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# Synthesis, structural characterization and electrochemical activity of oxidovanadium(IV/V) complexes of a diprotic ONS chelating ligand

Manas Sutradhar<sup>a,b</sup>, Tannistha Roy Barman<sup>a</sup>, Gurunath Mukherjee<sup>a</sup>, Michael G.B. Drew<sup>c</sup>, Saktiprosad Ghosh<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Calcutta, University College of Science, 92, Acharya Prafulla Chandra Road, Kolkata 700009, India <sup>b</sup> Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University of Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany <sup>c</sup> School of Chemistry, The University of Reading, P.O. Box 224 Whiteknights, Reading RG6 6AD, UK

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# ABSTRACT

The present work reports the chemistry of a few oxidovanadium(IV) and (V) complexes of the ONS chelating ligand S-benzyl- $\beta$ -N-(2-hydroxyphenylethylidine) dithiocarbazate (H<sub>2</sub>L). Major objective of this work is to arrive at some general conclusions about the influence of binding environment generated by the replacement of an O-donor center by a S-donor point in a ligand (of a similar arrangement of the other O- and N-donor points) on the redox behavior and on the structural features of comparable [VO(OEt)(ONS)] and [VO(OEt)(ONO)] complexes. Synthesis, characterization by various physicochemical techniques (UV-Vis, IR, EPR and elemental analysis), exploration of electrochemical activity of the oxidovanadium(V) complex [V<sup>V</sup>O(OEt)L] (1), the mixed ligand complex [V<sup>V</sup>O(N-O)L] (3) (where N–O is the mono anion of 8-hydroxyquinoline) and a binuclear complex [V<sup>V</sup>O(OEt)L]\_2(µ-4,4'-bipy) (2) are reported. Similar studies on of mixed ligand oxidovanadium(IV) complexes of the formula [V<sup>V</sup>O(N-N)L] (4,5) (where N–N = 2,2'-bipy and o-phen) are also presented here. The [V<sup>V</sup>O(OEt)L] complex is pentacoordinated and distorted square pyramidal, while the [V<sup>IV</sup>(N–N)L] complexes are hexacoordinated and octahedral. Structural features of the complex 1 were compared with the corresponding aspects of the previously reported analogous complex [V<sup>V</sup>O(OEt)(ONO)] (1').

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# 1. Introduction

Compared to chemistry of vanadium ligated to various types of N–O donor ligands [1–33] vanadium complexes in total or partial sulfur coordination have received much less attention. It is rather surprising because some vanadium complexes in total or partial sulfur environment were known for the last three decades. Such vanadium complexes are found to be involved in conducting vanadium-sulfur materials [34], in the removal of vanadium from crude oils [35], as catalysts for oxidizing sulfides to sulfoxides [36]. The thiolato complexes containing vanadium(III) [37], vanadium(IV) [38], oxidovanadium(IV) [38,39] and vanadium(V) [40] cores are also reported along with a structurally characterized V(V) thiolate complex [40] and the VO<sup>3+</sup> complex [VO(SCH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>N] [41]. A few other vanadium-sulfur systems also received limited attention [42-50]. From 1997 onwards Chaudhury and his group explored synthesis, structural characterization, magnetic, chemical, electrochemical and photochemical properties of oxidovanadium com-

E-mail address: ghosh\_sakti@vsnl.net (S. Ghosh).

plexes involving a series of tridentate ONS donor ligands [51–57]. In this backdrop and in continuation of our work in the complex chemistry of vanadium in +3, +4 and +5 oxidation states [3,10,27,28,30–33], specially in the form of oxidovanadium species, the present study of oxidoalkoxido containing vanadium complexes involving a ONS donor ligand are under taken. The complex [VO(OEt)L] (1) [where H<sub>2</sub>L is a diprotic tridentate ONS ligand, S-benzyl- $\beta$ -N-(2-hydroxyphenylethylidine) dithiocarbazate] is pentacoordinate and so has one position vacant in the coordination octahedron which can be utilized as a substrate binding site for neutral monodentate N-heterocyclic bases and are also amenable to the formation of binuclear complexes utilizing suitable neutral exobidentate ligands like 4,4'-bipyridine. The present work reports the findings enumerated below: (a) synthesis, structural characterization, examination of chemical and electrochemical properties of the monooxidoalkoxidovanadium(V) complex [VO(OEt)L] (1), the mixed ligand oxidovanadium(V) complex [VO(N-O)L] (**3**), a binuclear complex  $[VO(OEt)L]_2(\mu-4,4'-bipy)$  (**2**) and the mixed ligand oxidovanadium(IV) complexes of the type [VO(N-N)L] (4,5) where H<sub>2</sub>L is a diprotic tridentate ONS donor ligand, N-O = 8-hydroxy quinoline and N-N = 2,2'-bipyridine, 1,10-phenanthroline.





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# 2.1. Materials

[VO(acac)<sub>2</sub>] was prepared as described in literature [58] and was used as the source of vanadium. Reagent grade solvents were dried and distilled prior to use. All other chemicals were reagent grade, obtained from commercial sources and used without further purification. Spectroscopic grade solvents were used for spectral measurements.

# 2.2. Preparations

#### 2.2.1. Synthesis of the ligand $H_2L$

The Schiff base ligand, S-benzyl- $\beta$ -N-(2-hydroxyphenylethylidine) dithiocarbazate (H<sub>2</sub>L) was prepared by using a reported procedure [59]. Yield ~80%, m. p. ~148 °C. *Anal.* Calc. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>OS<sub>2</sub>: C, 60.76; H, 5.06; N, 8.86. Found: C; 60.71, H, 5.63; N, 8.82%. IR (KBr pellet, cm<sup>-1</sup>): 3436 cm<sup>-1</sup> for  $\nu$ (O–H), 3171 cm<sup>-1</sup> for  $\nu$ (N–H), 1600 cm<sup>-1</sup> for  $\nu$ (C=N), 1309 for cm<sup>-1</sup>  $\nu$ (C=S). <sup>1</sup>H NMR  $\delta$ <sub>H</sub> (300 MHz; DMSO d<sub>6</sub>; Me<sub>4</sub>Si): 11.26 (1H, s, OH), 11.25 (1H, s, NH), 7.41–6.82 (9H, m, C<sub>6</sub>H<sub>4</sub>), 4.51 (2H, s, -CH<sub>2</sub>–), 2.47 (3H, s, -CH<sub>3</sub>=CN–).

### 2.2.2. Synthesis of the oxidovanadium(V) complex [VO(OEt)L] (1)

The ligand H<sub>2</sub>L (0.32 g, 1.02 mmol) was dissolved in 30 ml of ethanol and 0.27 g (1.02 mmol) of vanadium(IV) acetylacetonate was added to this solution and the mixture was refluxed for 4 h on a steam bath. The color of the solution changed from yellow-green to dark brown. The solution was filtered and allowed to evaporate slowly at room temperature. After 2–3 days yellowish brown single crystals, suitable for X-ray diffraction analysis separated out. Yield: 70%. *Anal.* Calc. for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>V: C, 50.70; H, 4.46; N, 6.57; V, 11.97. Found: C, 50.68; H, 4.54; N, 6.54; V, 11.94%. IR (KBr pellet, cm<sup>-1</sup>): 3435 cm<sup>-1</sup> for v(O–H), 1595 cm<sup>-1</sup> for v(C=N), 1237 cm<sup>-1</sup> for v(C–O enolic), 1042 cm<sup>-1</sup> for v(N–N), 993 cm<sup>-1</sup> for v(V=O). <sup>1</sup>H NMR  $\delta_{\rm H}$  (300 MHz; DMSO d<sub>6</sub>; Me<sub>4</sub>Si): 10.92 (1H, s, OH), 10.09 (1H, s, NH), 7.43–6.92 (9H, m,C<sub>6</sub>H<sub>4</sub>), 4.54 (2H, s, –CH<sub>2</sub>–), 2.73 (3H, s, –CH<sub>3</sub>C=N–).

# 2.2.3. Synthesis of the oxidovanadium(V) complex $[VO(OEt)L]_2(\mu-4,4'-bipy)$ (2)

To 30 ml ethanolic solution of complex 1 (0.412 g, 1.0 mmol), 4,4'- bipyridine (0.078 g, 0.50 mmol) was added and the mixture was refluxed for 5 h on a steam bath. The mixture was cooled, filtered and the filtrate allowed to evaporate slowly in a refrigerator. After 5–6 days reddish brown solid separated out. Yield: 68%. *Anal.* Calc. for  $C_{46}H_{46}N_6O_6S_4V_2$ : C, 54.76; H, 4.56; N, 8.33; V, 10.12. Found: C, 54.76; H, 4.56; N, 8.30; V, 10.12%. IR (KBr pellet, cm<sup>-1</sup>): 3437 cm<sup>-1</sup> for  $\nu$ (O–H), 1589 cm<sup>-1</sup> for  $\nu$ (C–O enolic), 1072 cm<sup>-1</sup> for  $\nu$ (N–N), 967 cm<sup>-1</sup> for  $\nu$ (V=O).

 $^1H$  NMR  $\delta_{\rm H}$  (300 MHz; DMSO d<sub>6</sub>; Me<sub>4</sub>Si): 7.92–6.64 (26H, m, C<sub>6</sub>H<sub>4</sub>), 5.44 (4H, q, CH<sub>2</sub>, OEt), 4.56 (4H, s, –CH<sub>2</sub>–), 2.74 (6H, s, –CH<sub>3</sub>C=N–), 1.71 (6H, t, CH<sub>3</sub>, OEt).

# 2.2.4. Synthesis of the oxidovanadium(V) complex [VO(8-HQ)L] (3)

The ligand H<sub>2</sub>L (0.32 g, 1.02 mmol) was dissolved in 30 ml of ethanol, 0.27 g (1.02 mmol) of vanadium(IV) acetylacetonate was added to it and the mixture was refluxed for 1 h on a steam bath. The color of the solution changed from yellow-green to brown. To this brown solution 0.15 g (1.03 mmol) 8-hydroxy quinoline was added and refluxing was continued for 5 h. The solution was filtered and allowed to evaporate slowly at room temperature. After 2–3 days bluish brown solid separated out. Yield: 76%. *Anal.* Calc. for  $C_{25}H_{20}N_3O_3S_2V$ : C, 57.03; H, 3.99; N, 7.98; V, 9.96. Found: C, 57.01; H, 3.95; N, 7.93; V, 9.64%. IR (KBr pellet, cm<sup>-1</sup>): 3373 cm<sup>-1</sup> for v(O-H), 1601 cm<sup>-1</sup> for v(C=N), 1252 cm<sup>-1</sup> for

v(C–O enolic), 1046 cm<sup>-1</sup> for v(N–N), 960 cm<sup>-1</sup> for v(V=O). <sup>1</sup>H NMR  $\delta_{\rm H}$  (300 MHz; DMSO d<sub>6</sub>; Me<sub>4</sub>Si): 7.89–6.57 (15H, m, C<sub>6</sub>H<sub>4</sub>), 4.56 (2H, s, –CH<sub>2</sub>–), 2.74 (3H, s, –CH<sub>3</sub>C=N–).

# 2.2.5. Synthesis of the oxidovanadium(IV) complexes [VO(o-phen)L] (4) and [VO(2,2'- bipy)L] (5)

These two complexes were obtained as orange red crystalline solids utilizing the same method mentioned in the preparation of complex **3** using *o*-phenanthroline for **4** and 2,2'-bipyridine for **5** in place of 8-hydroxyquinoline and acetonitrile as the reaction medium.

*Complex* **4**: Yield: 70%. *Anal.* Calc. for  $C_{28}H_{22}N_4O_2S_2V$ : C, 59.89; H, 3.92; N, 9.98; V, 9.09. Found: C, 59.86; H, 3.94; N, 9.96; V, 9.07%. IR (KBr pellet, cm<sup>-1</sup>): 3423 cm<sup>-1</sup> for v(O-H), 1597 cm<sup>-1</sup> for v(C=N), 1238 cm<sup>-1</sup> for v(C-O enolic), 1062 cm<sup>-1</sup> for v(N-N), 957 cm<sup>-1</sup> for v(V=O).

*Complex* **5**: Yield: 73%. *Anal.* Calc. for  $C_{26}H_{22}N_4O_2S_2V$ : C, 58.10; H, 4.09; N, 10.43; V, 9.49. Found: C, 58.08; H, 4.11; N, 10.43; V, 9.46%. IR (KBr pellet, cm<sup>-1</sup>): 3436 cm<sup>-1</sup> for v(O-H), 1595 cm<sup>-1</sup> for v(C=N), 1242 cm<sup>-1</sup> for v(C-O enolic), 1068 cm<sup>-1</sup> for v(N-N), 958 cm<sup>-1</sup> for v(V=O).

# 2.3. Physical measurements

Elemental analyses (C, H and N) were done with a Perkin-Elmer 2400 CHNS/O analyzer and vanadium contents (%) of the complexes were determined gravimetrically [60] as V<sub>2</sub>O<sub>5</sub>. Electronic spectra of the complexes in acetonitrile were recorded on a Hitachi U-3501 spectrophotometer and IR spectra (as KBr pellets) were recorded using a Perkin Elmer RXI FT-IR spectrophotometer. The <sup>1</sup>H NMR Spectra were recorded on a Bruker Model Advance DPX300 Spectrometer. Electrochemical measurements were performed with a PAR model 362 scanning potentiostat and cyclic voltammograms were recorded at 25 °C in the designated solvent under dry dintrogen with the electroactive component at ca 10<sup>-3</sup> M. Tetraethyl ammonium perchlorate (NEt<sub>4</sub>ClO<sub>4</sub>, 0.1 M) was used as the supporting electrolyte. EPR spectra were obtained at X-band frequencies on a Varian E-109C spectrometer around 110 K. The experiments were carried out using a Varian variable temperature accessory. This accessory utilizes open gas-flow system and uses liquid nitrogen as coolant. Nitrogen gas is used to cool the sample. The calibrant was TCNE (g = 2.00277). For electrochemical investigations a three-electrode configuration was employed with platinum working electrode, a calomel reference electrode, and a platinum auxiliary electrode. The Ferrocene/Ferrocenium (Fc/Fc<sup>+</sup>) couple was used as the internal standard [61]. Room temperature magnetic susceptibilities of complexes were measured in polycrystalline state on a PAR 155 vibrating sample magnetometer using  $Hg[Co(SCN)_4]$  as the calibrant.

#### 2.4. X-ray crystallography

Diffraction data for suitable single crystals of complexes **1** and **5** were measured with Mo K $\alpha$  radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. A total of 95 frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program [62]. The structures were solved using direct methods with the SHELX-86 program [63]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the DIFABS program [64]. The structures were generated

using ORTEP-3 [66]. Crystallographic data are summarized in Tables 1 and 2.

#### Table 2

Selected dimensions in complexes **1**, **1**′ and **5** (distances, Å, angles °).

# 3. Results and discussion

The monooxidoethoxidovanadium(V) complex [VO(OEt)L] (1) was obtained as yellowish brown crystalline solid by refluxing an equimolar solution of [VO(acac)<sub>2</sub>] and the ligand H<sub>2</sub>L in ethanol medium  $[(L)^{2-}$  = dianion of the ONS donor ligand ] in ~70% yield. V(IV) was found to be oxidized to V(V) during the reaction period. Similar complexes containing other coordinated alkoxides could also be prepared easily using appropriate alcohols. However, detailed characterization of the other alkoxido complexes are not reported because of their very similar properties. Complex (1) was used as the precursor for preparing the binuclear oxidovanadium(V) complex  $[VO(OEt)L]_2(\mu-4,4'-bipy)$  (2) by refluxing [VO(OEt)L] and 4,4'-bipy in 2:1 molar ratio in ethanol in 65-70% vield. However, as single crystals of proper quality could not be obtained, structure of this compound could not be solved. The mixed ligand oxidovanadium(V) complex [VO(8-HQ)L] (3) was isolated as bluish brown microcrystals in 76% yield by refluxing [VO(acac)<sub>2</sub>] and H<sub>2</sub>L in 1:1 molar proportion in ethanol for 1 hour followed by addition of 1 mole 8-hydroxyguinoline (8-HQH) and further refluxing for 5 h. Single crystals fit for X-ray diffraction study could not be obtained. Mixed ligand oxidovanadium(IV) complexes [VO(o-phen)L](4) and [VO(2,2'-bipy)L](5) were obtained as orange red solids in 70-75% yield following the same method as in the case of complex 3 using acetonitrile in place of ethanol as the reaction medium and 1,10-phenanthroline (o-phen) or 2,2'-bipyridine (bipy) instead of 8-hydroxyquinoline. Single crystals of 5 were obtained and its crystal and molecular structure was determined. The synthetic route to all the complexes are summarized in Scheme 1.

# 3.1. Crystal structure of the complexes

Structure determination of **1** and **5** by X-ray crystallography showed that the coordination mode of the ligand  $H_2L$  remained same in both V(V) and V(IV) complexes though **1** is pentacoordinated and has a distorted square pyramidal structure, while **5** is hexacordinated and is distorted octahedral. Metric dimensions of the corresponding bond lengths and bond angles are given in Table

#### Table 1

Crystal data and structure determination summery of complexes 1 and 5.

	1	5
Empirical formula	C <sub>18</sub> H <sub>19</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> V	C <sub>26</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub> V
Formula weight	426.43	537.56
Crystal system	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /a (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
a (Å)	7.3241(12)	9.1267(11)
b (Å)	22.633(4)	12.4132(13)
<i>c</i> (Å)	11.705(2)	21.842(2)
α (°)	(90)	(90)
β (°)	98.828(15)	95.322(9)
γ (°)	(90)	(90)
V (Å <sup>3</sup> )	1917.3(6)	2463.9(5)
Ζ	4	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.477	1.449
Data/restraints/param	5633/0/235	7042/0/316
Number of observed reflections $[I > 2\sigma(I)]$	1512	3752
R(F), $wR(F)$ (obsd data) <sup>a</sup>	0.0448, 0.0821	0.1026, 0.1864
$R(F^2)$ , $wR(F^2)$ (all data) <sup>b</sup>	0.1463, 0.0909	0.1799, 0.2087
R <sub>int</sub>	0.087	0.083
Peaks in final difference map (e A <sup>-3</sup> )	0.68, -0.43	0.93, -0.47
Goodness-of-fit on F <sup>2</sup>	0.515	1.095

<sup>a</sup>  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$ 

<sup>b</sup>  $wR(F^2) = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^4]^{1/2}.$ 

Selected dimensions in complexes 1, 1 and 5 (distances, 7, angles ).					
	1	1′	5		
Bond distances					
V(1)-O(2)	1.802(2)	1.8547(16)	1.942(4)		
V(1)-O(35)	1.591(2)	1.5809(17)	1.595(3)		
V(1)-O(23)	1.7706(18)	1.7430(16)	-		
V(1)-S(14)	2.3310(11)	1.9477(16)*	2.4563(16)		
V(1)-N(11)	2.159(2)	2.1331(19)	2.090(4)		
V(1)-N(23)	-	-	2.343(4)		
V(1)-N(30)	-	-	2.138(4)		
Bond angles					
S14-V1-02	134.36(8)	147.77(6)*	158.92(11)		
S14-V1-023	84.18(7)	92.82(7)*	. ,		
S14-V1-035	110.34(8)	102.15(7)*	97.14(14)		
S14-V1-N11	78.74(7)	73.89(6)*	80.58(11)		
02-V1-023	101.24(9)	101.24(9)			
02-V1-035	111.61(10)	111.61(10)	101.95(17)		
02-V1-N11	82.31(9)	82.31(9)	85.82(15)		
023-V1-035	105.31(10)	105.31(10)			
023-V1-N11	158.79(9)	158.79(9)			
035-V1-N11	92.46(10)	92.46(10)	105.19(17)		
S14-V1-N23			81.04(11)		
S14-V1-N30			97.15(11)		
02-V1-N23			82.45(15)		
02-V1-N30			90.13(15)		
035-V1-N23			166.35(18)		
035-V1-N30			94.84(17)		
N11-V1-N23			87.92(15)		
N11-V1-N30			159.97(15)		
N23-V1-N30			72.09(14)		

Consider O(14) instead of S(14) for 1'.

2. On careful inspection of the data presented in Table 2 it is found that the V1–O2 distance [1.942(4)Å] in **5** is a bit longer than the corresponding distance [1.802(2) Å] in **1**. Also, the V1-S14 distance [2.4563(16) Å] in **5** is longer than that of the corresponding bond [2.3310(11) Å] in **1**. When we focus our attention on the length of the V=O bonds we notice the same trend but the magnitude of difference is lower. However, in case of the V1-N11 bonds, V1–N11 in **1** is slightly longer than that in **5** indicating that this bond is stronger in 5 which may be attributed to the effect of coordination of the chelating secondary ligand 2,2'-bipyridine. Thus, the presence of a secondary chelating ligand in the coordination environment of the central vanadium atom leads to noticeable changes in the lengths of the bonds that the ligand makes with the vanadium center. It is also noted that the deviation of vanadium acceptor center in 5 from the equatorial plane [0.5211 Å] is higher than that of the vanadium center in **1**, both being displaced towards the axial vanadyl oxygen (O35).

# 3.1.1. Description of crystal structure [VO(OEt)L] (1)

The yellow-brown complex [VO(OEt)L] (1) crystallizes in the monoclinic system with the space group  $P2_1/a$ . A perspective view of this complex is shown in Fig. 1 and important bond parameters are presented in Tables 1 and 2. The vanadium(V) center is present in a distorted square pyramidal VO<sub>3</sub>NS coordination with the four basal positions occupied by the three donor points O2 (phenoxide oxygen), N11 (imine nitrogen), S14 (thioenolate sulfur)of the tridentate ligand and O23 of the coordinated alkoxide moiety. The axial site is occupied by the vanadyl oxygen O35 which forms angles in the range  $92.46^{\circ}(10)-111.61^{\circ}(10)$  with the previously defined basl plane. The deviation of these four points from the leastsquares plane O2, N11, S14, and O23 are 0.2402, -0.2323, 0.2178, -0.2257 Å, respectively. Magnitude of the trans angle O23-V1-N11 [158.79°(9)] indicates that the V1 center is displaced towards the apical oxido-oxygen atom O35 and lies 0.5211 Å out of the plane. The V=O distance of 1.591(2) Å is not uncommon.



Scheme 1. Synthesis of the complexes 1-5.

# 3.1.2. Description of crystal structure [VO(2,2'-bipy)L] (5)

The brown complex **5** crystallizes in monoclinic system with space group  $P_{1/c}$ . Molecular structure and atom labeling scheme of **5** is illustrated in Fig. 2 and metric dimensions are presented in Tables 1 and 2. In contrast to the complex **1**, the vanadium (IV) center of **2** is hexacoordinated and is present in a distorted octahedral VO<sub>2</sub>N<sub>3</sub>S coordination with the O2, N11, S14 atoms of the ligand and N30 of the bipyridine molecule constituting the equatorial plane. Vanadyl oxygen O35 occupies the axial position which forms angle in the 94.84(17)–105.19(17) range with the basal plane defined previously. The second nitrogen atom N23 of the bipyridine moiety is situated trans to the vanadyl oxygen O35 and the *trans* angle O35–V1–N23 is 166.35°(18). The V1–N23 bond [2.343(4) Å] is considerably longer than the V1–N30 bond [2.138(4) Å] due to trans influence of the V=O moiety.

Unequal lengths of all bonds involving the vanadium(V) center and the six donor points signify distortion of coordination octahedron. The tridentate ONS ligand forms one six membered and one five membered chelate ring at the vanadium(V) acceptor center, the corresponding bite angles being 82.31°(9) and 80.58°(11), respectively the two axial positions are occupied by the oxido oxygen atom O35 and nitrogen atom N23 of the secondary ligand bipyridine. The short V1–O35 distance of 1.595(3) Å indicate the presence of vanadium oxygen double bond commonly found in five and six coordinated complexes of V(IV) and V(V). The V1–S14 bond length of 2.4563(16) Å is slightly longer than the corresponding vanadium thioenolate bond distance usually found in five and six coordinated V(IV) and V(V) complexes of ONS donor ligands [47,49,50]. It was noted that oxidation of vanadium(IV) to vanadium(V) in complexes **1**, **2** and **3** took place in ethanol medium while in acetonitrile medium vanadium(IV) did not get oxidized to vanadium(V).

# 3.1.3. Structural comparison of [VO(OEt)(ONS)] (1) versus [VO(OEt)(ONO)] (1')

It is expected that substitution of an 'O' donor point by an 'S' donor center in a similar chelating ligand would generate significant alteration in structure and properties of comparable complexes of the same metal ion in the same oxidation state. From this point of view, it appears worthwhile to compare the structures of the two complexes [VO(OEt)(ONS)] (1) and [VO(OEt)(ONO)] (1'). ORTEP diagram of 1 and 1' are shown side by side in Fig. 1 and metric values of the bond lengths and bond angles are presented in Table 2. A careful inspection of the structural data of 1 and 1' reveals that maior structural features as well as the values of the corresponding bond distances and bond angles are fairly close. The coordination geometry of both the complexes are also very similar, both having distorted square pyramidal structure. Calculated  $\tau$  values are 0.407 (1) and 0.183 (1') also guantify distortion of 1 and 1' from perfect square pyramidal geometry. Similarity in redox behavior is clearly reflected in the irreversible one electron reduction step at 0.43 V for (1) and at 0.42 V for (1'). In their IR spectra the v(V=0) mode



Fig. 1. Molecular structure and atom-numbering scheme for the complex 1 and complex 1' with thermal ellipsoids drawn at the 30% probability level.



Fig. 2. Molecular structure and atom-numbering scheme for the complex 5 with thermal ellipsoids drawn at the 30% probability level.

is observed at the same frequency [30] of 993 cm<sup>-1</sup>. Therefore, one is tempted to comment that in these two cases substitution of an oxygen donor point by a sulfur donor point in a multidentate chelating ligand forming similar metallocycles with an identical acceptor center may not always lead to major change of structural, electrochemical and spectroscopic properties.

# 3.2. IR and <sup>1</sup>H NMR spectroscopy

IR spectra of the complexes **1–5** display features characteristic of the dianionic tridentate ONS mode of ligation through the phenolate oxygen, imine nitrogen and the thioenolate sulfur. Compound **1**, **2** and **3** also display a strong band in the 954–993 cm<sup>-1</sup> range due to the terminal v(V=O) mode. In the two vanadium(IV) complexes **4** and **5** the v(V=O) is found at slightly lower frequencies (954 and 958 cm<sup>-1</sup>).

The <sup>1</sup>H NMR data of the free ligand  $H_2L$  in  $d_6$ -DMSO and its oxidovanadium(V) complexes **1**, **2** and **3** are given in the experimental section. The free ligand displays two characteristic resonances, one with a sharp feature at 10.92 ppm and the other with a broad peak at 10.09 ppm due to phenolic OH and NH functionalities, respectively, which are missing in the spectra of the complexes indicating that the coordinated ligand is dianionic. Besides having all the

### Table 3

Cyclic voltammetric data<sup>a</sup> and UV-Vis spectral data<sup>a</sup> of the vanadium(V) complexes 1-5.

$\begin{array}{c c} \mbox{Compound} & E_{1/2}, V \\ (\Delta E_p^{b},  mV) & \lambda_{max}  (nm)  (\varepsilon,  L  M^{-1}  cm^{-1}) \\ \hline \\ \begin{tabular}{lllllllllllllllllllllllllllllllllll$			
	Compound	$E_{1/2}, V$ $(\Delta E_p^{b}, mV)$	$\lambda_{\max} (nm) (\varepsilon, L M^{-1} cm^{-1})$
$ \begin{bmatrix} VO(OEt)L]_2(\mu-4,4'-bipy) & 0.424(96) & 396 (9,886), 306 (11,328) \\ (2) & & & & & & & & & & & & & & & & & & &$	[VO(OEt)L] (1)	0.432(102)	392 (10,744), 300 (40,844)
[VO(8-HQ)L] ( <b>3</b> ) 0.461(136) 396 (10,375), 315 (18,427), 243 (49,948) [VO(o-phen)L] ( <b>4</b> ) 0.418(123) 800 (147), 402 (11,054), 306 (34,637) [VO(2,2'-bipy)L] ( <b>5</b> ) 0.421(127) 800 (130.7), 404 (10,251), 306 (32,517)	[VO(OEt)L] <sub>2</sub> (µ-4,4'- bipy) (2)	0.424(96)	396 (9,886), 306 (11,328)
[VO(o-phen)L] ( <b>4</b> ) 0.418(123) 800 (147), 402 (11,054), 306 (34,637) [VO(2,2'-bipy)L] ( <b>5</b> ) 0.421(127) 800 (130.7), 404 (10,251), 306 (32,517)	[VO(8-HQ)L] ( <b>3</b> )	0.461(136)	396 (10,375), 315 (18,427), 243 (49,948)
[VO(2,2'-bipy)L] ( <b>5</b> ) 0.421(127) 800 (130.7), 404 (10,251), 306 (32,517)	[VO(o-phen)L] ( <b>4</b> )	0.418(123)	800 (147), 402 (11,054), 306 (34,637)
	[VO(2,2'-bipy)L] ( <b>5</b> )	0.421(127)	800 (130.7), 404 (10,251), 306 (32,517)

<sup>a</sup> In acetonitrile; scan rate 50 mV s<sup>-1</sup>,  $E_{1/2}$  is calculated as the average of anodic ( $E_{pa}$ ) and cathodic ( $E_{pc}$ ) peak potentials.

<sup>b</sup>  $\Delta E_p = E_{pa} - E_{pc}$ .

remaining peaks of the coordinated ONS ligand, the spectrum of **1** displays a quartet at 5.42 ppm (J = 7.2 Hz) and a triplet at 1.69 ppm (J = 7.0 Hz) due to the methylene and methyl protons, respectively, of the coordinated ethoxy group.

# 3.3. Electronic spectra

Electronic spectral data of the vanadium(V) complexes **1**, **2** and **3** are presented in Table 3 along with those of vanadium(IV) complexes **4** and **5**. The V(V) complexes in acetonitrile solution display a strong absorption around 400 nm which is due to PhO<sup>-</sup>  $\rightarrow$  V(d $\pi$ ) LMCT transition and two other absorption band in 300–243 nm region corresponding to intraligand transitions. The vanadium(IV) complexes **4** and **5** exhibit an additional low intensity band at *ca* 800 nm due to ligand field transition  $d_{xz}$ ,  $d_{yz} \rightarrow d_{xy}$  of the VO<sup>2+</sup> center. The strong band observed at ~400 is due to enolate oxygen to vanadium(IV) transition. Bands observed around 300 nm and below are due to intraligand transitions.

# 3.4. Electrochemistry

Cyclic voltammograms of all the reported complexes are recorded in acetonitrile solution with  $Et_4NClO_4$  as the supporting electrolyte at a platinum working electrode. The corresponding data are presented in Table 3. All the three vanadium(V) complexes exhibit identical one-electron response corresponding to the V(V)/ V(IV) reduction process in the 0.42–0.46 v range versus SCE.  $\Delta E_p$ values indicate quasireversible nature of the reduction process in case of **1** (Fig. 3), **2** and **3**. In case of the two vanadium(IV)



Fig. 3. Cyclic voltammogram of complex 1 in CH<sub>3</sub>CN.



Fig. 4. Cyclic voltammogram of complex 5 in CH<sub>3</sub>CN.

complexes **4** and **5** (Fig. 4) one-electron oxidation is observed at 0.418 and 0.421 v, respectively. One-electron nature is inferred by comparison with the authentic one-electron system  $[Fc^+/Fc]$  under identical conditions. It is to be noted that the binuclear complex **2** undergo one-step two-electron reduction at +0.424 v probably due to the centrosymmetric character of the complex, which is observed in similar type complexes involving ONO chelating ligand [32].

### 3.5. Magnetic moment and EPR studies

The two oxidovanadium(IV) complexes, **4** and **5**, exhibit room temperature magnetic moment values of 1.71 B.M. and 1.68 B.M., respectively (Table 4) as expected for spin only value of a  $d^1$  system.

EPR spectral parameters of **4** and **5** are practically identical (Table 4). EPR spectrum is recorded of **5** in dichloromethane at room temperature and at ~110 K. The room temperature spectrum exhibits eight line pattern  $[g_{av} = 1.983$  for **4** and 1.985 for **5**;  $A_{av} = 81.3 \times 10^{-4} \text{ cm}^{-1}$  for **4** and  $84.0 \times 10^{-4} \text{ cm}^{-1}$  for **5**] typical of one unpaired electron being coupled to a single <sup>51</sup>V (I = 7/2) nucleus. The spectrum at ~110 K displays axial anisotropy with two sets of eight line pattern corresponding to resonance parameters:  $g_{\parallel} 1.953$ ,  $A_{\parallel} 152 \times 10^{-4} \text{ cm}^{-1}$  and  $g_{\perp} 1.999$ ,  $A_{\perp} 45.8 \times 10^{-4} \text{ cm}^{-1}$  for **4** and  $g_{\parallel} 1.974$ ,  $A_{\parallel} 154 \times 10^{-4} \text{ cm}^{-1}$  and  $g_{\perp} 1.990$ ,  $A_{\perp} 48.7 \times 10^{-4} \text{ cm}^{-1}$  for **5**. It may be mentioned that the experimental  $A_{\parallel}$  are in accord with the calculated coupling constants ( $153 \times 10^{-4} \text{ cm}^{-1}$ ), calculated from the additivity rule with the equatorial ligand set found in the solid state crystal structure.

# 4. Conclusion

This work reports synthesis and characterization of three five coordinated distorted square planar oxidovanadium(V) complexes [VO(OEt)L] (1), the binuclear V(V)–V(V) complex [VO(OEt)L]<sub>2</sub>- $\mu$ -(4,4'-bipy) (2) and the six coordinate mixed ligand complex [VO(8-HQ)L] (3). Two six coordinate oxidovanadium(IV) complexes [VO(o-phen)L] (4) and [VO(2,2'-bipy)L] (5) are also discussed. Of these five complexes, 1 and 5 are structurally characterized by single crystal X-ray crystallography. We have recently reported preparation, structural characterization and chemical reactivity of binuclear complexes of the type [VO(OEt)L]<sub>2</sub>- $\mu$ -(4,4'-bipy) (where H<sub>2</sub>L = a diprotic tridentate ONO donor ligand) which is similar to 2 which is expected to have a similar structure.

#### Table 4

Magnetic moment data<sup>a</sup> and EPR<sup>b</sup> data for the complexes (4) and (5).

Compound	r. t.	r. t.		~110 K			
	$\mu_{\rm eff}$ <sup>a</sup> (B.M.)	$g_{\rm av}~(10^{-4}~{ m cm}^{-1})$	$A_{\rm av} (10^{-4}{\rm cm}^{-1})$	$g_{  } (10^{-4} \mathrm{cm}^{-1})$	$A_{  } (10^{-4} \mathrm{cm}^{-1})$	$g_{\perp}^{\ c} (10^{-4}  cm^{-1})$	$A_{\perp}^{\rm d} (10^{-4}  {\rm cm}^{-1})$
[VO( <i>o</i> -phen)L] ( <b>4</b> ) [VO(2,2'-bipy)L] ( <b>5</b> )	1.71 1.68	1.983 1.985	81.3 84.0	1.953 1.974	152 154	1.999 1.990	45.8 48.7

<sup>a</sup> In solid state.

 $^{\rm b}~$  In dichloromethane (at room temperature and  ${\sim}110$  K).

<sup>c</sup>  $g_{av} = (g_{||} + 2g_{\perp})/3.$ 

<sup>d</sup>  $A_{av} = (A_{||} + 2A_{\perp})/3.$ 

Cyclic voltametric study of **2** reveals only a single two-electron reductive response suggesting a centrosymmetric structure just like the corresponding structurally characterized and previously reported binuclear complex involving the ONO donor ligand. To our knowledge, complex **2** is the first report of a bipyridine bridged binuclear oxidovanadium(V) complex of a diprotic tridentate ONS donor ligand.

It is noted that the use of acetonitrile in place of ethanol (which is the source of EtO<sup>-</sup> donor) did not promote spontaneous oxidation of V(IV) to V(V) and leads to the formation of non-alkoxido oxidovanadium(IV) complexes 4 and 5. This finding underscores the ability of the alkoxido (ethoxido) group to prefer higher oxidation state of vanadium. The oxidovanadium(IV) complexes are subjected to EPR and magnetic susceptibility studies and the results correspond to the presence of an oxidovanadium(IV) center in all of them with their EPR pattern indicative of a single d electron interacting with one <sup>51</sup>V center. Comparison of the structural features of the complex 1 (involving a ONS donor ligand) with that of the previously reported complex 1' (involving a ONO donor ligand) indicates that contrary to the established belief that presence of one or more sulfur donor centers in the coordination zone of a metal accepter center exert significant influence on spectroscopic, electrochemical and structural characteristics of the resultant complex, substitution of an oxygen donor atom of a ONO donor ligand by a sulfur atom in the present case does not result any significant difference in the structural features, electrochemical and spectroscopic properties of the corresponding oxidovanadium(V) complex.

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#### **Appendix A. Supplementary material**

CCDC 735908 and 735909 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.06.025.

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