

# Synthesis, spectral and structural studies of oxovanadium(IV/V) complexes derived from 2-hydroxyacetophenone-3-hydroxy-2-naphthoylhydrazone: polymorphs of oxovanadium(V) complex [VOL(OCH<sub>3</sub>)]

M. R. Prathapachandra Kurup · E. B. Seena · Mini Kuriakose

Received: 30 August 2009 / Accepted: 11 January 2010 / Published online: 9 February 2010  
© Springer Science+Business Media, LLC 2010

**Abstract** Oxovanadium(IV/V) complexes of 2-hydroxyacetophenone-3-hydroxy-2-naphthoylhydrazone (H<sub>2</sub>L) have been synthesized and characterized. The complexes were characterized by elemental analyses, IR, electronic and EPR spectra. The oxovanadium(V) complex [VOL(OCH<sub>3</sub>)] is crystallized in two polymorphic forms, denoted by **1a** and **1b**, with space groups *Pn*2<sub>1</sub>a and *P*<sub>1</sub>, respectively. Both have distorted square pyramidal structures.

**Keywords** Oxovanadium(IV/V) complexes · 2-Hydroxyacetophenone · 3-Hydroxy-2-naphthoylhydrazide · Crystal structures

## Introduction

Hydrazones and their metal complexes are widely studied due to their versatile applications in the field of analytical and medicinal chemistry [1, 2]. Compounds containing hydrazide and acylhydrazone moieties and their complexes possess biological activity, especially as potential inhibitors for many enzymes. These ligands due to their facile keto-enol tautomerisation and the availability of several potential donor sites can coordinate with metals in many ways. Hydrazone ligands can act as bidentate, tridentate or tetradentate ligands depending on the nature of heterocyclic ring substituents attached to the hydrazone unit. The ligands in the coordination sphere can exist in the neutral or

anionic form depending on the reaction conditions employed [3].

The complexes of metal-hydrazones continue to attract considerable attention owing to their interesting biological activities and potential applications in industry [4]. The richness and importance of vanadate chemistry have emerged for quite some time [5–7]. In continuation of our work on the synthesis and characterization of aroyl hydrazones and their coordination compounds [8–12], we report here the synthesis and characterization of oxovanadium (IV/V) complexes of 2-hydroxyacetophenone-3-hydroxy-2-naphthoylhydrazone (H<sub>2</sub>L) along with the crystal structure of an oxovanadium(V) complex existing in two polymorphic forms. In addition to the azomethine nitrogen and carbonyl oxygen, the coordinating capacity of the ligand has been enhanced by the presence of coordinating oxygen in the phenyl ring of aromatic ketone.

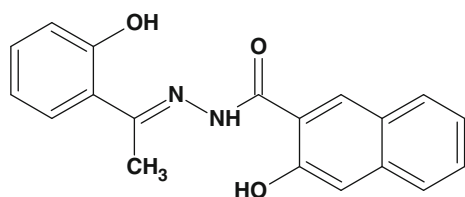
## Experimental

### Materials and physical measurements

The chemicals 2-hydroxyacetophenone (SRL), 3-hydroxy-2-naphthoylhydrazide (Fluka) were used without further purification. All the solvents were purified using standard methods before use.

Elemental analyses of the ligand and complexes were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a JASCO FT/IR-4100 type A spectrometer in the range 4000–400 cm<sup>-1</sup> using KBr pellets. Electronic spectra were recorded on a Cary 5000 version 1.09 UV–VIS–NIR spectrophotometer using DMF as the solvent. The EPR spectra of the complexes in the solid state at 298 K and in

M. R. P. Kurup (✉) · E. B. Seena · M. Kuriakose  
Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682-022, Kerala, India  
e-mail: mrp@cusat.ac.in; mrp\_k@yahoo.com



**Fig. 1** Structure of the ligand ( $H_2L$ )

DMF at 77 K were recorded on a Varian E-112 spectrometer using TCNE as the standard, with 100 kHz modulation frequency and 9.1 GHz microwave frequency at the SAIF, IIT Bombay, India.

#### Synthesis of oxovanadium(IV/V) complexes

The ligand  $H_2L$  was synthesized as already reported [13] (Fig. 1). The complexes **1a** and **1b** are different polymorphs of the same compound obtained by different procedures. The complex  $[VOL(OCH_3)]$  (**1a**) was prepared by refluxing a mixture of 1 mmol of the  $VOSO_4 \cdot H_2O$  in methanol and 1 mmol of the ligand ( $H_2L$ ) in methanol for 4 h. Dark red plate crystals suitable for X-ray analysis were obtained from a solution of the compound in a mixture of  $CH_2Cl_2/CH_3OH$  in 1:1 ratio. The complex  $[VOL(OCH_3)]$  (**1b**) was prepared by adding 1 mmol of the  $VO(acac)_2$  in methanol to 1 mmol of the ligand ( $H_2L$ ) in methanol. On slow evaporation, dark red block crystals suitable for X-ray analysis were obtained. The complexes  $[VOLbipy] \cdot 1/2 H_2O$  (**2**) and  $[VOLphen] \cdot 1/2 H_2O$  (**3**) were prepared by refluxing 1 mmol each of  $VOSO_4 \cdot H_2O$  in aqueous solution, heterocyclic base (bipy/phen) in solid form and the ligand ( $H_2L$ ) in methanol for 4 h.

$[VOL(OCH_3)]$  (**1**): Found (Calcd): C, 58.48(58.10); H, 4.86(4.67); N, 6.48(6.49).

$[VOLbipy] \cdot 1/2 H_2O$  (**2**): Found (Calcd): C, 63.62(63.28); H, 3.79(4.21); N, 10.20(10.18).

$[VOLphen] \cdot 1/2 H_2O$  (**3**): Found (Calcd): C, 62.25(62.63); H, 5.37(4.58); N, 9.99(9.42).

#### X-ray structure determinations

Dark red crystals of the compounds **1a** and **1b** having approximate dimensions of  $0.37 \times 0.33 \times 0.30 \text{ mm}^3$  and  $0.36 \times 0.33 \times 0.21 \text{ mm}^3$ , respectively, were sealed in glass capillaries. The crystallographic data and structure refinement parameters for the complexes **1a** and **1b** are given in Table 1. The X-ray diffraction data of the compounds were measured at 120(2) K; data acquisition, cell refinement and data reduction were done using the CrysAlis CCD, Oxford Diffraction Ltd. [14]. The structure was solved by direct methods and full-matrix least-squares

refinement using SHELX97 [15] package. The positions of all the non-hydrogen atoms were included in the full-matrix least-squares refinement using SHELX97 program, and all the hydrogen atoms were fixed in calculated positions for compounds **1a** and **1b**.

#### Crystal structures

The molecular structure of the compound **1a** along with atom numbering scheme is given in Fig. 2. This compound crystallizes in the orthorhombic crystal system with space group  $Pn2_1a$ . The vanadium atom in this molecule is five-coordinate, existing in a distorted square pyramidal geometry in which the basal plane is defined by phenoxy oxygen (O1), azomethine nitrogen (N1), enolic oxygen (O2) derived from the tridentate ligand and the oxygen atom (O4) of the methoxide; the apical position is occupied by the oxo group (O5). The terminal V1–O5 (oxo) distance is 1.584(2) Å, V1–O1 (phenoxy) is 1.8177(19) Å, V1–O2 (ketoxy) is 1.924(2) Å and V1–O4 (methoxy) is 1.772(2) Å; these agree well with the corresponding values reported for related systems [16].

The greatest distortion from ideal geometry is manifested in the O1–V1–O2 angle of  $138.73(11)^\circ$ , which arises as a result of the restricted bite angle of the tridentate ligand. The coordination mode of the tridentate ligand leads to the formation of both five- and six-membered rings. The relatively short C7–N1 and C9–N2 bond distances of 1.303(4) and 1.294(4) Å, respectively, coupled with the N1–N2 distance of 1.393(4) Å, indicate that there is conjugation along the backbone of the tridentate ligand; the value of the C7–N1–N2–C9 torsion angle is  $-175.1(3)^\circ$ .

The mean plane deviation calculations show that the atoms in the basal plane O1, N1, O2 and O4 comprising the square planes are 0.1019, 0.1683, 0.1323 and 0.1384 Å, respectively, and the V1 atom lies 0.4908 Å above this plane in the direction of the O5 atom. Ring puckering analyses and least-square plane calculations show that the ring Cg(1) comprising of atoms V1, O2, C9, N2 and N1 confirms an ‘envelope’ conformation (‘E’ configuration) [17].

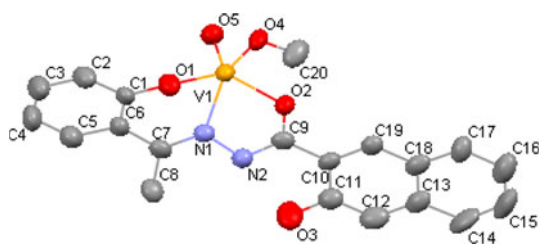
Figure 3 shows the contents of the unit cell packing. The assemblage of molecules in the respective manner in the unit cell is resulted by the  $\pi$ – $\pi$  and C–H $\cdots$  $\pi$  interactions. The centroid Cg(1) is involved in  $\pi$ – $\pi$  interaction with Cg(4) at a distance of 3.7108 Å and C–H $\cdots$  $\pi$  interactions C(8)–H(8)  $\rightarrow$  Cg(5) at a distance of 2.74 Å contribute stability to the unit cell packing. The unit cell comprises two molecules, and an intramolecular hydrogen bonding interaction occurs between O3(H) and N2 at a distance of 2.630(4) Å with an angle of  $148^\circ$ . An intermolecular hydrogen bonding interaction is also observed between C14–H14 and O5 at a distance of 3.430(5) Å with an angle of  $149^\circ$  (symmetry operation:  $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ).

**Table 1** Crystal data and structure refinement parameters for the complexes **1a** and **1b**

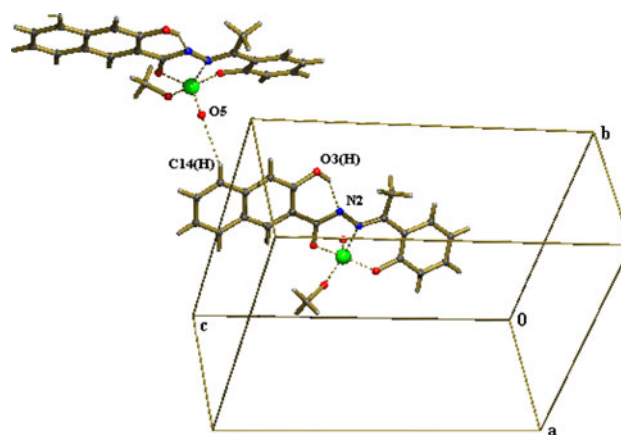
	[VOL(OCH <sub>3</sub> )] <b>1a</b>	[VOL(OCH <sub>3</sub> )] <b>1b</b>
Empirical formula	C <sub>20</sub> H <sub>17</sub> N <sub>2</sub> O <sub>5</sub> V	C <sub>20</sub> H <sub>17</sub> N <sub>2</sub> O <sub>5</sub> V
Formula weight	416.30	416.30
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pn</i> 2 <sub>1</sub> <i>a</i>	<i>P</i> <sub>1</sub>
Unit cell dimensions	<i>a</i> = 7.2653(2) Å <i>b</i> = 14.4911(4) Å <i>c</i> = 17.1643(6) Å $\alpha$ = 90.00° $\beta$ = 90.00° $\gamma$ = 90.00°	<i>a</i> = 7.3185(7) Å <i>b</i> = 15.710(3) Å <i>c</i> = 16.378(3) Å $\alpha$ = 104.619(17)° $\beta$ = 101.257(11)° $\gamma$ = 97.057(12)°
Volume, <i>Z</i>	1807.09(9) Å <sup>3</sup> , 4	1757.5(5) Å <sup>3</sup> , 4
Calculated density	1.530 Mg/m <sup>3</sup>	1.573 Mg/m <sup>3</sup>
Absorption coefficient	0.585 mm <sup>-1</sup>	0.601 mm <sup>-1</sup>
<i>F</i> (000)	856	856
Crystal size	0.37 × 0.33 × 0.30 mm <sup>3</sup>	0.36 × 0.33 × 0.21 mm <sup>3</sup>
$\theta$ range for data collection	3.04–24.98°	3.12–24.99°
Index ranges	−8 ≤ <i>h</i> ≤ 8, −17 ≤ <i>k</i> ≤ 17, −19 ≤ <i>l</i> ≤ 20	−8 ≤ <i>h</i> ≤ 8, −18 ≤ <i>k</i> ≤ 18, −18 ≤ <i>l</i> ≤ 19
Reflections collected/unique	3166/2861	6202/5440
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3166/1/259	6174/0/517
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.121	1.035
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0396 <i>wR</i> 2 = 0.0792	<i>R</i> 1 = 0.0277 <i>wR</i> 2 = 0.0744
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0466 <i>wR</i> 2 = 0.0835	<i>R</i> 1 = 0.0329 <i>wR</i> 2 = 0.0774

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

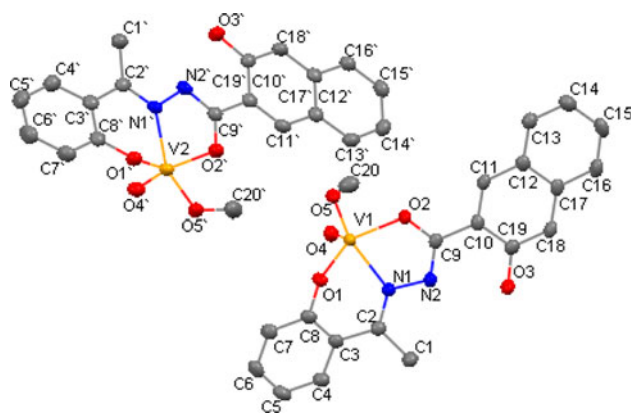
$$wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

**Fig. 2** Molecular structure of **1a**

The molecular structure of the compound **1b** is same as that of **1a**, but the asymmetric unit of **1b** contains two independent molecules (Fig. 4). However, there are only minor differences between the molecules in the asymmetric unit. This compound crystallizes in the triclinic crystal system with space group *P*<sub>1</sub>. The coordination around the central vanadium atom (V1) is same as that of **1a** and having distorted square pyramidal geometry in which the basal plane is defined by O1, N1 and O2 atoms from the

**Fig. 3** Partial unit cell packing of **1a** with intra- and intermolecular hydrogen bonding interactions

tridentate ligand and the oxygen atom (O5) of the methoxide; the apical position is occupied by the oxo (O4) group. The bond lengths [V1–O4 (oxo) = 1.5877(12) Å,



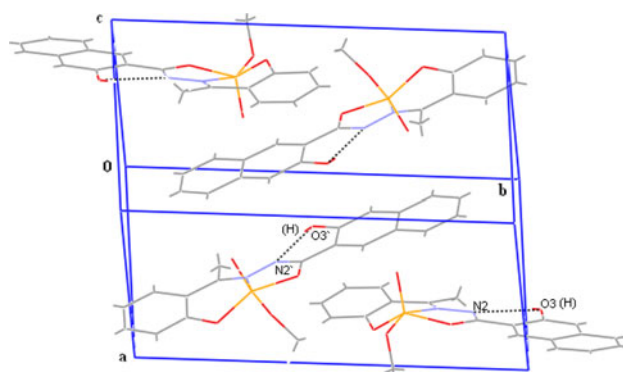
**Fig. 4** Molecular structure of **1b**

V1–O1 (phenoxy) = 1.8267(13) Å, V1–O2 (ketoxy) = 1.9192(12) Å and V1–O5 (methoxy) = 1.7618(13) Å, V1–N1 = 2.0939(16) Å, and the bond angle with greatest distortion from ideal geometry [O1–V1–O2 = 137.16(6)°] of **1b** is slightly different from **1a**. The selected bond lengths and bond angles of compounds **1a** and **1b** are presented in Table 2. The four vanadium–oxygen bond lengths in the complexes **1a** and **1b** are in the order: oxo < methoxide < phenolate < enolate, which is most probably due to the order of O → V  $\pi$ -bonding. In **1b**, the least-squares plane through the O1, N1, O2 and O5 atoms comprising the square planes are 0.1037, 0.1564, 0.1290 and 0.1163 Å, respectively, and the V1 atom lies 0.5183 Å above this plane in the direction of the O4 atom; comparable values for the second molecule are 0.0636, 0.0912, 0.0712 and 0.0696 Å, respectively, and the V2 atom lies 0.4874 Å above this plane in the direction of the O4' atom. As compared to **1a**, the deviations are almost the same in **1b**. Ring puckering analyses and least-square plane calculations show that the ring Cg(1) comprising of atoms V1, O2, C9, N2 and N1 and Cg(7) comprising of atoms V2, O2', C9', N2' and N1' confirm 'E' conformation (envelope on V1 and V2, respectively) [17].

Figure 5 shows the contents of the unit cell packing. The assemblage of molecules in the respective manner in the unit cell is resulted by the  $\pi$ - $\pi$ , C–H $\cdots$  $\pi$  and hydrogen bonding interactions. The centroid Cg(4) is involved in  $\pi$ - $\pi$  interaction with Cg(4) of the neighbouring unit at a distance of 3.6788(12) Å and C–H $\cdots$  $\pi$  interaction C(1)–H(1A) → Cg(5) at a distance of 2.59 Å contribute stability to the unit cell packing. The unit cell comprises four molecules, and an intramolecular hydrogen bonding interaction occurs between O3(H) and N2 at a distance of 2.589(2) Å with an angle of 150°. Similarly for the second molecule in the asymmetric unit [O3'(H) and N2' at a distance of 2.569(2) Å with an angle of 152°], an intermolecular hydrogen bonding interaction is also observed between C(14)–H(14) and O(3) at a distance of 3.266(2) Å

**Table 2** Selected bond lengths (Å) and bond angles (°) for **1a** and **1b**

<b>1a</b>	<b>1b(I)</b>	<b>1b(II)</b>			
V1–O1	1.8177(19)	V1–O4	1.5877(12)	V2–O4'	1.5861(13)
V1–O2	1.924(2)	V1–O5	1.7618(13)	V2–O5'	1.7585(13)
V1–N1	2.090(3)	V1–O1	1.8267(13)	V2–O1'	1.8339(13)
O1–C1	1.344(4)	V1–O2	1.9192(12)	V2–O2'	1.9299(13)
O2–C9	1.314(4)	V1–N1	2.0939(16)	V2–N1'	2.0835(15)
O4–C20	1.406(4)	O1–C8	1.346(2)	O1'–C8'	1.341(2)
O3–C11	1.356(4)	O2–C9	1.306(2)	O2'–C9'	1.308(2)
N1–C7	1.303(4)	N1–C2	1.305(2)	N1'–C2'	1.305(2)
N1–N2	1.393(4)	N1–N2	1.387(2)	N1'–N2'	1.388(2)
N2–C9	1.294(4)	N2–C9	1.300(2)	N2'–C9'	1.299(2)
O5–V1–O4	105.29(12)	O4–V1–O5	106.16(6)	O4'–V2–O5'	106.69(6)
O5–V1–O1	106.70(11)	O4–V1–O1	108.19(6)	O4'–V2–O1'	105.44(6)
O4–V1–O1	100.80(11)	O5–V1–O1	98.07(6)	O5'–V2–O1'	97.90(6)
O5–V1–O2	110.12(11)	O4–V1–O2	110.55(6)	O4'–V2–O2'	108.05(6)
O4–V1–O2	87.01(10)	O5–V1–O2	88.21(6)	O5'–V2–O2'	88.73(6)
O1–V1–O2	138.73(11)	O1–V1–O2	137.16(6)	O1'–V2–O2'	142.28(6)
O5–V1–N1	95.41(11)	O4–V1–N1	97.19(6)	O4'–V2–N1'	98.27(6)
O4–V1–N1	156.49(11)	O5–V1–N1	155.04(6)	O5'–V2–N1'	153.66(6)
O1–V1–N1	83.40(11)	O1–V1–N1	82.57(6)	O1'–V2–N1'	83.14(6)
O2–V1–N1	75.30(10)	O2–V1–N1	75.19(5)	O2'–V2–N1'	75.41(6)



**Fig. 5** Partial unit cell packing of **1b** with intramolecular hydrogen bonding interactions

with an angle of 152° (symmetry operation: 1 – x, –y, 2 – z). The  $\pi$ - $\pi$ , C–H $\cdots$  $\pi$  and hydrogen bonding interactions for the compounds **1a** and **1b** are given in Table 3.

**Table 3** Interaction parameters of the compounds **1a** and **1b**

$\pi$ - $\pi$ interactions				
Cg(I)-Res(1)⋯Cg(J)	Cg-Cg (Å)	$\alpha$ (°)	$\beta$ (°)	
Cg(1) [1] → Cg(4) <sup>a</sup> ( <b>1a</b> )	3.7108	8.88	18.23	
Cg(4) [1] → Cg(4) <sup>b</sup> ( <b>1b</b> )	3.6788	0.04	23.91	
C-H⋯ $\pi$ interactions				
X-H(I)⋯Cg(J)	H⋯Cg (Å)	X-H⋯Cg (°)	X⋯Cg (Å)	
C(8)-H(8) → Cg(5) <sup>a</sup> ( <b>1a</b> )	2.74	145	3.599 (4)	
C(1)-H(1A) → Cg(5) <sup>c</sup> ( <b>1b</b> )	2.59	155	3.486 (2)	
H bonding				
D-H⋯A	D-H	H⋯A	D⋯A	D-H⋯A
O(3)-H(103)⋯N(2) ( <b>1a</b> )	0.75(4)	1.96(4)	2.630(4)	148(4)
C(14)-H(14)⋯O(5) <sup>d</sup> ( <b>1a</b> )	0.95	2.58	3.430(5)	149
O(3)-H(03)⋯N(2) ( <b>1b</b> )	0.70(3)	1.96(3)	2.589(2)	150(3)
O(3')-H(03')⋯N(2') ( <b>1b</b> )	0.77(3)	1.86(3)	2.569(2)	152(3)
C(14)-H(14)⋯O(3) <sup>e</sup> ( <b>1b</b> )	0.93	2.41	3.266(2)	152

D donor, A acceptor, Cg centroid,  $\alpha$  dihedral angles between planes I and J,  $\beta$  angle Cg(I)-Cg(J)

Equivalent position codes:  $a = 1/2 + x, y, 3/2 - z$ ;  $b = -x, -y, 2 - z$ ;  $c = 1 - x, -y, 2 - z$ ;  $d = -1/2 - x, 1/2 + y, 1/2 + z$ ;  $e = 1 - x, -y, 2 - z$

Cg(1) = V(1), O(2), C(9), N(2), N(1);

Cg(4) = C(10), C(11), C(12), C(13), C(18), C(19);

Cg(4) = C(10), C(11), C(12), C(17), C(18), C(19);

Cg(5) = C(13), C(14), C(15), C(16), C(17), C(18);

Cg(5) = C(12), C(13), C(14), C(15), C(16), C(17)

### Spectral details

Selected vibrational bands of the free ligand and its vanadium complexes, which are useful for determining the mode of coordination of the ligands, are given in Table 4. In the IR spectra of the complexes, the shifting of  $\nu(\text{C}=\text{N})$  (azomethine) of the ligand to lower wavenumbers in the metal complexes (1597–1602  $\text{cm}^{-1}$ ) indicates the coordination of azomethine nitrogen to the metal [12, 18]. A new band appearing in the 1237–1239  $\text{cm}^{-1}$  region in the complexes (**1–3**) was assigned to the  $\nu(\text{C}-\text{O})$  (enolato) mode. The bands in the regions 501–510 and 421–428  $\text{cm}^{-1}$  can be assigned to the stretching modes of the metal to ligand bonds,  $\nu(\text{V}-\text{O})$  and  $\nu(\text{V}-\text{N})$ , respectively.

**Table 4** Selected IR bands ( $\text{cm}^{-1}$ ) with tentative assignments of oxovanadium(IV/V) complexes

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{V}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{V}-\text{O})$	$\nu(\text{V}-\text{N})$
H <sub>2</sub> L	1643	1604	–	–	–	–
[VOL(OCH <sub>3</sub> )] ( <b>1</b> )	–	1597	993	1237	510	428
[VOLbipy]·1/2H <sub>2</sub> O ( <b>2</b> )	–	1600	960	1240	502	420
[VOLphen]·1/2H <sub>2</sub> O ( <b>3</b> )	–	1602	956	1239	501	421

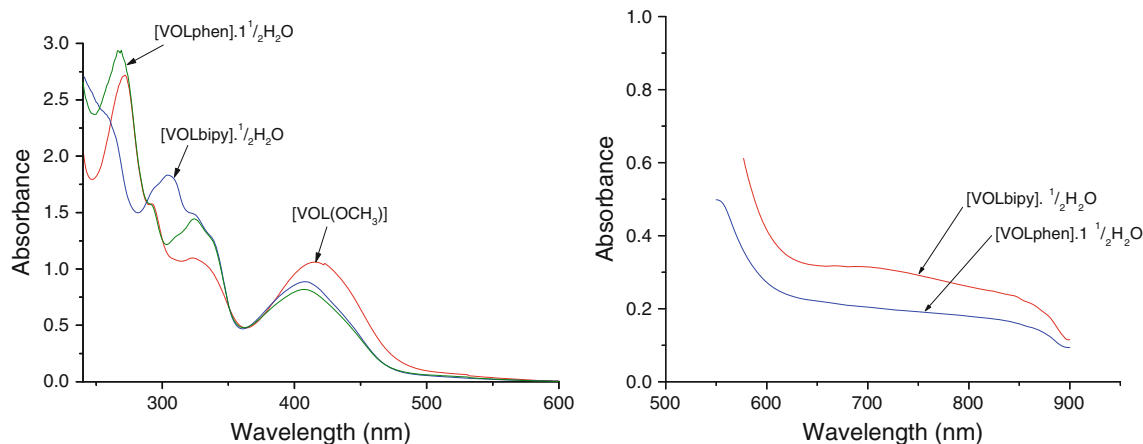
The complexes containing lattice water have IR bands in the range 3200–3500  $\text{cm}^{-1}$ . Here in the complexes **2** and **3**, broad bands are observed at 3467 and 3418  $\text{cm}^{-1}$  indicating the presence of lattice water in these molecules. The complexes **2** and **3** display bands at 1468 and 687; 1462 and 681  $\text{cm}^{-1}$  indicate the coordination of bipyridine and phenanthroline. In addition, the compounds exhibit a strong band in the 956–993  $\text{cm}^{-1}$  region due to the terminal V=O stretching [19–21].

The electronic spectra of the complexes in DMF solution are presented in the Table 5. The electronic spectra give much insight into the coordination geometry around the metal centre. The broad band at ca. 36760  $\text{cm}^{-1}$  can be attributed to the  $\pi \rightarrow \pi^*$  transition of the pyridyl ring of bipyridine/phenanthroline and imine function of the hydrazone ligand. The oxovanadium(IV)/(V) complexes (**1–3**) have broad bands in the range 32500–33000  $\text{cm}^{-1}$  corresponding to  $\pi \rightarrow \pi^*$  transition (pyridyl ring of bipyridine/phenanthroline and imine function of the hydrazone ligand) and are shifted to longer wavelength region as compared to the ligands. In ligands (hydrazone and bipyridine/phenanthroline),  $n \rightarrow \pi^*$  transitions due to pyridyl nitrogen and imine functions are at ca. 32100  $\text{cm}^{-1}$ , and in complexes this band is shifted and is in the range 29500–32000  $\text{cm}^{-1}$ . In complexes (**1–3**), an intense band at ca. 24440  $\text{cm}^{-1}$  is assignable to the phenolic oxygen  $\rightarrow \text{V}_{(\text{d}\pi)}$  ligand to metal charge transfer (LMCT) band [22, 23]. The compound [VOL(OCH<sub>3</sub>)] (**1**) is oxovanadium(V) complex, and d-d transitions are absent. In complexes **2** and **3**, an absorption band at ca. 11650  $\text{cm}^{-1}$  can be assigned to the electronic transition  ${}^2\text{B}_2 \rightarrow {}^2\text{E}$  ( $d_{xy} \rightarrow d_{xz}, d_{yz}$ ). In complex **2**, a signal at 14180  $\text{cm}^{-1}$  is observed due to  ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$  ( $d_{xy} \rightarrow d_{x^2-y^2}$ ). However, the band due to  ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$  ( $d_{xy} \rightarrow d_{z^2}$ ) is merged with LMCT band and observed as broad band in both complexes **2** and **3**, and in complex **3** the band due to  ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$  ( $d_{xy} \rightarrow d_{x^2-y^2}$ ) is also merged. These values are consistent with distorted octahedral structure for complexes **2** and **3** [8]. Representative spectra of the complexes (**1–3**) are presented in Fig. 6.

In complex **1**, vanadium is in +5 oxidation state and therefore EPR silent. EPR spectra of oxovanadium(IV) complexes **2** and **3** were recorded in polycrystalline state at 298 K and in DMF solution at 77 K. In polycrystalline state at 298 K, the complexes **2** and **3** are isotropic with

**Table 5** Electronic spectral assignments ( $\text{cm}^{-1}$ ) of oxovanadium(IV/V) complexes

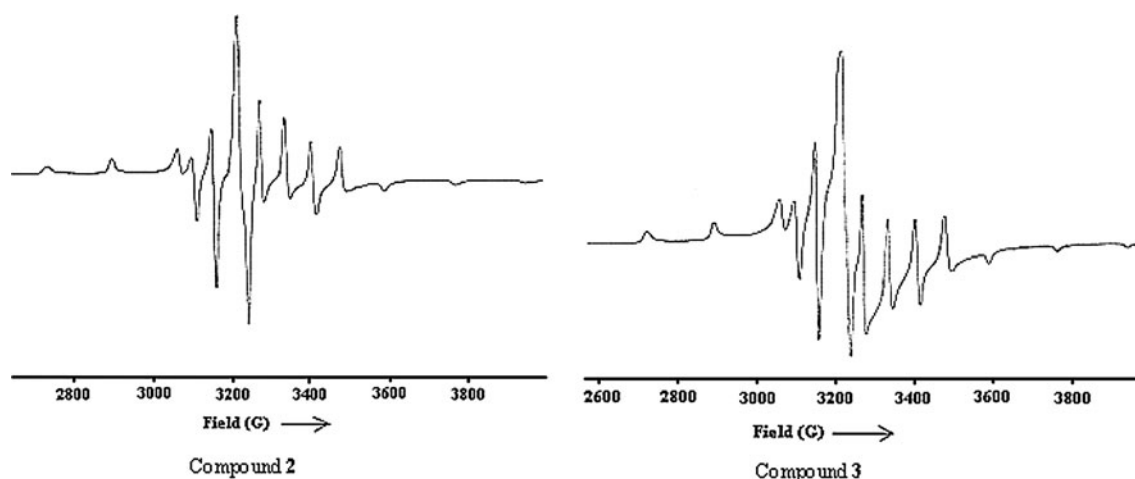
Compound	$\pi-\pi^*$	$n-\pi^*$	LMCT	d-d
$\text{H}_2\text{L}$	36760	32100	–	–
$[\text{VOL}(\text{OCH}_3)]$ ( <b>1</b> )	35710	32890, 31740, 29850	23750	–
$[\text{VOLbipy}] \cdot 1/2\text{H}_2\text{O}$ ( <b>2</b> )	34120, 32890	30770, 29580	24500	14180, 11800
$[\text{VOLphen}] \cdot 1/2\text{H}_2\text{O}$ ( <b>3</b> )	34240	30760, 29500	24390	11500

**Fig. 6** Electronic spectra of the complexes **1–3**

$g_{\text{iso}} = 1.990$ . In frozen DMF solution at 77 K, two sets of eight line spectra showing hyperfine splitting for the  $^{51}\text{V}$  nucleus ( $I = 7/2$ ) are obtained in the complexes (**2** and **3**). The  $g$  values calculated are  $g_{\parallel} = 1.947$  and  $1.958$  and  $g_{\perp} = 1.984$  and  $1.983$ , respectively, for complexes **2** and **3**. The corresponding coupling constants ( $A_{\parallel}$  and  $A_{\perp}$ ) are found to be 173.5, 170.7 and 57.1, 56.1 ( $\times 10^{-4} \text{ cm}^{-1}$ ), respectively [24–26]. The EPR spectra of the complexes **2** and **3** in DMF at 77 K are given in Fig. 7. The spectral parameters of the complexes **2** and **3** are given in Table 6.

### Supplementary data

CCDC 683391 and 683390 contain the supplementary crystallographic data for  $[\text{VOL}(\text{OCH}_3)]$  (**1a**) and  $[\text{VOL}(\text{OCH}_3)]$  (**1b**), respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2, IEZ, UK; Fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

**Fig. 7** EPR spectra of the complexes in DMF at 77 K

**Table 6** EPR spectral assignments of oxovanadium(IV) complexes in polycrystalline state at 298 K and DMF solution at 77 K

Compound	Polycrystalline state (298 K)	DMF solution (77 K)			
		$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^a$	$A_{\perp}^a$
[VOLbipy]· $\frac{1}{2}$ H <sub>2</sub> O ( <b>2</b> )	1.990 ( $g_{\text{iso}}$ )	1.947	1.984	173.5	57.1
[VOLphen]· $\frac{1}{2}$ H <sub>2</sub> O ( <b>3</b> )	1.990 ( $g_{\text{iso}}$ )	1.958	1.983	170.7	56.1

<sup>a</sup> Expressed in units of cm<sup>-1</sup> multiplied by a factor of 10<sup>-4</sup>

**Acknowledgement** M.R.P. Kurup is thankful to the CSIR, New Delhi, India [01(1963)/05/EMR-II] for financial assistance. We are thankful to the National Single Crystal X-ray diffraction Facility, IIT, Bombay, India, for providing single crystal XRD results.

## References

- Rath SP, Mondal S, Chakravorthy A (1997) *Inorg Chim Acta* 263:247
- Beraldo H, Gambino D (2004) *Mini Rev Med Chem* 4:159
- Hirao T, Mori M, Oshiro Y (1990) *J Org Chem* 55:358
- Hirao T, Fujii T, Tanaka T, Oshiro Y (1994) *J Chem Soc Perkin Trans* 1:3
- Fulwood R, Schmidt H, Rehder D (1995) *J Chem Soc Chem Commun* 1443
- Echert H, Das N (1994) *Inorg Chem* 33:2427
- Agedom G, Sreedhara A, KiviKoski J, Valkonen J, Hmainen EK, Rao CP (1996) *Inorg Chem* 35:5674
- Sreeja PB, Kurup MRP (2005) *Spectrochim Acta* A61:331
- Seena EB, Mathew N, Kuriakose M, Kurup MRP (2008) *Polyhedron* 27:1455
- Kuriakose M, Kurup MRP, Suresh E (2007) *Struct Chem* 18:579
- Mathew N, Kuriakose M, Seena EB, Kurup MRP (2007) *Acta Cryst E* 63:2190
- Mangalam NA, Sivakumar S, Sheeja SR, Kurup MRP, Tiekink ERT (2009) *Inorg Chim Acta* 362:4191
- Liu WY, Li YZ (2004) *Acta Cryst E* 60:o694
- CrysAlis CCD (2006) CrysAlis RED Versions 1.171.29.2 (CrysAlis171. NET). Oxford Diffraction Ltd, Abingdon, Oxfordshire, England
- Sheldrick GM (1997) SHELXL97 SHELXS97. University of Göttingen, Germany
- Tang ZX, Ping ZX, Ming WD, Zheng ZQ, Mei CS, Qin YY, Zhong LC (2002) *Chin J Struct Chem* 21:629
- Cremer D, Pople JA (1975) *J Am Chem Soc* 97:1354
- Reena TA, Seena EB, Kurup MRP (2008) *Polyhedron* 27:3461
- Bhattacharya S, Ghosh T (1999) *Indian J Chem* 38A:601
- Tsiamis C, Voulgaropoulos B, Christos D, Vonstas GP, Kavounis CA (2000) *Polyhedron* 19:2003
- Baran EJ (2001) *J Coord Chem* 54:215
- Walker FA, Carlin RL, Rieger PH (1966) *J Chem Phys* 45:4181
- Kuriakose M, Kurup MRP, Suresh E (2007) *Polyhedron* 26:2713
- Hausan GR, Kabanos TA, Kkeramidas AD, Mentazafos D, Terzis A (1992) *Inorg Chem* 31:2587
- Ghosh T, Bhattacharya S, Das A, Mukherjee G, Drew MGB (2005) *Inorg Chim Acta* 358:989
- Raman N, Raja JD, Sakthivel A (2007) *J Chem Sci* 119:303