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Journal of Molecular Structure 794 (2006) 24-34

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

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

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Received 7 October 2005; received in revised form 23 December 2005; accepted 23 January 2006 Available online 28 February 2006

## Abstract

Four new oxovanadium(IV) complexes, formed by the interaction of vanadyl sulfate pentahydrate and the Schiff bases derived from 3-methyl-1-phenyl-4-valeryl-2-pyrazolin-5-one and the sulfa drugs, N-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulfadiazine (L<sup>1</sup>H), N-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulfadiazine (L<sup>3</sup>H) and N'(-3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulphanilamide (L<sup>3</sup>H) and N'(-3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulphamethoxazole (L<sup>4</sup>H) in aqueous ethanol are described. The resulting complexes were characterized by elemental analyses, molar conductances, magnetic and decomposition temperature measurements, cyclic voltammetry, electron spin resonance, infrared and electronic spectral studies. They have the composition [VO(L)<sub>2</sub>]·H<sub>2</sub>O, where LH=Schiff base L<sup>1</sup>H, L<sup>2</sup>H, L<sup>3</sup>H or L<sup>4</sup>H mentioned above. A square–pyramidal structure having a slight  $\cdots$ V=O $\cdots$ V=O $\cdots$  type interaction has been proposed for these complexes.

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Keywords: Oxovanadium(IV) complexes; Sulfa drug based ligands; Bioinorganic; Medicinal relevance; 3D molecular modeling

# 1. Introduction

Pyrazolone derivatives have been extensively investigated on account of their wide range of pharmacological activities [1]. 4-Acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones have been investigated as extractants for metals from acidic solutions [2]. The metal complexes of Schiff bases derived from sulfa drugs have gained considerable importance due to their pronounced biological activity [3]. There are several reports on the Schiff base complexes of metal derived from sulfa drugs [4–7]. They have been found to possess effective fungicidal activity [4].

Recognition of vanadium as an essential trace element found in living organisms [8–12] has generated increasing interest in the structure and function of its complexes. Tunicates accumulate vanadium(V) from the marine environment and store it in their blood cells in the reduced tetra- and trivalent state [9]. However, the vanadium metabolism of the tunicates remains unclear [9] as tunichromes present in tunicates in vitro are able to reduce V(V)-V(IV) only, and not further to V(III). The mushroom accumulates vanadium to produce amavadin [8,9]. Spectroscopic investigations have shown a distinct preference of this metal center for N- and/or O-coordinated environments [13-16]. This is consistent with combination of hard acid (VO<sup>2+</sup>) and hard (N and O ligands) bases [17]. There is heightened interest in the biological chemistry due to the recent discovery of two types of vanadium-dependent enzymes: vanadium nitrogenase [18] and vanadium haloperoxidases [19]. Although in recent years a number of vanadium complexes have been synthesized and characterized as models of amavadin and vanadium-dependent metalloenzymes, the biological role of vanadium in living organisms and also in both reductive and oxidative catalytic transformations is still obscure and debatable [20].

The last decade is characterized by a continuing increase in interest in the bioinorganic chemistry of vanadium as documented by the appearance of four monographs [21–24].

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Studies on the interaction of vanadium with biologically important ligands aimed at finding structural and/or functional models of biogenic compounds are numerous and have been the subject of several reviews [8–12,18,19,25–28].

There has been great interest in the past two decades in the mechanism of the insulin-like function of vanadium and in developing new vanadium compounds as potential insulin adjuvants [29] or replacement in the treatment of diabetes, most notably when administered orally. Still, gastrointestinal absorption (by passive diffusion) of vanadium is usually poor and depends on the chemical nature, solubility, and speciation of the metal ion complex. 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 [30,31] have been prepared, viz. VO(O<sub>4</sub>), VO(S<sub>2</sub>N<sub>2</sub>), VO(S<sub>4</sub>), VO(N<sub>3</sub>O), and  $VO(N_2O_2)$ , and the relationship between their structures and insulin-mimetic activities has been examined by evaluating both in vivo and in vitro results. Among others, bis (maltolato) oxovanadium(IV) (BMOV) [VO  $(O_4)$  type] proved to be potent in decreasing the blood glucose level with high efficiency without any overt toxic [31] side effect. Vanadium compounds as insulin mimics have been recently reviewed [32-34].

Considering the pronounced biological activity of sulfa drug Schiff base complexes, in view of the importance of vanadium compounds, and also extending the search for more efficacious vanadium compounds, a study was undertaken of the coordination chemistry of oxovanadium(IV) complexes  $\{[VO(N_2O_2)]$  type $\}$  involving pyrazolone-based sulfa drug Schiff bases, viz. *N*-(3'-methyl-1'-phenyl-4'-valerylidene-2'pyrazolin-5'-one)sulfadiazine (L<sup>1</sup>H), *N*-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulfaguanidine (L<sup>2</sup>H), *N*-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulphanilamide (L<sup>3</sup>H) and *N*'(-3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulphamethoxazole (L<sup>4</sup>H) (Fig. 1).

# $H_{3}C \xrightarrow{H_{9}C_{4}} N \xrightarrow{N}{2}_{1} O \xrightarrow{N}{N} O \xrightarrow{N}{N} (L^{1}H) : -N \xrightarrow{N}{N} (L^{2}H) \xrightarrow{N}{N} O \xrightarrow{N}{N} (L^{4}H) : -NH \xrightarrow{N}{N} O \xrightarrow{N}{N} (L^{4}H) \xrightarrow{N}{N} O \xrightarrow{N} O \xrightarrow{N}{N} O \xrightarrow{N} O \xrightarrow{N}$

Fig. 1. Structures of sulfa drug Schiff bases.

### 2. Experimental

# 2.1. Materials

Vanadyl sulfate pentahydrate (Thomas Baker Co., Ltd, Mumbai), 3-methyl-1-phenyl-2-pyrazolin-5-one (Johnson Chemicals Co., Mumbai), sulpha drugs (sulfadiazine, sulfaguanidine, sulfanilamide and sulfamethoxazole, Sigma Chemicals Co., USA) and valeryl chloride (Fluka Chemie A.G, Switzerland), were used as supplied. All other chemicals used were of analytical reagent grade.

# 2.2. Preparation of 3-methyl-1-phenyl-4-valeryl-2-pyrazolin-5-one (mpvpH)

This compound was prepared by the acylation of 3-methyl-1-phenyl-2-pyrazolin-5-one with valeryl chloride in dimethylformamide by the method reported by Jensen [35].

### 2.3. Synthesis of sulfa drug Schiff bases

The Schiff bases of sulfa drugs were prepared as follows: an ethanolic solution (15 mL) of mpvpH (2.58 g, 1 mmol), was added to the solution ( $\sim 20$  mL) of sulphadiazine (2.50 g, 1 mmol), sulfaguanidine (2.14 g, 1 mmol), sulfamethoxazol (2.53 g, 1 mmol) in ethanol or sulphanilamide (1.72 g, 1 mmol) in acetone. The resulting solution was refluxed with stirring for 6–7 h and then filtered to remove insoluble sulpha drug if any. The filtrate so obtained was concentrated on a water bath and left overnight at room temperature when colored crystals of the Schiff bases separated out from their respective solutions. The crystals thus obtained were washed with ethanol–water (1:1) and dried in vacuo. They were recrystallised from ethanol. The characterization data of Schiff bases are given in Table 1.

### 2.4. Synthesis of complexes

The following general procedure was used in the synthesis of all of the complexes. The salt  $VOSO_4 \cdot 5H_2O$  (0.253 g, 1 mmol) was dissolved in water (5 mL) and the solution was added to a warmed, stirred ethanolic solution (~25 mL) of the corresponding Schiff bases L<sup>1</sup>H (0.980 g, 2 mmol), L<sup>2</sup>H (0.908 g, 2 mmol), L<sup>3</sup>H (0.824 g, 2 mmol), or L<sup>4</sup>H (0.986 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 any unreacted ligand and the metal salt. The product was dried in vacuo. The analytical data of the complexes are given in Table 2.

### 2.5. Analyses

Carbon, hydrogen and nitrogen were determined microanalytically at the Central Drug Research Institute, Lucknow. A 100 mg sample of the compound was placed in a silica crucible, decomposed by gentle heating and then adding 1–2 mL of concentrated HNO<sub>3</sub>, 2–3 times. An orange colored

Table 1					
Characterization	data	of the	synthesized	Schiff bases	

Ligand	Empirical formula (for- mula wt.)	Mp (°C)	Yield (%)	Color	Found (calcd, %)			$\nu$ (C=N)	ν(C–O)	$\nu(\text{NH})/\text{NH}_2$	ν(OH)	$\nu(C=N^2)$
- 1					С	Н	Ν	(Azometh)	(Enolic)			(cyclic)
$L^{1}H$	C <sub>25</sub> H <sub>26</sub> N <sub>6</sub> O <sub>3</sub> S (490)	180	65	Middle buff	61.22 (61.22)	5.10 (5.31)	17.14 (17.14)	1628s	1228m	3250w	3410br	1580s
$L^2H$	C <sub>22</sub> H <sub>26</sub> N <sub>6</sub> O <sub>3</sub> S (454.00)	175	62	Sand stone	58.34 (58.15)	5.62 (5.73)	18.28 (18.50)	1645s	1145m	3344w	3410br	1588s
L <sup>3</sup> H	$C_{21}H_{24}N_4O_3S$ (412)	165	60	Light yellow	60.92 (61.17)	5.65 (5.83)	13.71 (13.59)	1614s	1241m	3366w; 3260w	3450br	1590s
$L^4H$	$C_{25}H_{27}N_5O_4S$ (493)	170	65	Ivory	60.72 (60.85)	5.62 (5.48)	14.32 (14.20)	1620s	1178m	3233w	3433br	1584s

L<sup>1</sup>H, *N*-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulfadiazine; L<sup>2</sup>H, *N*-(3'-methyl-1'-phenyl-4'-valerylidene-2'-pyrazolin-5'-one)sulfaguanidine; L<sup>3</sup>H, *N*-(3'-methyl-1'-phenyl-

 Table 2

 Elemental analysis and some physical properties of the synthesized complexes

Sr. no. Complex (empirical formula) (mol. wt.)		Found (calcd,	(calcd, %)			Colour	Decomp.	$\Lambda_{\rm M}$	Yield (%)	$\mu_{\rm eff}$ (BM)
		С	Н	Ν	V		temp. (°C)	$(\Omega^{-1} \operatorname{cm}^2 - \operatorname{mol}^{-1})$		
(1)	$[VO(L^{1})_{2}] \cdot H_{2}O(C_{50}H_{52}N_{12}O_{8}S_{2}V)$ (1062.94)	56.14 (56.45)	4.76 (4.89)	15.64 (15.81)	4.58 (4.79)	Daffodil yellow	110	28.7	45	1.64
(2)	$[VO(L^2)_2] \cdot H_2O(C_{44}H_{52}N_{12}O_8S_2V)$ (990.94)	53.47 (53.28)	5.14 (5.25)	16.64 (16.95)	5.37 (5.14)	Golden green	105	22.6	50	1.58
(3)	$[VO(L^3)_2] \cdot H_2O (C_{42}H_{48}N_8O_8S_2V) (906.94)$	55.29 (55.57)	5.40 (5.29)	12.19 (12.35)	5.31 (5.62)	Greenish yellow	115	31.5	55	1.65
(4)	$[VO(L^4)_2] \cdot H_2O(C_{50}H_{54}N_{10}O_{10}S_2V) (1068.94)$	56.41 (56.13)	5.14 (5.05)	13.28 (13.10)	4.89 (4.77)	Golden green	110	20.4	55	1.61

Table 3 Important IR spectral bands (cm<sup>-1</sup>) of the synthesized complexes

Sr. no.	Complex	$\nu$ (C=N) azomethine (s)	v(C–O) enolic	ν(OH)	v(V=O)	$\nu$ (C=N <sub>2</sub> ) cyclic	<i>v</i> (NH)/NH <sub>2</sub>
(1)	$[VO(L^1)_2] \cdot H_2O$	1603s	1258m	3410br	913m	1583s	3258w
(2)	$[VO(L^2)_2] \cdot H_2O$	1612s	1156m	3416br	903m	1585s	3336, 3245w
(3)	$[VO(L^3)_2] \cdot H_2O$	1606s	1293m	3413br	904m	1586s	3350w; 3283w
(4)	$[VO(L^4)_2] \cdot H_2O$	1607s	1224m	3400br	903m	1585s	3293w

mass (V<sub>2</sub>O<sub>5</sub>) was obtained after decomposition 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 [36] using 0.02 M KMnO<sub>4</sub> solution as an oxidizing agent in the presence of sulfurous acid. Based on the following redox reactions, the amount of vanadium in the sample solution was calculated using the standard [36] relationship: 1 mL of 0.02 M KMnO<sub>4</sub>=0.0051 g vanadium

 $2VO_3^{-*} + H_2SO_3 + 4H^+ \rightarrow 2VO^{2+} + SO_4^{2-} + 3H_2O$ 

 $MnO_4^- + 5VO^{2+} + 6H_2O \rightarrow 5VO_3^- + Mn^{2+} + 12H^+$ 

\*in aqueous solution  $V_2O_5$  exists as vanadate ( $VO_3^-$ ) [36].

## 2.6. Physical methods

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/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 performed 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



Fig. 2. IR spectrum of  $L^4H$ .

system. A three-electrode system consisting of (i) a platinum disk working electrode, (ii) a platinum wire counter electrode and (iii) an 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. Molecular modeling studies

The 3D molecular modeling of a representative compound was carried out on a CS Chem 3D Ultra Molecular Modeling and Analysis Program [37]. It an interactive graphics program that allows rapid structure building, geometry optimization with minimum energy and molecular display. It has ability to handle transition metal compounds.

### 3. Results and discussion

The oxovanadium(IV) sulfa drug complexes were prepared according to the following equation



Fig. 3. IR spectrum of  $[VO(L^4)_2] \cdot H_2O$ .

 Table 4

 Electronic spectral data of the synthesized complexes

Compound no.	Compound	$\lambda_{\text{Max}}$ (nm)	$\nu (\mathrm{cm}^{-1})$	$\varepsilon$ , $(L \mathrm{cm}^{-1} \mathrm{mol}^{-1})$	Peak assignment
(1)	$[VO(L^1)_2] \cdot H_2O$	284	35211	2993	Charge transfer transition
		307	32573	3176	Charge transfer transition
		460	21739	177	$b_2 \rightarrow a_1^*$
(2)	$[VO(L^2)_2] \cdot H_2O$	295	33898	3033	Charge transfer transition
		314	31847	2919	Charge transfer transition
		475	21052	133	$b_2 \rightarrow a_1^*$
(3)	$[VO(L^3)_2] \cdot H_2O$	285	35087	3862	Charge transfer transition
		302	33112	4546	Charge transfer transition
		327	30581	4004	Charge transfer transition
		448	23364	342	$b_2 \rightarrow a_1^*$
(4)	$[VO(L^4)_2] \cdot H_2O$	310	32258	4720	Charge transfer transition
		335	29850	3945	Charge transfer transition
		350	28571	3880	Charge transfer transition
		560	17857	135	$b_2 \rightarrow a_1^*$

$$VOSO_4 \cdot 5H_2O + 2LH \xrightarrow[Reflux]{H_2O, C_2H_5OH} [VO(L)_2] \cdot H_2O + H_2SO_4$$

where  $LH = L^{1}H$ ,  $L^{2}H$ ,  $L^{3}H$  or  $L^{4}H$ .

The complexes obtained in this investigation are colored solids (see Table 2 for colors). Their decomposition temperatures are given in Table 2. The complexes are soluble in DMF, DMSO and acetonitrile but insoluble in ethanol, methanol and chloroform. The following physical studies have been employed in the characterization of these complexes.

### 3.1. Infrared spectral studies

The important spectral bands of the synthesized ligands as well as the complexes are presented in Tables 1 and 3, respectively. All of the Schiff base ligands in the present nvestigation exhibit a broad band centered at  $3410-3450 \text{ cm}^{-1}$ . This suggests the presence of a strongly hydrogen-bonded OH group [38]. This indicates the involvement of the 5-OH group in intramolecular hydrogen bonding with the lone pair of azomethine nitrogen. It also suggests that the ligands exist in enol form in the solid state [16].



Fig. 4. Electron spectrum of  $[VO(L^3)_2] \cdot H_2O$ .

The Schiff base ligands, L<sup>1</sup>H to L<sup>4</sup>H contain six potential donor sites: (i) the enolic oxygen; (ii) the cyclic nitrogen N<sup>1</sup>; (iii) the cyclic nitrogen N<sup>2</sup>; (iv) the azomethine nitrogen; (v) the sulfonamide (SO<sub>2</sub>NH) oxygen or nitrogen and; (vi) the ring nitrogen of sulfa drug. All the Schiff base ligands show a sharp and strong band due to  $\nu$ (C=N) of the azomethine group at 1614–1645 cm<sup>-1</sup>. The observed low-energy shift of this band in the chelates and appearing at 1603–1612 cm<sup>-1</sup> suggests the coordination of the azomethine nitrogen [16].

The  $\nu$ (C=N<sup>2</sup>) (cyclic) band arising from the pyrazolone moiety of the ligands appears at 1580–1590 cm<sup>-1</sup> and does not show any appreciable change in their position in the complexes. This observation indicates the non-participation of the ring nitrogen N<sup>2</sup> in coordination. The coordination of the ring nitrogen N<sup>1</sup> is unfavorable due to the presence of the bulky phenyl ring attached to it.

The  $\nu$ (NH) mode of the sulfonamide group/amino group in the uncoordinated Schiff bases remains unchanged in the spectra of their complexes (see Tables 1 and 3). This suggests that the sulfonamide nitrogen/amino group is not taking part in coordination. The band at ~1386 cm<sup>-1</sup> in the ligands is assigned to  $\nu_{as}$ (O=S=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.



Fig. 5. ESR spectrum of  $[VO(L^3)_2] \cdot H_2O$ .

Table 5 Cyclic voltammetric data of some oxovanadium(IV) complexes

Compound	Compound	V(IV)/V(V)			V(IV)/V(III)				
no.		$E_{\rm pc}(\rm mV)$	$E_{\rm pa}({\rm mV})$	$E_{\rm r}({\rm mV})$	$\Delta E_{\rm p}({\rm mV})$	E <sub>pa</sub> (mV)	$E_{\rm pc}({\rm mV})$	$E_{\rm r}({\rm mV})$	$\Delta E_{\rm p}({\rm mV})$
(1)	$[VO(L^1)_2] \cdot H_2O$	462	373	417.5	89	-760	-680	-720	80
(4)	$[VO(L^4)_2] \cdot H_2O$	425	340	382.5	85	-675	-580	-627.5	95

Supporting electrolyte: tetrabutylammonium tetrafluoroborate,  $[CH_3(CH_2)_3]_4NBF_4$  (50 mmol); concentration of complexes: 1 mmol; all the potentials are referenced to the Ag/AgCl electrode;  $E_r=0.5(E_{pa}+E_{pc})$ , where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic potentials.

The reaction of the enolic Schiff bases with VO<sup>2+</sup> ion with elimination of a proton is revealed by the presence of a new band in the complexes at 1156–1293 cm<sup>-1</sup> as compared to that of the Schiff bases at 1145–1241 cm<sup>-1</sup> due to the  $\nu$ (C–O) (enolic) [39]. The appearance of a broad band due to  $\nu$ (OH) at 3400–3416 cm<sup>-1</sup> in the complexes may be due to a lattice water molecule attached with the complexes. The low decomposition temperatures of the complexes (105–115 °C) (see Table 2) also support the presence of lattice water in these complexes.

Most of the oxovanadiun(IV) complexes exhibit a strong band near 1000 cm<sup>-1</sup>, which has been assigned to  $\nu$ (V=O) [40]. In contrast, several oxovanadium(IV) complexes have been reported in which this stretching mode appears at quite lower [41] wave numbers, around 900 cm<sup>-1</sup>. The shift of  $\nu$ (V=O) band to lower wave numbers has been suggested due to the presence of a slight  $\cdots$ V=O $\cdots$ V=O $\cdots$  type interaction occurring between vanadyl oxygen of one molecule with a vanadium metal in another molecule [42]. In the present work, the  $\nu$ (V=O) mode is found at 903–913 cm<sup>-1</sup>. This shift of  $\nu$ (V=O) mode to lower wave numbers suggests the presence of a slight  $\cdots$ V=O $\cdots$ V=O $\cdots$  type interaction in these complexes. The IR spectra of the Schiff base L<sup>4</sup>H and its complex, [VO(L<sup>4</sup>)<sub>2</sub>] $\cdot$ H<sub>2</sub>O are given in Figs. 2 and 3, respectively.

### 3.2. Conductance measurements

The observed molar conductances of these complexes in  $10^{-3}$  molar DMF solutions are in the range 20.4–31.5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (Table 2) and are consistent with the non-electrolytic nature of these complexes [43]. Such a non-zero molar conductance value for each of the 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 [43] type.

### 3.3. Magnetic measurements

The oxovanadium(IV) ion belongs to the S=1/2 system. The magnetically dilute oxovanadium(IV) complexes usually exhibit magnetic moments to their spin-only value of 1.73 BM. The observed magnetic moments of the complexes under study are found in the range 1.61–1.65 BM. These results suggest that an interaction [42] of the of the type  $\cdots$ V=O $\cdots$ V=O $\cdots$  is taking place in these complexes. Such a result has recently been reported by Maurya et al. [41] in some oxovanadium(IV) complexes involving Schiff bases derived from 4-butyryl-3-methyl-1-phenyl-2-pyrazolin-5-one and certain aromatic amines.

# 3.4. Electronic spectral studies

The electronic spectra of these compounds were recorded in  $10^{-3}$  molar dimethylformamide solutions in the range 200–800 nm. The  $\lambda_{max}$  of electronic spectral peaks and respective molar extinction coefficients along with their tentative assignments are given in Table 4. Besides high intensity charge transfer transitions, all these complexes displayed one low intensity d–d transition which may be assigned to  $b_2 \rightarrow 1a_1^*$  [44] transition. The assignment of  $b_2 \rightarrow 1a_1^*$ transition in each case assumes idealized  $C_{2\nu}$  symmetry. These spectra are typical of oxovanadium(IV) complexes [15,45]. The electronic spectrum of compound (3) is shown in Fig. 4.

### 3.5. ESR spectral studies

The liquid nitrogen temperature X-Band EPR Spectrum (Fig. 5) of a representative compound,  $[VO(L^3)] \cdot H_2O$ , was recorded in frozen DMF solution, without DPPH using the microwave frequency 9.17 GHz. The spectrum shows an eight-line pattern, characteristic of an unpaired electron being coupled with a vanadium nuclear spin (I=7/2). The oxovanadium(IV) ion belongs to the 3d<sup>1</sup> system and the vanadium nucleus has 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  $2 \times 7/2 + 1 = 8$  lines. The observed spectral parameters for this compound are:  $g_{\perp} = 2.003$ ,  $g_{\parallel} = 1.974$ ,  $g_{av} = 1.993$ . The observed  $g_{av}$  value deviates from the free ion value 2.0036, and this suggests that





Fig. 7. 3D Structure of  $[VO(L^3)_2]$  (3).

the complex is appreciably covalent [46]. The 'g'-value so obtained is comparable with the g values reported earlier for oxovanadium(IV) complexes [16,45].

### 3.6. Cyclic voltammetric studies

Cyclic voltammetric measurements of two representative complexes, (1) and (4), were carried out on an ECDA-001 basic electrochemistry system in order to assess the suitability of ligand environments in the present complexes to facilitate electron transfer reactions. The complexes were dissolved in acetonitrile and the cyclic voltammogram were recorded in the scan range 1500 to -1000 mV. The oxidations and reductions of these complexes were achieved by waves with  $E_r$  values in the range

from 382.5 to 417.5 mV (oxidation) and from -627.5 to -720 mV (reduction) against the saturated Ag/AgCl electrode (Table 5). These two complexes showed redox couples with peak-to-peak separation values ( $\Delta E_p$ ) ranging from 80 to 95 mV, indicating a single-step one-electron transfer process [47]. Thus, the positive  $E_r$  values (382.5–417.5 mV) may be assigned to the metal centered oxidation [48] of V(IV)–V(V) in which the stereo structures of parent and oxidized species are expected to be similar. The negative  $E_r$  potentials (-627.5 to -720 mV) may be assigned to the conversion [48] of V(IV)–V(III). Besides establishing (+IV) oxidation state, these observations conclude that the ligand environments present in these two complexes facilitate electron transfer reactions. This study gives some insight in the vanadium metabolism of the tunicates (9) that

Table 6				
Various bond	lengths of com	pound	$[VO(L^3)_2]$	(3)

S. no.	Atoms	Actual bond length	Optimal bond length	S. no.	Atoms	Actual bond length	Optimal bond length
1	H(79)-C(25)	1.1	1.1	58	H(77)–C(19)	1.113	1.113
2	C(25)-C(24)	1.337	1.42	59	H(91)-C(41)	1.113	1.113
3	C(23)-S(20)	1.79	-	60	H(78)-C(24)	1.1	1.1
4	C(58)–C(57)	1.337	1.42	61	H(90)–C(41)	1.113	1.113
5	C(5)–N(1)	1.266	1.462	62	C(40)-H(89)	1.113	1.113
6	N(8)-S(20)	1.696	-	63	C(18)–C(13)	1.337	1.42
7	H(96)-C(46)	1.1	1.1	64	C(10)–H(64)	1.113	1.113
8	H(94)-C(44)	1.1	1.1	65	C(11)–H(65)	1.113	1.113
9	C(48)–H(99)	1.113	1.113	66	C(52)–C(53)	1.337	1.42
10	H(101)–C(53)	1.1	1.1	67	H(70)-C(14)	1.1	1.1
11	C(34) - N(30)	1.266	1.462	68	N(27)–H(80)	1.05	1.05
12	C(15)–C(14)	1.337	1.42	69	C(48)–H(98)	1.113	1.113
13	H(85)–C(38)	1.113	1.113	70	C(23)–C(29)	1.337	1.42
14	S(49)–O(51)	1.45	1.45	71	C(54)–H(102)	1.1	1.1
15	H(86)-C(39)	1.113	1.113	72	S(20) - O(21)	1.45	1.45
16	C(28) - C(29)	1.337	1.42	73	H(82)-C(28)	1.1	1.1
17	U(60) - V(59)	1.5996	-	74	C(32)-C(33)	1.337	1.503
18	H(62) = C(9)	1.113	1.115	15	C(40) = H(88)	1.113	1.115
19	C(32) - C(48) C(10) U(62)	1.49/	1.497	70 77	C(33) = C(30) C(41) = U(02)	1.337	1.505
20	$C(10) - \Pi(03)$ C(55) - C(57)	1.115	1.115	70	$C(41) = \Pi(92)$ C(26) = C(28)	1.115	1.115
21	U(33) = U(37) U(71) = U(15)	1.557	1.42	78	C(20) = C(20)	1.337	1.42
22	H(71)-C(13) S(40) N(37)	1.1	1.1	80	V(23) = V(24) N(1) N(2)	1.557	1.42
23	C(47) = C(46)	1.090	-	81	$\Gamma(1) = \Gamma(2)$ $\Gamma(3) = \Gamma(2)$	1.014	1.420
24	C(47) = C(40) C(58) = C(52)	1.337	1.42	82	N(30) - N(31)	1.20	1.20
25	C(12) - H(69)	1.113	1.113	83	C(10) - C(9)	1.523	1.523
20	C(55) - C(54)	1 337	1.115	84	C(10) - C(11)	1.523	1.523
28	N(8) - V(59)	1.9264	_	85	C(26) - N(27)	1.266	1.462
29	C(7)-C(9)	1.497	1.497	86	C(58) - H(106)	1.1	1.1
30	C(36) - N(37)	1.377	_	87	C(18) - C(17)	1.337	1.42
31	H(87)-C(39)	1.113	1.113	88	C(45)-C(46)	1.337	1.42
32	V(59)–O(6)	1.86	_	89	C(34)–O(35)	1.355	1.355
33	C(13)–N(1)	1.266	1.462	90	C(40)–C(39)	1.523	1.523
34	C(17)-H(73)	1.1	1.1	91	C(16)-C(15)	1.337	1.42
35	C(47)-H(97)	1.1	1.1	92	C(17)–C(16)	1.337	1.42
36	H(104)-N(56)	1.05	1.05	93	C(3)–C(4)	1.337	1.503
37	C(5)–C(4)	1.337	1.337	94	C(19)–C(3)	1.497	1.497
38	C(5)–O(6)	1.355	1.355	95	C(12)-H(68)	1.113	1.113
39	C(48)–H(100)	1.113	1.113	96	C(12)-H(67)	1.113	1.113
40	H(76)-C(19)	1.113	1.113	97	C(7)–C(4)	1.337	1.503
41	H(75)–C(19)	1.113	1.113	98	N(8)–C(7)	1.377	-
42	C(12)-C(11)	1.523	1.523	99	C(11)–H(66)	1.113	1.113
43	C(13)-C(14)	1.337	1.42	100	V(59)–N(37)	2.0946	-
44	C(18)–H(74)	1.1	1.1	101	H(95)-C(45)	1.1	1.1
45	C(47)-C(42)	1.337	1.42	102	C(43)–H(93)	1.1	1.1
46	C(52)–S(49)	1.79	-	103	C(43)–C(44)	1.337	1.42
47	H(84)-C(38)	1.113	1.113	104	H(83)–C(29)	1.1	1.1
48	N(27) - H(81)	1.05	1.05	105	N(30) - C(42)	1.266	1.462
49	H(103) - N(56)	1.05	1.05	106	C(43) - C(42)	1.337	1.42
50	H(61)-C(9)	1.113	1.113	107	S(49) = O(50)	1.45	1.45
51	U(35) - V(59)	1.80	-	108	C(40) - C(41)	1.523	1.523
52 52	H(105)-C(57)	1.1	1.1	109	C(38) - C(39)	1.525	1.523
55 54	C(10) - H(72)	1.1	1.1	110	S(20) - O(22)	1.45	1.45
34 55	C(55) = N(50)	1.200	1.402	111	C(30) - C(38)	1.497	1.497
55 56	C(34) - C(33)	1.337	1.42	112	C(44) = C(45)	1.337	1.42
57	C(32) - IN(31) C(26) - C(25)	1.337	1.42	115	C(33)-C(34)	1.337	1.337

the vanadium(IV) formed from vanadium(V) of the marine environment in the initial reduction could become ligated in such a way as to lower its reduction potential to the required trivalent state. 3.7. 3D molecular modeling and analysis

In view the penta-coordination of all the complexes (vide infra), and also taking into account of the well established

Table 7 Various bond angles of compound  $[VO(L^3)_2]$  (3)

S. no.	Atoms	Actual bond angles	Optimal bond angles	S. no.	Atoms	Actual bond angles	Optimal bond angles
1	H(90)–C(41)–H(91)	109.442	109	101	C(34)–N(30)–N(31)	111	124
2	H(91)-C(41)-H(92)	109.52	109	102	C(34)-N(30)-C(42)	124.5	124
3	C(40)-C(41)-H(91)	109.442	110	103	C(42)–N(30)–N(31)	124.5	124
4	H(90)-C(41)-H(92)	109.462	109	104	C(32)-C(33)-C(36)	128.998	120
5	C(40)-C(41)-H(90)	109.5	110	105	C(32)-C(33)-C(34)	111	120
6	C(40)-C(41)-H(92)	109.462	110	106	C(34)-C(33)-C(36)	119.998	120
7	H(88)-C(40)-H(89)	109.52	109.4	107	O(35)-C(34)-N(30)	124.698	-
8	H(89)-C(40)-C(39)	109.462	109.41	108	C(33)-C(34)-N(30)	110.999	120
9	C(41)-C(40)-H(89)	109.462	109.41	109	C(33)-C(34)-O(35)	124.3	124.3
10	H(88)-C(40)-C(39)	109.442	109.41	110	H(82)-C(28)-C(29)	120	120
11	C(41)-C(40)-H(88)	109.442	109.41	111	C(26)-C(28)-C(29)	120	-
12	C(41)-C(40)-C(39)	109.5	109.5	112	C(26)-C(28)-H(82)	120	120
13	H(86)-C(39)-H(87)	109.52	109.4	113	H(80)–N(27)–H(81)	120	118.8
14	C(40)–C(39)–H(86)	109.442	109.41	114	C(26)–N(27)–H(81)	120	-
15	H(86)–C(39)–C(38)	109.442	109.41	115	C(26)–N(27)–H(80)	120	-
16	C(40)–C(39)–H(87)	109.462	109.41	116	C(25)-C(26)-C(28)	120	120
17	H(87)-C(39)-C(38)	109.462	109.41	117	C(25)-C(26)-N(27)	120	120
18	C(40)-C(39)-C(38)	109.5	109.5	118	N(27) - C(26) - C(28)	120	120
19	H(69)-C(12)-C(11)	109.462	110	119	H(79)-C(25)-C(24)	120	120
20	H(69)-C(12)-H(68)	109.52	109	120	H(79)-C(25)-C(26)	120	120
21	H(67)-C(12)-H(69)	109.462	109	121	C(26)-C(25)-C(24)	120	-
22	C(11)-C(12)-H(68)	109.442	110	122	C(23) = C(29) = C(28)	120	-
23	H(67) - C(12) - C(11)	109.5	110	123	H(83) = C(29) = C(28)	119.999	120
24	H(6/)-C(12)-H(68)	109.442	109	124	C(23) = C(29) = H(83)	120.001	120
25	C(12) = C(11) = H(03) C(12) = C(11) = C(10)	109.442	109.41	125	H(78) = C(24) = C(25)	119.999	120
20	C(12) = C(11) = C(10) C(12) = C(11) = H(66)	109.5	109.5	120	U(23) = U(24) = U(23)	120	-
21	C(12) = C(11) = H(00) C(10) = C(11) = H(65)	109.402	109.41	127	R(78) - C(24) - C(23) S(20) - C(23) - C(20)	120.001	120
20	H(65) - C(11) - H(65)	109.442	109.41	120	S(20)-C(23)-C(29) S(20)-C(23)-C(24)	120	_
30	$\Gamma(00) = C(11) = \Pi(00)$ $\Gamma(10) = C(11) = \Pi(66)$	109.32	109.4	130	C(24) = C(23) = C(24)	120	120
31	H(64) = C(10) = H(63)	109.402	109.41	131	C(18) - C(17) - H(73)	120	120
32	C(9) - C(10) - H(63)	109.32	109.41	132	C(16) - C(17) - H(73)	120	120
33	C(11)-C(10)-H(63)	109.442	109.41	132	C(18) - C(17) - C(16)	120	-
34	H(64)-C(10)-C(9)	109.462	109.41	134	H(72)-C(16)-C(15)	120	120
35	C(11)-C(10)-H(64)	109.462	109.41	135	C(17)–C(16)–H(72)	120	120
36	C(11)-C(10)-C(9)	109.5	109.5	136	C(17)-C(16)-C(15)	120	_
37	C(55)-C(57)-C(58)	120	_	137	H(71)–C(15)–C(14)	120	120
38	C(58)-C(57)-H(105)	120	120	138	C(16)-C(15)-C(14)	120	-
39	C(55)-C(57)-H(105)	120.001	120	139	H(71)-C(15)-C(16)	120	120
40	H(104)-N(56)-H(103)	120	118.8	140	C(13)-C(18)-H(74)	120	120
41	C(55)-N(56)-H(104)	120	-	141	C(17)-C(18)-H(74)	120	120
42	C(55)-N(56)-H(103)	120.001	-	142	C(13)-C(18)-C(17)	120	-
43	C(54)-C(55)-C(57)	120.001	120	143	C(13)-C(14)-C(15)	120	-
44	N(56)-C(55)-C(57)	119.999	120	144	H(70)-C(14)-C(15)	120	120
45	C(54)-C(55)-N(56)	120	120	145	C(13)-C(14)-H(70)	120	120
46	C(55)-C(54)-C(53)	120	-	146	S(49)-N(37)-C(36)	110.267	-
47	C(55)-C(54)-H(102)	120.001	120	147	S(49)-N(37)-V(59)	110.267	-
48	H(102)-C(54)-C(53)	120	120	148	V(59)–N(37)–C(36)	106.168	-
49	C(52)–C(58)–C(57)	120	-	149	C(34)–O(35)–V(59)	109.5	-
50	H(106)-C(58)-C(57)	120	120	150	N(8)–V(59)–O(60)	19.5526	-
51	C(52)-C(58)-H(106)	120	120	151	O(60)–V(59)–O(6)	90	-
52	C(54)–C(53)–H(101)	120	120	152	O(60)–V(59)–O(35)	89.9999	-
53	C(52)–C(53)–H(101)	120	120	153	O(60) - V(59) - N(37)	100.509	-
54	C(54)-C(53)-C(52)	120	-	154	N(8) - V(59) - O(6)	82.2944	-
<b>33</b>	C(58) = C(52) = S(49)	120	-	155	N(8) - V(59) - O(35)	109.5	-
56	C(58) = C(52) = C(53)	120	120	156	N(8) - V(59) - N(37)	102.675	-
5/	S(49) = C(52) = C(53)	120	-	157	U(35) - V(59) - U(6)	109.5	-
38 50	U(47) - U(40) - H(90)	120	120	158	N(37) - V(39) - U(6)	33.4308 77.7856	_
39 60	H(90) - C(40) - C(45)	120	120	159	U(35) - V(59) - N(37)	100 52	_
61	U(47) = U(40) = U(43) U(05) = U(45) = U(45)	120	-	161	C(23) = S(20) = IN(8)	109.32	_
62	$\Gamma(93) = C(43) = C(40)$ $\Gamma(44) = C(45) = C(46)$	120	120	167	C(23) = S(20) = O(21)	109.402	_
02	C(++) = C(+3) = C(+0)	120	-	102	U(23) - 3(20) - U(22)	107.402	-

Table 7	(continued)
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S. no.	Atoms	Actual bond angles	Optimal bond angles	S. no.	Atoms	Actual bond angles	Optimal bond angles
63	H(95)-C(45)-C(44)	120	120	163	N(8)-S(20)-O(21)	109.442	_
64	C(43)-C(44)-H(94)	120	120	164	N(8)-S(20)-O(22)	109.442	_
65	H(94)-C(44)-C(45)	120	120	165	O(21)–S(20)–O(22)	109.5	-
66	C(43)-C(44)-C(45)	120	_	166	H(62)–C(9)–C(7)	109.462	109.41
67	H(97)-C(47)-C(46)	120	120	167	H(62)–C(9)–H(61)	109.52	109.4
68	C(42)-C(47)-C(46)	120	-	168	H(62)-C(9)-C(10)	109.462	109.41
69	H(97)-C(47)-C(42)	120	120	169	H(61)–C(9)–C(7)	109.442	109.41
70	H(93)-C(43)-C(44)	120	120	170	C(10)-C(9)-C(7)	109.5	109.5
71	C(42)-C(43)-H(93)	120	120	171	C(10)–C(9)–H(61)	109.442	109.41
72	C(42)-C(43)-C(44)	120	-	172	S(20)-N(8)-V(59)	110.042	-
73	C(47)-C(42)-N(30)	120	120	173	S(20)–N(8)–C(7)	110.041	-
74	C(47)-C(42)-C(43)	120	120	174	C(7)-N(8)-V(59)	107.085	_
75	N(30)-C(42)-C(43)	120	120	175	N(1)-C(13)-C(14)	120	120
76	C(32)-C(48)-H(99)	109.442	110	176	C(18)-C(13)-N(1)	120	120
77	H(99)-C(48)-H(100)	109.52	109	177	C(18)-C(13)-C(14)	120	120
78	H(98)-C(48)-H(99)	109.442	109	178	C(9)-C(7)-C(4)	118.5	121.4
79	C(32)-C(48)-H(100)	109.462	110	179	N(8)-C(7)-C(9)	118.5	_
80	C(32)-C(48)-H(98)	109.5	110	180	N(8)-C(7)-C(4)	123	_
81	H(98)-C(48)-H(100)	109.462	109	181	C(5)-O(6)-V(59)	109.5	_
82	C(32)-N(31)-N(30)	108.832	115	182	N(1)-C(5)-C(4)	111	120
83	N(37)-S(49)-O(51)	109.442	_	183	N(1)-C(5)-O(6)	124.698	_
84	C(52)-S(49)-O(51)	109.462	-	184	C(4)-C(5)-O(6)	124.298	124.3
85	O(50)-S(49)-O(51)	109.5	116.6	185	H(75)-C(19)-H(76)	109.442	109
86	C(52)-S(49)-N(37)	109.52	-	186	H(77)-C(19)-H(76)	109.52	109
87	O(50)-S(49)-N(37)	109.442	-	187	H(76)–C(19)–C(3)	109.442	110
88	C(52)-S(49)-O(50)	109.462	-	188	H(77)-C(19)-H(75)	109.462	109
89	H(84)-C(38)-H(85)	109.52	109.4	189	H(75)-C(19)-C(3)	109.5	110
90	H(85)-C(38)-C(39)	109.462	109.41	190	H(77)–C(19)–C(3)	109.462	110
91	C(36)-C(38)-H(85)	109.462	109.41	191	C(5)-C(4)-C(3)	111	120
92	H(84)-C(38)-C(39)	109.441	109.41	192	C(5)-C(4)-C(7)	119.999	120
93	C(36)-C(38)-H(84)	109.442	109.41	193	C(7)-C(4)-C(3)	128.998	120
94	C(36)-C(38)-C(39)	109.5	109.5	194	C(13)–N(1)–C(5)	128.353	124
95	C(33)-C(36)-N(37)	123	-	195	C(5)-N(1)-N(2)	103.293	124
96	N(37)-C(36)-C(38)	118.5	-	196	C(13)–N(1)–N(2)	128.353	124
97	C(33)-C(36)-C(38)	118.5	121.4	197	N(2)-C(3)-C(4)	111	120
98	C(48)-C(32)-N(31)	130.916	115.1	198	C(19)-C(3)-N(2)	124.5	115.1
99	C(33)-C(32)-C(48)	130.915	121.4	199	C(19)-C(3)-C(4)	124.5	121.4
100	C(33)-C(32)-N(31)	98.169	120	200	N(1)-N(2)-C(3)	103.707	115

square pyramidal structure [49] of bis(picolinato)oxovanadium(IV) (Fig. 6) [having a monoprotic bidentate (O, N-donor) picolinate ligand, similar to monoprotic (O, N-donor)  $L^{1}H$ ,  $L^{2}H$ ,  $L^{3}H$  or  $L^{4}H$  ligand in the present investigation], the molecular modeling of a representative compound,  $[VO(L^3)_2]$ (3), is based on its square pyramidal structure. The details of bond lengths and bond angles as per the 3D structure (Fig. 7) are given in Tables 6 and 7, 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, 313 measurements of the bond lengths, plus the bond angles are listed in the Tables 6 and 7. Except few cases, optimal values (most favorable) of both the bond lengths and the bond angles are given in the tables along with the actual ones. 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 (3) as well as of the others, are acceptable.

### 4. Conclusion

The satisfactory analytical data and all the studies presented above suggests that the present complexes may be formulated as  $[VO(L)_2] \cdot H_2O$ , where  $LH = L^1H$ ,  $L^2H$ ,  $L^3H$ or L<sup>4</sup>H. Keeping in view of the  $\nu$ (V=O) mode at quite lower values around  $900 \text{ cm}^{-1}$  and the observed magnetic moments of the complexes in the range 1.61-1.65 BM, and considering the well established square pyramidal structure [49] of bis(picolinato)oxovanadium(IV) (Fig. 6) in the solid state [involving a monoprotic bidentate (O, N-donor) picolinate ligand, similar to monoprotic bidentate (O, N-donor) LH ligands in the present investigation], a square based pyramidal structure (Fig. 8) having a slight ... V=O... V=O··· type interaction has been proposed for these complexes. X-ray crystallographic studies, which might confirm the proposed structures, could not be carried out as suitable crystals were not obtained.



Fig. 8. Suggested structure of complexes.

# Acknowledgements

The authors are thankful to Dr S.M. Paul Khurana, Vicechancellor of this University, for encouragement, and Professor K.K. Verma, Head, Department of Chemistry, for laboratory facilities and helpful discussion. We are grateful to the Department of Science and Technology, New Delhi, India, for financial assistance. Analytical facilities provided by the Central Drug Research Institute, Lucknow, India, and the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai, India, are gratefully acknowledged.

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