn}_2\text{L}(\text{OAc})_2]\text{ClO}_4\}_n$ (1).

Mn(1)–O(1)	1.939(2)	Mn(2)–O(1)	2.217(2)
Mn(1)–O(2)	1.909(2)	Mn(2)–O(2)	2.366(2)
Mn(1)–O(3)	2.142(2)	Mn(2)–O(4)	2.153(3)
Mn(1)–O(5)	2.154(2)	Mn(2)–O(6) ^a	2.104(2)
Mn(1)–N(1)	2.015(3)	Mn(2)–N(3)	2.204(3)
Mn(1)–N(2)	2.023(3)	Mn(2)–N(4)	2.301(3)
O(1)–Mn(1)–O(2)	83.92(9)	O(1)–Mn(2)–O(2)	68.22(7)
O(1)–Mn(1)–O(3)	93.77(10)	O(1)–Mn(2)–O(4)	100.60(10)
O(1)–Mn(1)–O(5)	94.22(9)	O(1)–Mn(2)–O(6) ^a	106.19(9)
O(1)–Mn(1)–N(1)	88.69(10)	O(1)–Mn(2)–N(3)	131.04(9)
O(1)–Mn(1)–N(2)	175.22(10)	O(1)–Mn(2)–N(4)	79.53(9)
O(2)–Mn(1)–O(3)	90.06(10)	O(2)–Mn(2)–O(4)	77.17(9)
O(2)–Mn(1)–O(5)	95.13(9)	O(2)–Mn(2)–O(6) ^a	162.29(9)
O(2)–Mn(1)–N(1)	171.97(10)	O(2)–Mn(2)–N(3)	77.21(8)
O(2)–Mn(1)–N(2)	91.49(11)	O(2)–Mn(2)–N(4)	113.79(9)
O(3)–Mn(1)–O(5)	170.88(10)	O(4)–Mn(2)–O(6) ^a	87.77(11)
O(3)–Mn(1)–N(1)	87.29(11)	O(4)–Mn(2)–N(3)	104.37(11)
O(3)–Mn(1)–N(2)	84.87(12)	O(4)–Mn(2)–N(4)	167.72(11)
O(5)–Mn(1)–N(1)	88.52(10)	O(6) ^a –Mn(2)–N(3)	116.13(10)
O(5)–Mn(1)–N(2)	87.50(12)	O(6) ^a –Mn(2)–N(4)	80.46(10)
N(1)–Mn(1)–N(2)	95.82(12)	N(3)–Mn(2)–N(4)	84.15(10)
Mn(1)–O(1)–Mn(2)	100.71(9)	Mn(1)–O(2)–Mn(2)	96.56(9)

^a Symmetry transformation used to generate the equivalent atom: $x, -y+1/2, z-1/2$.

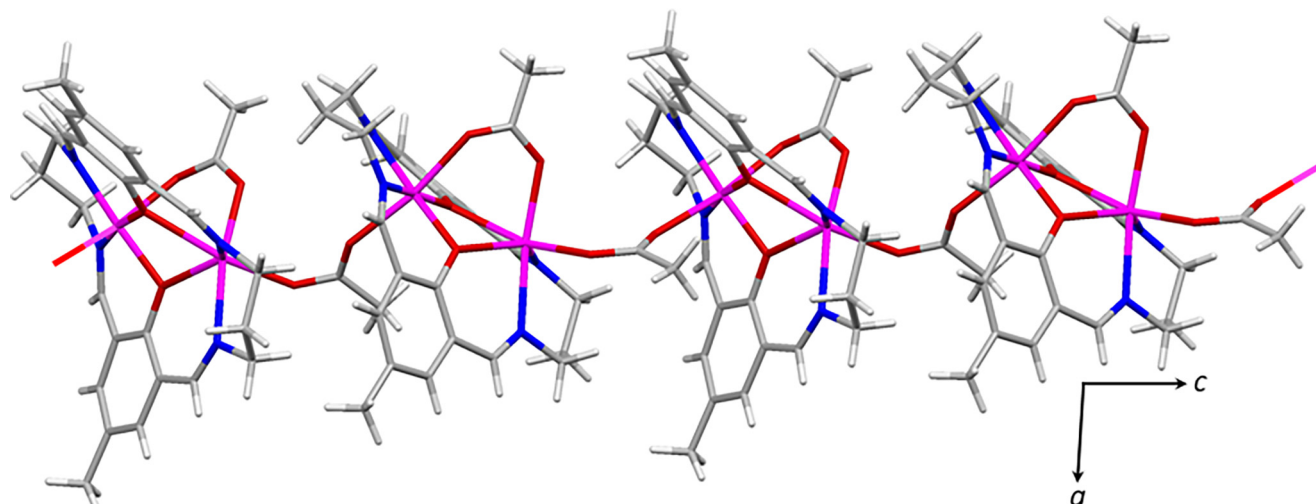


Fig. 3. The linear polymeric structure of $[\text{Mn}_2\text{L}(\text{OAc})_2]^+{}_n$.

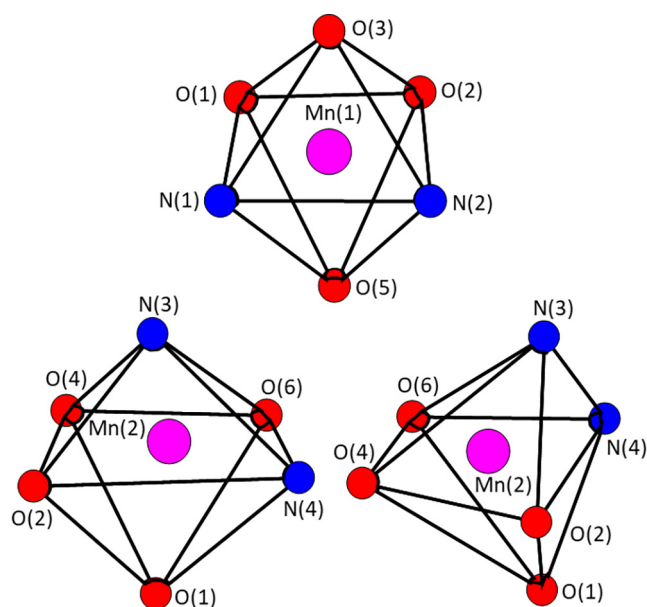


Fig. 4. The coordination spheres around the manganese(III) (top) and manganese (II) (bottom) in $[\text{Mn}_2\text{L}(\text{OAc})_2]^+$.

out in future. Nevertheless, the weak intra-dinuclear ferromagnetic and inter-molecular antiferromagnetic interactions are consistent with the observed χ_{MT} versus T curve profile. Similar weak interaction is also reported for complexes of the same mixed-valent $\{\text{Mn}_2(\mu\text{-O}(\text{phenoxo}))_2(\mu\text{-carboxylate})\}^{2+}$ core with analogous $\text{N}_2\text{O}_2\text{N}_2$ -donor Robson macrocycle [21] where the geometric parameters of the tribridged dimetal core are very similar to those of **1**.

3.4. Spectroscopic characteristics

The infrared spectrum of **1** was collected within the range $4000\text{--}500\text{ cm}^{-1}$ (Fig. S1, Supplementary material). Absence of any band assignable to the phenolic-OH is consistent with the deprotonated state of the two phenol functionalities of the macrocyclic ligand. A large number of bands having various intensities have been observed between 1650 and 500 cm^{-1} . Except for the following few, no attempt has been made to assign the remaining bands. A strong band observed at 1635 cm^{-1} is attributed to the azome-

thine ($\text{HC}=\text{N}$) double bond [20,21,31,34,35]. Two more strong bands appeared at 1543 and 1412 cm^{-1} are assigned to the acetate asymmetric and symmetric stretches, respectively [21,35,42,43]. The presence of the uncoordinated perchlorate counter anion is indicated by a very strong band and a sharp medium intensity band at 1084 cm^{-1} and at 621 cm^{-1} , respectively [21,35,36,44,45].

The electronic spectrum of **1** was recorded in methanol. The spectrum displays two strong bands centered at 370 and 260 nm (Fig. S2, Supplementary material). The lower energy strong band is likely to be primarily due to ligand-to-metal charge transfer transition with some contribution from the manganese(III) ($S = 2$) centered d-d transition in its long tail, which is extended up to the visible region [21,31,33,48]. The higher energy very strong broad band is attributed to the macrocyclic ligand centered π to π^* transition [20,21,31,34].

X-band EPR spectrum of **1** was recorded in frozen methanol solution at 77 K . The spectrum is typical for a complex of high-spin manganese(II) (Fig. S3, Supplementary material). It shows a strong six-line hyperfine structure at $g \approx 2.0$ due to the allowed $\Delta M_I = 0$ transitions. In between the six lines there are some weak fine structures. The forbidden $\Delta M_I = 1$ transitions are expected to appear as weak ten-line structure together with the six-line pattern [30,32]. The spectrum clearly indicates that there is essentially no or very weak spin-coupling between the manganese(II) and manganese(III) centers in **1**. Thus the spectrum is consistent with the very small spin-coupling constants obtained from the variable temperature magnetic susceptibility data of **1** (*vide supra*). It may be noted that analogous weakly coupled mixed-valent manganese(II)-manganese(III) complexes in frozen solution display very similar EPR spectra [30,32,48].

3.5. Redox properties

Cyclic voltammetric measurements were performed at room temperature (298 K) with a methanol solution of **1** ($1 \times 10^{-3}\text{ M}$) containing Bu_4NClO_4 (0.1 M) as the supporting electrolyte using a glassy-carbon working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1} . Under identical condition the ferrocenium/ferrocene (Fc^+/Fc) couple was observed at $E_{1/2} = 0.19\text{ V}$ ($\Delta E_p = 190\text{ mV}$). There is no oxidation response for the complex on the anodic side of the reference electrode. However, on the cathodic side, it displays a quasi-reversible reduction at $E_{1/2} = -0.03\text{ V}$ ($\Delta E_p = 230\text{ mV}$) and an irreversible reduction at -1.16 V (Fig. 7). The peak currents of

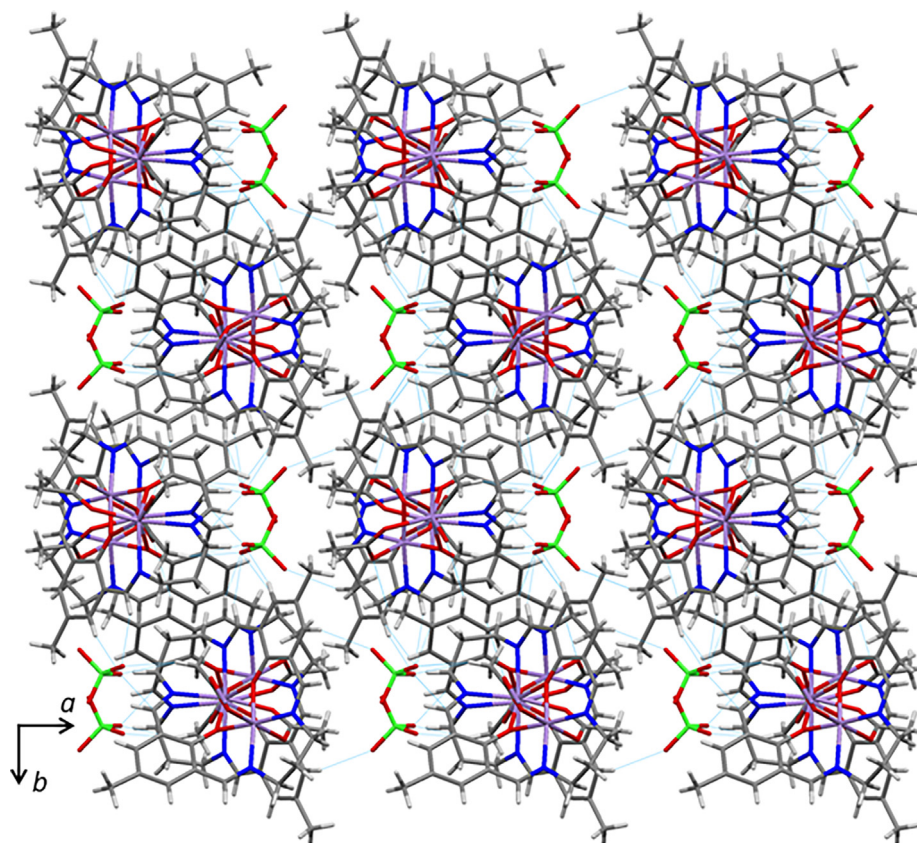


Fig. 5. The three dimensional network structure of $\{[Mn_2L(OAc)_2]ClO_4\}_n$ viewed along the c -axis.

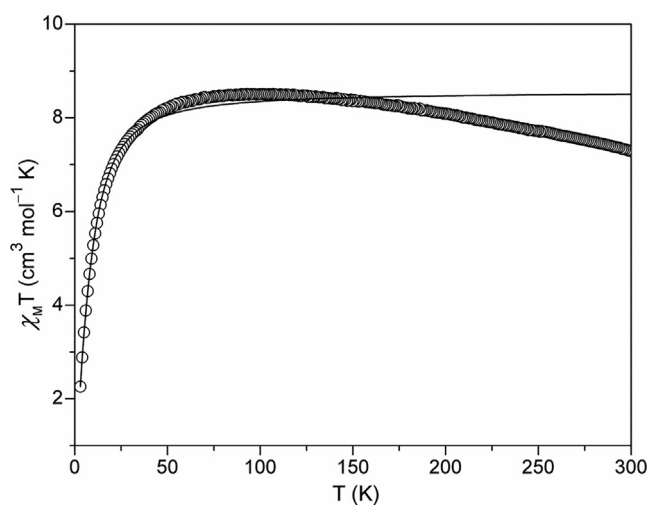


Fig. 6. The product of molar paramagnetic susceptibility and temperature plot for $\{[Mn_2L(OAc)_2]ClO_4\}_n$. The solid line was generated from the best fit parameters given in the text.

the quasi-reversible response are comparable with those of the Fc^+/Fc couple and other known one-electron redox processes under comparable conditions [49–51]. In contrast, the irreversible response has relatively much larger cathodic peak current. There is no report of any ligand reduction near 0.0 V for dimanganese complexes with analogous macrocyclic Schiff base ligands [20,30–32]. On the other hand, metal centered one-electron redox response having an $E_{1/2}$ value at a little higher potential range (0.03 V vs Fc^+/Fc , 0.08 V vs Ag^+/Ag , 0.6 V vs NHE and 0.11–0.29 V vs SCE) has been reported for analogous Robson-type diman-

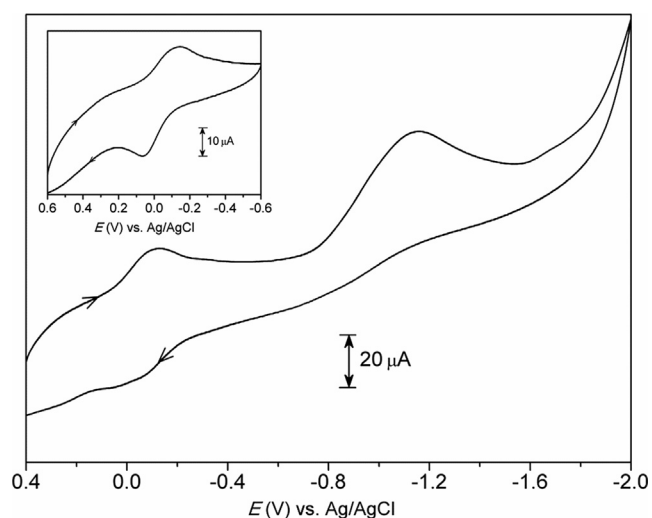


Fig. 7. Cyclic voltammogram of $\{[Mn_2L(OAc)_2]ClO_4\}_n$ in methanol using the experimental conditions described in the text. Inset: The quasi-reversible metal centered reduction.

ganes(II,II) complexes [20,30–32,48]. Thus the first quasi-reversible reduction of **1** is assigned to a metal centered $Mn(II)/Mn(III)/Mn(II)Mn(II)$ redox couple. The second irreversible reduction at -1.16 V with high peak current is attributed to the reduction of the azomethine fragments of L^{2-} [48].

3.6. Catecholase like activity

The catecholase mimicking activity of **1** was investigated using 3,5-di-*tert*-butylcatechol (3,5-DTBC) as the model substrate. The

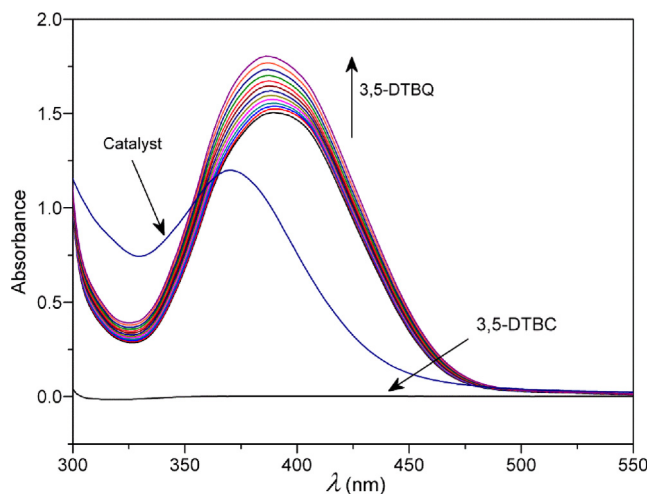


Fig. 8. Change of absorbance of 3,5-DTBQ band around 390 nm after the addition of 100 equivalents of 3,5-DTBC to a methanol solution of **1** (1×10^{-4} M). The spectra were recorded at time intervals of 5 min.

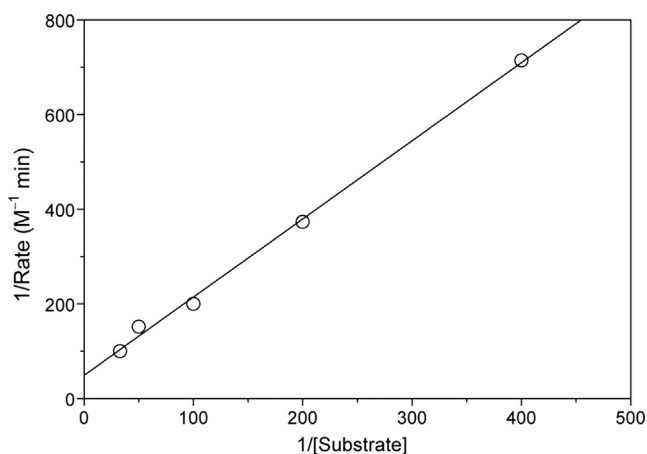


Fig. 9. Lineweaver–Burk plot. The straight line represents a linear least-squares fit.

reactions were carried out by adding 3,5-DTBC to 1×10^{-4} M solutions of the complex in methanol at 298 K under aerobic conditions. The formation of the 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-DTBQ) was followed spectrophotometrically over a period of 1 h (Fig. 8). Dependence of the reaction rate and the various kinetic parameters on the substrate concentration has been determined by treating the catalyst with 25, 50, 100, 200 and 300 molar equivalents of 3,5-DTBC. The rates of the reactions were calculated from the change in absorbance (at 382 nm) against time plots. Using Michaelis–Menten equation and the Lineweaver–Burk plot (Fig. 9), the kinetic parameters Michaelis–Menten constant (K_M), maximum velocity (V_{max}) and the turnover number (k_{cat}) were calculated as 33.6×10^{-3} M, 20.3×10^{-3} M min $^{-1}$ and 1.2×10^4 h $^{-1}$, respectively. Till now a large number of manganese(II/III/IV) complexes having a variety of nuclearities such as mono-, di-, tri-, tetra-, hexa- and octanuclear and two mixed-valent manganese (II/III) polymeric complexes have been reported to exhibit very low to very high catecholase activities with turnover numbers (k_{cat}) in the range 1.7 to 1.32×10^6 h $^{-1}$ [21,52–55]. The k_{cat} value of **1** indicates that its catalytic efficiency in oxidation of catechol to quinone is the fifth best amongst the above mentioned complexes [54].

4. Conclusions

A one-dimensional coordination polymer of a monocationic bis (phenoxo)-acetato bridged dimanganese(II/III) complex with a Robson-type macrocyclic L^{2-} as the principal ligand, acetate as coligand and perchlorate as counter anion was synthesized and structurally characterized. In this polymeric complex, $\{[Mn^{II}Mn^{III}L(OAc)_2]ClO_4\}_n$, half of the acetates act as intra-dinuclear bridges, while the other half provide the inter-dinuclear bridges. In the chain-like structure, the Mn...Mn distance alternates between long and short values. The microanalytical data and the spectroscopic features are consistent with the formula of the complex. Magnetic susceptibility measurements reveal that the bis(phenoxo)-acetato bridged metal centers in the repetitive dinuclear unit of the polymeric chain are weakly ferromagnetically coupled, while a weak antiferromagnetic interaction is operative in and between the polymeric chains. The complex is redox active and shows a metal centered and a ligand centered reduction responses. It exhibits an excellent catalytic activity in aerobic oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butyl-1,2-benzoquinone.

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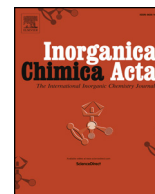
Appendix A. Supplementary data

CCDC 1890524 contains the supplementary crystallographic data for $\{[Mn^{II}Mn^{III}L(OAc)_2]ClO_4\}_n$ (**1**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Additional supplementary data (Table S1 and Figs. S1–S3) to this article can be found online at <https://doi.org/10.1016/j.poly.2019.04.003>.

References

- [1] A.E. Martell, J. Perutka, D. Kong, *Coord. Chem. Rev.* 216–217 (2001) 55.
- [2] K.D. Demadis, C.M. Hartshorn, T.J. Meyer, *Chem. Rev.* 101 (2001) 2655.
- [3] W.R. Browne, R. Hage, J.G. Vos, *Coord. Chem. Rev.* 250 (2006) 1653.
- [4] M. Shibasaki, S. Matsunaga, *J. Synth. Org. Chem. Jpn.* 68 (2010) 1142.
- [5] F. Habib, M. Murugesu, *Chem. Soc. Rev.* 42 (2013) 3278.
- [6] L.J. Daumann, G. Schenk, D.L. Ollis, L.R. Gahan, *Dalton Trans.* 43 (2014) 910.
- [7] S. Mameria, D. Specklin, R. Welter, *C.R. Chim.* 18 (2015) 1370.
- [8] T. Inatomi, Y. Koga, K. Matsubara, *Molecules* 23 (2018) 140.
- [9] L. Habala, F. Devinsky, A.E. Egger, *J. Coord. Chem.* 71 (2018) 907.
- [10] S. Rej, H. Tsurugi, K. Mashima, *Coord. Chem. Rev.* 355 (2018) 223.
- [11] N.H. Pilkington, R. Robson, *Aust. J. Chem.* 23 (1970) 2225.
- [12] B. Dutta, P. Bag, B. Adhikary, U. Flörke, K. Nag, *J. Org. Chem.* 69 (2004) 5419.
- [13] N.E. Borisova, M.D. Reshetova, Y.A. Ustynyuk, *Chem. Rev.* 107 (2007) 46.
- [14] K.K. Nanda, R. Das, K. Venkatsubramanian, K. Nag, *Proc. Indian Acad. Sci. Chem. Sci.* 106 (1994) 673.
- [15] A.J. Atkins, D. Black, A.J. Blake, A. Marin-Becerra, S. Parsons, I. ena kuiz-Ramirez, M. Schröder, *Chem. Commun.* (1996) 457.
- [16] H. Okawa, H. Furutachi, D.E. Fenton, *Coord. Chem. Rev.* 174 (1998) 51.
- [17] W. Huang, H.-B. Zhu, S.-H. Gou, *Coord. Chem. Rev.* 250 (2006) 414.
- [18] V. Lozan, C. Loose, J. Kortus, B. Kersting, *Coord. Chem. Rev.* 253 (2009) 2244.
- [19] D. Venegas-Yazigi, D. Aravena, E. Spodine, E. Ruiz, S. Alvarez, *Coord. Chem. Rev.* 254 (2010) 2086.
- [20] S. Kal, A.S. Filatov, P.H. Dinolfo, *Inorg. Chem.* 52 (2013) 13963, and references therein.
- [21] A. Jana, N. Aliaga-Alcalde, E. Ruiz, S. Mohanta, *Inorg. Chem.* 52 (2013) 7732.
- [22] L. Mandal, S. Mohanta, *Dalton Trans.* 43 (2014) 15737.
- [23] S. Sasmal, S. Roy, L. Carrella, A. Jana, E. Rentschler, S. Mohanta, *Eur. J. Inorg. Chem.* (2015) 680.

- [24] A. Asokan, B. Varghese, A. Caneschi, P.T. Manoharan, *Inorg. Chem.* 37 (1998) 228.
- [25] W. Huang, S. Gou, D. Hu, S. Chantrapromma, H.-K. Fun, Q. Meng, *Inorg. Chem.* 40 (2001) 1712.
- [26] Q.R. Cheng, H. Zhou, Z.Q. Pan, G.Y. Liao, Z.G. Xu, *Polyhedron* 81 (2014) 668.
- [27] M. Pascu, M. Andruh, A. Müller, M. Schmidtman, *Polyhedron* 23 (2004) 673.
- [28] W. Huang, Z. Chu, S. Gou, T. Ogawa, *Polyhedron* 26 (2007) 1483.
- [29] J. Pan, L. Cheng, H. Zhou, Z.-Q. Pan, Q.-M. Huang, X.-L. Hu, *Polyhedron* 29 (2010) 1588.
- [30] H.-R. Chang, S.K. Larsen, P.D.W. Boyd, C.G. Pierpont, D.N. Hendrickson, *J. Am. Chem. Soc.* 110 (1988) 4565.
- [31] A.J. Downard, V. McKee, S. Tandon, *Inorg. Chim. Acta* 173 (1990) 181.
- [32] H. Wada, K. Motoda, M. Ohba, H. Sakiyama, N. Matsumoto, H. Ōkawa, *Bull. Chem. Soc. Jpn.* 68 (1995) 1105.
- [33] T. Aono, H. Wada, M. Yonemura, M. Ohba, H. Ōkawa, D.E. Fenton, *J. Chem. Soc., Dalton Trans.* (1997) 1527.
- [34] J.-C. Jiang, Z.-L. Chu, W. Huang, G. Wang, X.-Z. You, *Inorg. Chem.* 49 (2010) 5897.
- [35] Y.-F. Chen, L. Wei, J.-L. Bai, H. Zhou, Q.-M. Huang, J.-B. Li, Z.-Q. Pan, *J. Coord. Chem.* 64 (2011) 1153.
- [36] D. Luneau, J.-M. Savariault, P. Cassoux, J.-P. Tuchagues, *J. Chem. Soc. Dalton Trans.* (1988) 1225.
- [37] APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2016.
- [38] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 64 (2008) 112.
- [39] L.J. Farrugia, *J. Appl. Crystallogr.* 45 (2012) 849.
- [40] F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P.M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Crystallogr.* 41 (2008) 466.
- [41] W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81.
- [42] S. Pal, M.M. Olmstead, W.H. Armstrong, *Inorg. Chem.* 34 (1995) 4708.
- [43] A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* (2009) 622.
- [44] S.G. Sreerama, S. Pal, *Eur. J. Inorg. Chem.* (2004) 4718.
- [45] S. Maloth, S.K. Kurapati, S. Pal, *J. Coord. Chem.* 68 (2015) 1402.
- [46] G.V.R. Chandramouli, C. Balagopalakrishna, M.V. Rajasekharan, P.T. Manoharan, *Computers Chem.* 20 (1996) 353.
- [47] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Comput. Chem.* 20 (1999) 1391.
- [48] J.C. da Rocha, G. Poneti, J.G. Ferreira, R.R. Ribeiro, F.S. Nunes, *J. Braz. Chem. Soc.* 25 (2014) 1528.
- [49] S.G. Sreerama, S. Pal, *Inorg. Chem.* 41 (2002) 4843.
- [50] A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* (2009) 5391.
- [51] A.K. Srivastava, S. Ghosh, S. Jana, S. Pal, *Inorg. Chim. Acta* 483 (2018) 329.
- [52] P. Chakraborty, S. Majumder, A. Jana, S. Mohanta, *Inorg. Chim. Acta* 410 (2014) 65.
- [53] P. Chakraborty, I. Majumder, K.S. Banu, B. Ghosh, H. Kara, E. Zangrando, D. Das, *Dalton Trans.* 45 (2016) 742.
- [54] S.K. Dey, A. Mukherjee, *Coord. Chem. Rev.* 310 (2016) 80.
- [55] S. Ganguly, P. Kar, M. Chakraborty, A. Ghosh, *New J. Chem.* 42 (2018) 9517.



Research paper

Coordination mode variation of oximate in complexes of $\text{VO}(\text{OMe})^{2+}$ and VO_2^+ with biacetylmonoxime salicyloylhydrazone: Structural confirmation, properties and photocatalytic applications

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ABSTRACT

Reaction of equimolar amounts of bis(acetylacetonato)oxidovanadium(IV) $[\text{VO}(\text{acac})_2]$ with biacetylmonoxime salicyloylhydrazone (H_3L , where three dissociable protons represent the oxime, the amide and the phenol protons) in methanol produced the dimeric oxidomethoxido vanadium(V) complex $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) in 55% yield, while the same reaction in presence of two mole equivalents of KOH afforded a pervanadyl complex $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2-MeOH**) in 60% yield. Both complexes were characterized by elemental analysis, mass spectrometry, magnetic susceptibility and electrical conductivity measurements, differential scanning calorimetry, various spectroscopy (IR, UV-Vis and ^1H NMR) and cyclic voltammetry. The diamagnetic complexes are brown in color. In solution, **1** is non-electrolytic, while **2-MeOH** behaves as 1:1 electrolyte. In solid state, they remain thermally stable up to 132 and 269 °C, respectively. X-ray crystal structures of both **1** and **2-MeOH** were determined. In the centrosymmetric edge-shared bioctahedral **1**, $(\text{HL})^{2-}$ acts as fused 5,6-membered chelate rings forming amidate-O, imine-N and oximate-O donor. In contrast, $(\text{HL})^{2-}$ acts as fused 5,5-membered chelate rings forming amidate-O, imine-N and oximate-N donor in trigonal-bipyramidal $[\text{VO}_2(\text{HL})]^-$. The infrared and ^1H NMR spectroscopic features of **1** and **2-MeOH** are consistent with their molecular structures. The electronic spectra of them in acetonitrile display several strong absorption bands within 452–207 nm. Cyclic voltammograms of the complexes and H_3L in acetonitrile solutions show irreversible reduction responses with the E_{pc} values in the potential range -0.9 to -1.5 V (vs. Ag/AgCl). Both complexes exhibit decent catalytic activity for photodegradation of rhodamine B (RhB) under visible light irradiation.

1. Introduction

Coordination complexes of vanadium are of continued interest because of their relevance to several biological processes such as haloperoxidation [1–4], nitrogen fixation [5–7], insulin mimicking [8–10] and anticancer activity [11,12]. In addition, a large number of vanadium complexes with a variety of ligands have found significant applications as catalysts in a wide range of organic transformation reactions [13,14]. As a consequence, synthesis of new coordination complexes of vanadium is receiving considerable attention to develop better functional and structural mimics of vanadium containing metalloenzymes and more efficient catalysts [15–18]. We have been working on oxidovanadium(IV/V) complexes with tri- and tetradentate Schiff bases derived by condensation reactions of acid hydrazides with *ortho*-hydroxy-aryl-aldehydes, such as pyridine-2-aldehyde and α - and β -diketones during the past couple of decades [19–23]. This type of

hydrazine based Schiff base ligands are known to exhibit non-innocent character [24,25]. These ligands being amide-O coordinating also provide the scope to study the effect of amide protonation state on the geometric and redox features of their complexes [26,27]. The ambidentate oxime containing ligands are well known to provide high-valent highly reactive metal ion complexes as well as oximate bridged polynuclear complexes [28–33]. The Schiff base 2-hydroxy-*N'*-(3-(hydroxyimino)butan-2-ylidene)benzohydrazide (IUPAC name) or biacetylmonoxime salicyloylhydrazone (H_3L) contains both the O-coordinating amide and the oxime functionalities (Chart 1). Several structurally characterized transition metal ion (V(V), Fe(III), Ni(II), Zn(II) and Ru(II)) [34–41] and one rare earth metal ion (Dy(III)) [42] complexes have been reported with this Schiff base. The tridentate ligand coordinates the metal center via the amidate-O, imine-N and oxime- or oximate-N and forms fused 5,5-membered chelate rings in all these complexes [36–42] except for the vanadium(V) complexes

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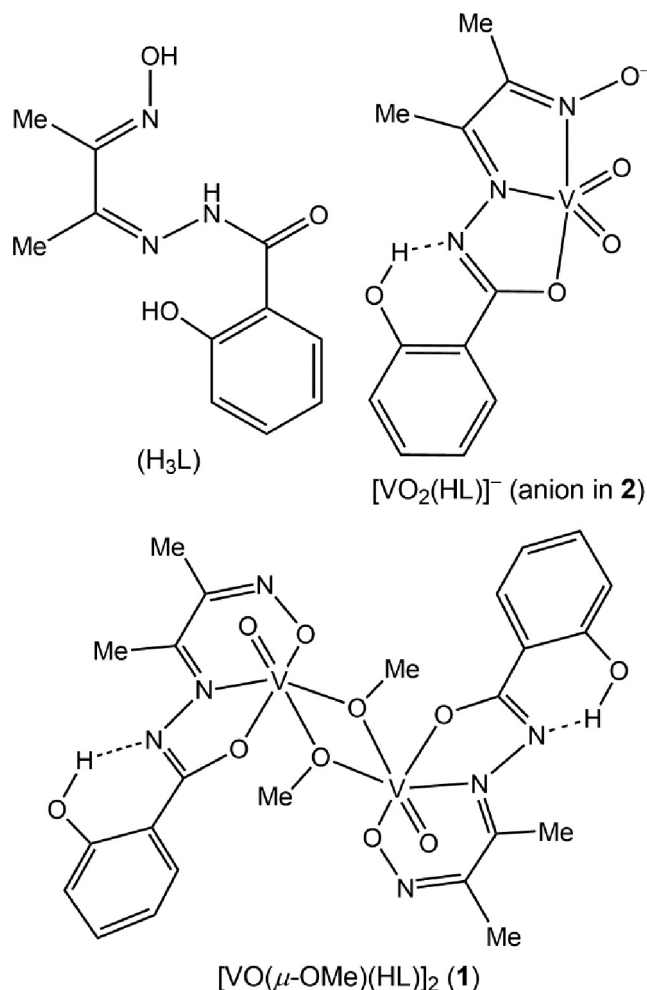


Chart 1. Chemical structure diagrams of biacetylmonoxime salicyloylhydrazone (H₃L) and the complexes [VO(μ-OMe)(HL)]₂ and [VO₂(HL)]⁻ derived from it.

[34,35]. In the vanadium(V) complexes, it acts as fused 5,6-membered chelate ring forming amidate-O, imine-N and oximate-O donor. It may be noted that vanadium(V) has the smallest effective ionic radius when compared with that of the other five metal ions [43]. It is generally observed that the large metal ions prefer to form 5-membered chelate ring, while 6-membered chelate ring is more stable with small metal ions [44,45]. Thus the oximate-O coordination and formation of the fused 5,6-membered chelate ring only in the vanadium(V) complexes is not inexplicable. In this work, we report a dimeric oxidomethoxido vanadium(V) complex [VO(μ-OMe)(HL)]₂ (**1**) and a solvated dioxido vanadium(V) complex K[VO₂(HL)]·MeOH (2·MeOH) with H₃L (Chart 1). In these two complexes, the oxime functionality of the tridentate ligand (HL)²⁻ exhibits the rare ambidentate behavior for the same metal ion. In the following sections, synthesis, X-ray crystal structures and physical properties of **1** and 2·MeOH are described. The photocatalytic activities of the two complexes in degradation of the organic dye rhodamine B (RhB) have been also evaluated.

2. Experimental

2.1. Materials

As reported in literature, biacetylmonoxime salicyloylhydrazone (H₃L) was prepared in ~70% yield by condensation reaction of equimolar amounts of biacetyl monoxime and salicyloylhydrazine in methanol [37]. Bis(acetylacetonato)oxidovanadium(IV), [VO(acac)₂], was

synthesized by following a literature procedure [46]. All other reagents and solvents used in this work were of analytical grade available commercially and were used as received without further purification.

2.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used for the microanalytical (CHN) measurements. High resolution mass spectra were recorded with a Bruker Maxis (ESI-TOF analyzer) spectrometer. A Sherwood Scientific balance was used for the measurement of magnetic susceptibilities. The solution electrical conductivities were measured using a Digisun DI-909 conductivity meter. Powder X-ray diffraction experiments were performed using a Bruker D8 Advance X-ray diffractometer. A TA Instruments Discovery DSC 250 was used for differential scanning calorimetric (DSC) measurements. The infrared spectra were collected on a Bruker TENSOR II FT-IR spectrophotometer. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used for electronic spectroscopic measurements. The ¹H NMR (400 MHz) spectra were collected on a Bruker NMR spectrometer. A CH Instruments model 620A electrochemical analyzer was used for the cyclic voltammetric experiments.

2.3. Synthesis of [VO(μ-OMe)(HL)]₂ (**1**)

A methanol solution (10 ml) of [VO(acac)₂] (80 mg, 0.3 mmol) was added to a methanol solution (10 ml) of H₃L (70 mg, 0.3 mmol) and the mixture was stirred at room temperature under aerobic conditions for 6 h. The resulting brown solution was allowed to evaporate slowly at room temperature (298 K) in air. The dark brown crystalline material separated in about 4–5 days was collected by filtration, washed with cold methanol and dried in air. Yield: 55 mg (55%). Anal. Calcd for C₂₄H₂₈N₆O₁₀V₂ (%): C, 43.52; H, 4.26; N, 12.69. Found: C, 43.58; H, 4.29; N, 12.61. HRMS in MeCN *m/z* found (calcd) for C₂₄H₂₉N₆O₁₀V₂ ([M + H]⁺): 663.4496 (663.0824). Selected IR bands: ν (cm⁻¹) = 3225 (O–H), 1623 & 1589 (C=N), 1254 (N–O), 974 (V=O). UV-Vis in MeCN: λ_{max} (nm) (ϵ (10⁴ M⁻¹ cm⁻¹)) = 375^{sh} (1.05), 270 (2.85), 207 (2.97). ¹H NMR in CDCl₃: δ (ppm) (*J* (Hz)) = 10.02 (s, 1H, phenolic-OH), 7.34 (6) (dd → t, 1H, *H* at *para* to amide), 7.33 (6) (d, 1H, *H* at *ortho* to amide), 6.92 (6) (d, 1H, *H* at *ortho* to phenolic-OH), 6.65 (6) (dd → t, 1H, *H* at *para* to phenolic-OH), 3.42 (s, 3H, OCH₃), 2.56 (s, 3H, H₃CC=NO), 1.94 (s, 3H, H₃CC=N). CV in MeCN: *E*_{pc} (V) = -1.34.

2.4. Synthesis of K[VO₂(HL)]·MeOH (2·MeOH)

A methanol solution (5 ml) of KOH (34 mg, 0.6 mmol) was added dropwise to a methanol solution (5 ml) of H₃L (70 mg, 0.3 mmol) with stirring. To the resulting light yellow solution, [VO(acac)₂] (80 mg, 0.3 mmol) was added and the mixture was stirred at room temperature (298 K) under aerobic conditions for 6 h. The brown reaction mixture was then kept at room temperature (298 K) in air for slow evaporation. The brown crystalline material precipitated in about 4–5 days was collected by filtration, washed with cold methanol and dried in air. Yield: 70 mg (60%). Anal. Calcd for C₁₂H₁₅N₃O₆KV (%): C, 37.21; H, 3.90; N, 10.85. Found C, 37.28; H, 3.86; N, 10.92. HRMS in MeOH *m/z* found (calcd) for C₁₁H₁₁N₃O₅V ([M]⁻): 316.0138 (316.0138). Selected IR bands: ν (cm⁻¹) = 3260 (O–H), 1621 & 1590 (C=N), 1253 (N–O), 939 & 915 (VO₂). UV-Vis in MeCN: λ_{max} (nm) (ϵ (10³ M⁻¹ cm⁻¹)) = 452 (5.8), 320 (7.8), 252 (10.4), 207 (23.3). ¹H NMR in (CD₃)₂SO: δ (ppm) (*J* (Hz)) = 11.78 (s, 1H, phenolic-OH), 7.72 (6, 2) (dd, 1H, *H* at *ortho* to amide), 7.37 (6, 2) (td, 1H, *H* at *para* to amide), 6.94 (6) (d, 1H, *H* at *ortho* to phenolic-OH), 6.90 (6, 2) (td, 1H, *H* at *para* to phenolic-OH), 2.43 (s, 3H, H₃CC=NO), 1.84 (s, 3H, H₃CC=N). CV in MeCN: *E*_{pc} (V) = -0.9.

2.5. X-ray crystallography

Single crystals of both $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2-MeOH**) were collected from the crystalline materials obtained during their syntheses. Unit cell determination and intensity data collection for both **1** and **2-MeOH** were performed using a BRUKER D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite monochromated Mo K α Radiation ($\lambda = 0.71073 \text{ \AA}$). The APEX3 software package [47] was used for data collection, integration, reduction and absorption correction. Each structure was solved by direct method and refined on F^2 by full matrix least-squares procedures. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the phenolic hydroxyl group in each of **1** and **2-MeOH** and the hydrogen atom of the methanolic hydroxyl group in **2-MeOH** were found in the corresponding difference maps and refined with $U_{\text{iso}} = 1.5 \times U_{\text{eq}}$ of the oxygen atoms to which they are attached. All other hydrogen atoms in both structures were included at idealized positions using a riding model. The SHELX-97 programs [48] accessed via the WinGX software suite [49] were used for structure solution and refinement. Structural illustrations were prepared using the Mercury package [50]. Selected crystallographic data are listed in Table 1.

2.6. Photocatalysis

Organic dye rhodamine B (RhB) was chosen for the heterogeneous photodegradation experiment. The powdered complex catalyst (10 mg) was suspended in a 1 μM aqueous solution of the dye (20 ml) and the suspension was magnetically stirred under aerobic conditions for $\frac{1}{2}$ h in dark to establish the adsorption/desorption equilibrium between the dye and the surface of the catalyst. The mixture was then irradiated with visible light with continuous stirring. After every 15 min of interval about 1 ml of the suspension was collected and centrifuged to remove the catalyst particulates and the clear solution obtained was used for spectrophotometric analysis. The degradation of RhB with the increase of irradiation time was monitored by measuring the change in the absorbance of its characteristic absorption band at 554 nm.

Table 1
Selected crystallographic data for **1** and **2-MeOH**.

Complex	1	2-MeOH
Chemical formula	$\text{C}_{24}\text{H}_{28}\text{N}_6\text{O}_{10}\text{V}_2$	$\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_6\text{KV}$
Formula weight	662.40	387.31
Crystal system	Monoclinic	Triclinic
Space Group	$P2_1/c$	$P\bar{1}$
<i>a</i> (Å)	7.4157(4)	7.0018(11)
<i>b</i> (Å)	18.5212(10)	11.234(2)
<i>c</i> (Å)	10.5562(5)	11.442(2)
α (°)	90	106.503(5)
β (°)	101.830(2)	106.104(5)
γ (°)	90	96.228(5)
<i>V</i> (Å ³)	1419.07(13)	811.7(3)
<i>Z</i>	2	2
ρ (g cm ⁻³)	1.550	1.585
μ (mm ⁻¹)	0.724	0.900
Reflections collected	36,866	26,078
Reflections unique	2882	3338
Reflections [$I \geq 2\sigma(I)$]	2752	3058
Data/parameters	2882/196	3338/217
<i>R</i> ₁ , <i>wR</i> ₂ [$I \geq 2\sigma(I)$]	0.0291, 0.0834	0.0298, 0.0801
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0305, 0.0845	0.0330, 0.0823
GOF on F^2	1.078	1.056
Largest diff. peak/hole (e Å ⁻³)	0.388/−0.325	0.410/−0.348

3. Results and discussion

3.1. Synthesis and characterization

The reaction of biacetylmonoxime salicyloylhydrazone (H_3L) and $[\text{VO}(\text{acac})_2]$ in 1:1 mole ratio in methanol in presence of air produced $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) in decent yield. On the other hand, if two mole equivalents of KOH was added in the above reaction mixture the product formed was $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2-MeOH**) in similar yield. The elemental (CHN) analysis data of both complexes are in good agreement with their molecular formulas. The high resolution electrospray ionization mass spectra of both species further confirm their molecular formulas (Figs. S1 and S2, supplementary material). The base peak appeared at $m/z = 663.4496$ in the spectrum of **1** recorded in the positive ionization mode. This value is consistent with the protonated species $[\text{1} + \text{H}]^+$. The spectrum of **2-MeOH** collected in negative ionization mode displayed the base peak at $m/z = 316.0138$ corresponding to the complex anion $[\text{VO}_2(\text{HL})]^-$. Room temperature (298 K) magnetic susceptibility measurements with the powdered samples of the two complexes showed their diamagnetic character. Both complexes are brown in color and highly soluble in methanol, acetonitrile, dimethylformamide and dimethylsulfoxide. In acetonitrile solution, **1** is electrically non-conducting, whereas the molar conductivity ($\Lambda_{\text{M}} = 130 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of **2-MeOH** indicates 1:1 electrolytic behavior [51]. The molecular formulas, diamagnetic character and the solution electrical conductivity behaviors suggest the +5 oxidation state of the vanadium centers in both **1** and **2-MeOH**. As the complexes were synthesized under aerobic conditions, oxygen in air is the most likely oxidizing agent for the oxidation of the tetravalent vanadium of the starting material to the pentavalent state in the products. In this context, it may be noted that although no base was used for the synthesis of **1**, but in all likelihood, the initial neutral synthesis reaction mixture became basic with the progress of the reaction due to complete reduction of oxygen and generation of the weak base (acac^-) from the dissociation of the starting material $[\text{VO}(\text{acac})_2]$. This basicity appears to be strong enough for the deprotonation of both H_3L and the bridging methanol leading to the formation of the methoxido bridged dinuclear **1**.

3.2. Description of X-ray molecular structures

The dimeric complex $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) crystallizes in the monoclinic $P2_1/c$ space group with one half of the molecule in the asymmetric unit. On the other hand, the solvated mononuclear ionic complex $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2-MeOH**) crystallizes in the triclinic $P\bar{1}$ space group and here the asymmetric unit contains the complete formula unit and one methanol molecule. The thermal ellipsoid plots of **1** and **2-MeOH** are illustrated in Figs. 1 and 2, respectively. The metal centered bond parameters of **1** and **2-MeOH** are listed in Tables 2 and 3, respectively. In general, the $\text{V}=\text{O}$ and the vanadium to other coordinating atom bond lengths in both complexes are comparable with the corresponding bond lengths in the vanadium(V) complexes with analogous ligands [19–23,34,35]. For further support of the pentavalent state of vanadium in each of **1** and **2-MeOH**, the bond valence sum calculations were performed using the EXPO2014 software [52]. The values for the oxidation state of vanadium in **1** and **2** were found to be 5.12 and 5.04, respectively.

The two halves of the dimeric molecule of **1** are related by an inversion center (Fig. 1). In the asymmetric unit, the meridionally spanning $(\text{HL})^{2-}$ coordinates to the metal center via the amidate-O, the imine-N and the oximate-O atoms (O(2), N(2) and O(1)) and forms fused 5,6-membered chelate rings. The methoxido-O (O(5)) occupies the fourth equatorial position of a NO_3 square-plane (rms deviation = 0.03 Å) and the oxido group (O(4)) occupies the apical position to complete a square-pyramidal NO_5 coordination environment around the metal center. As generally observed in square-pyramidal geometry,

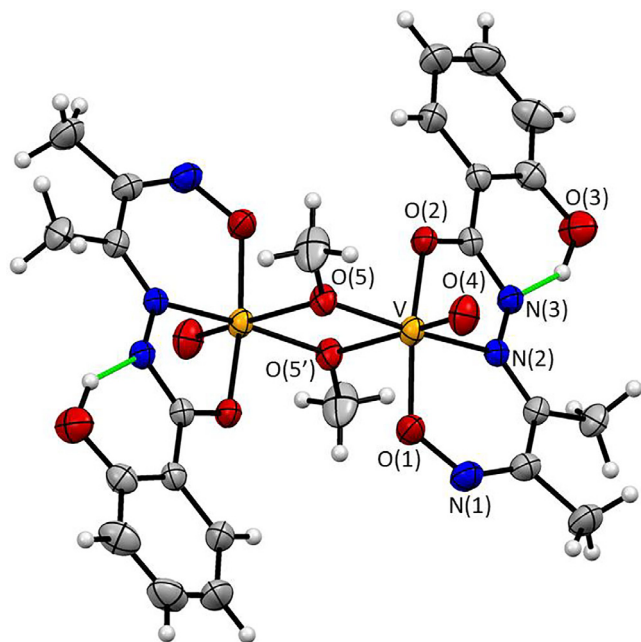


Fig. 1. The molecular structure of $[\text{VO}(\mu\text{-Ome})(\text{HL})]_2$ (**1**). The non-hydrogen atoms are displayed by their 40% probability thermal ellipsoids and only the non-carbon atoms are labeled for clarity.

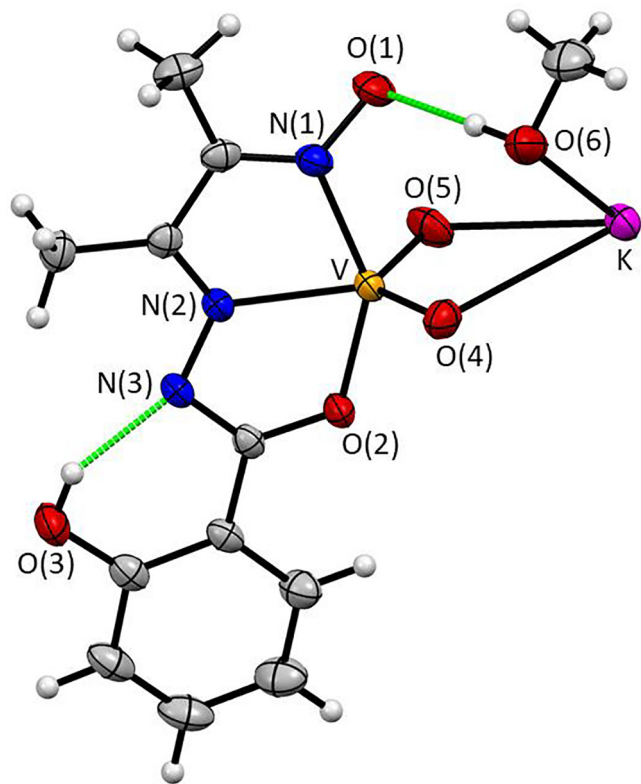


Fig. 2. The asymmetric unit of $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2·MeOH**). Thermal ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level and the carbon atoms are not labeled for clarity.

here also the vanadium atom is shifted towards the apical oxido group by 0.33 Å. Two such inversion symmetry related square-pyramidal units form the dimeric molecule where the sixth coordination sites *trans* to the oxido groups of the metal centers are occupied by the methoxido-O atoms in a reciprocal manner (Fig. 1). As a result, a divanadium(V)

Table 2

Selected bond parameters (Å and °) for $[\text{VO}(\mu\text{-Ome})(\text{HL})]_2$ (**1**).

V–O(1)	1.8217(12)	V–O(2)	1.9652(11)
V–O(4)	1.5818(13)	V–O(5)	1.8307(11)
V–O(5) ^a	2.3256(11)	V–N(2)	2.1054(13)
O(1)–V–O(2)	148.82(5)	O(1)–V–O(4)	99.90(7)
O(1)–V–O(5)	106.81(5)	O(1)–V–O(5) ^a	79.89(5)
O(1)–V–N(2)	80.42(5)	O(2)–V–O(4)	100.64(6)
O(2)–V–O(5)	90.98(5)	O(2)–V–O(5) ^a	80.99(4)
O(2)–V–N(2)	74.70(5)	O(4)–V–O(5)	103.21(6)
O(4)–V–O(5) ^a	176.47(6)	O(4)–V–N(2)	94.86(6)
O(5)–V–O(5) ^a	73.56(5)	O(5)–V–N(2)	158.81(5)
O(5) ^a –V–N(2)	88.59(4)		

^a Symmetry transformation used: 1 – x, 1 – y, 1 – z.

Table 3

Selected bond parameters (Å and °) for $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2·MeOH**).

V–O(2)	1.9647(13)	V–O(4)	1.6202(13)
V–O(5)	1.6242(14)	V–N(1)	2.0846(16)
V–N(2)	2.0844(14)		
O(2)–V–O(4)	103.03(6)	O(2)–V–O(5)	102.01(7)
O(2)–V–N(1)	146.74(6)	O(2)–V–N(2)	73.94(5)
O(4)–V–O(5)	110.38(8)	O(4)–V–N(1)	96.89(6)
O(4)–V–N(2)	120.45(7)	O(5)–V–N(1)	95.52(7)
O(5)–V–N(2)	128.71(7)	N(1)–V–N(2)	73.02(6)

core, $\{\text{OV}(\mu\text{-Ome})_2\text{VO}\}^{4+}$, is formed at the center of **1** and each metal center in it resides in a distorted octahedral NO_5 coordination sphere. On the whole, two $(\text{HL})^{2-}$, two methoxido groups and the two oxido O-atoms constitute an edge-shared bioctahedral coordination geometry ($\text{NO}_3\text{VO}_2\text{VO}_3\text{N}$). The central $\text{V}_2(\mu\text{-Ome})_2$ moiety has a pair of short (1.8307(11) Å) and a pair of long (2.3256(11) Å) V–O bond lengths. The longer ones are *trans* to the corresponding oxido groups. The V...V distance is 3.3422(5) Å. The uncoordinated phenolic-OH groups of the two $(\text{HL})^{2-}$ are involved in intramolecular strong hydrogen bonds with the uncoordinated amidate-N atoms. In this O–H...N hydrogen bond, the O...N distance and the O–H...N angle are 2.5653(18) Å and 146(3)°, respectively.

The perspective view of the asymmetric unit of **2·MeOH** is depicted in Fig. 2. In contrast to **1**, here the vanadium atom of the anion $[\text{VO}_2(\text{HL})]^-$ is penta-coordinated and the $(\text{HL})^{2-}$ coordinates to the metal center through the amidate-O, the imine-N and the oximate-N atoms (O(2), N(2) and N(1)) and creates fused 5,5-membered chelate rings. The two oxido groups (O(4) and O(5)) occupy the other two coordination sites. Based on the value of τ (0.61) [53], the N_2O_3 coordination geometry around vanadium center is best described as trigonal bipyramidal, where N(2), O(4) and O(5) create the trigonal equatorial-plane and N(1) and O(2) occupy the axial positions. In the asymmetric unit, the counter cation K^+ is coordinated by the two oxido groups and a methanol oxygen (O(6)). In addition to these three O-atoms, five more symmetry related O-atoms coordinate to the potassium atom. These are one oximate-O (O(1)), one phenol-O (O(3)), one more methanol-O and two more oxido groups. The K–O distances are in the range 2.7203(17) – 3.0740(18) Å. The KO_8 polyhedron is shown in Fig. 3. It has one tetragonal plane and ten trigonal planes. Continuous shape measures (CShM) calculations were performed to classify the observed polyhedron using the SHAPE 2.1 software [54]. The best description of the geometry around potassium is found to be distorted gyrobifastigium or Johnson solid J26 (Fig. 3 and Table S1, supplementary material) [55]. As observed in **1**, here also an intramolecular O–H...N hydrogen bond involving the phenolic-OH and the amidate-N atom is present (Fig. 2). The O...N distance and the O–H...N angle are 2.590(2) Å and 145(3)°, respectively. The methanol-OH is also involved in hydrogen bonding with the uncoordinated oximate-O atom. Here the O...O distance and the O–H...O angle are 2.745(2) Å and 174(3)°, respectively.

The crystal packing of **2·MeOH** reveals a two-dimensional

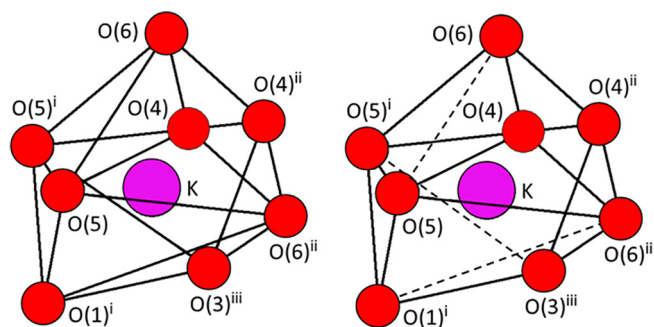


Fig. 3. The coordination polyhedron observed (left) and the calculated gyrobifastigium geometry shown by solid lines (right) around K in $K[VO_2(HL)] \cdot MeOH$ (2-MeOH). Symmetry transformations used to generate the equivalent atoms: ⁱ -x, -y, -z + 1; ⁱⁱ -x + 1, -y, -z + 1 and ⁱⁱⁱ x, y - 1, z.

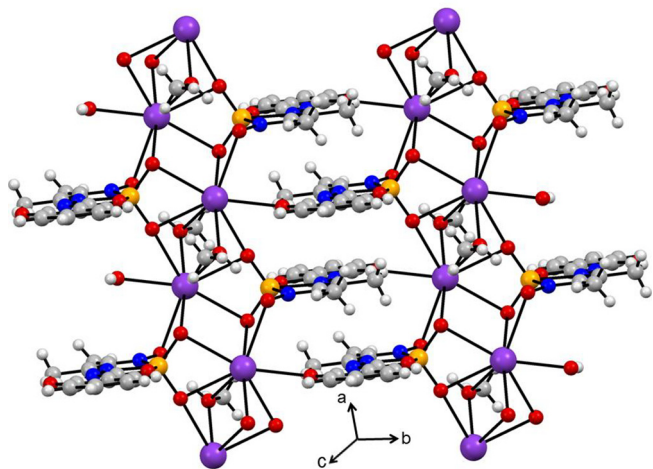


Fig. 4. Two-dimensional network structure of $K[VO_2(HL)] \cdot MeOH$ (2-MeOH).

coordination network structure (Fig. 4). The KO_8 polyhedra are interconnected in a linear fashion. In this chain structure, the K...K distance is alternating between 3.8104(10) and 4.2245(10) Å due to alternating four and two bridging atoms. In the first case, the bridging atoms are two vanadium-bound oxido and two methanol-O atoms, while, in the second case, these are two vanadium-bound oxido atoms. The complex anions are in a one-dimensional stacked columnar structure in between the $(KO_8)_n$ chains. As a result, alternating interconnected $(KO_8)_n$ and $\{[VO_2(HL)]^-\}_n$ chains assemble a two-dimensional network structure.

To examine whether the bulk material is composed of only the X-ray structurally characterized complex or a mixture of more than one complex, room temperature powder X-ray diffraction patterns of the bulk samples of both **1** and 2-MeOH were recorded using Cu K α radiation ($\lambda = 1.5406$ Å) and the experimental patterns were compared with the corresponding simulated patterns generated from the single crystal X-ray structures (Fig. S3, supplementary material). Essentially, in each case, there is a one-to-one correspondence between the peaks in the calculated pattern and those in the experimental pattern. This similarity clearly indicates the phase purity of the bulk materials for both **1** and 2-MeOH.

3.3. Thermal studies

Thermal stability of both complexes has been investigated by differential scanning calorimetry under nitrogen over the temperature range of 30–400 °C at a scan rate of 5 °C min⁻¹. The thermograms of **1** and 2-MeOH are depicted in Fig. S4 (supplementary material). Complex **1** shows an exothermic peak at 169 °C preceded by a shoulder at ~158 °C, a relatively much less intense peak at 215 °C, a broad peak

centered at ~280 °C and another small peak at 325 °C. On the other hand, 2-MeOH displays a sharp exothermic peak at 271 °C followed by a very weak shoulder like peak at ~280 °C. In each case, the first major peak is likely to be associated with the thermal decomposition process of the complex. Thus the ionic 2-MeOH is thermally much more stable than the neutral **1**.

3.4. Spectroscopic characteristics

Infrared spectra of **1** and 2-MeOH were recorded in the ATR mode (Figs. S5 and S6, supplementary material). Both spectra show a broad band at ~3240 cm⁻¹ due to the hydrogen bonded hydroxyl groups. Two medium intensity bands are observed at ~1620 and ~1590 cm⁻¹. Similar bands are assigned to the C=N(imine) and C=N(oxime) stretches, respectively [38,41]. A strong band observed at ~1254 cm⁻¹ is most likely associated with the oximate N–O stretching [28]. A strong band at 974 cm⁻¹ displayed by **1** is attributed to the V=O stretching [19,22,23,34,35]. The asymmetric and symmetric stretching bands of VO_2^+ unit in 2-MeOH appear as two strong bands at 939 and 915 cm⁻¹ [20,21].

Electronic spectra of both complexes collected using their corresponding acetonitrile solutions are illustrated in Fig. 5. The spectrum of **1** displays a strong absorption shoulder at 375 nm with a long tail extending into the visible region and two very strong bands at 270 and 207 nm. In contrast, 2-MeOH shows three strong bands at 452, 320 and 262 nm and a very strong band at 207 nm. The absorptions observed above 300 nm are attributed to ligand-to-metal charge transfer bands and the two higher energy bands observed below 300 nm are assigned to ligand-centered transitions [19–23,34,35].

The ¹H NMR spectra of **1** and 2-MeOH were recorded in CDCl₃ and (CD₃)₂SO, respectively (Figs. S7 and S8, supplementary material). The chemical shift data with the tentative assignments are listed in the experimental section with the respective complexes. The spectrum of **1** is consistent with its centrosymmetric dimeric structure. The free Schiff base (H_3L) is known to display three singlets each of one-proton at δ 11.33, 11.62 and 11.72 ppm for the amide-NH, the oxime-OH and the phenolic-OH protons, respectively [42]. In contrast, both **1** and 2-MeOH show only one sharp singlet at δ 10.02 and 11.78 ppm, respectively. Appearance of a single peak is consistent with the deprotonation of the amide-NH and the oxime-OH and the protonated state of the phenol functionality of the tridentate ligand $(HL)^{2-}$ in both complexes. Two three-proton singlets observed at δ 1.94 and 2.56 ppm for **1** and δ 1.84 and 2.43 ppm for 2-MeOH are attributed to the protons of the methyl groups at the imine and the oximate ends, respectively. The protons of the metal coordinated methoxido group of **1** are observed as a three-

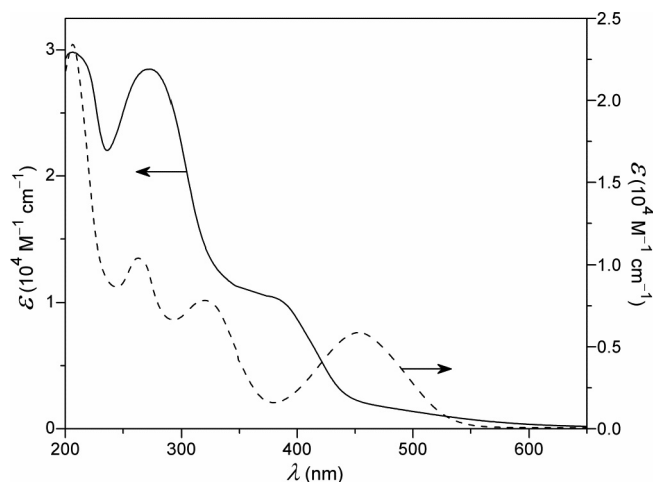


Fig. 5. Electronic spectra of $[VO(\mu-OME)(HL)]_2$ (**1**) (—) and $K[VO_2(HL)] \cdot MeOH$ (2-MeOH) (---) in acetonitrile.

proton singlet at δ 3.42 ppm. The four aromatic ring protons of **1** and 2-MeOH appear with the expected splitting patterns in the chemical shift ranges δ 6.65–7.34 and 6.90–7.72 ppm, respectively. No signal assignable to the methanol methyl protons is observed in the spectrum of 2-MeOH. Perhaps it is masked by the intense water signal at δ 3.33 ppm. Overall, the spectra of the two complexes are consistent with their corresponding molecular structures.

3.5. Redox properties

Electron transfer characteristics of **1**, 2-MeOH and the Schiff base H_3L were examined by cyclic voltammetry. Each three-electrode measurement was carried out at room temperature (298 K) with 1×10^{-3} M acetonitrile solution of the compound containing Bu_4NClO_4 (0.1 M) as the supporting electrolyte using a glassy carbon working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1} . Under identical conditions, the ferrocenium/ferrocene (Fc^+/Fc) couple was observed at $E_{1/2} = 0.58 \text{ V}$ ($\Delta E_p = 150 \text{ mV}$). The cyclic voltammograms of **1**, 2-MeOH and the Schiff base H_3L are illustrated in Fig. S9 (supplementary material). Complex **1** displays an irreversible reduction at $E_{pc} = -1.34 \text{ V}$. However, 2-MeOH shows a broad reduction peak near -0.9 V followed by a continuous increase of current. The free Schiff base H_3L also displays two irreversible broad reduction responses at -0.9 and -1.5 V . Thus the reductions observed for the complexes are very likely to be ligand centered rather than metal centered.

3.6. Photocatalytic activities

Photocatalysts are of immense contemporary interest because of their applications in effective handling of environmental pollution problems. They can be used for removal of various toxic pollutants by their degradation, generation of bio-fuels and valuable chemicals by degradation of plant biomass and for water splitting to produce clean fuel hydrogen [56–65]. In recent times, oxidovanadium(V) complexes and divanadium(V) pentoxide have found visible light driven photocatalytic applications in degradation of lignin like molecules and organic dyes [59–65]. A shoulder band at 375 nm with the tail extending up to $\sim 450 \text{ nm}$ is the lowest energy optical absorption for **1**, while that for 2-MeOH is at 452 nm (*vide supra*). Because of these absorptions, both complexes have been examined for their photocatalytic activities in degradation of the organic dye rhodamine B (RhB) under visible light irradiation. The degradation reactions performed were heterogeneous in nature. The water insoluble powdered catalyst (**1** or 2-MeOH) was added to the aqueous solution of RhB solution and the suspension was stirred and irradiated with visible light. The dye degradation was monitored spectrophotometrically. The variation of the spectroscopic profile of RhB with time in presence of the catalyst 2-MeOH is depicted in Fig. 6, while that for **1** as catalyst is shown in Fig. S10 (supplementary material). In 2 h, the extents of degradation of RhB are 84% and 91% for **1** and 2-MeOH, respectively. In the control experiment without catalyst, the decrease in the concentration of RhB solution in 2 h of exposure to light is significantly smaller (13%). The changes in the dye concentrations with the increase of irradiation time in absence and in presence of catalysts are shown in Fig. 7.

Assuming pseudo-first-order degradation of RhB, the degradation rate constants (k) for the two catalysts have been calculated using the equation $-\ln(C/C_i) = kt$ (C_i = initial concentration and C = concentration at time t). The k values obtained are $0.012(2)$ and $0.016(2) \text{ min}^{-1}$ for **1** and 2-MeOH, respectively. These rates are comparable with the rates reported for vanadium-doped nanomaterials catalyzed RhB degradation reactions under visible light irradiation [62–65]. The first absorption maxima (452 nm) of 2-MeOH is in the visible region, while that (375 nm) of **1** is in the violet end of the visible light. The band gap energies for these ligand-to-metal charge transfer bands calculated using the Tauc plot method are 2.87 and 2.42 eV for **1**

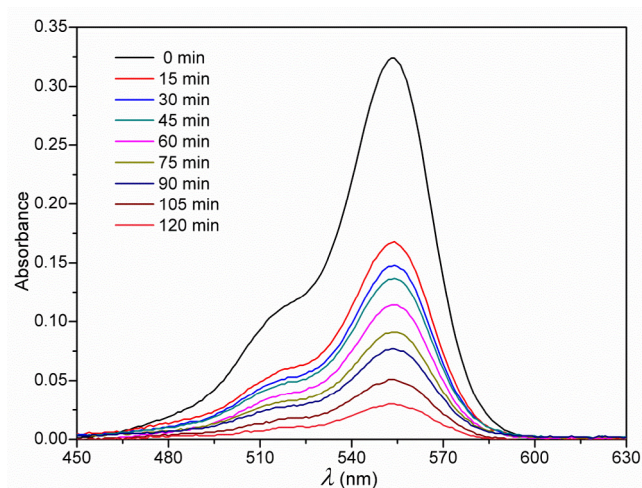


Fig. 6. Visible light driven catalytic degradation of rhodamine B (RhB) in presence of $K[VO_2(HL)] \cdot MeOH$ (2-MeOH) as catalyst using the experimental conditions described in the text.

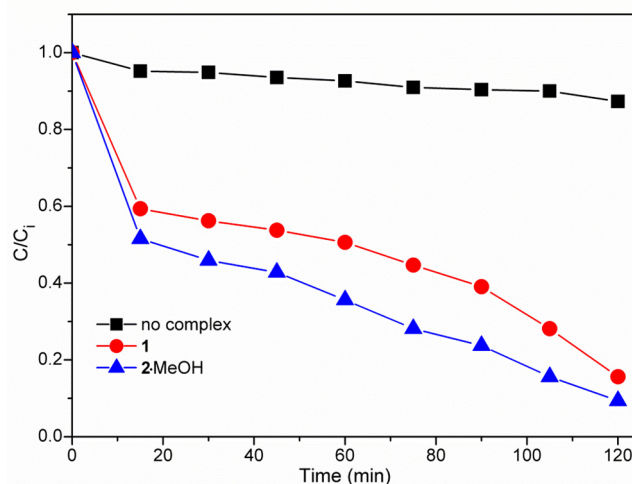


Fig. 7. Change of rhodamine B (RhB) concentration in absence and in presence of catalysts (**1** and 2-MeOH) as a function of irradiation time. C and C_i represent the dye concentrations after and before irradiation, respectively.

and 2-MeOH, respectively. Slightly better photocatalytic activity of 2-MeOH than **1** is likely to be due to the difference in their absorption maxima, and hence the corresponding band gap energies [66].

Close to 90% of each of the two complex catalysts was collected after the catalytic reaction by filtration. The infrared and 1H NMR spectra of the recovered samples showed no significant variation when compared with the corresponding spectra of the complexes before the reactions. Therefore, both complexes are recyclable and they can be reused for further catalytic cycles. Each of the two recovered catalysts was used for second time in the degradation reaction of RhB. In this second cycle, the degradation percentages of the dye were found to be 2–3% lower (82 and 88% for **1** and 2-MeOH, respectively) than those observed in the first cycle.

It has been proposed that in photocatalytic dye degradation using oxidovanadium(V) species as catalyst, the first step is an electron transfer from the photoexcited dye (RhB^*) to the oxidovanadium(V) species and hydrogen abstraction leading to the oxidation of oxidovanadium(IV) species, dye radical cation and water [61]. In the present system, it is very likely that the degradation of the dye begins in a similar fashion. Here, the catalytic reactions were performed under aerobic conditions and therefore the dissolved oxygen can regenerate

the catalyst by oxidizing the reduced complex (**1** or **2**) and itself getting reduced to reactive oxygen species such as superoxide or peroxide. These reactive species can complete the oxidative degradation of the dye radical cation. In the control experiment using either of the two catalysts under nitrogen atmosphere in presence of light, there is no significant variation of the absorption spectrum of the dye. Thus aerobic conditions are crucial for effective degradation of the dye.

4. Conclusions

Two complexes having the formulas $[\text{VO}(\mu\text{-OMe})(\text{HL})]_2$ (**1**) and $\text{K}[\text{VO}_2(\text{HL})]\cdot\text{MeOH}$ (**2-MeOH**) with the Schiff base biacetylmonoxime salicyloylhydrazone (H_3L) have been reported. The X-ray molecular structures of **1** and **2-MeOH** revealed the ambidentate coordination behavior of the oximate group (O and N) of $(\text{HL})^{2-}$. The centrosymmetric dimeric **1** is an edge-shared bioctahedral complex. Here $(\text{HL})^{2-}$ has a fused 5,6-membered chelate rings forming amidate-O, imine-N and oximate-O coordination mode. On the other hand, in **2-MeOH**, the distorted trigonal bipyramidal monoanionic complex $[\text{VO}_2(\text{HL})]^-$ contains the fused 5,5-membered chelate rings forming amidate-O, imine-N and oximate-N donor $(\text{HL})^{2-}$. The counter cation K^+ in **2-MeOH** is in distorted gyrobifastigium O_8 coordination sphere. In the crystal lattice, **2-MeOH** forms two-dimensional coordination polymeric network structure. Physical and spectroscopic characteristics of the two complexes are in good agreement with their molecular formulas and structures. Both complexes are photocatalytically active and visible light induced photodegradation of rhodamine B up to 84 and 91% has been achieved in 2 h using **1** and **2-MeOH**, respectively as catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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Appendix A. Supplementary data

CCDC 1943839 and 1943840 contain the supplementary crystallographic data for **1** and **2-MeOH**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing to data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033. Additional supplementary data (Table S1 and Figs. S1–S10) to this article can be found online at <https://doi.org/10.1016/j.ica.2019.119344>.

References

- [1] D. Rehder, *Bioinorganic Vanadium Chemistry*, Wiley, Chichester, 2008.
- [2] M.R. Maurya, *J. Chem. Sci.* 123 (2011) 215–228.
- [3] C. Leblanc, H. Vilter, J.-B. Fournier, L. Delage, P. Potin, E. Rebuffet, G. Michel, P.L. Solari, M.C. Feiters, M. Czjzek, *Coord. Chem. Rev.* 301–302 (2015) 134–146.
- [4] C.C. McLauchlan, H.A. Murakami, C.A. Wallace, D.C. Crans, *J. Inorg. Biochem.* 186 (2018) 267–279.
- [5] B.J. Hales, Vanadium nitrogenase, in: B.E. Smith, R.L. Richards, W.E. Newton (Eds.), *Catalysts for Nitrogen Fixation*, Springer, Dordrecht, 2004, pp. 255–279.
- [6] Y. Hu, C.C. Lee, M.W. Ribbe, *Dalton Trans.* 41 (2012) 1118–1127.
- [7] Y. Tanabe, Y. Nishibayashi, *Coord. Chem. Rev.* 381 (2019) 135–150.
- [8] Y. Shechter, I. Goldwasser, M. Mironchik, M. Fridkin, D. Gefel, *Coord. Chem. Rev.*

- 237 (2003) 3–11.
- [9] T. Scior, J.A. Guevara-Garcia, Q.-T. Do, P. Bernard, S. Laufer, *Curr. Med. Chem.* 23 (2016) 2874–2891.
- [10] T. Jakusch, T. Kiss, *Coord. Chem. Rev.* 351 (2017) 118–126.
- [11] I. Kostova, *Anti-Cancer Agents Med. Chem.* 9 (2009) 827–842.
- [12] E. Kioseoglou, S. Petanidis, C. Gabriel, A. Salifoglou, *Coord. Chem. Rev.* 301–302 (2015) 87–105.
- [13] H. Pellissier, *Coord. Chem. Rev.* 284 (2015) 93–110.
- [14] R.R. Langeslay, D.M. Kaphan, C.L. Marshall, P.C. Stair, A.P. Sattelberger, M. Delferro, *Chem. Rev.* 119 (2019) 2128–2191.
- [15] D.C. Crans, J.J. Smee, Vanadium, in: J.A. McCleverty, T.J. Meyer (Eds.), *Comprehensive Coordination Chemistry II*, Elsevier, 2003.
- [16] R.L. Richards, Vanadium: inorganic & coordination chemistry, *Encyclopedia of Inorganic Chemistry*, John Wiley & Sons, Ltd, Brighton, UK, 2006.
- [17] P. Galloni, V. Conte, B. Floris, *Coord. Chem. Rev.* 301–302 (2015) 240–299.
- [18] M.R. Maurya, *Coord. Chem. Rev.* 383 (2019) 43–81.
- [19] N.R. Sangeetha, S. Pal, *Bull. Chem. Soc. Jpn.* 73 (2000) 357–363.
- [20] S.N. Pal, K.R. Radhika, S. Pal, *Z. Anorg. Allg. Chem.* 627 (2001) 1631–1637.
- [21] A. Sarkar, S. Pal, *Polyhedron* 26 (2007) 1205–1210.
- [22] A. Sarkar, S. Pal, *Inorg. Chim. Acta* 362 (2009) 3807–3812.
- [23] A.K. Srivastava, S. Ghosh, S. Jana, S. Pal, *Inorg. Chim. Acta* 483 (2018) 329–336.
- [24] A. Mukhopadhyay, S. Pal, *Eur. J. Inorg. Chem.* (2009) 4141–4148.
- [25] W. Kaim, *Dalton Trans.* 48 (2019) 8521–8529.
- [26] N.R. Sangeetha, C.K. Pal, P. Ghosh, S. Pal, *J. Chem. Soc., Dalton Trans.* (1996) 3293–5296.
- [27] S.N. Pal, S. Pal, *J. Chem. Soc., Dalton Trans.* (2002) 2102–2108.
- [28] A. Chakravorty, *Coord. Chem. Rev.* 13 (1974) 1–46.
- [29] V.Y. Kukushkin, A.J.L. Pomberio, *Coord. Chem. Rev.* 181 (1999) 147–175.
- [30] P. Chaudhuri, *Coord. Chem. Rev.* 243 (2003) 143–190.
- [31] C.J. Milios, T.C. Stamatatos, S.P. Perlepes, *Polyhedron* 25 (2006) 134–194.
- [32] S.G. Sreerama, S. Pal, *Inorg. Chem.* 41 (2002) 4843–4845.
- [33] S.G. Sreerama, S. Pal, *Eur. J. Inorg. Chem.* (2004) 4718–4723.
- [34] S.P. Dash, S. Pasayat, Saswati, H.R. Dash, S. Das, R.J. Butcher, R. Dinda, *Polyhedron* 31 (2012) 524–529.
- [35] M. Sutradhar, T.R. Barman, S. Ghosh, M.G.B. Drew, *J. Mol. Struct.* 1037 (2013) 276–282.
- [36] Z.-J. Xiao, S.-X. Liu, C.C. Lin, *Chinese J. Inorg. Chem.* 20 (2004) 513–518.
- [37] S. Naskar, D. Mishra, R.J. Butcher, S.K. Chattopadhyay, *Polyhedron* 26 (2007) 3703–3714.
- [38] N. Chitrapriya, V. Mahalingam, M. Zeller, K. Natarajan, *Inorg. Chim. Acta* 363 (2010) 3685–3693.
- [39] M. Sutradhar, L.M. Carrella, E. Rentschler, *Eur. J. Inorg. Chem.* (2012) 4273–4278.
- [40] S. Martínez, F. Igoa, I. Carrera, G. Seoane, N. Veiga, A.S.S. De Camargo, C. Kremer, J. Torres, *J. Coord. Chem.* 71 (2018) 874–889.
- [41] N. Chitrapriya, V. Mahalingam, L.C. Channels, M. Zeller, F.R. Fronczek, K. Natarajan, *Inorg. Chim. Acta* 361 (2008) 2841–2850.
- [42] J.-P. Costes, C. Duhayon, *Eur. J. Inorg. Chem.* (2014) 4745–4749.
- [43] R.D. Shannon, *Acta Crystallogr. Sect. A* 32 (1976) 751–767.
- [44] R.D. Hancock, *Pure Appl. Chem.* 58 (1986) 1445–1452.
- [45] R.D. Hancock, *Chem. Soc. Rev.* 42 (2013) 1500–1524.
- [46] R.A. Rowe, M.M. Jones, *Inorg. Synth.* 5 (1957) 113–116.
- [47] APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2016.
- [48] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 64 (2008) 112–122.
- [49] L.J. Farrugia, *J. Appl. Crystallogr.* 45 (2012) 849–854.
- [50] F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P.M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Crystallogr.* 41 (2008) 466–470.
- [51] W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81–122.
- [52] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, *J. Appl. Cryst.* 46 (2013) 1231–1235.
- [53] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, *J. Chem. Soc., Dalton Trans.* (1984) 1349–1356.
- [54] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, SHAPE, version 2.1, Universitat de Barcelona, Barcelona, Spain, 2013.
- [55] D. Casanova, M. Llunell, P. Alemany, S. Alvarez, *Chem. Eur. J.* 11 (2005) 1479–1494.
- [56] Q.-Q. Xiao, D. Liu, Y.-L. Wei, G.-H. Cui, *Polyhedron* 158 (2019) 342–351.
- [57] X.-J. Wei, D. Liu, Y.-H. Li, G.-H. Cui, *J. Solid State Chem.* 272 (2019) 138–147.
- [58] S. Ghosh, A.K. Srivastava, S. Pal, *New J. Chem.* 43 (2019) 970–978.
- [59] S. Gazi, W.K.H. Ng, R. Ganguly, A.M.P. Moeljadi, H. Hirao, H.S. Soo, *Chem. Sci.* 6 (2015) 7130–7142.
- [60] S. Gazi, M. Dokić, A.M.P. Moeljadi, R. Ganguly, H. Hirao, H.S. Soo, *ACS Catal.* 7 (2017) 4682–4691.
- [61] Y. Li, J.-L. Kuang, Y. Lu, W.-B. Cao, *Acta Metall. Sin. (Engl. Lett.)* 30 (2017) 1017–1026.
- [62] X. Hu, T. Mohamood, W. Ma, C. Chen, J. Zhao, *J. Phys. Chem. B* 110 (2006) 26012–26018.
- [63] A.A. Taha, A.A. Hriez, Y.-N. Wu, H. Wang, F. Li, *J. Colloid Interface Sci.* 417 (2014) 199–205.
- [64] D. Lu, B. Zhao, P. Fang, S. Zhai, D. Li, Z. Chen, W. Wu, W. Chai, Y. Wu, N. Qi, *Appl. Surf. Sci.* 359 (2015) 435–448.
- [65] M. Epifani, S. Kaciulis, A. Mezzi, D. Altamura, C. Giannini, R. Díaz, C. Force, A. Genç, J. Arbiol, P. Siciliano, E. Comini, I. Concina, *Sci. Rep.* 7 (2017) 44763.
- [66] A. Hassan, T. Iqbal, M.B. Tahir, S. Afsheen, *Int. J. Energy Res.* 43 (2019) 9–28.



One-dimensional manganese(III) and iron(III) coordination polymers assembled by N₂O₂-donor Schiff bases and 4,4'-bipyridine: syntheses, structures and properties

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Abstract. Reactions of Mn(ClO₄)₂·6H₂O and Fe(ClO₄)₃·6H₂O with the tetradentate N₂O₂-donor Schiff bases *N,N'*-bis(salicylidene)-*ortho*-phenylenediamine and *N,N'*-bis(salicylidene)ethylenediamine (H₂salophen and H₂salen, where 2 Hs represent the two dissociable phenolic protons), respectively and the bridging ligand 4,4'-bipyridine (bipy) in presence of triethyl amine in methanol under ambient conditions produce one dimensional coordination polymers {[Mn(salophen)(μ-bipy)]ClO₄}_n (**1**) and {[Fe(salen)(μ-bipy)]ClO₄}_n (**2**) in ~60% yields. Both complexes have been characterized by elemental analysis and spectroscopic (IR and DR) measurements. The linear polymeric structures of **1** and **2** have been confirmed by single-crystal X-ray crystallography. The metal centres in these polymers are in distorted octahedral N₄O₂ coordination spheres. Each of the two dibasic tetradentate ligands (salophen²⁻ and salen²⁻) forms an ONNO square-plane around the metal centre, while the two axial coordination sites are occupied by N-atoms of the two bridging bipy ligands. Variable temperature magnetic susceptibility measurements reveal the high-spin configuration of manganese(III) and iron(III) and Curie paramagnetic behaviour of each of the two coordination polymers.

Keywords. Manganese(III); Iron(III); Schiff bases; 4,4'-bipyridine; Coordination polymers; Crystal structures; Physical properties.

1. Introduction

Since the first classification of infinite linear inorganic chain compounds as coordination polymers in 1964,¹ the design and synthesis of polymeric coordination compounds have attracted immense attention due to their interesting solid-state assembly patterns and the consequent electronic, optical and magnetic properties.^{2–11} The network structures and the physical properties of these compounds have led to their applications in a wide variety of research areas such as gas absorption, separation and storage; molecule-based conductors, magnets and sensors; nonlinear optical materials and catalysis.^{6–11} As a result, there is a constant effort for new coordination polymers having potential for use as functional materials and

efficient catalysts. We have been working on structural aspects and catalytic applications of coordination polymers involving some 3d metal ions for quite some time.^{12–14} Herein, we report two analogous one-dimensional coordination polymers of manganese(III) and iron(III) having the formulas {[Mn(salophen)(μ-bipy)]ClO₄}_n (**1**) and {[Fe(salen)(μ-bipy)]ClO₄}_n (**2**) assembled from square-planar N₂O₂ coordination geometry forming Schiff bases *N,N'*-bis(salicylidene)-*ortho*-phenylenediamine (H₂salophen) and *N,N'*-bis(salicylidene)ethylenediamine (H₂salen), respectively and the bridging ligand 4,4'-bipyridine (bipy) (Figure 1). In the following account, syntheses, single-crystal X-ray structures and the physical properties of **1** and **2** have been described.

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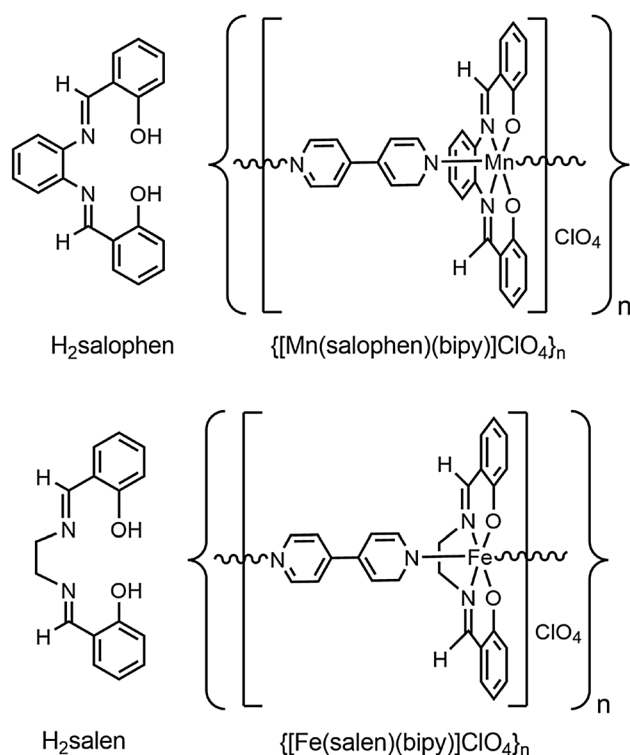


Figure 1. Chemical structure diagrams of the teradentate Schiff bases and the corresponding one-dimensional manganese(III) and iron(III) coordination polymers.

2. Experimental

2.1 Materials

The Schiff bases H_2salen and $H_2salophen$ were prepared from two-mole equivalents of salicylaldehyde and one mole equivalent of ethylene diamine and *ortho*-phenylenediamine, respectively in methanol by following a reported procedure.¹⁵ All other chemicals used in this work were of analytical grade available commercially and were used as received without any further purification. Solvents used were purified by standard methods.¹⁶

2.2 Physical measurements

Elemental (CHN) analyses were performed with the help of a Thermo Finnigan Flash EA1112 series elemental analyser. A Quantum Design SQUID-VSM instrument was used for solid-state variable temperature magnetic susceptibility measurements. The infrared spectra were recorded in ATR mode on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer. The electronic spectra were recorded in the solid-state diffuse-reflectance spectroscopy (DRS)

mode with the help of a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere.

2.3 Synthesis of $\{[Mn(salophen)(\mu\text{-}bipy)]ClO_4\}_n$ (1)

To a suspension of $H_2salophen$ (95 mg, 0.3 mmol) in 10 mL of methanol NEt_3 (60 mg, 0.6 mmol) and 4,4'-bipyridine (bipy) (47 mg, 0.3 mmol) were added and stirred for 10 min. To the resulting mixture a methanol solution (10 mL) of $Mn(ClO_4)_2 \cdot 6H_2O$ (110 mg, 0.3 mmol) was added and stirred in the air at room temperature (298 K) for 2 h. The brown solution obtained was filtered and the filtrate was kept for slow evaporation. The dark crystalline material separated in about 7–10 days was collected by filtration and dried in vacuum. Yield: 120 mg (64%). Anal. Calcd for $C_{30}H_{22}N_4O_6ClMn$: C, 57.66; H, 3.55; N, 8.97. Found: C, 57.62; H, 3.56; N, 8.91. Selected IR bands: ν (cm^{-1}) = 1599 (azomethine-CN), 1064 and 621 (ClO_4^-). UV-Vis (diffuse reflectance) bands: λ_{max} (nm) = 570^{sh}, 450^{sh}, 350, 252.

2.4 Synthesis of $\{[Fe(salen)(\mu\text{-}bipy)]ClO_4\}_n$ (2)

The iron(III) coordination polymer was also synthesized in methanolic medium by using H_2salen , NEt_3 , 4,4'-bipyridine (bipy) and $Fe(ClO_4)_3 \cdot 6H_2O$ in the same mole ratio and the same procedure as described for **1**. Yield: 105 mg (60%). Anal. Calcd for $C_{26}H_{22}N_4O_6ClFe$: C, 54.05; H, 3.84; N, 9.70. Found: C, 54.15; H, 3.86; N, 9.62. Selected IR bands: ν (cm^{-1}) = 1617 (azomethine-CN), 1083 and 618 (ClO_4^-). UV-Vis (diffuse reflectance) bands: λ_{max} (nm) = 580^{sh}, 442, 345, 248.

2.5 X-ray crystallography

A single crystal of $\{[Mn(salophen)(\mu\text{-}bipy)]ClO_4\}_n$ (**1**) suitable for X-ray data collection was collected from the crystalline material obtained from its synthesis reaction mixture. On the other hand, X-ray quality crystals of $\{[Fe(salen)(\mu\text{-}bipy)]ClO_4\}_n$ (**2**) were grown by slow evaporation of its solution in acetonitrile. Complex **1** crystallized as it is without any solvent molecule, while complex **2** formed an acetonitrile solvate **2**· CH_3CN . X-ray intensity data for both crystals were collected at 298 K on a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an INCOATEC microfocus source for graphite-monochromated Mo $K\alpha$ radiation (λ =

0.71073 Å). Data collection and reduction were performed with the help of APEX3 package.¹⁷ Absorption corrections were applied using the SADABS program.¹⁸ Each of the two structures was solved by direct method and refined on F^2 by full-matrix least-squares procedures. All non-hydrogen atoms of **1** and except for the non-hydrogen atoms of the two half-occupancy CH₃CN molecules, which were refined isotropically, the remaining non-hydrogen atoms of **2**·CH₃CN were refined with anisotropic thermal parameters. All hydrogen atoms of both structures were included in the structure factor calculations at idealized positions by using a riding model. The SHELX-97 programs¹⁹ available in the WinGX package²⁰ were used for structure solution and refinement. The structural illustrations were prepared using the Mercury package.²¹ Selected crystal data and refinement summary for both structures are listed in Table 1.

3. Results and Discussion

3.1 Synthesis and characterization

{[Mn(salophen)(μ-bipy)]ClO₄}_n (**1**) and {[Fe(salen)(μ-bipy)]ClO₄}_n (**2**) were synthesized in decent yields (64 and 60%, respectively) by reacting hexahydrated manganese(II) and iron(III) perchlorates,

the corresponding Schiff bases H₂salophen and H₂salen, 4,4'-bipyridine and triethylamine in 1:1:1:2 mole ratio in methanol at room temperature (300 K) under aerobic conditions. Both **1** and **2** are brown in colour. The elemental (CHN) analysis data of the two compounds are in good agreement with their molecular formulas. In the solid state, room temperature (300 K) magnetic moments of the repetitive mononuclear units are 4.61 and 6.02 μ_B for **1** and **2**, respectively. These values are close to the spin-only magnetic moments of 4.89 and 5.92 μ_B calculated for $S = 2$ and $S = 5/2$ spin states for the manganese(III) and iron(III) centres in **1** and **2**, respectively. In the case of **1**, it is very likely that the oxygen in air oxidized the manganese centre from bivalent state to the trivalent state during its synthesis from manganese(II) perchlorate under aerobic conditions.

3.2 X-ray structures

The structures of **1** and **2**·CH₃CN were solved in the space groups $P2_1/c$ and $P\bar{1}$, respectively. The asymmetric unit of **1** contains two repetitive units of the polymer, while that of **2**·CH₃CN contains one repetitive unit of the polymer and two half occupancy acetonitrile molecules. In both coordination polymers, the perchlorate ions are somewhat close to the metal coordinated polarized azomethine C–H groups

Table 1. Selected crystal data and structure refinement summary.

Complex	1	2 ·CH ₃ CN
Chemical formula	C ₃₀ H ₂₂ N ₄ O ₆ ClMn	C ₂₈ H ₂₅ N ₅ O ₆ ClFe
Formula weight	624.91	618.83
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
<i>a</i> (Å)	11.7703(5)	9.6938(18)
<i>b</i> (Å)	30.1432(16)	11.533(3)
<i>c</i> (Å)	16.4637(8)	15.084(3)
α (°)	90	102.352(13)
β (°)	99.697(2)	102.883(12)
γ (°)	90	105.925(13)
Volume (Å ³)	5757.8(5)	1511.2(5)
<i>Z</i>	8	2
ρ (g cm ^{−3})	1.442	1.360
μ (mm ^{−1})	0.602	0.635
Reflections collected	208861	49255
Reflections unique	10099	5285
Reflections [$I \geq 2\sigma(I)$]	8068	3800
Data / restr. / param.	10099/0/757	5285/0/369
<i>R</i> 1, <i>wR</i> 2 [$I \geq 2\sigma(I)$]	0.0648, 0.1945	0.0950, 0.2421
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0813, 0.2063	0.1283, 0.2594
GoF on F^2	1.062	1.095
Max./Min. $\Delta\rho$ (e Å ^{−3})	1.698/−0.688	1.222/−0.586

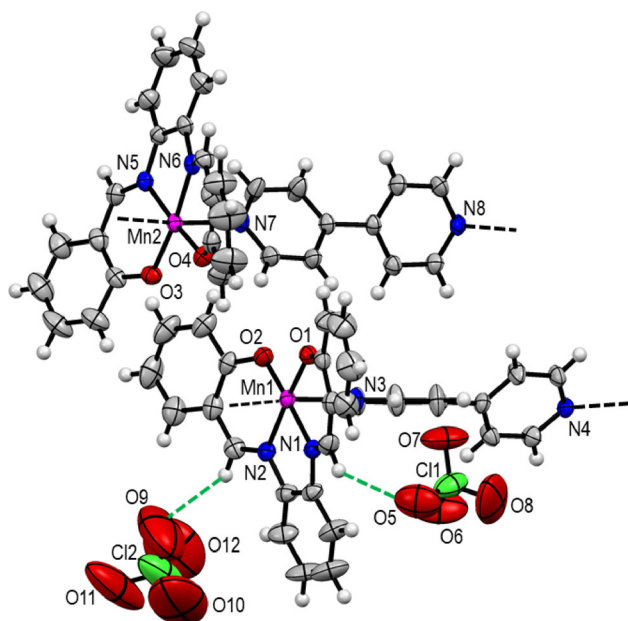


Figure 2. The asymmetric unit of **1** with the atom labelling scheme. Thermal ellipsoids of all non-hydrogen atoms are drawn at the 50% probability level. For clarity only the non-carbon atoms are labelled.

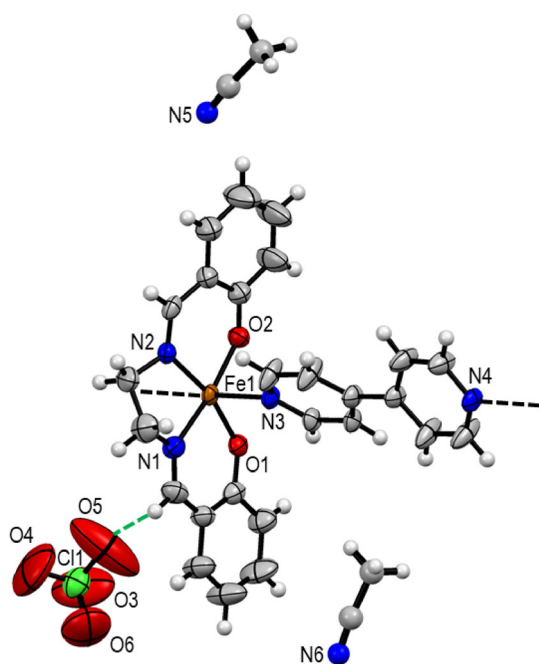


Figure 3. The asymmetric unit of **2**·CH₃CN with the atom labelling scheme. Thermal ellipsoids of all non-hydrogen atoms except for those of the two half-occupancy CH₃CN molecules are drawn at the 50% probability level. For clarity the carbon atoms are not labelled.

indicating hydrogen bonding interactions. The shortest C...O distances and the corresponding C–H...O angles are in the ranges 3.360(14)–3.618(16) Å and

123–163°, respectively. However, no significant close contact could be detected for the two half-occupancy acetonitrile molecules with the complex cation or perchlorate ion in **2**·CH₃CN. The structures of the asymmetric units of **1** and **2**·CH₃CN are illustrated in Figures 2 and 3, respectively. Metal centred geometric parameters of both are listed in Table 2. In the asymmetric unit of **1**, the bond lengths and angles associated with the manganese centres of the two repetitive cations are very similar. In each of [Mn(salophen)(μ-bipy)]⁺ and [Fe(salen)(μ-bipy)]⁺, the metal ion is in a distorted octahedral N₄O₂ coordination sphere assembled by the N₂O₂-donor Schiff base ligand and two N-atoms of the two bridging 4,4'-bipyridine molecules. The tetradentate Schiff base forms an ONNO square-plane around the metal centre. There is no deviation of the metal ion from this square-plane. The rms deviations from the mean plane constituted by the metal centre and the four coordinating atoms are about 0.03 and 0.07 Å for **1** and **2**, respectively. The N-atoms of two symmetry related 4,4'-bipyridine molecules satisfy the two axial positions of the metal centre in each of the planar {Mn(salophen)}⁺ and {Fe(salen)}⁺ units. As a result infinite linear chains of [Mn(salophen)(μ-bipy)]⁺ and [Fe(salen)(μ-bipy)]⁺ are formed in the crystal lattices of **1** and **2**·CH₃CN, respectively (Figure 4). The bridging 4,4'-bipyridine moieties are twisted in both complexes. The twisting is relatively more in **1** than in **2**. In the asymmetric unit of **1**, the dihedral angles between the two pyridine rings are 49.7(2)° and 37.8(2)° in the first and the second [Mn(salophen)(μ-bipy)]⁺ units, respectively, whereas, in [Fe(salen)(μ-bipy)]⁺, the dihedral angle is 28.2(4)°. The metal to coordinating atom distances observed for [Mn(salophen)(μ-bipy)]⁺ and [Fe(salen)(μ-bipy)]⁺ are comparable with bond lengths reported for manganese(III) and iron(III) complexes, respectively, having similar coordinating atoms.^{22–25} Bond valence sum calculations were also carried out using the EXPO2014²⁶ software for further confirmation of the oxidation states. The values obtained are 3.21 and 3.19 for the two metal centres of the two [Mn(salophen)(μ-bipy)]⁺ units present in the asymmetric unit of **1**, whereas that is 2.99 for iron in [Fe(salen)(μ-bipy)]⁺ present in the asymmetric unit of **2**·CH₃CN.

3.3 Spectroscopic properties

Infrared spectra of **1** and **2** were recorded in the range 4000–400 cm^{−1}. Both spectra display a large number of bands of various intensities (Figure 5). No attempt

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**·CH₃CN.

[Mn(salophen)(μ-bipy)]ClO ₄ (1)			
Mn(1)–O(1)	1.871(3)	Mn(2)–O(3)	1.886(3)
Mn(1)–O(2)	1.879(3)	Mn(2)–O(4)	1.865(3)
Mn(1)–N(1)	1.984(3)	Mn(2)–N(5)	1.977(3)
Mn(1)–N(2)	1.983(3)	Mn(2)–N(6)	1.994(3)
Mn(1)–N(3)	2.315(3)	Mn(2)–N(7)	2.334(3)
Mn(1)–N(4') ^a	2.396(3)	Mn(2)–N(8') ^a	2.390(3)
O(1)–Mn(1)–O(2)	95.05(13)	O(3)–Mn(2)–O(4)	94.10(12)
O(1)–Mn(1)–N(1)	91.91(13)	O(3)–Mn(2)–N(5)	91.80(13)
O(1)–Mn(1)–N(2)	173.09(14)	O(3)–Mn(2)–N(6)	172.84(13)
O(1)–Mn(1)–N(3)	90.74(13)	O(3)–Mn(2)–N(7)	91.72(12)
O(1)–Mn(1)–N(4') ^a	89.19(12)	O(3)–Mn(2)–N(8') ^a	89.32(12)
O(2)–Mn(1)–N(1)	172.87(13)	O(4)–Mn(2)–N(5)	172.81(13)
O(2)–Mn(1)–N(2)	91.41(13)	O(4)–Mn(2)–N(6)	92.69(13)
O(2)–Mn(1)–N(3)	92.10(12)	O(4)–Mn(2)–N(7)	94.21(12)
O(2)–Mn(1)–N(4') ^a	91.52(12)	O(4)–Mn(2)–N(8') ^a	88.72(12)
N(1)–Mn(1)–N(2)	81.70(14)	N(5)–Mn(2)–N(6)	81.27(13)
N(1)–Mn(1)–N(3)	89.32(12)	N(5)–Mn(2)–N(7)	89.73(12)
N(1)–Mn(1)–N(4') ^a	87.06(12)	N(5)–Mn(2)–N(8') ^a	87.23(12)
N(2)–Mn(1)–N(3)	86.57(13)	N(6)–Mn(2)–N(7)	90.02(12)
N(2)–Mn(1)–N(4') ^a	93.09(12)	N(6)–Mn(2)–N(8') ^a	88.59(12)
N(3)–Mn(1)–N(4') ^a	176.38(12)	N(7)–Mn(2)–N(8') ^a	176.82(12)
[Fe(salen)(μ-bipy)]ClO ₄ ·CH ₃ CN (2·CH ₃ CN)			
Fe(1)–O(1)	1.871(4)	Fe(1)–O(2)	1.906(4)
Fe(1)–N(1)	2.123(6)	Fe(1)–N(2)	2.097(5)
Fe(1)–N(3)	2.231(5)	Fe(1)–N(4') ^b	2.232(5)
O(1)–Fe(1)–O(2)	105.9(2)	O(1)–Fe(1)–N(1)	88.7(2)
O(1)–Fe(1)–N(2)	165.0(2)	O(1)–Fe(1)–N(3)	90.24(19)
O(1)–Fe(1)–N(4') ^b	88.80(19)	O(2)–Fe(1)–N(1)	164.5(2)
O(2)–Fe(1)–N(2)	89.0(2)	O(2)–Fe(1)–N(3)	86.6(2)
O(2)–Fe(1)–N(4') ^b	90.8(2)	N(1)–Fe(1)–N(2)	76.8(2)
N(1)–Fe(1)–N(3)	88.1(2)	N(1)–Fe(1)–N(4') ^b	94.8(2)
N(2)–Fe(1)–N(3)	92.9(2)	N(2)–Fe(1)–N(4') ^b	88.8(2)
N(3)–Fe(1)–N(4') ^b	176.9(2)		

Symmetry transformations used to generate equivalent atoms: ^a x + 1, y, z. ^b x, y + 1, z.

was made to assign all the bands except for a selected few. The free Schiff bases H₂salophen and H₂salen are reported to show the phenolic-OH stretches as a broad band centred at 3450 and 3318 cm^{−1}, respectively.^{27,28} As expected no such band is present in the spectra of **1** and **2** due to the deprotonation of the phenolic-OH groups in both compounds. A sharp and strong band observed at 1599 cm^{−1} for **1** is assigned to the azomethine C=N group. This C=N stretching band in **1** is about 11 cm^{−1} lower than that in the free H₂salophen.²⁷ Similarly **2** displays a sharp and strong band at 1617 cm^{−1}, which is about 15 cm^{−1} lower than that in the corresponding free Schiff base.²⁸ The shift of the C=N stretch to lower energy in each of the two polymers is consistent with the coordination of the azomethine-N atom to the metal centre. The presence of the perchlorate ion in **1** and **2** is indicated by a very strong and broad band centred at ~1070 cm^{−1} and a sharp strong band at ~620 cm^{−1}.

The optical features of **1** and **2** were determined by UV–Vis diffuse reflectance spectroscopy using BaSO₄ as the reference. The spectral profiles are very similar except for some shift in the band positions and variations in their relative intensities (Figure 6). Both compounds display a weak shoulder at ~575 nm, followed by a relatively strong absorption at ~455 nm and two very strong absorptions at ~348 and ~250 nm. The electronic spectra of H₂salophen and H₂salen are known to show three strong absorptions in the range 368–214 nm.^{27,29} A ligand centred absorption band of the 4,4'-bipyridine has been reported to be observed at 363 nm.³⁰ Thus, for **1** and **2**, the two bands in the ultraviolet region (~348 and ~250 nm) are assigned to ligand centred transitions and the two visible region absorptions (~575 and ~455 nm) are attributed to ligand-to-metal charge transfer (LMCT) transitions. Previously reported manganese(III) and iron(III) complexes with salen type ligands display LMCT bands in the comparable wavelength range.^{24,25,31}

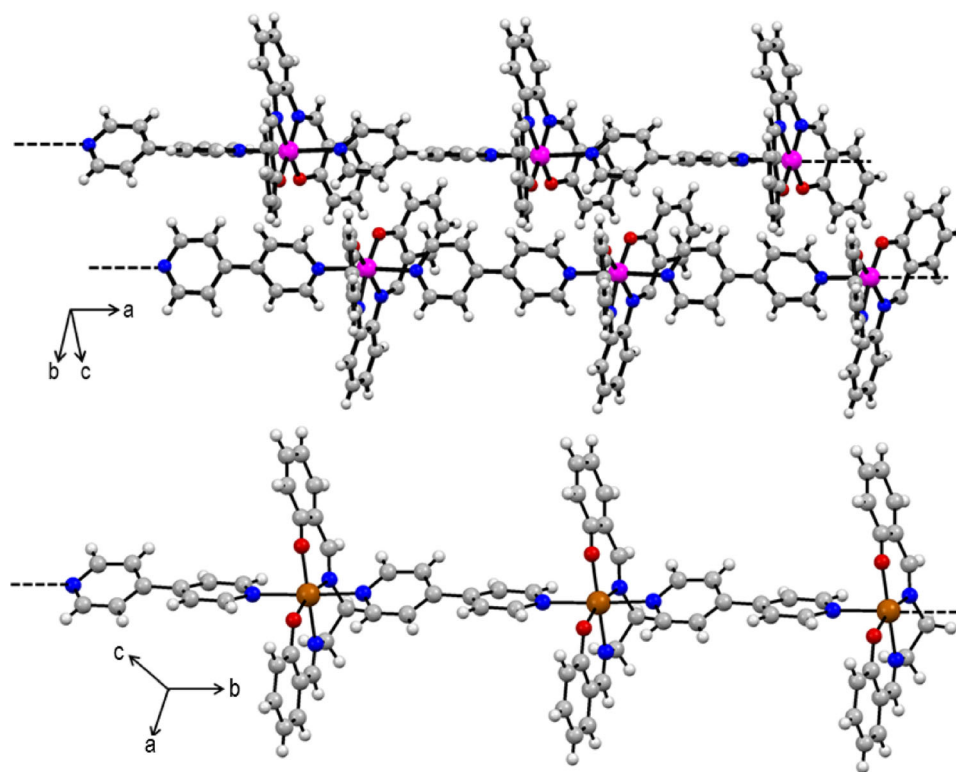


Figure 4. One-dimensional linear structures of $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]^+\}_n$ (top) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]^+\}_n$ (bottom).

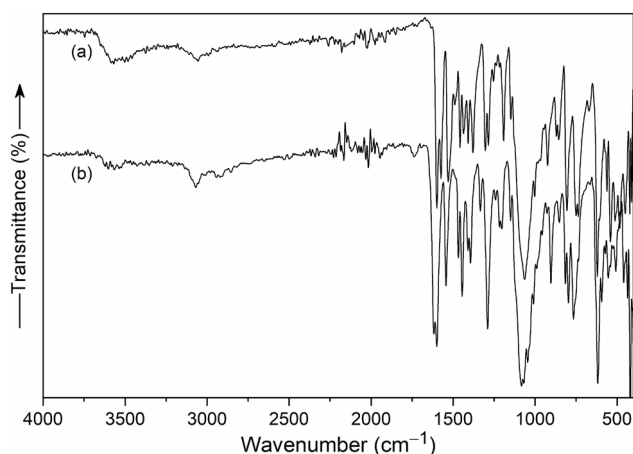


Figure 5. Infrared spectra of (a) $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) and (b) $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**).

3.4 Magnetic properties

The magnetic properties of **1** and **2** were investigated by variable temperature magnetic susceptibility measurements with their powdered samples in the temperature range 5–300 K at a constant magnetic field of 1000 Oe. The effective magnetic moment (μ_{eff}) of the repetitive unit of **1** is found to be $4.61 \mu_{\text{B}}$ at 300 K, which is somewhat lower than the calculated spin-only value

($4.89 \mu_{\text{B}}$) of high-spin manganese(III) ($S = 2$). There is essentially no change in the magnetic moment with lowering of temperature down to 65 K, where μ_{eff} is $4.59 \mu_{\text{B}}$ (Figure 7). On further lowering the temperature it increases slightly and becomes $4.65 \mu_{\text{B}}$ at 20 K and then decreases rapidly to a value of $4.34 \mu_{\text{B}}$. In case of the repetitive unit of **2**, the μ_{eff} is $6.02 \mu_{\text{B}}$ at 300 K, which is very close to the spin-only value ($5.92 \mu_{\text{B}}$) of high-spin iron(III) ($S = 5/2$). With lowering of temperature the μ_{eff} decreases and reaches the value of $5.91 \mu_{\text{B}}$ at 50 K and then increases slightly to $5.94 \mu_{\text{B}}$ at 20 K (Figure 7). Below 20 K the μ_{eff} decreases rather sharply to a value of $5.68 \mu_{\text{B}}$ at 5 K. The extents of overall decrease of the μ_{eff} values due to lowering of temperature from 300 to 5 K are 0.27 and $0.34 \mu_{\text{B}}$ for **1** and **2**, respectively. Thus it appears that there is no significant spin-spin interaction in either of the two coordination polymers. The inverse molar magnetic susceptibility values of the repetitive units of **1** and **2** are plotted against temperature (Figure 7). A near perfect linear plot has been obtained for each of **1** and **2**. In both cases, the data were fitted using the expression for the Curie–Weiss law. The Curie (C in $\text{cm}^3 \text{K mol}^{-1}$) and Weiss (θ in K) constants obtained are 2.65 and -0.40 for **1** and 4.55 and -1.87 for **2**. The linear plots and the intercepts very close to the origin indicate the Curie paramagnetic behaviour of

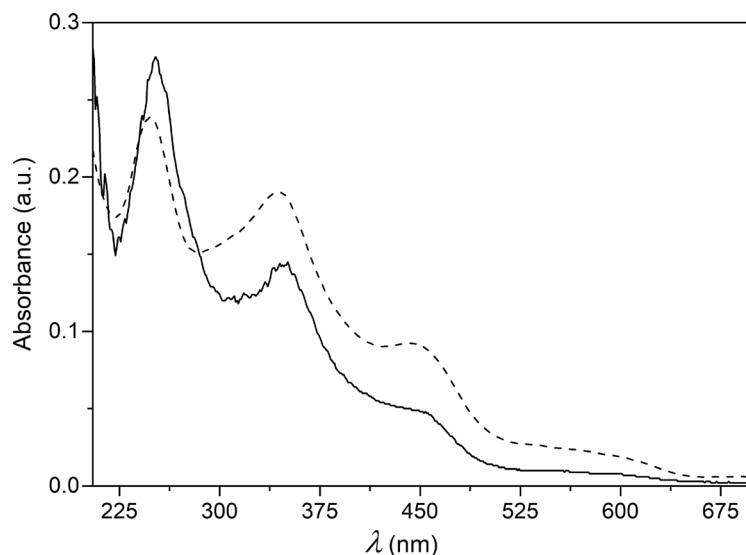


Figure 6. Diffuse reflectance spectra of $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) (solid trace) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) (dashed trace).

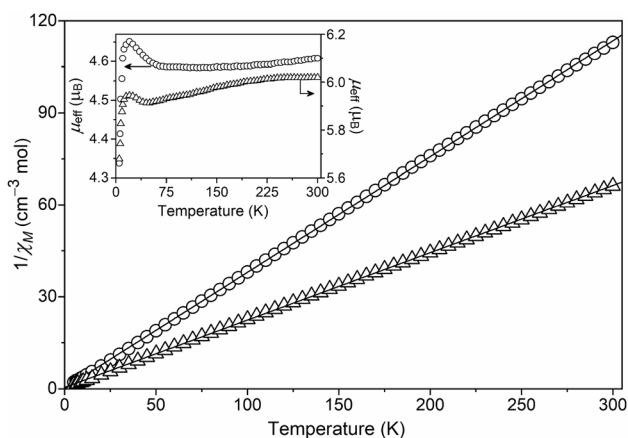


Figure 7. Inverse molar magnetic susceptibility as a function of temperature for $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) (O) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) (Δ). The straight lines represent linear least-squares fits. Inset: Variation of effective magnetic moments with temperature for $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) (O) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) (Δ).

both coordination polymers. The μ_{eff} calculated from the above mentioned values of C are 4.60 and 6.03 μ_{B} for **1** and **2**, respectively. Generally very weak or no spin-spin interactions are reported for 4,4'-bipyridine bridged complexes.^{23,32} A possible explanation proposed for such magnetic behaviour is as follows.³² The single bond character of the C–C bond (1.477(5) and 1.491(5) Å in **1** and 1.482(9) Å in **2**) between the two pyridine rings of the bridging 4,4'-bipyridine allows unhindered twisting of the two pyridine rings around this C–C bond (*vide supra*) and therefore prevents the super-exchange pathway *via* the pyridine ring π -electrons for effective spin-spin interaction between the bridged metal ions.

4. Conclusions

Syntheses and characterization of two one-dimensional coordination polymers of formulas $\{[\text{Mn}(\text{salophen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**1**) and $\{[\text{Fe}(\text{salen})(\mu\text{-bipy})]\text{ClO}_4\}_n$ (**2**) with N_2O_2 -donor Schiff base ligands (salophen²⁻ and salen²⁻) and 4,4'-bipyridine (bipy) are reported. Structures of both coordination polymers were determined by single crystal X-ray crystallography. In each structure, the twisted 4,4'-bipyridine molecules act as bridges by occupying the axial coordination sites of the metal ions of the planar $\{\text{M}(\text{salophen/salen})\}^+$ units and assemble the one-dimensional linear structures of $\{[\text{M}(\text{salophen/salen})(\mu\text{-bipy})]\}^+_n$. Microanalytical and the solid state infrared and electronic spectroscopic characteristics of both polymeric compounds are consistent with their structures. Variable temperature magnetic susceptibility studies revealed the $S = 2$ and $5/2$ spin states of the metal ions in **1** and **2**, respectively and their Curie paramagnetic character due to twisting of the bridging 4,4'-bipyridine, which does not allow any super-exchange induced spin-spin interaction between the metal ions.

Supplementary Information (SI)

CCDC 2077457 and 2077458 contain the supplementary crystallographic data for **1** and **2**·CH₃CN, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing to data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12

Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033.

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References

- Bailar JC Jr 1964 In *Preparative Inorganic Reactions* Vol. 1 WL Jolly (Ed.) (Interscience: New York) pp. 1–25
- Murugavel R, Anantharaman G, Krishnamurthy D, Sathiyendiran M and Walawalkar MG 2000 Extended metal–organic solids based on benzenepolycarboxylic and aminobenzoic acids *Proc. Indian Acad. Sci. (Chem. Sci.)* **112** 273
- Rajput L, Sarkar M and Biradha K 2010 Assembling one-dimensional coordination polymers into three-dimensional architectures via hydrogen bonds *J. Chem. Sci.* **122** 707
- Dzhardimalieva GI and Uflyand IE 2017 Design and synthesis of coordination polymers with chelated units and their applications in nanomaterials science *RSC Adv.* **7** 42242
- Engel ER and Scott JL 2020 Advances in the green chemistry of coordination polymer materials *Green Chem.* **22** 3693
- Chen C-T and Suslick KS 1993 One-dimensional coordination polymers: Applications to material science *Coord. Chem. Rev.* **128** 293
- Batten SR, Neville SM and Turner DR 2009 *Coordination Polymers: Design, Analysis and Application* (Cambridge: RSC Publishing)
- Mas-Ballesté R, Gómez-Herrero J and Zamora F 2010 One-dimensional coordination polymers on surfaces: towards single molecule devices *Chem. Soc. Rev.* **39** 4220
- Leong WL and Vittal JJ 2011 One-Dimensional Coordination Polymers: Complexity and Diversity in Structures, Properties, and Applications *Chem. Rev.* **111** 688
- Loukopoulos E and Kostakis GE 2018 Review: Recent advances of one-dimensional coordination polymers as catalysts *J. Coord. Chem.* **71** 371
- Liu J-Q, Luo Z-D, Pan Y, Singh AK, Trivedi M and Kumar A 2020 Recent developments in luminescent coordination polymers: Designing strategies, sensing application and theoretical evidences *Coord. Chem. Rev.* **406** 213145
- Sangeetha NR and Pal S 2000 Dimeric and polymeric square-pyramidal copper(II) complexes containing equatorial–apical chloride or acetate bridges *Polyhedron* **19** 1593
- Das S, Maloth S and Pal S 2011 Nickel(II) Coordination Polymers – 4,4'-Bipyridine-Connected Six- and Four-fold Metal–succinate Helices and Their Corresponding Chiral and Achiral Networks *Eur. J. Inorg. Chem.* 4270
- Srivastava AK, Ghosh S and Pal S 2019 A one-dimensional polymeric mixed-valent Mn(II)Mn(III) complex with a macrocyclic compartmental ligand: Structure, properties and catecholase like activity *Polyhedron* **172** 112
- Zhou L, Feng Y, Cheng J, Sun N, Zhou X and Xiang H 2012 Simple, selective, and sensitive colorimetric and ratiometric fluorescence/phosphorescence probes for platinum(II) based on Salen-type Schiff bases *RSC Adv.* **2** 10529
- Perrin DD, Armarego WLF and Perrin DP 1983 *Purification of Laboratory Chemicals* (Oxford: Pergamon)
- APEX3: Program for Data Collection on Area Detectors, 2014 Bruker Analytical X-ray Systems Inc., Madison Wisconsin, USA
- Sheldrick GM 1997 *SADABS. Program for Area Detector Absorption Correction* (University of Göttingen: Göttingen)
- Sheldrick GM 2008 A short history of SHELX *Acta Crystallogr. Sect. A* **64** 112
- Farrugia LJ 1999 WinGX suite for small-molecule single-crystal crystallography *J. Appl. Crystallogr.* **32** 837
- Macrae F, Bruno IJ, Chisholm JA, Edgington PR, Cabel PM, Pidcock E, et al. 2008 New features for the visualization and investigation of crystal structures *J. Appl. Crystallogr.* **41** 466
- Zhou Y-X, Zheng X-F, Han D, Zhang H-Y, Shen X-Q, Niu C-Y, et al. 2006 Syntheses and Crystal Structures of Fe(III) and Mn(III) Complexes with Salen Ligands: [Fe(salen)Cl]·CH₃CN and [Mn(salen)(SCN)(CH₃OH)]·CH₃CN *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **36** 693
- Deawati Y, Onggo D, Mulyani I, Hastiawan I, Kurnia D, Lönnecke P, et al. 2018 Synthesis, crystal structures, and superoxide dismutase activity of two new multinuclear manganese(III)-salen-4,4'-bipyridine complexes *Inorg. Chim. Acta* **482** 353
- Shova S, Vlad A, Cazacu M, Krzystek J, Bucinsky L, Breza M, et al. 2017 A five-coordinate manganese(III) complex of a salen type ligand with a positive axial anisotropy parameter *D Dalton Trans.* **46** 11817
- Cozzolino M, Leo V, Tedesco C, Mazzeo M and Lamberti M 2018 Salen, salan and salalen iron(III) complexes as catalysts for CO₂/epoxide reactions and ROP of cyclic esters *Dalton Trans.* **47** 13229
- Altomare A, Cuocci C, Giacovazzo C, Moliterni A, Rizzi R, Corriero N and Falcicchio A 2013 EXPO2013: a kit of tools for phasing crystal structures from powder data *J. Appl. Crystallogr.* **46** 1231

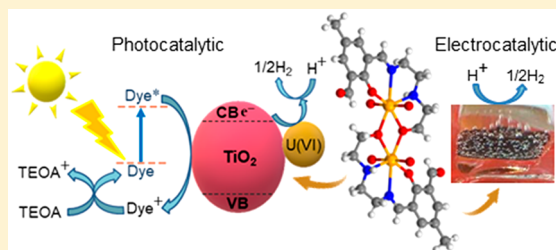
27. Koley MK, Sivasubramanian SC, Varghese B, Manoharan PT and Koley AP 2012 A paramagnetic octahedral trans-dihydroxy chromium(IV) complex with dianionic tetradentate Schiff base salophen and crystal structure of its *trans*-diisothiocyanato analog *J. Coord. Chem.* **65** 3623
28. Hu X-M, Xue L-W, Zhao G-Q and Yang W-C 2015 Synthesis, Crystal Structure and Antimicrobial Activity of a Hetero Trinuclear Manganese(III)-Iron(II) Complex Derived from *N,N'*-Bis(5-methylsalicylidene)-1,2-diaminoethane *Bull. Chem. Soc. Ethiop.* **29** 407
29. Gao T, Yang Y, Sun W-B, Li G-M, Hou G-F, Yan PF, et al. 2013 Syntheses, structure and near-infrared (NIR) luminescence of Er₂, Yb₂, ErYb of homodinuclear and heterodinuclear lanthanide(III) complexes based on salen ligand *CrystEngComm* **15** 6213
30. Xiu-min S, Hai-yan W, Yan-bing L, Jing-xiu Y, Lei C, Ge H, et al. 2010 Spectroscopic studies on Co(II), Ni(II), Zn(II) complexes with 4,4'-bipyridine *Chem. Res. Chin. Univ.* **26** 1011
31. Kurahashi T and Fujii H 2012 Comparative Spectroscopic Studies of Iron(III) and Manganese(III) Salen Complexes Having a Weakly Coordinating Triflate Axial Ligand *Bull. Chem. Soc. Jpn.* **85** 940
32. Li M-X, Xie G-Y, Gu Y-D, Chen J and Zheng P-J 1995 Synthesis, characterization and magnetic properties of one-dimensional 4,4'-bipyridine bridged manganese(II) complex: crystal structure of [Mn(μ -4,4'-bipy)(4,4'-bipy)(NCS)₂(H₂O)₂]_n *Polyhedron* **14** 1235

A Diuranyl(VI) Complex and Its Application in Electrocatalytic and Photocatalytic Hydrogen Evolution from Neutral Aqueous Medium

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S Supporting Information

ABSTRACT: The reaction of equimolar amounts of $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 2,6-diformyl-4-methylphenol, and *N*-(hydroxyethyl)-ethylenediamine in methanol affords a dinuclear *trans*-uranyl(VI) complex of the molecular formula $[(\text{UO}_2)_2(\mu\text{-L})_2]$ ($\text{L}^{2-} = 2\text{-formyl-4-methyl-6-}((2\text{-(2-oxidoethylamino)ethylimino)methyl)phenolate}$) in 65% yield. Detailed structural elucidation of the complex was performed by using single-crystal X-ray crystallographic and spectroscopic studies. In $[(\text{UO}_2)_2(\mu\text{-L})_2]$, the metal centers are in edge-shared pentagonal-bipyramidal N_2O_5 coordination spheres assembled by the two meridional ONNO-donor bridging L^{2-} and two pairs of mutually trans oriented oxo groups. The complex is redox active and displays two successive metal-centered one-electron reductions at $E_{\text{pc}} = -0.71$ and -1.03 V in *N,N*-dimethylformamide solution. The redox-active complex was used as a heterogeneous catalyst for electrochemical hydrogen evolution from aqueous medium at pH 7 with a turnover frequency (TOF) of 384 h^{-1} and a Tafel slope of 274 mV dec^{-1} . The Faradaic efficiency of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ was found to be 84%. Beyond the electrocatalytic response, the $[(\text{UO}_2)_2(\mu\text{-L})_2]\text{-TiO}_2\text{-N719}$ composite also exhibited significant heterogeneous photocatalytic hydrogen evolution activity in neutral aqueous medium under visible light and provided a yield of $3439\text{ }\mu\text{mol g}_{\text{cat}}^{-1}$ of H_2 in 4 h with a TOF of 172 h^{-1} and apparent quantum yield (AQY) of 7.6%.



■ INTRODUCTION

One of the major concerns of the present day is to have a source of clean and green energy. Hydrogen is not only an environmentally friendly and renewable source of energy without emission of any carbon-based greenhouse gas during combustion but it also has the highest gravimetric energy density for any fuel known to date.¹ In nature, hydrogenase enzymes utilize iron and/or nickel cofactors to produce hydrogen from neutral aqueous medium with turnover frequencies (TOFs) ranging from 100 to 10000 s^{-1} .² However, the complexity of the macromolecules as well as their inefficiency to work under aerobic conditions has restricted their practical usage. Thus, immense efforts have been devoted to the development of efficient, robust, and inexpensive catalysts for the production of hydrogen from water.^{3,4} Hydrogen can be generated by both photocatalytic and electrocatalytic water-splitting reactions. The platinum-based electrocatalysts are considered to be ideal for hydrogen production because they have low overpotentials along with Tafel slopes as low as 30 mV dec^{-1} , but then again, they suffer the problem of high cost due to the low abundance of platinum.^{5,6} Several other earth-abundant 3d and 4d transition metal containing catalysts under both homogeneous and heterogeneous conditions have been shown to be quite efficient and robust in aqueous as well as nonaqueous medium.^{3,4,6}

Fujishima and Honda carried out the first photoelectrochemical water splitting reaction in 1972, using a TiO_2 electrode as anode and a platinum electrode as cathode.⁷ However, the reaction has a low quantum efficiency. Among the various semiconductors available, TiO_2 possesses better light-harvesting capacity and low Fermi energy levels to undergo water-splitting reactions. However, its major drawback is the high band gap (3.2 eV), which obstructs light absorption from the visible region. To overcome this drawback, there is a continuous quest for the design and synthesis of new photocatalysts which not only possess better light-harvesting ability but also can absorb visible light, which is about 40% of the total sunlight.^{3,8,9}

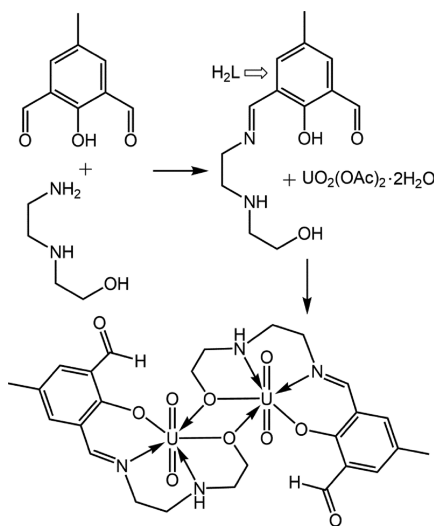
Depleted uranium forms a major source of radioactive waste all over the world. Thus, the utilization of uranium as a catalyst toward hydrogen production from water can be considered as a major step forward toward a clean and green environment. The application of low-valent uranium as a catalyst in electrolytic water reduction has been recently reported by Meyer and co-workers,¹⁰ and it happens to be the first report on uranium acting as an electrocatalyst for the hydrogen evolution reaction (HER). In the present article, we report the synthesis, characterization, X-ray crystal structure, and physical properties of a high-valent dinuclear *trans*-uranyl(VI) complex with

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the molecular formula $[(\text{UO}_2)_2(\mu\text{-L})_2]$ (H_2L is 2-hydroxy-3-((2-(2-hydroxyethylamino)ethylimino)methyl)-5-methylbenzaldehyde, where the two Hs represent the dissociable phenolic and alcoholic protons) (Scheme 1) and its use for efficient reduction of water to hydrogen by both electrocatalytic and photocatalytic methods.

Scheme 1. Synthesis of $[(\text{UO}_2)_2(\mu\text{-L})_2]$



EXPERIMENTAL SECTION

Materials. 2,6-Diformyl-4-methylphenol was prepared by following a reported procedure.¹¹ All other chemicals and solvents used in this work were of reagent grade and were used as received without any further purification.

Physical Measurements. Elemental (CHN) analysis data were obtained with the help of a Thermo Finnigan Flash EA1112 series elemental analyzer. Solid-state magnetic susceptibility measurements were performed with a Sherwood Scientific balance. A Digisun DI-909 conductivity meter was used for solution electrical conductivity measurements. Mass spectra were recorded with a Bruker Maxis (ESI-TOF analyzer) spectrometer. A Thermo Scientific Nicolet iSS FT-IR spectrophotometer was used to record the infrared (IR) spectra in ATR mode. A Shimadzu UV-3600 UV-vis-NIR spectrophotometer was used to collect the electronic absorption spectra. Cyclic and differential pulse voltammetric (CV and DPV) measurements with *N,N*-dimethylformamide solutions of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ were carried out using a CH Instruments Model 620A electrochemical analyzer. A Varian 720-ES ICP-OES spectrometer was used for determination of the uranium content. XPS measurements were carried out on a Thermo Scientific K-Alpha⁺ spectrometer. Gas chromatographic measurements were performed using a PerkinElmer Clarus 590 gas chromatograph equipped with a thermal conductivity detector and a molecular sieve 5 Å column. Diffuse reflectance spectra were recorded using BaSO_4 as the reference on a PerkinElmer Lambda 750 UV-vis-NIR spectrophotometer fitted with an integrating sphere. A Newport 450 W xenon lamp was used for photocatalytic experiments.

Synthesis of $[(\text{UO}_2)_2(\mu\text{-L})_2]$. A solution of *N*-(hydroxyethyl)-ethylenediamine (42 mg, 41 μL , 0.4 mmol) in methanol (10 mL) was added to a methanol solution (10 mL) of 2,6-diformyl-4-methylphenol (66 mg, 0.4 mmol), and the mixture was boiled under reflux for 1 h. To the resulting solution was added a solution of $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (170 mg, 0.4 mmol) in methanol (10 mL) dropwise, and the mixture was refluxed for another 3 h. A microcrystalline orange solid that separated on cooling to room temperature (298 K) was collected by filtration and dried in air. For recrystallization, the solid obtained was dissolved in an *N,N*-dimethylformamide/methanol (1/1) mixture and allowed to evapo-

rate slowly. The crystalline material that deposited in about 8–10 days was collected by filtration and dried under vacuum. Yield: 135 mg (65%). Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_{10}\text{U}_2$ (1036.61): C, 30.12; H, 3.11; N, 5.40. Found: C, 30.19; H, 3.07; N, 5.48. Selected IR data (ν (cm^{-1})): 3225 (N–H), 2831 ((O)C–H), 1676 (C=O), 1625 (C=N), 886 (UO_2). UV-vis data (λ_{max} (nm) (ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$))): 465 (0.9), 396 (4.1), 372 (4.7). ESI-MS (m/z): calcd for $\text{C}_{26}\text{H}_{33}\text{N}_4\text{O}_{10}\text{U}_2^+$ 1037.3212, found 1037.3099. CV data (E_{pc} (V)): −0.71, −1.03. DPV data (E_{p} (V)): −0.56, −0.86.

X-ray Crystallography. A single crystal suitable for X-ray data collection was selected from the recrystallized sample of the complex. Unit cell determination and the intensity data collection at room temperature (298 K) were performed on a Bruker D8 Quest diffractometer fitted with a Photon 100 CMOS area detector and an Incoatec microfocus source for graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data acquisition, integration, and reduction were done using the APEX3 software package.¹² An empirical multiscan absorption correction was applied to the data using the SADABS program.¹³ The structure was solved by direct methods in space group $P2_1/c$ and refined on F^2 using full-matrix least-squares procedures. The asymmetric unit contains half of the dinuclear molecule. All of the non-hydrogen atoms were refined using anisotropic displacement parameters, whereas the hydrogen atoms were placed at idealized positions and were refined as riding atoms. The SHELX-97 programs¹⁴ provided in the WinGX software suite¹⁵ were used for structure solution and refinement. Structural illustrations were prepared using the Mercury package.¹⁶ Significant crystal and refinement data are summarized in Table 1.

Table 1. Selected Crystal Data for $[(\text{UO}_2)_2(\mu\text{-L})_2]$

chem formula	$\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_{10}\text{U}_2$
formula wt	1036.62
cryst syst	monoclinic
space group	$P2_1/c$
<i>a</i> (Å)	7.6504(6)
<i>b</i> (Å)	7.4471(5)
<i>c</i> (Å)	26.094(2)
β (deg)	98.150(3)
<i>V</i> (Å ³)	1471.63(19)
<i>Z</i>	2
ρ (g cm ^{−3})	2.339
μ (mm ^{−1})	11.052
no. of rflns collected	54912
no. of unique rflns	2588
no. of rflns with $I \geq 2\sigma(I)$	2276
no. of data/restraints/params	2588/0/191
<i>R</i> ₁ , <i>wR</i> ₂ ($I \geq 2\sigma(I)$)	0.0283, 0.0584
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0356, 0.0603
GOF on F^2	1.191
largest diff peak/hole (e Å ^{−3})	1.008/−1.546

Electrocatalytic Studies. All of the electrochemical hydrogen evolution studies were done with the help of a Zahner Zanium electrochemical workstation using a three-electrode system. The measurements were carried out using a $[(\text{UO}_2)_2(\mu\text{-L})_2]$, carbon black and Nafion coated fluorine doped tin oxide (FTO) glass plate as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl reference electrode in 0.1 M phosphate buffer of pH 7 (unless otherwise mentioned) at room temperature (298 K). Sample preparation for the coating of the FTO plate was as follows: to a mixture of 4 mg of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ and 1 mg of carbon black in 1 mL of an ethanol/water (3/2 v/v) mixture was added 10 μL of 5 wt % Nafion, and the whole mixture was sonicated for 2 h. A 30 μL portion of this mixture was then coated on a FTO plate of area 0.2 cm². The coating on the FTO plate surface was then dried by an IR lamp. The area of the electrode was maintained at 0.2 cm² for all of the electrochemical experiments unless mentioned otherwise. The open-

circuit potential was used as the initial potential for all of the cyclic voltammetric measurements using the surface-coated FTO electrode. All electrode potentials were converted to the reversible hydrogen electrode (RHE) scale using the equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.2$.

Preparation of Dye-Adsorbed Composite Photocatalyst. N719 dye (1.19 mg, 1 μmol) was dissolved in an ethanol/acetonitrile mixture (20 mL, 1/1 v/v). To this solution were added $[(\text{UO}_2)_2(\mu\text{-L})_2]$ (5.5 mg, 5.3 μmol) and TiO_2 (100 mg, 1.25 mmol), and the mixture was stirred at room temperature (298 K) in the dark for 24 h. The solvent was then evaporated by rotavaporation, and the solid obtained was dried under vacuum at 50–60 °C. The product thus obtained was tested for photocatalytic activity. The same experimental conditions and procedures were used for the preparation of all other composite photocatalysts having different dyes such as 4-hydroxycoumarin and Coumarin 343.

Photocatalytic Studies. The photocatalytic hydrogen evolution experiments were carried out in a quartz reactor. The photocatalyst (10 mg) was added to an aqueous solution (20 mL) of triethanolamine (TEOA) (10 vol %), and the mixture was sonicated for complete dispersion of the catalyst. The pH of the mixture in the reactor was maintained at 7 using 1 M hydrochloric acid, and it was purged with nitrogen for 30 min. The mixture was then stirred and irradiated with light from a 450 W xenon lamp. The hydrogen production rate was analyzed by sampling the evolved gas at periodic intervals (every 1 h) using online gas chromatography.

RESULTS AND DISCUSSION

Synthesis and Characterization. The complex $[(\text{UO}_2)_2(\mu\text{-L})_2]$ was synthesized in good yield (65%) by reacting $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ with in situ prepared 2-hydroxy-3-((2-(2-hydroxyethylamino)ethylimino)methyl)-5-methylbenzaldehyde (H_2L) from 2,6-diformyl-4-methylphenol and *N*-(hydroxyethyl)ethylenediamine in methanol under reflux conditions (Scheme 1). The molecular formula of the complex is in good agreement with the elemental analysis data. The complex is insoluble in common organic solvents and is sparingly soluble in *N,N*-dimethylformamide and dimethyl sulfoxide. In solution, it is electrically nonconducting. A room-temperature magnetic susceptibility measurement indicates its diamagnetic character. The nonelectrolytic behavior and the diamagnetic nature of the complex are consistent with its neutral molecular formula and the +6 oxidation state of the metal centers, respectively.

X-ray Structure. The structure of the dinuclear $[(\text{UO}_2)_2(\mu\text{-L})_2]$ is illustrated in Figure 1. Selected bond parameters are given in Table 2. The halves of the dinuclear molecule are related by an inversion center. Coordination of the metal centers by the two meridionally spanning L^{2-} ligands through their bridging ethoxide O, secondary amine N, azomethine N, and phenolate O atoms results in the formation of fused 5,5,6-membered chelate rings and two edge-shared pentagonal N_2O_3 planes (rms deviation 0.99 Å). Four oxo groups occupy the axial sites of the two metal atoms and complete the edge-shared pentagonal-bipyramidal N_2O_5 coordination spheres around the two uranium atoms (Figure 1). It may be noted that not many structurally characterized discrete diuranyl(VI) complexes having such an edge-shared pentagonal-bipyramidal molecular structure are known.¹⁷ The four-membered bridging U_2O_2 unit is perfectly planar, and the $\text{U}\cdots\text{U}$ distance and $\text{U}-\text{O}-\text{U}$ and $\text{O}-\text{U}-\text{O}$ angles are 3.9067(5) Å and 111.2(2)° and 68.8(2)°, respectively. The $\text{U}(1)-\text{O}(1)$ and $\text{U}(1)-\text{O}(1')$ bond lengths are comparable with the uranium(VI) to bridging alkoxide O distances observed before.^{17c,18} Overall the $\text{U}=\text{O}$, $\text{U}-\text{O}(\text{phenolate})$,

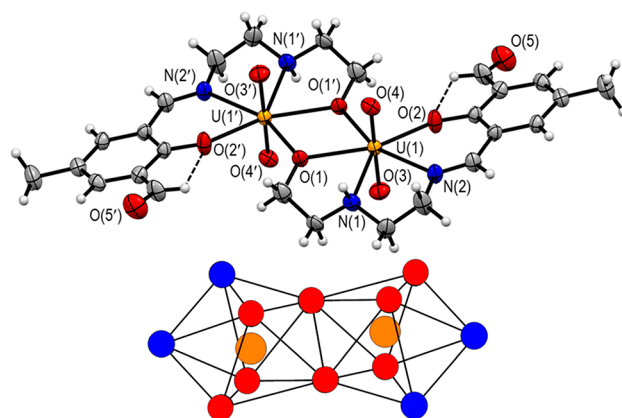


Figure 1. ORTEP drawing of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ (top) and the edge-shared pentagonal-bipyramidal N_2O_5 coordination spheres around the uranium atoms (bottom). In the ORTEP drawing, all of the non-hydrogen atoms are represented by their 40% probability thermal ellipsoids and only the noncarbon atoms are labeled for clarity.

$\text{U}-\text{N}(\text{azomethine})$, and $\text{U}-\text{N}(\text{amine})$ bond lengths in $[(\text{UO}_2)_2(\mu\text{-L})_2]$ are within the ranges reported for uranium(VI) complexes having similar coordinating atoms.^{17–19}

The dinuclear complex molecule contains two types of potential hydrogen bond donors, the formyl C–H and the secondary amine N–H groups, and several O atoms that can act as hydrogen bond acceptors. Thus, the structure was further scrutinized for intermolecular hydrogen-bonding interactions and the resulting supramolecular self-assembled structure. Interestingly, the formyl group is coplanar with rest of the six-membered chelate ring forming fragment of L^{2-} and the formyl $\text{C}(13)-\text{H}$ is oriented toward $\text{O}(2)$, the metal-coordinated phenolate O (Figure 1). This orientation indicates that, instead of any intermolecular interaction, it participates in an intramolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding interaction. Here the $\text{H}\cdots\text{O}$ distance is 2.53 Å and the $\text{C}\cdots\text{O}$ distance and the $\text{C}-\text{H}\cdots\text{O}$ angle are 2.835(8) Å and 99°, respectively. On the other hand, out of the two amine groups only one ($\text{N}(1)-\text{H}$) participates in an intermolecular strong $\text{N}-\text{H}\cdots\text{O}$ interaction with $\text{O}(4)$, one of the two metal-bound oxo groups. Here the $\text{N}\cdots\text{O}$ and $\text{H}\cdots\text{O}$ distances are 3.041(8) and 2.18 Å, respectively, while the $\text{N}-\text{H}\cdots\text{O}$ angle is 157°. Due to this hydrogen bonding there is a small difference (by 0.016 Å) in the two $\text{U}=\text{O}$ lengths (Table 2). This intermolecular $\text{N}-\text{H}\cdots\text{O}$ interaction leads to a one-dimensional array of the complex molecules in the crystal lattice (Figure 2).

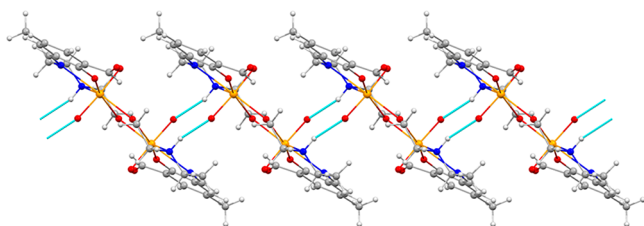
Mass, Infrared, and Electronic Spectra. For further confirmation of the molecular formula and the molecular weight of the bulk sample, $[(\text{UO}_2)_2(\mu\text{-L})_2]$ was subjected to mass spectrometric measurement using its *N,N*-dimethylformamide solution. The spectrum displays the molecular ion (MH^+) as the base peak with the expected isotopic pattern at an m/z value of 1037.3099 (Figure S1, Supporting Information).

The infrared spectrum of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ displays several bands with various intensities in the range 4000–500 cm^{-1} (Figure S2, Supporting Information). Except for a few characteristic bands, no attempt was made to assign the remaining bands. The medium-intensity band at 3225 cm^{-1} is attributed to the secondary amine N–H stretch, and it is followed by the C–H stretching band of the free aldehyde at 2831 cm^{-1} .²⁰ The sharp band at 1675 cm^{-1} reveals the

Table 2. Selected Bond Parameters (Å and deg) for $[(\text{UO}_2)_2(\mu\text{-L})_2]$

U(1)–O(1)	2.396(4)	U(1)–O(1') ^a	2.339(4)
U(1)–O(2)	2.229(5)	U(1)–O(3)	1.761(5)
U(1)–O(4)	1.777(5)	U(1)–N(1)	2.554(5)
U(1)–N(2)	2.574(5)		
O(1)–U(1)–O(1') ^a	68.80(17)	O(1)–U(1)–O(2)	157.15(16)
O(1)–U(1)–O(3)	90.2(2)	O(1)–U(1)–O(4)	90.17(19)
O(1)–U(1)–N(1)	65.43(16)	O(1)–U(1)–N(2)	131.24(16)
O(1') ^a –U(1)–O(2)	88.39(16)	O(1') ^a –U(1)–O(3)	93.8(2)
O(1') ^a –U(1)–O(4)	90.82(19)	O(1') ^a –U(1)–N(1)	134.19(16)
O(1') ^a –U(1)–N(2)	159.11(16)	O(2)–U(1)–O(3)	89.9(2)
O(2)–U(1)–O(4)	91.6(2)	O(2)–U(1)–N(1)	137.27(17)
O(2)–U(1)–N(2)	71.58(17)	O(3)–U(1)–O(4)	175.1(2)
O(3)–U(1)–N(1)	84.6(2)	O(3)–U(1)–N(2)	92.1(2)
O(4)–U(1)–N(1)	91.2(2)	O(4)–U(1)–N(2)	84.0(2)
N(1)–U(1)–N(2)	66.34(17)	U(1)–O(1)–U(1') ^a	111.20(17)

^aSymmetry transformation used to generate the equivalent atom: (') $-x + 1, -y + 1, -z + 1$.

Figure 2. One-dimensional chain-like assembly of $[(\text{UO}_2)_2(\mu\text{-L})_2]$.

presence of the uncoordinated carbonyl (C=O) functionality. The azomethine (HC=N) stretch appears as a strong sharp band at 1625 cm^{-1} .^{17g,19a,c} The characteristic strong band at 886 cm^{-1} is assigned to the asymmetric stretching vibration of the *trans*- UO_2 moiety.^{17f,g,19a,c}

The electronic spectrum of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ was taken in *N,N*-dimethylformamide solution. The spectrum shows a broad shoulder at $\sim 465\text{ nm}$ followed by one more shoulder

at $\sim 396\text{ nm}$ and an absorption maximum at 372 nm (Figure S3, Supporting Information). The molar extinction coefficients of these absorptions are in 3 orders of magnitude. Similar absorptions for *trans*-uranyl(VI) complexes with Schiff base ligands have been shown to be due to electronic transitions from the filled p orbitals of metal coordinated O atoms to the empty f orbitals of the uranium(VI) center.^{17g,19a,c,21}

Redox Properties. The electron transfer characteristics of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ have been examined by cyclic and differential pulse voltammetry. The measurements were carried out at 298 K with an $\sim 1\text{ mM}$ *N,N*-dimethylformamide solution of the complex containing *n*- Bu_4NClO_4 (0.1 M) as the supporting electrolyte using a glassy-carbon working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode under a nitrogen atmosphere. Under identical conditions, a cyclic voltammogram (CV) of an $\sim 1\text{ mM}$ *N,N*-dimethylformamide solution of ferrocene (Fc) displayed the Fc^+/Fc couple at $E_{1/2} = 0.61\text{ V}$ ($\Delta E_p = 100\text{ mV}$). The CV of ferrocene and the CV

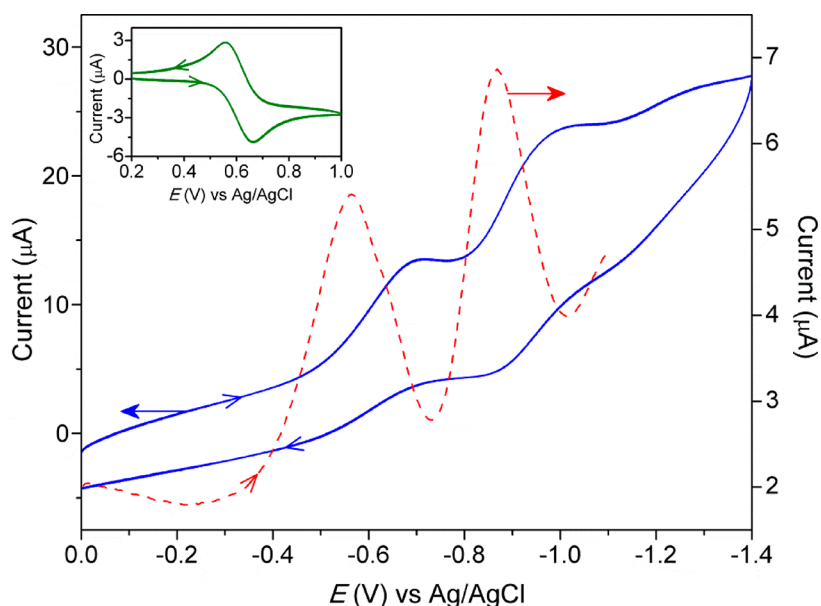


Figure 3. Cyclic (blue solid line) and differential pulse (red dashed line) voltammograms of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ in Me_2NCHO under the experimental conditions described in the text. Inset: Cyclic voltammogram (green solid line) of ferrocene under identical conditions.

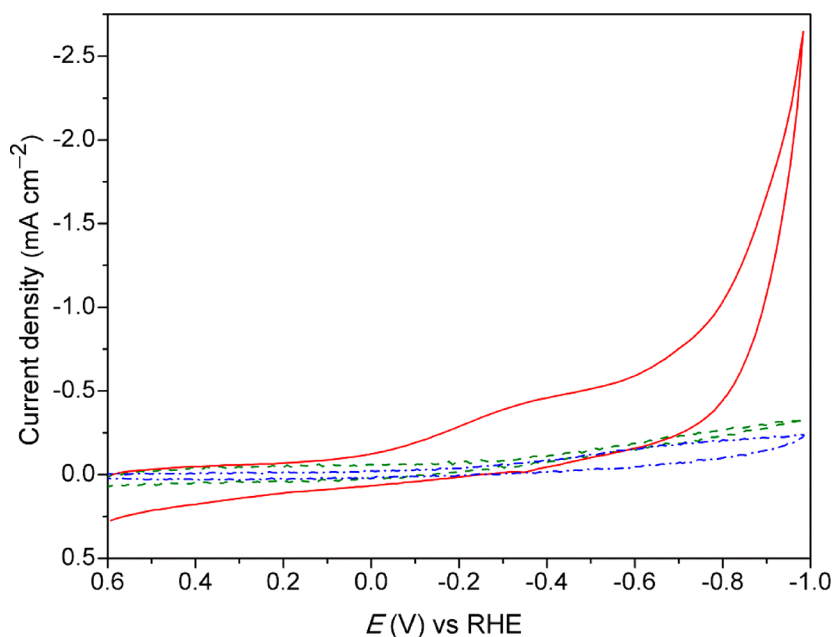


Figure 4. Cyclic voltammograms at a scan rate of 100 mV s^{-1} using a carbon black/Nafion/ $[(\text{UO}_2)_2(\mu\text{-L})_2]$ /FTO electrode (red solid line) and carbon black/Nafion/FTO electrode (green dashed line) in phosphate buffer of pH 7 and a carbon black/Nafion/ $[(\text{UO}_2)_2(\mu\text{-L})_2]$ /FTO electrode (blue dot-dashed line) in acetonitrile.

and the differential pulse voltammogram (DPV) of the complex are illustrated in Figure 3. The complex displays an irreversible reduction at $E_{\text{pc}} = -0.71$ and a quasi-reversible reduction at $E_{1/2} = -0.93 \text{ V}$ ($\Delta E_p = 200 \text{ mV}$). For the second reduction the cathodic peak current (i_{pc}) is significantly larger than the anodic peak current (i_{pa}). Nevertheless, the i_{pc} values of both of these reductions are comparable with the peak currents (i_{pa} and i_{pc}) of ferrocene. This similarity of peak currents suggests that each of the two reductions of the complex is one electron in nature. In the DPV, the reduction peaks are relatively well resolved and they appear at -0.56 and -0.86 V with comparable peak currents. Complexes of *trans*-uranyl(VI) complexes with Schiff bases are known to display $\text{U(VI)} \rightarrow \text{U(V)}$ reduction in a similar potential range.^{17g,19} Thus the two reductions observed for the present complex are attributed to $\text{U(VI)}\text{--U(VI)} \rightarrow \text{U(V)}\text{--U(VI)} \rightarrow \text{U(V)}\text{--U(V)}$ processes.

Electrocatalytic Hydrogen Evolution. The electrochemical hydrogen evolution experiments were performed using 0.1 M phosphate buffer at pH 7. The CV recorded using a $[(\text{UO}_2)_2(\mu\text{-L})_2]$, carbon black, and Nafion mixture coated FTO working electrode shows a single broad reduction response at -0.32 V (vs RHE) followed by a sharp increase in the cathodic current, which indicates the initiation of the hydrogen evolution reaction (HER) on the working electrode (Figure 4). Chromatographic analysis of the evolved gas collected in the electrolysis experiments (vide infra) confirmed the HER (Figure S4, Supporting Information). Considering that $[(\text{UO}_2)_2(\mu\text{-L})_2]$ in *N,N*-dimethylformamide solution displays metal-centered reductions on the cathodic side of the reference electrode (vide supra), the broad reduction observed with the surface-coated FTO electrode is also attributed to a metal-centered process. This reduced complex catalyst coated on the electrode surface can then produce hydrogen and go back to the original oxidized form. Controlled experiments were performed with blank FTO as well as with carbon black and Nafion coated FTO. A negligible increment

in the cathodic current confirms the fact that HER activity does not take place in the absence of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ (Figure 4). Also to further confirm the fact that the production of hydrogen is due to water reduction alone, the electrocatalytic process was carried out in acetonitrile medium instead of phosphate buffer, keeping the remaining conditions the same. There was no increment in the catalytic current when the medium was only acetonitrile (Figure 4). However, subsequent additions of phosphate buffer (pH 7) into the acetonitrile medium led to an increase in the catalytic current (Figure S5, Supporting Information).

To get a better measure of the electrocatalytic activity of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ in the HER the Tafel equation $\eta = a + b \log i$ (where η = overpotential, i = measured current density, b = Tafel slope, and a = constant) has been employed (Figure 5). A low η value, a large exchange current density (i_0 , current density at $\eta = 0$), and a low b value indicate better hydrogen evolution and hence a better catalytic activity.^{4,22} In the

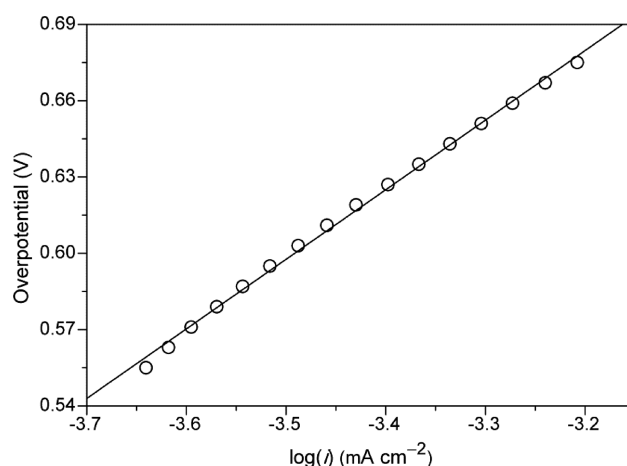


Figure 5. Tafel plot of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ in 0.1 M phosphate buffer.

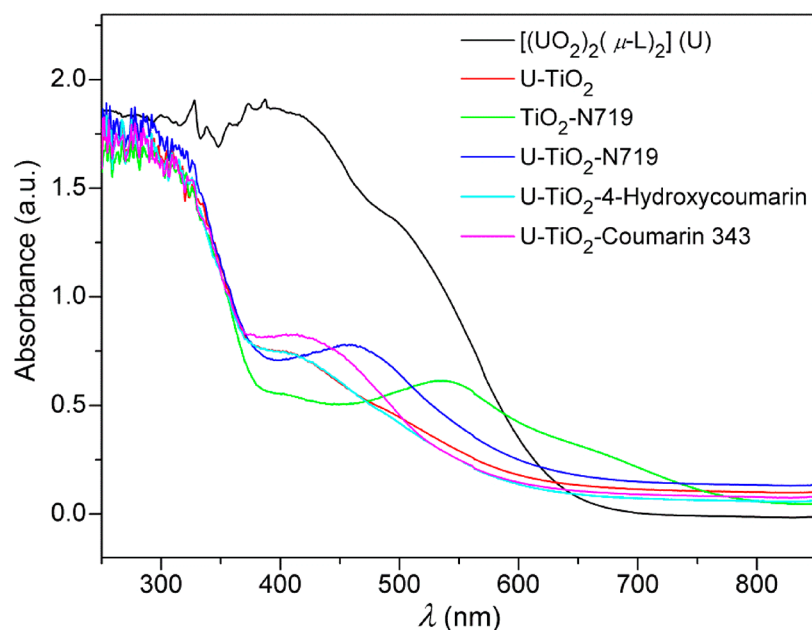


Figure 6. Diffuse reflectance spectra (DRS) of different catalyst composites.

present case, the values of η (corresponding to a current density of 1 mA cm^{-2}), i_0 , and b are found to be 0.73 V , $2.07 \times 10^{-6} \text{ A cm}^{-2}$ and 274 mV dec^{-1} , respectively. These values clearly show a decent catalytic activity of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ toward electrocatalytic hydrogen production at neutral pH.

The effectiveness of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ as a HER electrocatalyst has been evaluated by determining the Faradaic efficiency and the TOF value. Constant current electrolysis (CCE) was performed to determine the Faradaic efficiency of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ in the HER. The Faradaic efficiency was calculated as 84% (Supporting Information). The turnover frequency (TOF) was determined by using the equation $\text{TOF} = I/Q$, where I is the steady-state current (in A) in the constant potential electrolysis (CPE) plot (vide infra) and Q is the charge (in C) calculated from the reduction peak in the CV recorded under noncatalytic conditions (acetonitrile medium) with a $[(\text{UO}_2)_2(\mu\text{-L})_2]$, carbon black and Nafion mixture coated FTO working electrode (Supporting Information). The value of TOF obtained is 384 h^{-1} . A comparison of both Faradaic efficiency and the TOF values of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ with the corresponding values of the previously reported metal-centered HER catalysts clearly indicates that the present catalyst is quite noteworthy.^{4,22}

Another important feature which defines a good catalyst is its stability and robustness under the given experimental conditions. Constant-potential electrolysis (CPE) was performed to gain insights into the stability of the present catalyst. CPE was conducted at an onset potential of -1.1 V for a period of 12 h. The current was constant with negligible change for the whole range of 12 h, confirming the robust nature as well as the durability of the catalyst (Figure S6, Supporting Information). The CVs taken before and after CPE were almost identical with each other with a slight decrease in the current density, indicating no significant change in the catalyst. ICP analysis of the electrolyte solution after 12 h of CPE showed the presence of approximately 0.4% of the total metal content of the electrode surface and therefore confirms negligible leaching of the catalyst and very good electrochemical stability of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ for showing HER activity.

Thus, both electrolysis (CPE and CCE) experiments clearly indicate the high stability and competence of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ as a HER catalyst.

To understand whether HER causes any change in the catalyst $[(\text{UO}_2)_2(\mu\text{-L})_2]$, the surface analyses of the $[(\text{UO}_2)_2(\mu\text{-L})_2]$, carbon black, and Nafion mixture coated FTO electrode were done before electrolysis as well as after running 500 CV cycles by X-ray photoelectron spectroscopy (XPS). Both spectra are presented in Figure S7 (Supporting Information). There is essentially no difference between the two spectral profiles. The binding energies of the two major peaks in each spectrum reveal the presence of uranium only in the +6 oxidation state.²³ For a better comparison, both curves were fitted and the best fits led to the same number of satellite peaks in each of them. In the two deconvoluted spectra, there are little variations in the relative intensities of the resolved peaks and small differences (within 0.1–0.7 eV) in the peak maxima. However, the absence of any new peak in the spectrum obtained after CV cycles indicates that there is effectively no significant alteration in the composition of the complex catalyst due to the HER.

Photocatalytic Hydrogen Production. One of the major prerequisites for a good composite photocatalyst for hydrogen evolution from water is that it should absorb in the visible region. We have prepared some binary and ternary composite materials using TiO_2 as catalyst, $[(\text{UO}_2)_2(\mu\text{-L})_2]$ as cocatalyst, and the dyes N719, 4-hydroxycoumarin, and coumarin 343 as photosensitizers. Diffuse reflectance spectroscopy was used to study the absorption features of these composite materials. All of the spectra are illustrated in Figure 6. The dye-sensitized composite materials display broad absorption bands in the wavelength range of 370–650 nm, and hence they can be activated in the visible region, which in turn indicates their potential light-harvesting ability for solar energy conversion. The band gap energies of the complex $[(\text{UO}_2)_2(\mu\text{-L})_2]$ and the composites have been calculated by using Tauc plots (Figure S8). The value for the complex has been obtained as 1.78 eV, whereas for the composite materials it is in a narrow range of 2.50–2.66 eV.

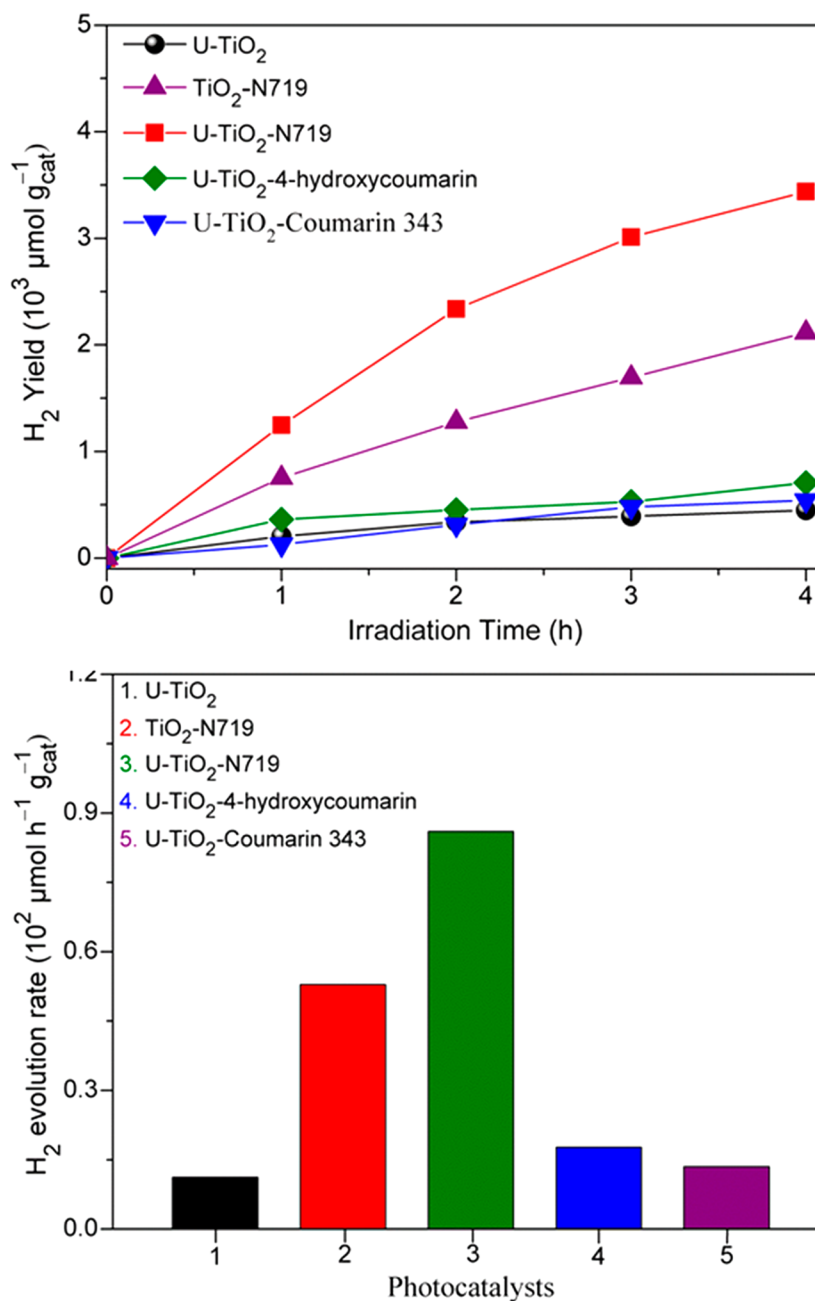


Figure 7. Kinetic profile (top) and bar graph representation (bottom) of the photocatalytic hydrogen production activity under the reaction conditions as described in the text.

The hydrogen production activity of a dye-sensitized composite photocatalyst depends not only on the type of dye being used but also on the photocatalytic reaction conditions such as dye/cocatalyst loading, nature of the sacrificial electron donor (SED), wavelength of the illuminating light, and time.^{8,9} Herein we have used the binary and ternary composite materials described above with triethanolamine (TEOA) as the SED for the photocatalytic hydrogen evolution experiments at neutral pH under visible light irradiation for a period of 4 h. The results are summarized in Figure 7 and Table 3. The expressions used for the calculation of turnover numbers (TON) and apparent quantum yields (AQY) are provided in the Supporting Information. The composite U-TiO₂ (U represents the cocatalyst [(UO₂)₂(μ-L)₂]) without any dye showed very little photocatalytic

Table 3. Photocatalytic Hydrogen Evolution Activity of the Composites

composite	H ₂ yield ^a (μmol g _{cat} ⁻¹)	TON	AQY (%)
U-TiO ₂	449		1.0
TiO ₂ -N719	2117	423	4.7
U-TiO ₂ -N719	3439	688	7.6
U-TiO ₂ -4-hydroxycoumarin	708	142	1.6
U-TiO ₂ -coumarin 343	541	108	1.2

^aReaction conditions: 10 mg of composite in 20 mL of 10 vol % TEOA aqueous solution at pH 7 (attained by using 1 M aqueous HCl solution) under 4 h of light irradiation (λ > 420 nm).

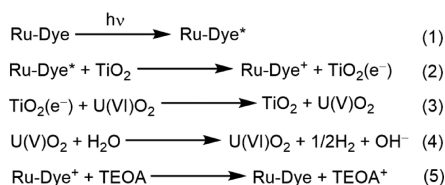
activity. Almost similar results were observed for the composites U-TiO₂-coumarin 343 and U-TiO₂-4-hydroxycou-

marin. In these three cases, the H_2 yields and AQY values were obtained within the ranges 449–708 $\mu\text{mol g}_{\text{cat}}^{-1}$ and 1.0–1.6%, respectively, after 4 h of visible light irradiation (Table 3). The corresponding TON values for the two dye-containing ternary composites were obtained as 108 and 142. In comparison, the binary composite TiO_2 -N719 exhibited a considerable amount of H_2 production (2117 $\mu\text{mol g}_{\text{cat}}^{-1}$) with a much higher TON (423) and AQY (4.7%) in 4 h of photolysis. However, a maximum H_2 yield of 3439 $\mu\text{mol g}_{\text{cat}}^{-1}$ with TON and AQY values as high as 688 and 7.6%, respectively, were obtained with the U- TiO_2 -N719 composite in the same 4 h of photolysis. These values indicate a very decent photocatalytic hydrogen production ability of the U- TiO_2 -N719 combination.^{8,9}

The photoactivity of a dye-sensitized semiconductor is strongly influenced by the attachment modes among the dye, semiconductor, and coexisting species (such as the SED and the cocatalyst) in the suspension systems, which dominate the charge generation, separation, transfer, and recombination. All three ternary composites used in this work contain the same cocatalyst $[(\text{UO}_2)_2(\mu\text{-L})_2]$, and all of the reactions were performed in aqueous TEOA (SED) solution under long-term (4 h) irradiation. The superior photocatalytic activity of the U- TiO_2 -N719 combination in comparison to the other two composites is most likely due to the effective surface binding of the carboxyl anchoring groups of N719 (a Ru(II) complex having visible light absorption capability within 400–600 nm) onto the semiconductor TiO_2 . In all probability, the low efficiency of each of the other two composites containing the dyes 4-hydroxycoumarin and coumarin 343 results from the low injection yields of photoinduced electrons across the dye–semiconductor interface due to relatively poor attachment of the dye to TiO_2 .

A possible reaction sequence for the photocatalytic hydrogen production has been given in Scheme 2. Upon visible light

Scheme 2. Possible Mechanism for the Photocatalytic Evolution of Hydrogen



irradiation of N719, the Ru-dye, electron transfer takes place from the HOMO to the LUMO and the excited species Ru-dye^* is formed (eq 1). Oxidation of Ru-dye^* by the semiconductor TiO_2 results in the formation of the oxidized dye Ru-dye^+ and the reduced species $\text{TiO}_2(\text{e}^-)$ (eq 2). In the third step (eq 3), the cocatalyst U(VI) -complex gets reduced to a U(V) -containing species with regeneration of the semiconductor catalyst TiO_2 . The U(V) -containing species then reduces the water molecule to hydrogen (eq 4). The oxidized Ru-dye^+ takes up the electron from a sacrificial electron donor (TEOA) (eq 5), and the process of photocatalytic hydrogen generation continues.

CONCLUSIONS

A dinuclear *trans*-uranyl(VI) complex of formula $[(\text{UO}_2)_2(\mu\text{-L})_2]$ has been reported. The X-ray crystal structure reveals meridional fused 5,5,6-membered chelate rings forming an

ONNO-coordination mode of the bridging ligands L^{2-} and the formation of an edge-shared pentagonal N_2O_3 plane around each *trans*- UO_2^{2+} unit. In the crystal lattice, the dinuclear molecules form a supramolecular chainlike structure via intermolecular $\text{N}\cdots\text{H}-\text{O}$ hydrogen-bonding interactions. The spectroscopic features of the complex are consistent with its X-ray molecular structure. The complex exhibited decent activity in electrocatalytic as well as photocatalytic hydrogen evolution reaction in neutral aqueous medium. In the electrocatalytic process, the complex exhibits a Faradaic efficiency of 84% with a TOF as high as 384 h^{-1} . On the other hand, using the complex- TiO_2 -N719 composite in photocatalytic hydrogen production under visible light irradiation a TOF of 172 h^{-1} with an apparent quantum yield of 7.6% has been obtained. To the best of our knowledge, $[(\text{UO}_2)_2(\mu\text{-L})_2]$ is the first *trans*-uranyl(VI) complex that can act as both an electrocatalyst and a photocatalyst for the hydrogen evolution reaction in neutral aqueous medium.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01726.

Procedures followed for hydrogen evolution experiments, the equations used to calculate various parameters, and additional figures as described in the text (PDF)

Accession Codes

CCDC 1921042 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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REFERENCES

- (a) Lubitz, W.; Tumas, W. Hydrogen: An Overview. *Chem. Rev.* 2007, 107, 3900–3903. (b) Dutta, S. A review on production, storage of hydrogen and its utilization as an energy resource. *J. Ind. Eng.*

- Chem.* **2014**, *20*, 1148–1156. (c) Staffell, I.; Scamman, D.; Abad, A. V.; Balcombe, P.; Dodds, P. E.; Ekins, P.; Shah, N.; Ward, K. R. The role of hydrogen and fuel cells in the global energy system. *Energy Environ. Sci.* **2019**, *12*, 463–491.
- (2) (a) Frey, M. Hydrogenases: Hydrogen-activating enzymes. *ChemBioChem* **2002**, *3*, 153–160. (b) Evans, D. J.; Pickett, C. J. Chemistry and the hydrogenases. *Chem. Soc. Rev.* **2003**, *32*, 268–275.
- (3) (a) Ismail, A. A.; Bahnemann, D. W. Photochemical splitting of water for hydrogen production by photocatalysis: A review. *Sol. Energy Mater. Sol. Cells* **2014**, *128*, 85–101. (b) Rajaambal, S.; Sivarajani, K.; Gopinath, C. S. Recent developments in solar H₂ generation from water splitting. *J. Chem. Sci.* **2015**, *127*, 33–47. (c) Jafari, T.; Moharreri, E.; Amin, A. S.; Miao, R.; Song, W.; Suib, S. L. Photocatalytic Water Splitting—The Untamed Dream: A Review of Recent Advances. *Molecules* **2016**, *21*, 900. (d) Takanabe, K. Photocatalytic Water Splitting: Quantitative Approaches toward Photocatalyst by Design. *ACS Catal.* **2017**, *7*, 8006–8022. (e) Wang, Z.; Li, C.; Domen, K. Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting. *Chem. Soc. Rev.* **2019**, *48*, 2109–2125.
- (4) (a) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. Complexes of earth-abundant metals for catalytic electrochemical hydrogen generation under aqueous conditions. *Chem. Soc. Rev.* **2013**, *42*, 2388–2400. (b) Zeng, M.; Li, Y. Recent advances in heterogeneous electrocatalysts for the hydrogen evolution reaction. *J. Mater. Chem. A* **2015**, *3*, 14942–14962. (c) Zou, X.; Zhang, Y. Noble metal-free hydrogen evolution catalysts for water splitting. *Chem. Soc. Rev.* **2015**, *44*, 5148–5180.
- (5) Kunimatsu, K.; Senzaki, T.; Tsushima, M.; Osawa, M. A combined surface-enhanced infrared and electrochemical kinetics study of hydrogen adsorption and evolution on a Pt electrode. *Chem. Phys. Lett.* **2005**, *401*, 451–454 and references therein.
- (6) Haddad, A. Z.; Cronin, S. P.; Mashuta, M. S.; Buchanan, R. M.; Grapperhaus, C. A. Metal-Assisted Ligand-Centered Electrocatalytic Hydrogen Evolution upon Reduction of a Bis(thiosemicarbazonato)-Cu(II) Complex. *Inorg. Chem.* **2017**, *56*, 11254–11265.
- (7) Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38.
- (8) (a) Maeda, K.; Eguchi, M.; Youngblood, W. J.; Mallouk, T. E. Niobium oxide nanoscrolls as building blocks for dye-sensitized hydrogen production from water under visible light irradiation. *Chem. Mater.* **2008**, *20*, 6770–6778. (b) Peng, T.; Ke, D.; Cai, P.; Dai, K.; Ma, L.; Zan, L. Influence of different ruthenium(II) bipyridyl complex on the photocatalytic H₂ evolution over TiO₂ nanoparticles with mesostructures. *J. Power Sources* **2008**, *180*, 498–505. (c) Abe, R.; Shinmei, K.; Harac, K.; Ohtani, B. Robust dye-sensitized overall water splitting system with two-step photoexcitation of coumarin dyes and metal oxide semiconductors. *Chem. Commun.* **2009**, 3577–3579. (d) Tran, P. D.; Xi, L.; Batabyal, S. K.; Wong, L. H.; Barber, J.; Loo, J. S. C. Enhancing the photocatalytic efficiency of TiO₂ nanopowders for H₂ production by using non-noble transition metal co-catalysts. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11596–11599. (e) Tanaka, A.; Sakaguchi, S.; Hashimoto, K.; Kominami, H. Preparation of Au/TiO₂ with metal cocatalysts exhibiting strong surface plasmon resonance effective for photoinduced hydrogen formation under irradiation of visible light. *ACS Catal.* **2013**, *3*, 79–85. (f) Abe, R.; Shinmei, K.; Koumura, N.; Hara, K.; Ohtani, B. Visible-Light-Induced Water Splitting Based on Two-Step Photoexcitation between Dye-Sensitized Layered Niobate and Tungsten Oxide Photocatalysts in the Presence of a Triiodide/Iodide Shuttle Redox Mediator. *J. Am. Chem. Soc.* **2013**, *135*, 16872–16884. (g) Mongal, B. N.; Tiwari, A.; Malapaka, C.; Pal, U. Ruthenium(III)-bis(phenolato)bipyridine/TiO₂ hybrids: unprecedented photocatalytic hydrogen evolution. *Dalton Trans* **2019**, *48*, 10070.
- (9) (a) Abe, R. J. Hydrogen Evolution from Water under Visible-Light Irradiation Using Keggin-Type Platinum-Coordinated Phospho-(II)-, Silico-, and Germanotungstates as Co-Catalysts. *J. Photochem. Photobiol., C* **2010**, *11*, 179–209. (b) Chen, X. B.; Shen, S. H.; Guo, L. J.; Mao, S. S. Semiconductor based photocatalytic hydrogen generation. *Chem. Rev.* **2010**, *110*, 6503–6570. (c) Qu, Y.; Duan, X. Progress, challenge and perspective of heterogeneous photocatalysts. *Chem. Soc. Rev.* **2013**, *42*, 2568–2580. (d) Zhang, X. H.; Peng, T. Y.; Song, S. S. Recent advances in dye sensitized semiconductor systems for photocatalytic hydrogen production. *J. Mater. Chem. A* **2016**, *4*, 2365–2402. (e) Junge, H.; Rockstroh, N.; Fischer, S.; Brückner, A.; Ludwig, R.; Lochbrunner, S.; Kühn, O.; Beller, M. Light to Hydrogen: Photocatalytic Hydrogen Generation from Water with Molecularly-Defined Iron Complexes. *Inorganics* **2017**, *5*, 14.
- (10) Halter, D. P.; Heinemann, F. W.; Bachmann, J.; Meyer, K. Uranium-mediated electrocatalytic dihydrogen production from water. *Nature* **2016**, *530*, 317–321.
- (11) Gagné, R. R.; Spiro, C. L.; Smith, T. J.; Hamann, C. A.; Thies, W. R.; Shiemke, A. K. The Synthesis, Redox Properties, and Ligand Binding of Heterobinuclear Transition-Metal Macrocyclic Ligand Complexes. Measurement of an Apparent Delocalization Energy in a Mixed-Valent $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}$ Complex. *J. Am. Chem. Soc.* **1981**, *103*, 4073–4081.
- (12) APEX3: Program for Data Collection on Area Detectors; Bruker AXS Inc.: Madison, WI, USA, 2016.
- (13) Sheldrick, G. M. SADABS: Program for Area Detector Absorption Correction; University of Göttingen: Göttingen, Germany, 1997.
- (14) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.
- (15) Farrugia, L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **2012**, *45*, 849–854.
- (16) Macrae, F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; Cabe, P. M.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. New Features for the Visualization and Investigation of Crystal Structures. *J. Appl. Crystallogr.* **2008**, *41*, 466–470.
- (17) (a) Åberg, M. The Crystal Structure of $[(\text{UO}_2)_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_4]$. *Acta Chem. Scand.* **1969**, *23*, 791–810. (b) Jiang, J.; Sarsfield, M. J.; Renshaw, J. C.; Livens, F. R.; Collison, D.; Charnock, J. M.; Helliwell, M.; Eccles, H. Synthesis and Characterization of Uranyl Compounds with Iminodiacetate and Oxydiacetate Displaying Variable Denticity. *Inorg. Chem.* **2002**, *41*, 2799–2806. (c) Masci, B.; Thuéry, P. Uranyl complexes with the pyridine-2,6-dicarboxylato ligand: new dinuclear species with $\text{r}^{-2,2}$ -peroxide, -2-hydroxide or -2-methoxide bridges. *Polyhedron* **2005**, *24*, 229–237. (d) Lyczko, K.; Steczek, L. Crystal Structure of a Hydroxo-bridged Dimeric Uranyl Complex with a 2,2y:6;2-Terpyridine Ligand. *J. Struct. Chem.* **2017**, *58*, 102–106. (e) Hadjithoma, S.; Papanikolaou, M. G.; Leontidis, E.; Kabanos, T. A.; Keramidis, A. D. Bis(hydroxylamino)triazines: High Selectivity and Hydrolytic Stability of Hydroxylamine-Based Ligands for Uranyl Compared to Vanadium(V) and Iron(III). *Inorg. Chem.* **2018**, *57*, 7631–7643. (f) Zhao, X.; Zhang, D.; Yu, R.; Chen, S.; Zhao, D. TetrahydrosalenUranyl(VI) Complexes: Crystal Structures and Solution Binding Study. *Eur. J. Inorg. Chem.* **2018**, *2018*, 1185–1191. (g) Ghosh, S.; Srivastava, A. K.; Pal, S. Dihydroxo-bridged diuranyl(VI) complexes with 2-((2-(6-chloropyridazin-3-yl)hydrazono)methyl)4-R-phenols: structural insights and visible light driven photocatalytic activities. *New J. Chem.* **2019**, *43*, 970–978.
- (18) Burns, C. J.; Sattelberger, A. P. Uranium(VI)-Oxo-Alkoxide Cluster Synthesis via Ligand Redistribution. *Inorg. Chem.* **1988**, *27*, 3692–3693.
- (19) (a) Asadi, Z.; Asadi, M.; Zeinali, A.; Ranjeshshorkaei, M.; Fejfarova, K.; Eigner, V.; Dusek, M.; Dehnokhalaji, A. Synthesis, structural investigation and kinetic studies of uranyl(VI) unsymmetrical Schiff base complexes. *J. Chem. Sci.* **2014**, *126*, 1673–1683. (b) Camp, C.; Chatelain, L.; Mougel, V.; Pécaut, J.; Mazzanti, M. Ferrocene-Based Tetradentate Schiff Bases as Supporting Ligands in Uranium Chemistry. *Inorg. Chem.* **2015**, *54*, 5774–5783. (c) Ghosh, S.; Kurapati, S. K.; Ghosh, A.; Srivastava, A. K.; Pal, S. Di- -acetato Diuranyl(VI) Complexes with *N*-(2-pyridyl)-*NN*-(5-R-salicylidene)hydrazines: Syntheses, Structures, Properties and Extraction Studies. *ChemistrySelect* **2018**, *3*, 4865–4872.
- (20) Kemp, W. *Organic Spectroscopy*, 2nd ed.; Macmillan: Hampshire, 1987; pp 46–51.

(21) (a) Volkovich, V. A.; Griffiths, T. R.; Frayand, D. J.; Thied, R. C. The electronic spectra of alkali metal uranates and band assignments: an analysis of their diffuse reflectance spectra. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5182–5191. (b) Almond, P. M.; Albrecht-Schmitt, T. E. Hydrothermal Syntheses, Structures, and Properties of the New Uranyl Selenites $\text{Ag}_2(\text{UO}_2)(\text{SeO}_3)_2$, $\text{M}[(\text{UO}_2)(\text{HSeO}_3)(\text{SeO}_3)]$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$), and $\text{Pb}(\text{UO}_2)(\text{SeO}_3)_2$. *Inorg. Chem.* **2002**, *41*, 1177–1183.

(22) (a) Fang, Y.-H.; Liu, Z.-P. Tafel Kinetics of Electrocatalytic Reactions: From Experiment to First-Principles. *ACS Catal.* **2014**, *4*, 4364–4376. (b) Shinagawa, T.; Garcia-Esparza, A. T.; Takanabe, K. Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion. *Sci. Rep.* **2015**, *5*, 13801.

(23) Ilton, E. S.; Bagus, P. S. XPS determination of uranium oxidation states. *Surf. Interface Anal.* **2011**, *43*, 1549–1560.

Inorganic Chemistry

Di- μ -acetato Diuranyl(VI) Complexes with *N*-(2-pyridyl)-*N'*-(5-*R*-salicylidene)hydrazines: Syntheses, Structures, Properties and Extraction StudiesSabari Ghosh, Sathish Kumar Kurapati, Arpita Ghosh, Ankit Kumar Srivastava, and Samudranil Pal^{*,[a]}

Reactions of equimolar amounts of $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and *N*-(2-pyridyl)-*N'*-(5-*R*-salicylidene)hydrazines (HL^n ; $n = 1-3$ for $R = \text{H}$, Me, and OMe, respectively) in methanol produced $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}^n)_2]$ (**1-3** for $n = 1-3$) in ~70% yields. Elemental analysis, various spectroscopic, and electrochemical measurements were used to characterize **1-3**. X-ray crystal structures revealed an 8-membered $\text{U}(\text{OCO})_2\text{U}$ ring with a chair conformation and pentagonal-bipyramidal UN_2O_5 coordination spheres in each of **1-3**. The $\text{N}_2\text{N}_2\text{O}$ -donor (L^n) and the two O-atoms of the two bridging (OAc^-) form the pentagonal plane around the U-atom of *trans*-(UO_2)²⁺. Intermolecular H-bonding assisted self-assembly of the complexes lead to 1- and 2-dimensional supramolecular structures. Infrared (IR) and proton nuclear

magnetic resonance (¹HNMR) spectra of **1-3** are consistent with their molecular structures. The electronic spectra showed four strong absorption bands in the range 466–288 nm. The complexes undergo two irreversible reductions near -0.65 and -0.88 V (vs. Ag/AgCl). Time-dependent density functional theory (TD-DFT) calculations suggest that a ligand centered transition causes the highest energy absorption band, while, the remaining three are ligand-to-metal charge transfer (LMCT) bands and the two successive reductions are due to $\text{U(VI)}\text{-U(VI)} \rightarrow \text{U(V)}\text{-U(VI)} \rightarrow \text{U(V)}\text{-U(V)}$ processes. A maximum extraction of 98% of *trans*-(UO_2)²⁺ from the aqueous layer was observed in two-phase extraction studies.

Introduction

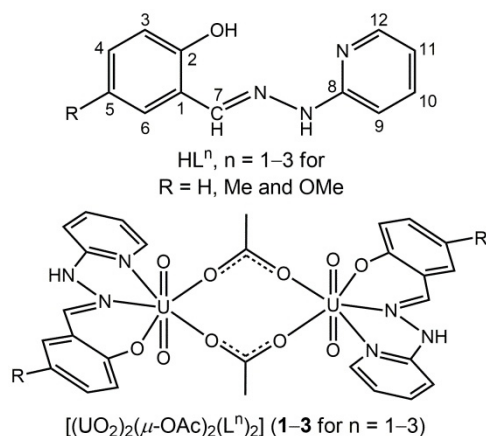
Uranium is one of the most widely explored and chemically exploited f-block elements. Naturally occurring uranium has essentially two isotopes, about 99.3% of the non-fissile U-238 and only about 0.7% of the fissile U-235. Human ingestion of uranium is mostly through underground water sources which are in the vicinity of the uranium-rich regions. Prolonged consumption and exposure to this heavy radioactive metal can lead to adverse health conditions.^[1] It is also important to note that due to the steady and steep growth in electricity consumption there is an increasing demand of uranium as fuel for nuclear power plants. Thus, synthesis of stable environment friendly complexes of uranium and development of advanced techniques for uranium extraction from underground as well as seawater, in both micro as well as macro level, are crucial and challenging from not only the environmental point of view but also for use in energy production.^[2] Among the varied oxidation states of uranium spanning the range from +2 to +6, the most stable and common is the +6. In this oxidation state, uranium exists as the uranyl(VI) ion, (UO_2)²⁺, where the two oxo groups are mutually *trans*-oriented. In comparison to the other well-known dioxo-metal ions such as (VO_2)⁺, (MoO_2)²⁺, and (WO_2)²⁺ where the two oxo groups are *cis* to each other,^[3] the

coordination chemistry of *trans*-(UO_2)²⁺ is much less explored.^[4] The structures of *trans*-uranyl(VI) complexes are essentially decided by the local geometry of the uranium center. The *trans*-orientation of the oxo groups restricts ligand coordination to the metal center at the equatorial plane only and gives rise to the possibilities of various coordination environments ranging from tetragonal six-coordination or octahedral to pentagonal seven-coordination or pentagonal-bipyramidal to hexagonal eight-coordination or hexagonal-bipyramidal. In recent years, among the chelating organic ligands, Schiff-Bases have attracted considerable interest in exploring the coordination chemistry of the linear uranyl(VI) ion.^[5] The primary reasons are as follows: Schiff bases are easy to design and synthesize; their steric and electronic characteristics can be tuned by changing substituents; they can provide very stable complexes and hence can act as an efficient sequestering agent for the extraction of the *trans*-uranyl(VI) dication. Hydrazine based Schiff bases and their complexes with various transition metal ions have been widely studied due to the variety in their coordination chemistry as well as their applications in the fields of biological, materials and pharmaceutical research.^[6] We have been working on the oxo-vanadium and oxo-molybdenum complexes with this class of Schiff bases for the past several years.^[7] These ligands have turned out to be excellent in coordinating and stabilizing *cis*-dioxomolybdenum(VI) (*cis*- MoO_2^{2+}) and a variety of oxo-vanadium(IV/V) units. In the case of oxo-vanadium complexes, the solvent used for the synthetic reaction plays the key role in deciding the type of oxo-metal ion to be stabilized by ligand complexation. Generally oxo-

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alkoxo-vanadium(V) ($\text{VO}(\text{OR})^{2+}$) complexes have been isolated from protic alcohol media, while *cis*-dioxovanadium(V) (*cis*- VO_2^+) or dinuclear oxo-bridged oxovanadium(V) ($\text{OV}(\mu\text{-O})\text{VO}^{4+}$) complexes have been obtained from non-protic medium such as acetonitrile. The N,N,O-donor *N*-(2-pyridyl)-*N'*-(5-*R*-salicylidene)hydrazines (HL^n ; where H represents the dissociable phenolic proton and $n=1-3$ for $R = \text{H}, \text{Me}, \text{and OMe}$, respectively) (Scheme 1) belong to this class of Schiff bases.



Scheme 1. Chemical structure diagrams of HL^n and $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}^n)_2]$.

These Schiff bases (HL^n) are known to exhibit amine-imine and also imine-azo tautomerism processes involving the 2-pyridine-NH- and the $-\text{NH}-\text{N}=\text{CH}-$ fragments, respectively.^[7e,f,8] In the present work, we have investigated the coordination chemistry of *trans*- $(\text{UO}_2)^{2+}$ with HL^n and isolated three new dinuclear diacetato bridged complexes having the general molecular formula $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}^n)_2]$ (**1-3** for $n=1-3$) (Scheme 1). It may be noted that examples of discrete dinuclear complexes of $\{\text{O}_2\text{U}(\mu\text{-OAc})_2\text{UO}_2\}^{2+}$ core having pentagonal-bipyramidal metal centers, which are stable in both solid and solution states, are very rare. To the best of our knowledge, till date, only five X-ray structurally characterized complexes of this diacetato-bridged diuranyl(VI) core have been reported in literature.^[9] But the ligands around the pentagonal-bipyramidal metal centers are either monodentate solvents/phosphine-oxide or monodentate/bidentate carboxylate ligands in all five complexes. We have also examined the dicationic *trans*-uranyl(VI) extraction abilities of HL^n from aqueous medium using both quantitative gravimetric filtration as well as sequential extraction methods. In the following account, we have described the synthetic details, physical properties and X-ray structures of complexes **1-3** and the extraction characteristics of HL^n .

Results and Discussion

Synthesis and Characterization

Complexes with the general molecular formula as $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}^n)_2]$ (**1-3**) have been synthesized in good yields (68-70%) by treating the corresponding Schiff bases (HL^n , $n=1-3$) with

$\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in hot methanol under aerobic conditions. They have been isolated as brown solids. The elemental analysis data of **1-3** are in good agreement with their corresponding molecular formulas. Magnetic susceptibility measurements with powdered samples of the complexes at room temperature revealed their diamagnetic character. Thus the uranium center in each of **1-3** is in +6 oxidation state. All three complexes are insoluble in most of the common organic solvents except for dimethylformamide (DMF) and dimethylsulfoxide (DMSO). In these two solvents, they are highly soluble and provide yellow to yellow-brown solutions. The complexes behave as non-electrolytes in solution. The non-electrolytic nature of **1-3** is consistent with them being neutral species as indicated by their molecular formulas.

X-ray Molecular Structures

The structures of **1** and **3** were determined in orthorhombic *Pbca* and triclinic $P\bar{1}$ space groups, respectively, while that of the solvated species **2**·4MeOH was solved in the triclinic space group $P\bar{1}$. Selected crystallographic data for **1**, **2**·4MeOH, and **3** are summarized in Table S1 (supporting information). The molecular structures of all three dinuclear complexes are very similar. The structures of the unsolvated complexes (**1** and **3**) are illustrated in Figure 1 and the structure of the solvated

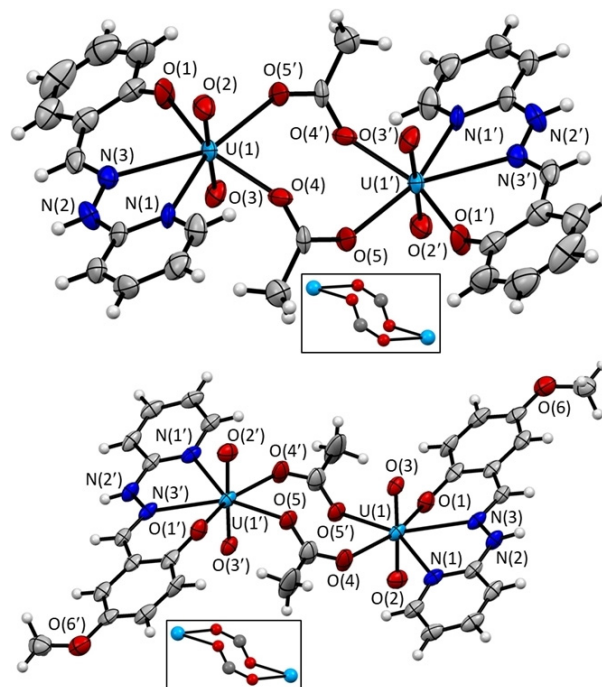


Figure 1. Molecular structures of $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}^1)_2]$ (**1**) (top) and $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}^3)_2]$ (**3**) (bottom). All the non-hydrogen atoms in each structure are represented by their 50% probability thermal ellipsoids. For clarity only the non-carbon atoms are labelled. Insets: the chair conformations of the $\text{U}_2\text{C}_2\text{O}_4$ rings.

complex (**2**-4MeOH) is provided in Figure 2. The bond lengths and angles associated with the uranium centers for all three

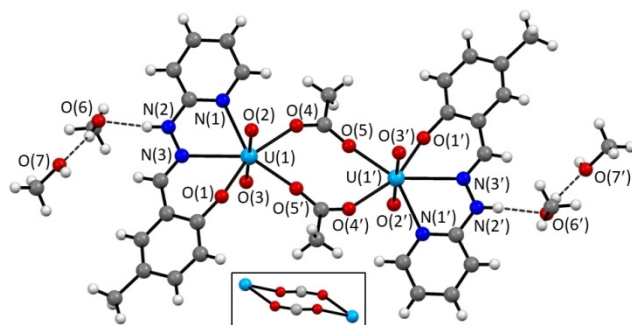


Figure 2. The structure of $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}')_2]\cdot 4\text{MeOH}$ (**2**-4MeOH). For clarity only the non-carbon atoms are labelled. Inset: the chair conformation of the $\text{U}_2\text{C}_2\text{O}_4$ ring.

Table 1. Selected bond lengths [Å] and angles [°] for **1**, **2**-4MeOH, and **3**.

Complex	1	2 -4MeOH	3
U(1)-O(1)	2.178(13)	2.224(10)	2.217(5)
U(1)-O(2)	1.769(12)	1.790(13)	1.777(5)
U(1)-O(3)	1.795(12)	1.801(13)	1.774(4)
U(1)-O(4)	2.302(13)	2.356(12)	2.351(5)
U(1)-O(5) ^[a]	2.371(12)	2.311(12)	2.338(4)
U(1)-N(1)	2.564(15)	2.582(13)	2.594(5)
U(1)-N(3)	2.650(14)	2.625(11)	2.609(5)
O(1)-U(1)-O(2)	89.5(6)	88.0(5)	87.0(2)
O(1)-U(1)-O(3)	90.9(6)	92.7(5)	94.6(2)
O(1)-U(1)-O(4)	159.2(5)	157.7(4)	158.10(18)
O(1)-U(1)-O(5) ^[a]	79.8(5)	80.4(4)	80.68(17)
O(1)-U(1)-N(1)	125.1(5)	127.2(4)	127.96(18)
O(1)-U(1)-N(3)	67.4(5)	68.3(4)	69.53(16)
O(2)-U(1)-O(3)	178.6(6)	178.7(5)	178.2(2)
O(2)-U(1)-O(4)	95.1(5)	90.0(5)	89.3(2)
O(2)-U(1)-O(5) ^[a]	85.1(6)	90.2(6)	89.09(19)
O(2)-U(1)-N(1)	81.3(5)	83.2(6)	84.18(19)
O(2)-U(1)-N(3)	100.1(5)	100.7(5)	101.59(19)
O(3)-U(1)-O(4)	84.0(5)	89.7(5)	88.9(2)
O(3)-U(1)-O(5) ^[a]	93.7(5)	90.9(5)	90.34(19)
O(3)-U(1)-N(1)	99.5(5)	95.5(5)	95.47(18)
O(3)-U(1)-N(3)	81.3(5)	78.6(4)	79.80(18)
O(4)-U(1)-O(5) ^[a]	80.5(5)	77.4(4)	77.68(17)
O(4)-U(1)-N(1)	75.6(4)	74.6(4)	72.96(18)
O(4)-U(1)-N(3)	131.1(4)	133.8(4)	132.31(17)
O(5) ^[a] -U(1)-N(1)	151.2(5)	151.2(5)	149.91(19)
O(5) ^[a] -U(1)-N(3)	146.6(5)	146.2(4)	147.54(17)
N(1)-U(1)-N(3)	61.4(4)	62.6(4)	62.42(18)

[a] Symmetry transformations: $-x, -y + 1, -z + 1$ for **1**; $-x + 1, -y, -z + 1$ for **2**-4MeOH; and $-x, -y + 2, -z + 1$ for **3**.

complexes are listed in Table 1. In **2**-4MeOH, the methanol molecules exist as dimers via O-H...O interactions. Two such methanol dimers are attached to either side of **2** through two N-H...O interactions (Figure 2).

In each of **1**–**3**, the two halves of the complex molecule, i.e. the two $\{(trans\text{-UO}_2)(\text{OAc})(\text{L}')\}$ fragments, are related by an inversion center. As a result, the metal atoms of the two $trans\text{-}(\text{UO}_2)^{2+}$ units are bridged by two acetate groups and a central $\{\text{O}_2\text{U}(\mu\text{-OAc})_2\text{UO}_2\}^{2+}$ core is formed in each molecule (Figures 1 and 2). In this central core of **1**–**3**, the conformation of the centrosymmetric eight-membered $\text{U}_2\text{C}_2\text{O}_4$ ring can be best described as chair (Figures 1 and 2, insets). The dihedral angle between the UO_2 plane and the mean plane containing C_2O_4 (rms deviations: 0.12–0.45 Å) decreases in the order **1** (43.3(5)°) > **3** (33.8(3)°) > **2** (14.9(6)°). These dihedral angles indicate that the flattening of both ends of the chair or in other words the planarity of the $\text{U}_2\text{C}_2\text{O}_4$ ring increases in the order **1** < **3** < **2**. Interestingly, the metal...metal distance decreases with the increase of the planarity of the $\text{U}_2\text{C}_2\text{O}_4$ ring. The U(1)–U(1') distances are 5.7561(9), 5.5444(5), and 5.3547(9) Å in **1**, **3**, and **2**, respectively. The uranium centers are in distorted pentagonal-bipyramidal N_2O_5 coordination sphere. The planar ligand (L') acts as pyridine-N, azomethine-N, and phenolate-O donor and forms fused 5,6-membered chelate rings at the metal center. The (L') and two O-atoms of the two bridging acetate groups form the equatorial pentagonal N_2O_3 plane (rms deviations: 0.23–0.28 Å) around the uranium atom of the $trans\text{-}(\text{UO}_2)^{2+}$ unit. In all of **1**–**3**, the O=U=O angles are very close to the ideal value of 180° and the U=O bond lengths are comparable to those found in $trans\text{-}(\text{UO}_2)^{2+}$ complexes.^[5,9] The remaining metal centered bond lengths and angles involving the coordinating atoms of (L') and the bridging acetate groups (Table 1) are within the ranges reported for complexes of $trans\text{-}(\text{UO}_2)^{2+}$ containing pentagonal-bipyramidal uranium centers having similar coordinating atoms.^[5a–h,j–o,9]

Supramolecular Self-assembly

All of **1**, **2**-4MeOH, and **3** contain classical (hydrazinic-NH or methanolic-OH) as well as non-classical (CH) hydrogen bond donor functionalities and also hydrogen bond acceptors such as oxo groups and phenolate-O atoms. Hence, each structure has been scrutinized for intermolecular hydrogen bonding interactions and if there is any such interaction then what type of supramolecular self-assembly pattern it leads to. Indeed there are three types of hydrogen bonds namely N-H...O, O-H...O, and C-H...O. The geometric parameters for these hydrogen bonding interactions are summarized in Table 2.

Table 2. Hydrogen bonding parameters for **1**, **2**-4MeOH, and **3**.

Complex	D-H...A	D...A [Å]	∠DHA [°]
1	N(2)-H...O(3) ^[a]	3.099(18)	165
2 -4MeOH	N(2)-H...O(6)	2.798(16)	173
	O(6)-H...O(7)	2.612(9)	166
	O(7)-H...O(1) ^[a]	2.763(18)	162
3	C(6)-H...O(3) ^[a]	3.318(8)	135
	C(12)-H...O(3) ^[a]	3.403(8)	138

[a] Symmetry transformations used: $-x + 1/2, y - 1/2, z$ for **1**; $-x, -y, -z$ for **2**-4MeOH; $-x, -y + 1, -z + 1$ for **3**.

In the case of **1**, one of the two metal bound oxo groups is hydrogen bonded with the hydrazinic-NH of (L^1). As the donor and the acceptor are approximately orthogonal to each other, this intermolecular N-H...O interaction directs the self-assembly of **1** into a two-dimensional sheet-like structure (Figure 3).

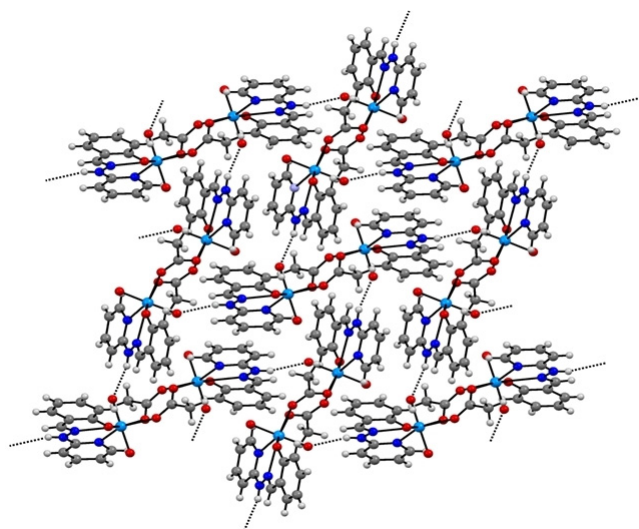


Figure 3. Intermolecular N-H...O interaction assisted two-dimensional sheet structure of $[(UO_2)_2(\mu-OAc)_2(L^1)_2]$ (**1**).

The solvent molecules dictate the self-assembly and the supramolecular structure of **2**·4MeOH. Every pair of dinuclear molecules of **2** are bridged by two methanol dimers, which are O-H...O hydrogen bonded, through N-H...O and O-H...O hydrogen bonds involving the hydrazinic-NH group and the phenolate-O atom of each tridentate ligand (L^2) of **2** as donor and acceptor, respectively. These two intermolecular hydrogen bonding interactions lead to a one-dimensional chain-like $-(MeOH)_2\text{-}2\text{-(MeOH)}_2-$ array in the crystal lattice (Figure 4).

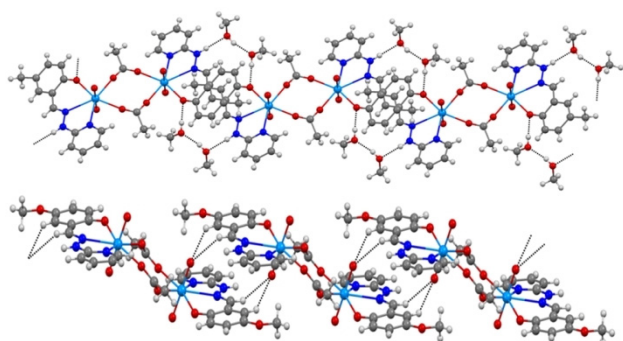


Figure 4. One-dimensional orderings of $[(UO_2)_2(\mu-OAc)_2(L^2)_2]\cdot 4MeOH$ (**2**·4MeOH) via O-H...O and N-H...O hydrogen bonds (top) and $[(UO_2)_2(\mu-OAc)_2(L^3)_2]$ (**3**) through intermolecular bifurcated C-H...O...H-C hydrogen bond (bottom).

Interestingly, unlike **1** and **2**·4MeOH, the hydrazinic-NH of (L^3) in **3** does not participate as donor to any intermolecular hydrogen bonding interaction. Instead, the metal coordinated polarized azomethine-CH and the nearest phenolate ring CH that is *ortho* to both azomethine group and the methoxy substituent of the tridentate ligand are involved in a bifurcated hydrogen bond^[10] with one of the metal bound oxo groups. As a consequence of this intermolecular single acceptor and two donors interaction on either side of each dinuclear **3**, a one-dimensional chain-like structure is formed in the crystal lattice (Figure 4).

Spectroscopic Characterization

Infrared spectra of **1**–**3** were recorded using KBr disks in the range 4000–400 cm^{-1} . Each spectrum displays a large number of bands with various intensities. A representative spectrum is shown in Figure 5. Except for few selected bands, no attempt

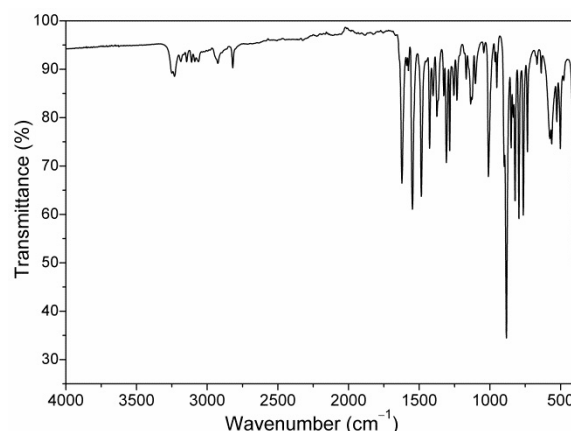


Figure 5. Infrared spectrum of $[(UO_2)_2(\mu-OAc)_2(L^2)_2]$ (**2**) in KBr disk.

has been made to assign the remaining bands. None of the complexes displays any band assignable to the phenolic-OH group of the free Schiff base (HL^n). Thus the phenolic-OH is deprotonated and the Schiff base is monoanionic ($(L^n)^-$) in the complex. A weak and broad band observed in the range 3308–3234 cm^{-1} is assigned to the hydrazinic-NH of (L^n).^[7e,f,j] A sharp and strong band displayed at around 1621 cm^{-1} by all three complexes is attributed to the metal coordinated azomethine ($-HC=N-$) group of their respective ligands.^[5,7e,f,j,8b] Two strong bands are observed in the ranges 1545–1528 and 1427–1422 cm^{-1} in each spectrum. These two bands are assigned to the asymmetric and symmetric stretches, respectively of the carboxylate fragment of the bridging acetate group.^[11] The typical strong band due to the asymmetric stretching vibration of the *trans*-uranyl(VI) moiety has been observed within 899–883 cm^{-1} .^[5]

The electronic absorption spectra of **1**–**3** were recorded using their DMF solutions. The spectral profiles of all three complexes are very similar. The spectrum of **1** is displayed in

Figure 6. A strong band at ~ 435 nm preceded by a shoulder at ~ 458 nm and two more strong bands at 360 and ~ 290 nm are

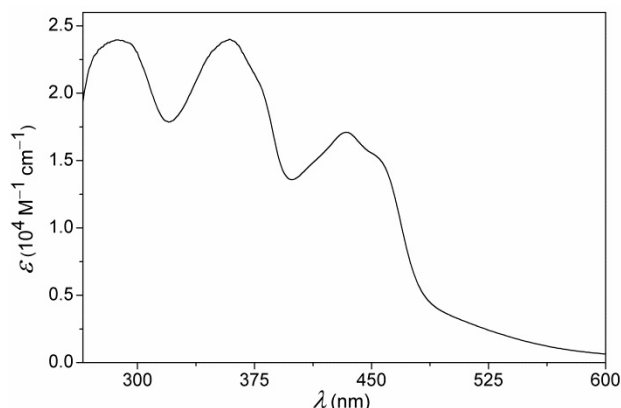


Figure 6. Electronic spectrum of $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}^1)_2]$ (**1**) in DMF.

observed in each spectrum. The free Schiff bases (HL^n) display a very strong band within 351–335 nm, a shoulder or band at ~ 312 nm and another strong absorption at ~ 240 nm.^[7] Comparison of the spectra of HL^n with those of the complexes (**1–3**) indicates that the shoulder and the band at ~ 458 and ~ 435 nm, respectively are very likely to be due to ligand to metal charge transfer transitions.^[5,7] To find out the origins of the remaining bands and for a better overall perception of the electronic spectra, TD-DFT calculations were carried out for **1** and **3** in DMF solution. Calculated band positions with the corresponding oscillator strengths and the percentages of contributing transitions along with the experimental band positions are summarized in Table S2 (supporting information). The calculated and experimental λ_{max} values complement each other very well. The compositions of the molecular orbitals involved in the contributing transitions (Table S3, supporting information) indicate that the highest energy absorption (at ~ 290 nm) is due to a ligand centered transition, while the remaining three lower energy absorptions are due to ligand-to-metal charge transfer transitions.

The ^1H NMR spectra of all the complexes were recorded in DMSO-d_6 solutions using tetramethylsilane as the internal standard. The comparable spectral traces and the similar chemical shift values are consistent with similar type of coordination modes of the ligands (L^{1-3}) in **1–3**. The spectra also indicate that both halves of each of the three dinuclear complexes are equivalent. The chemical shift values with the tentative assignments are provided in the experimental section under the respective complexes (supporting information). As expected, due to the deprotonation upon metal coordination the spectra of **1–3** are devoid of the phenol proton resonance observed for the free Schiff bases (HL^{1-3}) at $\delta \sim 10.88$ ppm. The hydrazinic-NH proton of HL^n resonates as a singlet at $\delta \sim 10.24$ ppm, while the corresponding singlet of (L^n) in the complexes shifts slightly upfield to $\delta \sim 9.99$ ppm. The singlet due to the resonance of the azomethine proton of HL^n appears

at $\delta \sim 8.27$ ppm. In contrast, the singlet corresponding to the azomethine proton of (L^n) in the complexes appeared at $\delta \sim 8.84$ ppm. The observed downfield shift is consistent with the N-coordination of the azomethine and hence the deshielding of the azomethine proton. The three-proton singlet observed at $\delta \sim 2.32$ ppm is assigned to the bridging acetate methyl group in **1–3**. The protons of the methyl substituent at C^5 of (L^2) in **2** resonate as a singlet at $\delta \sim 2.37$ ppm, whereas the protons of the methoxy substituent at C^5 of (L^3) in **3** are observed as singlet at $\delta \sim 3.78$ ppm. The chemical shifts and splitting patterns of the remaining aromatic protons of the tridentate ligands in **1–3** are unexceptional.

Redox Behavior

Cyclic and differential pulse voltammetric measurements with the Schiff bases (HL^{1-3}) and their complexes (**1–3**) were performed using their corresponding $\sim 10^{-3}$ M DMF solutions containing tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte with a Pt-disk working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode under nitrogen atmosphere at 298 K. Under identical experimental conditions the ferrocenium/ferrocene (Fc^+/Fc) couple was observed at $E_{1/2} = 0.61$ V with a peak-to-peak separation (ΔE_p) of 110 mV. Cyclic voltammograms of all the complexes are very similar and display two broad overlapping cathodic peaks and essentially no or very weak anodic peak on reverse scan. The cathodic peak potentials (E_{pc}) are about -0.7 and -1.0 V. The differential pulse voltammograms of **1–3** display two well-resolved peaks at potentials around -0.65 and -0.88 V. The voltammograms of a representative complex is shown in Figure 7. Considering that the present complexes are diacetate

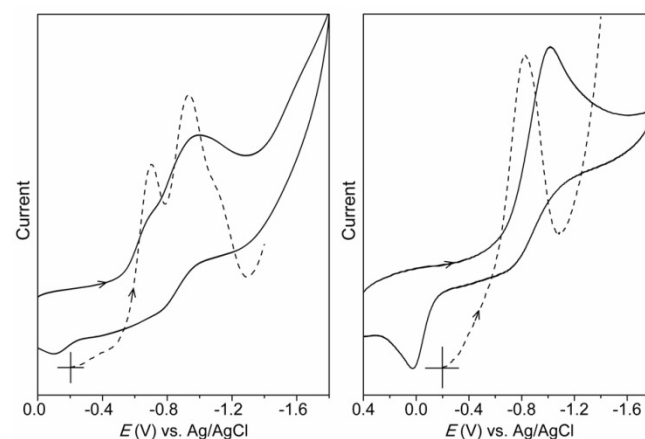


Figure 7. Cyclic and differential pulse voltammograms of $[(\text{UO}_2)_2(\mu\text{-OAc})_2(\text{L}^3)_2]$ (**3**) (left) and HL^1 (right) in DMF.

bridged dinuclear species and complexes of $\text{trans-(UO}_2\text{)}^{2+}$ with Schiff bases are known to display U(VI) to U(V) reduction response at comparable potential range,^[5g-j,q,r] the reductions observed for **1–3** can be assigned as $\text{U(VI)} \rightarrow \text{U(V)}$.

and $U(V)-U(VI) \rightarrow U(V)-U(V)$ processes. However, the free Schiff bases (HL^n) are also redox active and display a single reduction response having large peak-to-peak separation (E_{pc} and E_{pa} values are around -1.02 and -0.04 V, respectively) and cathodic peak current (i_{pc}) to anodic peak current (i_{pa}) ratio. The i_{pc} values of the Schiff bases are higher than those of the corresponding complexes. As expected the differential pulse voltammograms of HL^{1-3} show a single peak within -0.80 to -0.84 V. The voltammograms of HL^1 are illustrated in Figure 7. Generally the reduction of metal coordinated ligand is expected to be easier and hence to be observed at higher potential than its reduction in the free state. Therefore, for **1-3** the first reduction can be assigned as a ligand centered process, while the second reduction can be due to a metal centered $UO_2^{2+} \rightarrow UO_2^+$ process. A similar situation of ligand reduction followed by metal reduction has been reported for a pentagonal-bipyramidal mononuclear complex of $trans-(UO_2)^{2+}$ containing a redox-active tetradentate N_4 -donor Schiff base as primary ligand and a monodentate chloride as an ancillary ligand.^[5q] Thus for the present complexes there are two possibilities, i.e. both reductions are metal centered or the first reduction is ligand centered and the second reduction is metal centered. To decide between the above two possibilities the characteristics of the unoccupied molecular orbitals shown by the TD-DFT calculations have been examined. The compositions of LUMO to LUMO + 7 (Table S3) indicate that at the present level of theory they are all metal centered in both **1** and **3**. The locations of the LUMO in the two complexes are illustrated in Figure 8. Thus

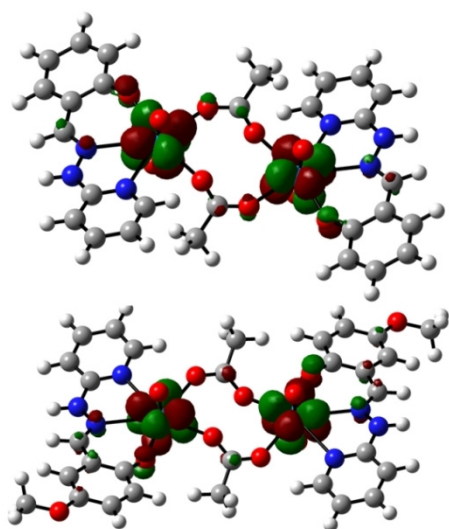


Figure 8. LUMOs of $[(UO_2)_2(\mu-OAc)_2(L^1)_2]$ (**1**) (top) and $[(UO_2)_2(\mu-OAc)_2(L^3)_2]$ (**3**) (bottom).

the two closely spaced reductions are assigned to the successive reductions of the two metal centers in each of **1-3**.

To gain further insight, constant potential (at -1.3 V) coulometric reductions of **1-3** and one of the three Schiff bases (HL^1) were performed using a Pt wire-gauze working electrode. The overall n -values (the ratio of Q_{obsd} to Q_{calcd} for 1 e transfer)

for the two successive reductions of the three complexes have been found to be in the range 1.8-2.1. In contrast, the n -value for the single reduction displayed by HL^1 is 3.1. The difference in the n -values of the complexes and the Schiff base, together with the TD-DFT results indicate that the coordinated ligands are not involved in any of the two reductions observed for the complexes. Hence, the two successive electron transfer responses of the complexes are indeed due to two metal centered single electron transfers, i.e. stepwise $U(VI)-U(VI) \rightarrow U(V)-U(VI) \rightarrow U(V)-U(V)$ reductions.

Extraction Studies

Extraction abilities of HL^n for the *trans*-uranyl(VI) dication from aqueous medium have been investigated. Two methods were employed for the extraction process. These two methods are: gravimetric separation and sequential extraction using $CHCl_3$ as the organic layer.

In the gravimetric separation, a solution of the respective Schiff base (HL^n) in an organic solvent (MeOH or CH_2Cl_2 or $CHCl_3$) was mixed with an aqueous solution of $UO_2(OAc)_2 \cdot 2H_2O$ and stirred for a specific duration (15, 30, 45, and 60 min). The amount of the complex precipitated after each duration was quantitatively measured to determine the extent of extraction. The infrared spectra of the precipitates confirm their identities as $[(UO_2)_2(\mu-OAc)_2(L^n)_2]$ (**1-3**). The results are summarized in Table S4 (supporting information). In general, the two-phase solvent systems $H_2O-CH_2Cl_2$ and $H_2O-CHCl_3$ show better results of extraction as compared to the H_2O-CH_3OH mixture. The maximum extraction of 98% of $trans-(UO_2)^{2+}$ was achieved in 60 min. using HL^2 as the ligand and $H_2O-CHCl_3$ as the reaction medium. A comparative study showing the extents of extraction of $trans-(UO_2)^{2+}$ using different solvent mixtures and HL^2 as the extractant is graphically represented in Figure 9.

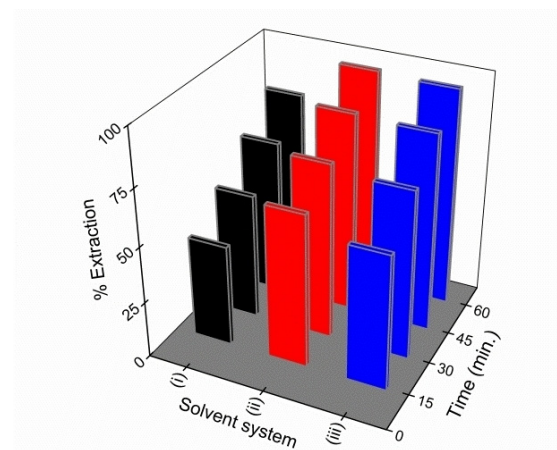


Figure 9. *trans*-uranyl(VI) dication extraction by HL^2 in the solvent systems (i) MeOH- H_2O , (ii) $CHCl_3$ - H_2O , and (iii) CH_2Cl_2 - H_2O .

Considering that in the gravimetric separation method the best extraction was achieved with the use of HL^2 , only this

Schiff base was employed in the sequential extraction method. Here a CHCl_3 solution of HL^2 was used as the organic layer for the extraction of $\text{trans-(UO}_2)_2^{2+}$ from an aqueous solution having pH 6. The absorption bands in the electronic spectrum of the CHCl_3 layer recorded after extraction confirm the formation of **2** in the organic phase (Figure S1, supporting information). The progress of extraction was followed by monitoring the 429 nm band^[12] in the electronic spectrum of the aqueous phase after each extraction (Figure 10). The

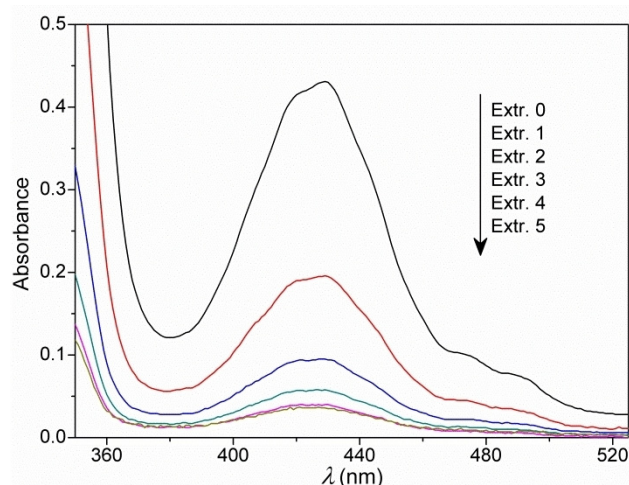


Figure 10. Electronic spectroscopic profiles of the aqueous phase (pH 6) containing $\text{UO}_2(\text{OAc})_2$ recorded after sequential extractions of *trans*-uranyl(VI) dication using CHCl_3 solutions of HL^2 .

absorbance values and the extraction data are listed in Table S5 (supporting information). The maximum extraction (55%) of the $\text{trans-(UO}_2)_2^{2+}$ from the aqueous layer to the organic layer occurred in the first extraction. The amount of *trans*-uranyl(VI) dication in the aqueous phase gradually decreased with successive extractions with CHCl_3 solutions of HL^2 . Total 91% $\text{trans-(UO}_2)_2^{2+}$ could be removed from the aqueous phase in four extractions. After the fourth extraction there was very little change in the *trans*-uranyl(VI) dication content of the aqueous phase in the following extraction attempts.

Thus the present Schiff bases (HL^n) turned out to be effective extractants for the extraction of $\text{trans-(UO}_2)_2^{2+}$ from aqueous phase. All three compounds showed excellent extraction abilities. The maximum extents of extraction in the above mentioned two-phase extraction studies are very good ($> 90\%$) in both methods. These results are better or comparable to the previously reported extraction studies using Schiff bases.^[5d,f,m]

Conclusions

Stabilization and isolation of the rare $\{\text{O}_2\text{U}(\mu\text{-OAc})_2\text{UO}_2\}^{2+}$ core using the deprotonated N,N,O-donor Schiff bases *N*-(2-pyridyl)-*N'*-(5-*R*-salicylidene)hydrazines (HL^n where $R = \text{H, Me, and OMe}$) as ligands have been demonstrated. The discrete dinuclear complexes isolated have the general molecular formula $[(\text{UO}_2)_2$

$(\mu\text{-OAc})_2(\text{L}^n)_2]$. X-ray crystallographic studies revealed pentagonal-bipyramidal N_2O_5 coordination sphere around each metal center and a chair conformation of the central eight-membered $\text{U}(\text{OCO})_2\text{U}$ ring in each complex. In the crystal lattice, the complexes form two-dimensional and one-dimensional supramolecular structures through intermolecular regular and bifurcated hydrogen bonding interactions. The infrared and proton NMR spectroscopic characteristics of all the complexes are in good agreement with their molecular structures. All three complexes display four strong electronic absorption bands and two closely spaced reduction responses at the cathodic side of Ag/AgCl. Theoretical calculations show that the first three absorption bands are of ligand-to-metal charge transfer character, while, the highest energy band is due to a ligand centered transition and the two successive electron transfer processes are due to $\text{U(VI)-U(VI)} \rightarrow \text{U(V)-U(VI)} \rightarrow \text{U(V)-U(V)}$ reductions. Constant potential coulometric measurements confirm an overall stoichiometry of two electrons for the stepwise reductions of the two metal centers. Very effective extraction of $\text{trans-(UO}_2)_2^{2+}$ from the aqueous layer has been achieved using the Schiff bases (HL^n) as the extractants in two-phase extraction studies.

Supporting Information Summary

Experimental section containing the materials used, a general procedure for the synthesis of the complexes (**1-3**), spectroscopic and electrochemical data of **1-3**, physical measurements, extraction methods employed, and procedures for X-ray crystallographic studies and theoretical calculations; selected crystallographic data (Table S1); DFT calculated data (Tables S2 and S3); and extraction data (Tables S4 and S5, and Figure S1). CCDC 1811353, 1811354, and 1811355 contain the supplementary crystallographic data for **1**, **2**·4MeOH, and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Dinuclear uranyl(VI) complexes • Extraction • Physical properties • Schiff bases • X-ray structures

- [1] D. Brugge, V. Buchner, *Rev. Environ. Health* **2011**, *26*, 231–249.
- [2] a) J. R. Kumar, J.-S. Kim, J.-Y. Lee, H.-S. Yoon, *Sep. Purif. Rev.* **2011**, *40*, 77–125; b) R. Gilligan, A. N. Nikoloski, *Miner. Eng.* **2015**, *71*, 34–48; c) A. Basu, S. T. Brown, J. N. Christensen, D. J. DePaolo, P. W. Reimus, J. M. Heikoop, G. Woldegabriel, A. M. Simmons, B. M. House, M. Hartmann, K. Maher, *Environ. Sci. Technol.* **2015**, *49*, 5939–5947; d) D. K. Singh, S. Mondal, J. K. Chakravarty, *Solvent Extr. Ion Exch.* **2016**, *34*, 201–225; e) F. Endrizzi, C. J. Leggett, L. Rao, *Ind. Eng. Chem. Res.* **2016**, *55*, 4249–4256.
- [3] a) B. Mondal, M. G. B. Drew, T. Ghosh, *Inorg. Chim. Acta* **2010**, *363*, 2296–2306; b) M. R. Maurya, *J. Chem. Sci.* **2011**, *123*, 215–228; c) M. Sutradhar, A. J. L. Pombeiro, *Coord. Chem. Rev.* **2014**, *265*, 89–124; d) R. D. Chakravarthy, D. K. Chand, *J. Chem. Sci.* **2011**, *123*, 187–199; e) B. I. Ceylan, N. G. Deniz, S. Kahraman, B. Ulkuseven, *Spectrochim. Acta Part A* **2015**, *141*, 272–277; f) A. A. Eagle, E. R. T. Tiekink, C. G. Young, *Inorg. Chem.* **1997**, *36*, 6315–6322; g) Y.-L. Wong, J.-F. Ma, F. Xue, T. C. W. Mak, D. K. P. Ng, *Organometallics* **1999**, *18*, 5075–5079; h) V. S. Sergienko, *Russ. J. Inorg. Chem.* **2000**, *45*, 537–564; i) Y.-L. Wong, L. H. Tong, J. R. Dilworth, D. K. P. Ng, H. K. Lee, *Dalton Trans.* **2010**, *39*, 4602–4611; j) V. Vrdoljak, J. Pisk, D. Agustin, P. Novak, J. P. Vuković, D. Matković-Čalogović, *New J. Chem.* **2014**, *38*, 6176–6185.
- [4] a) M. R. Maurya, R. C. Maurya, *Rev. Inorg. Chem.* **1995**, *15*, 1–108; b) J. L. Sessler, P. J. Melfi, G. D. Pantos, *Coord. Chem. Rev.* **2006**, *250*, 816–843; c) P. A. Giesting, P. C. Burns, *Crystallogr. Rev.* **2006**, *12*, 205–255; d) K.-X. Wang, J.-S. Chen, *Acc. Chem. Res.* **2011**, *44*, 531–540; e) R. J. Baker, *Chem. Eur. J.* **2012**, *18*, 16258–16271; f) K. Kiegiel, L. Steczek, G. Zakrzewska-Trznadel, *J. Chem.* **2013**, 762819, doi: 10.1155/2013/762819; g) A. G. Beirakhov, I. M. Orlova, Y. N. Mikhailov, *Russ. J. Inorg. Chem.* **2014**, *59*, 1679–1690; h) T. Loiseau, I. Mihalcea, N. Henry, C. Volkringer, *Coord. Chem. Rev.* **2014**, 266–267, 69–109.
- [5] a) A. K. Sah, C. P. Rao, P. K. Saarenketo, E. K. Wegelius, E. Kolehmainen, K. Rissanen, *Eur. J. Inorg. Chem.* **2001**, 2773–2781; b) C. C. Gatto, E. S. Lang, A. Kupfer, A. Hagenbach, U. Abram, Z. Anorg. Allg. Chem. **2004**, *630*, 1286–1295; c) P. L. Arnold, A. J. Blake, C. Wilson, J. B. Love, *Inorg. Chem.* **2004**, *43*, 8206–8208; d) M. S. Bharara, K. Strawbridge, J. Z. Vilsek, T. H. Bray, A. E. V. Gorden, *Inorg. Chem.* **2007**, *46*, 8309–8315; e) M. S. Bharara, S. A. Tonks, A. E. V. Gorden, *Chem. Commun.* **2007**, 4006–4008; f) M. S. Bharara, K. Heflin, S. Tonks, K. L. Strawbridge, A. E. V. Gorden, *Dalton Trans.* **2008**, 2966–2973; g) H. C. Hardwick, D. S. Royal, M. Helliwell, S. J. A. Pope, L. Ashton, R. Goodacre, C. A. Sharrad, *Dalton Trans.* **2011**, *40*, 5939–5952; h) Z. Asadi, M. Asadi, A. Zeinali, M. Ranjeshshorkaei, K. Feifarova, V. Eigner, M. Dusek, A. Dehnokhalaji, *J. Chem. Sci.* **2014**, *126*, 1673–1683; i) M. Azam, S. I. Al-Resayes, G. Velmurugan, P. Venuvanalingam, J. Wagler, E. Kroke, *Dalton Trans.* **2015**, *44*, 568–577; j) C. Camp, L. Chatelain, V. Mougél, J. Pécaut, M. Mazzanti, *Inorg. Chem.* **2015**, *54*, 5774–5783; k) Y. Zhang, D. J. Fanna, N. D. Shepherd, I. Karatchevtseva, K. Lu, L. Kong, Jason R. Price, *RSC Adv.* **2016**, *6*, 75045–75053; l) M. Azam, G. Velmurugan, S. M. Wabaidur, A. Trzesowska-Kruszynska, R. Kruszynski, S. I. Al-Resayes, Z. A. Al-Othman, P. Venuvanalingam, *Sci. Rep.* **2016**, *6*, 32898:1–13, doi: 10.1038/srep32898; m) H. B. T. Jeazet, K. Gloe, T. Doert, J. Mizera, O. N. Kataeva, S. Tsushima, G. Bernhard, J. J. Weigand, L. F. Lindoy, K. Gloe, *Polyhedron* **2016**, *103*, 198–205; n) L. Pavelek, V. Ladányi, M. Nečas, S. Vallová, K. Wichterle, *Polyhedron* **2016**, *107*, 89–96; o) A. Akbari, A. Fasihizad, M. Ahmadi, B. Machura, *Polyhedron* **2017**, *128*, 188–197; p) E. E. Hardy, K. M. Wyss, M. A. Eddy, A. E. V. Gorden, *Chem. Commun.* **2017**, *53*, 5718–5720; q) J. R. Pankhurst, N. L. Bell, M. Zegke, L. N. Platts, C. A. Lamfsus, L. Maron, L. S. Natrajan, S. Sproules, P. L. Arnold, J. B. Love, *Chem. Sci.* **2017**, *8*, 108–116; r) J. E. Niklas, B. H. Farnum, J. D. Gorden, A. E. V. Gorden, *Organometallics* **2017**, *36*, 4626–4634.
- [6] a) A.-M. Stadler, J. Harrowfield, *Inorg. Chim. Acta* **2009**, *362*, 4298–4314; b) L. D. Popov, A. N. Morozov, I. N. Shcherbakov, Y. P. Tupolova, V. V. Lukov, V. A. Kogan, *Russ. Chem. Rev.* **2009**, *78*, 643–658; c) N. P. Belskaya, W. Dehaen, V. A. Bakulev, *ARKIVOC* **2010**, *i*, 275–332; d) J. R. Dilworth, R. Hueting, *Inorg. Chim. Acta* **2012**, *389*, 3–15; e) R. Narang, B. Narasimhan, S. Sharma, *Curr. Med. Chem.* **2012**, *19*, 569–612; f) P. Zhang, L. Zhang, J. Tang, *Curr. Inorg. Chem.* **2013**, *3*, 101–111; g) M. M. E. Shakhodofa, M. H. Shtaiwi, N. Morsy, T. M. A. Abdel-rassel, *Main Group Chem.* **2014**, *13*, 187–218; h) X. Su, I. Aprahamian, *Chem. Soc. Rev.* **2014**, *43*, 1963–1981.
- [7] a) N. R. Sangeetha, S. Pal, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 357–363; b) N. R. Sangeetha, V. Kavita, S. Wocadlo, A. K. Powell, S. Pal, *J. Coord. Chem.* **2000**, *51*, 55–66; c) S. N. Pal, S. Pal, *Acta Crystallogr. Sect. C* **2001**, *57*, 141–142; d) S. N. Pal, K. Radhika, S. Pal, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1631–1637; e) A. Sarkar, S. Pal, *Polyhedron* **2006**, *25*, 1689–1694; f) A. Sarkar, S. Pal, *Polyhedron* **2007**, *26*, 1205–1210; g) A. Sarkar, S. Pal, *Inorg. Chim. Acta* **2008**, *361*, 2296–2304; h) A. Sarkar, S. Pal, *Inorg. Chim. Acta* **2009**, *362*, 3807–3812; i) A. Sarkar, S. Pal, *Eur. J. Inorg. Chem.* **2009**, 5391–5398; j) S. K. Kurapati, U. Ugandhar, S. Maloth, S. Pal, *Polyhedron* **2012**, *42*, 161–167.
- [8] a) M. F. Zady, J. L. Wong, *J. Org. Chem.* **1976**, *41*, 2491–2495; b) K. Nagaraju, R. Raveendran, S. N. Pal, S. Pal, *Polyhedron* **2012**, *33*, 52–59; c) C. Basu, S. Chowdhury, R. Banerjee, H. S. Evans, S. Mukherjee, *Polyhedron* **2007**, *26*, 3617–3624; d) D. Debnath, S. Roy, B.-H. Li, C.-H. Lin, T. K. Misra, *Spectrochim. Acta, Part A* **2015**, *140*, 185–197.
- [9] a) C. Panattoni, R. Graziani, G. Bandoli, B. Zarli, G. Bombieri, *Inorg. Chem.* **1969**, *8*, 320–325; b) V. I. Spitsyn, V. V. Kolesnik, V. É. Mistryukov, I. A. Yuranov, Y. N. Mikhailov, K. M. Dunaeva, *Russ. Chem. Bull.* **1982**, *31*, 715–719; c) I. A. Charushnikova, N. N. Krot, Z. A. Starikova, *Radiochemistry* **2008**, *50*, 117–120; d) P. D. Bernardo, P. L. Zanonato, F. Benetollo, A. Melchior, M. Tolazzi, L. Rao, *Inorg. Chem.* **2012**, *51*, 9045–9055; e) L. B. Serezhkina, M. S. Grigor'ev, N. A. Shimin, V. V. Klepov, V. N. Serezhkin, *Russ. J. Inorg. Chem.* **2015**, *60*, 672–683.
- [10] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, New York, **1999**.
- [11] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, **1986**, p. 233.
- [12] a) Z. Libuš, *J. Inorg. Nucl. Chem.* **1962**, *24*, 619–631; b) A. Günther, G. Geipel, G. Bernhard, *FZR-IRC Annu. Rep.* **2004**, *24*; c) M. Glorius, H. Moll, G. Bernhard, *Radiochim. Acta* **2007**, *95*, 151–157; d) P. K. Mohapatra, D. R. Raut, A. Sengupta, *Sep. Purif. Technol.* **2014**, *133*, 69–75.

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Dihydroxo-bridged diuranyl(vi) complexes with 2-((2-(6-chloropyridazin-3-yl)hydrazono)methyl)-4-R-phenols: structural insights and visible light driven photocatalytic activities†

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Two new dihydroxo-bridged diuranyl(vi) complexes with the molecular formula $[(\text{UO}_2)_2(\mu\text{-OH})_2(\text{L}^n)_2]$ (**1** and **2**) were synthesized in good yields (~64%) by reacting equimolar amounts of $[\text{UO}_2(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$ and 2-((2-(6-chloropyridazin-3-yl)hydrazono)methyl)-4-R-phenols (HL^n where $n = 1$ and 2 for $\text{R} = \text{H}$ and OMe , respectively) in dimethylformamide. Both complexes were characterized by elemental analysis, and various spectroscopic and cyclic voltammetric measurements. The X-ray crystal structures of the two complexes crystallized as solvated species showed the rare $\{(\text{UO}_2)_2(\mu\text{-OH})_2\}^{2+}$ core where each metal centre is in a distorted pentagonal-bipyramidal N_2O_5 coordination sphere assembled by two axial oxo atoms, two equatorial bridging hydroxo-O atoms and the equatorial N,N,O-donor $(\text{L}^n)^-$. The solvated complexes assemble through intermolecular bifurcated $\text{N-H} \cdots (\text{O}, \text{O})$ and simple $\text{O-H} \cdots \text{O}$ and $\text{N-H} \cdots \text{O}$ hydrogen bonding interactions and form supramolecular one-dimensional chain-like and three-dimensional network structures in the crystal lattices. The infrared and proton NMR spectroscopic characteristics of the two complexes corroborate their molecular structures. The electronic spectra of **1** and **2** display three strong absorption bands in the range of 405–301 nm. A metal centred irreversible reduction having a E_{pc} of approximately -1.06 V (vs. Ag/AgCl) was observed in the cyclic voltammograms of **1** and **2**. Both complexes are photocatalytically active in the degradation of rhodamine B (RhB) and methylene blue (MB) under visible light irradiation. Photodegradation of RhB up to a maximum of 96% and that of MB up to a maximum of 85% was achieved in 150 and 180 min, respectively, using **2** as a catalyst.

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Introduction

Uranium is one of the most abundant and extensively studied metals in the actinide series. In uranium chemistry, the *trans*-uranyl(vi) dication is the leading functional unit, where hexavalent uranium is bonded to two mutually *trans*-oriented oxo atoms. The strongly covalent U–O bonds in *trans*-(UO_2)²⁺ are particularly short and exhibit remarkable thermal and chemical stability, contributing various interesting physicochemical properties to it and its complexes.¹ As a consequence, uranyl coordination complexes and uranyl–organic-framework materials have found a variety of applications that range from photoluminescence to photochemical reactions to photocatalysis.^{2,3} Thus, in search of new and more effective *trans*-uranyl(vi) dication

containing species, their coordination chemistry has emerged as one of the actively pursued areas of inorganic chemistry.⁴ Photocatalysis is the phenomenon of catalyzing reactions in the presence of light of a suitable wavelength. Photocatalysts have gained tremendous interest primarily because of their effective use in solving environmental pollution problems. The significant factors upon which the photocatalytic activity of a substance depends are the desired band gap, reusability, surface morphology and stability.⁵ Over the past few decades, TiO_2 has emerged as an excellent photocatalyst for a variety of applications such as water splitting, degradation of pollutants, organic synthesis and phototherapy.⁶ But, TiO_2 is an active photocatalyst only under ultraviolet light, which somewhat confines its practical applications. Thus, there is an increasing demand for band gap-tunable photocatalysts for visible light-driven catalytic processes.⁷ In the present work, we have explored the coordination chemistry of the *trans*-uranyl(vi) dication with 2-((2-(6-chloropyridazin-3-yl)hydrazono)methyl)-4-R-phenols (HL^n) ($n = 1$ and 2 for $\text{R} = \text{H}$ and OMe , respectively) and isolated two dinuclear complexes with the molecular formula

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† Electronic supplementary information (ESI) available: Irradiation time dependent spectral changes for the dyes in the presence of catalysts (Fig. S1–S3) and X-ray crystallographic data in CIF format. CCDC 1870329 and 1870330. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8nj05038d

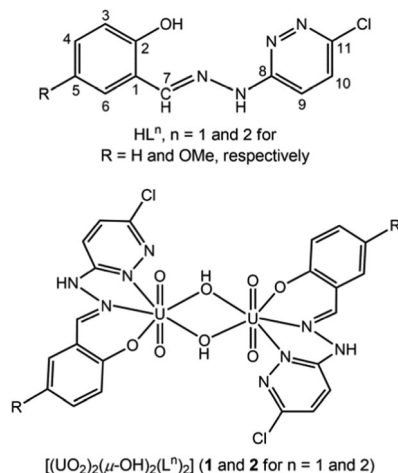


Chart 1 Chemical structure diagrams of 2-((2-(6-chloropyridazin-3-yl)-hydrazono)methyl)-4-R-phenols (HLⁿ) and their corresponding complexes [(UO₂)₂(μ-OH)₂(Lⁿ)₂].

[(UO₂)₂(μ-OH)₂(Lⁿ)₂] (1 and 2 for $n = 1$ and 2 , respectively) (Chart 1). The visible light-induced photocatalytic abilities of these two complexes have also been examined by performing the photodegradation of rhodamine B (RhB) and methylene blue (MB) solutions. Herein, we report the synthesis, X-ray structures, physical properties and photocatalytic activities of [(UO₂)₂(μ-OH)₂(L^{1/2})₂] (1 and 2).

Experimental section

Materials

3-Hydrazino-6-chloropyridazine was prepared by following a reported procedure.⁸ All other chemicals and solvents used in this work were of reagent grade, available commercially, and used as received without further purification.

Physical measurements

Elemental (CHN) analysis data were obtained using a Thermo Finnigan Flash EA1112 series elemental analyzer. A Shimadzu LCMS 2010 liquid chromatograph mass spectrometer was used for the purity verification of the Schiff bases (HL^{1/2}). Solid-state magnetic susceptibility measurements were performed using a Sherwood Scientific balance. A Digisun DI-909 conductivity meter was used for solution electrical conductivity measurements. A Thermo Scientific Nicolet iS5 FT-IR spectrophotometer was used to record the infrared spectra. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used to record the electronic spectra. The ¹H (400 MHz) NMR spectra were recorded using a Bruker NMR spectrometer. Cyclic voltammetric measurements were carried out using a CH Instruments model 620A electrochemical analyzer.

Synthesis of the complexes [(UO₂)₂(μ-OH)₂(Lⁿ)₂] (1 and 2)

Complexes 1 and 2 were synthesized using the following general procedure. Solid UO₂(OAc)₂·2H₂O (0.25 mmol) was added to a hot dimethylformamide solution (8 mL) of the corresponding HLⁿ ($n = 1$ or 2) (0.25 mmol) in a 25 mL beaker. The color of the

mixture immediately turned deep brown. The solution was then heated in a boiling water bath for about 45 min and filtered hot to remove any solid present. The filtrate was kept at room temperature (298 K) for slow evaporation. In about 3–4 weeks, the separated brown crystalline material was collected by filtration, washed with methanol and finally dried in a vacuum.

[(UO₂)₂(μ-OH)₂(L¹)₂] (1). Yield 65%. Anal. calcd for C₂₂H₁₈Cl₂N₈O₈U₂: C, 24.71; H, 1.70; N 10.48. Found C, 24.35, H, 1.76, N, 10.23. Selected IR data (ν (cm⁻¹)): 3460 (O–H), 3278 (N–H), 1620 (C=N), 891, 872 (UO₂). UV-Vis data (λ_{max} (nm) (ϵ (10⁴ M⁻¹ cm⁻¹)): 405 (4.59)^{sh}, 367 (7.85), 301 (10.97). ¹H NMR data (δ (ppm) (J (Hz))): 11.14 (s, 1H, NH), 9.02 (s, 1H, H⁷), 7.71 (8) (d, 1H, H¹⁰), 7.47 (8) (d, 1H, H⁹), 7.41 (8) (dd → t, 1H, H⁴), 6.99 (8) (d, 1H, H⁶), 6.97 (8) (d, 1H, H³), 6.69 (8) (dd → t, 1H, H⁵). CV data (E_{pc} and E_{pa} (V)): −1.01 and −0.47.

[(UO₂)₂(μ-OH)₂(L²)₂] (2). Yield 63%. Anal. calcd for C₂₄H₂₂Cl₂N₈O₁₀U₂: C, 25.52; H, 1.96, N, 9.92. Found: C, 25.21; H, 1.93, N, 9.56. Selected IR data (ν (cm⁻¹)): 3470 (O–H), 3240 (N–H), 1618 (C=N), 899 (UO₂). UV-Vis data (λ_{max} (nm) (ϵ (10⁴ M⁻¹ cm⁻¹)): 405 (6.98)^{sh}, 375 (9.52), 302 (11.59). ¹H NMR data (δ (ppm) (J (Hz))): 10.60 (s, 1H, NH), 8.97 (s, 1H, H⁷), 7.29 (3) (d, 1H, H⁶), 7.11 (s, 1H, μ-OH), 7.10 (8) (d, 1H, H¹⁰), 7.03 (8,3) (dd, 1H, H⁴), 6.92 (8) (d, 1H, H⁹), 6.87 (8) (d, 1H, H³), 3.75 (s, 3H, −OCH₃). CV data (E_{pc} and E_{pa} (V)): −1.11 and −0.50.

X-ray crystallography

Single crystals of both complexes suitable for X-ray data collection were collected from the crystalline materials separated in the synthetic reaction mixtures. In each case, the crystal was taken from the mother liquor, coated with silicone oil and then mounted on a glass fibre using epoxy. Both 1 and 2 crystallized as solvated species, which are 1·H₂O·2Me₂NCHO and 2·1.5H₂O, respectively. Unit cell determination and intensity data collection for each of 1·H₂O·2Me₂NCHO and 2·1.5H₂O were performed at room temperature (298 K) using a Bruker D8 Quest diffractometer fitted with a Photon 100 CMOS area detector and an Incoatec microfocus source for graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The APEX3 software package⁹ was used for data acquisition, integration and reduction. The SADABS program¹⁰ was employed for absorption correction. In the case of 1·H₂O·2Me₂NCHO, some residual absorption effects were treated with an additional correction using the XABS2 program.¹¹ Both structures were solved by a direct method and refined using F^2 using full-matrix least-squares procedures. In each structure, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecules were located using difference maps and placed at idealized positions, while the remaining hydrogen atoms were included at idealized positions using a riding model. All hydrogen atoms were refined as riding atoms with the relative isotropic thermal parameters of their parent atoms. The SHELX-97 programs¹² available in the WinGX software suite¹³ were used for structure solution and refinement. Structural illustrations were prepared using the Mercury package.¹⁴ The selected crystallographic data for 1·H₂O·2Me₂NCHO and 2·1.5H₂O are listed in Table 1.

Table 1 Selected crystal data and structure refinement summary

Complex	1·H ₂ O·2Me ₂ NCHO	2·1.5H ₂ O
Chemical formula	C ₂₈ H ₃₄ Cl ₂ N ₁₀ O ₁₁ U ₂	C ₂₄ H ₂₃ Cl ₂ N ₈ O _{11.5} U ₂
Formula weight	1233.61	1154.46
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	7.0485(5)	15.4436(13)
<i>b</i> (Å)	14.7628(11)	14.7742(12)
<i>c</i> (Å)	18.7692(14)	15.3194(12)
α (°)	73.799(3)	90
β (°)	89.767(3)	113.786(2)
γ (°)	89.067(3)	90
Volume (Å ³)	1875.2(2)	3198.5(5)
<i>Z</i>	2	4
ρ (g cm ^{−3})	2.185	2.397
μ (mm ^{−1})	8.837	10.352
Reflections collected	64 327	20 243
Reflections unique	6603	2812
Reflections [<i>I</i> ≥ 2 σ (<i>I</i>)]	5938	2219
Data/parameter	6603/482	2812/219
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0307, 0.0710	0.0355, 0.0791
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0351, 0.0728	0.0536, 0.0857
GoF on <i>F</i> ²	1.086	1.039
Max./min. $\Delta\rho$ (e Å ^{−3})	3.227/−1.941	0.927/−1.002

Detailed X-ray crystallographic data for 1·H₂O·2Me₂NCHO and 2·1.5H₂O have been deposited with the Cambridge Crystallographic Data Centre under the deposition numbers CCDC 1870329 and 1870330, respectively.†

Photocatalysis

Organic dyes rhodamine B (RhB) and methylene blue (MB) were selected for heterogeneous photodegradation experiments. The powdered complex catalyst (20 mg) was suspended in an aqueous solution of the dye (40 mL, conc. 10 ppm) and stirred for 1/2 h in the dark to ensure appropriate adsorption/desorption equilibrium of the dye on the catalyst surface. The mixture was then exposed to irradiation of visible light with continuous stirring. After every 1/2 h interval, a portion of the solution was pipetted out and filtered. The clear dye solution obtained after filtration was used for spectrophotometric analysis. The degradation of the dyes with the increase of the irradiation time was followed by measuring the changes in the absorption intensities at λ_{max} values of 554 and 664 nm for RhB and MB, respectively.

Results and discussion

Synthesis and characterization

Schiff bases (HL^{1/2}) were prepared in fairly high yields (~80%) by condensation reactions of equimolar amounts of 3-hydrazino-6-chloropyridazine and the corresponding 5-R-salicylaldehydes (R = H and OMe) in ethanol by following a procedure very similar to that reported earlier.^{8,15} Complexes having the general molecular formula [(UO₂)₂(μ-OH)₂(Lⁿ)₂] (1 (*n* = 1) and 2 (*n* = 2)) were synthesized in good yields (~64%) by treating the corresponding Schiff bases (HL^{1/2}) with UO₂(OAc)₂·2H₂O in dimethylformamide. The elemental analysis data of 1 and 2 are in good agreement with their molecular formulas. Room temperature magnetic susceptibility measurements on the powdered samples of the

two complexes indicate their diamagnetic character and hence the +6 oxidation state of uranium in each. Both complexes are insoluble in most common organic solvents except for dimethylformamide and dimethylsulfoxide. In solution, each of the two complexes is electrically non-conducting. The non-electrolytic behaviour of 1 and 2 is consistent with their molecular formulas as neutral species.

X-ray molecular structures

The structures of 1·H₂O·2Me₂NCHO and 2·1.5H₂O were solved in the triclinic *P* $\bar{1}$ and monoclinic *C*2/*c* space groups, respectively. The asymmetric unit of the first crystal contains one complete molecule of the dinuclear complex 1, one water molecule and two dimethylformamide molecules. On the other hand, the asymmetric unit of the second crystal contains one-half of the dinuclear complex 2, one-half of a water molecule and a second water molecule having one-quarter occupancy. The two halves of the molecule of 2 are related by an inversion centre, while a two-fold axis passes through the O-atom of each water molecule. The structures of 1·H₂O·2Me₂NCHO and 2·1.5H₂O are illustrated in Fig. 1. The bond lengths and bond angles associated with the metal centres for 1 and 2 are listed in Tables 2 and 3, respectively. In the case of 1·H₂O·2Me₂NCHO, the water molecule acts as a bridge between the two dimethylformamide molecules by forming two O–H...O hydrogen bonds with the two dimethylformamide O-atoms. One end of this Me₂NCHO...HOH...OHCNMe₂ ensemble is connected to the complex molecule through a N–H...O interaction involving the

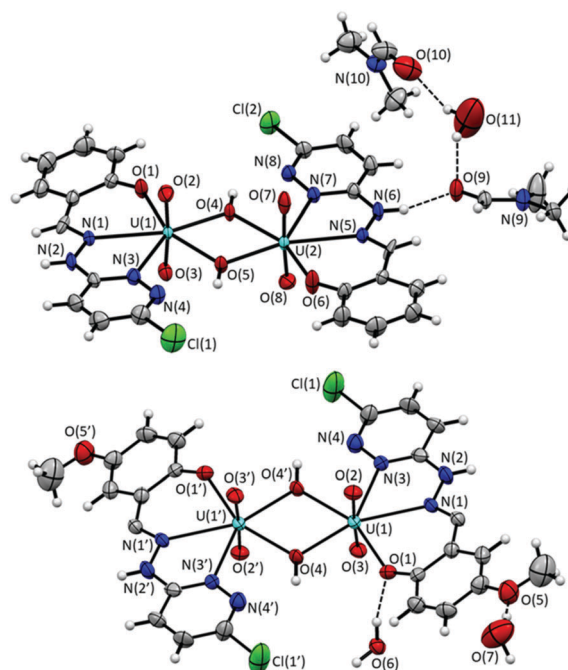


Fig. 1 The structures of [(UO₂)₂(μ-OH)₂(L¹)₂]·H₂O·2Me₂NCHO (1·H₂O·2Me₂NCHO) (top) and [(UO₂)₂(μ-OH)₂(L²)₂]·1.5H₂O (2·1.5H₂O) (bottom). In both structures, all the non-hydrogen atoms are represented by their 40% probability thermal ellipsoids and only the non-carbon atoms are labelled for clarity.

Table 2 Selected bond parameters (Å and °) for 1·H₂O·2Me₂NCHO

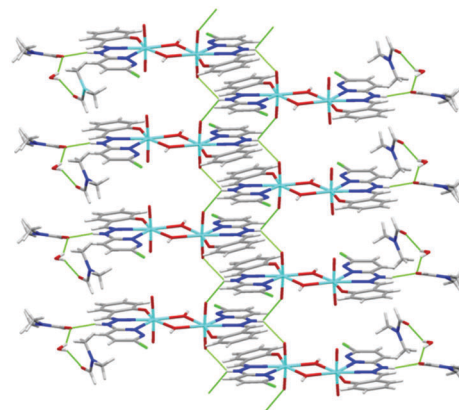
U(1)–O(1)	2.220(5)	U(2)–O(4)	2.356(4)
U(1)–O(2)	1.799(5)	U(2)–O(5)	2.336(4)
U(1)–O(3)	1.773(5)	U(2)–O(6)	2.202(5)
U(1)–O(4)	2.293(4)	U(2)–O(7)	1.737(6)
U(1)–O(5)	2.335(4)	U(2)–O(8)	1.782(5)
U(1)–N(1)	2.632(5)	U(2)–N(5)	2.621(5)
U(1)–N(3)	2.584(6)	U(2)–N(7)	2.582(5)
O(1)–U(1)–O(2)	88.8(2)	O(4)–U(2)–O(5)	66.63(15)
O(1)–U(1)–O(3)	91.8(2)	O(4)–U(2)–O(6)	155.29(17)
O(1)–U(1)–O(4)	86.77(17)	O(4)–U(2)–O(7)	89.3(2)
O(1)–U(1)–O(5)	154.40(16)	O(4)–U(2)–O(8)	91.6(2)
O(1)–U(1)–N(1)	69.24(17)	O(4)–U(2)–N(5)	134.53(16)
O(1)–U(1)–N(3)	130.01(18)	O(4)–U(2)–N(7)	72.60(16)
O(2)–U(1)–O(3)	174.1(2)	O(5)–U(2)–O(6)	88.68(17)
O(2)–U(1)–O(4)	94.3(2)	O(5)–U(2)–O(7)	91.8(2)
O(2)–U(1)–O(5)	91.5(2)	O(5)–U(2)–O(8)	93.4(2)
O(2)–U(1)–N(1)	91.2(2)	O(5)–U(2)–N(5)	158.74(16)
O(2)–U(1)–N(3)	84.4(2)	O(5)–U(2)–N(7)	139.21(16)
O(3)–U(1)–O(4)	91.5(2)	O(6)–U(2)–O(7)	90.5(3)
O(3)–U(1)–O(5)	90.5(2)	O(6)–U(2)–O(8)	90.9(3)
O(3)–U(1)–N(1)	83.5(2)	O(6)–U(2)–N(5)	70.11(18)
O(3)–U(1)–N(3)	90.8(2)	O(6)–U(2)–N(7)	132.11(18)
O(4)–U(1)–O(5)	67.67(15)	O(7)–U(2)–O(8)	174.7(2)
O(4)–U(1)–N(1)	155.26(17)	O(7)–U(2)–N(5)	87.1(2)
O(4)–U(1)–N(3)	143.04(17)	O(7)–U(2)–N(7)	88.6(2)
O(5)–U(1)–N(1)	136.32(16)	O(8)–U(2)–N(5)	88.5(2)
O(5)–U(1)–N(3)	75.42(17)	O(8)–U(2)–N(7)	86.6(2)
N(1)–U(1)–N(3)	61.51(18)	N(5)–U(2)–N(7)	62.02(17)

Table 3 Selected bond parameters (Å and °) for 2·1.5H₂O

U(1)–O(1)	2.251(6)	U(1)–O(2)	1.775(6)
U(1)–O(3)	1.776(6)	U(1)–O(4)	2.322(5)
U(1)–O(4') ^a	2.350(6)	U(1)–N(1)	2.612(7)
U(1)–N(3)	2.613(7)		
O(1)–U(1)–O(2)	92.6(3)	O(1)–U(1)–O(3)	87.2(3)
O(1)–U(1)–O(4)	86.1(2)	O(1)–U(1)–O(4') ^a	155.5(2)
O(1)–U(1)–N(3)	69.6(2)	O(1)–U(1)–N(3)	129.6(2)
O(2)–U(1)–O(3)	176.6(3)	O(2)–U(1)–O(4)	92.9(3)
O(2)–U(1)–O(4') ^a	90.7(3)	O(2)–U(1)–N(1)	82.5(3)
O(2)–U(1)–N(3)	94.6(3)	O(3)–U(1)–O(4)	90.4(3)
O(3)–U(1)–O(4') ^a	90.8(3)	O(3)–U(1)–N(1)	94.2(3)
O(3)–U(1)–N(3)	82.9(3)	O(4)–U(1)–O(4') ^a	69.4(2)
O(4)–U(1)–N(1)	155.0(2)	O(4)–U(1)–N(3)	143.0(2)
O(4') ^a –U(1)–N(1)	134.9(2)	O(4') ^a –U(1)–N(3)	74.3(2)
N(1)–U(1)–N(3)	62.0(2)		

^a Symmetry transformation used: $-x + 3/2, -y + 1/2, -z$.

O-atom of one Me₂NCHO and the hydrazinic N–H of the U(2) bound (L¹)[–] (Fig. 1). On the other hand, in 2·1.5H₂O, the full occupancy water molecule is hydrogen bonded to the metal coordinated phenolate O-atom and the water molecule having half-occupancy is hydrogen bonded to the O-atom of the methoxy substituent of (L²)[–] (Fig. 2). The structures of the two dinuclear complex molecules are very similar. The metal centres are in distorted pentagonal-bipyramidal N₂O₅ coordination spheres. The fused 5,6-membered chelate rings forming pyridazine-N, azomethine-N and phenolate-O donors (Lⁿ)[–] and the two bridging hydroxo-O atoms form a pentagonal N₂O₃ plane (rms deviations 0.03–0.16 Å), and the two oxo atoms occupy the axial positions. U₂(μ-OH)₂ is essentially planar (rms deviation 0.02 Å) in 1 and perfectly planar in 2. The U–O(H)–U bridge angles (113.2(2) and 112.4(2)°) in 1 are slightly larger than the bridge angle (110.6(2)°) in centrosymmetric 2. As a consequence,

Fig. 2 One-dimensional chain-like assembly of [(UO₂)₂(μ-OH)₂(L¹)₂]·H₂O·2Me₂NCHO (1·H₂O·2Me₂NCHO).

the U···U distance in 1 (3.8821(4) Å) is a little longer than that in 2 (3.8405(7) Å). It should be noted that very few structurally characterized discrete diuranyl(vi) complexes containing the {(UO₂)₂(μ-OH)₂}²⁺ core are known.¹⁶ Overall, the U–OH bond lengths, U–O(H)–U bridge angles and the U···U distances in the {(UO₂)₂(μ-OH)₂}²⁺ fragment of 1 and 2 are within the corresponding ranges reported earlier for complexes of this core.¹⁶ In 1, the average of the U=O bond lengths for U(1) (1.786(5) Å) is significantly longer than that for U(2) (1.760(6) Å). This difference is most likely due to the involvement of the oxo atoms O(2) and O(3) attached to U(1) in the intermolecular N–H···O hydrogen bonding interactions as acceptors (*vide infra*). In the centrosymmetric 2, the average of the U=O bond lengths is 1.776(6) Å. Overall, the U=O bond lengths in 1 and 2 are within the range found in *trans*-uranyl(vi) dication complexes.^{16–18} The *trans*-O=U=O angles (174.1(2)–176.6(3)°) are slightly different from the ideal value of 180°. The remaining bond lengths and angles associated with the uranium centres and the N,N,O-donor (Lⁿ)[–] are comparable with the corresponding bond parameters reported for the complexes of *trans*-(UO₂)²⁺ having pentagonal-bipyramidal uranium centres and similar coordinating atoms containing Schiff base ligands.^{17,18}

Hydrogen bonding and self-assembly

In both structures, the complex molecules and the lattice solvent molecules have several classical hydrogen bond donors such as N–H and O–H and acceptors such as O- and Cl-atoms. Thus, the two structures were scrutinized for intermolecular hydrogen bonding interactions and if any were found, then how they directed the supramolecular self-assembly process was investigated. The intermolecular hydrogen bonds found are O–H···O and bifurcated O–H···O···H–N and N–H···(O,O) in 1·H₂O·2Me₂NCHO and O–H···O and N–H···O in 2·1.5H₂O. The geometric parameters for these intermolecular hydrogen bonds are listed in Table 4 and the supramolecular structures assembled by them are described below.

In 1·H₂O·2Me₂NCHO, the hydrogen bonded ensemble of lattice solvent molecules (Me₂NCHO···HOH···OHNCMe₂) that is connected to the U(2) side of 1 *via* the N–H···O interaction

Table 4 Hydrogen bonding parameters for **1**·H₂O·2Me₂NCHO and **2**·1.5H₂O^a

Complex	D–H···A	D···A (Å)	∠DHA (°)
1 ·H ₂ O·2Me ₂ NCHO	N(6)–H(6)···O(9)	2.758(8)	163
	O(11)–H(11A)···O(9)	3.017(13)	153
	O(11)–H(11B)···O(10)	2.750(16)	142
	N(2)–H(2A)···O(2) ⁱ	2.964(7)	133
	N(2)–H(2A)···O(3) ⁱⁱ	3.093(8)	127
2 ·1.5H ₂ O	O(6)–H(6A)···O(1)	2.705(7)	161
	O(7)–H(7A)···O(5)	2.94(2)	158
	N(2)–H(2A)···O(6) ⁱⁱⁱ	2.844(10)	174

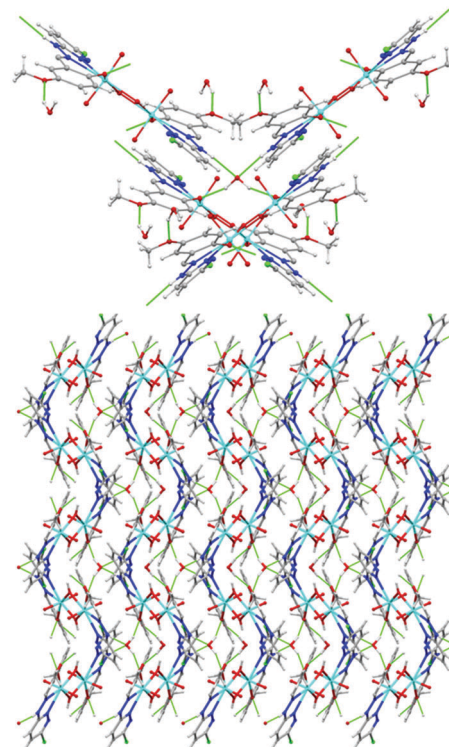
^a Symmetry transformations used: (i) $-x + 1, -y + 1, -z + 1$. (ii) $-x + 2, -y + 1, -z + 1$. (iii) $-x + 1, -y, -z$.

(Fig. 1) does not participate in any further intermolecular interaction. However, on the other side of the solvated dinuclear molecule, the hydrazinic N–H of the U(1) coordinated (L^1)[−] and the U(1) bound oxo atoms O(2) and O(3) participate in three bifurcated N–H···(O,O) hydrogen bonding interactions with two neighbouring inversion symmetry-related molecules in a reciprocal manner. This intermolecular N–H···(O,O) interaction leads to a one-dimensional assembly of **1**·H₂O·2Me₂NCHO in the crystal lattice (Fig. 2).

In **2**·1.5H₂O, the two-fold symmetric half-occupancy water molecule acts as a donor in two O–H···O hydrogen bonds involving the O-atoms of the methoxy substituents on the salicylidene moieties of (L^2)[−] of two complex molecules. This water molecule is not involved in any other hydrogen bonding. The formation of a one-dimensional chain like array of **2**·0.5H₂O due to the above-mentioned intermolecular O–H···O interactions cannot be counted because of the positional disorder of the water molecule. On the other hand, the second two-fold symmetric but full occupancy water molecule participates in the maximum possible, that is, four hydrogen bonding interactions. These are two O–H···O interactions as the donor and two N–H···O interactions as the acceptor. In the former, the uranium coordinated phenolate-O atom of (L^2)[−] is the acceptor and in the latter, the hydrazinic N–H of (L^2)[−] is the donor. Thus, each full occupancy water molecule is connected to four complex molecules that are tetrahedrally oriented around the water O-atom, and a butterfly-like motif is formed (Fig. 3, top). The interconnection of these motifs *via* these four intermolecular hydrogen bonding interactions leads to an overall three-dimensional network of **2**·1.5H₂O in the crystal lattice (Fig. 3, bottom).

Spectroscopic characterizations

The infrared spectra of **1** and **2** were recorded in ATR mode in the range of 4000–550 cm^{−1}. A large number of bands with various intensities were observed in each spectrum. No attempt has been made to assign all the bands except for a few characteristic bands. Both complexes display a broad band at ~3465 cm^{−1}. A similar band observed for dihydroxo-bridged complexes was attributed to the bridging-OH groups.^{16g,19} A weak and somewhat broad band observed at ~3260 cm^{−1} has been assigned to the hydrazinic-NH of (L^n)[−].^{15,20} The sharp and strong band at ~1619 cm^{−1} displayed by both complexes is attributed to the metal coordinated azomethine (–HC=N–) group of (L^n)[−].^{15,18,19}

**Fig. 3** Butterfly-like motif (top) and the three-dimensional network of [(UO₂)₂(μ-OH)₂(L²)₂].1.5H₂O (**2**·1.5H₂O) viewed along the *a*-axis (bottom).

The spectrum of **1** displays two closely spaced strong bands at 891 and 872 cm^{−1}, while the spectrum of **2** displays a single strong band at 899 cm^{−1}. The asymmetric stretching vibration of the *trans*-uranyl(vi) moiety is generally observed in this region as a strong band.^{16g,h,17,18} The observation of two closely spaced bands in the case of **1** is most likely due to the difference in the two average U=O bond lengths at the two uranium centres caused by the participation of the oxo atoms of one metal centre in intermolecular hydrogen bonding interactions (*vide supra*).

The electronic spectra of both **1** and **2** were recorded in dimethylformamide. The spectral profiles of the two complexes are very similar (Fig. 4). They display a somewhat broad and strong band centred at ~370 nm (367 and 375 nm for **1** and **2**, respectively), which is preceded by a shoulder at ~405 nm and followed by another strong band at ~302 nm. The free Schiff bases (HL^{1/2}) in dimethylformamide display two strong bands having almost equal intensities at ~350 and ~300 nm. A comparison of the spectra of the complexes with those of the Schiff bases clearly indicates that for **1** and **2**, the absorption at ~302 nm is due to a ($L^{1/2}$)[−] centred transition. The absorption bands in the longer-wavelength ultraviolet region for the *trans*-diuranyl(vi) dication containing species are characteristic of charge transfer transitions involving the U=O bonds.²¹ Thus, the absorption band of **1** and **2** at ~370 nm, which is red-shifted in comparison to the corresponding absorption of the Schiff bases at ~350 nm, has most likely a combined ($L^{1/2}$)[−] centred and *trans*-(UO₂)²⁺ centred charge transfer character. In the visible region, the shoulder at 405 nm

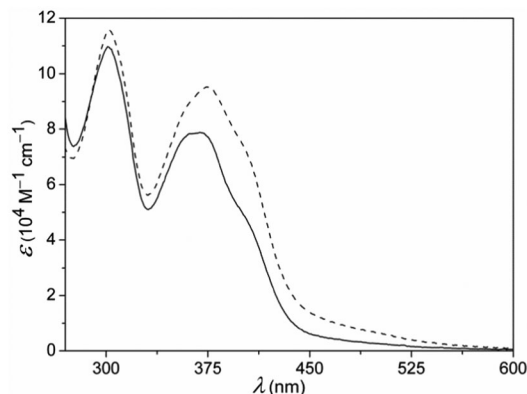


Fig. 4 Electronic spectra of $[(\text{UO}_2)_2(\mu\text{-OH})_2(\text{L}^1)_2]$ (**1**) (—) and $[(\text{UO}_2)_2(\mu\text{-OH})_2(\text{L}^2)_2]$ (**2**) (---) in dimethylformamide.

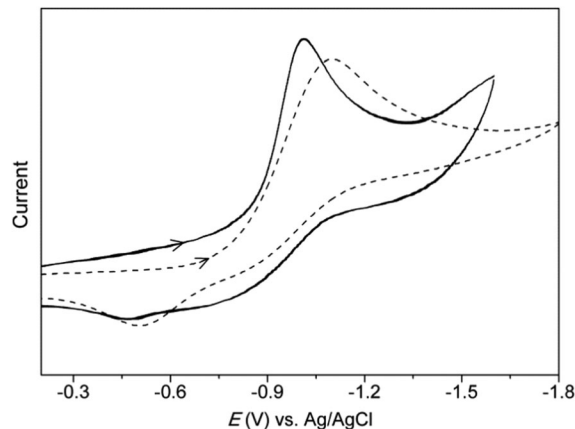


Fig. 5 Cyclic voltammograms of $[(\text{UO}_2)_2(\mu\text{-OH})_2(\text{L}^1)_2]$ (**1**) (—) and $[(\text{UO}_2)_2(\mu\text{-OH})_2(\text{L}^2)_2]$ (**2**) (---) in dimethylformamide.

has been assigned to a primarily phenolate-to-metal charge transfer transition.

The ^1H NMR spectra of **1** and **2** were recorded in DMSO-d_6 solutions. Both spectra clearly indicate that in solution, the two halves of the centrosymmetric complex molecule are equivalent. The chemical shift values with tentative assignments are provided in the Experimental section under the respective complexes. The absence of any signal assignable to the phenol proton resonance¹⁵ is consistent with the deprotonated state of the Schiff base ligand in both complexes. The hydrazinic N–H appears as a singlet at δ 11.14 and 10.60 ppm for **1** and **2**, respectively. The azomethine ($-\text{HC}=\text{N}-$) proton (H^7) of **1** and **2** resonates as a singlet at δ 9.02 and 8.97 ppm, respectively. A singlet observed at δ 7.11 ppm for **2** is assigned to the bridging hydroxyl group proton.²² However, no such signal was observed for **1**. The protons of the methoxy substituent in **2** are observed as a singlet at δ 3.75 ppm. In both complexes, the aromatic protons of $(\text{L}^1)^-$ and $(\text{L}^2)^-$ appear with the expected splitting patterns in the ranges δ 7.71–6.69 and 7.29–6.87 ppm, respectively.

Redox properties

The redox properties of **1** and **2** were investigated by cyclic voltammetric measurements using their corresponding dimethylformamide solutions ($\sim 10^{-3}$ M) containing tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte with a Pt-disk working electrode, a Pt-wire auxiliary electrode and a Ag/AgCl reference electrode under nitrogen atmosphere at 298 K. Under identical conditions, the $E_{1/2}$ and $\Delta E_p (= E_{pa} - E_{pc})$ values for the ferrocenium/ferrocene (Fc^+/Fc) couple were 0.50 V and 150 mV, respectively. The cyclic voltammograms of the two complexes are very similar. They display a cathodic peak and a well separated weak anodic peak in the reverse scan (Fig. 5). The cathodic peak potential (E_{pc}) is -1.01 and -1.10 V and the corresponding anodic peak potential (E_{pa}) is -0.47 and -0.50 V for **1** and **2**, respectively. The cathodic peak currents of both complexes are comparable with those of the Fc^+/Fc couple and other known one electron transfer processes under similar conditions.^{18,23} The free Schiff bases show an irreversible reduction response, having relatively broader peaks at more cathodic potentials (average E_{pc} and E_{pa} values are around -1.55

and -0.82 V, respectively) under the same experimental conditions. Upon comparison of the reduction responses displayed by the complexes with those of $\text{HL}^{1/2}$ and considering that the complexes of $\text{trans-(UO}_2\text{)}^{2+}$ with ligands having comparable coordinating atoms are known to show a uranium(vi) to uranium(v) reduction in a similar potential range, the reductions observed for **1** and **2** were assigned to a metal centred process.^{17a,18} This assignment was further substantiated by the 90 mV cathodic shift of the E_{pc} of **2** compared to that of **1** due to the presence of the electron releasing methoxy group *para* to the phenolate-O of the ligand $(\text{L}^2)^-$ in **2**.

Photocatalytic activities

The electronic transition within the $\text{U}=\text{O}$ double bond was considered to be the key for the photocatalytic activities of the complexes of the *trans*-diuranyl(vi) dication.^{2,3} The transition that gives rise to the absorption band of **1** and **2** at 367 and 375 nm, respectively, has a partial $\text{trans-(UO}_2\text{)}^{2+}$ centred character (*vide supra*). The appearance of this band near to the violet end of the visible light accompanied by the shoulder in the visible region at ~ 405 nm prompted us to examine the photocatalytic potentials of **1** and **2** by visible light irradiation. Herein, we have chosen rhodamine B (RhB) and methylene blue (MB) as model pollutants for the photo-degradation experiments. The photocatalytic reactions were heterogeneous in nature where the catalyst powder (**1** or **2**) was suspended in the dye solution and stirred in the presence of white visible light. The degradation of the dye (RhB or MB) with the increase in the irradiation time was monitored spectrophotometrically. The change in the spectroscopic profile of RhB with time in the presence of **2** as a catalyst under light is illustrated in Fig. 6. The irradiation time dependent spectral changes for RhB in the presence of **1** as the catalyst and those of MB in the presence of **1** as well as **2** as the catalyst are depicted in Fig. S1–S3, respectively (ESI[†]). In the control experiments without catalysts in the presence of light, the variation in the absorption spectrum of either of the two dyes is insignificant. The degradation of RhB is as high as 96% in 150 min with **2** as the catalyst, whereas with **1** as the catalyst, the degradation was 80% over the span of 180 min.

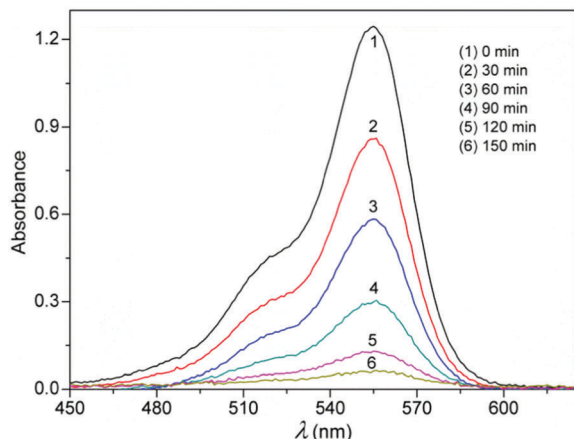


Fig. 6 Photocatalytic degradation of rhodamine B (RhB) under visible light irradiation using $[(\text{UO}_2)_2(\mu\text{-OH})_2(\text{L}^2)_2]$ (**2**) as a catalyst.

In the case of MB, the degradation was 71% in 210 min and 85% in 180 min for **1** and **2**, respectively. Thus, **2** is a relatively more effective catalyst in the photodegradation of both dyes (Fig. 7). This difference in the activities is consistent with the appearance of the first absorption band in the ultraviolet region for **2** at a slightly lower energy than that for **1** and the higher extinction coefficients of this band and the ~ 405 nm shoulder of **2** compared to those of **1**. In general, the photocatalytic dye degradation abilities of **1** and **2** are better than or comparable with the previously reported uranyl containing catalysts.^{2c,3a,b,e-g}

In order to account for the reusability of **1** and **2** as catalysts, they were recovered after the reactions by filtration. About 85% of the catalysts was recovered. The NMR spectra of the recovered samples were essentially identical to the spectra of the complexes before the reaction. Thus, the complexes remained intact throughout the catalysis and they can be recycled and reused for further catalytic cycles.

The mechanism suggested for the photocatalytic dye degradation primarily involves two processes – electron transfer and

hydrogen abstraction.^{2,3} Upon photoexcitation of the *trans*-(UO_2)²⁺ containing species, the electrons get promoted from the highest bonding molecular orbital primarily possessing a coordinated oxygen character to the lowest antibonding molecular orbital localized at the uranium atom, and thereby the excited *trans*-(UO_2)²⁺ containing species is generated. In the presence of a suitable guest like the dye molecule, the hole in the highest bonding molecular orbital gets filled by an electron from the α -CH of the dye while the promoted electron still remains in the antibonding molecular orbital. As a result, a dye degradation intermediate and a proton are produced. Since the antibonding molecular orbital in the reduced photo-excited *trans*-(UO_2)²⁺ containing species is higher in energy, the electron in it is not stable and hence it reduces the dissolved oxygen to reactive oxygen species such as superoxide or peroxide. These reactive species are responsible for the oxidation and complete degradation of the dye molecules. Thus, aerobic conditions are essential because in the absence of oxygen, the reduced photo-excited *trans*-(UO_2)²⁺ containing species will not be oxidized back to the original *trans*-(UO_2)²⁺ containing catalyst and there will be no generation of reactive oxygen species to carry on the dye degradation process further.

Conclusions

Two complexes having the general molecular formula $[(\text{UO}_2)_2(\mu\text{-OH})_2(\text{L}^n)_2]$ containing the rare di- μ -hydroxo-diuranyl(vi) core with the Schiff base system 2-((2-(6-chloropyridazin-3-yl)hydrazono)-methyl)-4-R-phenol (HL^n) have been synthesized. The X-ray structures of the solvated complexes revealed the meridionally spanning fused 5,6-membered chelate rings forming the N,N,O-donor coordination mode of $(\text{L}^n)^-$ and the pentagonal bipyramidal N_2O_5 coordination sphere around the metal centres in each of the two complexes. Supramolecular self-assembly *via* intermolecular simple and bifurcated hydrogen bonding interactions leads to one-dimensional chain-like and three-dimensional network structures in the crystal lattices of the two solvated complexes. The spectroscopic features of both complexes are consistent with their molecular structures. The redox active complexes display a metal centred one-electron reduction process. Utilizing the visible region absorption shoulder and a strong absorption band close to the high-energy end of the visible light of both complexes, their excellent photocatalytic activities in the degradation of organic dyes in the presence of visible light have been demonstrated.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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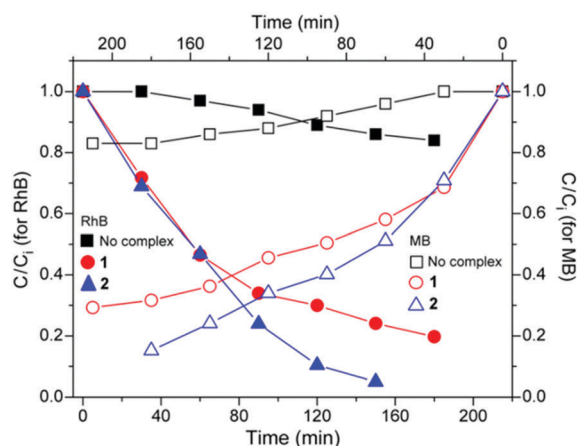


Fig. 7 Change of dye (RhB and MB) concentrations with and without the catalyst (**1** and **2**) as a function of irradiation time. C and C_i represent the dye concentrations after and before irradiation, respectively.

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Notes and references

- (a) R. G. Denning, *Struct. Bonding*, 1992, **79**, 215–276; (b) R. G. Denning, *J. Phys. Chem. A*, 2007, **111**, 4125–4143.
- (a) H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, 1974, **3**, 139–165; (b) H. D. Burrows and M. da Graça Miguel, *Adv. Colloid Interface Sci.*, 2001, **89–90**, 485–496; (c) K.-X. Wang and J.-S. Chen, *Acc. Chem. Res.*, 2011, **44**, 531–540; (d) R. J. Baker, *Chem. – Eur. J.*, 2012, **18**, 16258–16271; (e) Z. R. Ismagilov and S. V. Lazareva, *Catal. Rev.: Sci. Eng.*, 2013, **55**, 135–209; (f) L. Yong, S. Jing, M. Ellen, Z. GuoQing and L. Jun, *Sci. China: Chem.*, 2013, **56**, 1671–1681.
- (a) Z.-T. Yu, Z.-L. Liao, Y.-S. Jiang, G.-H. Li, G.-D. Li and J.-S. Chen, *Chem. Commun.*, 2004, 1814–1815; (b) Z.-T. Yu, Z.-L. Liao, Y.-S. Jiang, G.-H. Li and J.-S. Chen, *Chem. – Eur. J.*, 2005, **11**, 2642–2650; (c) S. Kannan, A. E. Vaughn, E. M. Weis, C. L. Barnes and P. B. Duval, *J. Am. Chem. Soc.*, 2006, **128**, 14024–14025; (d) S. Tsushima, *Inorg. Chem.*, 2009, **48**, 4856–4862; (e) W. Yang, W. G. Tian, X. X. Liu, L. Wang and Z. M. Sun, *Cryst. Growth Des.*, 2014, **14**, 5904–5911; (f) H.-H. Li, X.-H. Zeng, H.-Y. Wu, X. Jie, S.-T. Zheng and Z.-R. Chen, *Cryst. Growth Des.*, 2015, **15**, 10–13; (g) M. Azam, G. Velmurugan, S. M. Wabaidur, A. Trzesowska-Kruszynska, R. Kruszynski, S. I. Al-Resayes, Z. A. Al-Othman and P. Venuvanalingam, *Sci. Rep.*, 2016, **6**(32898), 1–13, DOI: 10.1038/srep32898.
- (a) M. R. Maurya and R. C. Maurya, *Rev. Inorg. Chem.*, 1995, **15**, 1–108; (b) J. L. Sessler, P. J. Melfi and G. D. Pantos, *Coord. Chem. Rev.*, 2006, **250**, 816–843; (c) P. A. Giesting and P. C. Burns, *Crystallogr. Rev.*, 2006, **12**, 205–255; (d) K.-X. Wang and J.-S. Chen, *Acc. Chem. Res.*, 2011, **44**, 531–540; (e) R. J. Baker, *Chem. – Eur. J.*, 2012, **18**, 16258–16271; (f) K. Kiegiel, L. Steczek and G. Zakrzewska-Trznadel, *J. Chem.*, 2013, 762819; (g) A. G. Beirakhov, I. M. Orlova and Y. N. Mikhailov, *Russ. J. Inorg. Chem.*, 2014, **59**, 1679–1690; (h) T. Loiseau, I. Mihalcea, N. Henry and C. Volkringer, *Coord. Chem. Rev.*, 2014, **266–267**, 69–109.
- (a) M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69–96; (b) H. Kirsch, *Angew. Chem., Int. Ed.*, 2013, **52**, 812–847; (c) T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 2014, **43**, 7520–7535.
- (a) A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobiol., C*, 2000, **1**, 1–21; (b) G. Burgeth and H. Kisch, *Coord. Chem. Rev.*, 2002, **230**, 41–47; (c) X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891–2959; (d) C. L. Pang, R. Lindsay and G. Thornton, *Chem. Soc. Rev.*, 2008, **37**, 2328–2353; (e) G. S. Mital and T. Manoj, *Chin. Sci. Bull.*, 2011, **56**, 1639–1657; (f) M. A. Lazar, S. Varghese and S. S. Nair, *Catalysts*, 2012, **2**, 572–602; (g) Z. F. Yin, L. Wu, H. G. Yang and Y. H. Su, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4844–4858.
- (a) S. G. Kumar and L. G. Devi, *J. Phys. Chem. A*, 2011, **115**, 13211–13241; (b) D. Pei and J. Luan, *Int. J. Photoenergy*, 2012, 262831; (c) Y.-Q. Zou, J.-R. Chen and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2013, **52**, 11701–11703; (d) P. Kanhere and Z. Chen, *Molecules*, 2014, **19**, 19995–20022; (e) S. N. Tijare, S. Bakardjieva, J. Subrt, M. V. Joshi, S. S. Rayalu, S. Hishita and N. Labhsetwar, *J. Chem. Sci.*, 2014, **126**, 517–525; (f) R. S. Jack, G. A. Ayoko, M. O. Adebajo and R. L. Frost, *Environ. Sci. Pollut. Res.*, 2015, **22**, 7439–7449; (g) R. Fagan, D. E. McCormack, D. D. Dionysiou and S. C. Pillai, *Mater. Sci. Semicond. Process.*, 2016, **42**, 2–14; (h) *Semiconductor Photocatalysis: Materials, Mechanisms and Applications*, ed. W. Cao, IntechOpen, London, 2016.
- K. R. Grünwald, M. Volpe, P. Cias, G. Gescheidt and N. C. Mösch-Zanetti, *Inorg. Chem.*, 2011, **50**, 7478–7488.
- APEX3, *Program for Data Collection on Area Detectors*, Bruker AXS Inc., Madison, Wisconsin, USA, 2016.
- G. M. Sheldrick, *SADABS, Program for Area Detector Absorption Correction*, University of Göttingen, Göttingen, Germany, 1997.
- S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53–56.
- G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
- L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849–854.
- F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466–470.
- U. M. Rafi, D. Mahendiran, A. K. Haleel, R. P. Nankar, M. Doble and A. K. Rahiman, *New J. Chem.*, 2016, **40**, 2451–2465.
- (a) M. Åberg, *Acta Chem. Scand.*, 1969, **23**, 791–810; (b) J. Jiang, M. J. Sarsfield, J. C. Renshaw, F. R. Livens, D. Collison, J. M. Charnock, M. Helliwell and H. Eccles, *Inorg. Chem.*, 2002, **41**, 2799–2806; (c) A. Fischer and G. Palladino, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m1542–m1544; (d) B. Masci and P. Thuéry, *Polyhedron*, 2005, **24**, 229–237; (e) V. Cocalia, M. Smiglak, S. P. Kelley, J. L. Shamshina, G. Gurau and R. D. Rogers, *Eur. J. Inorg. Chem.*, 2010, 2760–2767; (f) N. D. Shepherd, Y. Zhang, I. Karatchevtseva, J. R. Price, L. Kong, N. Scales and G. R. Lumpkin, *Polyhedron*, 2016, **113**, 88–95; (g) K. Lyczko and L. Steczek, *J. Struct. Chem.*, 2017, **58**, 102–106; (h) S. Hadjithoma, M. G. Papanikolaou, E. Leontidis, T. A. Kabanos and A. D. Keramidas, *Inorg. Chem.*, 2018, **57**, 7631–7643.
- (a) Z. Asadi, M. Asadi, A. Zeinali, M. Ranjkeshshorkaei, K. Fejfarova, V. Eigner, M. Dusek and A. Dehnokhalaji, *J. Chem. Sci.*, 2014, **126**, 1673–1683; (b) M. Azam, S. I. Al-Resayes, A. Trzesowska-Kruszynska and R. Kruszynski, *Polyhedron*, 2017, **124**, 177–183; (c) X. Zhao, D. Zhang, R. Yu, S. Chen and D. Zhao, *Eur. J. Inorg. Chem.*, 2018, 1185–1191.
- S. Ghosh, S. K. Kurapati, A. Ghosh, A. K. Srivastava and S. Pal, *Chemistry Select*, 2018, **3**, 4865–4872 and references therein.

- 19 (a) J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, 1965, **4**, 1382–1386; (b) D. L. Perry, *Inorg. Chim. Acta*, 1982, **65**, L211–L213.
- 20 (a) N. R. Sangeetha, C. K. Pal, P. Ghosh and S. Pal, *J. Chem. Soc., Dalton Trans.*, 1996, 3293–5296; (b) A. Sarkar and S. Pal, *Polyhedron*, 2006, **25**, 1689–1694; (c) A. Sarkar and S. Pal, *Polyhedron*, 2007, **26**, 1205–1210; (d) S. K. Kurapati, U. Ugandhar, S. Maloth and S. Pal, *Polyhedron*, 2012, **42**, 161–167; (e) K. Nagaraju, R. Raveendran, S. N. Pal and S. Pal, *Polyhedron*, 2012, **33**, 52–59.
- 21 (a) V. A. Volkovich, T. R. Griffiths, D. J. Fray and R. C. Thied, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5182–5191; (b) P. M. Almond and T. E. Albrecht-Schmitt, *Inorg. Chem.*, 2002, **41**, 1177–1183.
- 22 A. F. Oliveri, L. A. Wills, C. R. Hazlett, M. E. Carnes, I.-Y. Chang, P. H.-Y. Cheong and D. W. Johnson, *Chem. Sci.*, 2015, **6**, 4071–4085.
- 23 (a) R. Raveendran and S. Pal, *Eur. J. Inorg. Chem.*, 2008, 5540–5546; (b) R. Raveendran and S. Pal, *J. Organomet. Chem.*, 2009, **694**, 1482–1486; (c) K. Nagaraju and S. Pal, *Inorg. Chim. Acta*, 2014, **413**, 102–108; (d) S. K. Kurapati and S. Pal, *Dalton Trans.*, 2015, **44**, 2401–2408.

Nickel(II) complexes with N,O-donor thiopseudourea ligands: Syntheses, structures, and catalytic applications in Kumada–Corriu cross-coupling reactions

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Synthesis, characterization, and physical properties of benzyl-*N'*-(4-*R*-benzoyl)-*N*-(2,6-diisopropylphenyl)carbamimidothioates, HL¹ (R = H) and HL² (R = Cl), and their nickel(II) complexes having the general molecular formula [Ni(L^{1/2})₂] (**1** and **2**) have been reported. Elemental analysis, magnetic susceptibility, solution electrical conductivity, and various spectroscopic (IR, UV–Vis, and ¹H NMR) measurements were used to characterize HL¹, HL², and the two complexes (**1** and **2**). The molecular structures of all four compounds were determined by single-crystal X-ray crystallographic studies. The structures of HL¹ and HL² showed the imino-ketone form of both compounds. In each of **1** and **2**, the six-membered chelate ring forming iminolate-O and azomethine-N donor two (L^{1/2})[−] ligands form a square-planar *trans*-N₂O₂ coordination environment around the metal center. The spectroscopic characteristics of HL¹, HL², **1**, and **2** are consistent with their molecular structures. Both complexes were successfully employed as efficient catalysts in Kumada–Corriu C–C cross-coupling reactions of aryl bromides with phenylmagnesium bromide. The reactions provided biaryl products in good to excellent yields with a good substrate scope.

KEYWORDS

crystal structure, Kumada–Corriu reaction, nickel(II), NO-donor, thiopseudourea

1 | INTRODUCTION

Transition metal catalyzed cross-coupling reaction leading to the formation of C–C bond is a powerful and widely used tool for the synthesis of natural products and a variety of complex and structurally intricate organic compounds with potential for use as agrochemicals, pharmaceuticals, and functional materials.^[1,2] The biaryl frameworks are widespread and play important roles in deciding the properties and activities of these types of compounds. Hence, in recent years, the syntheses of biaryls via C–C cross-coupling reactions have attracted

particular attention.^[2] Generally, complexes of palladium, the 4d-block transition metal in Group 10, are found to be the most efficient catalysts for the various cross-coupling reactions. However, due to the high cost of palladium, there is a continuous quest for less expensive and environment friendly alternative to these palladium catalysts. As a result, complexes of nickel, the lightest and inexpensive member of Group 10, have attracted immense attention as catalysts for cross-coupling reaction.^[3–6] The first nickel catalyzed C–C cross-coupling reaction using alkyl or aryl halides, and Grignard reagents were reported independently by

Tamao et al.^[3] and Corriu and Masse^[4] in 1972. Since then, a large number of nickel complexes with a variety of ligands such as Schiff bases, monophosphines/diphosphines/triphosphines, diamines, β -diketonates, *N*-heterocyclic carbenes, and various pincer ligands have been employed for this cross-coupling reaction.^[5,6] Thiourea, isothiurea, and thiopseudourea derivatives are of considerable interest for their complexation behaviors and applications as catalysts as well as for their biological and biochemical properties leading to various therapeutic and diagnostic applications.^[7–9] In this work, we have examined the coordination behavior of two thiopseudoureas benzyl-*N'*-(4-*R*-benzoyl)-*N*-(2,6-diisopropylphenyl)carbamimidothioates (HL^n , where $n = 1$ and 2 for $R = H$ and Cl , respectively) toward nickel(II) (Scheme 1) and the catalytic activities of the resulting complexes in Kumada–Corriu cross-coupling reaction. The deprotonated thiopseudourea system (L^n)[−] can act as a bidentate six-membered chelate ring forming ligand in two ways: via iminolate-O and thioether-S coordination or via iminolate-O and azomethine-N coordination. Considering the moderately soft character of nickel(II) and the sterically crowded environment of the azomethine-N, it was anticipated that (L^n)[−] may prefer the O,S-coordination mode rather than the O,N-coordination mode. In a somewhat similar situation, it has been found that *N,N*-dialkyl/diaryl-*N'*-(aryl)thioureates (L)[−] provide square-planar nickel(II) complexes [NiL_2], where (L)[−] coordinates the metal center through the O-atom and the less crowded S-atom instead of the N-atom containing two alkyl groups.^[7] It may be noted that like the present ligand system, each of these thioureates (L)[−] also forms six-membered chelate ring at the metal center in either O,S- or O,N-coordination

mode. Interestingly, the present thiopseudourea ligand system (L^n)[−] behaves in the opposite way and acts as O,N-donor in the two complexes having the general formula [$Ni(L^n)_2$] (**1** and **2** where $n = 1$ and 2, respectively) (Scheme 1). Herein, we report the syntheses, characterization, and X-ray structures of $HL^{1/2}$ and their complexes [$Ni(L^{1/2})_2$] (**1** and **2**). Application of both complexes as effective catalysts in Kumada–Corriu C–C cross-coupling reactions of aryl bromides with phenylmagnesium bromide has been demonstrated.

2 | EXPERIMENTAL

2.1 | Materials

Aryl halides and phenylmagnesium bromide for the cross-coupling reactions were procured from Sigma-Aldrich and were used as received. The *N*-(4-*R*-benzoyl)-*N'*-(2,6-diisopropylphenyl)thioureas ($R = H$ and Cl) were prepared in about 90% yields from 4-*R*-benzoyl chlorides ($R = H$ and Cl), NH_4SCN , and 2,6-diisopropylaniline by following a reported procedure.^[9] All other chemicals used in this work were of reagent grade available commercially and were used without further purification. All solvents used were purified by standard methods.^[10]

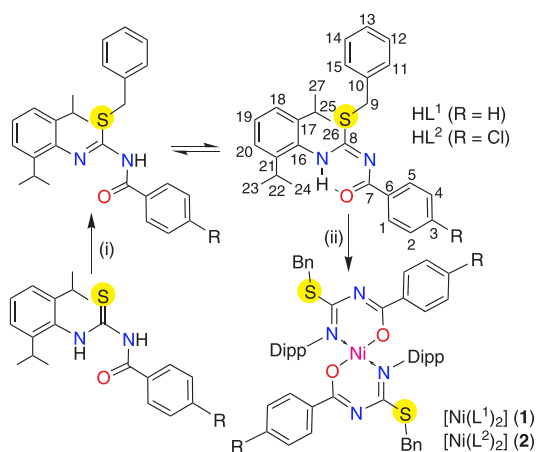
2.2 | Physical measurements

Elemental (CHN) analyses were performed on a Thermo Finnigan Flash EA1112 series elemental analyzer. A Sherwood scientific balance was used for the magnetic susceptibility measurements. A Digisun DI-909 conductivity meter was used to measure the electrical conductivities in solution. The infrared spectra were recorded with a Bruker TENSOR II FT-IR spectrophotometer. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used to collect the electronic spectra. The ¹H NMR spectra were recorded using a Bruker NMR spectrometer.

2.3 | Synthetic procedures

2.3.1 | Benzyl-*N'*-(4-*R*-benzoyl)-*N*-(2,6-diisopropylphenyl)carbamimidothioates (HL^n)

Benzyl bromide (0.36 ml, 518 mg, 3 mmol) was added dropwise to a solution of *N*-(4-*R*-benzoyl)-*N'*-(2,6-diisopropylphenyl)thiourea ($R = H$ or Cl) (3 mmol) and NaH (60% in mineral oil, 200 mg, 5 mmol) in tetrahydrofuran (50 ml) and stirred at 0°C for 3 h. The



SCHEME 1 Syntheses of $HL^{1/2}$ and [$Ni(L^{1/2})_2$] (**1** and **2**):

(i) $PhCH_2Br$ and NaH in tetrahydrofuran at 0°C for 3 h.

(ii) $Ni(OAc)_2 \cdot 4H_2O$ in $MeOH-CHCl_3$ (1:1) at 50°C for 24 h

reaction mixture was then neutralized with aqueous NH_4Cl , and the organic layer was extracted with ethyl acetate (2×50 ml), dried over MgSO_4 , filtered, and finally, the filtrate was evaporated to dryness in vacuum to obtain the crude product. It was then purified by column chromatography on silica gel using ethyl acetate-*n*-hexane mixture (1:9) as the eluent. The solution obtained was evaporated to dryness and the product was isolated as white solid.

HL¹: Yield 1.1 g (85%). Anal. Calcd for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{OS}$ (430.59) (%): C, 75.31. H, 7.02. N, 6.51. Found (%): C, 75.26. H, 7.12. N, 6.63. Selected IR bands (cm^{-1}): 3165 (NH), 1653 (C=O), 1598 (C=N). ^1H NMR (CDCl_3 , 500 MHz, δ [J], ppm [Hz]): 12.45 (s, 1H, NH), 8.38 (8) (d, 2H, $\text{H}^{1,5}$), 7.55 (8) (t, 1H, H^3), 7.48 (8) (dd $\rightarrow$ t, 2H, $\text{H}^{2,4}$), 7.39–7.35 and 7.29–7.23 (both m, 3H, 3H, $\text{H}^{11-15,19}$), 7.21 (8) (d, 2H, $\text{H}^{18,20}$), 4.55 (s, 2H, $\text{H}^{9a,b}$), 3.14 (7) (sep, 2H, $\text{H}^{22,25}$), 1.25 (7) (d, 6H, Me-protons of dipp), 1.18 (7) (d, 6H, Me-protons of dipp).

HL²: Yield 1.2 g (86%). Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{ClOS}$ (465.03) (%): C, 69.73. H, 6.29. N, 6.02. Found (%): C, 69.85. H, 6.35. N, 6.12. Selected IR bands (cm^{-1}): 3199 (NH), 1686 (C=O), 1598 (C=N). ^1H NMR (CDCl_3 , 500 MHz, δ [J], ppm [Hz]): 12.40 (s, 1H, NH), 8.29 (9) (d, 2H, $\text{H}^{1,5}$), 7.44 (9) (d, 2H, $\text{H}^{2,4}$), 7.40–7.33 and 7.30–7.24 (both m, 3H, 3H, $\text{H}^{11-15,19}$), 7.22 (8) (d, 2H, $\text{H}^{18,20}$), 4.52 (s, 2H, $\text{H}^{9a,b}$), 3.13 (7) (sep, 2H, $\text{H}^{22,25}$), 1.26 (7) (d, 6H, Me-protons of dipp), 1.18 (7) (d, 6H, Me-protons of dipp).

2.3.2 | $[\text{Ni}(\text{L}^1/\text{L}^2)_2]$ (1 and 2)

A methanol solution (30 ml) of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (249 mg, 1 mmol) was added to a chloroform solution (30 ml) of HL^n (2 mmol), and the mixture was stirred at 50°C for 24 h. The reaction mixture was then evaporated under reduced pressure, and the solid obtained was washed with water and then dried in a vacuum desiccator. The dry solid was dissolved in chloroform (15 ml). To this chloroform solution methanol (15 ml) was added with stirring. The light brown solid separated was collected by filtration and dried in air.

$[\text{Ni}(\text{L}^1)_2]$ (1): Yield 630 mg (69%). Anal. Calcd for $\text{C}_{54}\text{H}_{58}\text{N}_4\text{O}_2\text{S}_2\text{Ni}$ (917.87) (%): C, 70.66. H, 6.37. N, 6.10. Found (%): C, 70.65. H, 6.52. N, 6.15. Selected IR band (cm^{-1}): 1589 (C=N). UV-Vis (CHCl_3 ; λ_{max} (nm) (ϵ [$\text{M}^{-1} \text{cm}^{-1}$])): 600^{sh} (47), 502 (131), 395^{sh} (2.7×10^3), 355^{sh} (1.3×10^4), 330^{sh} (1.9×10^4), 303 (2.8×10^4), 253 (2.1×10^4). ^1H NMR (CDCl_3 ; 500 MHz, δ [J], ppm [Hz]): 7.42 (9) (t, 1H, H^{19}), 7.28 (8) (t, 1H, H^3), 7.23–7.16 (m, 7H, $\text{H}^{1,2,4,5,11,13,15}$), 7.04 (9) (dd $\rightarrow$ t, 2H, $\text{H}^{12,14}$), 6.74 (9) (d, 2H, $\text{H}^{18,20}$), 4.35 (s, 2H, $\text{H}^{9a,b}$), 4.15 (9) (sep, 2H,

$\text{H}^{22,25}$), 1.42 (9) (d, 6H, Me-protons of dipp), 1.33 (9) (d, 6H, Me-protons of dipp).

$[\text{Ni}(\text{L}^2)_2]$ (2): Yield 690 mg (70%). Anal. Calcd for $\text{C}_{54}\text{H}_{56}\text{N}_4\text{O}_2\text{Cl}_2\text{S}_2\text{Ni}$ (986.76) (%): C, 65.73. H, 5.72. N, 5.68. Found (%): C, 65.46. H, 5.85. N, 5.58. Selected IR band (cm^{-1}): 1579 (C=N). UV-Vis (CHCl_3 ; λ_{max} (nm) (ϵ [$\text{M}^{-1} \text{cm}^{-1}$])): 600^{sh} (56), 502 (152), 400^{sh} (2.3×10^3), 357^{sh} (1.2×10^4), 330^{sh} (1.8×10^4), 304 (2.3×10^4), 252 (1.7×10^4). ^1H NMR (CDCl_3 ; 500 MHz, δ [J], ppm [Hz]): 7.42 (8) (t, 1H, H^{19}), 7.24–7.16 (m, 7H, $\text{H}^{1,5,11-15}$), 6.99 (9) (d, 2H, $\text{H}^{2,4}$), 6.61 (8) (d, 2H, $\text{H}^{18,20}$), 4.30 (s, 2H, $\text{H}^{9a,b}$), 4.11 (7) (sep, 2H, $\text{H}^{22,25}$), 1.40 (7) (d, 6H, Me-protons of dipp), 1.33 (7) (d, 6H, Me-protons of dipp).

2.4 | X-ray crystallography

X-ray quality single crystals of HL^1 and HL^2 were obtained by slow evaporation of their solutions in ethyl acetate-*n*-hexane (1:10) mixture, whereas those for $[\text{Ni}(\text{L}^1)_2]$ (1) and $[\text{Ni}(\text{L}^2)_2]$ (2) were grown by slow evaporation of their solutions in chloroform-methanol (1:1) mixture. Unit cell determination and intensity data collection for each crystal were carried out at room temperature (298 K) on a Bruker D8 Quest diffractometer fitted with a Photon 100 CMOS area detector and an Incoatec Micro-focus Source for graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data acquisition, integration, and reduction were performed using the APEX3 software package.^[11] The SADABS program^[12] was employed for an empirical absorption correction. In the case of HL^1 , some residual absorption effect was treated with an additional correction using the XABS2 program.^[13] All four structures were solved by direct method and refined on F^2 using full-matrix least-squares procedures. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at idealized positions and refined as riding atoms with relative isotropic thermal parameters of their parent atoms. The SHELX-97 programs^[14] available in the WinGX software suite^[15] were used for structure solution and refinement. Mercury package^[16] was used to prepare the structural illustrations. Selected crystallographic data for all four structures are listed in Table 1.

2.5 | General procedure for the Kumada-Corriu cross-coupling reaction

A mixture of aryl bromide (1.0 mmol), phenylmagnesium bromide (1.2 mmol), and the nickel complex catalyst (1 or 2) (0.05 or 0.1 mol%) in tetrahydrofuran (2 ml) was stirred at room temperature (25°C) under nitrogen

TABLE 1 Selected crystallographic data for HL¹, HL², [Ni(L¹)₂] (**1**), and [Ni(L²)₂] (**2**)

Compound	HL ¹	HL ²	1	2
Chemical formula	C ₂₇ H ₃₀ N ₂ OS	C ₂₇ H ₂₉ N ₂ OClS	C ₅₄ H ₅₈ N ₄ O ₂ S ₂ Ni	C ₅₄ H ₅₆ N ₄ O ₂ Cl ₂ S ₂ Ni
Formula weight	430.59	465.03	917.87	986.76
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.591(2)	10.8061(4)	9.2963(10)	8.4743(6)
<i>b</i> (Å)	10.479(2)	11.2035(5)	10.5788(11)	12.5662(9)
<i>c</i> (Å)	13.109(3)	12.1252(5)	13.5217(14)	12.8658(9)
α (°)	72.223(7)	73.437(2)	68.971(3)	97.861(2)
β (°)	86.174(9)	71.818(1)	80.553(4)	106.032(2)
γ (°)	85.211(7)	71.212(2)	80.439(4)	97.242(2)
<i>V</i> (Å ³)	1249.1(5)	1292.25(9)	1216.0(2)	1284.96(16)
<i>Z</i>	2	2	1	1
ρ (g cm ⁻³)	1.145	1.195	1.253	1.275
μ (mm ⁻¹)	0.149	0.249	0.529	0.606
Reflections collected	17,449	31,846	34,745	45,530
Reflections unique	4228	4526	4259	4463
Reflections $I \geq 2\sigma(I)$	2289	3848	3451	4215
Parameters	280	293	290	299
<i>R</i> 1, <i>wR</i> 2 ($I \geq 2\sigma(I)$)	0.0909, 0.1645	0.0470, 0.1182	0.0549, 0.1465	0.0342, 0.0911
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1962, 0.2038	0.0557, 0.1243	0.0702, 0.1599	0.0364, 0.0929
GOF on <i>F</i> ²	1.048	1.052	1.078	1.049
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.403, -0.308	0.432, -0.440	0.915, -0.860	0.401, -0.397

atmosphere for the required time. After that, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using *n*-hexane as the eluent to isolate the cross-coupled product.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and some properties

Reactions of equimolar amounts of benzyl bromide and *N*-(4-*R*-benzoyl)-*N'*-(2,6-diisopropylphenyl)thiourea (*R* = H and Cl) in presence of excess (1.7 times) NaH in tetrahydrofuran provided HL¹ and HL² in high yields (~85%) (Scheme 1). The complexes **1** and **2** were synthesized in good yields (~70%) by reacting one mole equivalent of Ni(OAc)₂·4H₂O with two mole equivalents of HL¹ and HL², respectively, in MeOH–CHCl₃ (1:1) mixture. The elemental analysis data of all four compounds are in good agreement with the corresponding molecular formulas. Magnetic susceptibility measurements with powdered samples of both complexes revealed their

diamagnetic character. The complexes are insoluble in most of the common organic solvents such as methanol, ethanol, acetonitrile, dimethylsulfoxide, and *N,N*-dimethylformamide. However, they readily dissolve in dichloromethane and chloroform and provide brown solutions. In solution, they are electrically non-conducting. The use of bivalent nickel starting material for synthesis and the diamagnetic and nonelectrolytic character indicate that both **1** and **2** are square-planar nickel(II) complexes.

3.2 | X-ray structures

All of HL¹, HL², **1**, and **2** crystallize in the triclinic *P* $\bar{1}$ space group. The asymmetric units of HL¹ and HL² contain one complete molecule of the corresponding compounds. On the other hand, each of the two complex molecules is centrosymmetric, and the metal center resides at the inversion center. Thus, the asymmetric units of both **1** and **2** have half of the corresponding complex molecules. The molecular structures of HL¹ and HL² are illustrated in Figure 1, whereas those of **1** and **2** are

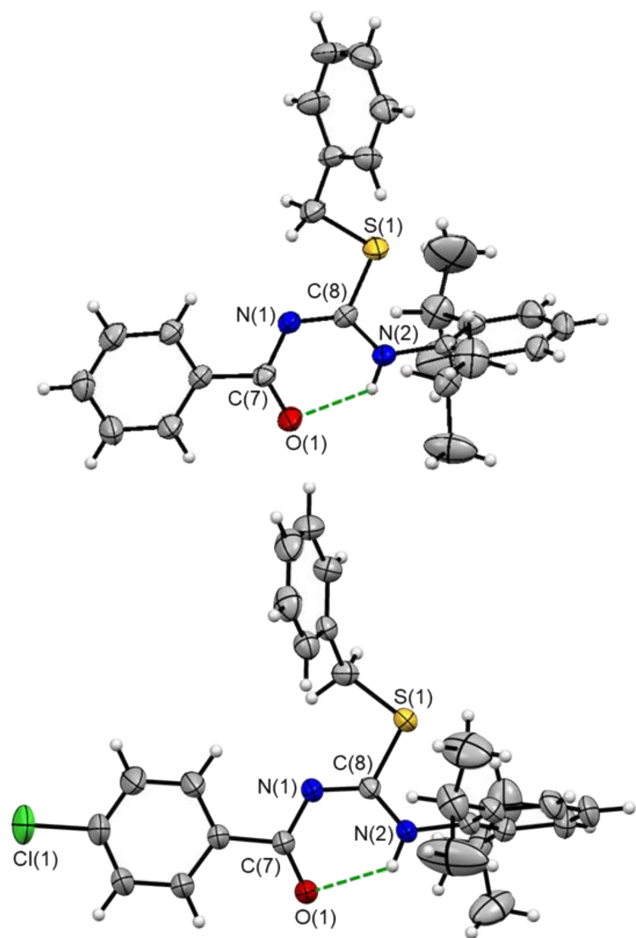


FIGURE 1 Molecular structures of HL^1 (top) and HL^2 (bottom). All nonhydrogen atoms are represented by their thermal ellipsoids at the 40% probability level. Only selected atoms are labeled for clarity

shown in Figure 2. Selected bond parameters are listed in Tables 2 and 3.

Both HL^1 and HL^2 can have two forms amide and imino-ketone (Scheme 1) due to amine-imine tautomerism.^[17] The X-ray structures revealed that both molecules exist in the imino-ketone form (Figure 1). The shorter C(8)—N(1) bond length compared with the C(8)—N(2) bond length indicates the double bond character of the former (Table 2). The C(7)—O(1) and C(7)—N(1) bond lengths are consistent with double and single bond characters, respectively. There is an intramolecular N—H...O hydrogen bond involving the amine and the keto-O leading to the formation of a planar six-membered ring (rms deviations: 0.02 and 0.08 Å for HL^1 and HL^2 , respectively) in each structure. The N...O distance and the N—H...O angle are 2.638(3) Å and 128° for HL^1 and 2.677(2) Å and 126° for HL^2 . It appears that the imino-ketone form is favored over the amide form due to this N—H...O

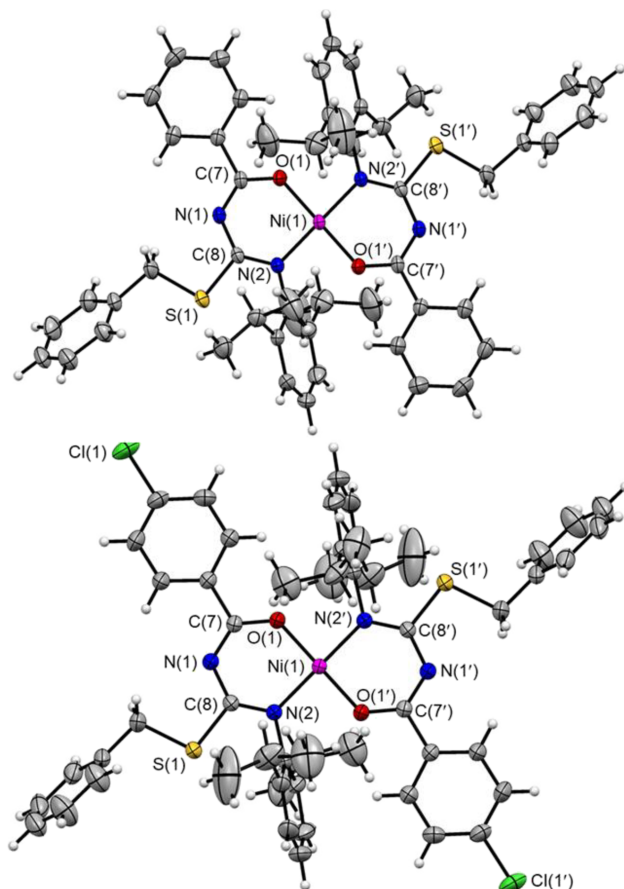


FIGURE 2 Perspective views of $[\text{Ni}(\text{L}^1)_2]$ (**1**) (top) and $[\text{Ni}(\text{L}^2)_2]$ (**2**) (bottom). The thermal displacement ellipsoids of the nonhydrogen atoms are drawn at the 40% probability level. Only selected atoms are labeled for clarity

interaction. The remaining intramolecular bond lengths and angles are unexceptional in both structures.

The structures of **1** and **2** confirm the deprotonation of the migratory proton and the monoanionic state of the ligands (L^1)[−] and (L^2)[−] (Figure 2). In the complexes, the C(7)—O(1) bond length is ~0.04 Å longer and C(7)—N(1) bond length is ~0.06 Å shorter compared with the corresponding bond lengths in HL^1 and HL^2 (Table 2). Hence, the imino-ketone fragment of the ligand is in the iminolate state in both **1** and **2**.^[18,19] In contrast to HL^1 and HL^2 , the C(8)—N(1) is longer and C(8)—N(2) is shorter in **1** and **2** (Table 2) indicating the single and double bond characters, respectively. In each centrosymmetric complex, the ligand coordinates the metal center through the iminolate-O and the azomethine-N atoms and forms a six-membered chelate ring with bite angle close to 90° (Table 3). Because of the inversion center at the coordinated metal atom, two ligands form a near perfect square-planar *trans*-NiN₂O₂ coordination geometry (Figure 2). The Ni—N and Ni—O bonds lengths are very similar in **1** and **2**, and they are within the ranges

TABLE 2 Selected bond lengths (Å) and angles (°) for HL¹, HL², **1**, and **2**

Compound	HL ¹	HL ²	[Ni(L ¹) ₂] (1)	[Ni(L ²) ₂] (2)
C(7)—O(1)	1.239(4)	1.229(2)	1.278(3)	1.272(2)
C(7)—N(1)	1.373(4)	1.364(2)	1.308(3)	1.309(2)
C(8)—N(1)	1.314(4)	1.312(2)	1.341(3)	1.343(2)
C(8)—N(2)	1.326(4)	1.327(2)	1.320(4)	1.314(2)
C(8)—S(1)	1.766(3)	1.768(2)	1.774(3)	1.771(2)

TABLE 3 Metal centered bond lengths (Å) and angles (°) for **1** and **2**

Complex	1	2
Ni(1)—O(1)	1.8215(19)	1.8342(12)
Ni(1)—N(2)	1.911(2)	1.9000(13)
Ni(1)—O(1') ^a	1.8215(19)	1.8342(12)
Ni(1)—N(2') ^a	1.911(2)	1.9000(13)
O(1)—Ni(1)—N(2)	91.58(9)	91.64(5)
O(1)—Ni(1)—O(1') ^a	180.000(1)	180.00(7)
O(1)—Ni(1)—N(2') ^a	88.42(9)	88.36(5)
N(2)—Ni(1)—O(1') ^a	88.42(9)	88.36(5)
N(2)—Ni(1)—N(2') ^a	180.0	180.00(9)
O(1') ^a —Ni(1)—N(2') ^a	91.58(9)	91.64(5)

^aSymmetry transformations used to generate equivalent atoms: $-x, -y, -z + 2$ for **1** and $-x, -y, -z$ for **2**.

observed for nickel(II) square-planar complexes with ligands having comparable coordinating atoms.^[19,20]

A possible explanation for the observed O,N-coordination mode instead of the O,S-coordination mode of (L^{1/2})[−] in **1** and **2** despite relatively more steric crowding around N-atom compared with that around S-atom is as follows. The delocalization of the negative charge by resonance is possible only in the O,N-coordination mode, but not in the O,S-coordination mode (Scheme 1). Further the C—O and C—N bond lengths in the six-membered chelate rings of the two complexes are in the range 1.272(2)–1.343(2) Å. However, the average C(8)—S(1) bond is ~0.46 Å longer than these bonds in HL^{1/2} as well as in the corresponding complexes **1** and **2** (Table 2). Hence, it is very likely that the effective delocalization of the negative charge of the ligand with the formation of a relatively more uniform six-membered chelate ring leads to the O,N-coordination mode over the O,S-coordination mode of (L^{1/2})[−] in the present complexes. In the previously reported square-planar nickel(II) complexes with *N,N*-dialkyl/diaryl-*N'*-(aroyl)

thioureaates,^[7] which are somewhat analogous to the present ligands, the opposite O,S-coordination was preferred over the O,N-coordination. In these complexes, resonance delocalization of the negative charge of the ligand is possible only in the O,S-coordination mode but not in the O,N-coordination mode. Thus, it appears that the coordination mode of the reported thioureaates as well as the present deprotonated thiopseudoureas is dictated by the delocalization of the ligand negative charge and not by the steric crowding around the coordinating atom.

3.3 | Spectroscopic properties

Infrared spectra of HL¹, HL², **1**, and **2** were recorded in the range 4000–500 cm^{−1} using the ATR mode (Figures S1 and S2). The spectra display several bands of various intensities. No attempt was made to assign all the bands except for the following few. Both HL¹ and HL² show a somewhat broad band at ~3180 cm^{−1} due to the N—H stretching. Two medium intensity bands at ~1670 and 1598 cm^{−1} are assigned to the C=O and C=N stretches, respectively.^[18,19] In contrast, neither of **1** and **2** displays the N—H and C=O stretching bands. Absence of these bands indicates the deprotonation of HL¹ and HL² and formation of the iminolate states (L¹)[−] and (L²)[−] in the complexes. A medium intensity band observed at ~1584 cm^{−1} for both complexes is attributed to the metal coordinated C=N stretching.^[18,19]

The electronic absorption spectra of **1** and **2** were recorded using their chloroform solutions. The spectral profiles of the two complexes are very similar (Figure 3). In each spectrum, two low intensity absorptions, a shoulder at 600 nm and a peak at 502 nm, are followed by three strong shoulders at ~400, ~355, and 330 nm and two very strong peaks at 303 and ~250 nm. Square-planar nickel(II) complexes are reported to exhibit weak spin-allowed ligand field transitions in the range 645–460 nm.^[19a,b,20] Thus, the first two weak absorptions are assigned to ligand field transitions. Considering that each of HL¹ and HL² in chloroform displays an absorption

FIGURE 3 Electronic spectra of $[\text{Ni}(\text{L}^1)_2]$ (**1**) (—) and $[\text{Ni}(\text{L}^2)_2]$ (**2**) (-----) in chloroform

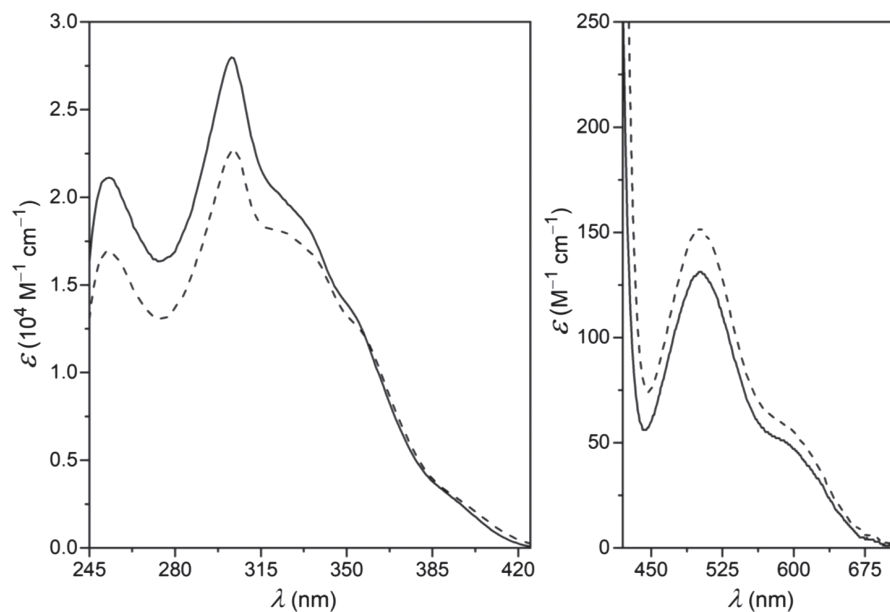
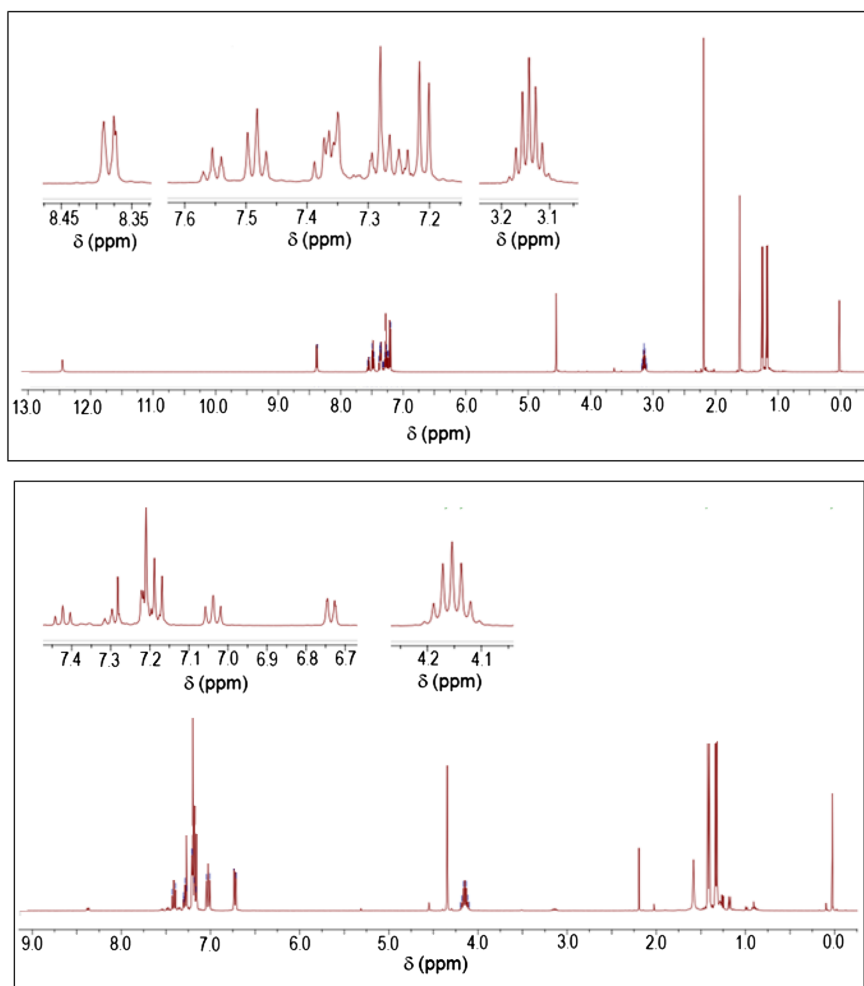


FIGURE 4 ^1H NMR spectra of HL^1 (top) and $[\text{Ni}(\text{L}^1)_2]$ (**1**) (bottom) in CDCl_3



maximum at ~ 295 nm followed by a shoulder at ~ 260 nm both being very strong, three strong shoulders observed for the complexes are attributed to ligand-to-metal charge transfer transitions^[19,20] and the last two

very strong highest energy peaks are assigned to intra-ligand transitions.

The proton NMR spectra of HL^1 , HL^2 , **1**, and **2** were recorded in CDCl_3 . The chemical shift data (numbering

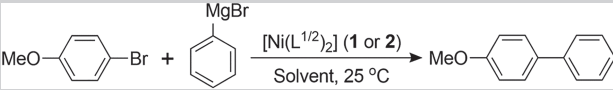
scheme in Scheme 1) are given in Section 2 under the respective compounds, and the spectra of HL¹ and **1** are depicted in Figure 4, whereas the spectra of HL² and **2** are shown in Figure S3. The spectrum of each of the two complexes **1** and **2** clearly indicates that in solution also the two ligands are equivalent as observed in the corresponding X-ray structure. Both thiopseudoureas HL¹ and HL² display a singlet at ~12.43 ppm due to the NH group. As expected, neither of **1** and **2** shows this signal due to the deprotonation of the NH group and the monoanionic state of the ligand. The tertiary H-atoms of the two isopropyl groups of HL¹ and HL² appear as a two-proton septate at ~3.14 ppm, whereas the two-proton septate for the same H-atoms is shifted downfield by ~1 ppm in the cases of **1** and **2**. Unlike the single signal for the tertiary H-atoms, the methyl protons of the two isopropyl groups resonate as two closely spaced six-proton doublets for all four compounds. These two doublets are observed at ~1.25 and 1.18 ppm for the thiopseudoureas (HL¹ and HL²), while they move slightly downfield to ~1.41 and 1.33 ppm for the complexes (**1** and **2**). The methylene protons of the benzyl group appear as a two-proton singlet at ~4.54 ppm for HL¹ and HL². However, in contrast to the protons of the isopropyl groups, the two-proton singlet due to the benzylic methylene protons in the complexes (**1** and **2**) appears slightly upfield at ~4.33 ppm. The aromatic protons of HL¹ and HL² resonate in the range 7.21–8.38 ppm whereas those for **1** and **2** are observed in relatively upfield and somewhat narrow range of 6.61–7.42 ppm with the expected splitting patterns.

3.4 | Catalytic studies

Optimization of the reaction conditions for C–C cross-coupling was performed using 1-bromo-4-methoxybenzene (1.0 mmol) and phenylmagnesium bromide (1.2 mmol) as the model substrates and the complexes **1** and **2** as catalysts in 2 ml of solvent (toluene and or tetrahydrofuran) (Table 4). All the reactions were carried out at room temperature (25°C). Using toluene as solvent and 0.05 mol% of **1** under nitrogen atmosphere, 80% yield was obtained in 24 h (Entry 1). In the mixed solvent toluene–tetrahydrofuran (1:1), the yield decreased considerably (Entry 2). In contrast, better yield (88%) was obtained in much less time in pure tetrahydrofuran (Entry 3). However, if the reaction was conducted in air keeping all other conditions the same as in Entry 3, the yield decreased drastically (Entry 4). Doubling of the catalyst loading increased the yield but by a very small amount (4%). Both **1** and **2** showed good and comparable catalytic activities and provided the coupling product in essentially the same yield (88 and 90%) under the same conditions (Entries 3 and 6). The homo-coupling product biphenyl was also produced but in very little amount (~4%). Therefore, the conditions used for Entry 3 were found to be optimal for reactions of phenylmagnesium bromide with aryl bromides using **1** or **2** as catalyst.

The substrate scope of the above coupling reaction was probed using **1** as the catalyst. The results are summarized in Table 5. Reactions of phenylmagnesium bromide with *para*-substituted bromobenzenes (4-F, 4-Cl, 4-Me, and 4-OMe) and 2-bromonaphthalene produced

TABLE 4 Optimization of reaction conditions

					
Entry	Catalyst	Catalyst loading (mol%)	Solvent	Time (h)	Yield ^a (%)
1	[Ni(L ¹) ₂] (1)	0.05	Toluene	24 ^b	80
2	[Ni(L ¹) ₂] (1)	0.05	Toluene–THF (1:1)	24 ^b	68
3	[Ni(L ¹) ₂] (1)	0.05	THF	6 ^b	88
4	[Ni(L ¹) ₂] (1)	0.05	THF	12 ^c	40
5	[Ni(L ¹) ₂] (1)	0.10	THF	6 ^b	92
6	[Ni(L ²) ₂] (2)	0.05	THF	6 ^b	90

Note: BrC₆H₄OMe: 1.0 mmol; phenylmagnesium bromide: 1.2 mmol; solvent: 2 ml.

^aIsolated yield.

^bIn nitrogen.

^cIn air.

TABLE 5 Coupling reactions of phenylmagnesium bromide with various aryl bromides

Entry	Aryl bromide	Product	Time (h)	Yield ^a (%)
1	1-Bromo-4-fluorobenzene	4-Fluorobiphenyl	6	96 ^b
2	1-Bromo-4-chlorobenzene	4-Chlorobiphenyl	6	94 ^b
3	1-Bromo-4-methylbenzene	4-Methylbiphenyl	6	93 ^b
4	1-Bromo-4-methoxybenzene	4-Methoxybiphenyl	6	88 ^b
5	2-Bromonaphthalene	2-Phenyl-naphthalene	6	86 ^b
6	1-Bromo-3-methylbenzene	3-Methylbiphenyl	12	92 ^b
7	1-Bromo-3-methoxybenzene	3-Methoxybiphenyl	12	88 ^b
8	1-Bromo-2-methylbenzene	2-Methylbiphenyl	24	86 ^c
9	1-Bromo-2-methoxybenzene	2-Methoxybiphenyl	24	83 ^c

Note: Aryl bromide: 1.0 mmol; phenylmagnesium bromide: 1.2 mmol; THF: 2 ml.

^aIsolated yield.

^b[Ni(L¹)₂]: 0.05 mol%.

^c[Ni(L¹)₂]: 0.1 mol%.

the desired products in 86–96% yields in 6 h (Entries 1–5). The reactions of *meta*-substituted bromobenzenes (3-Me and 3-OMe) with phenylmagnesium bromide also provided high yields (92% and 88%) of the corresponding products (Entries 6 and 7) but in double reaction time (12 h) compared with that (6 h) required for the reactions of the *para*-substituted bromobenzenes with the same Grignard reagent. In contrast, the cross-coupling reactions of *ortho*-substituted bromobenzenes (2-Me and 2-OMe) with phenylmagnesium bromide require much longer reaction time (24 h) and double catalyst loading (0.1 mol%) compared with those needed for the coupling of *para*- and *meta*-substituted bromobenzenes with phenylmagnesium bromide to afford the products 2-methylbiphenyl and 2-methoxybiphenyl in slightly lower yields of 86% and 83%, respectively (Entries 8 and 9). The observed increase in the reaction time and the catalyst loading with the change of the substituent position on the bromobenzene from *para* to *meta* to *ortho* is in all likelihood to be due to the gradual increase of the steric hindrance. It may be noted that room temperature cross-coupling reactions for the synthesis of biaryls using nickel complexes as catalysts are not very common.^[5,6] The present catalyst system not only works at room temperature but also provides as good as or improved yields when compared with the yields reported so far for nickel complex catalyzed reactions.

4 | CONCLUSIONS

In summary, two thiopseudoureas HL¹ and HL² and their corresponding nickel(II) complexes [Ni(L¹)₂] and [Ni(L²)₂] have been successfully synthesized and characterized. The microanalytical data and diamagnetic and non-electrolytic characteristics of the two complexes indicate +2 oxidation state and square-planar coordination environment of the metal center in each complex. The X-ray structures of HL^{1/2} showed the imino-ketone tautomeric form of both thiopseudoureas in the solid state, whereas the X-ray structures of [Ni(L^{1/2})₂] confirmed the iminolate-O and azomethine-N donor coordination mode of the ligands (L^{1/2})[−] and a square-planar *trans*-N₂O₂ coordination geometry for both complexes. The spectroscopic features of all four compounds corroborate the corresponding molecular structures. Both complexes exhibit efficient catalytic activity toward Kumada–Corriu cross-coupling reactions of phenylmagnesium bromide with a variety of aryl bromides at room temperature. The reactions provided good to excellent yields of the biaryls.

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AUTHOR CONTRIBUTIONS

Kinche Shakunthala: Investigation. **Ankit Kumar Srivastava:** Investigation. **G. Narendra Babu:** Investigation. **Srinivas Keesara:** Investigation. **Samudranil Pal:** Conceptualization; supervision.

DATA AVAILABILITY STATEMENT

CCDC 2049212–2049215 contain the supplementary crystallographic data for HL¹, HL², [Ni(L¹)₂] (1), and [Ni(L²)₂] (2). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Additional data (Figures S1–S8) that support the findings of this study are available in the supplementary material of this article.

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REFERENCES

- [1] a) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. b) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417. c) C. C. C. J. Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem., Int. Ed.* **2012**, *51*, 5062. d) S. Xu, E. H. Kim, A. Wei, E. Negishi, *Sci. Technol. Adv. Mater.* **2014**, *15*, 044201. e) A. de Meijere, S. Bräse, M. Oestreich (Eds), *Metal Catalyzed Cross-Coupling Reactions and More*, Wiley-VCH **2014**. f) M. Busch, M. D. Wodrich, C. Corminboeuf, *ACS Catal.* **2017**, *7*, 5643. g) I. Kanwal, A. Mujahid, N. Rasool, K. Rizwan, A. Malik, G. Ahmad, S. A. A. Shah, U. Rashid, N. M. Nasir, *Catalysts* **2020**, *10*, 443. h) U. S. Kanchana, E. J. Diana, T. V. Mathew, G. Anilkumar, *Appl. Organomet. Chem.* **2020**, *34*, e5983.
- [2] a) S. P. Stanforth, *Tetrahedron* **1998**, *54*, 263. b) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359. c) G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447. d) H. Aldemir, R. Richarz, T. A. M. Gulder, *Angew. Chem., Int. Ed.* **2014**, *53*, 8286. e) J. Wencel-Delord, A. Panossian, F. R. Leroux, F. Colobert, *Chem. Soc. Rev.* **2015**, *44*, 3418. f) S. Yuan, J. Chang, B. Yu, *Top. Curr. Chem.* **2020**, *378*, 23.
- [3] K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374.
- [4] R. J. P. Corriu, J. P. Masse, *J. Chem. Soc., Chem. Commun.* **1972**, 144.
- [5] a) B. M. Rosen, K. W. Quasdorf, D. A. Wilson, N. Zhang, A.-M. Resmerita, N. K. Garg, V. Percec, *Chem. Rev.* **2011**, *111*, 1346. b) X. Hu, *Chem. Sci.* **2011**, *2*, 1867. c) M. M. Heravi, P. Hajiabbasi, *Monatsh. Chem.* **2012**, *143*, 1575. d) S. Z. Tasker, E. A. Standley, T. F. Jamison, *Nature* **2014**, *509*, 299. e) Z. Li, L. Liu, *Chin. J. Catal.* **2015**, *36*, 3. f) M. M. Heravi, V. Zadsirjan, P. Hajiabbasi, H. Hamidi, *Monatsh. Chem.* **2019**, *150*, 535. g) K. E. Poremba, S. E. Dibrell, S. E. Reisman, *ACS Catal.* **2020**, *10*, 8237.
- [6] a) V. P. W. Böhm, T. Weskamp, C. W. K. Gstöttmayr, W. A. Herrmann, *Angew. Chem., Int. Ed.* **2000**, *39*, 1602. b) F.-L. Qing, R. Wang, B. Li, X. Zheng, W.-D. Meng, *J. Fluorine Chem.* **2003**, *120*, 21. c) Z.-X. Wang, L. Wang, *Chem. Commun.* **2007**, 2423. d) J. Berding, T. F. van Dijkman, M. Lutz, A. L. Spek, E. Bouwman, *Dalton Trans.* **2009**, 6948. e) N. Şahin, H. E. Moll, D. Sémeril, D. Matt, İ. Özdemiir, C. Kaya, L. Toupet, *Polyhedron* **2011**, *30*, 2051. f) W. Dai, J. Xiao, G. Jin, J. Wu, S. Cao, *J. Org. Chem.* **2014**, *79*, 10537. g) V. Kuchtanin, L. Kleščiková, M. Šoral, R. Fischer, Z. Růžicková, E. Rakovský, J. Moncol, P. Segla, *Polyhedron* **2016**, *117*, 90. h) L. Iffland, A. Petuker, M. van Gastel, U.-P. Apfel, *Inorganics* **2017**, *5*, 78. i) M. Mastalir, K. Kirchner, *Monatsh. Chem.* **2017**, *148*, 105. j) K. Matsubara, H. Yamamoto, S. Miyazaki, T. Inatomi, K. Nonaka, Y. Koga, Y. Yamada, L. F. Veiros, K. Kirchner, *Organometallics* **2017**, *36*, 255.
- [7] a) R. del Campo, J. J. Criado, E. Garcia, M. R. Hermosa, A. Jiménez-Sánchez, J. L. Manzano, E. Monte, E. Rodríguez-Fernández, F. Sanz, *J. Inorg. Biochem.* **2002**, *89*, 74. b) G. Binzet, G. Kavak, N. Külcü, S. Özbey, U. Flörke, H. Arslan, *J. Chem.* **2013**, 536562. and references therein
- [8] a) T. Iwamoto, T. Watano, M. Shigekawa, *J. Biol. Chem.* **1996**, *271*, 22391. b) T. P. Prakash, A. Püschl, M. Manoharan, *Nucleos. Nucleot. Nucl. Acids* **2007**, *26*, 149. c) M. Ferreira, L. S. Assunção, A. H. Silva, F. B. Filippin-Monteiro, T. B. Creczynski-Pasa, M. M. Sá, *Eur. J. Med. Chem.* **2017**, *129*, 151. d) J. Merad, J.-M. Pons, O. Chuzel, C. Bressy, *Eur. J. Org. Chem.* **2016**, 5589.
- [9] a) K. Srinivas, P. Srinivas, P. S. Prathima, K. Balaswamy, B. Sridhar, M. M. Rao, *Catal. Sci. Technol.* **2012**, *2*, 1180. b) S. Thogiti, S. P. Parvathaneni, S. Keesara, *J. Organomet. Chem.* **2016**, *822*, 165.
- [10] D. D. Perrin, W. L. F. Armarego, D. P. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon **1983**.
- [11] APEX3, Program for Data Collection on Area Detectors, Bruker AXS Inc., Madison, Wisconsin, USA, **2016**.

- [12] G. M. Sheldrick, SADABS, program for area detector absorption correction, University of Göttingen, Göttingen, Germany, **1997**.
- [13] S. Parkin, B. Moezzi, H. Hope, *J. Appl. Crystallogr.* **1995**, 28, 53.
- [14] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, 64, 112.
- [15] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, 45, 849.
- [16] F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. M. Cabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* **2008**, 41, 466.
- [17] N. Phukan, J. B. Baruah, *Cryst. Eng. Comm.* **2016**, 18, 3877.
- [18] a) S. Das, S. Pal, *J. Organomet. Chem.* **2004**, 689, 352. b) S. Das, S. Pal, *J. Organomet. Chem.* **2006**, 691, 2575. c) A. R. B. Rao, S. Pal, *J. Organomet. Chem.* **2013**, 731, 67.
- [19] a) A. Mukhopadhyay, G. Padmaja, S. N. Pal, S. Pal, *Inorg. Chem. Commun.* **2003**, 6, 381. b) A. Mukhopadhyay, S. Pal, *Polyhedron* **2004**, 23, 1997. c) A. Mukhopadhyay, S. Pal, *Eur. J. Inorg. Chem.* **2006**, 4879. d) A. Mukhopadhyay, S. Pal, *Eur. J. Inorg. Chem.* **2009**, 4141. e) T. Ghosh, A. Mukhopadhyay, K. S. C. Dargaiah, S. Pal, *Struct. Chem.* **2010**, 21, 147. f) G. N. Babu, S. Pal, *J. Chem. Sci.* **2017**, 129, 1105.
- [20] a) A. la Cour, M. Findeisen, R. Hazell, L. Hennig, C. E. Olsen, O. Simonsen, *J. Chem. Soc., Dalton Trans.* **1996**, 3437. b) C. Lochenie, S. Schlamp, A. P. Railliet, K. Robeyns, B. Weber, Y. Garcia, *Cryst. Eng. Comm.* **2014**, 16, 6213.

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Functionalized naphthalenediimide based supramolecular charge-transfer complexes via self-assembly and their photophysical properties†

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We report here the design and syntheses of a naphthalenediimide (NDI)-N functionalized organic fluorophore, **1**, and its supramolecular CT complexes [(1.2H)²⁺·(PA)⁻]₂ (**2**) and [(1.2H)²⁺·(3,5-DNSA)⁻]₂ (**3**), self-assembled from **1** as an electron acceptor (A) and picric acid (PA) or 3,5-dinitrosalicylic acid (3,5-DNSA) as a donor (D), with a very large Stokes shift (>170 nm) and significant fluorescence lifetime (~1.55 ns). NDI is functionalized with phenylpyridyl units (chromophore) to extend the π -conjugation and thus provide a suitable platform for strong C–H $\cdots$ π and $\pi\cdots\pi$ stacking interactions, which are the prime requirements for any compound to be used as a fluorescent probe. The organic fluorophore, **1**, and its supramolecular CT complexes **2** and **3** exhibit decent electronic properties as suggested by DFT, cyclic voltammetry, and fluorescence studies. Moreover, compounds **1–3** were also exploited as fluorescent probes for cell imaging under normal cell isolation and with time-bound exposure.

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Introduction

The construction of well-organized inter- or intramolecular charge-transfer complexes (CTCs) is one of the rapidly growing areas for contemporary researchers working in the domain of chemical and biological sciences due to their fascinating photophysical properties.^{1–5} It is a well-known fact that intermolecular CTCs are composed of electron-rich (donor; D) and electron-poor (acceptor; A) π -conjugated molecules, which are associated through favorable supramolecular noncovalent interactions such as hydrogen bonding, π - π stacking, and electrostatic interactions.^{6–9} However, in intramolecular CT complexes, one part of the same photophysical system behaves as a donor (D) and another part as an acceptor (A).^{10,11} Therefore, the key aspect of the design of such CTC systems is controlling D and A to optimize efficient electron transfer between them.¹²

In this regard, several photophysical systems such as covalently linked porphyrin arrays,¹³ π -stacked molecules,¹⁴ dendrimers,¹⁵ chromophoric polymers,¹⁶ self-assembled structures,^{17,18} and hybrid organic–inorganic structures^{19,20} have been synthesized and successfully used as a fluorescent probe for a diverse range of applications such as organic electronics,²¹ photovoltaic devices,²² flexible displays²³ and imaging applications.^{24,25} Several reports are available in the literature wherein naphthalenediimide (NDI) based chromophores show a strong tendency towards self-assembly and form a stacked structure in a size-dependent manner.^{26–30} Moreover, the stacking pattern plays a vital role in their applicability towards a particular application.^{31,32} Nevertheless, the interactions are moderated by the electrostatic complementarity of the stacked structure.³³ Furthermore, it is an evident fact that a good fluorescent probe must feature a (i) large Stokes shift,^{34,35} (ii) high physiological stability, (iii) fluorogenic behavior, (iv) high quantum yield of fluorescence and so on.²⁵ Therefore it is essential to understand the structure–function relationships of such type of photofunctional systems to design, optimize and control their electronic functions.^{36,37} The properties of such type of probe strongly depends on the efficient charge separation in donor–acceptor (D–A) systems.^{38,39} The association of D and A molecules often results in the modification of the electronic structure of the D–A system and the formation of charge transfer (CT) complexes.²⁵

So, based on the vast utilities of organic fluorescent probes, we report here the design and syntheses of an NDI-N

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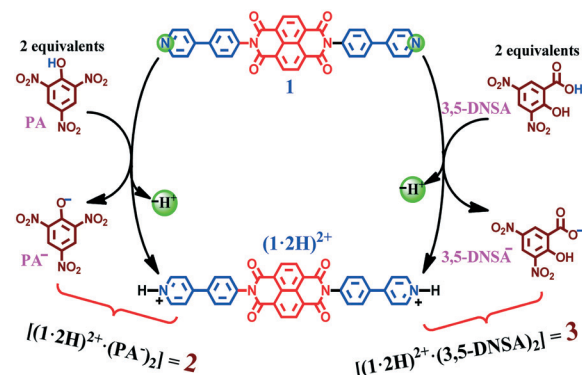
† Electronic supplementary information (ESI) available: Additional experimental data and characterization details, thermal analysis, UV-vis, HRMS data, powder XRD analysis, additional crystallographic packing images and bonding parameters, Hirshfeld surface analysis, electrochemical behavior and fluorescence images. CCDC 1975049–1975051. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ce01719a

functionalized organic fluorophore, **1** (ref. 40), and its intermolecular D-A CT complexes $[(1\cdot 2H)^{2+}\cdot(PA^-)_2]$ (**2**) and $[(1\cdot 2H)^{2+}\cdot(3,5\text{-DNSA}^-)_2]$ (**3**). CT complexes **2** and **3** self-assembled from **1** as an electron acceptor (A), and PA or 3,5-DNSA as a donor (D), in their ionic form in solution (Schemes 1 and 2). NDI is functionalized with phenylpyridyl units with an aim to extend the π -conjugation and thus provide a suitable platform for C-H $\cdots\pi$ and $\pi\cdots\pi$ stacking interactions along with facile charge-transfer, which are the prime requirements for any fluorescent probe. Moreover, **1**–**3** were also exploited as fluorescent probes for the cell imaging of rat brain. The preliminary results are very promising and will help contemporary researchers of the field to design advanced CTC based fluorescent probes for biological application in the near future.

Results and discussion

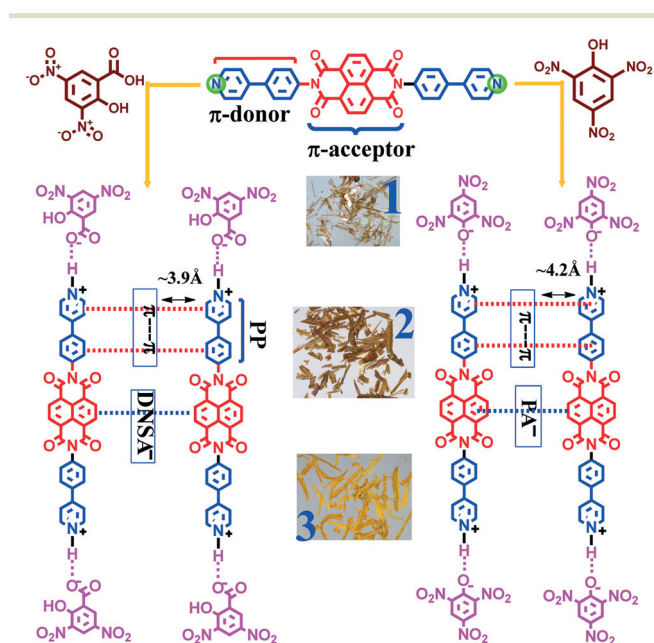
Synthesis and characterization

The details of the synthesis of the precursor, 4-(pyridin-4-yl)aniline, are provided in the ESI† (Scheme S1). Meanwhile, the preparation of fluorophore **1** and CT complexes **2** and **3** is provided in the Experimental section (Scheme 1). For all the compounds, characterization details are provided in the ESI† (Fig. S1–S19). The precursor, 4-(pyridin-4-yl)aniline, was prepared by the Suzuki–Miyaura coupling of 4-iodoaniline with 4-pyridylboronic acid in a 1:1.2 molar ratio in a DMF–water system at 70–80 °C.⁴¹ Afterwards, **1** was synthesized by refluxing 4-(pyridin-4-yl)aniline with 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) in a 1:2 molar ratio in DMF for 24 h. The CT complexes **2** and **3** were prepared by stirring **1** and respectively PA or 3,5-DNSA in a



Scheme 2 Plausible mechanistic pathway of proton transfer from PA or 3,5-DNSA to **1** and generation of charged species in solution during the intermolecular D-A CT complex formation.

1:2 molar ratio in DMSO for 1 h at room temperature (Scheme 1). Precursor 4-(pyridin-4-yl)aniline shows a characteristic ν_{N-H} band at 3313 cm^{-1} (Fig. S1†). Meanwhile, the corresponding ^1H NMR spectrum shows a singlet at δ 5.54 ppm, which is ascribed to the $-\text{NH}_2$ proton (Fig. S2†). The FT-IR spectra of **1**–**3** display strong bands between 1707–1717 cm^{-1} and 1673–1677 cm^{-1} , which are assigned to $\nu_{C=N}$ and $\nu_{C=O}$, respectively (Fig. S5†). The ^1H NMR spectrum of **1** shows five types of signals, indicating the presence of five types of protons (Fig. S9†) due to the highly symmetrical nature of **1**. The formal 1:2 stoichiometry was confirmed for CT complexes **2** and **3** by elemental analysis, HRMS, DFT calculations and X-ray diffraction analysis. Further, to probe the 1:2 stoichiometry and to understand the mode of interaction between PA or 3,5-DNSA and **1** in solution, ^1H NMR spectra were recorded for **2** and **3**. Interestingly, **2** does not show a signal for the phenolic proton, which indicates the transfer of a phenolic proton from PA to the 1-pyridyl-N atom, resulting in the formation of charged species: PA^- and $\{1\cdot 2H\}^{2+}$ in solution, which helps in intermolecular D-A CT complex formation (Scheme 2). Notably, after CTC formation, PA displays significant chemical shifts ($\Delta\delta_H$) for its aromatic proton in the ^1H NMR spectrum (Fig. S11†), as the characteristic singlet for the aromatic proton of PA, which appears at $\sim$ 8.61 ppm (before complexation), shifts significantly to 8.47 ppm ($\Delta\delta_H = 0.14$ ppm), indicating the complexation of **2** (Fig. S12†).⁴² Meanwhile, the integration of the aromatic protons of PA in **2** suggests 1:2 stoichiometry. Interestingly, the upfield shifts in the $\Delta\delta_H$ values, instead of expected downfield shifts (for PA protons), indicate the increase of electron density (due to formation of picrate ions, PA^-), which induces PA (PA^- in solution) to behave as D in place of its well-known electron acceptor nature. In a similar fashion, **3** displays no signal for the carboxylic acid proton of 3,5-DNSA in its ^1H NMR spectrum, thus suggesting the transfer of this proton from 3,5-DNSA to the 1-pyridyl-N atom and generation of charged species, $3,5\text{-DNSA}^-$ and $\{1\cdot 2H\}^{2+}$ in solution, which assisted in intermolecular D-A CT complex formation. Further, **3** also exhibits considerable $\Delta\delta_H$ shifts, as



Scheme 1 Schematic illustration of the formation of CT complexes **2** and **3** using **1**. In both cases, **1** acts as an acceptor (A) and PA and 3,5-DNSA work as a donor (D) in their anionic form.

the characteristic singlets of 3,5-DNSA, which appear at 8.72 and 8.67 ppm (before complexation), shift to 8.64 and 8.60 ppm ($\Delta\delta_{\text{H}} = 0.08$ and 0.07 ppm, respectively) after complexation (Fig. S14 and S15†). In addition, upfield shifts in $\Delta\delta_{\text{H}}$ values indicate the increase of electron density (due to the formation of 3,5-dinitrosalicylate ions), which induces 3,5-DNSA (3,5-DNSA[−] in solution) to behave as D in place of its famous electron acceptor nature. Notably, the H_a protons of **1** are shifted 0.03–0.05 ppm downfield in both CTC (Fig. S12 and S14†), thereby further supporting the transfer of a proton from the concerned PA or 3,5-DNSA to N_{Pyridyl} of **1**. These ¹H NMR findings are well supported by DFT calculations and single-crystal X-ray analysis. Moreover, the HRMS spectra of **2** and **3** display $[M + 2H]^{2+}$ peaks at m/z 1206.2561 and 1102.2565, which are ascribed to $[(1\cdot 2H)^{2+}\cdot(PA^-)_2]$ and $[(1\cdot 2H)^{2+}\cdot(3,5\text{-DNSA}^-)_2]$, respectively, thereby providing additional proof for 1:2 complexation (Fig. S18 and S19†).^{43,44}

The parent compound **1** displays a peak at $m/z = 573.1561$, which corresponds to $[M + H]^+$ (Fig. S17†). Notably, numerous attempts have also been made to prepare intermolecular D·A CT complexes of **1** with other well-known acceptors such as 2,2'-(cyclohexa-2,5-diene-1,4-diylidene) dimalononitrile (TCNQ; $7.29 \times 10.23 \text{ \AA}^2$), 2,5-dihydroxyterephthalic acid ($8.62 \times 10.28 \text{ \AA}^2$), and potassium 6-methyl-4-methylene-4*H*-1,2,3-oxathiazin-3-ide-2,2-dioxide (acesulfame-K; $8.43 \times 8.96 \text{ \AA}^2$), and donors such as naphthalene ($7.28 \times 8.98 \text{ \AA}^2$) and anthracene ($7.28 \times 11.33 \text{ \AA}^2$); however, all our efforts were in vain (see Scheme S2† for details). We believe that the similar shape and size (see Scheme S2 and Table S1†) along with the strong proton donating tendency of PA ($9.50 \times 9.79 \text{ \AA}^2$) and 3,5-DNSA ($9.48 \times 10.09 \text{ \AA}^2$) might be responsible for their selectivity towards the formation of intermolecular D·A CT complexes **2** and **3**.

Structural description of **1**

Single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of a DMSO solution after two weeks. The structural analysis reveals that compound **1** crystallizes in the monoclinic cell system with space group $P2_1/c$. The asymmetric unit consists of one and a half

molecules of **1**, as one of the naphthalenic ring centroids is located over an inversion center. The molecular structure of **1** is depicted in Fig. 1. The phenylpyridyl moieties are nearly planar as the dihedral angle between the planes of the two rings lies in the range $6.0\text{--}15.4^\circ$. The dihedral angles between the NDI core and phenylpyridyl moiety are $\sim 89.35^\circ$ and $\sim 88.11^\circ$ indicating that both moieties are almost perpendicular and this orientation allows the core NDI-Hs to form C–H $\cdots\pi$, N $\cdots$ H–C and C–H $\cdots$ O interactions (Fig. 1). The strong to moderate C–H $\cdots\pi$ ($2.739\text{--}3.524 \text{ \AA}$) interactions between the aryl hydrogens and the phenylpyridyl rings of the adjacent molecules are responsible for the formation of a 3D architecture as shown in Fig. S20.† Moreover, the carbonyl O atoms are hydrogen-bonded ($2.339\text{--}2.530 \text{ \AA}$) to pyridyl CH and NDI core CH of the adjacent molecules (Table S2†), further supporting the framework as shown in Fig. S20.† Due to the orthogonality of the phenylpyridyl rings with the NDI core, there is no probability for $\pi\cdots\pi$ interactions between the adjacent molecules. In addition, the Hirshfeld surface was mapped with d_{norm} and 2D fingerprint plots were generated using Crystal Explorer 3.1 (ref. 45) to visualize the intermolecular interactions. The Hirshfeld surface analysis shown in Fig. S21† suggests that the majority of intermolecular interactions in the crystal packing were contributed by C–H (33.7%) and O–H (20%) contacts, thereby further strengthening the crystal packing.

Structural description of **2**

Single crystals of **2** suitable for X-ray diffraction analysis were obtained by slow evaporation of a DMSO solution after two weeks. The structural analysis reveals that **2** crystallizes in the monoclinic cell system with space group $I2/a$. The asymmetric unit consists of half a molecule of the bi-protonated form of **1** (as a naphthalenic ring centroid is located over an inversion center), a picrate anion, one lattice occluded DMSO and one water molecule. The molecular structure of **2** is depicted in Fig. 2. The phenylpyridyl moieties in **2** lost their planarity as the dihedral angle between the planes of the two rings is 31.7° . The dihedral angle between the NDI core and phenyl ring of the phenylpyridyl moiety is 68.8° . This orientation allows the core NDI-Hs to form C–H $\cdots$ O interactions (Fig. 2) and strong $\pi\cdots\pi$ ($3.317\text{--}3.419 \text{ \AA}$) interactions between the centroids of the picrate rings and the NDI core. The phenylpyridyl rings also interact *via* weak $\pi\cdots\pi$ ($4.192 \text{ \AA}$) interactions between the adjacent molecules (Fig. 2c). These strong to weak $\pi\cdots\pi$ interactions resulted in a 2D network as shown in Fig. 2c. The protonated pyridyl groups are strongly H-bonded to the phenolic and nitro O atoms in bifurcated mode. The lattice occluded water and DMSO connect the adjacent molecules *via* C–H $\cdots$ O interactions. The Hirshfeld surface analysis shown in Fig. S21† suggests that a majority of intermolecular interactions in the crystal packing were contributed by C–H (8.9%) and O–H (38.9%) contacts, thereby further strengthening the crystal packing.

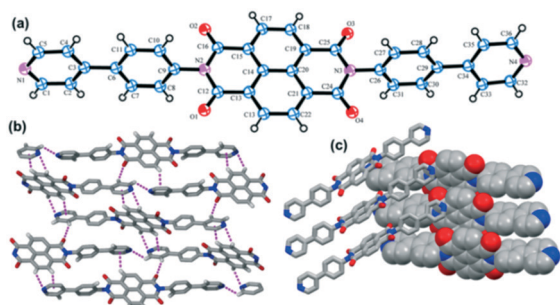


Fig. 1 (a) ORTEP diagram of one of the components of **1** (probability level 50%). (b) C–H $\cdots\pi$, N $\cdots$ H–C and C–H $\cdots$ O interactions. (c) The herringbone arrangement viewed down along the *a*-axis.

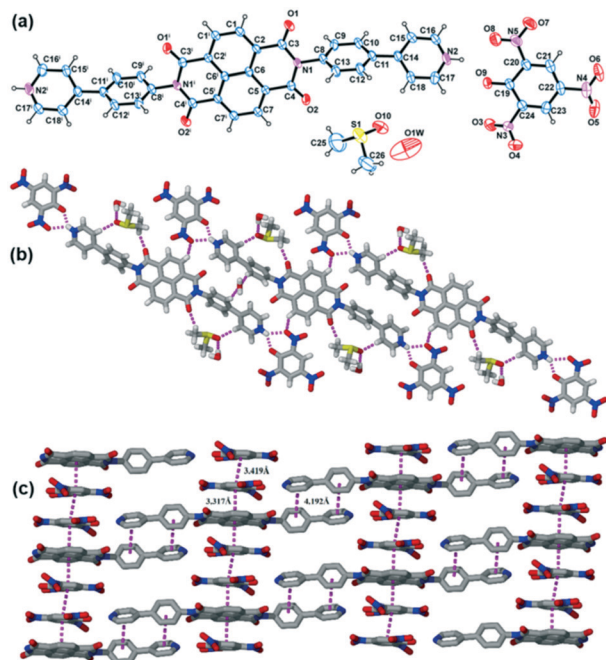


Fig. 2 (a) ORTEP diagram of **2** (probability level 50%). Symmetry equivalent positions are (i) $3/2 - x, 3/2 - y, 3/2 - z$. (b) 2D H-bonding network. (c) 2D sheet formation due to the $\pi \cdots \pi$ stacking viewed down along the a -axis.

Structural description of **3**

Single crystals of **3** suitable for X-ray diffraction analysis were obtained by slow evaporation of a DMSO solution after two weeks. The structural analysis reveals that compound **3** crystallizes in the orthorhombic cell system with space group *Cccm*. The asymmetric unit consists of a quarter of a molecule of **1**, half a 3,5-DNSA molecule and three quarters of a lattice water molecule. A mirror plane (perpendicular to 001) bisects **1** and the 3,5-DNSA molecules. A two-fold axis also passes through molecule **1**. The molecular structure of **3** is depicted in Fig. 3. The orientation of the phenylpyridyl moieties is almost similar to that of **2** (the dihedral angle between the planes of the two rings is 35.9°). The dihedral angle between the NDI core and phenyl ring of the phenylpyridyl moiety of **3** is 62.3° . The 3,5-DNSA molecule is highly disordered and modeled over two positions with half occupancy. Compound **1** is biprotonated and strongly hydrogen-bonded to the lattice water and the disordered 3,5-DNSA molecules. The crystal structure analysis reveals the strong $\pi \cdots \pi$ interaction between the adjacent 3,5-DNSA molecules, and the NDI core and the 3,5-DNSA molecules ($3.862 \text{ \AA}$ and $4.109 \text{ \AA}$, respectively) resulting in the stacking of the NDI core and the 3,5-DNSA molecules (Fig. 3b). This stacking is further strengthened by the weak $\pi \cdots \pi$ interactions between the phenylpyridyl rings ($3.904 \text{ \AA}$) and results in the formation of a three-dimensional network (Fig. 3c). The crystal packing reveals the formation of channels running along the a -axis containing lattice water molecules.

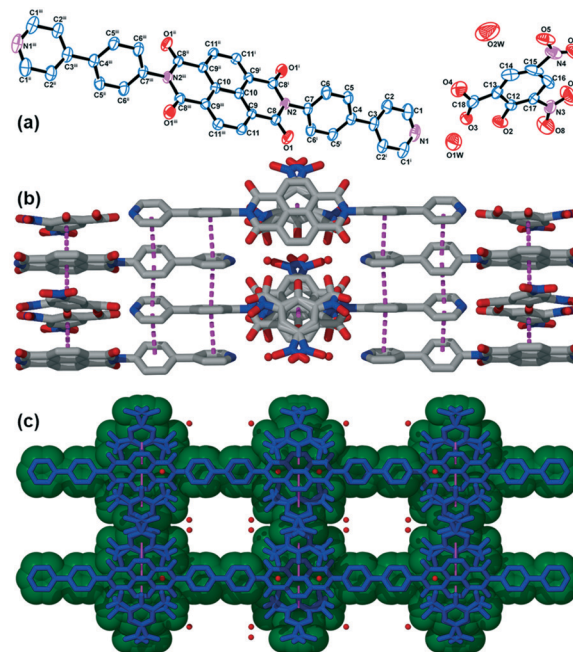


Fig. 3 (a) ORTEP diagram of **3** (probability level 50%). Symmetry equivalent positions are (i) $1/2 - x, 1/2 - y, z$; (ii) $1/2 - x, 1/2 - y, 2 - z$; (iii) $x, y, 2 - z$. (b) Stacking interactions between **1** and 3,5-DNSA molecules. (c) Channels running along the a -axis containing lattice water.

Thermal and PXRD analyses

The thermal stability of any organic compound is one of the essential features for their use as a functional material. Therefore, **1–3** were employed towards thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) and their plots are shown in Fig. S22 and S23 in the ESI.† Notably, **2** exhibits stability up to 370°C , with an initial weight loss of *ca.* 10.71% (*obs.* 10.85%) in the temperature range $30\text{--}200^\circ\text{C}$. This weight loss is assigned to the loss of one H_2O molecule and one DMSO molecule. In a similar fashion, **3** shows stability up to 380°C , with an initial weight loss of *ca.* 6.54% (*obs.* 6.50%). This weight loss is ascribed to the loss of four lattice occluded water molecules. However, due to the poor crystallographic data, the occupancy of one of the lattice water molecules needs to be fixed as half. This resulted in the count of water molecules per unit cell being three. Meanwhile, the loss of water molecules at higher temperatures might be due to the strong hydrogen bonding interaction with the 3,5-DNSA molecule. Moreover, **1** displays stability up to 400°C without any initial weight loss. These observations are intensely sustained by single-crystal X-ray crystallography. DSC findings also suggested that **2** and **3** loses the concerned solvent molecules in their first transition in the exothermic region. Moreover, to see the crystallinity and phase purity of these materials, PXRD patterns were recorded. The PXRD patterns of **1–3** fitted nicely with the simulated one (Fig. S24–S26†), obtained from the single-crystal X-ray data, thus confirming that the concerned materials retained their crystalline phase purity during the bulk synthesis.

DFT calculations

To assess the positions and energies of frontier molecular orbitals (FMO) for 1–3, density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d,p) level using the Gaussian 09 program (see the ESI† for details). Full geometry optimization was done for all these molecules. In all cases, the geometry of the concerned optimized molecule is very close to the single-crystal X-ray structure. DFT calculations for 2 and 3 reveal that the NDI-N substituted phenylpyridyl units deviate from perpendicularity to the NDI core, thus providing a suitable platform for electronic interaction between the NDI core and *N*-substituents. Notably, in both CT complexes, the pyridyl-N atoms are protonated. The presence of a +ve charge on the pyridyl-N atoms in combination with the geometrical arrangements force the substituents to pull conjugated electrons from the NDI core, thus increasing its π -acidity. As shown in Fig. 4, the electron distribution of the lowest unoccupied molecular orbital (LUMO) is spread over the NDI core, whereas in the case of the highest-occupied molecular orbital (HOMO), it is spread over the pendent phenylpyridyl substituents. Notably, the intermolecular D-A CT complexation greatly affects the FMO energies as the HOMO and LUMO energies of 2 (HOMO: -6.35 eV; LUMO: -3.16 eV; HOMO–LUMO gap: 3.19 eV) shifted upfield compared to those of 1 (HOMO: -6.73 eV; LUMO: -3.54 eV; gap: 3.19 eV). This upfield shift in FMO energies may be attributed to the $\pi\cdots\pi$ stacking arrangements. Comparatively, 3 presents a lower HOMO and LUMO energy (HOMO: -9.12 eV; LUMO: -6.97 eV; HOMO–LUMO gap: 2.15 eV) with a narrower band-gap induced by extension of the π -electron system (Table 2).

Electronic and optical properties

To prove the DFT findings and the possibility of using 1–3 as fluorescent probes, UV-vis absorption and emission profiles of 1–3 were recorded in DMSO. As shown in Fig. 5a, 1–3 show

two intense absorption bands each at 360 nm (363 nm for 3) and 380 nm (Table 2). The major absorption peaks are assigned to the spin-allowed π – π^* transition of the NDI core. Notably, in comparison to the parent NDA,⁴⁶ in 1–3, the absorption band red-shifted (bathochromic shift) to 360 nm with additional absorption at 380 nm. The bathochromic shifts of 7–10 nm in 1–3 are attributed to the presence of phenylpyridyl groups on the NDI core, which provides an opportunity for additional intermolecular interactions due to the increment in the conjugation length.⁴⁷ The optical band gaps for 1–3 estimated from the edge of end absorption (Fig. 5a) are found to be *ca.* 2.92 eV, 2.63 eV and 2.86 eV, respectively, which are quite consistent with the HOMO–LUMO band gap values estimated from DFT calculations. The optical band gaps for 1–3 were calculated using Tauc plots and details are provided with Fig. S27 in the ESI.†^{48,49} It should be noted that the presence of phenylpyridyl groups on the NDI core plays a crucial role in the energy gap distribution.

The fluorescence spectra of 1–3 exhibit a broad emission between 425 nm and 550 nm, when excited in prevailing absorption bands at 360 or 370 nm (Fig. 5b). This broad and strong fluorescence response corresponds to electron-rich strong π – π electron conjugation.⁴⁷ Notably, the studied materials also exhibit a very large Stokes shift (170–180 nm), which is a prime requirement for any material to be used for precise fluorescence imaging (Tables 2 and S4†). The quantum yields of 1–3 were determined to be 0.05, 0.89 and 0.10 in DMSO, with perylene in ethanol ($\Phi_f = 0.92$) as reference.⁵⁰

The absolute quantum yield of 3 is relatively lower than that of 2, largely due to intensive non-classical π – π interactions around the fluorophore scaffolds which are relatively less in the case of 2, wherein only the NDI core interacts with the PA[−] anion as the phenylpyridyl units are more twisted at a distance of 4.2 Å. However, in 3, both the NDI rings and phenylpyridyl rings are involved in strong π – π

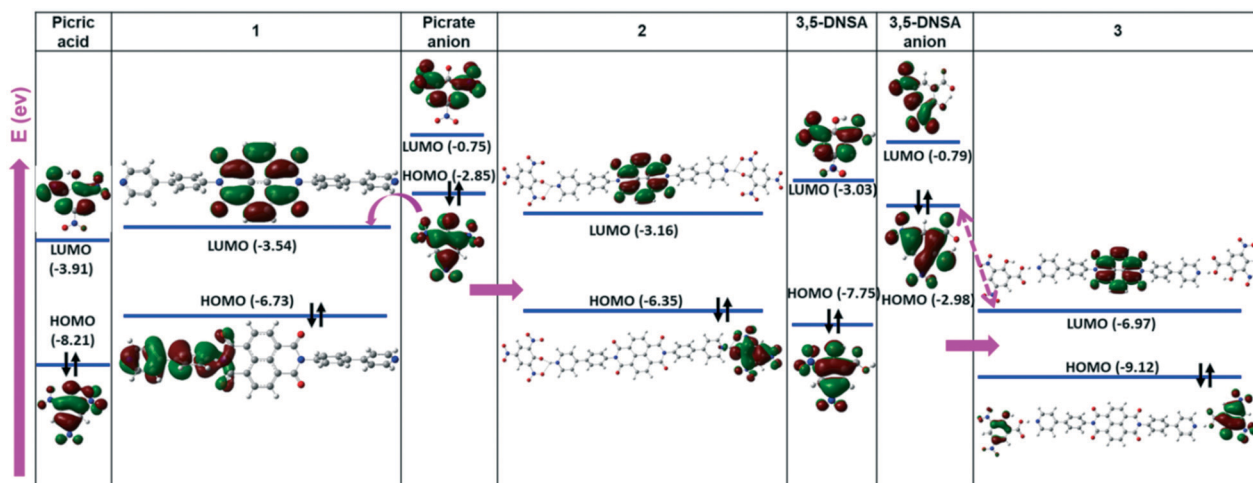


Fig. 4 Pictorial representation of the CT phenomenon in 2 and 3 in the ground state which occurs from the HOMO of picrate and 3,5-dinitrosalicylate anion to the LUMO of 1.

Table 1 Crystal data and structure refinement for compounds **1–3**

Identification code	1	2	3
CCDC no	1975049	1975050	1975051
Empirical formula	C ₃₆ H ₂₀ N ₄ O ₄	C ₅₂ H ₄₀ N ₁₀ O ₂₁ S ₂	C ₅₀ H ₂₆ N ₈ O ₂₁
Formula weight	572.56	1205.06	1074.79
Temperature [K]	298	138	138
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>I</i> 2/ <i>a</i>	<i>Cccm</i>
<i>a</i> /Å	13.1438(7)	16.6037(3)	7.7993(3)
<i>b</i> /Å	17.2839(10)	10.0174(2)	22.8606(8)
<i>c</i> /Å	17.6953(11)	32.0776(5)	33.5658(11)
α /deg	90	90	90
β /deg	104.028(6)	100.676(2)	90
γ /deg	90	90	90
Volume/Å ³	3900.1(4)	5242.98(17)	5984.7(4)
<i>Z</i>	6	4	4
ρ_{calc} g cm ^{−3}	1.463	1.527	1.193
μ /mm ^{−1}	0.098	0.196	0.096
<i>F</i> (000)	1776	2488	2200
Crystal size/mm ³	0.4 × 0.1 × 0.03	0.2 × 0.15 × 0.12	0.2 × 0.05 × 0.05
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
2 θ range for data collection/deg	6.39 to 54.95	6.384 to 50.698	6.612 to 50.696
Index ranges	−16 ≤ <i>h</i> ≤ 16, −22 ≤ <i>k</i> ≤ 20, −22 ≤ <i>l</i> ≤ 22	−19 ≤ <i>h</i> ≤ 19, −12 ≤ <i>k</i> ≤ 12, −38 ≤ <i>l</i> ≤ 38	−9 ≤ <i>h</i> ≤ 9, −26 ≤ <i>k</i> ≤ 27, −40 ≤ <i>l</i> ≤ 39
Reflections collected	33 236	34 355	35 813
Independent reflections	8322 [<i>R</i> _{int} = 0.0864, <i>R</i> _{sigma} = 0.1196]	4784 [<i>R</i> _{int} = 0.0437, <i>R</i> _{sigma} = 0.0297]	2805 [<i>R</i> _{int} = 0.0716, <i>R</i> _{sigma} = 0.0352]
Data/restraints/parameters	8322/0/596	4784/3/392	2805/281/253
Goodness-of-fit on <i>F</i> ²	0.866	1.109	1.493
Final <i>R</i> indices [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0631, <i>wR</i> ₂ = 0.1304	<i>R</i> ₁ = 0.0429, <i>wR</i> ₂ = 0.1136	<i>R</i> ₁ = 0.1258, <i>wR</i> ₂ = 0.3764
Final <i>R</i> indices [all data]	<i>R</i> ₁ = 0.1990, <i>wR</i> ₂ = 0.1682	<i>R</i> ₁ = 0.0535, <i>wR</i> ₂ = 0.1202	<i>R</i> ₁ = 0.1621, <i>wR</i> ₂ = 0.3999
Largest peak/hole/e Å ^{−3}	0.20/−0.23	0.29/−0.45	0.80/−0.29

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(|F_o|^2 - |F_c|^2)_2] / \sum [wF_o] \}^{1/2}$.

Table 2 Summary of the electronic/optical properties of **1–3**^a

	λ_{max} (nm)	$E_{\text{LUMO}}^{\text{CV}}$	$E_{\text{HOMO}}^{\text{CV}}$	E_{g}^{UV}	$E_{\text{LUMO}}^{\text{Th}}$	$E_{\text{HOMO}}^{\text{Th}}$	E_{g}^{Th}	Fluorescence properties (λ_{ex}) [nm]	Fluorescence quantum yields (ϕ_{F})	Fluorescence life time τ_{avg} (ns)	Stokes shifts (nm)
1	360, 380	−4.59	−7.46	2.92	−3.54	−6.73	3.19	541 (370)	0.05	0.69	171
2	360, 380	−4.65	−7.29	2.63	−3.16	−6.35	3.19	532 (360)	0.89	1.55	172
3	363, 380	−4.48	−7.28	2.86	−6.97	−9.12	2.15	550 (370)	0.10	1.14	180

^a Energies are in eV; $E_{\text{red1}}^{\text{CV}} = -5.1 - E_{\text{red1}}^{1/2}$, $E_{\text{HOMO}}^{\text{CV}} = E_{\text{LUMO}}^{\text{CV}} - E_{\text{g}}^{\text{UV}}$; E_{g}^{UV} , optical band gap determined by the onset of absorption in the UV-vis spectra (the details of the calculation of E_{g}^{UV} values are provided in the ESI†); E_{Th} , theoretical calculation using the B3LYP/6-31G(d,p) basis set; $E_{\text{g}}^{\text{Th}} = E_{\text{LUMO}}^{\text{Th}} - E_{\text{HOMO}}^{\text{Th}}$. Molar extinction coefficients $\epsilon_{360} = 39\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_{380} = 35\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ (for **1**); $\epsilon_{360} = 145\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_{380} = 145\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ (for **2**); $\epsilon_{363} = 78\,889 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_{380} = 64\,444 \text{ L mol}^{-1} \text{ cm}^{-1}$ (for **3**), respectively.

interaction with the DNSA anion and phenylpyridyl units, respectively.^{52–55}

Furthermore, to display molecular interactions in probes **1–3**, time-resolved fluorescence decay profiles were analyzed in DMSO and provided in Fig. S28,† whereas, their fluorescence lifetime τ_{avg} (ns) and respective deconvoluted data are presented in Tables 2 and S4,† respectively. As shown in Fig. S28,† these probes show a multi-exponential decay pattern. This might be due to the existence of various H-bonded species in the concerned probes. Importantly, **2** and **3** exhibit a quite better fluorescence lifetime (1.55 and 1.14 ns, respectively) than parent **1** (0.69 ns). This significant difference observed in the fluorescence lifetimes for

intermolecular D-A CT self-assembly might be due to the presence of strong *face-to-face* and *edge-to-face* $\pi \cdots \pi$ stacking.

Cyclic voltammetry studies

NDI derivatives are well-known for their photophysical properties and interesting charge transfer phenomenon.^{26–30} To illustrate the electron-transfer phenomenon, cyclic voltammograms (CVs) of **1–3** were recorded in DMSO using Ag/AgCl as the reference electrode and are depicted in Fig. 5c. As shown in Fig. 5c, compound **1** exhibited a quasi-reversible reduction potential at an $E_{1/2} = -0.507$ (0.26) V vs. a Fc/Fc⁺ [Fc: ferrocene; 0.52 (0.16) V] couple. This low reduction

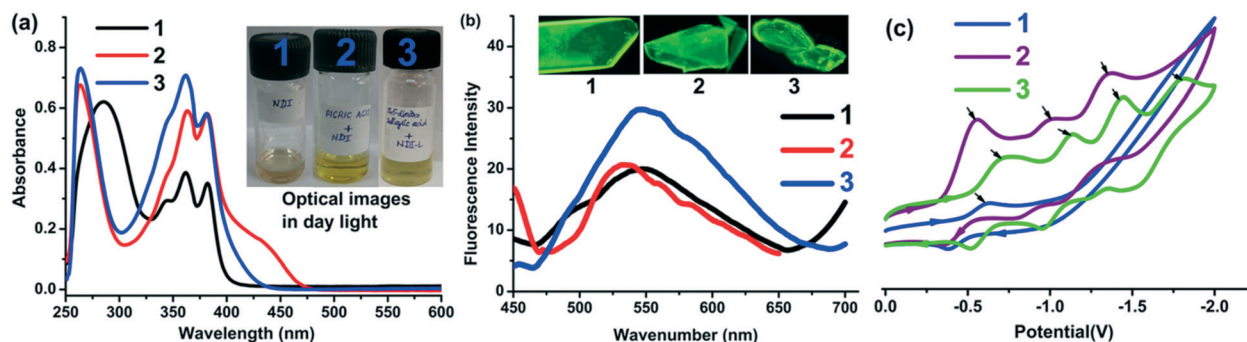


Fig. 5 (a) UV-vis absorption spectra of 1–3 in DMSO. The concentrations of the solutions used for UV-vis measurements of 1–3 are 1×10^{-5} , 0.4×10^{-5} and 0.9×10^{-5} M, respectively. Inset shows the optical images of the solutions of 1–3 in DMSO in daylight; the solutions are of the same conc. of 4.7×10^{-4} M. (b) Emission spectra of 1–3 excited at 360 nm (2.08×10^{-2} mM). The inset shows the fluorescence microscopy images of the respective crystals. (c) Cyclic voltammetry of 1–3 in DMSO (1×10^{-3} M) containing 0.1 M $\{(Bu_4N)^+ \cdot ClO_4^-\}$ as the supporting electrolyte and using Ag/AgCl as the reference electrode.

potential value of 1 indicates the generation of anion radicals $[1]^-$.⁵⁶ Notably, the CV of CT complex 2 showed three successive reduction potentials at $E_{1/2} = -0.452$ (0.21), -0.885 (0.23) and -0.122 (0.26) V. The low values of the 1st, 2nd and 3rd reduction potentials of 2 indicate the generation of anion radicals $[2]^-$ and $[2]^{2-}$, respectively. Under identical conditions, 3 exhibits four successive reduction peaks at $E_{1/2} = -0.616$ (0.18), -1.040 (0.17), -1.344 (0.20), and -1.675 (0.27) V (Fig. 5c) corresponding to the formation of four radical anions. A closer look on the CVs of 1–3 revealed that the 1st reduction potential of 2 and 3 significantly shifted towards the more negative side, which indicates the better stability of the CT complex anion radicals $[2]^-$ and $[3]^-$ compared to $[1]^-$.⁵⁶ It is also observed that the CV significantly changes after the formation of CT complexes, demonstrating that the electronic properties of 1 have been significantly altered, which is possible through a conformation that includes charge transfer. Moreover, the gradual shift in reduction potentials to more negative values indicates the strong influence of the electron-donating character of the concerned picric acid or 3,5-dinitrosalicylate ion on the NDI core and thus on their redox properties.⁵⁷ These observations are well sustained by 1H NMR spectroscopy and DFT calculations. Notably, both PA and 3,5-DNSA exhibit only two successive reduction peaks in their potential window (Fig. S29†).

Fluorescence cell imaging

The fluorescence properties and large Stokes shift (>170 nm) of 1–3 encouraged us to exploit these materials as a fluorescent probe for cell imaging. As shown in Fig. S30,† 1–3 display excellent cell permeability due to their ability to diffuse rapidly and stain all the neuronal cells and thus are efficient enough to be used in the biological system. The live (green colour), dead (red colour) and necrotic cells (yellow colour) are visible in Fig. S30,† which indicates that the experimental probes 1–3 can be used as a marker for live, dead and necrotic cells. In addition, they have shown similar

properties to those of commercially available acridine orange (AO) and ethidium bromide (EB). A closer look at the stained fluorescence images indicates that our probes 1–3 are also compatible to be used as a biological probe, as the number of visible live cells is higher with probes 1–3 in comparison to that with commercial AO. Interestingly, 2 and 3 showed enhanced staining under identical conditions (Fig. S30b and c†). This might be due to the strong $\pi \cdots \pi$ stacking interactions.⁵⁸ Furthermore, the rate of apoptosis was also counted in different treatment groups over time. As shown in Fig. 6a, the number of live cells is higher with 2 and 3 in the initial 15 min, whereas after 1 h, 1–3 exhibits an almost similar influence on brain cells to that of AO (Fig. 6b). Furthermore, considering their application in cell imaging, the toxicity of the probes 1–3 was evaluated from the number of live cells detected in a sample of 50 total cells (Fig. 6).⁵⁹ The % of live cells detected after staining is 58%, 82% and 78% for 1, 2 and 3, respectively. These data showed that experimental probes 2 and 3 are relatively non-toxic by displaying a greater percentage of live cells as compared to fluorophore 1. Finally, these results revealed that 1–3 can be used as biocompatible fluorescent markers.

Experimental section

Materials and methods

The starting materials such as 4-iodoaniline, 4-pyridylboronic acid, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) and anhydrous DMF were purchased from Sigma-Aldrich. However, picric acid (PA), 3,5-dinitrosalicylic acid (3,5-DNSA), $PdCl_2$ (anhydrous), K_2CO_3 and triphenylphosphine were purchased from TCI and AVRA Chemicals, respectively, and used as received. The solvents were of analytical grade and purified wherever necessary per the standard literature.⁶⁰ The microanalytical data were obtained with a FLASH EA 1112 Series CHNS analyzer. The NMR spectroscopic measurements were carried out with a Bruker Avance 400/500 MHz spectrometer. The FTIR spectra were recorded with a Perkin-Elmer FTIR 2000 spectrometer.

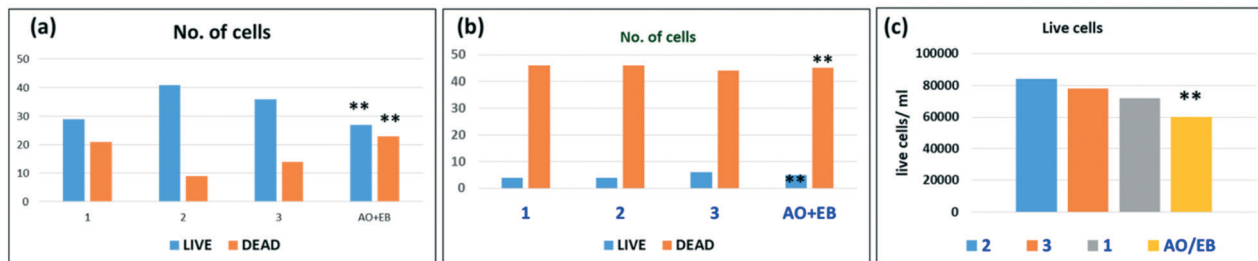


Fig. 6 Number of live and dead cells after 15 min (a) and 1 h (b) of exposure. (c) Number of live cells per mL under different treatments. **Incubation with control (AO/EB) for 5 min.

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on an SDT Q600 (V20.9 Build 20) instrument (Artisan Technology Group, Champaign, IL) under a N_2 atmosphere with a heating rate of $10^\circ C$ per min. HRMS (ESI-TOF) of 1–3 was performed using a Bruker Compass Data Analysis 4.0 equipment. The powder X-ray diffraction patterns were recorded on a Bruker D8-Advance diffractometer using graphite-monochromated Cu K α 1 ($\lambda = 1.5406 \text{ \AA}$) and K α 2 ($\lambda = 1.54439 \text{ \AA}$) radiation. The samples were ground and subjected to the range $\theta = 5\text{--}50^\circ$ with a scan rate of 1° min^{-1} at room temperature.

Synthesis of 2,7-bis(4-(pyridin-4-yl)phenyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (1)⁴⁰

Compound 1 was synthesized by refluxing 4-(pyridin-4-yl)aniline (0.263 g, 1.55 mmol) with NDA (0.200 g, 0.73 mmol) in 10 mL of DMF in the presence of 4–5 drops of glacial acetic acid as a catalyst at $80\text{--}90^\circ C$ in an oil bath for 10 h (Scheme S1†). The progress of the reaction was monitored by TLC. After completion of the reaction, the product was filtered off, washed with diethyl ether and dried under vacuum. Yield, 0.279 g (50%; based on NDA, pale yellow, crystalline solid). FT-IR spectrum (selected peaks, ν , cm^{-1}): 1717 (C=O), 1676 (C=N). Anal. calcd. for $C_{36}H_{20}N_4O_4$: C, 75.51%; H, 3.52%; N, 9.79%. Found. C, 75.42%; H, 3.48%; N, 9.65%. 1H NMR (400 MHz, DMSO- d_6) δ_{ppm} 8.99–9.01 (d, 4H, H_a), 8.73 (d, 4H, H_c), 8.55–8.56 (d, 4H, H_b), 8.22–8.24 (d, 4H, H_c), 7.73–7.75 (d, 4H, H_d). ^{13}C NMR (101 MHz, DMSO- d_6) δ_{ppm} 124.7, 126.8, 129.4, 130.9, 134.8, 137.7, 142.4, 155.5, 158.1, 162.6. UV-vis (DMSO, $1.0 \times 10^{-5} \text{ mol L}^{-1}$) λ/nm ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$) 360, 380 (39 000, 35 000). ESI-TOF (m/z): $[M + H]^+$ calcd for $C_{36}H_{20}N_4O_4H^+$ 573.1562; found 573.1561.

Synthesis of charge-transfer complex $[(1\cdot 2H)^{2+} \cdot (PA^-)_2]$ (2)

Complex 2 was synthesized by mixing a standard solution of 1 (0.060 g, 0.01 mmol) in 10 mL of DMSO (5–6 drops of H_2SO_4) with a standard solution of PA (0.04 g, 0.02 mmol) in 5 mL of DMSO (Scheme 1). The resulting solution was stirred for 1 h and then kept for 6–7 days at room temperature. Needle shaped yellow coloured crystals suitable for single crystal X-ray analysis were isolated. Yield, 0.05 g (43%; based on NDA). FT-IR spectrum (selected peaks, ν , cm^{-1}): 1709

(C=O), 1677 (C=N). Anal. calcd. for $C_{52}H_{38}N_{10}O_{21}S_2$: C, 51.92%; H, 3.18%; N, 11.64%. Found. C, 51.82%; H, 3.12%; N, 11.56%. 1H NMR (500 MHz, DMSO- d_6) δ_{ppm} 9.01–9.03 (d, 4H, H_a), 8.76 (d, 4H, H_c), 8.56–8.57 (d, 4H, H_b), 8.45–8.48 (br, 4H, H_f), 8.23–8.25 (d, 4H, H_c), 7.76–7.79 (d, 4H, H_d). ^{13}C NMR (101 MHz, DMSO- d_6) δ_{ppm} 123.6, 124.1, 125.3, 126.8, 126.9, 127.1, 130.3, 130.5, 135.1, 138.4, 141.7, 144.1, 153.3, 160.8, 162.8. UV-vis (DMSO, $0.4 \times 10^{-5} \text{ mol L}^{-1}$) λ/nm ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$) 360, 380 (145 000 for both). ESI-TOF (m/z): $[M + 2H]^{2+}$ calcd. for $C_{52}H_{40}N_{10}O_{21}S_2H_2^+$ 1206.1967; found 1206.2561.

Synthesis of charge-transfer complex $[(1\cdot 2H)^{2+} \cdot (3,5\text{-DNSA}^-)_2]$ (3)

Complex 3 was synthesized using the same protocol except for using a standard solution of 3,5-DNSA (0.047 g, 0.02 mmol) in place of PA (Scheme 1). The resulting solution was stirred for 1 h and then kept for 6–8 days at room temperature. Needle shaped light brown coloured crystals were obtained within 6–8 days and were washed with methanol and ether, filtered off and dried under vacuum. Yield, 0.038 g (33%; based on NDA). FT-IR spectrum (selected peaks, ν , cm^{-1}): 1708 (C=O), 1673 (C=N). Anal. calcd. for $C_{50}H_{36}N_8O_{22}$: C, 54.55%; H, 3.30%; N, 10.18%. Found. C, 54.72%; H, 2.52%; N, 10.12%. 1H NMR (500 MHz, DMSO- d_6) δ_{ppm} 9.02–9.04 (d, 4H, H_a), 8.75 (d, 4H, H_c), 8.64–8.65 (m, 2H, H_b), 8.60–8.61 (m, 2H, H_b), 8.48–8.50 (m, 4H, H_c), 8.23–8.26 (dd, 4H, H_f), 7.76–7.78 (d, 4H, H_d). ^{13}C NMR (126 MHz, DMSO- d_6) δ_{ppm} 120.9, 124.4, 125.9, 127.1, 127.5, 129.1, 130.4, 130.8, 131.0, 135.3, 139.1, 143.7, 143.8, 163.3, 167.2, 169.5. UV-vis (DMSO, $0.9 \times 10^{-5} \text{ mol L}^{-1}$) λ/nm ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$) 363, 380 (78 889 and 64 444). ESI-TOF (m/z): $[M + 2H]^+$ calcd. for $C_{50}H_{36}N_8O_{22}H_2^+$ 1102.2100; found 1102.2565 and $[M + Na]^+$ calcd. for $C_{50}H_{36}N_8O_{22}Na$ 1123.1841; found 1122.6665.

Caution! Picric acid (PA) used in this study is well-known for its toxic and explosive nature. Therefore, it must be used in a small quantity and handled with care.

Single crystal X-ray crystallography

Suitable single crystals of 1–3 were selected for the data collection. The data for 1 were collected at 298 K, whereas those for 2 and 3 were collected at 138 K on a Rigaku SuperNova HyPix3000 diffractometer with monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Diffraction data were

processed using CrysAlisPro v39.31,⁶¹ followed by empirical absorption correction with the included Scale3 ABSPACK program.⁶¹ The structures were solved by intrinsic phasing with the SHELXS structure solution program and the refinement procedure by the full-matrix least-squares method based on F^2 values against all reflections was performed with SHELXL-2014/7,⁶² using the Olex2 GUI.⁶³ Details of the crystallographic data collection and structural solution parameters for 1–3 are provided in Table 1. Meanwhile, Table S2† contains H-bonding and short contact details for 1–3.

Optical spectroscopy

The UV-visible and fluorescence spectra were recorded using a Perkin-Elmer Lambda-25 and Cary Eclipse fluorescence spectrophotometer, respectively, with a slit width of 5 nm. Time-resolved fluorescence decay measurements were performed based on time-resolved intensity decay by the method of time-correlated single-photon counting (TCSPC) on a Horiba Jobin Yvon Fluoro Cube fluorescence lifetime system using a diode laser at 360 nm (IBH NanoLED, UK) as the excitation light source with a TBX-04 photon detector.

Computational methods

DFT calculations have been carried out by employing the unrestricted B3LYP^{64,65} hybrid functional using the Gaussian 09, revision B.01, package.⁶⁶ All geometry optimization calculations were performed with the B3LYP exchange–correlation functional.^{64,65} The methods used were Becke's three-parameter hybrid exchange functional, the nonlocal correlation provided by the Lee, Yang, and Parr expression, and the Vosko, Wilk, and Nusair 1980 correlation functional (III) for local correction. The basis set 6-31G(d,p) is used for all atoms. The coordinates are generated from the X-ray structure of 1–3 (see the ESI† for coordinates). All the structures were optimized in the gas phase.

Cyclic voltammetry

Cyclic voltammetry measurements were performed with the help of a CH Instruments model 620A electrochemical analyzer at room temperature (298 K) with an HPLC grade DMSO solution of corresponding compounds 1–3 (1×10^{-3} M) containing Bu_4NClO_4 (0.1 M) as the supporting electrolyte using a glassy carbon working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1} . There is no response on the anodic side (oxidation), but there is a nice quasi-reversible couple found on the cathodic side (reduction).

Preparation of standard solutions

A standard solution of 1 with a concentration of 1.04×10^{-2} mM was prepared by dissolving 0.060 g of 1 in 10 mL of DMSO and then adding 5–6 drops of conc. H_2SO_4 and stirring till dissolved. Meanwhile, a standard solution of picric acid of 2.08×10^{-2} mM concentration was prepared by

dissolving 0.04 g of picric acid in 5 mL of DMSO. In a similar manner, a standard solution of 3,5-dinitrosalicylic acid of 2.08×10^{-2} mM concentration was prepared by dissolving 0.047 g of 3,5-dinitrosalicylic acid in 5 mL of DMSO.

Cell isolation and imaging

To determine the role of experimental probes 1–3 as a fluorescent probe, cellular imaging of rat brain has been conducted and the results were compared with those from the commercially available standard fluorescent dyes acridine orange (AO) and ethidium bromide (EB) used for staining of neuronal cells. Neuronal cells were isolated from brain tissue and were immediately suspended in PBS (isolated cells were centrifuged to remove cellular debris).⁶⁷ Further, the suspended cells were incubated with the fluorescent probes, *i.e.* 1–3 (1 mg mL^{-1}), AO ($1 \mu\text{g mL}^{-1}$) and EB ($1 \mu\text{g mL}^{-1}$), for 5 min and later were washed and examined under a fluorescence microscope at various wavelengths to determine the rate of apoptosis. The cells which appeared green in colour were live, yellow were necrotic and dead appeared red when stained with 1–3, AO and EB. For quantification of the extent of apoptosis, a total of 50 cells from six different slides in each treatment were observed and photographed at 20 fold magnification using fluorescence microscopy.

Conclusions

In conclusion, we have successfully designed and synthesized three fluorescent probes 1–3 with a very large Stokes shift ($>170 \text{ nm}$). The aim of functionalization of the NDI-core with phenylpyridyl groups is to increase the length of the parent organic system and π -electron conjugation, and most importantly, to develop *face-to-face* and *edge-to-face* $\pi \cdots \pi$ stacking, which is a vital requirement for any organic material to be used as a fluorescent probe. The key driving force for the formation of intermolecular D–A CT complexes 2 and 3 are the proton donating and accepting capacity of PA and 3,5-DNSA, and 1, respectively, resulting in the generation of charged species in solution [PA^- or $3,5\text{-DNSA}^-$ and $(1 \cdot 2\text{H})^{2+}$]. Importantly, probes 1–3 can stain neuronal cells under normal cell isolation and with time-bound exposure, and the results are very promising. Furthermore, this work provides a platform for researchers to design and develop more advanced NDI functionalized fluorescent probes for advanced stage applications in the near future.

Author contributions

Pooja Rani: experimental work and formal analysis. Dr. Ahmad Husain: crystallographic work and DFT calculations. Ananya Shukla: performed biological work. Dr. Neha Singla: supervised and written the biological part. Ankit Kumar Srivastava: performed the cyclic voltammetry study. Dr. Gulshan Kumar: contributed in the synthesis of 1–3. Dr. K. K. Bhasin:

project supervision. Dr. Girijesh Kumar: concept design and project supervision. This manuscript was written with the contribution of all authors and they have given approval to the final version.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 J. S. Brooks, *Chem. Soc. Rev.*, 2010, **39**, 2667–2694.
- 2 L. Sun, W. Zhu, W. Wang, F. Yang, C. Zhang, S. Wang, X. Zhang, R. Li, H. Dong and W. Hu, *Angew. Chem., Int. Ed.*, 2017, **56**, 7831–7835.
- 3 E. M. S. Stennett, M. A. Ciuba and M. Levitus, *Chem. Soc. Rev.*, 2014, **43**, 1057–1075.
- 4 Y. Li, T. Liu, H. Liu, M.-Z. Tian and Y. Li, *Acc. Chem. Res.*, 2014, **47**, 1186–1198.
- 5 Y. Wang, L. Sun, C. Wang, F. Yang, X. Ren, X. Zhang, H. Dong and W. Hu, *Chem. Soc. Rev.*, 2019, **48**, 1492–1530.
- 6 S. Guha, F. S. Goodson, L. J. Corson and S. Saha, *J. Am. Chem. Soc.*, 2012, **134**, 13679–13691.
- 7 R.-B. Lin, Y. He, P. Li, H. Wang, W. Zhou and B. Chen, *Chem. Soc. Rev.*, 2019, **48**, 1362–1389.
- 8 M. A. Kobaisi, R. S. Bhosale, M. E. El-Khouly, D. D. La, S. D. Padghan, S. V. Bhosale, L. A. Jones, F. Antolasic, S. Fukuzumi and S. V. Bhosale, *Sci. Rep.*, 2017, **7**, 16501.
- 9 N. S. S. Kumar, M. D. Gujrati and J. N. Wilson, *Chem. Commun.*, 2010, **46**, 5464–5466.
- 10 D.-G. Chen, T.-C. Lin, Y.-A. Chen, Y.-H. Chen, T.-C. Lin, Y.-T. Chen and P.-T. Chou, *J. Phys. Chem. C*, 2018, **122**, 12215–12221.
- 11 S. Grimme, *Angew. Chem., Int. Ed.*, 2008, **47**, 3430–3434.
- 12 Z. Yang, Z. Mao, Z. Xie, Y. Zhang, S. Liu, J. Zhao, J. Xu, Z. Chi and M. P. Aldred, *Chem. Soc. Rev.*, 2017, **46**, 915–1016.
- 13 A. Takai, M. Chkounda, A. Eggenspieler, C. P. Gros, M. Lachkar, J.-M. Barbe and S. Fukuzumi, *J. Am. Chem. Soc.*, 2010, **132**, 4477–4489.
- 14 S. T. Schneebeli, M. Kamenetska, Z. Cheng, R. Skouta, R. A. Friesner, L. Venkataraman and R. Breslow, *J. Am. Chem. Soc.*, 2011, **133**, 2136–2139.
- 15 D. Astruc, E. Boisselier and C. Ornelas, *Chem. Rev.*, 2010, **110**, 1857–1959.
- 16 J. M. Lupton, *ChemPhysChem*, 2012, **13**, 901–907.
- 17 B. Rybtchinski, L. E. Sinks and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2004, **126**, 12268–12269.
- 18 M. D. Ward and P. R. Raithby, *Chem. Soc. Rev.*, 2013, **42**, 1619–1636.
- 19 G. J. A. A. Soler-Illia and O. Azzaroni, *Chem. Soc. Rev.*, 2011, **40**, 1107–1150.
- 20 Q. Cheng, Z. Cao, A. Hao, Y. Zhao and P. Xing, *ACS Appl. Mater. Interfaces*, 2020, **12**, 15491–15499.
- 21 A. Pron, P. Gawrys, M. Zagorska, D. Djurado and R. Demadrille, *Chem. Soc. Rev.*, 2010, **39**, 2577–2632.
- 22 H. Yao, J. Wang, Y. Xu, S. Zhang and J. Hou, *Acc. Chem. Res.*, 2020, **53**, 822–832.
- 23 Y. Woo, W. Hong, S. Y. Yang, H. J. Kim, J.-H. Cha, J. E. Lee, K. J. Lee, T. Kang and S.-Y. Choi, *Adv. Electron. Mater.*, 2018, **4**, 1800251.
- 24 J. Zhang, L. Ning, J. Liu, J. Wang, B. Yu, X. Liu, X. Yao, Z. Zhang and H. Zhang, *Anal. Chem.*, 2015, **87**, 9101–9107.
- 25 T. D. Ashton, K. A. Jolliffe and F. M. Pfeffer, *Chem. Soc. Rev.*, 2015, **44**, 4547–4595.
- 26 S. Kumar, J. Shukla, Y. Kumar and P. Mukhopadhyay, *Org. Chem. Front.*, 2018, **5**, 2254–2276.
- 27 A. Das and S. Ghosh, *Chem. Commun.*, 2016, **52**, 6860–6872.
- 28 H. Chen, W. Zhang, M. Li, G. He and X. Guo, *Chem. Rev.*, 2020, **120**, 2879–2949.
- 29 M. A. Kobaisi, S. V. Bhosale, K. Latham, A. M. Raynor and S. V. Bhosale, *Chem. Rev.*, 2016, **116**, 11685–11796.
- 30 Z. Guo, S. Park, J. Yoon and I. Shin, *Chem. Soc. Rev.*, 2014, **43**, 16–29.
- 31 T. Hayashia and M. Kinoshita, *Phys. Chem. Chem. Phys.*, 2016, **18**, 32406–32417.
- 32 P. M. Alvey, J. J. Reczek, V. Lynch and B. L. Iverson, *J. Org. Chem.*, 2010, **75**, 7682–7690.
- 33 J. K. Klosterman, Y. Yamauchi and M. Fujita, *Chem. Soc. Rev.*, 2009, **38**, 1714–1725.
- 34 D. Dahal, L. McDonald, S. Pokhrel, S. Paruchuri, M. Konopka and Y. Pang, *Chem. Commun.*, 2019, **55**, 13223–13226.
- 35 X. Peng, F. Song, E. Lu, Y. Wang, W. Zhou, J. Fan and Y. Gao, *J. Am. Chem. Soc.*, 2005, **127**, 4170–4171.
- 36 Y.-J. Lu, Q. Deng, D.-P. Hu, Z.-Y. Wang, B.-H. Huang, Z.-Y. Du, Y.-X. Fang, W.-L. Wong, K. Zhang and C.-F. Chow, *Chem. Commun.*, 2015, **51**, 15241–15244.
- 37 H. Chen, W. Lin, W. Jiang, B. Dong, H. Cui and Y. Tang, *Chem. Commun.*, 2015, **51**, 6968–6971.
- 38 J. S. Ward, R. S. Nobuyasu, A. S. Batsanov, P. Data, A. P. Monkman, F. B. Dias and M. R. Bryce, *Chem. Commun.*, 2016, **52**, 2612–2615.

- 39 N. Karton-Lifshin, L. Albertazzi, M. Bendikov, P. S. Baran and D. Shabat, *J. Am. Chem. Soc.*, 2012, **134**, 20412–20420.
- 40 Y. Hirose, I. Yagi, S. Hirata, H. Mogi, M. Bando and O. Enoki, PCT Int. ppl., 2018, WO2018016570A1 20180125.
- 41 Q.-L. Luo, J.-P. Tan, Z.-F. Li, W.-H. Nan and D.-R. Xiao, *J. Org. Chem.*, 2012, **77**, 8332–8337.
- 42 A. I. Vedernikov, E. N. Ushakov, A. A. Efremova, L. G. Kuz'mina, A. A. Moiseeva, N. A. Lobova, A. V. Churakov, Y. A. Strelenko, M. V. Alfimov, J. A. K. Howard and S. P. Gromov, *J. Org. Chem.*, 2011, **76**, 6768–6779.
- 43 G. Kumar, R. Guda, A. Husain, R. Bodapati and S. K. Das, *Inorg. Chem.*, 2017, **56**, 5017–5025.
- 44 P. Rani, A. Sharma, A. Husain, G. Kumar, H. Kaur, K. K. Bhasin and G. Kumar, *CrystEngComm*, 2019, **21**, 7447–7459.
- 45 M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, *CrystalExplorer17*, University of Western Australia, 2017.
- 46 G. Kumar, R. Guda, A. Husain, R. Patra, Kirandeep and M. Kasula, *Photochem. Photobiol. Sci.*, 2019, **18**, 1333–1341.
- 47 A. Pron, P. Gawrys, M. Zagorska, D. Djurado and R. Demadrille, *Chem. Soc. Rev.*, 2010, **39**, 2577–2632.
- 48 J. Tauc, *Mater. Res. Bull.*, 1968, **3**, 37–46.
- 49 C. Coluccini, N. Manfredi, M. M. Salamone, R. Ruffo, M. G. Lobello, F. De Angelis and A. Abboto, *J. Org. Chem.*, 2012, **77**, 7945–7956.
- 50 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.
- 51 C. M. Cardona, L. Wei, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367–2371.
- 52 T.-B. Ren, W. Xu, W. Zhang, X.-X. Zhang, Z.-Y. Wang, Z. Xiang, L. Yuan and X.-B. Zhang, *J. Am. Chem. Soc.*, 2018, **140**, 7716–7722.
- 53 X. Lv, C. Gao, T. Han, H. Shi and W. Guo, *Chem. Commun.*, 2020, **56**, 715–718.
- 54 N. Zhao, S. Xuan, F. R. Fronczek, K. M. Smith and M. G. H. Vicente, *J. Org. Chem.*, 2017, **82**, 3880–3885.
- 55 X. Liu, Q. Qiao, W. Tian, W. Liu, J. Chen, M. J. Lang and Z. Xu, *J. Am. Chem. Soc.*, 2016, **138**, 6960–6963.
- 56 S. Guha and S. Saha, *J. Am. Chem. Soc.*, 2010, **132**, 17674–17677.
- 57 C. Röger and F. Würthner, *J. Org. Chem.*, 2007, **72**, 8070–8075.
- 58 I. Roy, S. Bobbala, J. Zhou, M. T. Nguyen, S. K. M. Nalluri, Y. Wu, D. P. Ferris, E. A. Scott, M. R. Wasielewski and J. F. Stoddart, *J. Am. Chem. Soc.*, 2018, **140**, 7206–7212.
- 59 B. S. Cummings and R. G. Schnellmann, *Curr. Protoc. Pharmacol.*, 2004, **25**, 12.8.1–12.8.22.
- 60 W. L. F. Armarego, *Purification of Laboratory Chemicals (Eighth Edition)*, Elsevier, Oxford, 8th edn, 2017.
- 61 *CrysAlisPro*, Rigaku Oxford Diffraction/Agilent Technologies UK Ltd, Yarnton, England, 2019.
- 62 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
- 63 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- 64 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789.
- 65 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 66 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *GAUSSIAN 09, Revision A.02*, Gaussian, Inc., Wallingford, CT, 2009.
- 67 M. Nikodemova and J. J. Watters, *Neuroscience*, 2011, **190**, 67–74.



Syntheses, crystal structures, optical, and theoretical study of two ternary chalcogenides CsSc₅Te₈ and Cs_{0.6(1)}Ti₆Se₈ with tunnel structures

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ABSTRACT

Single crystals of two new chalcogenides CsSc₅Te₈ and Cs_{0.6(1)}Ti₆Se₈ were synthesized by the high-temperature solid-state sealed tube method using a reactive flux (CsCl) at 1223 K. The crystal structures of CsSc₅Te₈ and Cs_{0.6(1)}Ti₆Se₈ were determined by single-crystal X-ray diffraction method. The compound CsSc₅Te₈ crystallizes in the monoclinic space group C_{2h}^3-C2/m with the lattice parameters $a = 21.3376(15)$ Å, $b = 4.1434(3)$ Å, $c = 10.2853(7)$ Å, and $\beta = 103.925(2)^\circ$ having the two formula units ($Z = 2$). The asymmetric unit of CsSc₅Te₈ contains eight crystallographically independent atomic sites: Cs1 (site symmetry: $2/m$), Sc1 (m), Sc2 (m), Sc3 ($2/m$), Te1 (m), Te2 (m), Te3 (m), and Te4 (m). The structure of CsSc₅Te₈ is built up of the three-dimensional anionic framework of $[\infty [\text{Sc}_5\text{Te}_8]]^{1-}$ where the Sc atoms are octahedrally coordinated with six Te atoms forming the one-dimensional tunnels approximately along the b -axis where the Cs⁺ cations are present. The compound Cs_{0.6(1)}Ti₆Se₈ crystallizes in the Nb₃Te₄ structure type with $Z = 1$, in the hexagonal space group $C_{6h}^2-P6_3/m$ having cell dimensions of $a = b = 9.9520(1)$ Å and $c = 3.5710(1)$ Å. The asymmetric unit of Cs_{0.6(1)}Ti₆Se₈ structure is composed of four crystallographically independent sites with atoms Cs1 (site symmetry: $\bar{6}$), Ti1 ($m..$), Se1 ($m..$), and Se2 ($\bar{6}$). The Ti atoms are making distorted octahedral units by coordinating with six Se atoms. These TiSe₆ distorted octahedra share edges and corners with the adjacent TiSe₆ units to form three-dimensional anionic networks that generate one-dimensional tunnels approximately along the c -direction. The optical absorption measurements show that CsSc₅Te₈ is a semiconductor having a direct bandgap of 1.2(1) eV at room temperature consistent with the DFT studies.

1. Introduction

Over the last few decades, a variety of new solid-state metal oxides and chalcogenides with channel (or tunnel) structures were synthesized, and their crystal chemistry was studied in detail to understand the structure-property relationship of these compounds. Examples of such channel structure types include hollandites [1], psilomelanes [2], and the structures that are related to TiV₅S₈ [3] and TiCr₃S₅ [4]. The main frameworks of these structures are composed of the metal and ligand-based octahedra. Furthermore, the arrangement of these octahedra in these structures varies depending on the structure type, which in turn controls the size of the one-dimensional tunnels that can host a

variety of cations (e.g., K⁺, Cs⁺, Tl⁺, etc.) or neutral molecules (e.g., H₂O). The mineral hollandite was initially structurally characterized by Byström. The hollandite type structures have a general formula of $A_xM_8O_{16}$ ($A = \text{Na, K, Rb, Cs, Sr, and Ba}$; $M = \text{Ti, V, Cr, Mn, and Si}$) in which tunnels can accommodate bigger cations like alkali and alkaline-earth metals [5]. The main framework of hollandite based structures is formed by condensation of edge-sharing MO₆ octahedral units, making a 2×2 tunnel of four double strings. Hollandite based compounds mainly crystallize either in the tetragonal space group $I4/m$ or in the monoclinic space group $I2/m$. On the other hand, psilomelane structure type compounds crystallize in the $A2/m$ space group of the monoclinic crystal system. (Ba, H₂O)₂Mn₅O₁₀ is a typical example of a

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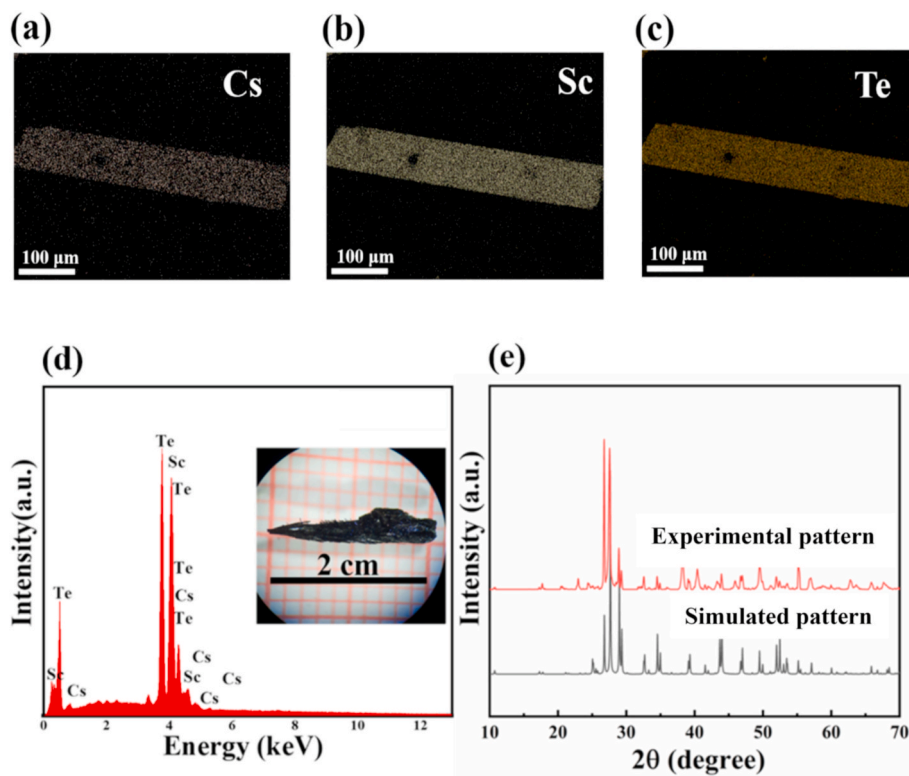


Fig. 1. (a)–(c) Elemental mapping of a typical black plate-shaped single crystal of CsSc_5Te_8 showing the homogenous distribution of Cs, Sc, and Te. (d) The EDS spectrum obtained from a point on a typical single crystal of CsSc_5Te_8 that was hand-picked from the lump of single crystals (inset picture), and (e) the experimental PXRD pattern of CsSc_5Te_8 collected on ground single crystals along with the simulated PXRD pattern.

psilomelane structure type compound [2] where Ba and water molecules are present in the tunnels that are formed by the framework of edge-sharing MnO_6 based octahedra.

Many of these metal oxides, which belong to the hollandite and psilomelanes family of compounds, are found as minerals in contrast to the chalcogen ($Q = \text{S}, \text{Se}, \text{and Te}$) based compounds with tunnel structures that were discovered mainly by the exploratory solid-state syntheses. Examples of these metal chalcogenides include AT_5Q_8 ($A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Cd}, \text{Sn}, \text{Pb}, \text{and Tl}; T = \text{Cr}, \text{Ti}, \text{and V}$) [3,6–9] and AT_6Q_8 ($A = \text{K}, \text{Rb}, \text{Cs}, \text{and Tl}; T = \text{V}, \text{Ti}, \text{and Cr}$) [10–13]. These metal chalcogenides with one-dimensional (1D) tunnel structures are of great interest as they show interesting properties which include immobilization of radioactive waste [14,15], 1D-ionic conductor [16], metallic [3,17], magnetic [17–19], optical [20], and transport properties [17,21].

The physical properties of the chalcogenides with tunnel structures can be fine-tuned with the proper choice and concentration of the guest species that occupy the tunnels. The low-temperature ion-exchange method is one of the effective routes to synthesize such compounds. For instance, Tl^{1+} cations act as a guest and reside in the tunnels of the host matrix V_5S_8 in the TlV_5S_8 structure, and the amount of the Tl atoms in this structure can be varied using the ion-exchange method. Some metastable phases such as $\text{Tl}_x\text{V}_5\text{S}_8$ and $\text{Tl}_x\text{V}_6\text{S}_8$ [22,23] could only be synthesized using the electrochemical method. Compounds of type $\text{M}_x\text{Ti}_6\text{Se}_8$ ($M = \text{H}_2\text{O}, \text{K}, \text{Tl}, \text{etc.}$) have also been synthesized using topotactic redox reaction [24]. Thus, depending on the molar ratios and size of the guest species, many novel ternary metal chalcogenides with diverse structure types can be stabilized. For example, three types of a ternary transition metal or lanthanide (III) based chalcogenides are reported where alkali metal cations are present in a poorer ratio than trivalent transition metals or lanthanides. $\text{Cs}_3\text{Y}_7\text{Se}_{12}$ and $\text{A}_3\text{M}_7\text{Q}_{12}$ ($A = \text{K}, \text{Rb}, \text{Cs}; M = \text{Sm}, \text{Gd}, \text{Tb}$) [25,26] structure types consist of the “triple” channels, that can host three A^+ cations simultaneously. Similarly double-channels (e.g., CsEr_3Se_5) [25] and single-channel (e.g., RbSc_5Te_8

[6]) containing chalcogenides are also known.

This report presents the crystal structure and characterization of two chalcogenides CsSc_5Te_8 and $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$, which belong to the family of tunnel structures. The single crystals of these two compounds were obtained from the reactive molten flux method. Although the synthesis of polycrystalline $\text{Cs}_x\text{Ti}_6\text{Se}_8$ [10] samples that belong to the Nb_3Te_4 structure type [27] is reported earlier using the ion exchange method but their crystal structures are not determined using the single-crystal X-ray diffraction (SXRD) method. We report the crystal structure of cesium deficient $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ using the SXRD study for the first time. The crystal structure of the new compound CsSc_5Te_8 is also established using the SXRD study. CsSc_5Te_8 crystallizes in the TlV_5S_8 [3] structure type and is the first compound known in the Cs–Sc–Te ternary system [28]. We also present the optical bandgap of CsSc_5Te_8 using the UV–visible absorption spectroscopy and its electronic structure using the DFT study.

2. Experimental

2.1. Syntheses

For the chemical reactions, the following reactants were used as supplied: cesium chloride (99.9%, SRL), scandium arc cast pellet (99.9%, Alfa Aesar), tellurium pieces (99.999%, Sigma Aldrich), selenium powder (99.5%, Sigma Aldrich), and titanium powder (99.99%, Alfa Aesar). Cesium chloride powder was preheated overnight to remove moisture and then stored in an argon-filled glove box for further use. All the other reactants were loaded inside the argon-filled glove box. Scandium arc cast pellet was shaved inside an argon-filled glove box, and the metal shavings were used in the reaction.

2.1.1. Synthesis of single crystals of CsSc_5Te_8

Our group has been actively working on the exploratory syntheses in the Cs–M–Q ($M = 3d$ transition metals) ternary system to discover new

compounds. One of the reactions in these attempts yielded a black lump consisting of black plate-shaped crystals of CsSc₅Te₈. This new ternary compound was first obtained from the molten flux reaction of Sc (22.5 mg, 0.500 mmol), Te (127.5 mg, 0.999 mmol), and CsCl (150 mg, 0.891 mmol) that acted as a reactant as well as a molten flux. The chemical manipulations of all the reactants were carried out inside the argon-filled glove box. The reaction mixture was taken in a 6 mm (outer diameter) carbon-coated fused silica tube having a length of around 155 mm. The loaded tube was connected to a vacuum line and evacuated (ca. 10⁻⁴ Torr) before sealing the tube using a flame torch with a gas mixture of oxygen (oxidizer) and liquefied petroleum gas (fuel). The sealed tube was kept vertically inside a programmable muffle furnace for the heat treatment, where it was first heated to 1223 K in 48 h, and the temperature was held constant at 1223 K for 96 h. The temperature of the furnace was then gradually cooled down to 1023 K with a rate of 4 K/h and annealed at this temperature for 96 h, followed by slow cooling to 673 K at a rate of 5 K/h. Finally, the reaction mixture was radiatively cooled down to room temperature by switching off the furnace. The reaction product was opened under ambient conditions and analyzed under an optical microscope. A black lump consisting of plate-type crystals (Fig. 1d) was found as the major product of the reaction, along with the white sticky powder. These black plate-shaped crystals were carefully picked and affixed to a stub on a carbon tape for elemental analysis using energy dispersive X-ray spectroscopic (EDS) studies. An octane elite (EDAX Inc., USA) spectrometer that was attached to the field-emission scanning electron microscope (FE-SEM) (Make: JEOL, Japan; Model: JSM 7800F) was used for the elemental study. The EDS data were collected with an accelerating voltage of 15–20 kV. The EDS analysis of these crystals was performed by choosing multiple random points on the various selected crystals. The approximate ratio of ≈1:3:5 of the black crystals was found for the elements Cs, Sc, and Te (Fig. 1d) that corresponds to the CsSc₅Te₈ composition. An EDS spectrum collected on a typical crystal of CsSc₅Te₈ is shown in Fig. 1d. The results of the elemental mapping of this crystal are also presented in Fig. 1a–c that shows the homogenous distribution of Cs, Sc, and Te elements in the crystal.

2.1.2. Synthesis of single crystals of Cs_{0.6(1)}Ti₆Se₈

Black plate-shaped crystals of Cs_{0.6(1)}Ti₆Se₈ were first obtained during the exploration of the ternary Cs–Ti–Se system using a solid-state reaction that was loaded with Ti (8.0 mg, 0.1671 mmol), Se (39.7 mg, 0.503 mmol), and CsCl (70 mg, 0.416 mmol) inside an argon-filled glove box into a carbon-coated 6 mm fused silica tube. The tube was subsequently sealed by a flame torch (ca. 10⁻⁴ Torr) and placed inside a cylindrical alumina crucible to keep it in the vertical position. The alumina cylinder containing the tube was placed inside a programmable chamber furnace for heat treatment. The temperature of the furnace was firstly ramped to 1223 K (in 30 h), and the temperature was held constant for 146 h. In the second step, the temperature was allowed to cool down very slowly at a rate of 2.3 K/h to reach 873 K and annealed for 96 h. After that, the reaction temperature again cooled to 573 K at a rate of 6.25 K/h, and finally, the furnace was turned off. The reaction product contained black needle-shaped crystals. The energy dispersive spectroscopic study revealed that the average composition of the black crystals is close to Cs_{0.6}Ti₆Se₈.

2.2. Single-crystal X-ray diffraction studies of CsSc₅Te₈ and Cs_{0.6(1)}Ti₆Se₈

Single-crystal X-ray diffraction data set of a plate-shaped crystal of CsSc₅Te₈ was collected at 298(2) K on a Bruker D8 Quest diffractometer equipped with a Photon 100 CMOS area detector and an INCOATEC microfocus X-ray radiation source for graphite monochromated Mo-*K* α radiation ($\lambda = 0.71073$ Å). APEX3 software package was used for the intensity data acquisition, data reduction, and cell refinement [29]. A suitable sized single crystal of CsSc₅Te₈ was picked at the tip of a glass

Table 1

Crystallographic data and structure refinement details for CsSc₅Te₈ and Cs_{0.6(1)}Ti₆Se₈.

Compound	CsSc ₅ Te ₈	Cs _{0.6(1)} Ti ₆ Se ₈
Space group	<i>C</i> _{2h} – <i>C2/m</i>	<i>C</i> _{6h} – <i>P6₃/m</i>
<i>a</i> (Å)	21.3376(15)	9.9520(1)
<i>b</i> (Å)	4.1434(3)	9.9520(1)
<i>c</i> (Å)	10.2853(7)	3.5710(1)
β (°)	103.925(2)	90
<i>V</i> (Å ³)	882.60(11)	306.30(1)
<i>Z</i>	2	1
ρ (g cm ⁻³)	5.187	5.415
μ (mm ⁻¹)	16.78	29.20
<i>T</i> (K)	298(2)	100(2)
<i>R</i> (<i>F</i>) ^a	0.027	0.013
<i>R</i> _w (<i>F</i> _o ²) ^b	0.082	0.031

$$\lambda = 0.71073 \text{ Å}$$

$$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ for } F_o^2 > 2\sigma(F_o^2).$$

$$^b R_w(F_o^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{1/2}. \text{ For } F_o^2 < 0, w = 1/[\sigma^2(F_o^2) + (rP)^2 + mP], \text{ where } P = (F_o^2 + 2F_c^2)/3. \text{ The values of } r \text{ are } 0.050 \text{ and } 0.0168, \text{ respectively for CsSc}_5\text{Te}_8 \text{ and Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8 \text{ while the values of } m \text{ are } 1.1464 \text{ and } 0.2434, \text{ respectively for CsSc}_5\text{Te}_8 \text{ and Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8.$$

Table 2

Selected interatomic lengths (Å) for CsSc₅Te₈ and Cs_{0.6(1)}Ti₆Se₈.

CsSc ₅ Te ₈	Distances (Å)	Cs _{0.6(1)} Ti ₆ Se ₈	Distances (Å)
Sc1–Te2	2.8529(8) × 1	Ti1–Se1	2.5565(3) × 2
Sc1–Te2	2.8651(5) × 2	Ti1–Se1	2.5617(4) × 1
Sc1–Te4	2.9442(8) × 1	Ti1–Se1	2.6559(4) × 1
Sc1–Te3	3.0141(6) × 2	Ti1–Se2	2.6060(3) × 2
Sc2–Te1	2.8426(6) × 2	Cs1–Se1	3.3011(2) × 3
Sc2–Te3	2.9373(8) × 1	Cs1–Se1	3.7530(2) × 6
Sc2–Te3	3.0347(7) × 2	Ti1...Ti1	3.2627(6) × 2
Sc2–Te4	2.8944(7) × 1	Cs1...Cs1	3.5711(1)
Sc3–Te1	2.9201(3) × 2		
Sc3–Te4	2.9061(2) × 4		
Cs1–Te1	3.9361(3) × 4		
Cs1–Te2	4.0823(3) × 4		
Cs1–Te4	4.1140(3) × 2		
Sc1...Sc1	3.8989(9)		
Sc1...Sc2	3.6534(12)		
Sc3...Sc2	3.9767(8)		
Cs1...Cs1	4.1434(3)		

fiber under Paratone oil. Single crystal data were collected with a scan width of 0.5° with a scan time of 12 s/frame, and the crystal to detector distance was fixed to 40 mm.

The single-crystal data for CsSc₅Te₈ was first integrated with a primitive triclinic setting. The XPREP program [30] indicated a base centered *C*-cell as per the observed extinction conditions. On account of systematic absences, the XPREP program suggested *C2* (chiral), *C2/m* (centrosymmetric), and *Cm* (non-centrosymmetric) space groups. Centrosymmetric *C2/m* space group was selected based on the intensity of statistics value [$|E^2 - 1| = 1.247$]. The crystal structure of CsSc₅Te₈ was established by the use of the SHELX-14 suite of programs. The crystal structure's atomic positions were successfully located by the direct method using the SHELXS program [31]. The resulting eight atomic positions were then assigned to the respective atoms based on the interatomic distances. The least-square refinement of the structure model was further carried out with the help of the SHELXL program package [32]. The absorption correction was performed by SADABS [33] using the multi-scan method. Anisotropic displacement parameters, extinction corrections, and weight corrections were further performed to finalize the structure model. The atomic positions were standardized using STRUCTURE TIDY [34] of the PLATON program package [35]. ADDSYM [35] program of PLATON [35] did not find any missing symmetry. The Fourier difference map was nearly flat with the highest peak of 1.77 e⁻ Å⁻³ at (0.5786, 0.0000, 0.980), which is present

Table 3Fractional atomic coordinates and U_{eq} values for CsSc₅Te₈ structure.

Atoms	Wyckoff Position	x	y	z	U_{iso}/U_{eq}^a
Cs1	2d	0.000000	0.500000	0.500000	0.03022 (14)
Sc1	4i	0.29484 (4)	0.000000	0.65514 (8)	0.01179 (19)
Sc2	4i	0.34363 (4)	0.000000	0.02084 (9)	0.01149 (19)
Sc3	2a	0.000000	0.000000	0.000000	0.0111(2)
Te1	4i	0.08617 (2)	0.000000	0.81830 (3)	0.01189 (11)
Te2	4i	0.16474 (2)	0.000000	0.49905 (3)	0.01186 (11)
Te3	4i	0.23816 (2)	0.000000	0.15913 (3)	0.01009 (11)
Te4	4i	0.57458 (2)	0.000000	0.16650 (3)	0.01044 (11)

^a U_{iso}/U_{eq} is the one-third value of the trace of orthogonalized U_{ij} tensor.**Table 4**Fractional atomic coordinates and U_{eq} values for Cs_{0.6(1)}Ti₆Se₈ structure.

Atoms	Wyckoff Position	S.O.F.	x	y	z	U_{iso}/U_{eq}^a
Cs1	2a	0.298 (2)	0.000000	0.000000	0.250000	0.0699 (7)
Ti1	6h	1	0.86844 (4)	0.51066 (4)	0.250000	0.00495 (8)
Se1	6h	1	0.69636 (2)	0.64600 (2)	0.250000	0.00499 (6)
Se2	2c	1	0.333333	0.666667	0.250000	0.00409 (8)

^a U_{iso}/U_{eq} is the one-third value of the trace of orthogonalized U_{ij} tensor.

at 0.73 Å away from Te4. The deepest hole of $-1.38 \text{ e}^{-\text{Å}^{-3}}$ was observed at (0.4392, 0.5000, 0.4542), which is situated at 2.38 Å away from Te2. Further crystal structure refinement and structural details are given in Tables 1–3, and in the supporting information (S.I.).

A Bruker APEX2 Kappa diffractometer was employed to collect the single-crystal X-ray diffracted data of Cs_{0.6(1)}Ti₆Se₈ at 100(2) K. Graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ Å}$) was used for the data collection. The data were collected in ω and ϕ scans with a scan width of 0.3° , and the exposure time was 15 s/frame. During the experiment, the detector to crystal distance was 50 mm. APEX2 program [36] was used for data integration, reduction, and for cell refinement. Face indexed absorption correction was carried out using SADABS software [33]. The mean value $|E^2 - 1| = 0.860$ suggested a centrosymmetric space group. Based on the systemic absences, XPREP offered a total of thirteen space groups: three centrosymmetric ($P\bar{3}$, $P6/m$ and $P6_3/m$), one non-centrosymmetric $P(\bar{6})$, and nine chiral ($P3$, $P3_1$, $P3_2$, $P6$, $P6_3$, $P6_2$, $P6_4$, $P6_1$, and $P6_5$) space groups. The space group $P6_3/m$ with the highest symmetry among the suggested centrosymmetric space groups was used for the structure solution. The structure of Cs_{0.6(1)}Ti₆Se₈ was solved using the direct method with the help of the SHELXS program [31], which proposed four atomic positions as an initial solution. The atomic positions were assigned based on geometrical parameters such as bond distances and angles. The model structure was refined using the least square method with the help of the SHELXL program package [32]. Finally, the occupancy of the Cs1 atom was freely refined, which drastically improve the quality of the solved model. The R1 and wR2 values of 0.104 and 0.396, respectively, were reduced to 0.013 and 0.031 after freely refining the chemical occupancy of Cs1 atoms. The weight correction and anisotropic displacement parameters were further refined. The extinction correction was omitted in the final cycle of refinement as its value was very close to zero. The final refinement gives an occupancy of 0.298(2) for the Cs1 site with a cigar-shaped anisotropic

displacement parameter (ADP). The cigar-shaped ADP of Cs1 indicates that the Cs1 atoms are heavily disordered and behaving like a liquid in the channels. The Fourier difference map was approximately flat with the highest peak of $1.57 \text{ e}^{-\text{Å}^{-3}}$ at (0.0000, 0.0000, 0.0000), which is 0.89 Å away from Cs1. The deepest hole of $-0.81 \text{ e}^{-\text{Å}^{-3}}$ was located at (0.0000, 0.0000, 0.1273), which is 0.44 Å away from Cs1. The STRUCTURE TIDY [34] program of the PLATON [35] program suite was used to standardize the atomic positions. No missing symmetry was suggested by the ADDSYM [35] program of PLATON [35]. Also, the precession images did not show any additional reflections. Further crystal structure refinement and structural details are given in Tables 1, 2 and 4, and in the supporting information (S.I) file.

2.3. Powder X-ray diffraction study (PXRD)

The room temperature PXRD data of a homogenized powdered sample of CsSc₅Te₈ were carried out using a Rigaku Ultima IV diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ Å}$) source D/tex ultra-detector. The operating current and voltage were 40 mA and 40 kV, respectively. The PXRD data of powdered CsSc₅Te₈ was recorded over a 2θ range of 10° – 70° using a θ - 2θ geometry. The Match! version 3 software was used for phase identification.

2.4. Solid-state ultraviolet–visible near-infrared spectroscopy

Finely ground single crystals of CsSc₅Te₈ was used for the optical study at room temperature (298 K) by using the UV–vis–NIR spectrophotometer (JASCO V-770). Dry BaSO₄ was used as a standard reference for the data collection. The reflectance data as a function of wavelength were recorded over the wavelength region of 2000 nm (0.62 eV) to 200 nm (6.2 eV). The Kubelka-Munk equation [37] was used to convert reflectance data to absorption data.

$$\alpha/S = (1 - R)^2/2R$$

Here the symbols α , S , and R represent the absorption coefficient, scattering coefficient, and reflectance, respectively. The bandgap of CsSc₅Te₈ was estimated using the familiar Tauc plot:

$$(ah\nu)^n = A(h\nu - E_g)$$

Here, the symbols α , h , ν , A , and E_g are the absorption coefficient, Planck's constant, frequency of light, proportionality constant, and bandgap, respectively. The value of constant n decides the nature of the bandgap. The $n = 2$ value indicates a direct bandgap.

2.5. Computational methodology

The density functional theoretical (DFT) [38] calculations are performed using the plane-wave basis set formalism as implemented in the VASP package [39]. The interactions between the core and valence electrons are approximated using the projected augmented wave (PAW) method [40]. A plane-wave basis set with a kinetic energy cutoff of 300 eV (or higher) is used to expand the Kohn–Sham single-particle orbitals. The exchange-correlation (XC) interactions are described using (a) strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation (meta-GGA) [41], (b) modified Becke–Johnson (mBJ) [42] meta-GGA approximation, and (3) Perdew–Burke–Ernzerhoff (PBE) of generalized gradient approximation (GGA) [43]. The integrations in the reciprocal space are performed by sampling the Brillouin zone using $3 \times 15 \times 6$ Monkhorst-Pack k -point mesh. The lattice constants and the atomic positions in the unit cell are relaxed until the force on each atom is reduced to less than 0.01 eV/Å. Self-consistency in calculations is achieved by allowing the total energies to converge up to 10^{-7} eV/cell.

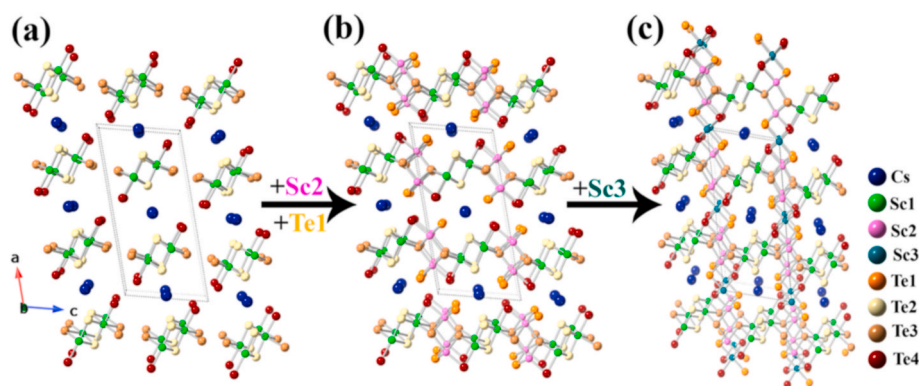


Fig. 2. Fragments of the CsSc_5Te_8 structure based on (a) $\frac{1}{\infty} [\text{Sc}(1)\text{Te}_3]^{3-}$, (b) $\frac{2}{\infty} [\text{Sc}(1)\text{Sc}(2)\text{Te}_4]^{2-}$, and (c) $\frac{3}{\infty} [\text{Sc}(1)_2\text{Sc}(2)_2\text{Sc}(3)\text{Te}_8]^{3-}$ substructures.

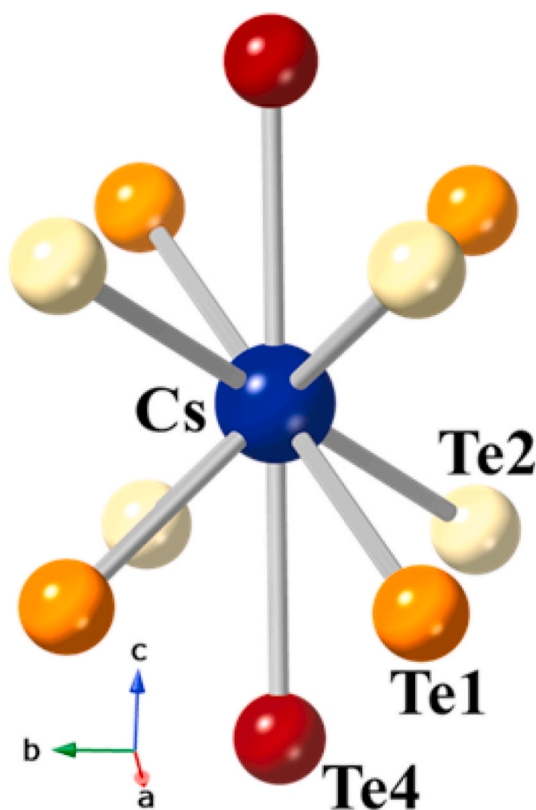


Fig. 3. The local coordination environment of Cs atom in CsSc_5Te_8 structure.

3. Results and discussion

3.1. Syntheses and crystal structures

Black color crystals of CsSc_5Te_8 and $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ were successfully synthesized by the molten flux method. An overnight dried CsCl powder was employed as a reactive molten flux in both the reactions at 1223 K. The crystals of CsSc_5Te_8 were air-stable for almost one week as analyzed by the unit cell determinations of single crystals. A black lump of CsSc_5Te_8 was ground and used for the PXRD analysis. The PXRD pattern shows the presence of a single phase of CsSc_5Te_8 . Some of the reflections' intensities did not match the calculated pattern due to the powder's preferred orientation (Fig. 1e). Attempts to synthesize monophasic polycrystalline sample of $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ were failed, and as a result physical properties of this compound could not be studied.

Crystal structure description of CsSc_5Te_8 . This new chalcogenide phase is the first ternary compound of the Cs–Sc–Te system. It crystallizes in

the monoclinic $C2/m$ space group with cell constants of $a = 21.3376(15)$ Å, $b = 4.1434(3)$ Å, $c = 10.2853(7)$ Å, and $\beta = 103.925(2)^\circ$ with two formula units per cell ($Z = 2$). The compound CsSc_5Te_8 is isostructural to TiV_5S_8 [3]. There are eight crystallographically independent sites in an asymmetric unit of the structure. These atomic positions are Cs1 (site symmetry: $2/m$), Sc1 (m), Sc2 (m), Sc3 ($2/m$), Te1 (m), Te2 (m), Te3 (m), and Te4 (m). The structure can be described as a three-dimensional anionic framework of $\frac{3}{\infty} [\text{Sc}_5\text{Te}_8]^{1-}$ units. There are one-dimensional tunnels in between the $\frac{3}{\infty} [\text{Sc}_5\text{Te}_8]^{1-}$ framework approximately along the [010] direction, where the Cs^+ cations are residing (Fig. 2c). Each of the Cs atoms is connected to ten Te atoms, forming a trans-face bicapped cubic CsTe_{10} unit (Fig. 3).

We next present a detailed description of the formation of the three-dimensional anionic framework of this structure. All Sc atoms of this structure are forming distorted octahedral ScTe_6 units by coordinating with six Te atoms. Thus, the basic building block of this structure is the ScTe_6 octahedron. Each Sc(1) atom is bonded to one Te4, two Te3, and three Te2 atoms. The Sc(1) Te_6 octahedron is connected to four nearest Sc(1) Te_6 octahedra via edge-sharing, thus forming double infinite chains of $\frac{1}{\infty} [\text{Sc}(1)\text{Te}_3]^{3-}$ if one ignores other atoms of the structure.

These $\frac{1}{\infty} [\text{Sc}(1)\text{Te}_3]^{3-}$ chains are running along the b -axis as shown in Fig. 2a. Similarly, Sc(2) Te_6 octahedra are also forming double chains $\frac{1}{\infty} [\text{Sc}(2)\text{Te}_3]^{3-}$ that are extended in the b -direction via edge-sharing with the nearest neighboring Sc(2) Te_6 octahedra. Each Sc(2) atom is connected to one Te4, two Te1, and three Te3 atoms. The Sc(2) and Te1 atoms act as a link between two $[\text{Sc}(1)\text{Te}_3]^{3-}$ chains to form infinite layers of $\frac{2}{\infty} [\text{Sc}(1)\text{Sc}(2)\text{Te}_4]^{2-}$ which are stacked along the c -axis (Fig. 2b). Interestingly, the Sc(1) Te_6 and Sc(2) Te_6 octahedra are connected by face-sharing ($2 \times \text{Te}_3$ and $1 \times \text{Te}_4$), which is relatively uncommon. The face-sharing of $M\text{Q}_6$ octahedra ($M = \text{metal}$) is rare in metal chalcogenides because this type of sharing is less stable than the edge- and vertex-sharing. Due to the face-sharing, the Sc(1) and Sc(2) atoms are closer (3.6531 Å) to each other as compared to homoatomic distances between other Sc atoms. There are only two compounds known among Sc-based chalcogenides that show face-sharing between Sc-octahedra: RbSc_5Te_8 [6] and Ba_3ScTe_5 [44] structures.

Finally, the Sc(3) atoms fill the empty octahedral holes, thus connecting the $\frac{2}{\infty} [\text{Sc}(1)\text{Sc}(2)\text{Te}_4]^{2-}$ layers to form a three-dimensional network of $\frac{3}{\infty} [\text{Sc}(1)_2\text{Sc}(2)_2\text{Sc}(3)\text{Te}_8]^{3-}$, which can also be written as $\frac{3}{\infty} [\text{Sc}_5\text{Te}_8]^{1-}$. The Sc(3) atoms are bonded to four Te4 and two Te1 atoms. Each Sc(3)-based octahedron is surrounded by two Sc(3) Te_6 and four Sc(2) Te_6 octahedra via sharing of six edges. The Sc–Te bond distances in this structure range from 2.8426(6) Å to 3.0347(7) Å, which are in good agreement with the previously reported Sc^{3+} –Te bond distances in RbSc_5Te_8 (2.843(1)–3.034(1) Å) [6], BaSc_2Te_4 (2.878(2)–

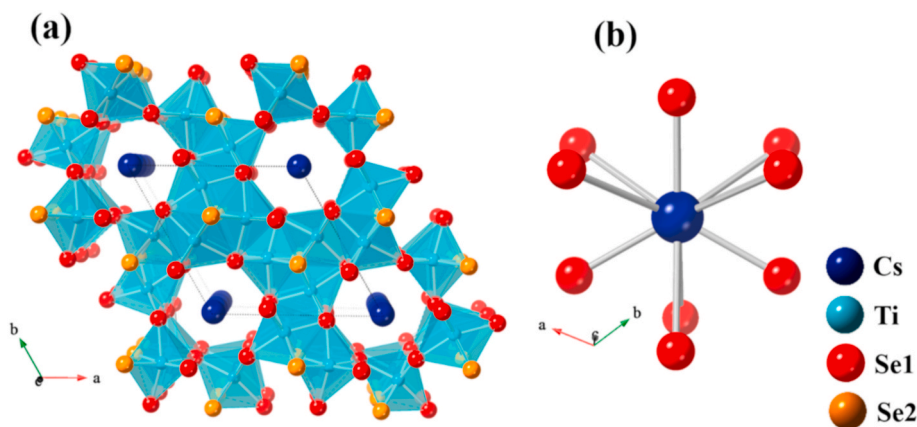


Fig. 4. (a) A polyhedral view of the unit cell of $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$, and (b) local coordination environment around Cs atom in $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$.

2.990(2) Å [45], SrSc_2Te_4 (2.891(2)–2.976(2) Å [45], TiScTe_2 (2.9341(6) Å [46], and Ba_3ScTe_5 (2.9568(7) Å [44]. The Cs–Te bond distances range from 3.9361(3) to 4.1140(3) Å are comparable with the bond distances found in CsTi_5Te_8 (3.7911(5)–3.9942(6) Å [7], $\text{Cs}_2\text{Mn}_3\text{Te}_4$ (3.8865(10)–3.9471(10) Å [47], and CsInTe_2 (3.787(2)–4.442(2) Å [48].

Crystal structure description of $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$. Its crystal structure is isotopic to the Nb_3Te_4 structure [27]. The crystal structure of $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ has been solved in the $C_{6h}^2-P6_3/m$ space group of the hexagonal crystal system having cell dimensions of $a = b = 9.9520(1)$ Å and $c = 3.5710(1)$ Å ($Z = 1$). There are four independent crystallographic sites in the asymmetric unit of $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ structure: Cs1 ($\bar{6}..$), Ti1 ($m..$), Se1 ($m..$), and Se2 ($\bar{6}..$). The Cs site's occupancy refinement in this structure reveals that it is partially filled ($\sim 30\%$). The structure of $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ could be described as a three-dimensional framework of $[\text{Ti}_6\text{Se}_8]^{0.6-}$ that is built up of face-, edge-, and vertex-sharing Ti-centered $[\text{TiSe}_6]$ distorted octahedra (Fig. 4a). Each Ti atom is bonded to four Se1 atoms and two Se2 atoms. The Ti–Se bond distances in $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ range from 2.5565(3) to 2.6559(4) Å, which are in good agreement with the previously reported compounds such as $\text{Ti}_{0.8}\text{Ti}_6\text{Se}_8$ (2.562(1)–2.661(3) Å [12] and $\text{Na}_2\text{Ti}_2\text{Se}_8$ (2.383(4) to 2.822(4) Å [49]. The Cs–Se bond distances observed in $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ structure can be compared with the $\text{Cs}_2\text{GdP}_2\text{Se}_7$ (3.559(2)–3.982(2) Å [50] and $\text{Cs}_2\text{Mo}_{12}\text{Se}_{14}$ (3.597(1)–3.791(1) Å [51].

The sharing of the TiSe_6 octahedra in this structure creates large one-dimensional hexagonal tunnels approximately along the c -direction, as shown in Fig. 4a. These tunnels accommodate Cs^+ cations that balance the electrical charge of the anionic $[\text{Ti}_6\text{Se}_8]^{0.6-}$ framework. Each of the cesium atoms is coordinated to nine selenium atoms forming a distorted tri-capped trigonal prism-like geometry (Fig. 4b). Interestingly, the Cs^+ cations in these large tunnels are disordered and behave like a liquid, as

evident from its elongated cigar-shaped anisotropic displacement parameter [$U_{33} = 0.198(2)$ at 100 K]. The similar higher anisotropic parameter values of alkali metals were also observed for compounds like $\text{K}_{0.52}\text{Ti}_6\text{Se}_8$ ($U_{33} = 0.12(3)$ at 100 K and $U_{33} = 0.41(9)$ at 293 K for K^+) [52,53] and $\text{Ti}_{0.7}\text{Nb}_6\text{Se}_8$ ($U_{33} = 0.51(9)$ for Ti^+ cations at 298 K) [54] structures.

3.2. Assignment of formal oxidation states in CsSc_5Te_8 and $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$

There is no homo-atomic bonding in the crystal structures of CsSc_5Te_8 and $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$. The charge balancing of the CsSc_5Te_8 compound is straightforward, as per the Zintl formalism [55]. The charge-balanced formula of CsSc_5Te_8 can be written as $[\text{Cs}^+(\text{Sc}^{3+})_5(\text{Te}^{2-})_8]$. However, the assignment of formal oxidation states of atoms in $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ is difficult due to occupational disorder of Cs sites in $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ and mixed valency of titanium atoms. The oxidation state of Cs and Se atoms can be assigned as +1 and –2, leaving an average charge of +2.57 on each Ti atom. The magnetic properties of $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ are expected to be interesting due to the mixed valency of Ti. Regrettably, this compound could not be obtained as a single phase for the physical property measurement.

3.3. Optical bandgap study of CsSc_5Te_8

A UV–vis–NIR spectrophotometer was used for the optical bandgap study on the ground single crystals of CsSc_5Te_8 at room temperature. The phase purity of this powder was established using the PXRD study (Fig. 1e). For the estimation of the direct bandgap, the Tauc plot was plotted, which exhibited the direct bandgap of 1.2(1) eV. The absorption spectra show the optical bandgap of 0.6(2) eV. The bandgap is consistent with the black color of CsSc_5Te_8 crystals and suggests that it is a

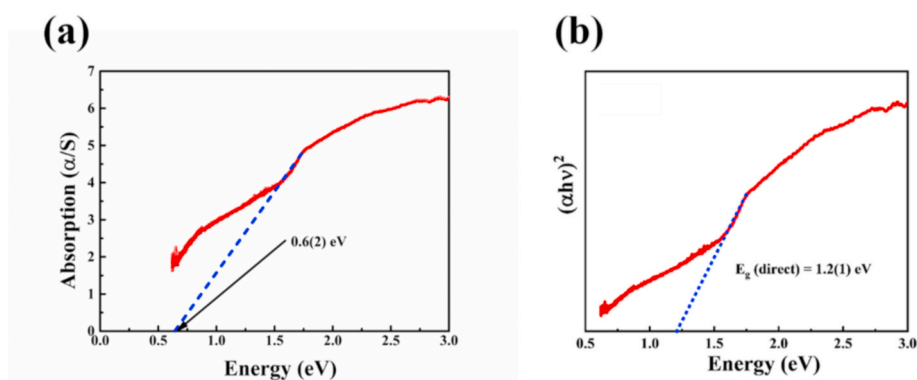


Fig. 5. (a) Optical absorption spectrum and (b) direct bandgap plot of CsSc_5Te_8 .

Table 5Computed lattices parameters, volume, and bandgap of CsSc₅Te₈.

		$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	β	$Vol.(\text{\AA}^3)$	E_g (eV)
Cal.	SCAN	21.516	4.170	10.383	103.993 ⁰	904.01	0.95
	PBE	21.530	4.179	10.404	104.00 ⁰	908.44	0.54
	mBJ	—	—	—	—	—	1.27
Exp.		21.3376	4.1434	10.2853	103.925 ⁰	882.60	1.2

Table 6The computed (SCAN meta-GGA) fractional atomic coordinates in CsSc₅Te₈ unit cell.

Site		x	y	z
Cs1	cal.	0.00000	0.50000	0.50000
	(exp.)	(0.00000)	(0.50000)	(0.50000)
Sc1	cal.	0.29442	0.00000	0.65540
	(exp.)	(0.29484)	(0.00000)	(0.65514)
Sc2	cal.	0.34403	0.00000	0.01812
	(exp.)	(0.34363)	(0.00000)	(0.02084)
Sc3	cal.	0.00000	0.00000	0.00000
	(exp.)	(0.00000)	(0.00000)	(0.00000)
Te1	cal.	0.08629	0.00000	0.82136
	(exp.)	(0.08617)	(0.00000)	(0.81830)
Te2	cal.	0.16522	0.00000	0.49692
	(exp.)	(0.16474)	(0.00000)	(0.49905)
Te3	cal.	0.23868	0.00000	0.15947
	(exp.)	(0.23816)	(0.00000)	(0.15913)
Te4	cal.	0.57469	0.00000	0.16650
	(exp.)	(0.57458)	(0.00000)	(0.16650)

semiconductor. An absorption spectrum and direct bandgap plot of CsSc₅Te₈ are depicted in Fig. 5.

3.4. Electronic structure of CsSc₅Te₈

Next, we discuss the results of the first-principles study of the crystal and electronic structure of CsSc₅Te₈. The lattice parameters and the bandgap computed using SCAN (meta-GGA), mBJ (meta-GGA), and PBE (GGA) schemes are shown in Table 5. The computed (SCAN) fractional atomic coordinates are given in Table 6.

As evident, the theoretical estimates of the lattice constants and

fractional atomic coordinates are in good agreement (~1%) with the experiments. The theoretical results are found to be in much better agreement with the experiments when computed using the SCAN meta-GGA scheme as compared to those computed using other schemes such as PBE-GGA, LDA, etc. The SCAN approximation is indeed expected to be superior as compared to other XC approximations since it is known to fulfill all known constraints that the exact density functional must fulfill [56]. The bandgap of CsSc₅Te₈ is found to be 0.95 eV, 0.54 eV, and 1.27 eV when computed using SCAN, PBE, and mBJ approximations. As can be seen, the SCAN and PBE computed bandgaps are underestimated as compared to the experimental value of ~1.2 eV. On the other hand, the mBJ computed bandgap is found marginally overestimated as compared to the experimental value. The mBJ potentials are expected to provide a better estimate of the bandgap as they approximate the atomic exact-exchange potentials locally in addition to a screening term. In the case of PBE (GGA) approximation, the computed bandgap is expected to be underestimated by at least ~50%.

The total and projected density of electronic states (DOS) of CsSc₅Te₈ are shown in Fig. 6a-d. The band structure along the high symmetry directions in the Brillouin zone is shown in Fig. 6e. The valence band (VB) extends from ~ -5.0 eV to 0 eV and is formed due to the hybridization between Te-5p and Sc-3d states. The band in the energy range -9.0 to -9.6 eV is primarily derived from Cs-5s states. The contribution to the valence band in the energy range -11.5 eV to -10.5 eV comes primarily from Te-5s states. Further, the conduction band (CB) is contributed primarily by Sc-3d states. Fig. 6e shows that the bandgap is direct with valence band maximum (VBM) and conduction band minimum (CBM) occurring at the Γ -point.

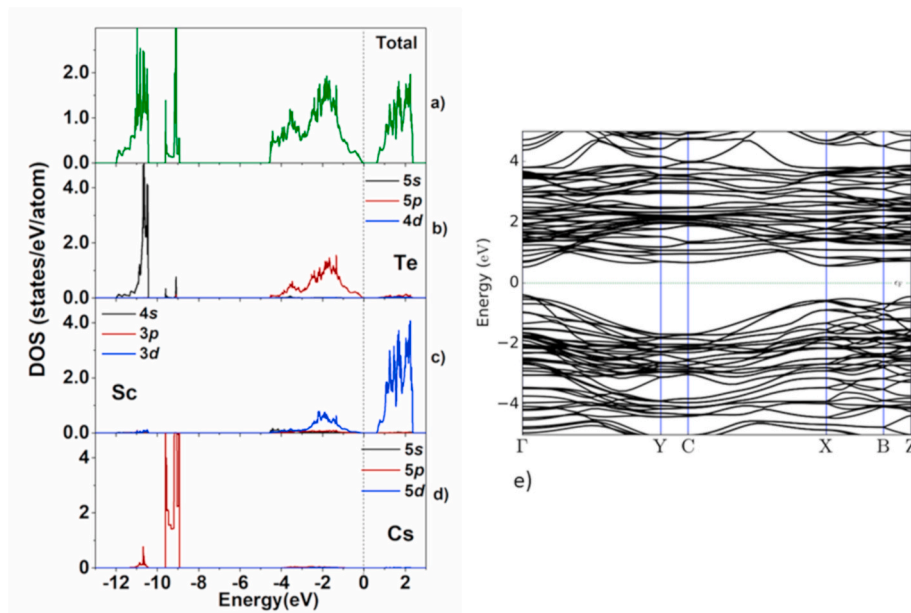


Fig. 6. (a) The total density of states of CsSc₅Te₈ (b) The partial density of states (PDOS) projected onto orbitals of Te atom, (c) Sc atom, and (d) Cs atom. The valence band maximum is indicated by the dotted line. (e) Band structure along the high symmetry.

4. Conclusions

We have successfully synthesized black plate-shaped single crystals of CsSc_5Te_8 and $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ at 1223 K by the solid-state method using sealed fused silica tubes as reaction vessels and CsCl as a reactive flux. Crystal structures of both the compounds were solved using the single-crystal X-ray diffraction technique, which showed CsSc_5Te_8 and $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ crystallize in the monoclinic and hexagonal space groups C_{2h}^3-C2/m and $C_{6h}^2-P6_3/m$, respectively. The asymmetric unit of CsSc_5Te_8 consist of eight crystallographically independent atomic sites: Cs1 (site symmetry: $2/m$), Sc1 (m), Sc2 (m), Sc3 ($2/m$), Te1 (m), Te2 (m), Te3 (m), and Te4 (m). While there are four crystallographically independent sites in the asymmetric unit of $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$: Cs1 ($\bar{6}$.), Ti1 (m .), Se1 (m .), and Se2 ($\bar{6}$.). The crystal structures of CsSc_5Te_8 and $\text{Cs}_{0.6(1)}\text{Ti}_6\text{Se}_8$ feature a three-dimensional anionic framework of ${}^\infty[\text{Sc}_5\text{Te}_8]^{1-}$ and ${}^\infty[\text{Ti}_6\text{Se}_8]^{0.6-}$, respectively, which are made up of distorted transition metal based octahedra. The sharing of these metal octahedra results in the formation of one-dimensional tunnels that are filled with the Cs^+ cations. Room temperature UV–vis–NIR absorption study on powdered single crystals of CsSc_5Te_8 confirms semiconducting nature with a direct bandgap of 1.2(1) eV, which augurs well with the black color of the compound. The DFT study of CsSc_5Te_8 shows that the valence band (VB) is formed due to the hybridization between $\text{Te-}5p$ and $\text{Sc-}3d$ states, and the value of the theoretical bandgap is in good agreement with the experimental value.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solidstatesciences.2021.106577>.

Author statement

This manuscript was written by the contribution of all authors. M. Ishtiyak and S. Jana carried out syntheses and crystal structure determination studies. G. Panigrahi studied the optical absorption and PXRD patterns. A. K. Srivastava collected the single-crystal data. S. Narayanswami and P. P. Bhattacharjee carried out elemental analysis using the EDS study. M. K. Nirajan calculated and studied the electronic structure using the DFT method. J. Prakash conceived the idea for this work and supervised the findings of this work, discussed the results, and commented on the manuscript.

References

- [1] M. Watanabe, Y. Fujiki, Y. Kanazawa, K. Tsukimura, The effects of cation substitution on the hollandite-type structure, *J. Solid State Chem.* 66 (1987) 56–63, [https://doi.org/10.1016/0022-4596\(87\)90220-9](https://doi.org/10.1016/0022-4596(87)90220-9).
- [2] A.D. Wadsley, The crystal structure of psilomelane, $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$, *Acta Crystallogr.* 6 (1953) 433–438, <https://doi.org/10.1107/S0365110X53001277>.
- [3] L. Fournès, M. Vlasse, M. Saux, Preparation, properties and crystal structure of TlV_5S_8 , *Mater. Res. Bull.* 12 (1977) 1–5, [https://doi.org/10.1016/0025-5408\(77\)90081-2](https://doi.org/10.1016/0025-5408(77)90081-2).
- [4] C. Platte, H. Sabrowsky, TlCr_3S_5 , das erste Thiochromat(III) mit Wabenstruktur, *Naturwissenschaften* 60 (1973) 474–475, <https://doi.org/10.1007/BF00592860>.
- [5] O. Tamada, N. Yamamoto, T. Mori, T. Endo, The crystal structure of $\text{K}_2\text{Cr}_6\text{O}_{16}$: the hollandite-type full cationic occupation in a tunnel, *J. Solid State Chem.* 126 (1996) 1–6, <https://doi.org/10.1006/jssc.1996.0301>.
- [6] J.-M. Babo, T. Schleid, Synthesis and crystal structure of the rubidium scandium telluride RbSc_5Te_8 , *Z. Anorg. Allg. Chem.* 634 (2008) 1463–1465, <https://doi.org/10.1002/zaac.200800048>.
- [7] D.L. Gray, J.A. Ibers, Synthesis and structure of CsTi_5Te_8 : relation to the TlV_5S_8 , TlCr_3S_5 , and similar channel structures, *J. Alloys Compd.* 440 (2007) 74–77, <https://doi.org/10.1016/j.jallcom.2006.09.022>.
- [8] K. Klepp, H. Boller, Channel structures based on octahedral frameworks: the crystal structure of TiTi_5Se_8 , TlV_5Se_8 , and TlCr_5Se_8 and its relationships to TlCr_3S_5 , hollandites, and psilomelane, *J. Solid State Chem.* 48 (1983) 388–395, [https://doi.org/10.1016/0022-4596\(83\)90096-8](https://doi.org/10.1016/0022-4596(83)90096-8).
- [9] T. Novet, M. Wagner, M. Jiang, D.C. Johnson, The preparation and properties of $\text{M}'\text{M}_5\text{X}_8$ ($\text{X} = \text{Se}, \text{Te}; \text{M} = \text{Cr}, \text{Ti}; \text{M}' = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Cd}, \text{Sn}, \text{Pb}$) via low temperature ion exchange reaction, *Mater. Res. Bull.* 30 (1995) 65–73, [https://doi.org/10.1016/0025-5408\(94\)00117-0](https://doi.org/10.1016/0025-5408(94)00117-0).
- [10] T. Ohtani, Y. Sano, K. Kodama, S. Onoue, H. Nishihara, Synthesis of new ternary tunnel chalcogenides by ion exchange reactions and deintercalation of the ternary chromium selenides, *Mater. Res. Bull.* 28 (1993) 501–508, [https://doi.org/10.1016/0025-5408\(93\)90133-X](https://doi.org/10.1016/0025-5408(93)90133-X).
- [11] T. Ohtani, S. Onoue, Preparation and magnetic properties of the new ternary chalcogenides isotypic with TlV_5S_8 and TlV_6S_8 , *Mater. Res. Bull.* 21 (1986) 69–76, [https://doi.org/10.1016/0025-5408\(86\)90031-0](https://doi.org/10.1016/0025-5408(86)90031-0).
- [12] W. Bensch, J. Koy, The single crystal structure of nonstoichiometric thallium hexatitanium octaselenide determined at different temperatures, *Mater. Res. Bull.* 27 (1992) 731–740, [https://doi.org/10.1016/0025-5408\(92\)90081-A](https://doi.org/10.1016/0025-5408(92)90081-A).
- [13] N.-H. Dung, V.-V. Tien, H.J. Behm, P.T. Beurskens, Superstructure with pseudo translation. II. Monopotassium pentachromium octaselenide: a tunnel structure, *Acta Crystallogr. C* 43 (1987) 2258–2260, <https://doi.org/10.1107/S0108270187088164>.
- [14] W. Sinclair, G.M. McLaughlin, A.E. Ringwood, The structure and chemistry of a barium titanate hollandite-type phase, *Acta Crystallogr. B* 36 (1980) 2913–2918, <https://doi.org/10.1107/S0567740880010515>.
- [15] A.E. Ringwood, S.E. Kesson, N.G. Ware, W. Hiberson, A. Major, Immobilisation of high level nuclear reactor wastes in SYNROC, *Nature* 278 (1979) 219–223, <https://doi.org/10.1038/278219a0>.
- [16] H.U. Beyeler, Cationic short-range order in the hollandite $\text{K}_{1.54}\text{Mg}_{0.77}\text{Tl}_{7.23}\text{O}_{16}$: evidence for the importance of ion-ion interactions in superionic conductors, *Phys. Rev. Lett.* 37 (1976) 1557–1560, <https://doi.org/10.1103/PhysRevLett.37.1557>.
- [17] S. Maier, R. Lefèvre, X. Lin, R. Nunna, D. Berthebaud, S. Hébert, A. Mar, F. Gascoin, The solid solution series $\text{Ti}_{(1-x)}\text{Cr}_x\text{Se}_8$: crystal structure, magnetic and thermoelectric properties, *J. Mater. Chem. C* 3 (2015) 10509–10517, <https://doi.org/10.1039/C5TC01766A>.
- [18] W. Bensch, J. Abart, E. Amberger, Magnetic properties in the series $\text{Ti}_x\text{V}_{6-y}\text{M}_y\text{S}_8$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}; 0 \leq y \leq 1$), *Solid State Commun.* 58 (1986) 631–635, [https://doi.org/10.1016/0038-1098\(86\)90235-8](https://doi.org/10.1016/0038-1098(86)90235-8).
- [19] W. Bensch, C. Näther, O. Helmer, C. Ritter, The magnetic structures of $\text{Ti}_x\text{Cr}_y\text{Se}_8$ ($x=1$ and 0.2) as determined by neutron scattering, *J. Alloys Compd.* 290 (1999) 41–51, [https://doi.org/10.1016/S0925-8388\(99\)00212-1](https://doi.org/10.1016/S0925-8388(99)00212-1).
- [20] P. Moetakef, L. Wang, A.E. Maughan, K.J. Gaskell, A.M. Larson, B.C. Hodges, E. Rodriguez, Tuning the electronic band structure of microporous titanates with the hollandite structure, *J. Mater. Chem. A* 3 (2015) 20330–20337, <https://doi.org/10.1039/C5TA05288B>.
- [21] H. Takahashi, N. Raghavendra, F. Gascoin, D. Pelloquin, S. Hébert, E. Guilmeau, Transport properties of an intermetallic with pseudo-hollandite structure as a potential thermoelectric material: the example of $\text{Ti}_x\text{Cr}_y\text{Se}_8$, *Chem. Mater.* 25 (2013) 1809–1815, <https://doi.org/10.1021/cm400365q>.
- [22] W. Schramm, R. Schöllhorn, H. Eckert, W. Müller-Warmuth, Nonstoichiometric channel chalcogenides $\text{Ti}_x\text{V}_5\text{S}_8$: topotactic redox reactions and NMR studies, *Mater. Res. Bull.* 18 (1983) 1283–1289, [https://doi.org/10.1016/0025-5408\(83\)90032-6](https://doi.org/10.1016/0025-5408(83)90032-6).
- [23] H. Eckert, W. Müller-Warmuth, W. Schramm, R. Schöllhorn, Nonstoichiometric channel chalcogenides $\text{Ti}_x\text{V}_6\text{S}_8$: topotactic redox reactions and NMR studies, *Solid State Ionics* 13 (1984) 1–6, [https://doi.org/10.1016/0167-2738\(84\)90055-9](https://doi.org/10.1016/0167-2738(84)90055-9).
- [24] W. Bensch, J. Koy, T. Braun, P. Hug, Chemical reactivity of $\text{K}_2\text{Ti}_6\text{Se}_8$ and the crystal structures of $(\text{H}_2\text{O})_{1.5}\text{Ti}_6\text{Se}_8$ and Ti_3Se_4 -channel compounds with the hexagonal Nb_3S_4 structure, *Solid State Ionics* 74 (1994) 141–148, [https://doi.org/10.1016/0167-2738\(94\)90204-6](https://doi.org/10.1016/0167-2738(94)90204-6).
- [25] S.-J. Kim, S.-J. Park, H. Yun, J. Do, Syntheses and crystal structures of new ternary selenides: $\text{Rb}_3\text{Yb}_2\text{Se}_{12}$ and CsEr_3Se_8 , *Inorg. Chem.* 35 (1996) 5283–5289, <https://doi.org/10.1021/ic960227o>.
- [26] O. Tougaï, H. Noël, J.A. Ibers, Serendipitous syntheses of the series $\text{Cs}_3\text{Ln}_7\text{Te}_{12}$ ($\text{Ln} = \text{Sm}, \text{Gd}, \text{Tb}$): compounds with large tunnels, *Solid State Sci.* 3 (2001) 513–518, [https://doi.org/10.1016/S1293-2558\(01\)01162-1](https://doi.org/10.1016/S1293-2558(01)01162-1).
- [27] K. Selte, A. Kjekshus, The crystal structures of Nb_3Se_4 and Nb_3Te_4 , *Acta Crystallogr.* 17 (1964) 1568–1572, <https://doi.org/10.1107/S0365110X64003875>.
- [28] A. Belsky, M. Hellenbrandt, V.L. Karen, P. Luksch, New developments in the Inorganic Crystal Structure Database (ICSD): accessibility in support of materials

- research and design, *Acta Crystallogr. B* 58 (2002) 364–369, <https://doi.org/10.1107/S0108768102006948>.
- [29] APEX3, Program for Data Collection on Area Detectors, Bruker AXS Inc., Madison, WI, USA, 2016.
- [30] G.M. Sheldrick, XPREP Version 2008/2, Bruker AXS Inc., Madison, 2008.
- [31] G.M. Sheldrick, A short history of *SHELX*, *Acta Crystallogr. A* 64 (2008) 112–122, <https://doi.org/10.1107/S0108767307043930>.
- [32] G.M. Sheldrick, Crystal structure refinement with *SHELXL*, *Acta Crystallogr. C* 71 (2015) 3–8, <https://doi.org/10.1107/S2053229614024218>.
- [33] G.M. Sheldrick, SADABS; Department of Structural Chemistry, University of Göttingen: Göttingen, Germany, 2008.
- [34] L.M. Gelato, E. Parthé, *STRUCTURE TIDY* - a computer program to standardize crystal structure data, *J. Appl. Crystallogr.* 20 (1987) 139–143, <https://doi.org/10.1107/S0021889887086965>.
- [35] A.L. Spek, Single-crystal structure validation with the program *PLATON*, *J. Appl. Crystallogr.* 36 (2003) 7–13, <https://doi.org/10.1107/S0021889802022112>.
- [36] Bruker APEX2 Version 2009.5-1 Data Collection and Processing Software, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, 2009.
- [37] G. Kortüm, *Reflectance Spectroscopy*, Springer, New York, 1969.
- [38] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) A1133–A1138, <https://doi.org/10.1103/PhysRev.140.A1133>.
- [39] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 54 (1996) 11169–11186, <https://doi.org/10.1103/PhysRevB.54.11169>.
- [40] P.E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50 (1994) 17953–17979, <https://doi.org/10.1103/PhysRevB.50.17953>.
- [41] J. Sun, A. Ruzsinszky, J.P. Perdew, Strongly constrained and appropriately normed semilocal density functional, *Phys. Rev. Lett.* 115 (2015), 036402, <https://doi.org/10.1103/PhysRevLett.115.036402>.
- [42] F. Tran, P. Blaha, Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential, *Phys. Rev. Lett.* 102 (2009) 226401, <https://doi.org/10.1103/PhysRevLett.102.226401>.
- [43] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868, <https://doi.org/10.1103/PhysRevLett.77.3865>.
- [44] M. Ishtiyak, G. Panigrahi, S. Jana, J. Prakash, A. Mesbah, C.D. Malliakas, S. Lebegue, J.A. Ibers, Modulated linear tellurium chains in Ba_3ScTe_5 : synthesis, crystal structure, optical and resistivity studies, and electronic structure, *Inorg. Chem.* 59 (2020) 2434–2442, <https://doi.org/10.1021/acs.inorgchem.9b03319>.
- [45] A. Assoud, N. Soheilnia, H. Kleinke, Thermoelectric properties of the new tellurides SrSc_2Te_4 and BaSc_2Te_4 in comparison to BaY_2Te_4 , *Intermetallics* 15 (2007) 371–376, <https://doi.org/10.1016/j.intermet.2006.08.006>.
- [46] C.L. Teske, W. Bensch, S. Mankovsky, H. Ebert, Preparation, crystal structure, physical properties and electronic band structure of TiScQ_2 (Q = S, Se and Te), *Z. Anorg. Allg. Chem.* 634 (2008) 445–451, <https://doi.org/10.1002/zaac.200700440>.
- [47] E.J. Wu, J.A. Ibers, $\text{Cs}_2\text{Mn}_3\text{Te}_4$, *Acta Crystallogr. C* 53 (1997) 993–994, <https://doi.org/10.1107/S010827019700098X>.
- [48] H. Lin, J.-N. Shen, L. Chen, L.-M. Wu, Quaternary supertetrahedra-layered telluride CsMnInTe_3 : why does this type of chalcogenide tilt? *Inorg. Chem.* 52 (2013) 10726–10728, <https://doi.org/10.1021/ic4018618>.
- [49] D. Kang, J.A. Ibers, Synthesis and characterization of sodium titanium selenide, $\text{Na}_2\text{Ti}_2\text{Se}_8$, a new one-dimensional solid-state polyselenide, *Inorg. Chem.* 27 (1988) 549–551, <https://doi.org/10.1021/ic00276a022>.
- [50] K. Chondroudis, M.G. Kanatzidis, New lanthanide selenophosphates. Influence of flux composition on the distribution of $[\text{PSe}_4]^{3-}/[\text{P}_2\text{Se}_6]^{4-}$ units and the stabilization of the low-dimensional compounds $\text{A}_3\text{RE}_2\text{P}_2\text{Se}_8$, and $\text{A}_2(\text{RE})\text{P}_2\text{Se}_7$ (A = Rb, Cs; RE = Ce, Gd), *Inorg. Chem.* 37 (1998) 3792–3797, <https://doi.org/10.1021/ic980025n>.
- [51] P. Gougeon, M. Potel, J. Padiou, M. Sergent, Synthesis, crystal structure and electrical properties of the first compound containing uniquely $\text{Mo}_{12}\text{Se}_{14}$ cluster units: $\text{Cs}_2\text{Mo}_{12}\text{Se}_{14}$, *Mater. Res. Bull.* 22 (1987) 1087–1093, [https://doi.org/10.1016/0025-5408\(87\)90238-8](https://doi.org/10.1016/0025-5408(87)90238-8).
- [52] W. Bensch, J. Koy, Crystal structure of potassium hexatitanium octaselenide, $\text{K}_{0.52}\text{Ti}_6\text{Se}_8$, at 100 K, *Z. Kristallogr. Krist.* 202 (1992) 300–301, <https://doi.org/10.1524/zkri.1992.202.3-4.300>.
- [53] W. Bensch, J. Koy, Crystal structure of potassium hexatitanium octaselenide, $\text{K}_{0.52}\text{Ti}_6\text{Se}_8$, at 293 K, *Z. Kristallogr. Krist.* 202 (1992) 298–299, <https://doi.org/10.1524/zkri.1992.202.3-4.298>.
- [54] H. Boller, K. Klepp, $\text{Ti}_x\text{Ti}_6\text{Se}_8$ and $\text{Ti}_x\text{Nb}_6\text{Se}_8$, two phases with filled up Nb_3Te_4 type of structure showing pronounced cation disorder, *Mater. Res. Bull.* 18 (1983) 437–442, [https://doi.org/10.1016/0025-5408\(83\)90135-6](https://doi.org/10.1016/0025-5408(83)90135-6).
- [55] R. Nesper, The Zintl-Klemm concept – a historical survey, *Z. Anorg. Allg. Chem.* 640 (2014) 2639–2648, <https://doi.org/10.1002/zaac.201400403>.
- [56] J. Sun, R.C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M.L. Klein, J.P. Perdew, Accurate first-principles structures and energies of diversely bonded systems from an efficient density functional, *Nat. Chem.* 8 (2016) 831–836, <https://doi.org/10.1038/nchem.2535>.