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ORIGINAL ARTICLE

Oxovanadium(IV) complexes of bioinorganic and medicinal relevance: Synthesis, characterization and 3D molecular modeling of some oxovanadium(IV) complexes involving O, N-donor environment of salicylaldehyde-based sulfa drug Schiff bases

R.C. Maurya *, J. Chourasia, D. Rajak, B.A. Malik, J.M. Mir, N. Jain, S. Batalia

Coordination and Bioinorganic Chemistry Laboratory, Department of P.G. Studies and Research in Chemistry and Pharmacy, R.D. University, Jabalpur 482 001, India

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O, N-donor sulfa drug based organic matrix;
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3D Molecular modeling

Abstract The present paper reports the synthesis and characterization of some new sulfa drug based Schiff base oxovanadium(IV) complexes of composition, $[VO(sal\text{-}sdz)_2(H_2O)]\cdot H_2O$, $[VO(sal\text{-}sgn)_2(H_2O)]\cdot H_2O$, $[VO(sal\text{-}snm)(H_2O)]\cdot H_2O$, $[VO(sal\text{-}smr)_2(H_2O)]\cdot H_2O$ and $[VO(dadps)(H_2O)]_2\cdot 2H_2O$, where sal-sdzH = N-(salicylidene)sulfadizine, sal-sgnH = N-(salicylidene)sulfaguanidine, sal-snmH = N-(salicylidene)sulfanilamide, sal-smrH = N-(salicylidene)sulfamerizine, sal-dadpsH_2 = N,N′-bis(salicylidene)-4,4′-diaminodiphenylsulfone, respectively. Complexes, (**1**)–(**4**) were prepared by the reaction of $VOSO_4\cdot 5H_2O$ with the Schiff bases in 1:2 metal-ligand ratio while complex (**5**) in 2:2 metal-ligand ratio in DMF-ethanol medium. The compounds so obtained were characterized by different physico-chemical studies, such as, elemental analysis, molar conductance and magnetic measurements, infrared, ESR, thermogravimetric studies, mass and electronic spectral studies. The overall IR studies conclude that the ligand in complex (**1**)–(**4**) behave as monobasic bidentate ON donor, while the ligand in the complex (**5**) behaves as dibasic tetradentate O_2N_2 donor. The 3D-molecular modeling and analysis for bond lengths and bond angles have also been

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* Corresponding author.
E-mail address: rcmaurya1@gmail.com (R.C. Maurya).

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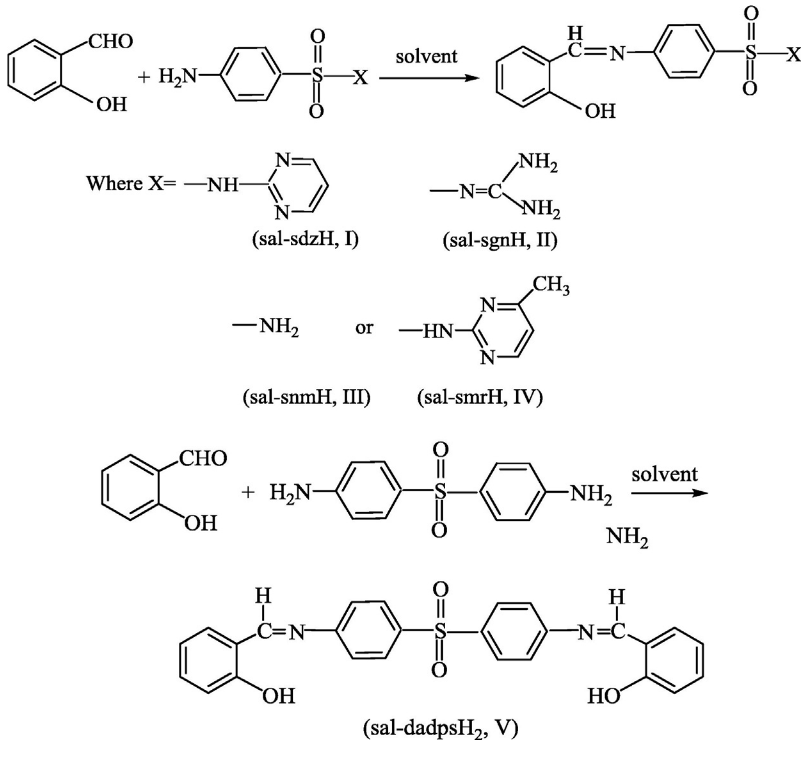
carried out for two representative compounds, [VO(sal-snm)$_2$(H$_2$O)]·H$_2$O (**3**) and [VO(dadps)(H$_2$O)]$_2$·2H$_2$O (**5**) to substantiate the proposed structures. Based on these studies suitable octahedral structures have been proposed for these complexes.

1. Introduction

Sulfa drugs are an important class of therapeutic (Pharmacopoeia of India, 1983) compounds. In combination with certain other drugs, they are used for the treatment of various bacterial infections. Study of the coordination behavior of sulfa drugs is of considerable interest because the coordination of metal ion is reported to enhance the biological activities of organic compounds.

The sulfa drugs, derivatives of a compound *p*-aminobenzenesulfonamide, commonly known as sulfanilamide, were the first effective chemotherapeutic agents to be widely used for the treatment of bacterial infection in humans. They are termed as sulfonamides, due to the presence of sulfonamide (Maurya and Patel, 1999) group (–SO$_2$NH$_2$). The derivatives of sulfonamide exhibit a range of bioactivities, including anti-angiogenic (Funahashi et al., 2002; Semba et al., 2004), anti-tumor (Semba et al., 2004; Sawiński and Gdaniec, 2005), anti-inflammatory and anti-analgesic (Chen et al., 2005), anti-tubercular (Gadad et al., 2004), anti-glaucoma (Agrawal et al., 2004), anti-HIV (Yeung et al., 2005), cytotoxic (Enćio et al., 2005), anti-microbial (Nieta et al., 2005) and anti-malarial (Domínguez et al., 2005) agents. The sulfonamide derivatives are also known to exhibit a wide variety of pharmacological activities (Yoshino et al., 1992; Toth et al., 1997; Medina et al., 1999) through exchanges of different functional groups without modification of the structural –S(O)2N(H)– feature.

There are several reports on the Schiff bases complexes of different metals derived from sulfa drugs (Singh et al., 1999, 2000; Mohamed and Gad-Elkareem, 2007; Sharaby, 2007; Mohamed



Scheme 1 Synthesis of sulfa drug Schiff base ligands.

Table 1 Characterization data of the synthesized Schiff bases.

S. no.	Ligands (empirical formula) (F.W.)	Found/calc. (%)				Color	Decom. temp. (°C)
		C	H	N	S		
I	(sal-sdzH) (C$_{17}$H$_{14}$N$_4$O$_3$S)(354)	57.55 (57.63)	3.79 (3.95)	15.75 (15.82)	8.99 (9.04)	Daffodil	260
II	(sal-sgnH) (C$_{14}$H$_{14}$N$_4$O$_3$S)(318)	52.70 (52.83)	4.29 (4.40)	17.52 (17.61)	9.95 (10.06)	Daffodil	250
III	(sal-snmH) (C$_{13}$H$_{12}$N$_2$O$_3$S)(276)	56.49 (56.52)	4.25 (4.35)	10.05 (10.14)	11.42 (11.59)	Daffodil	210
IV	(sal-smrH) (C$_{18}$H$_{16}$N$_4$O$_3$S)(368)	58.65 (58.70)	4.21 (4.35)	15.12 (15.22)	8.62 (8.70)	Primrose	265
V	(sal-dadpsH$_2$) (C$_{26}$H$_{20}$N$_2$O$_4$S)(456)	68.29 (68.42)	4.30 (4.39)	6.02 (6.14)	6.92 (7.02)	Canary yellow	260

Table 2 Analytical data and some physical properties of the synthesized complexes.

S. no.	Complex (empirical formula) (F.W.)	Analysis, found/calc. (%)					Color	Decom. temp.(°C)	ˆM (ohm^{1}cm^2 mol^{-1})	μ_{eff} (B.M.)
		C	H	N	S	V				
1.	$[VO(sal\text{-}sdz)_2(H_2O)]\cdot H_2O$ $(C_{34}H_{30}N_8O_9S_2V)$(808.94)	50.40 (50.44)	3.67 (3.71)	13.70 (13.85)	7.85 (7.91)	6.21 (6.30)	Green gold	230	14.1	1.71
2.	$[VO(sal\text{-}sgn)_2(H_2O)]\cdot H_2O(C_{28}H_{30}N_8O_9S_2V)$(736.94)	45.40 (45.59)	3.97 (4.07)	15.12 (15.20)	8.56 (8.68)	6.82 (6.91)	Olive green	190	17.4	1.68
3.	$[VO(sal\text{-}snm)_2(H_2O)]\cdot H_2O(C_{26}H_{26}N_4O_9S_2V)$(652.94)	47.70 (47.78)	3.85 (3.98)	8.49 (8.58)	9.75 (9.80)	7.70 (7.80)	Green gold	210	21.2	1.74
4.	$[VO(sal\text{-}smr)_2(H_2O)]\cdot H_2O$ $(C_{36}H_{34}N_8O_9S_2V)$(836.94)	51.50 (51.62)	3.98 (4.06)	13.21 (13.38)	7.58 (7.65)	6.02 (6.09)	Olive green	220	24.3	1.70
5.	$[VO(sal\text{-}dadps)(H_2O)]_2\cdot 2H_2O(C_{52}H_{44}N_4O_{14}S_2V_2)$(1113.88)	55.95 (56.02)	3.90 (3.95)	4.99 (5.03)	5.60 (5.75)	9.08 (9.15)	Green gold	220	20.5	1.61

and Sharaby, 2007; Mohamed et al., 2010; Maurya et al., 1994, 2007, 2010a,b, 2015a,b,c). The pronounced biological activity of the metal complexes of Schiff bases derived from sulfa drugs (Lal and Shukla, 1981; Jain and Chaturvedi, 1977) has led to considerable interest in their coordination chemistry. The Schiff bases derived by the condensation of sulfonamides with salicylaldehyde are not only good complexing agents (Roy and Mukherjee, 1955; Jain and Chaturvedi, 1975a,b, 1976), but also good bacteriocides (Tiwari and Mishra, 1980). Chelating ligands containing O and N donor atoms (Maurya et al., 2003) show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions (Syamal and Maurya, 1989; Maurya and Maurya, 1995). Aromatic hydroxyaldehydes form stable complexes and the presence of a phenolic hydroxyl group at their o-position imparts an additional donor site of the molecule making it bidentate. Such a molecule coordinates with the metal ion through the carbonyl oxygen and deprotonated hydroxyl group. The chelating properties of Schiff bases derived from *o*-hydroxyaldehydes and ketones are well established (Maurya et al., 1993, 1995; Agarwal et al., 1994).

The coordination chemistry (Maurya, 2003) of vanadium has acquired renewed interest since the discovery of vanadium in organisms such as certain ascidians and *Amanita muscaria* mushrooms and as a constituent of the cofactors in vanadate-dependent haloperoxidases and vanadium nitrogenase (Butler, 1999; Little and Butler, 2001; Roson et al., 1986; Rehder, 2003a,b). The role of vanadium complexes in catalytically conducted redox reactions (Ligtenbarg et al., 2003; Conte et al., 1997) potential pharmaceutical applications (Rehder, 2003a,b; Thompson and Orvig, 2004; Sakurai et al., 2002; Rehder et al., 2002; Melchier et al., 1999; Clarke et al., 1999) studies on the metabolism and detoxification of vanadium compounds under physiological conditions (Baran, 2000) and the stability and specification of vanadium complexes in biofluids (Kiss et al., 2003, 2000) have also influenced the study of the coordination chemistry of vanadium. Spectroscopic investigations have shown a distinct preference of this metal center for N and/or O coordination environment (Sivak et al., 1998; Asgedom et al., 1995). This is consistent with the combination of hard acid (VO^{+2}) and hard (N and O ligands) bases (Sakurai et al., 1998). Some vanadium complexes of O, N donor ligands have been reported recently (Sutradhar et al., 2006; Miyazaki et al., 2005; Sarkar and Pal, 2006; Hazara et al., 2007). Vanadium complexes with Schiff base were reported to exhibit a range of biological activities including anti-tuberculosis, antibacterial, and antifungal properties, (Hashidhara and Goudar, 2000; Maqsood et al., 2006). In contrast to O, N donor ligands, complexes of vanadium containing sulfur functionality have not received much attention (Samanta et al., 2003; Maurya et al., 2002a,b, 2003; Monga et al., 2005). Vanadium complexes having sulfur functionality have been found to be orally active insulin-mimetic agents in the treatment of diabetic model animals (Kotosh et al., 2004). In vanadium nitrogenase, the sulfur-vanadium bond has also been well established (Eady and Legh, 1994).

It has also been recognized that vanadium as a micronutrient, prevents the minor wear and tear of the essential critical molecules of the cell like DNA, proteins, etc., in humans (Fenech and Ferguson, 2001). Thus, it has a role in DNA maintenance reactions and may protect the genomic instability that may be leading to cancer (Ray et al., 2006).

A recent report from our laboratory, Maurya and Rajput (2006) has reported the synthesis and characterization of four new oxovanadium(IV) complexes, formed by the Schiff bases derived from 3-methyl-1-phenyl-4-valeryl-2-pyrazolin-5-one and the sulfa drugs. Another new series of four oxovanadium(IV) complexes involving O, N donor environment of pyrazolone based sulfa drugs Schiff bases has also been reported from our laboratory (Maurya et al., 2015a,b,c).

Considering the pronounced biological activity of the sulfa drug Schiff base complexes, in view of the importance of vanadium compound, and also extending our search for more efficacious vanadium compounds, a study was undertaken of the coordination chemistry of oxovanadium(IV) complexes involving salicylaldehyde based sulfadrug Schiff bases *viz*., N-(salicylidene)sulfadiazine (sal-sdzH, I), N-(salicylidene)sulfaguani dine (sal-sgnH, II), N-(salicylidene)sulfanilamide(sal-snmH, III), N-(salicylidene)sulfamerazine(sal-smrH, IV) and N,N′-bis(salicylidene)-4,4′-diaminodiphenylsulfone(sal-dadpsH$_2$, V) (Scheme 1).

2. Experimental

2.1. Materials used

Vanadyl sulfate pentahydrate (Thomas Baker Ltd., Mumbai), salicylaldehyde (E. Merck, Germany), sulfa drugs (sulfadiazine, sulfaguanidine, sulfanilamide, sulfamerazine, (Sigma Chemicals Co., USA), daphsone (Fluka Chemie A.G., Switzerland), ethanol (Bengal Chemicals and Pharmaceuticals Ltd., Kolkata), were used as supplied. All other chemicals used were of analytical reagent grade.

2.2. Synthesis of Schiff bases

The Schiff bases of sulfa drugs were prepared as follows: An ethanolic solution (10 mL) of salicylaldehyde (0.244 g, 0.209 mL, 2 mmol) was added to the ethanolic solution (~20 mL) of sulfadiazine (0.500 g, 2 mmol), sulfanilamide (0.344 g, 2 mmol), sulfaguanidine (0.428 g, 2 mmol), sulfamerizine (0.528 g, 2 mmol) or 4,4′-diaminodiphenylsulfone (0.248 g, 1 mmol). A colored solid mass separated out when the mixture was heated at 80 °C for ~20 min. It was filtered, washed several times with ethanol and diethyl ether and subsequently, dried over anhydrous $CaCl_2$ in a desiccator. The characterization data of Schiff bases are given in Table 1.

2.3. Synthesis of complexes

The following general procedure was used in the synthesis of all the complexes: A suspension of the Schiff base ligand sal-sdzH (0.708 g, 2 mmol), sal-sgnH (0.636 g, 2 mmol), sal-snmH (0.552 g, 2 mmol), sal-smrH (0.736 g, 2 mmol), and sal-dadpsH$_2$ (0.456 g, 1 mmol) in the minimum quantity of DMF was mixed with ethanol (~20 mL). The resulting mixture was refluxed with stirring on a magnetic stirrer equipped with heater for 1 h to get a clear solution. The salt of $VOSO_4{\cdot}5H_2O$ (0.253 g, 1 mmol) was dissolved in ethanol-water (4:1, 5 mL) and the solution so obtained was added to a hot, stirred ethanolic solution of the corresponding Schiff bases. The resulting solution was refluxed for 10–12 h, and then concentrated to half of its volume. The resulting colored precipitate was then filtered and washed several times with ethanol to remove any unreacted ligand and the metal salt. The product was dried *in vacuo*. The analytical data of the complexes are given in Table 2.

Table 3 Some important IR spectral bands (cm^{-1}) of the synthesized Schiff bases.

S. no.	Ligands	ν(C=N) (azomethine)	ν(C–O) (phenolic)	ν(NH)/NH$_2$	ν(OH) (phenolic)	ν$_{as}$(SO$_2$)	ν$_s$(SO$_2$)
I	sal-sdzH	1620	1490	3100	3480	1340	1160
II	sal-sgnH	1620	1480	3353 3240	3420	1300	1170
III	sal-snmH	1615	1490	3340 3240	3480	1310	1160
IV	sal-smrH	1620	1490	3240	3340	1310	1160
V	sal-dadpsH$_2$	1620	1480	–	3400 (br)	1320	1150

Table 4 Important IR spectral bands (cm^{-1}) of the synthesized complexes.

S. no.	Complex	ν(C=N) (azomethine)	ν(C–O) (phenolic)	ν (V=O)	ν(OH)(H$_2$O)	ν(NH)/NH$_2$	ν$_s$(SO$_2$)	ν$_{as}$(SO$_2$)	ν(V–O)	ν(V–N)
1	$[VO(sal\text{-}sdz)_2(H_2O)]{\cdot}H_2O$	1600	1440	945	3400	3100	1160	1340	580	450
2	$[VO(sal\text{-}sgn)_2(H_2O)]{\cdot}H_2O$	1580	1440	940	3400 3360	3360 3240	1150	1330	580	450
3	$[VO(sal\text{-}snm)_2(H_2O)]{\cdot}H_2O$	1580	1440	940	3400 3350	3350 3240	1150	1330	580	460
4	$[VO(sal\text{-}smr)_2(H_2O)]{\cdot}H_2O$	1590	1450	930	3500 3380	3240	1170	1325	580	470
5	$[VO(sal\text{-}dadps)(H_2O)]_2{\cdot}2H_2O$	1590	1450	980	3460 3380	–	1150	1300	550	450

2.4. Analyses

Carbon, hydrogen and nitrogen were determined micro-analytically at SAIF, Indian Institute of Technology, Mumbai. The vanadium content of each of the complexes was determined as follows. A 100 mg of sample of the compound was placed in a silica crucible, decomposed by gentle heating and then adding 1–2 mL of concentrated HNO_3, 2–3 times. An orangish mass (V_2O_5) was obtained after decomposing and complete drying. It was dissolved in the minimum amount of dilute H_2SO_4, and the solution so obtained was diluted with distilled water to 100 mL in a measuring flask. The vanadium content of each of the complexes was determined volumetrically using decinormal $KMnO_4$ solution as an oxidizing agent in the presence of sulfurous acid. The amount of vanadium in the sample solution was calculated using the standard (Furman, 1962) relationship: 1 mL of 0.1 N $KMnO_4$ = 5.094 mg vanadium.

2.5. Physical methods

The following physical methods were used in the present investigation. The solid-state infrared spectra were obtained using KBr pellets with a Perkin–Elmer model 1620 FT-IR spectrophotometer at the Central Drug Research Institute, Lucknow. Thermogravimetry of the complexes was performed on a Perkin–Elmer Thermoanalyser at S. A. I. F., Indian Institute of Technology, Mumbai. Electronic spectra were recorded on an ATI Unicam UV-1-100 UV/Visible Spectrophotometer in our laboratory. Conductance measurements were made in DMF solution using a Toshniwal conductivity bridge and dip-type cell with a smooth platinum electrode of cell constant 1.02. Magnetic measurements were done by a vibrating sample magnetometer at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai. The decomposition temperatures of the complexes were recorded by an electrically operated melting point apparatus (Kumar Industries, Mumbai) of heating capacity up to 360 °C. The X-Band and EPR spectra of the complexes were measured on a Bruker ESP X-Band EPR spectrometer using powdered samples at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai. The FAB mass spectrum of a representative complex was recorded on a JEOL SX 102/DA-6000 Mass Spectrometer/Data system using Argon/Xenon (6KV, 10 mA) as the FAB gas. The accelerating voltage was

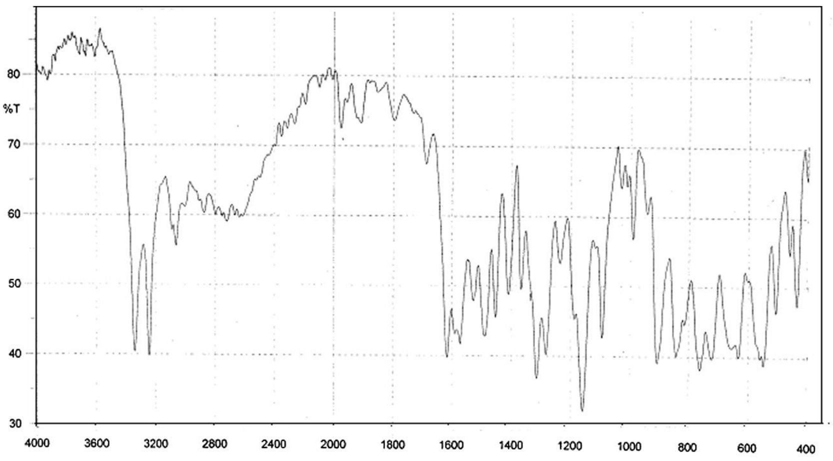


Figure 1 IR spectrum of sal-snmH.

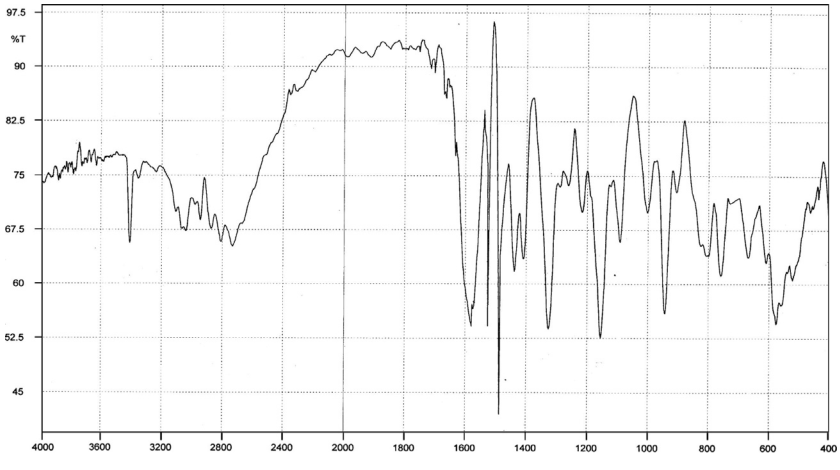


Figure 2 IR spectrum of $[VO(sal\text{-}snm)(H_2O)]\cdot H_2O$ (**3**).

10 KV and the spectrum was recorded at room temperature and *m*-nitrobenzyl alcohol (NBA) was used as the matrix.

2.6. 3D Molecular modeling studies

The 3D molecular modeling of one of the synthesized compound was carried out on CS Chem 3D Ultra Molecular Modeling and Analysis Program (http://www.cambridgesoft.com). It is an interactive graphics program that allows rapid structure building, geometry optimization and molecular display. It has the ability to handle transition metal compounds.

3. Results and discussion

The five sulfa drugs based Schiff base ligands, sal-sdzH, sal-sgnH, sal-snmH, sal-smrH and sal-dadpsH_2 were prepared by the interaction of salicylaldehyde and sulfa drugs in ethanol according to Scheme 1.

The micro-analytical data of these Schiff base ligands along with physical properties are given in Table 1. Some important IR spectral bands of these ligands are given in Table 3. The formation of these Schiff base ligands can be confirmed by the appearance of a strong band for ν(C=N) (Hazara et al., 2007; Hashidhara and Goudar, 2000) (azomethine) at 1615–1620 cm^{-1}. The IR spectra of these ligands also exhibit relevant bands for ν(OH) (phenolic), ν(C–O) (phenolic), ν(NH/NH_2), $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ (see Table 3), which also support the formation of Schiff base ligands.

The oxovanadium(IV) complexes were prepared according to the following equations:

$$VOSO_4 \cdot 5H_2O + 2LH \xrightarrow[\text{Reflux}]{H_2O,\text{Ethanol}} [VO(L)_2(H_2O)] \cdot H_2O + H_2SO_4$$

Where, LH = sal-sdzH (**1**), sal-sgnH (**2**), sal-snmH (**3**) or sal-smrH (**4**) and

$$2VOSO_4 \cdot 5H_2O + 2\text{sal} - \text{dadps}H_2 \xrightarrow[\text{Reflux}]{H_2O,\text{Ethanol}} [VO(\text{sal} - \text{dadps}) \times (H_2O)]_2 \cdot 2H_2O(5) + 2H_2SO_4$$

The resulting complexes are soluble in DMF and DMSO, partially soluble in acetonitrile and insoluble in ethanol, methanol and carbon tetrachloride. Their physical properties are given in Table 2. The complexes were characterized by the following studies:

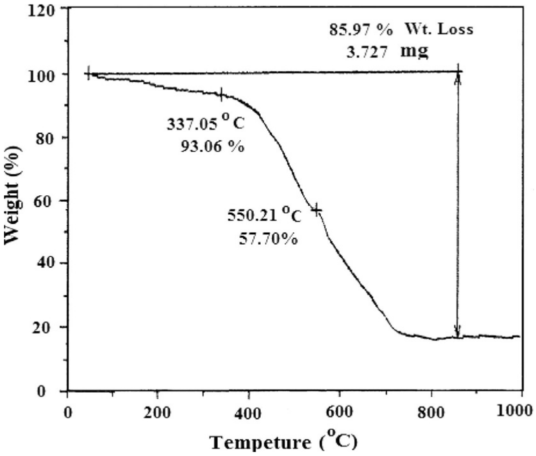


Figure 4 TG curve of $[VO(\text{sal-dadps})(H_2O)]_2 \cdot 2H_2O$ (**5**).

3.1. Infrared spectral studies

All the ligands except (sal-dadpsH_2 and sal-snmH) contain five donor sites: (i) the phenolic oxygen, (ii) the azomethine nitrogen, (iii) sulfonamide oxygens, (iv) sulfonamide nitrogen, (v) ring nitrogens in the case of sal-sdzH and sal-smrH or amino nitrogen in the case of sal-sgnH. The ligand, sal-snmH contains only four potential donor sites, (i)–(iv) given above. The remaining ligand, sal-dadpsH_2 possesses five potential donor sites (i) two azomethine nitrogens, (ii) two phenolic oxygens, (iii) sulfonamide oxygens. All the Schiff base ligands show a sharp and strong band due to ν(C=N) of the azomethine group at 1615–1620 cm^{-1}. The observed low energy shift (Maurya and Rajput, 2006) of this band in the complexes appearing at 1580–1600 cm^{-1}, suggests the coordination of azomethine nitrogen to the metal center. This is further supported by the appearance of a new band at 450–470 cm^{-1} due to the ν(V–N) band (Maurya et al., 2015a,b,c).

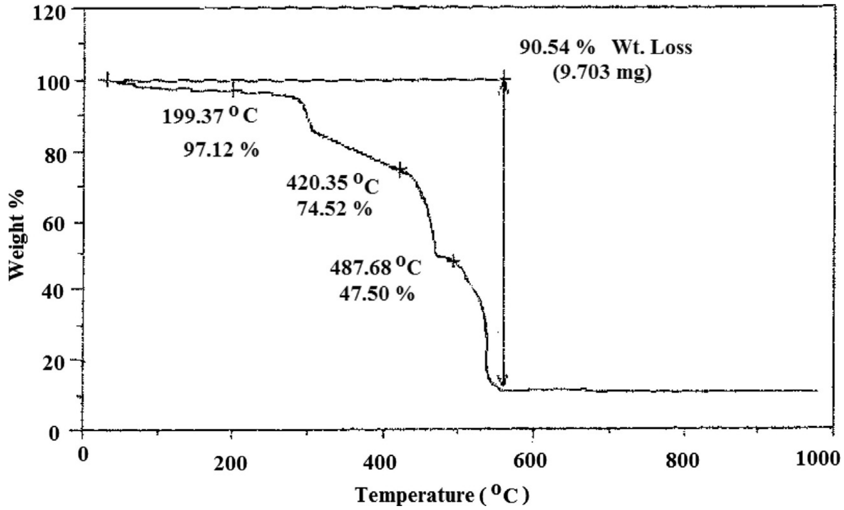


Figure 3 TG curve of $[VO(\text{sal-sdz})(H_2O)] \cdot H_2O$ (**1**).

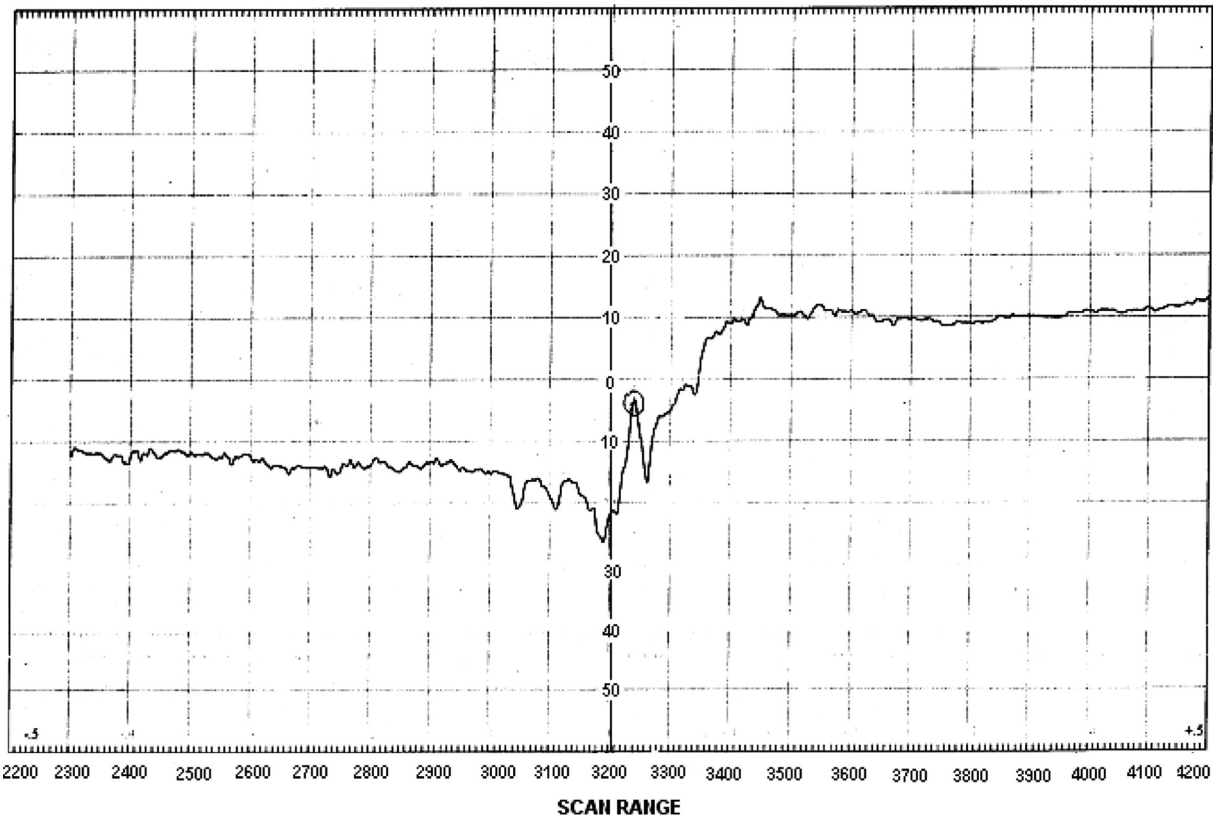


Figure 5 ESR spectrum of [VO(sal-sdz)(H_2O)]·H_2O (**1**).

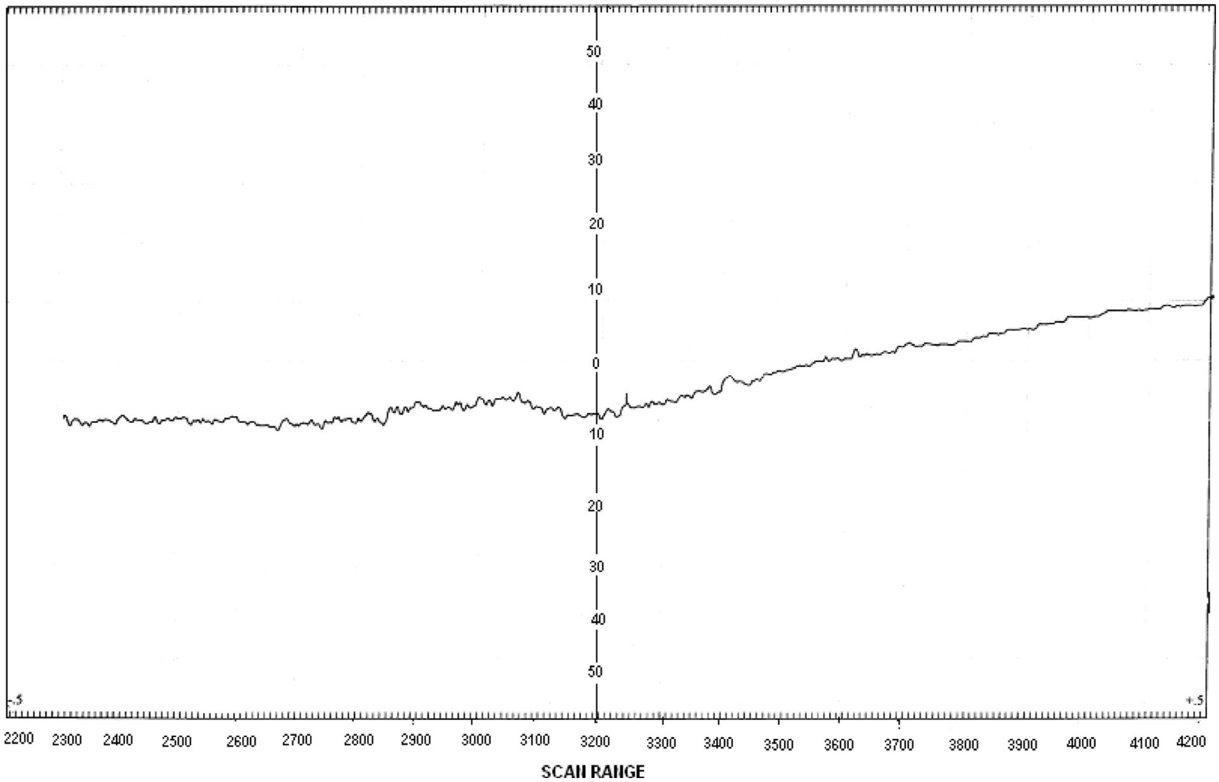


Figure 6 ESR spectrum of [VO(sal-dadps)(H_2O)]$_2$·2H_2O (**5**).

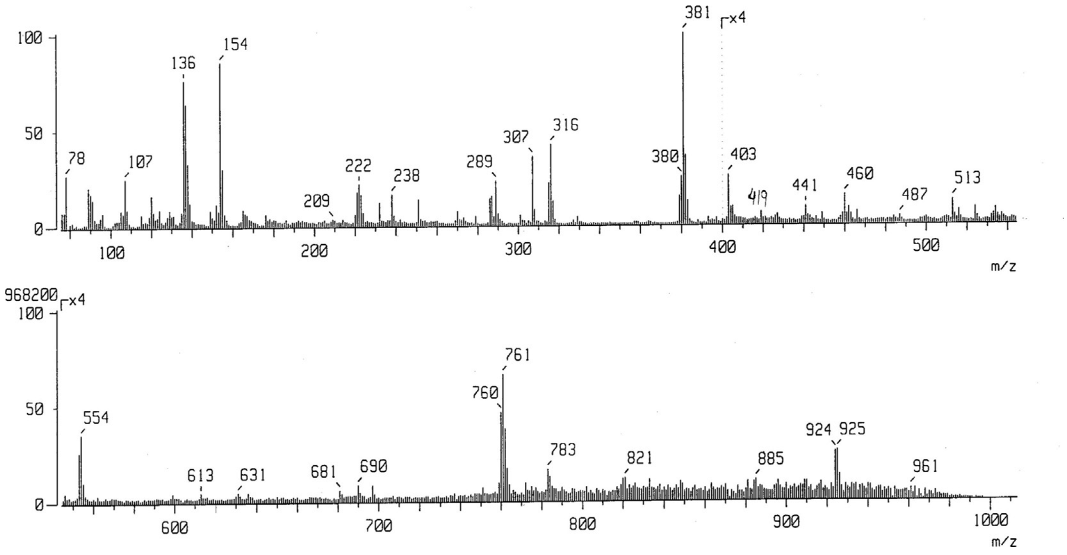


Figure 7 Mass spectrum of [VO(sal-sdz)(H_2O)]·H_2O (**1**).

Table 5 Electronic Spectral Peaks of the Synthesized Complexes.

Comp. no.	Complex	λ_{max} (nm)	ε (liter mol^{-1} cm^{-1})	Peak assignments
1	[VO(sal-sdz)$_2$(H_2O)]·H_2O	281	2446	Charge Transfer Transition
		303	2404	Charge Transfer Transition
		320	2340	Charge Transfer Transition
		430	1137	$b_2 \rightarrow {}^1a_1^*$
2	[VO(sal-sgn)$_2$(H_2O)]·H_2O	288	4770	Charge Transfer Transition
		304	3947	Charge Transfer Transition Charge
		322	3910	Transfer Transition
		339	290	$b_2 \rightarrow {}^1a_1^*$
		426	214	$b^2 \rightarrow b_1^*$
3	[VO(sal-snm)$_2$(H_2O)]·H_2O	285	2230	Charge Transfer Transition
		310	2170	Charge Transfer Transition Charge
		330	2125	Transfer Transition
		400	750	$b_2 \rightarrow {}^1a_1^*$
4	[VO(sal-smr)$_2$(H_2O)]·H_2O	300	2247	Charge Transfer Transition
		315	2183	Charge Transfer Transition Charge
		325	2119	Transfer Transition
		380	855	$b_2 \rightarrow {}^1a_1^*$
5	[VO(sal-dadps)(H_2O)]$_2$·2H_2O	288	2340	Charge Transfer Transition
		310	2204	Charge Transfer Transition
		335	2040	Charge Transfer Transition
		415	650	$b_2 \rightarrow {}^1a_1^*$

The ν(NH) mode of the sulfonamide group/amino group in the uncoordinated Schiff bases remains unchanged in the spectra of their complexes (see Tables 3 and 4). This suggests that the sulfonamide nitrogen or amino group is not taking part in coordination. The bands, in these ligands, due to $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ appear at 1300–1340 and 1150–1170 cm^{-1}, respectively. These remain almost unchanged in the spectra of complexes, indicating that sulfonamide oxygens are not participating in coordination. This is consistent with our previous observation (Maurya et al., 2003a) in sulfa drug based Schiff bases.

The characteristic phenolic ν(OH) mode in all the ligands due to the presence of a hydroxyl group at the *ortho* position, was observed at 3340–3480 cm^{-1}. A medium band at 1480–1490 cm^{-1} due to ν(C–O) of the phenolic group was also observed in these ligands. The band due to the phenolic (OH) group of these ligands should be absent in all of the complexes under study to indicate the coordination of the phenolic oxygen, after deprotonation, to the metal ion. But due to the presence of a broad band (*vide infra*) for lattice and coordinated water, it is difficult to confirm with certainty the coordination of the phenolic oxygen after deprotonation. However, such coordination is supported by the observed shift of the phenolic ν(C–O) band to a lower wave number (Maurya et al., 2008a,b) at 1440–1450 cm^{-1} in the complexes. The coordination of phenolic oxygen is further supported by the appearance of a non ligand band at 550–580 cm^{-1}, due to ν(V–O) (Maurya et al., 2003b) in the complexes. The band due to ν(C=N) ring appearing at 1580 and 1588 cm^{-1} in the ligands, sal-sdzH and sal-smrH remains unchanged in the respective complexes. This suggests that ring nitrogens of the ligand are not taking part in coordination. This is logical in terms of six-member

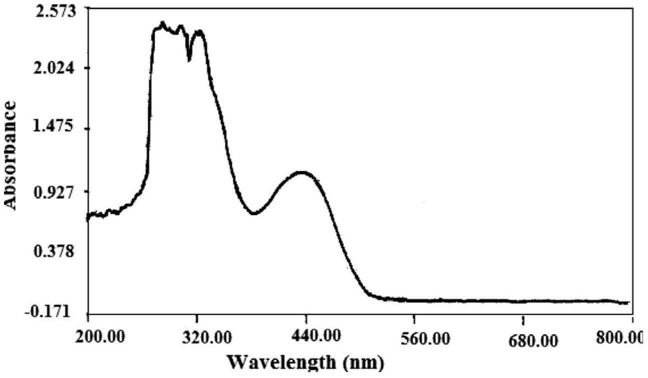


Figure 8 Electronic spectrum of [VO(sal-sdz)(H_2O)]·H_2O (**1**).

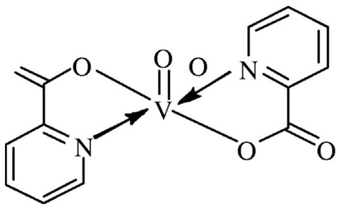


Figure 9 Structure of bis(picolinato)oxovanadium(IV).

chelate ring formation including metal on account of the bidentate coordination of azomethine nitrogen and phenyl oxygen from the *ortho* position.

The presence of lattice/coordinated water (Maurya et al., 2003a,b,c,d) in the complexes is revealed by the presence of either a broad band at 3400 cm^{-1} or two weak bands at 3400–3500 and 3350–3380 cm^{-1}.

Most of the oxovanadium(IV) complexes display a strong band near 1000 cm^{-1} assignable to ν(V=O) (Selbin, 1966). Contrary to this, several oxovanadium(IV) complexes have been reported in which this stretching mode appears at quite lower (Maurya and Rajput, 2006; Maurya et al., 2001) wave numbers around 900 cm^{-1} due to the presence of a ···V=O···V=O··· chain structure, which is formed by the interaction of vanadyl oxygen of one molecule with a vanadium metal in another molecule (Boas and Pessoa, 1987). In the complexes presented here, ν(V=O) is found at 930–980 cm^{-1}. This suggests the absence of a ···V=O···V=O··· chain. The presence of a coordinated water molecule in this complex (discussed above) supports this fact. The IR spectra of the Schiff base ligand (sal-snmH, III) and its complex, [VO(sal-snm)(H_2O)]·H_2O (**3**) are given in Figs. 1 and 2, respectively.

3.2. Thermogravimetric studies

Thermogravimetric analysis of two representative compounds, namely [VO(sal-sdz)$_2$(H_2O)]·H_2O (**1**) and [VO(sal-dadps) (H_2O)]$_2$·2H_2O (**5**) were recorded in the temperature range from ambient to 1000 °C at the heating rate of 15 °C/min. The compound (**1**) exhibits a weight loss of 4.66% at approximately

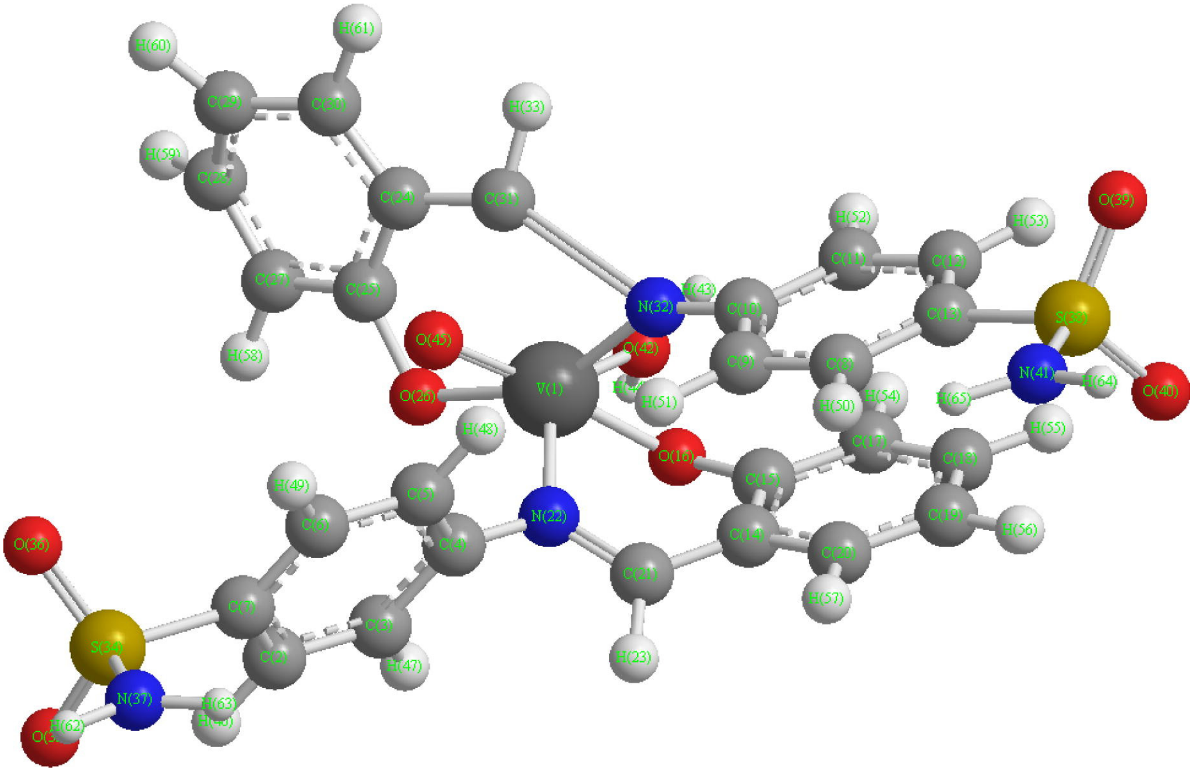


Figure 10 3D-Structure of compound (**3**).

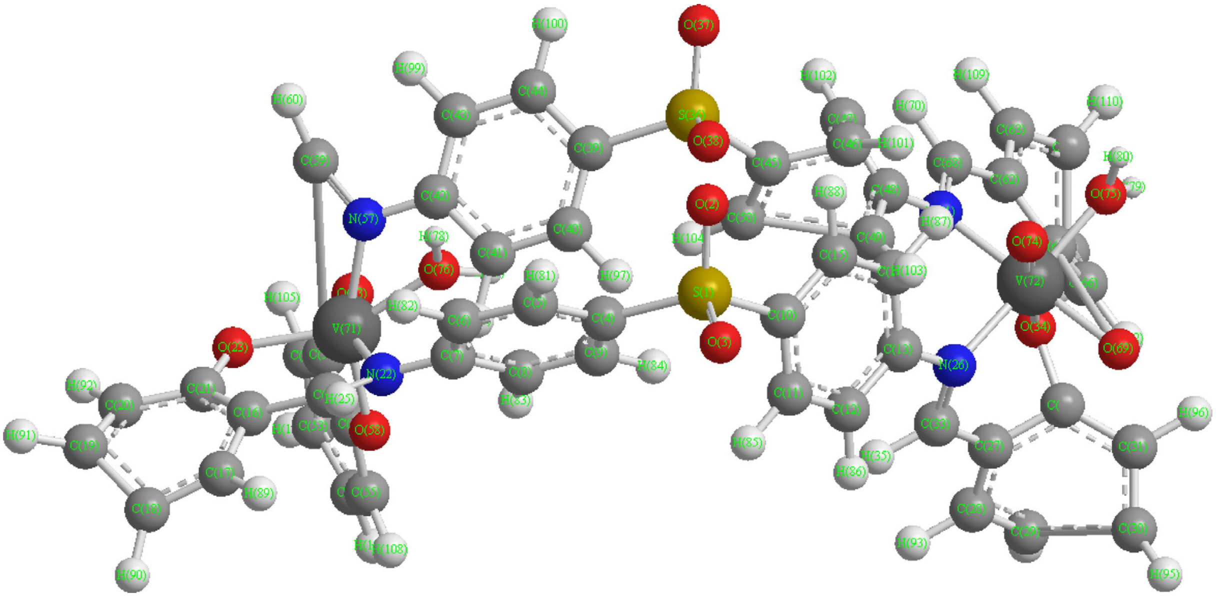


Figure 11 3D-Structure of compound (**5**).

277.00 °C (calcd. wt. loss for two moles of H_2O, 4.45%) corresponding to the removal of two molecules of water. As the compound starts loosing weight right from about 50.00 °C, one water molecule may be taken as lattice water and the other as the coordinated water. The second weight loss observed at 490.00 °C is found to be 51.48% against a calculated weight loss of 48.08% corresponding to the elimination of one ligand moiety. The final weight loss at approximately 573.13 °C has been found to be 90.54% against a calculated weight loss of 91.72% involving the removal of another ligand moiety. The final residue attaining a constant weight over 600.00 °C (obsd. = 9.46%) corresponds to V_2O_5

Table 6a$_1$ Various bond lengths of compound $[VO(sal\text{-}snm)_2(H_2O)]\cdot H_2O$ (**3**).

S. no.	Atoms	Actual bond length	Optimal bond length	S. No.	Atoms	Actual bond length	Optimal bond length
1	O(42)–H(44)	0.942	0.942	36	C(15)–C(17)	1.337	1.42
2	O(42)–H(43)	0.942	0.942	37	C(15)–O(16)	1.355	1.355
3	N(41)–H(65)	1.02	1.02	38	C(14)–C(21)	1.337	1.503
4	N(41)–H(64)	1.02	1.02	39	C(14)–C(20)	1.337	1.42
5	S(38)–N(41)	1.696		40	C(14)–C(15)	1.337	1.42
6	S(38)–O(40)	1.45	1.45	41	C(13)–S(38)	1.79	–
7	S(38)–O(39)	1.45	1.45	42	C(12)–H(53)	1.1	1.1
8	N(37)–H(63)	1.02	1.02	43	C(12)–C(13)	1.3949	1.42
9	N(37)–H(62)	1.02	1.02	44	C(11)–H(52)	1.1	1.1
10	S(34)–N(37)	1.696		45	C(11)–C(12)	1.3948	1.42
11	S(34)–O(36)	1.45	1.45	46	C(10)–N(32)	1.26	1.456
12	S(34)–O(35)	1.45	1.45	47	C(10)–C(11)	1.3948	1.42
13	C(31)–H(33)	1.1	1.1	48	C(9)–H(51)	1.1	1.1
14	C(31)–N(32)	2.3057	1.26	49	C(9)–C(10)	1.3949	1.42
15	C(30)–H(61)	1.1	1.1	50	C(8)–H(50)	1.1	1.1
16	C(29)–H(60)	1.1	1.1	51	C(13)–C(8)	1.3948	1.42
17	C(29)–C(30)	1.337	1.42	52	C(8)–C(9)	1.3948	1.42
18	C(28)–H(59)	1.1	1.1	53	C(7)–S(34)	1.79	–
19	C(28)–C(29)	1.4345	1.42	54	C(6)–H(49)	1.1	1.1
20	C(27)–H(58)	1.1	1.1	55	C(6)–C(7)	1.3949	1.42
21	C(27)–C(28)	1.337	1.42	56	C(5)–H(48)	1.1	1.1
22	C(25)–C(27)	1.337	1.42	57	C(5)–C(6)	1.3948	1.42
23	C(25)–O(26)	1.355	1.355	58	N(22)–C(4)	1.26	1.456
24	C(24)–C(31)	1.337	1.503	59	C(4)–C(5)	1.3948	1.42
25	C(24)–C(30)	1.337	1.42	60	C(3)–H(47)	1.1	1.1
26	C(24)–C(25)	1.337	1.42	61	C(3)–C(4)	1.3949	1.42
27	C(21)–H(23)	1.1	1.1	62	C(2)–H(46)	1.1	1.1
28	C(21)–N(22)	1.2782	1.26	63	C(7)–C(2)	1.3948	1.42
29	C(20)–H(57)	1.1	1.1	64	C(2)–C(3)	1.3948	1.42
30	C(19)–H(56)	1.1	1.1	65	V(1)–O(45)	1.5996	–
31	C(19)–C(20)	1.337	1.42	66	V(1)–O(42)	1.86	–
32	C(18)–H(55)	1.1	1.1	67	O(16)–V(1)	1.86	–
33	C(18)–C(19)	1.337	1.42	68	N(22)–V(1)	1.896	–
34	C(17)–H(54)	1.1	1.1	69	N(32)–V(1)	1.896	–
35	C(17)–C(18)	1.337	1.42	70	O(26)–V(1)	1.86	–

Table 6a$_2$ Various bond angles of compound [VO(sal-snm)$_2$(H$_2$O)]·H$_2$O (**3**).

S. no.	Atoms	Actual bond angles	Optimal bond angles
1	H(65)–N(41)–H(64)	119.9998	104.5
2	H(65)–N(41)–S(38)	120.0002	–
3	H(64)–N(41)–S(38)	120	–
4	H(63)–N(37)–H(62)	119.9999	104.5
5	H(63)–N(37)–S(34)	119.9995	–
6	H(62)–N(37)–S(34)	120.0006	–
7	H(60)–C(29)–C(30)	122.2431	120
8	H(60)–C(29)–C(28)	122.2429	120
9	C(30)–C(29)–C(28)	115.514	–
10	H(59)–C(28)–C(29)	122.2423	120
11	H(59)–C(28)–C(27)	122.2421	120
12	C(29)–C(28)–C(27)	115.5156	–
13	H(61)–C(30)–C(29)	120	120
14	H(61)–C(30)–C(24)	119.9997	120
15	C(29)–C(30)–C(24)	120.0003	–
16	H(58)–C(27)–C(28)	119.9995	120
17	H(58)–C(27)–C(25)	120.0002	120
18	C(28)–C(27)–C(25)	120.0003	–
19	C(27)–C(25)–O(26)	115.6993	124.3
20	C(27)–C(25)–C(24)	119.9989	120
21	O(26)–C(25)–C(24)	124.2997	124.3
22	N(41)–S(38)–O(40)	109.4417	–
23	N(41)–S(38)–O(39)	109.442	–
24	N(41)–S(38)–C(13)	109.5201	–
25	O(40)–S(38)–O(39)	109.4997	116.6
26	O(40)–S(38)–C(13)	109.4618	–
27	O(39)–S(38)–C(13)	109.462	–
28	S(38)–C(13)–C(12)	120.0007	–
29	S(38)–C(13)–C(8)	120.0001	–
30	C(12)–C(13)–C(8)	119.9992	120
31	H(53)–C(12)–C(13)	120.0008	120
32	H(53)–C(12)–C(11)	120.0013	120
33	C(13)–C(12)–C(11)	119.9979	
34	H(50)–C(8)–C(13)	119.9987	120
35	H(50)–C(8)–C(9)	119.9986	120
36	C(13)–C(8)–C(9)	120.0028	–
37	H(52)–C(11)–C(12)	119.9989	120
38	H(52)–C(11)–C(10)	119.9993	120
39	C(12)–C(11)–C(10)	120.0017	–
40	H(51)–C(9)–C(10)	120.0017	120
41	H(51)–C(9)–C(8)	120.0011	120
42	C(10)–C(9)–C(8)	119.9971	–
43	C(31)–C(24)–C(30)	119.9988	120
44	C(31)–C(24)–C(25)	119.9989	120
45	C(30)–C(24)–C(25)	119.9998	120
46	H(33)–C(31)–N(32)	105.7245	116.5
47	H(33)–C(31)–C(24)	105.7246	120
48	N(32)–C(31)–C(24)	148.5509	123.5
49	N(32)–C(10)–C(11)	119.9995	120
50	N(32)–C(10)–C(9)	119.9992	120
51	C(11)–C(10)–C(9)	120.0012	120
52	H(44)–O(42)–H(43)	120.0002	–
53	H(44)–O(42)–V(1)	120.0001	–
54	H(43)–O(42)–V(1)	119.9997	–
55	C(31)–N(32)–C(10)	148.1512	–
56	C(31)–N(32)–V(1)	63.698	–
57	C(10)—N(32)–V(1)	148.1508	–
58	C(25)–O(26)–V(1)	109.5002	–
59	H(56)–C(19)–C(20)	119.9995	120
60	H(56)–C(19)–C(18)	120.0004	120
61	C(20)–C(19)–C(18)	120.0001	–
62	H(55)–C(18)–C(19)	119.9998	120
63	H(55)–C(18)–C(17)	119.9999	120
64	C(19)–C(18)–C(17)	120.0003	–
65	H(54)–C(17)–C(18)	119.9999	120
66	H(54)–C(17)–C(15)	120.0003	120
67	C(18)–C(17)–C(15)	119.9997	–
68	C(15)–O(16)–V(1)	109.4996	–
69	H(57)–C(20)–C(19)	120	120
70	H(57)–C(20)–C(14)	120.0004	120
71	C(19)–C(20)–C(14)	119.9996	–
72	C(17)–C(15)–O(16)	115.6987	124.3
73	C(17)–C(15)–C(14)	120.0004	120
74	O(16)–C(15)–C(14)	124.2985	124.3
75	N(37)–S(34)–O(36)	109.4417	–
76	N(37)–S(34)–O(35)	109.4418	–
77	N(37)–S(34)–C(7)	109.5205	–
78	O(36)–S(34)–O(35)	109.4996	116.6
79	O(36)–S(34)–C(7)	109.4619	–
80	O(35)–S(34)–C(7)	109.462	–
81	S(34)–C(7)–C(6)	120.0002	–
82	S(34)–C(7)–C(2)	120.0002	–
83	C(6)–C(7)–C(2)	119.9996	120
84	H(49)–C(6)–C(7)	120.0013	120
85	H(49)–C(6)–C(5)	120.0012	120
86	C(7)–C(6)–C(5)	119.9976	–
87	H(46)–C(2)–C(7)	119.9986	120
88	H(46)–C(2)–C(3)	119.9985	120
89	C(7)–C(2)–C(3)	120.0029	–
90	H(48)–C(5)–C(6)	119.9989	120
91	H(48)–C(5)–C(4)	119.9993	120
92	C(6)–C(5)–C(4)	120.0018	–
93	H(47)–C(3)–C(4)	120.0015	120
94	H(47)–C(3)–C(2)	120.0016	120
95	C(4)–C(3)–C(2)	119.9969	–
96	C(21)–C(14)–C(20)	119.9989	120
97	C(21)–C(14)–C(15)	119.9987	120
98	C(20)–C(14)–C(15)	119.9999	120
99	H(23)–C(21)–N(22)	119.12	116.5
100	H(23)–C(21)–C(14)	119.12	120
101	N(22)–C(21)–C(14)	121.76	123.5
102	N(22)–C(4)–C(5)	119.9993	120
103	N(22)–C(4)–C(3)	119.9994	120
104	C(5)–C(4)–C(3)	120.0013	120
105	C(21)–N(22)–C(4)	119.1178	–
106	C(21)–N(22)–V(1)	121.7647	–
107	C(4)–N(22)–V(1)	119.1175	–
108	O(45)–V(1)–O(42)	135.6046	–
109	O(45)–V(1)–O(16)	174.2007	–
110	O(45)–V(1)–N(22)	89.1053	–
111	O(45)–V(1)–N(32)	95.7292	–
112	O(45)–V(1)–O(26)	65.4876	–
113	O(42)–V(1)–O(16)	44.9999	–
114	O(42)–V(1)–N(22)	135	–
115	O(42)–V(1)–N(32)	90.0001	–
116	O(42)–V(1)–O(26)	89.9998	–
117	O(16)–V(1)–N(22)	90.0001	–
118	O(16)–V(1)–N(32)	90.0002	–
119	O(16)–V(1)–O(26)	109.4998	–
120	N(22)–V(1)–N(32)	90.0001	–
121	N(22)–V(1)–O(26)	109.5001	–
122	N(32)–V(1)–O(26)	151.8308	–

(calcd. = 10.25%) (Maurya et al., 2015a,b,c). This weight loss data, thus, agree well with the IR results for this complex. The thermogram of compound, [VO(sal-sdz)$_2$(H$_2$O)]·H$_2$O (**1**) is given in Fig. 3.

The compound (**5**) shows a weight loss of 6.43% at 337.00 °C (calcd. wt. loss for four moles of water, 6.46%) corresponding to the removal of four water molecules similar to compound (**1**). It also starts loosing weight right from 50.00 °C. This suggests that two water molecules are lattice water and other two are coordinated. Taking the dimeric structure of the compound into account (*vide infra*), this seems to be logical. Another weight loss of 45.42% by this compound was noticed around 550.00 °C (calculated wt. loss of one ligand moiety, 47.22%), suggesting the removal of one ligand moiety from the complex. The final weight loss of 85.97% observed at ~700.00 °C (calcd. wt. loss for another ligand moiety, 87.98%), indicates the elimination of second ligand moiety from the complex. The final residue attaining a constant weight over 750 °C corresponds to (obsd. = 14.03%) V_2O_5 (calculated = 14.89%) (Maurya et al., 2015a,b,c). The

Table 6b$_1$ Various bond lengths of compound $[VO(sal\text{-}dadps)(H_2O)]_2{\cdot}2H_2O$ (**5**).

S. no.	Atoms	Actual bond length	Optimal Bond Length	S. No.	Atoms	Actual bond length	Optimal bond length
1	O(76)–H(78)	0.942	0.942	63	S(36)–C(45)	1.79	–
2	O(76)–H(77)	0.942	0.942	64	S(36)–C(39)	1.79	–
3	O(75)–H(80)	0.942	0.942	65	S(36)–O(38)	1.45	1.45
4	O(75)–H(79)	0.942	0.942	66	S(36)–O(37)	1.45	1.45
5	V(72)–O(75)	1.86	–	67	O(34)–V(72)	1.86	–
6	V(72)–O(74)	1.5996	–	68	C(33)–H(35)	1.1	1.1
7	V(71)–O(76)	1.86	–	69	O(34)–C(32)	1.3722	1.355
8	V(71)–O(73)	1.5996	–	70	C(31)–H(96)	1.1	1.1
9	O(69)–V(72)	1.86	–	71	C(31)–C(32)	1.337	1.42
10	C(68)–H(70)	1.1	1.1	72	C(30)–H(95)	1.1	1.1
11	O(69)–C(67)	3.4681	1.355	73	C(30)–C(31)	1.337	1.42
12	C(66)–H(112)	1.1	1.1	74	C(29)–H(94)	1.1	1.1
13	C(66)–C(67)	1.337	1.42	75	C(29)–C(30)	2.6164	1.42
14	C(65)–H(111)	1.1	1.1	76	C(28)–H(93)	1.1	1.1
15	C(65)–C(66)	1.337	1.42	77	C(28)–C(29)	1.337	1.42
16	C(64)–H(110)	1.1	1.1	78	C(27)–C(33)	1.337	1.503
17	C(64)–C(65)	1.6862	1.42	79	C(32)–C(27)	1.337	1.42
18	C(63)–H(109)	1.1	1.1	80	C(27)–C(28)	1.337	1.42
19	C(63)–C(64)	1.337	1.42	81	N(26)–V(72)	1.896	–
20	C(62)–C(68)	1.337	1.503	82	N(26)–C(33)	1.26	1.26
21	C(67)–C(62)	1.337	1.42	83	C(24)–H(25)	1.1	1.1
22	C(62)–C(63)	1.337	1.42	84	O(23)–V(71)	1.86	–
23	N(61)–V(72)	1.896		85	N(22)–V(71)	1.896	–
24	N(61)–C(68)	1.26	1.26	86	N(22)–C(24)	1.26	1.26
25	C(59)–H(60)	1.1	1.1	87	C(21)–O(23)	1.355	1.355
26	O(58)–V(71)	1.86		88	C(20)–H(92)	1.1	1.1
27	N(57)–V(71)	1.896		89	C(20)–C(21)	1.337	1.42
28	N(57)–C(59)	1.26	1.26	90	C(19)–H(91)	1.1	1.1
29	C(56)–O(58)	1.355	1.355	91	C(19)–C(20)	1.337	1.42
30	C(55)–H(108)	1.1	1.1	92	C(18)–H(90)	1.1	1.1
31	C(55)–C(56)	1.337	1.42	93	C(18)–C(19)	1.5533	1.42
32	C(54)–H(107)	1.1	1.1	94	C(17)–H(89)	1.1	1.1
33	C(54)–C(55)	1.337	1.42	95	C(17)–C(18)	1.337	1.42
34	C(53)–H(106)	1.1	1.1	96	C(16)–C(24)	1.4475	1.503
35	C(53)–C(54)	1.3514	1.42	97	C(21)–C(16)	1.337	1.42
36	C(52)–H(105)	1.1	1.1	98	C(16)–C(17)	1.337	1.42
37	C(52)–C(53)	1.337	1.42	99	C(15)–H(88)	1.1	1.1
38	C(51)–C(59)	4.3751	1.503	100	C(14)–H(87)	1.1	1.1
39	C(56)–C(51)	1.337	1.42	101	C(14)–C(15)	1.337	1.42
40	C(51)–C(52)	1.337	1.42	102	C(13)–N(26)	1.26	1.456
41	C(50)–H(104)	1.1	1.1	103	C(13)–C(14)	1.337	1.42
42	C(49)–H(103)	1.1	1.1	104	C(12)–H(86)	1.1	1.1
43	C(49)–C(50)	2.1434	1.42	105	C(12)–C(13)	1.337	1.42
44	C(48)–N(61)	1.26	1.456	106	C(11)–H(85)	1.1	1.1
45	C(48)–C(49)	1.337	1.42	107	C(11)–C(12)	1.3373	1.42
46	C(47)–H(102)	1.1	1.1	108	C(10)–C(15)	1.337	1.42
47	C(47)–C(48)	1.337	1.42	109	C(10)–C(11)	1.337	1.42
48	C(46)–H(101)	1.1	1.1	110	C(9)–H(84)	1.1	1.1
49	C(46)–C(47)	1.8878	1.42	111	C(8)–H(83)	1.1	1.1
50	C(45)–C(50)	1.337	1.42	112	C(8)–C(9)	1.337	1.42
51	C(45)–C(46)	1.337	1.42	113	N(22)–C(7)	1.26	1.456
52	C(44)–H(100)	1.1	1.1	114	C(7)–C(8)	1.337	1.42
53	C(43)–H(99)	1.1	1.1	115	C(6)–H(82)	1.1	1.1
54	C(43)–C(44)	1.337	1.42	116	C(6)–C(7)	1.337	1.42
55	N(57)–C(42)	1.26	1.456	117	C(5)–H(81)	1.1	1.1
56	C(42)–C(43)	1.337	1.42	118	C(5)–C(6)	1.3373	1.42
57	C(41)–H(98)	1.1	1.1	119	C(4)–C(9)	1.337	1.42
58	C(41)–C(42)	1.337	1.42	120	C(4)–C(5)	1.337	1.42
59	C(40)–H(97)	1.1	1.1	121	S(1)–C(10)	1.79	–
60	C(40)–C(41)	1.3371	1.42	122	S(1)–C(4)	1.79	–
61	C(39)–C(44)	1.337	1.42	123	S(1)–O(3)	1.45	1.45
62	C(39)–C(40)	1.337	1.42	124	S(1)–O(2)	1.45	1.45

thermogram of compound, $[VO(sal\text{-}dadps)(H_2O)]_2{\cdot}2H_2O$ (**5**) is given in Fig. 4.

3.3. ESR spectral studies

The liquid nitrogen temperature (LNT) X-Band ESR spectra of two representative compounds namely $[VO(sal\text{-}sdz)_2(H_2O)]{\cdot}H_2O$ (**1**) and $[VO(sal\text{-}dadps)(H_2O)]_2{\cdot}2H_2O$ (**5**) were recorded in powder form using TCNE (tetracynoethylene) as a marker. Both g|| and g⊥ components were resolved in compound (**1**). The observed spectral parameters for this compound are: $g\perp = 1.976$, $g\| = 1.966$, $g_{av} = 1.969$, $A\perp = 80$ G, $A\| = 70$ G and $A_{av} = 76.66$. The deviation of $g\|$, $g\perp$ and g_{av} values in the complex from the free ion value of 2.0027 suggests that the resulting complex is covalent (Dutta and Syamal, 1993) in nature. Furthermore, the feature of the spectrum of the complex is indicative of its monomeric structure (Maurya et al., 2002a,b).

The ESR spectrum of compound (**5**) does not exhibit usual shape of a paramagnetic sample. Instead, it shows a zigzag straight-line curve. This is most probably due to the partial pairing of two unpaired electron spins on two oxovanadium centers because of dimer formation involving ligand bridging. The ESR spectra of compound (**1**) and (**5**) are given in Figs. 5 and 6, respectively.

3.4. Mass spectral studies

In the FAB mass spectrum (Fig. 7) of a representative complex [VO(sal-sdz)$_2$(H_2O)]·H_2O the matrix peaks were supposed to appear at m/z 136, 137, 154, 289, 307 in the absence of any metal ion. If metal ions are present, these peaks may be shifted accordingly. Besides matrix peaks at 136, 137, 154, 289 and 307 m/z, and other spectral peaks were observed at 381, 419, 460, 613, 773 m/z in the compound in question which are most probably due to following types of ion associations:

(i) [Molecular ion]$^+$ (772.94) – $^*[C_4N_3H_4SO_2]^+$ (157) – $^{**}[C_{10}N_3H_9SO_2]^+$ (235) = 380.94 (~381).
(ii) [sal-sdz]$^+$ (353) + [V=O]$^+$ (66.94) – H^+ = 418.94 (~419).

Table 6b$_2$ Various bond angles of compound [VO(sal-dadps)(H_2O)]$_2$·2H_2O (**5**).

S. no.	Atoms	Actual bond angles	Optimal bond angles	S. No.	Atoms	Actual bond angles	Optimal bond angles
1	H(111)–C(65)–C(66)	126.8897	120	111	O(75)–V(72)–O(74)	82.1813	–
2	H(111)–C(65)–C(64)	126.8887	120	112	O(75)–V(72)–O(69)	88.922	–
3	C(66)–C(65)–C(64)	106.2217	–	113	O(75)–V(72)–N(61)	91.0778	–
4	H(110)–C(64)–C(65)	126.8892	120	114	O(75)–V(72)–O(34)	97.8186	–
5	H(110)–C(64)–C(63)	126.8892	120	115	O(75)–V(72)–N(26)	172.1064	–
6	C(65)–C(64)–C(63)	106.2216	–	116	O(74)–V(72)–O(69)	89.9999	–
7	H(112)–C(66)–C(67)	119.9995	120	117	O(74)–V(72)–N(61)	90.0002	–
8	H(112)–C(66)–C(65)	120.0002	120	118	O(74)–V(72)–O(34)	179.9998	–
9	C(67)–C(66)–C(65)	120.0003	–	119	O(74)–V(72)–N(26)	90	–
10	O(69)–C(67)–C(66)	111.531	124.3	120	O(69)–V(72)–N(61)	179.9997	–
11	O(69)–C(67)–C(62)	128.4687	124.3	121	O(69)–V(72)–O(34)	90	–
12	C(66)–C(67)–C(62)	119.9986	120	122	O(69)–V(72)–N(26)	90.0001	–
13	H(109)–C(63)–C(64)	120	120	123	N(61)–V(72)–O(34)	89.9999	–
14	H(109)–C(63)–C(62)	119.9998	120	124	N(61)–V(72)–N(26)	90.0002	–
15	C(64)–C(63)–C(62)	120.0002	–	125	O(34)–V(72)–N(26)	90.0001	–
16	H(107)–C(54)–C(55)	120.2968	120	126	H(35)–C(33)–C(27)	119.9998	120
17	H(107)–C(54)–C(53)	120.297	120	127	H(35)–C(33)–N(26)	119.9997	116.5
18	C(55)–C(54)–C(53)	119.4062	–	128	C(27)–C(33)–N(26)	120.0005	123.5
19	H(106)–C(53)–C(54)	120.3246	120	129	H(78)–O(76)–H(77)	119.9995	–
20	H(106)–C(53)–C(52)	120.3253	120	130	H(78)–O(76)–V(71)	120.0004	–
21	C(54)–C(53)–C(52)	119.3502	–	131	H(77)–O(76)–V(71)	120.0001	–
22	H(108)–C(55)–C(56)	120.0002	120	132	V(71)–O(58)–C(56)	109.5001	–
23	H(108)–C(55)–C(54)	120	120	133	V(71)–N(57)–C(59)	120.0003	–
24	C(56)–C(55)–C(54)	119.9999	–	134	V(71)–N(57)–C(42)	119.9998	–
25	O(58)–C(56)–C(55)	115.699	124.3	135	C(59)–N(57)–C(42)	114.9999	–
26	O(58)–C(56)–C(51)	124.3001	124.3	136	V(71)–O(23)–C(21)	109.4998	–
27	C(55)–C(56)–C(51)	119.9989	120	137	H(92)–C(20)–C(21)	120.0002	120
28	H(105)–C(52)–C(53)	119.9996	120	137	H(92)–C(20)–C(19)	120.0001	120
29	H(105)–C(52)–C(51)	120.0002	120	139	C(21)–C(20)–C(19)	119.9996	–
30	C(53)–C(52)–C(51)	120.0002	–	140	H(91)–C(19)–C(20)	124.6011	120
31	C(68)–C(62)–C(67)	119.9999	120	141	H(91)–C(19)–C(18)	124.6013	120
32	C(68)–C(62)–C(63)	119.9988	120	142	C(20)–C(19)–C(18)	110.7976	–
33	C(67)–C(62)–C(63)	119.9988	120	143	H(90)–C(18)–C(19)	124.6019	120
34	H(70)–C(68)–C(62)	119.9999	120	144	H(90)–C(18)–C(17)	124.6013	120
35	H(70)–C(68)–N(61)	120.0001	116.5	145	C(19)–C(18)–C(17)	110.7968	–
36	C(62)–C(68)–N(61)	120	123.5	146	O(23)–C(21)–C(20)	115.6987	124.3
37	H(103)–C(49)–C(50)	137.9078	120	147	O(23)–C(21)–C(16)	124.3003	124.3
38	H(103)–C(49)–C(48)	137.9074	120	148	C(20)–C(21)–C(16)	119.9989	120
39	C(50)–C(49)–C(48)	84.1848	–	149	H(89)–C(17)–C(18)	120	120
40	N(61)–C(48)–C(49)	119.9999	120	150	H(89)–C(17)–C(16)	120	120
41	N(61)–C(48)–C(47)	119.9986	120	151	C(18)–C(17)–C(16)	120	–
42	C(49)–C(48)–C(47)	119.999	120	152	C(24)–C(16)–C(21)	140.0803	120
43	H(102)–C(47)–C(48)	144.7547	120	153	C(24)–C(16)–C(17)	99.9193	120
44	H(102)–C(47)–C(46)	144.7544	120	154	C(21)–C(16)–C(17)	119.9995	120
45	C(48)–C(47)–C(46)	70.4909	–	155	O(76)–V(71)–O(73)	95.1862	–
46	H(104)–C(50)–C(49)	145.0758	120	156	O(76)–V(71)–O(58)	115.7977	–
47	H(104)–C(50)–C(45)	145.0758	120	157	O(76)–V(71)–N(57)	45.3302	–
48	C(49)–C(50)–C(45)	69.8484	–	158	O(76)–V(71)–O(23)	154.1071	–
49	H(101)–C(46)–C(47)	137.5888	120	159	O(76)–V(71)–N(22)	70.4684	–
50	H(101)–C(46)–C(45)	137.5891	120	160	O(73)–V(71)–O(58)	82.7958	–
51	C(47)–C(46)–C(45)	84.8221	–	161	O(73)–V(71)–N(57)	90.0001	–
52	C(50)–C(45)–C(46)	119.9986	120	162	O(73)–V(71)–O(23)	90	–
53	C(50)–C(45)–S(36)	119.9987	–	163	O(73)–V(71)–N(22)	159.2605	–
54	C(46)–C(45)–S(36)	120.0003	–	164	O(58)–V(71)–N(57)	159.2607	–
55	H(100)–C(44)–C(43)	119.9998	120	165	O(58)–V(71)–O(23)	90	–
56	H(100)–C(44)–C(39)	119.9998	120	166	O(58)–V(71)–N(22)	90	–
57	C(43)–C(44)–C(39)	120.0004	–	167	N(57)–V(71)–O(23)	109.4998	–
58	C(45)–S(36)–C(39)	109.5003	–	168	N(57)–V(71)–N(22)	90.0003	–
59	C(45)–S(36)–O(38)	109.4618	–	169	O(23)–V(71)–N(22)	109.5	–
60	C(45)–S(36)–O(37)	109.442	–	170	H(25)–C(24)–N(22)	124.6646	116.5
61	C(39)–S(36)–O(38)	109.4615	–	171	H(25)–C(24)–C(16)	124.664	120
62	C(39)–S(36)–O(37)	109.4419	–	172	N(22)–C(24)–C(16)	110.6714	123.5
63	O(38)–S(36)–O(37)	109.5197	116.6	173	V(72)–N(26)–C(33)	119.9996	–

Table 6b$_2$ (*continued*)

S. No.	Atoms	Actual bond angles	Optimal bond angles	S. No.	Atoms	Actual bond angles	Optimal bond angles
64	C(44)–C(39)–C(40)	119.9987	120	174	V(72)–N(26)–C(13)	120.0001	–
65	C(44)–C(39)–S(36)	120	–	175	C(33)–N(26)–C(13)	115.0003	–
66	C(40)–C(39)–S(36)	119.9988	–	176	H(87)–C(14)–C(15)	119.9999	120
67	H(97)–C(40)–C(41)	120.003	120	177	H(87)–C(14)–C(13)	119.9999	120
68	H(97)–C(40)–C(39)	120.0032	120	178	C(15)–C(14)–C(13)	120.0002	–
69	C(41)–C(40)–C(39)	119.9938	–	179	N(26)–C(13)–C(14)	119.9999	120
70	H(99)–C(43)–C(44)	120.0004	120	180	N(26)–C(13)–C(12)	119.9991	120
71	H(99)–C(43)–C(42)	120	120	181	C(14)–C(13)–C(12)	119.9984	120
72	C(44)–C(43)–C(42)	119.9996	–	182	H(86)–C(12)–C(13)	120.0079	120
73	H(98)–C(41)–C(42)	120.0008	120	183	H(86)–C(12)–C(11)	120.008	120
74	H(98)–C(41)–C(40)	120.0005	120	184	C(13)–C(12)–C(11)	119.9841	–
75	C(42)–C(41)–C(40)	119.9987	–	185	H(88)–C(15)–C(14)	120.0001	120
76	C(59)–C(51)–C(56)	106.5371	120	186	H(88)–C(15)–C(10)	120.0001	120
77	C(59)–C(51)–C(52)	133.4032	120	187	C(14)–C(15)–C(10)	119.9998	–
78	C(56)–C(51)–C(52)	120.0557	120	188	H(85)–C(11)–C(12)	120.0081	120
79	H(60)–C(59)–N(57)	145.4489	116.5	189	H(85)–C(11)–C(10)	120.0081	120
80	H(60)–C(59)–C(51)	145.4491	120	190	C(12)–C(11)–C(10)	119.9838	
81	N(57)–C(59)–C(51)	69.102	123.5	191	C(15)–C(10)–C(11)	119.9989	120
82	N(57)–C(42)–C(43)	119.9987	120	192	C(15)–C(10)–S(1)	119.9988	–
83	N(57)–C(42)–C(41)	119.9999	120	193	C(11)–C(10)–S(1)	119.9998	–
84	C(43)–C(42)–C(41)	119.9989	120	194	V(71)–N(22)–C(24)	119.9999	–
85	H(80)–O(75)–H(79)	119.9994	–	195	V(71)–N(22)–C(7)	119.9999	–
86	H(80)–O(75)–V(72)	120.0002	–	196	C(24)–N(22)–C(7)	115.0001	–
87	H(79)–O(75)–V(72)	120.0004	–	197	H(83)–C(8)–C(9)	120.0004	120
88	V(72)–O(69)–C(67)	42.58	–	198	H(83)–C(8)–C(7)	120.0001	120
89	V(72)–N(61)–C(68)	120.0001	–	199	C(9)–C(8)–C(7)	119.9995	–
90	V(72)–N(61)–C(48)	119.9996	–	200	N(22)–C(7)–C(8)	119.9996	120
91	C(68)–N(61)–C(48)	115	–	201	N(22)–C(7)–C(6)	119.9986	120
92	V(72)–O(34)–C(32)	97.6087	–	202	C(8)–C(7)–C(6)	119.9993	120
93	H(96)–C(31)–C(32)	119.9995	120	203	H(82)–C(6)–C(7)	120.0079	120
94	H(96)–C(31)–C(30)	120.0004	120	204	H(82)–C(6)–C(5)	120.0081	120
95	C(32)–C(31)–C(30)	120.0001		205	C(7)–C(6)–C(5)	119.984	–
96	H(95)–C(30)–C(31)	138.0414	120	206	H(84)–C(9)–C(8)	119.9997	120
97	H(95)–C(30)–C(29)	138.042	120	207	H(84)–C(9)–C(4)	120.0003	120
98	C(31)–C(30)–C(29)	83.9166	–	208	C(8)–C(9)–C(4)	120	–
99	H(94)–C(29)–C(30)	138.0414	120	209	H(81)–C(5)–C(6)	120.009	120
100	H(94)–C(29)–C(28)	138.0417	120	210	H(81)–C(5)–C(4)	120.0088	120
101	C(30)–C(29)–C(28)	83.9168	–	211	C(6)–C(5)–C(4)	119.9822	–
102	O(34)–C(32)–C(31)	138.4832	124.3	212	C(9)–C(4)–C(5)	120.0003	120
103	O(34)–C(32)–C(27)	101.0414	124.3	213	C(9)–C(4)–S(1)	119.9984	–
104	C(31)–C(32)–C(27)	119.9997	120	214	C(5)–C(4)–S(1)	119.9988	–
105	H(93)–C(28)–C(29)	119.9996	120	215	C(10)–S(1)–C(4)	109.5002	–
106	H(93)–C(28)–C(27)	120.0001	120	216	C(10)–S(1)–O(3)	109.4618	–
107	C(29)–C(28)–C(27)	120.0003	–	217	C(10)–S(1)–O(2)	109.4418	–
108	C(33)–C(27)–C(32)	120	120	218	C(4)–S(1)–O(3)	109.4619	–
109	C(33)–C(27)–C(28)	119.9989	120	219	C(4)–S(1)–O(2)	109.4418	–
110	C(32)–C(27)–C(28)	119.9986	120	220	O(3)–S(1)–O(2)	109.5198	116.6

(iii) [Molecular ion]$^+$ (772.94) – *[$C_4N_3H_4SO_2$]$^+$ (157) –**[$C_4N_3H_4SO_2$]$^+$ (157) = 458.94 ~ 460.
(iv) [Molecular ion]$^+$ (772.94) – *[$C_4N_3H_4SO_2$]$^+$ (157) – 3H$^+$ = 612.94 ~ 613.
(v) [Molecular ion]$^+$ (772.94) = 772.94 ~ 773.

* = From one diazine moiety; ** = from another diazine moiety.

From the above fragmentation patterns it appears that the mass spectral data are consistent with proposed formulation of the complex in question.

3.5. Electronic spectral studies

The electronic spectra of the complexes were recorded in 10^{-3} M dimethylformamide solutions in the range of 280–800 nm solutions, and the spectral data are given in Table 5. Besides high intensity charge transfer transitions, compound (**1**), (**3**), (**4**) and (**5**) displayed one low intensity d–d transition assignable to $b_2 \rightarrow {}^1a_1^*$ while compound (**2**) exhibited two low intensity d–d transitions at 339 and 426 nm assignable to $b_2 \rightarrow {}^1a_1^*$ and $b^2 \rightarrow b_1^*$, respectively (Maurya et al., 1997). The assignment of $b_2 \rightarrow {}^1a_1^*$ transition in each case assumes idealized C_2v symmetry. These spectra are typical of oxovanadium(IV) complexes (Maurya and Rajput, 2004; Dutta and Syamal, 1993). The electronic spectrum of compound, [VO(sal-sdz)$_2$(H_2O)]·H_2O (**1**) is shown in Fig. 8.

3.6. Magnetic studies

The observed magnetic moments of the compounds (**1**)–(**4**) at room temperature are in the range 1.68–1.74 B.M., expected for monomeric oxovanadium(IV) complexes. A low magnetic moment value of 1.61 B.M. of compound (**5**) suggests spin quenching most probably due to ligand bridged dimeric structure (Maurya et al., 2008b) for this complex. This is

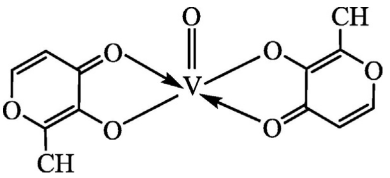


Figure 12 Structure of bis(maltolato)oxovanadium(IV).

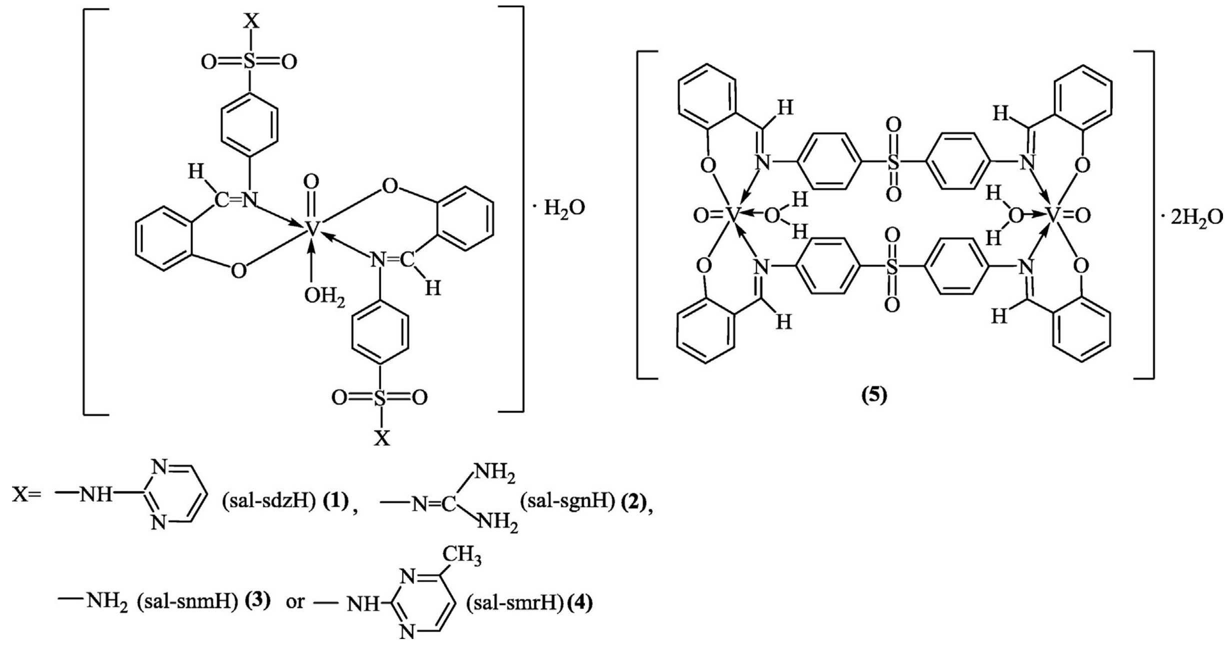


Figure 13 Proposed structure of complexes.

consistent with the zigzag straight line ESR spectrum of this compound (*vide supra*).

3.7. Conductance measurements

The observed molar conductance (14.1–24.3 ohm^{-1} cm^2 mol^{-1}) in 10^{-3} molar DMF solutions of these complexes are given in Table 2, and are consistent with the non-electrolytic (Geary, 1971) nature of these complexes. Such a non-zero molar conductance value for each complex in the present study is most probably due to the strong donor capacity of DMF, which may lead to the displacement of anionic ligand and change of electrolyte type.

4. 3D Molecular modeling

Keeping in view the hexa-coordination of all the complexes (*vide infra*) and also taking into account the well established crystal structure (Melchior et al., 1999) of bis(picolinato)oxovanadium(IV) (Fig. 9) (having a monoprotic bidentate (O, N)-donor) picolinate ligand, similar to monoprotic (O, N)-donor LH ligands in the present investigation, the molecular modelings of two representative compounds, [VO(sal-snm)$_2$(H_2O)]·H_2O (**3**) and [VO(sal-dadps)(H_2O)]$_2$·$2H_2O$ (**5**) were carried out with the CS Chem 3D Ultra Molecular Modeling and Analysis Program. These are based on their octahedral structures with axial oxo group and water molecule *trans* to O (oxo), and the two molecules of O,N-donor sal-snm/sal-dadps ligand at the equatorial positions in *cis* arrangement. Alternative structures of these compounds having water molecule *cis* to O (oxo) were not considered suitable due to steric reason of the ligand sal-snm/sal-dadps. The details of bond lengths, bond angles as per the 3D structures (Figs. 10 and 11) are given in Tables 6a$_1$,a$_2$, and Tables 6b$_1$,b$_2$, respectively. For convenience of looking over the different bond lengths and bond angles, the various atoms in the two compounds in question are numbered in Arabic numerals. Compound (**3**) displays a total of 192 measurements of the bond lengths (70 in number), plus the bond angles (122 in number), while compound (**5**) displays a total of 344 measurements of the bond lengths (124 in number), plus the bond angles (220 in number). Except few cases, optimal values of both the bond lengths and the bond angles are given in Tables 6a$_1$–b$_2$ along with the actual ones. The actual bond lengths/bond angles given in Tables 6a$_1$–b$_2$ are obtained as a result of energy optimization in CHEM 3D Ultra (http://www.cambridgesoft.com), while the optimal bond length/optimal bond angle values are the most desirable/favorable (standard) bond lengths/bond angles established by the builder unit of the CHEM 3D. The missing of some values of standard bond lengths/bond angles may be due to the limitations of the software, which we had already noticed in the modeling of other systems (Maurya et al., 2007, 2008, 2010a, 2015a,b,c). In most of the cases, the actual bond lengths and bond angles are close to the optimal values, and thus the proposed structures of compounds (**3**) and (**5**) (and also others) are acceptable (Maurya et al., 2007, 2008, 2010b, 2015a,b,c,d).

5. Conclusions

The satisfactory analytical data coupled with the studies presented above suggest that the complexes prepared in this investigation are of the general composition [VO(L)$_2$(H_2O)]·H_2O and [VO(sal-dadps)(H_2O)]$_2$·$2H_2O$, where, LH = sal-sdzH, sal-sgnH, sal-snmH or sal-smrH. Keeping in view the monomeric hexacoordination and the dimeric hexacoordination of compound, and the well documented crystal structure (Burguess et al., 1997) of bis(maltolato)-oxovanadium(IV) (BMOV) (Fig. 12) involving a monomeric bidentate (O, O) donor ligand (similar to (O, N)-donor in the present investigation), octahedral structures (Fig. 13) with an axial oxo group have been proposed for complexes (**1**)–(**5**). Maurya et al. have already proposed a similar octahedral structure (Maurya et al., 2002a,b) (for hexacoordination oxovanadium(IV) complexes).

In complex (**5**) the Schiff base ligand behaves as a dibasic tetradentate ligand which on reaction with VO^{2+} forms a stable binuclear oxovanadium(IV) complex. The neighboring vanadyl group participates in spin-spin exchange interaction (Maurya et al., 1997) leading to subnormal magnetic moment.

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