



ORIGINAL ARTICLE

Oxovanadium(IV) complexes of medicinal relevance: Synthesis, characterization, and 3D-molecular modeling and analysis of some oxovanadium(IV) complexes in O,N-donor coordination matrix of sulfa drug Schiff bases derived from a 2-pyrazolin-5-one derivative



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3D Molecular modeling

Abstract The present paper reports the synthesis and characterization of some new oxovanadium(IV) complexes of composition $[\text{VO}(\text{L})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, where $\text{LH} = N$ -(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)sulfadiazine (bumphp-sdzH), N -(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)sulfaguandine (bumphp-sgnH), N -(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)sulfani-lamide (bumphp-snmH), and N -(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)sulfamerazine (bumphp-smrH). These complexes were prepared by the reaction of vanadyl sulfate pentahydrate with the ligands in 1:2 metal–ligand ratios, in ethanol. The compounds so obtained were characterized by different physicochemical studies, such as, elemental analyses, molar conductance, and magnetic measurements, thermogravimetry, cyclic voltammetry, infrared, electron spin resonance, and electronic spectral studies. The overall IR studies conclude that the ligands in the present investigation behave as monobasic bidentate O,N-donors. The 3D molecular

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modeling and analysis for bond lengths and bond angles have also been carried out for one of the representative compounds, $[\text{VO}(\text{bump-}p\text{-sdz})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (**1**) to substantiate the proposed structure. Based on these studies suitable octahedral structures have been proposed for these complexes.

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1. Introduction

Acylpyrazolones, originally investigated by Jensen (1959a,b), have been employed for several applications (Marchetti et al., 2000a,b), viz., as pigments for dyes, as metal extractants from acidic solutions and also as sequestering agents toward polluting metal ions, such as cadmium and lead. These ligands have played and continue to play an important role in the development of coordination compounds that have found wide application in several fields, from new materials to catalysts, as precursors for CVD in the microelectronic industry and as potential antitumourals (Marchetti et al., 2005).

The pyrazolone derivatives have been reported to possess strong antibacterial, antihistaminic and antifungal, analgesic, antipyretic, anti-inflammatory, and anti-rheumatic activities (Merck Index, 1983). They also show antidiabetic (Goodman and Gilman, 1970), anticancer (Garg and Singh, 1970), and antineoplastic (Wilson and Bottiglieri, 1962) properties.

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; Sawinski et al., 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 (Encio 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 the modification of the structural $-\text{S}(\text{O})_2\text{N}(\text{H})-$ feature. The synthesis of metal sulfonamide compounds had received much attention due to the fact that sulfanilamides were the first effective chemotherapeutic agents to be employed for the prevention and cure of bacterial infections in humans (Mohamed and Gad-Elkareem, 2007). The pharmacological activity of these types of molecules is often enhanced by complexation with metal ions (Bult and Sigel, 1983; Casanova et al., 1983). Moreover, some metal complexes of these ligands have been found to promote rapid healing of burns in human and animals (De Oliveira et al., 2008; Baenziger et al., 1983).

Vanadium plays an important role in life and one of its most relevant properties identified thus far is its capacity to act as an insulin-enhancing agent, either in the form of its inorganic salts or complexes with organic ligands (Rangel et al., 2006). It has been observed that simple inorganic vanadium compounds are more toxic than vanadium compounds with organic ligands and the efficacy of metal based therapeutic agents' changes drastically by making changes in the organic ligands that are attached to the metal center (Mahroof-Tahir et al., 2005). For any complex considered for therapeutic use, it is important to consider the intrinsic toxicity of the ligand, especially if the treatment is predicted for long periods (Pressoa et al., 2003). Great efforts have, therefore, been made

to synthesize oxovanadium(IV) complexes of high biological activity and low toxicity which are readily absorbed. Many oxovanadium(IV) complexes with various coordination modes (Thompson and Orvig, 2001; Sakurai et al., 2002; Thompson et al., 1999; Maurya and Rajput, 2006; Ghosh et al., 2005) have been prepared, viz., $\text{VO}(\text{O}_4)$, $\text{VO}(\text{S}_2\text{N}_2)$, $\text{VO}(\text{S}_4)$, $\text{VO}(\text{N}_3\text{O})$, and $\text{VO}(\text{N}_2\text{O}_2)$, and the relationship between their structures and insulin-mimetic activities has been examined by evaluating both *in vivo* and *in vitro* results. The bis(ethylmaltoato)oxovanadium(IV) (BEOV) has completed phase I clinical trial in humans in the treatment of type-1 and type-2 diabetes mellitus (Thompson and Orvig, 2006).

Besides the antidiabetic action, vanadium complexes are known to possess potent anticancer activity (Kieler et al., 1965; Dessoize, 2004), which deserves increasing attention for the application to biomedical sciences (Etcheverry et al., 2008). Recent studies indicate the chemopreventive efficacy of vanadium in the inhibition of chemically induced carcinomas of the liver, colon, and mammary gland and has substantially documented the role of vanadium in the prevention of DNA-protein crosslinks, DNA chain break, chromosomal aberrations (Molinuevo et al., 2008; Chakraborty et al., 2006; Chattopadhyay et al., 2005; Kanna et al., 2004, 2005; Ray et al., 2004, 2005), reduction of tumor incidence and average number of tumors (33, Bishayee et al., 2000; Kanna et al., 2003), suppression of tumor marker genes like GST, GST-P, GGT, and MT (Ray et al., 2004). On the other hand, when using *in vitro* models it has been shown that some vanadium complexes displayed antitumoural actions (Barrio et al., 2003; D'Cruz and Uckun, 2002; Ding et al., 1999; Etcheverry et al., 2002; Evangelou et al., 2002; Molinuevo et al., 2004). Knowledge gained from *in vitro* studies has advanced vanadium research into the preclinical *in vivo* phase (Bishayee et al., 2010).

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).

Recent studies (D'Cruz et al., 2003; Shigeta et al., 2003) showed that oxovanadium complexes of thiourea and vanadium substituted polyoxotungstates exhibit potent anti-HIV properties toward infected immortalized T-cells. However, the instability of vanadium(IV) complexes under physiological conditions has been frequently encountered (Raymond et al., 2007). Some oxovanadium(IV) complexes of porphyrin derivatives $\{[\text{VO}(\text{N}_4)]\}$ type were evaluated for their inhibitory effects on HIV-1(BaL) (Human Immunodeficiency Virus) replication in Hut/CCR5 cells (Raymond et al., 2007).

Earlier reports from our laboratory described the synthesis and characterization of metal chelates of ruthenium(II) (Maurya et al., 1994), dioxomolybdenum(VI) (Maurya et al.,

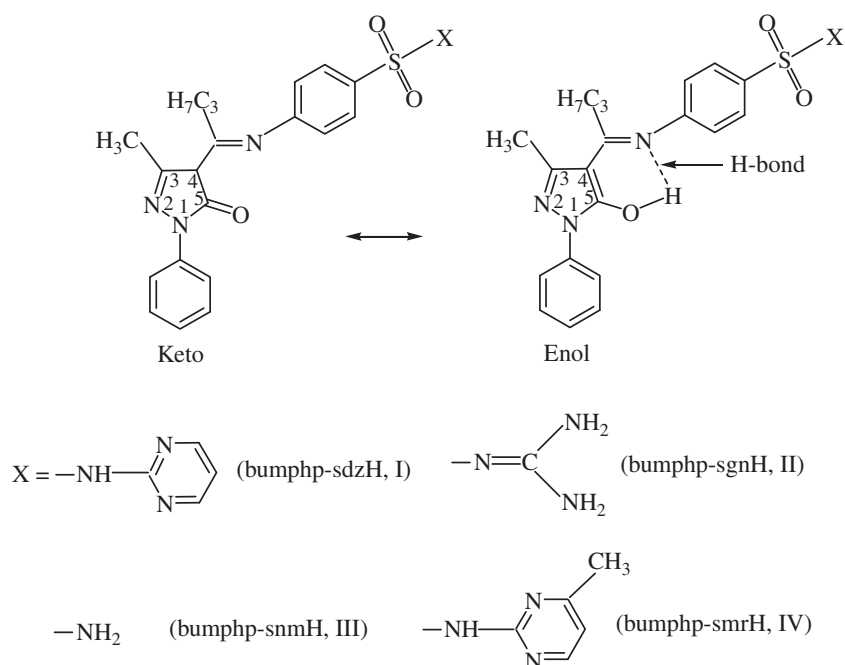


Figure 1 Keto-enol tautomerism and intramolecular hydrogen bonding in Schiff bases.

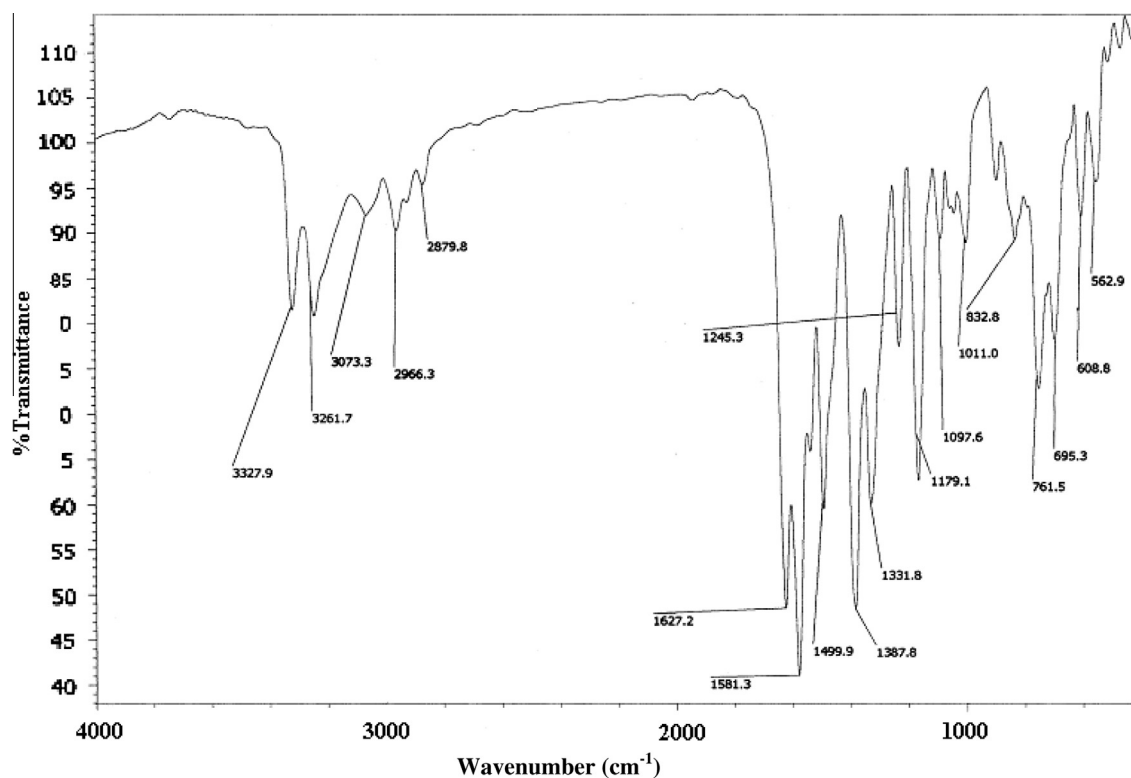


Figure 2 IR spectrum of bumphp-snmH (III).

2004, in press), oxovanadium(IV) (Maurya and Rajput, 2006), Cu(II), Ni(II), Co(II), Zn(II), Sm(III), Th(IV), and U(VI)O₂ (Maurya et al., 2007) chelates with some Schiff base ligands derived from sulfa drugs.

Considering the pronounced biological activity of acylpyrazolones, and of sulfa drug derivatives, in view of the importance of vanadium compounds mentioned above, and also extending our search for more efficacious vanadium compounds,

a study was undertaken of the coordination chemistry of oxovanadium(IV) complexes {[VO(N₂O₂)] type} involving pyrazolone based sulfa drug Schiff bases, viz., *N*-(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)sulfadiazine (bumphp-sdzH, I), *N*-(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)sulfaguanidine (bumphp-sgnH, II), *N*-(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)sulfanilamide (bumphp-snmH, III), and *N*-(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)sulfamerazine (bumphp-smrH, IV) (Fig. 1). The present communication describes the results of such a study.

2. Experimental

2.1. Materials

Vanadyl sulfate pentahydrate, calcium hydroxide, butyryl chloride, dimethyl formamide, sulfa drugs, viz., sulfamerazine (Thomas Baker Co. Ltd., Mumbai, India), sulfadiazine, sulphaguanidine and sulfanilamide (Sigma Chemicals Co., USA), and 3-methyl-1-phenyl-2-pyrazolin-5-one (Lancaster Research Chemicals, England) were used as supplied. All other chemicals used were of analytical grade.

2.2. Preparation of 3-methyl-1-phenyl-4-butyryl-2-pyrazolin-5-one (bumphpH)

It was prepared by the method reported elsewhere (Jensen, 1959a,b) with modification. Into a 1-L 3-necked quick fit flask containing DMF (100 mL) and carrying a dropping funnel, a mechanical stirrer, and a reflux condenser was placed 3-methyl-1-phenyl-2-pyrazolin-5-one (17 g, 0.098 mol). A solution was obtained by gentle heating and stirring. Calcium hydroxide (10 g, 0.14 mol) was added and butyryl chloride (10.33 mL) was added drop wise within 2–3 min. The reaction was exothermic and the reaction mixture became a paste. The mixture was allowed to cool and then refluxed with stirring for 1 h on a sand bath, during which period, the bright yellow complex, formed initially, turned yellowish brown. The complex was decomposed by pouring the reaction mixture into chilled dilute hydrochloric acid solution (500 mL, 2 N). A yel-

lowish brown solid settled, which was filtered on a sintered glass crucible, washed with distilled water until the washings were colorless and dried in air and recrystallized from *n*-heptane. Melting point, 65 °C, yield, 70%.

2.3. Synthesis of Schiff bases

The Schiff bases with sulfa drugs were prepared as follows: An ethanolic solution (15 mL) of bumphpH (0.488 g, 2 mmol) was added to the solution of sulfadiazine (0.500 g, 2 mmol), sulfanilamide (0.344 g, 2 mmol), sulfaguanidine (0.428 g, 2 mmol), or sulfamerazine (0.528 g, 2 mmol) in ethanol. The resulting solution was refluxed with stirring for 4–5 h and then filtered to remove the insoluble sulfa drug, if any. The filtrate so obtained was concentrated on a water bath and left overnight at room temperature when colored crystals of Schiff bases separated out from their respective solutions. The crystals thus obtained were washed with ethanol and dried *in vacuo*. The characterization data of Schiff bases are given in Tables 1 and 2.

2.4. Synthesis of complexes

The following general procedure was used in the synthesis of all the complexes. The salt VOSO₄·5H₂O (0.253 g, 1 mmol) was dissolved in 5 mL of water and this solution was added to a warmed, stirred ethanolic solution (~15 mL) of the corresponding Schiff bases, bumphp-sdzH (0.952 g, 2 mmol), bumphp-sgnH (0.880 g, 2 mmol), bumphp-snmH (0.796 g, 2 mmol) or bumphp-smrH (0.980 g, 2 mmol). The resulting solution was refluxed for 10–12 h and then concentrated to half of its volume. The resulting colored precipitate was filtered and washed several times with ethanol to remove the unreacted ligand and the metal salt. The product was dried *in vacuo*. The analytical data are given in Table 3.

2.5. Analyses

Carbon, hydrogen, and nitrogen were determined micro-analytically at SAIF, Indian Institute of Technology, Mumbai.

Table 1 Characterization data of the synthesized sulfa drug Schiff base ligands.

S. No.	Schiff bases (empirical formula) (F.W.)	Found/(calcd.)%			Color	Decomp. temp. (°C)
		C	H	N		
I	bumphp-sdzH (C ₂₄ H ₂₄ N ₆ SO ₃) (476)	60.12 (60.50)	5.38 (5.04)	17.30 (17.65)	Light golden yellow	200
II	bumphp-sgnH (C ₂₁ H ₂₄ N ₆ SO ₃) (440)	57.59 (57.27)	5.78 (5.45)	19.41 (19.09)	Yellow	150
III	bumphp-snmH (C ₂₀ H ₂₂ N ₄ SO ₃) (398)	60.13 (60.30)	5.38 (5.53)	14.39 (14.07)	Daffodil	181
IV	bumphp-smrH (C ₂₅ H ₂₆ N ₆ SO ₃) (490)	61.56 (61.22)	5.16 (5.31)	17.43 (17.14)	Yellow	190

Table 2 IR spectral data of the synthesized ligands.

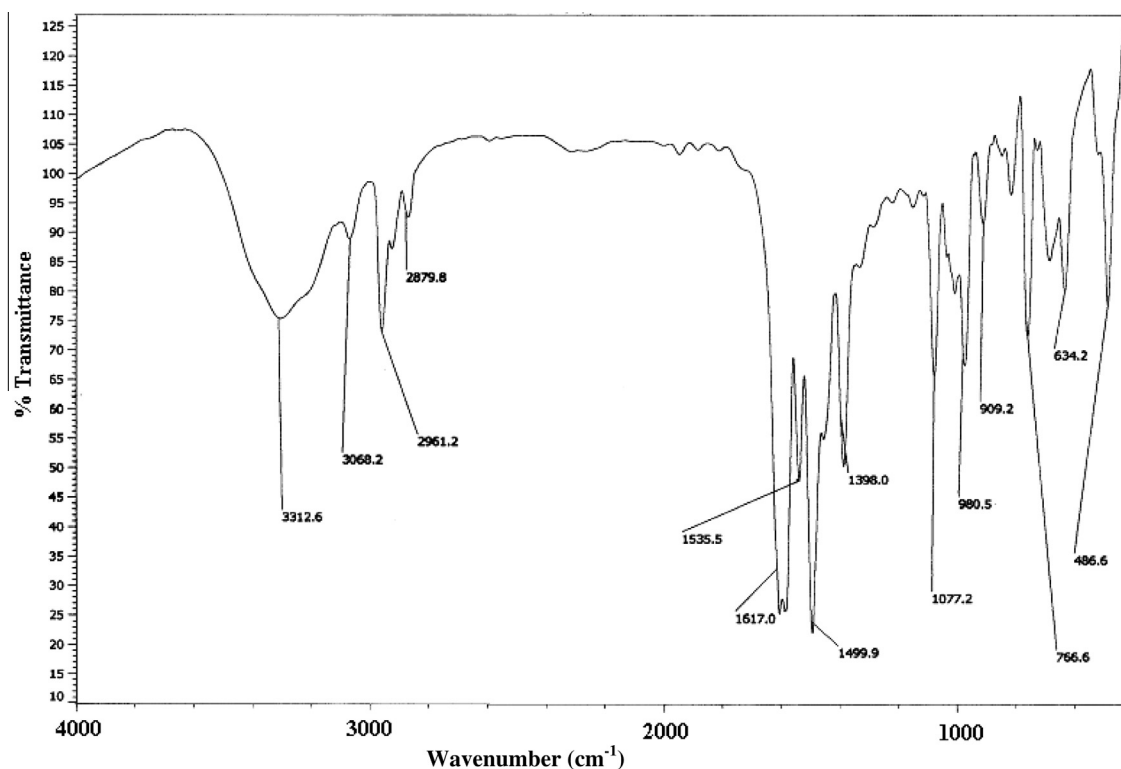
S. No.	Ligands	$\nu(\text{C}=\text{N})$ (azomethine)	$\nu(\text{C}=\text{O})$ (enolic)	$\nu(\text{C}=\text{N}_2)$ (cyclic)	$\nu(\text{NH})/(\text{NH}_2)$	$\nu(\text{OH})$	$\nu_{\text{as}}(\text{O}=\text{S}=\text{O})$
I	bumphp-sdzH	1630	1159	1591	3363	3435	1410
II	bumphp-sgnH	1627	1138	1595	3338 3216	3440	1388
III	bumphp-snmH	1627	1179	1581	3262	3328	1388
IV	bumphp-smrH	1628	1153	1596	3389	3486	1403

Table 3 Analytical data and some physical properties of the synthesized complexes.

S. No.	Complexes (empirical formula, F.W.)	Found/(calcd.)%				Color	Decomp. temp. (°C)	Yield (%)	A_m (Ohm ⁻¹ cm ² mol ⁻¹)	μ_{eff} (B. M.)
		C	H	N	V					
(1)	[VO(bumphp-sdz) ₂ (H ₂ O)]·H ₂ O (C ₄₈ H ₅₂ N ₁₂ O ₁₀ S ₂ V) (1070.94)	54.52 (54.74)	4.64 (4.75)	15.76 (15.96)	4.49 (4.84)	Peppermint	225	65	12.5	1.74
(2)	[VO(bumphp-sgn) ₂ (H ₂ O)]·H ₂ O (C ₄₂ H ₅₀ N ₁₂ O ₉ S ₂ V) (980.94)	51.69 (51.38)	5.32 (5.10)	17.27 (17.13)	5.37 (5.19)	Pastel green	210	40	16.3	1.75
(3)	[VO(bumphp-snm) ₂ (H ₂ O)]·H ₂ O (C ₄₀ H ₄₆ N ₈ O ₉ S ₂ V) (896.94)	53.29 (53.52)	5.37 (5.13)	12.24 (12.49)	5.79 (5.68)	Pistachio	200	50	14.2	1.78
(4)	[VO(bumphp-smr) ₂ (H ₂ O)]·H ₂ O (C ₅₀ H ₅₄ N ₁₂ O ₉ S ₂ V) (1080.94)	55.32 (55.51)	5.13 (5.00)	15.71 (15.54)	4.54 (4.71)	Pastel green	220	50	19.2	17.6

Table 4 Important IR spectral bands of the synthesized complexes.

S. No	Complexes	$\nu(\text{C}=\text{N})$ (azometh.)	$\nu(\text{C}-\text{O})$ (enolic)	$\nu(\text{C}=\text{N}_2)$ (cyclic)	$\nu(\text{V}=\text{O})$	$\nu(\text{V}-\text{O})$	$\nu(\text{V}-\text{N})$	$\nu(\text{OH})$	$\nu(\text{NH})/(\text{NH}_2)$
(1)	[VO(bumphp-sdz) ₂ (H ₂ O)]·H ₂ O	1615	1164	1591	975	639	486	3475 (br)	3348
(2)	[VO(bumphp-sgn) ₂ (H ₂ O)]·H ₂ O	1612	1150	1595	980	634	491	3470 (br)	3317 3245
(3)	[VO(bumphp-snm) ₂ (H ₂ O)]·H ₂ O	1617	1195	1585	980	634	486	3313 (br)	3230
(4)	[VO(bumphp-smr) ₂ (H ₂ O)]·H ₂ O	1607	1180	Merged with $\nu(\text{C}=\text{N})$	990	625	502	3450 (br)	3338

**Figure 3** IR spectrum of [VO(bumphp-snm)₂(H₂O)]·H₂O (3).

The vanadium content of each of the complexes was determined as follows. One hundred milligrams of the sample of the compound were placed in a silica crucible, decomposed by gentle heating and then was added 1–2 mL of concentrated HNO₃, 2–3 times. An orangish mass (V₂O₅) was obtained after decomposing and complete drying. It was dissolved in minimum amount of dilute H₂SO₄, 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 KMnO₄ solution as an oxidizing agent in the presence of sulfuric acid. The amount of vanadium in the sample solution was calculated using the standard (Furman, 1962) relationship: 1 mL of 0.1 N KMnO₄ = 5.094 mg vanadium.

Table 5 Electronic spectral data of the synthesized complexes.

S. No.	Complex	λ_{max} (nm.)	ϵ (L mol ⁻¹ cm ⁻¹)	Peak assignment
(1)	[VO(bumphp-sdz) ₂ (H ₂ O)]·H ₂ O	320 438.5	2492 341	Charge transfer transition $b_2 \rightarrow a_1^*$
(2)	[VO(bumphp-sgn) ₂ (H ₂ O)]·H ₂ O	328 440	2894 270	Charge transfer transition $b_2 \rightarrow a_1^*$
(3)	[VO(bumphp-snm) ₂ (H ₂ O)]·H ₂ O	333 433	3178 294	Charge transfer transition $b_2 \rightarrow a_1^*$
(4)	[VO(bumphp-smr) ₂ (H ₂ O)]·H ₂ O	332 427	3238 267	Charge transfer transition $b_2 \rightarrow a_1^*$

2.6. Physical methods

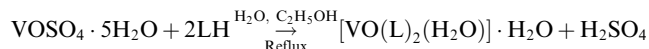
The following physical methods were used in the present investigation. Thermogravimetry of a complex was performed on a Perkin–Elmer Thermoanalyser at S. A. I. F., Indian Institute of Technology, Mumbai. The solid-state infrared spectra were obtained using KBr pellets with a Perkin–Elmer model 1620 FT-IR spectrophotometer at the Central Drug Research Institute, Lucknow. Electronic spectra were recorded on an ATI Unicam UV-1–100 UV/vis 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. Cyclic voltammetric measurements were carried out on an ECDA-001 basic electrochemistry system. A three-electrode system consisting of (i) a platinum disk working electrode, (ii) a platinum wire counter electrode and (iii) a Ag/AgCl reference electrode was used. A 10 mL glass cell with a Teflon cell cover holding working, counter, and reference electrodes and deoxygenating purge tube formed the sample cell. Prior to each run, the working electrode was polished using polishing nylon cloth over a glass plate. The sample solution was deoxygenated by passing purified nitrogen gas through the solution. 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.

2.7. 3D Molecular modeling studies

The 3D molecular modeling of one of the synthesized compounds was carried out on CS Chem 3D Ultra Molecular Modeling and Analysis Programme (www.cambridge-soft.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 oxovanadium(IV) complexes were prepared according to the following equations:



where LH = bumphp-sdzH (1), bumphp-sgnH (2), bumphp-snmH (3), bumphp-smrH (4).

The resulting complexes are soluble in DMF and DMSO, partially soluble in acetonitrile and insoluble in ethanol, methanol, and carbon tetrachloride. They are non-hygroscopic and colored solids. Their physical properties are given in Table 3.

3.1. Infrared spectral studies

The important spectral bands of the synthesized ligands as well as the complexes are presented in Tables 2 and 4, respectively. All of the Schiff base ligands in the present investigation exhibit a broad band centered at 3328–3486 cm⁻¹. This suggests the involvement of the 5-OH group in intramolecular hydrogen (Maurya et al., 1997) bonding with the lone pair of azomethine nitrogen. It also suggests that the ligands exist in enol form in the solid state (Maurya et al., 2002a,b,c).

The Schiff base ligands used in the present investigation contain six potential donor sites: (i) the enolic oxygen; (ii) the cyclic nitrogen, N¹; (iii) the cyclic nitrogen, N²; (iv) the azomethine nitrogen; (v) the sulfonamide (–SO₂NH) oxygen or nitrogen and; (vi) the ring nitrogen of sulfa drug. All the Schiff base ligands show a sharp and strong band due to $\nu(\text{C}=\text{N})$ of the azomethine group at 1627–1630 cm⁻¹. The observed low-energy shift of this band in the chelates and appearing at 1607–1617 cm⁻¹, suggests the coordination of the azomethine nitrogen (Maurya et al., 2002a,b,c).

The $\nu(\text{C}=\text{N}^2)$ (cyclic) band arising from the pyrazolone moiety of the ligands appears at 1581–1596 cm⁻¹ and does not show any appreciable change in its respective positions in the complexes. This observation indicates the non-participation of the ring nitrogen N² in coordination. The coordination of the ring nitrogen N¹ is unfavorable due to the steric demand of the bulky phenyl ring attached to it.

The $\nu(\text{NH})$ mode of the sulfonamide group/amino group in the uncoordinated Schiff bases remains almost unchanged in the spectra of their complexes (see Tables 2 and 4). This suggests that the sulfonamide nitrogen/amino group is not taking part in coordination. The band appearing at 1388–1410 cm⁻¹ in the ligands is assigned to $\nu_{\text{as}}(\text{O}=\text{S}=\text{O})$. This band remains almost at the same position in the complexes and hence suggests that the sulfonamide oxygen is not taking part in coordination with the metal center. The reaction of the enolic Schiff bases with VO²⁺ ion with the elimination of a proton is revealed by the presence of a new band in the complexes at 1150–1195 cm⁻¹ as compared to that of the Schiff bases at

1138–1179 cm^{-1} due to $\nu(\text{C}=\text{O})$ (enolic) (Maurya et al., 1996). The appearance of a broad band centered at 3313–3475 cm^{-1} and assignable as $\nu(\text{OH})$ suggests the presence of lattice/coordinated water molecules in the complexes.

Most of the oxovanadium(IV) complexes exhibit a strong band near 1000 cm^{-1} , which has been assigned to $\nu(\text{V}=\text{O})$ (Selbin, 1966). In contrast, several oxovanadium(IV) complexes have been reported in which this stretching mode appears at quite lower (Maurya et al., 2001) wave numbers, around 900 cm^{-1} . The shift of $\nu(\text{V}=\text{O})$ band to lower wave numbers has been suggested due to the presence of a slight $\cdots\text{V}=\text{O}\cdots\text{V}=\text{O}\cdots$ type interaction occurring between a vanadyl oxygen of one molecule with a vanadium metal in another molecule (Boas and Pessoa, 1987). In the present work, the $\nu(\text{V}=\text{O})$ mode is found at 975–990 cm^{-1} thereby suggesting the absence of $\cdots\text{V}=\text{O}\cdots\text{V}=\text{O}\cdots$ type interaction in these complexes. The IR spectra of the Schiff base ligand (bumphp-smnH, III) and its complex, $[\text{VO}(\text{bumphp-smn})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (3) are given in Figs. 2 and 3, respectively.

3.2. Electronic spectral studies

The electronic spectra of these compounds were recorded in 10^{-3} M dimethylformamide solutions in the range of 280–800 nm. The λ_{max} of the electronic spectral peaks and the respective molar extinction coefficients along with the tentative assignments are given in Table 5. Besides high intensity charge

transfer transitions, all these complexes displayed one low intensity d–d transition which may be assigned to $b_2 \rightarrow {}^1a_1^*$ transition (Lever, 1984). 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 et al., 1997). The electronic spectrum of the compound, $[\text{VO}(\text{bumphp-sgn})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (2) is shown in Fig. 4.

3.3. ESR spectral studies

The X-band EPR spectra of compounds, (2) and (4) were recorded using the microwave frequencies 9.09 GHz and 9.10 GHz, respectively in frozen DMF solution without DPPH at LNT. Each spectrum shows an eight-line pattern, a characteristic of an unpaired electron being coupled with a vanadium nuclear spin ($I = 7/2$). This means that the unpaired electron is in the vicinity of $I = 7/2$ of its own mother nucleus. Thus, the isotropic ESR spectrum of a magnetically dilute oxovanadium(IV) complex gives $(2 \times 7/2 + 1 = 8 \text{ lines})$. The calculated ESR parameters from the spectra of both the complexes are given in Table 6.

The observed g_{av} values for both the complexes deviate from the free ion value 2.0036, which suggest that the resulting complexes are covalent in nature (Dutta and Syamal, 1993). Moreover, the features of the spectra of these complexes

Table 6 ESR spectral parameters of the complexes.

Compound	$A_{\perp}$	$A_{\parallel}$	A_{av}	$g_{\perp}$	$g_{\parallel}$	g_{av}
$[\text{VO}(\text{bumphp-sgn})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$	180	240	200	1.898	1.896	1.897
$[\text{VO}(\text{bumphp-smr})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$	180	140	166.67	1.90	1.976	1.925

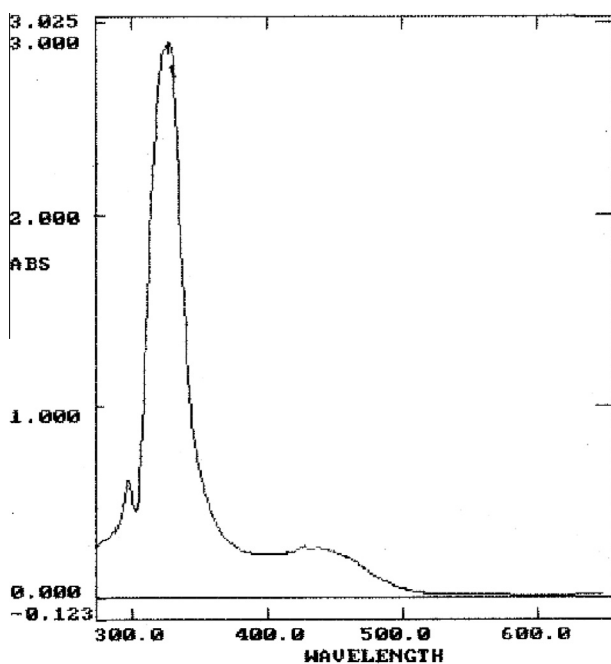


Figure 4 Electronic spectrum of $[\text{VO}(\text{bumphp-sgn})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (2).

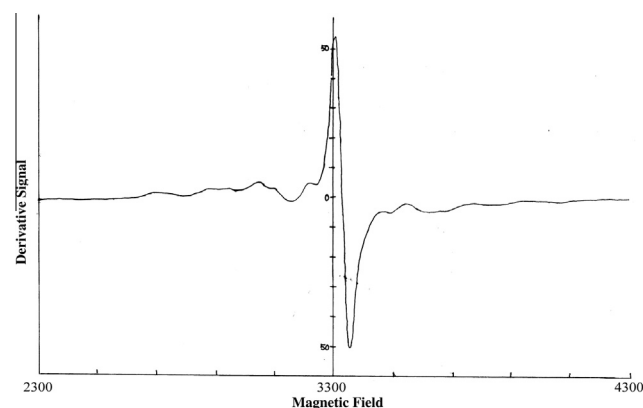


Figure 5a ESR spectrum of $[\text{VO}(\text{bumphp-sgn})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (2).

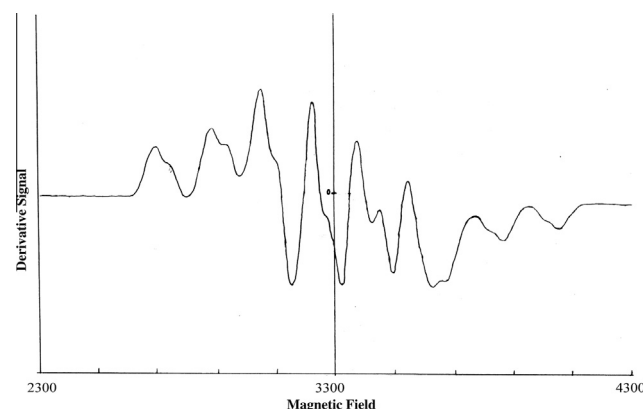


Figure 5b ESR spectrum of $[\text{VO}(\text{bumphp-smr})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (4).

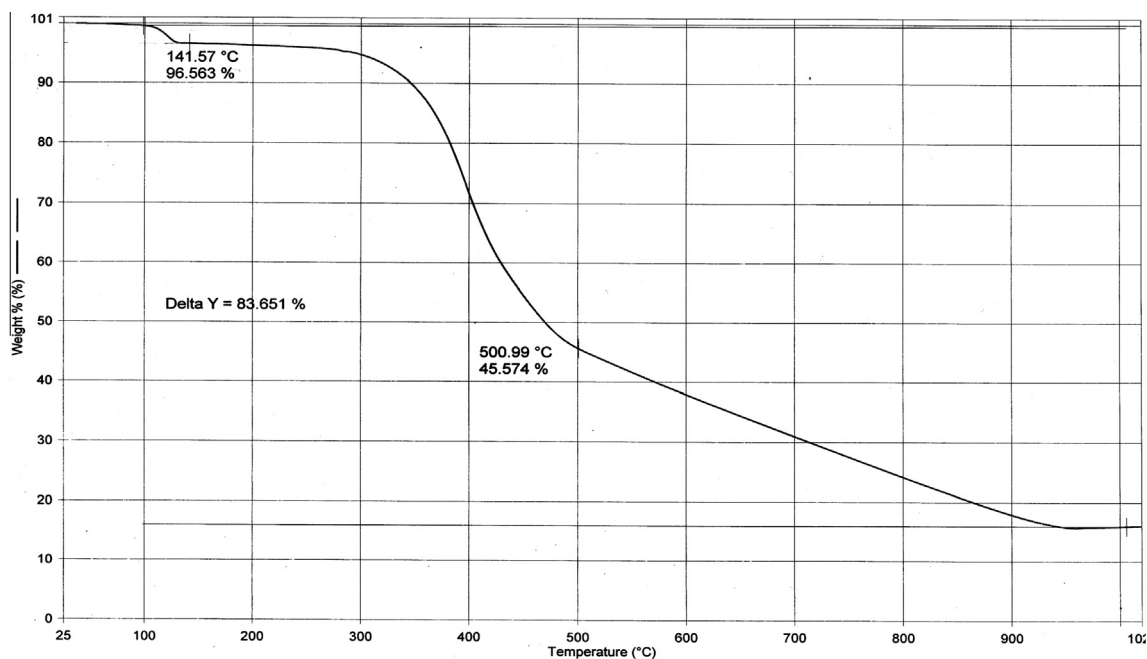


Figure 6 Thermogram of $[\text{VO}(\text{bumphp-snm})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (3).

Table 7 Some important parameters of cyclic voltammogram of the complexes.

Compd.	E_{pc}	E_{pa}	$E_r = \frac{E_{pc} + E_{pa}}{2}$	$E(E_{pc} - E_{pa})$	i_{pc}	i_{pa}	i_{pc}/i_{pa}
(1)	-711.5	-1115.4	-913.45	403.9	155.5	133.4	1.17
(3)	-615.3	-961.6	-788.45	346.3	160	220	0.73

Supporting electrolyte: tetrabutylammonium tetrafluoroborate, $[\text{CH}_3(\text{CH}_2)_3]_4\text{NBF}_4$ (50 mmol); concentration of complexes; 1 mmol; all the potentials are referenced to Ag/AgCl electrode; $E_r = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic potentials.

are indicative of monomeric oxovanadium(IV) complexes (Maurya et al., 2002a,b,c). The ESR spectrum of compounds, $[\text{VO}(\text{bumphp-sgn})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (2) and $[\text{VO}(\text{bumphp-smr})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (4) is given in Fig. 5a and b, respectively.

3.4. Thermogravimetric studies

The thermogram of one of the representative compounds, $[\text{VO}(\text{bumphp-snm})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (3) were recorded in the temperature range from 30 to 1000 °C at a heating rate of 15 °C/min. This compound shows a weight loss of 4% in the temperature range 80–140 °C (calcd. wt. loss for 2 mol of H_2O , 4%). As this weight loss starts from 80 °C and completes around 140 °C, this shows the presence (Maurya et al., 2003; Zhao et al., 2008) of one lattice water and one coordinated water molecule in the complex. After this weight loss, the compound remains stable up to 300 °C and thereafter, shows a steep weight loss. The ultimate weight loss of 84% at ~950 °C roughly corresponds to the removal of all the ligand moieties from the complex (calcd. wt. loss for removal of all the ligand moieties, 92.7%). The final residue attaining a constant weight (observed, 16%) over 950 °C roughly corresponds to V_2O_5 (calculated, 20.27%). This weight loss data, thus, agree well with the IR results for this complex. The thermogram of compound, $[\text{VO}(\text{bumphp-snm})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (3) is given in Fig. 6.

3.5. Magnetic measurements

The magnetically dilute oxovanadium(IV) complexes usually exhibit magnetic moments in line with spin-only value of 1.73 B.M. At room temperature, the observed value of the magnetic moments for the present complexes, are in the range 1.74–1.76 B.M. These data suggest that the complexes under this investigation are mononuclear (Dutta et al., 1997).

3.6. Conductance measurements

The observed molar conductances ($12.5\text{--}19.7\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) in 10^{-3} M DMF solutions of these Schiff base complexes are given in Table 3, and are consistent with the non-electrolytic nature of the complexes. Such a non-zero molar conductance value for each of the complexes 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 (Geary, 1971) type.

3.7. Cyclic voltammetric studies

Cyclic voltammetric measurements of two representative complexes, $[\text{VO}(\text{bumphp-sdz})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (1) and $[\text{VO}(\text{bumphp-snm})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (3), were carried out on an ECDA-001 basic electrochemistry system in order to assess the suitability of

Table 8 Various bond lengths of compound [VO(bumphp-sdz)₂(H₂O)]·H₂O (1).

S. No.	Atoms	Actual bond length	Optimal bond length	S. No.	Atoms	Actual bond length	Optimal bond length
1	C(76)–H(134)	1.113	1.113	71	C(36)–C(37)	1.337	1.42
2	C(76)–H(133)	1.113	1.113	72	C(35)–H(109)	1.1	1.1
3	C(76)–H(132)	1.113	1.113	73	C(35)–C(36)	1.337	1.42
4	C(76)–H(131)	1.113	1.113	74	C(34)–H(108)	1.1	1.1
5	C(2)–H(84)	1.113	1.113	75	C(34)–C(35)	1.337	1.42
6	C(2)–H(83)	1.113	1.113	76	C(33)–H(107)	1.1	1.1
7	C(2)–H(82)	1.113	1.113	77	C(33)–C(34)	1.337	1.42
8	C(2)–H(81)	1.113	1.113	78	C(32)–C(37)	1.337	1.42
9	C(1)–H(80)	1.113	1.113	79	C(32)–C(33)	1.337	1.42
10	C(1)–H(79)	1.113	1.113	80	C(31)–H(106)	1.113	1.113
11	C(1)–H(78)	1.113	1.113	81	C(31)–H(105)	1.113	1.113
12	C(1)–H(77)	1.113	1.113	82	C(30)–H(104)	1.113	1.113
13	N(75)–H(130)	1.05	1.05	83	C(30)–H(103)	1.113	1.113
14	C(74)–H(129)	1.1	1.1	84	C(30)–C(31)	1.523	1.523
15	C(73)–H(128)	1.1	1.1	85	C(29)–H(102)	1.113	1.113
16	C(73)–C(74)	0.9398	1.42	86	C(29)–H(101)	1.113	1.113
17	C(72)–H(127)	1.1	1.1	87	C(29)–H(100)	1.113	1.113
18	C(72)–C(73)	1.337	1.42	88	C(29)–C(30)	1.523	1.523
19	N(71)–C(72)	1.26	1.358	89	N(39)–C(28)	1.266	1.266
20	C(70)–N(75)	1.266	1.462	90	C(28)–C(31)	1.497	1.497
21	C(70)–N(71)	1.26	1.358	91	C(26)–O(27)	1.355	1.355
22	C(74)–N(69)	1.26	1.358	92	C(25)–C(28)	1.337	1.503
23	N(69)–C(70)	1.26	1.358	93	C(25)–C(26)	1.337	1.337
24	N(75)–S(66)	1.696	–	94	C(24)–C(38)	1.497	1.497
25	S(66)–O(68)	1.45	1.45	95	C(24)–C(25)	1.337	1.503
26	S(66)–O(67)	1.45	1.45	96	N(23)–C(24)	1.5526	1.26
27	C(65)–H(126)	1.1	1.1	97	N(22)–C(32)	1.266	1.462
28	C(64)–S(66)	1.79	–	98	N(22)–C(26)	1.266	1.462
29	C(64)–C(65)	1.337	1.42	99	N(22)–N(23)	1.23	1.426
30	C(63)–H(125)	1.1	1.1	100	N(39)–V(21)	2.075	–
31	C(63)–C(64)	1.337	1.42	101	V(21)–O(50)	1.86	–
32	C(62)–H(124)	1.1	1.1	102	V(21)–O(49)	1.5996	–
33	C(62)–C(63)	1.337	1.42	103	O(27)–V(21)	1.86	–
34	C(61)–C(62)	1.337	1.42	104	C(20)–H(99)	1.113	1.113
35	C(60)–H(123)	1.1	1.1	105	C(20)–H(98)	1.113	1.113
36	C(65)–C(60)	1.337	1.42	106	C(20)–H(97)	1.113	1.113
37	C(60)–C(61)	1.337	1.42	107	C(19)–H(96)	1.1	1.1
38	N(59)–H(122)	1.05	1.05	108	C(18)–H(95)	1.1	1.1
39	C(58)–H(121)	1.1	1.1	109	C(18)–C(19)	1.337	1.42
40	C(57)–H(120)	1.1	1.1	110	C(17)–H(94)	1.1	1.1
41	C(57)–C(58)	0.9398	1.42	111	C(17)–C(18)	1.337	1.42
42	C(56)–H(119)	1.1	1.1	112	C(16)–H(93)	1.1	1.1
43	C(56)–C(57)	1.337	1.42	113	C(16)–C(17)	1.337	1.42
44	N(55)–C(56)	1.26	1.358	114	C(15)–H(92)	1.1	1.1
45	C(54)–N(59)	1.266	1.462	115	C(15)–C(16)	1.337	1.42
46	C(54)–N(55)	1.26	1.358	116	C(14)–C(19)	1.337	1.42
47	C(58)–N(53)	1.26	1.358	117	C(14)–C(15)	1.337	1.42
48	N(53)–C(54)	1.26	1.358	118	C(13)–H(91)	1.113	1.113
49	O(50)–H(52)	0.986	–	119	C(13)–H(90)	1.113	1.113
50	O(50)–H(51)	0.986	–	120	C(12)–H(89)	1.113	1.113
51	N(59)–S(46)	1.696	–	121	C(12)–H(88)	1.113	1.113
52	S(46)–O(48)	1.45	1.45	122	C(12)–C(13)	1.523	1.523
53	S(46)–O(47)	1.45	1.45	123	C(11)–H(87)	1.113	1.113
54	C(45)–H(118)	1.1	1.1	124	C(11)–H(86)	1.113	1.113
55	C(44)–S(46)	1.79	–	125	C(11)–H(85)	1.113	1.113
56	C(44)–C(45)	1.337	1.42	126	C(11)–C(12)	1.523	1.523
57	C(43)–H(117)	1.1	1.1	127	V(21)–N(10)	1.8628	–
58	C(43)–C(44)	1.337	1.42	128	C(41)–N(10)	1.266	1.462
59	C(42)–H(116)	1.1	1.1	129	C(9)–C(13)	1.497	1.497
60	C(42)–C(43)	1.337	1.42	130	C(9)–N(10)	1.266	1.266
61	C(41)–C(42)	1.337	1.42	131	O(8)–V(21)	1.86	–
62	C(40)–H(115)	1.1	1.1	132	C(7)–O(8)	1.355	1.355
63	C(45)–C(40)	1.337	1.42	133	C(6)–C(9)	1.337	1.503
64	C(40)–C(41)	1.337	1.42	134	C(6)–C(7)	1.337	1.337
65	C(61)–N(39)	1.266	1.462	135	C(5)–C(20)	1.497	1.497

Table 8 (continued)

S. No.	Atoms	Actual bond length	Optimal bond length	S. No.	Atoms	Actual bond length	Optimal bond length
66	C(38)–H(114)	1.113	1.113	136	C(5)–C(6)	1.337	1.503
67	C(38)–H(113)	1.113	1.113	137	N(4)–C(5)	1.26	1.26
68	C(38)–H(112)	1.113	1.113	138	N(3)–C(14)	1.266	1.462
69	C(37)–H(111)	1.1	1.1	139	N(3)–C(7)	1.266	1.462
70	C(36)–H(110)	1.1	1.1	140	N(3)–N(4)	1.614	1.426

Table 9 Various bond angles of compound [VO(bumphp-sdz)₂(H₂O)]·H₂O (I).

S. No.	Atoms	Actual bond angles	Optimal bond angles	S. No.	Atoms	Actual bond angles	Optimal bond angles
1	H(134)–C(76)–H(133)	109.52	109.47	122	H(109)–C(35)–C(36)	119.9999	120
2	H(134)–C(76)–H(132)	109.4621	109.47	123	H(109)–C(35)–C(34)	120	120
3	H(134)–C(76)–H(131)	109.4618	109.47	124	C(36)–C(35)–C(34)	120.0001	–
4	H(133)–C(76)–H(132)	109.4417	109.47	125	H(108)–C(34)–C(35)	120.0004	120
5	H(133)–C(76)–H(131)	109.4417	109.47	126	H(108)–C(34)–C(33)	119.9996	120
6	H(132)–C(76)–H(131)	109.4999	109.47	127	C(35)–C(34)–C(33)	120	–
7	H(84)–C(2)–H(83)	109.52	109.47	128	H(111)–C(37)–C(36)	119.9993	120
8	H(84)–C(2)–H(82)	109.4619	109.47	129	H(111)–C(37)–C(32)	120.0003	120
9	H(84)–C(2)–H(81)	109.462	109.47	130	C(36)–C(37)–C(32)	120.0004	–
10	H(83)–C(2)–H(82)	109.4417	109.47	131	H(107)–C(33)–C(34)	119.9998	120
11	H(83)–C(2)–H(81)	109.4419	109.47	132	H(107)–C(33)–C(32)	120.0003	120
12	H(82)–C(2)–H(81)	109.4999	109.47	133	C(34)–C(33)–C(32)	119.9999	–
13	H(80)–C(1)–H(79)	109.5197	109.47	134	C(37)–C(32)–C(33)	119.9999	120
14	H(80)–C(1)–H(78)	109.4619	109.47	135	C(37)–C(32)–N(22)	120.0003	120
15	H(80)–C(1)–H(77)	109.4618	109.47	136	C(33)–C(32)–N(22)	119.9998	120
16	H(79)–C(1)–H(78)	109.4421	109.47	137	H(114)–C(38)–H(113)	109.5199	109
17	H(79)–C(1)–H(77)	109.4416	109.47	137	H(114)–C(38)–H(112)	109.462	109
18	H(78)–C(1)–H(77)	109.5001	109.47	139	H(114)–C(38)–C(24)	109.4619	110
19	H(129)–C(74)–C(73)	114.0213	120	140	H(113)–C(38)–H(112)	109.4419	109
20	H(129)–C(74)–N(69)	114.0215	116.5	141	H(113)–C(38)–C(24)	109.4419	110
21	C(73)–C(74)–N(69)	131.9572	123.5	142	H(112)–C(38)–C(24)	109.4998	110
22	H(128)–C(73)–C(74)	120.979	120	143	C(24)–N(23)–N(22)	108.8313	115
23	H(128)–C(73)–C(72)	120.978	120	144	C(62)–C(61)–C(60)	120.0004	120
24	C(74)–C(73)–C(72)	118.043	–	145	C(62)–C(61)–N(39)	120.0001	120
25	H(127)–C(72)–C(73)	120	120	146	C(60)–C(61)–N(39)	119.9995	120
26	H(127)–C(72)–N(71)	119.9999	116.5	147	H(106)–C(31)–H(105)	109.5206	109.4
27	C(73)–C(72)–N(71)	120.0001	123.5	148	H(106)–C(31)–C(30)	109.462	109.41
28	C(72)–N(71)–C(70)	115.0002	115	149	H(106)–C(31)–C(28)	109.4618	109.41
29	C(74)–N(69)–C(70)	114.9998	115	150	H(105)–C(31)–C(30)	109.4417	109.41
30	N(75)–C(70)–N(71)	120.0004	126	151	H(105)–C(31)–C(28)	109.4415	109.41
31	N(75)–C(70)–N(69)	119.9998	126	152	C(30)–C(31)–C(28)	109.4997	109.5
32	N(71)–C(70)–N(69)	119.9998	120	153	N(39)–C(28)–C(31)	120	125.3
33	H(130)–N(75)–C(70)	120.0004	118	154	N(39)–C(28)–C(25)	120.0001	120
34	H(130)–N(75)–S(66)	119.9996	–	155	C(31)–C(28)–C(25)	119.9999	121.4
35	C(70)–N(75)–S(66)	120	–	156	C(38)–C(24)–C(25)	130.9156	121.4
36	H(121)–C(58)–C(57)	114.0221	120	157	C(38)–C(24)–N(23)	130.9152	115.1
37	H(121)–C(58)–N(53)	114.0215	116.5	158	C(25)–C(24)–N(23)	98.1693	120
38	C(57)–C(58)–N(53)	131.9564	123.5	159	C(32)–N(22)–C(26)	124.5002	124
39	H(120)–C(57)–C(58)	120.9782	120	160	C(32)–N(22)–N(23)	124.4997	124
40	H(120)–C(57)–C(56)	120.9783	120	161	C(26)–N(22)–N(23)	111.0001	124
41	C(58)–C(57)–C(56)	118.0436	–	162	C(28)–C(25)–C(26)	119.9983	120
42	H(119)–C(56)–C(57)	119.9999	120	163	C(28)–C(25)–C(24)	128.9979	120
43	H(119)–C(56)–N(55)	120	116.5	164	C(26)–C(25)–C(24)	111.0003	120
44	C(57)–C(56)–N(55)	120.0001	123.5	165	O(27)–C(26)–C(25)	124.3002	124.3
45	C(56)–N(55)–C(54)	114.9999	115	166	O(27)–C(26)–N(22)	124.6986	–
46	C(58)–N(53)–C(54)	115.0001	115	167	C(25)–C(26)–N(22)	110.9991	120
47	N(59)–C(54)–N(55)	119.9999	126	168	H(95)–C(18)–C(19)	119.9998	120
48	N(59)–C(54)–N(53)	120.0001	126	169	H(95)–C(18)–C(17)	119.9999	120
49	N(55)–C(54)–N(53)	120	120	170	C(19)–C(18)–C(17)	120.0003	–
50	H(122)–N(59)–C(54)	119.9998	118	171	H(94)–C(17)–C(18)	120.0005	120
51	H(122)–N(59)–S(46)	120.0003	–	172	H(94)–C(17)–C(16)	120	120

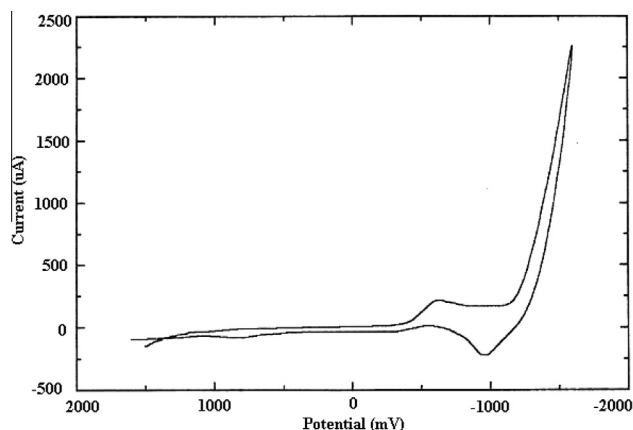
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Table 9 (continued)

S. No.	Atoms	Actual bond angles	Optimal bond angles	S. No.	Atoms	Actual bond angles	Optimal bond angles
52	C(54)–N(59)–S(46)	119.9999	–	173	C(18)–C(17)–C(16)	119.9995	–
53	H(102)–C(29)–H(101)	109.5203	109	174	H(93)–C(16)–C(17)	119.9998	120
54	H(102)–C(29)–H(100)	109.461	109	175	H(93)–C(16)–C(15)	119.9998	120
55	H(102)–C(29)–C(30)	109.462	110	176	C(17)–C(16)–C(15)	120.0004	–
56	H(101)–C(29)–H(100)	109.4418	109	177	H(96)–C(19)–C(18)	120.0001	120
57	H(101)–C(29)–C(30)	109.4421	110	178	H(96)–C(19)–C(14)	119.9999	120
58	H(100)–C(29)–C(30)	109.5	110	179	C(18)–C(19)–C(14)	120.0001	–
59	H(104)–C(30)–H(103)	109.52	109.4	180	H(92)–C(15)–C(16)	120.0007	120
60	H(104)–C(30)–C(31)	109.462	109.41	181	H(92)–C(15)–C(14)	119.9993	120
61	H(104)–C(30)–C(29)	109.462	109.41	182	C(16)–C(15)–C(14)	120	–
62	H(103)–C(30)–C(31)	109.4419	109.41	183	H(52)–O(50)–H(51)	119.9998	–
63	H(103)–C(30)–C(29)	109.4418	109.41	184	H(52)–O(50)–V(21)	120	–
64	C(31)–C(30)–C(29)	109.4996	109.5	185	H(51)–O(50)–V(21)	120.0003	–
65	H(87)–C(11)–H(86)	109.52	109	186	C(61)–N(39)–C(28)	121.5436	124
66	H(87)–C(11)–H(85)	109.4613	109	187	C(61)–N(39)–V(21)	121.544	–
67	H(87)–C(11)–C(12)	109.4615	110	188	C(28)–N(39)–V(21)	116.9124	–
68	H(86)–C(11)–H(85)	109.442	109	189	C(26)–O(27)–V(21)	109.4998	–
69	H(86)–C(11)–C(12)	109.4424	110	190	C(42)–C(41)–C(40)	119.9999	120
70	H(85)–C(11)–C(12)	109.5	110	191	C(42)–C(41)–N(10)	120	120
71	H(89)–C(12)–H(88)	109.5197	109.4	192	C(40)–C(41)–N(10)	120.0001	120
72	H(89)–C(12)–C(13)	109.4615	109.41	193	O(50)–V(21)–O(49)	128.1267	–
73	H(89)–C(12)–C(11)	109.4619	109.41	194	O(50)–V(21)–N(39)	134.7233	–
74	H(88)–C(12)–C(13)	109.4416	109.41	195	O(50)–V(21)–O(27)	102.8229	–
75	H(88)–C(12)–C(11)	109.4424	109.41	196	O(50)–V(21)–N(10)	121.5001	–
76	C(13)–C(12)–C(11)	109.5003	109.5	197	O(50)–V(21)–O(8)	129.5918	–
77	N(75)–S(66)–O(68)	109.4417	–	198	O(49)–V(21)–N(39)	97.0934	–
78	N(75)–S(66)–O(67)	109.4419	–	199	O(49)–V(21)–O(27)	90.0001	–
79	N(75)–S(66)–C(64)	109.52	–	200	O(49)–V(21)–N(10)	19.5346	–
80	O(68)–S(66)–O(67)	109.4999	116.6	201	O(49)–V(21)–O(8)	90.0001	–
81	O(68)–S(66)–C(64)	109.4619	–	202	N(39)–V(21)–O(27)	76.1516	–
82	O(67)–S(66)–C(64)	109.4619	–	203	N(39)–V(21)–N(10)	100.2237	–
83	H(126)–C(65)–C(64)	120.0002	120	204	N(39)–V(21)–O(8)	34.1154	–
84	H(126)–C(65)–C(60)	119.9995	120	205	O(27)–V(21)–N(10)	109.5001	–
85	C(64)–C(65)–C(60)	120.0003	–	206	O(27)–V(21)–O(8)	109.5002	–
86	S(66)–C(64)–C(65)	120.0001	–	207	N(10)–V(21)–O(8)	82.5412	–
87	S(66)–C(64)–C(63)	120.0002	–	208	H(91)–C(13)–H(90)	109.52	109.4
88	C(65)–C(64)–C(63)	119.9997	120	209	H(91)–C(13)–C(12)	109.4615	109.41
89	H(125)–C(63)–C(64)	119.9998	120	210	H(91)–C(13)–C(9)	109.4618	109.41
90	H(125)–C(63)–C(62)	120.0002	120	211	H(90)–C(13)–C(12)	109.4417	109.41
91	C(64)–C(63)–C(62)	119.9999	–	212	H(90)–C(13)–C(9)	109.4421	109.41
92	H(124)–C(62)–C(63)	119.9995	120	213	C(12)–C(13)–C(9)	109.5002	109.5
93	H(124)–C(62)–C(61)	120.0004	120	214	C(41)–N(10)–V(21)	118.6942	–
94	C(63)–C(62)–C(61)	120.0001	–	215	C(41)–N(10)–C(9)	118.6943	124
95	H(123)–C(60)–C(65)	120.0003	120	216	V(21)–N(10)–C(9)	122.6116	–
96	H(123)–C(60)–C(61)	120.0002	120	217	C(19)–C(14)–C(15)	119.9997	120
97	C(65)–C(60)–C(61)	119.9995	–	218	C(19)–C(14)–N(3)	120	120
98	N(59)–S(46)–O(48)	109.4422	–	219	C(15)–C(14)–N(3)	120.0003	120
99	N(59)–S(46)–O(47)	109.4417	–	220	C(13)–C(9)–N(10)	119.9999	125.3
100	N(59)–S(46)–C(44)	109.5202	–	221	C(13)–C(9)–C(6)	120	121.4
101	O(48)–S(46)–O(47)	109.4998	116.6	222	N(10)–C(9)–C(6)	120.0001	120
102	O(48)–S(46)–C(44)	109.4617	–	223	V(21)–O(8)–C(7)	109.4998	–
103	O(47)–S(46)–C(44)	109.4617	–	224	O(8)–C(7)–C(6)	124.2983	124.3
104	H(118)–C(45)–C(44)	120.0003	120	225	O(8)–C(7)–N(3)	124.6983	–
105	H(118)–C(45)–C(40)	120	120	226	C(6)–C(7)–N(3)	111	120
106	C(44)–C(45)–C(40)	119.9998	–	227	H(99)–C(20)–H(98)	109.5198	109
107	S(46)–C(44)–C(45)	119.9998	–	228	H(99)–C(20)–H(97)	109.4618	109
108	S(46)–C(44)–C(43)	119.9995	–	229	H(99)–C(20)–C(5)	109.4619	110
109	C(45)–C(44)–C(43)	120.0007	120	230	H(98)–C(20)–H(97)	109.4418	109
110	H(117)–C(43)–C(44)	120.0005	120	231	H(98)–C(20)–C(5)	109.4419	110
111	H(117)–C(43)–C(42)	120.0002	120	232	H(97)–C(20)–C(5)	109.5001	110
112	C(44)–C(43)–C(42)	119.9993	–	233	C(9)–C(6)–C(7)	119.9986	120

Table 9 (continued)

S. No.	Atoms	Actual bond angles	Optimal bond angles	S. No.	Atoms	Actual bond angles	Optimal bond angles
113	H(116)–C(42)–C(43)	119.9997	120	234	C(9)–C(6)–C(5)	128.998	120
114	H(116)–C(42)–C(41)	120	120	235	C(7)–C(6)–C(5)	111	120
115	C(43)–C(42)–C(41)	120.0003	120	236	C(14)–N(3)–C(7)	128.3535	124
116	H(115)–C(40)–C(45)	120.0002	120	237	C(14)–N(3)–N(4)	128.3536	124
117	H(115)–C(40)–C(41)	119.9998	120	237	C(7)–N(3)–N(4)	103.2929	124
118	C(45)–C(40)–C(41)	120	120	239	C(20)–C(5)–C(6)	124.5	121.4
119	H(110)–C(36)–C(37)	120.0002	120	240	C(20)–C(5)–N(4)	124.5001	115.1
120	H(110)–C(36)–C(35)	120.0001	120	241	C(6)–C(5)–N(4)	110.9999	120
121	C(37)–C(36)–C(35)	119.9997	120	242	C(5)–N(4)–N(3)	103.7073	115

**Figure 7** Cyclic voltammogram of $[\text{VO}(\text{bumphp-snm})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (3).

ligand environments in the present complexes to facilitate electron transfer reactions. The complexes were dissolved in dimethylformamide and the cyclic voltammograms were recorded in the scan range of 2000 to -2000 mV. The reduction of these

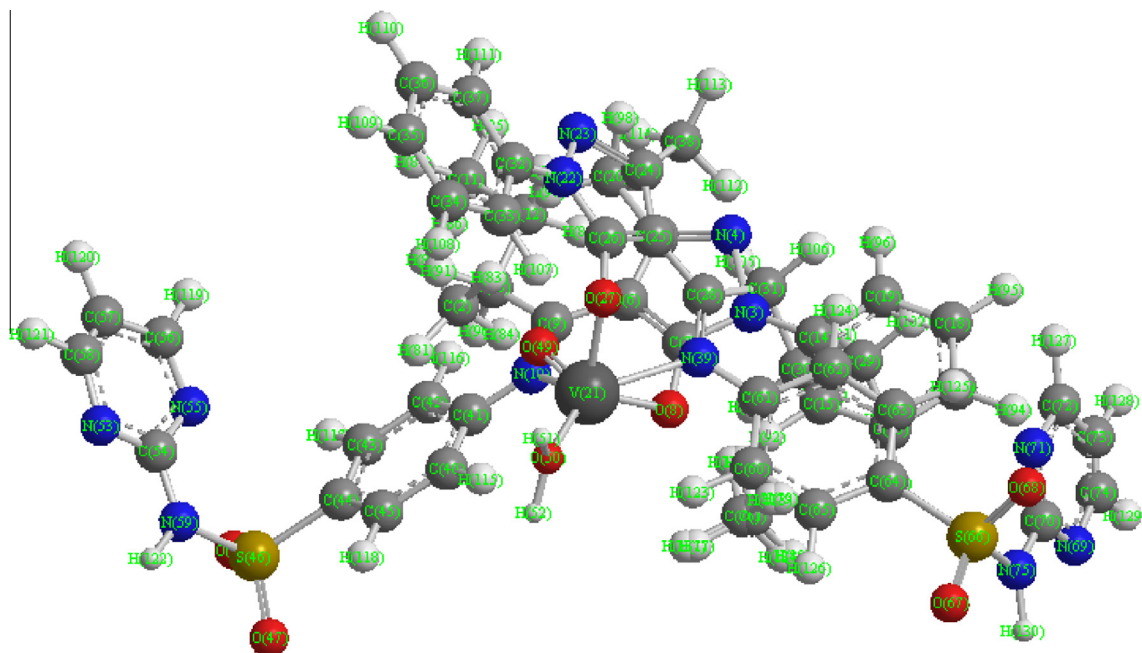
complexes to +III oxidation state (usually expected in such complexes) were achieved by waves with E_r values (Maurya and Rajput, 2004; Dai et al., 1996) in the range from -788.45 to -913.45 mV against the saturated Ag/AgCl electrode (Table 7). Other important parameters are also included in this table. The deviations of i_{pc}/i_{pa} from 1 in the present cases suggest that the redox couple is not reversible. This may be due to a slow electron transfer reaction. This is again reflected by the unusually high values of ΔE in the range of 346.3 – 403.9 mV, not following the reversibility criterion (Kissinger and Heineman, 1984),

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.059}{n}$$

The cyclic voltammogram of compound (3) is shown in Fig. 7.

3.8. 3D-Molecular modeling and analysis

In view of the hexa-coordination of all the complexes (vide infra), and also taking into account the well established square pyramidal structure (Sakurai et al., 1995) of bis(picolinato)oxovanadium(IV) [having two monoprotic bidentate (O,N-donor) picolinate ligand, similar to two monoprotic

**Figure 8** 3D structure of $[\text{VO}(\text{bumphp-sdz})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (1).

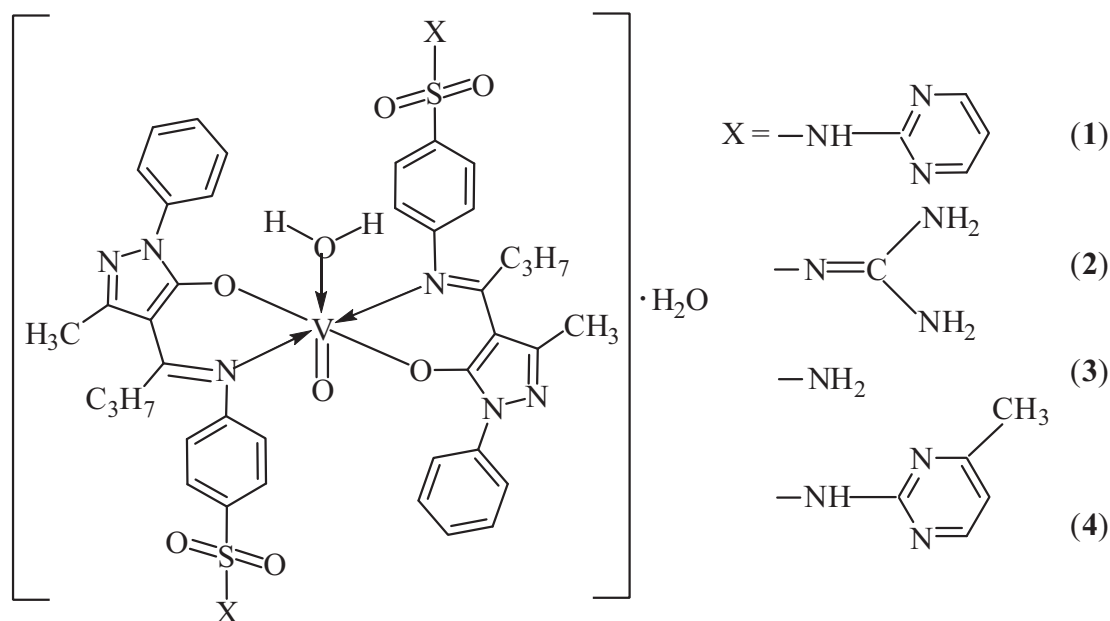


Figure 9 Proposed octahedral structure of oxovanadium(IV) complexes.

O,N-donor sulfa drug based Schiff base ligands (LH) used in the present investigation, and occupying equatorial positions *cis* to each other, and oxo group at one of the axial positions], the molecular modeling of a representative compound, [VO (bumphp-sdz)₂(H₂O)]·H₂O (**1**) is based on its octahedral structure with an axial oxo group and water molecule *trans* to O (oxo) and two O,N-donor LH ligands at the equatorial positions *cis* to each other. The details of bond lengths and bond angles as per the 3D structure (Fig. 8) are given in Tables 8 and 9, respectively. For convenience of looking over the different bond lengths and bond angles, the various atoms in the compound in question are numbered in Arabic numerals. In all, 382 measurements of the bond lengths (140 in number), plus the bond angles (242 in number) are listed in the Tables 8 and 9. Except few cases, optimal values of both the bond lengths and the bond angles are given in the Tables along with the calculated ones. The actual (calculated) bond lengths/bond angles given in Tables are obtained as a result of energy optimization in CHEM 3D Ultra, 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 modeling of other systems (Maurya et al., 2007, 2008, *in press*). In most of the cases, the actual bond lengths and bond angles are close to the optimal values, and thus the proposed structure of the compound (**1**) as well as of the others are acceptable (Maurya and Rajput, 2007; Maurya et al., 2007, 2008, *in press*).

4. 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(H₂O)]·H₂O, where LH = bumphp-sdzH (**1**), bumphp-sgnH (**2**), bumphp-smnH (**3**) or bumphp-smrH (**4**). Keeping view of the mono-

meric hexacoordination of all the complexes, and the well established square pyramidal structure (Sakurai et al., 1995) of bis(picolinato)oxovanadium(IV) [involving a monobasic bidentate (O,N)-donor picolinate ligand similar to monobasic (O,N)-donor sulfa drug Schiff base ligands LH in the present investigation, and occupying equatorial positions *cis* to each other, and oxo group at one of the axial positions], octahedral structures (Fig. 9) with an axial oxo group and a water molecule *trans* to O (oxo), and two O,N-donor LH ligands at the equatorial positions *cis* to each other, have been proposed for these complexes. We have already proposed a similar octahedral structure (Maurya et al., 2002a,b,c) for hexa-coordinated oxovanadium(IV) complexes of the compositions, [VO(L¹)₂(H₂O)] where, L¹H (O,N-donor) = *N*-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-*p*-anisidine, *N*-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-*m*-phenetidine or *N*-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-*p*-toluidine, and [VO(L²)(H₂O)], where L²H(O₂N₂) = *N*-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-*o*-phenylenediamine or *N*-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-*m*-phenylenediamine.

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