



# Synthesis and spectral investigations of vanadium(IV/V) complexes derived from an ONS donor thiosemicarbazone ligand

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## ABSTRACT

Four oxovanadium and one dioxovanadium complex with 2-hydroxyacetophenone *N*(4)-phenylthiosemicarbazone ( $H_2L$ ) which are represented as  $[VOLphen] \cdot 2H_2O$  (**1**),  $[VOLbipy]$  (**2**),  $[VOLdmbipy]$  (**3**),  $[VOL]_2$  (**4**) and  $[VO_2HL] \cdot CH_3OH$  (**5**) have been synthesized and characterized by elemental analyses, electronic, infrared and EPR spectral techniques. In all the complexes **1–4** the ligand coordinates through phenolic oxygen, azomethine nitrogen and thiolate sulfur. But in complex  $[VO_2HL] \cdot CH_3OH$ , coordination takes place in thione form instead of thiolate sulfur. All the complexes except  $[VO_2HL] \cdot CH_3OH$  are EPR active due to the presence of an unpaired electron. In frozen DMF at 77 K, all the oxovanadium(IV) complexes show axial anisotropy with two sets of eight line patterns.

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## 1. Introduction

Various metal complexes of thiosemicarbazones have been extensively studied during recent years, owing to their activity against small pox, virus disease and certain kinds of tumor [1]. The chemistry of oxovanadium(IV) has received considerable attention as the  $VO^{2+}$  unit can readily coordinate to four and five donor atoms to form  $VO_4$  and  $VO_5$  complexes, respectively. Additional interest has been generated in the coordination chemistry of oxovanadium(IV), oxovanadium(V) and dioxovanadium(V), as these complexes model vanadium containing enzymes and serve as good oxidation catalysts. Oxovanadium(IV) complexes find use in chemical reactivity studies either as models for V–O bond reactivity [2] or as potential free radicals.

Among the biological activities of vanadium, an intrinsic mimetic antidiabetic effect is the most striking, the effect being provided by the oxidation states of vanadic(III), vanadyl(IV) and vanadate(V) [3]. Medicinal applications of vanadium compounds have focused on their in vitro and in vivo activity in the treatment of insulin deficiency, type I diabetes and insulin tolerance, type II diabetes which is by far the more common form frequently found with elderly people and increasingly also a problem for obese young people [4]. In addition to the therapeutic effect of vanadium ion and vanadium complexes, these vanadium compounds have a pre-

ventive effect [3]. The literature survey revealed only few papers reporting the synthesis and characterization of oxovanadium(IV) complexes with thiosemicarbazones. Having all these facts in mind, it was thought worthwhile to study the coordination chemistry of oxovanadium(IV) complexes derived from 2-hydroxyacetophenone *N*(4)-phenylthiosemicarbazone as an ONS donor ligand. Moreover, we have isolated a dioxovanadium(V) complex also.

In the present article, synthesis and characterization of some vanadium(IV/V) complexes of 2-hydroxyacetophenone *N*(4)-phenylthiosemicarbazone are investigated with the help of physico-chemical techniques.

## 2. Experimental

### 2.1. Materials

$VOSO_4 \cdot H_2O$  (Sigma–Aldrich), vanadium(IV) oxide acetylacetonate, 4,4'-dimethyl 2,2'-bipyridine (dmbipy) (E-Merck), 1,10-phenanthroline (phen) (Universal Laboratories), 2,2'-bipyridine (bipy) (Qualigens) were of analar grade and were used as received. Solvents used were methanol and water.

### 2.2. Synthesis of the ligand and their complexes

The ligand 2-hydroxyacetophenone *N*(4)-phenylthiosemicarbazone ( $H_2L$ ) has been synthesized as reported by us earlier [5].

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### 2.3. Synthesis of complexes

The complexes [VOLphen]·2H<sub>2</sub>O (**1**), [VOLbipy] (**2**), [VOLdmbipy] (**3**) were prepared by refluxing 1 mmol each of VOSO<sub>4</sub>·H<sub>2</sub>O in aqueous solution, heterocyclic base (phen/bipy/dmbipy) in solid form and H<sub>2</sub>L in methanol for 3 h. The complexes [VOL]<sub>2</sub> (**4**), [VO<sub>2</sub>HL]·CH<sub>3</sub>OH (**5**) were prepared by refluxing 1 mmol of VOSO<sub>4</sub>·H<sub>2</sub>O for **4** and 1 mmol of vanadium(IV) oxide acetylacetonate for **5** in aqueous solution with 1 mmol of H<sub>2</sub>L in methanol for 3 h. The compounds formed were filtered, washed with methanol and ether and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

[VOLphen]·2H<sub>2</sub>O (**1**): Elemental Anal. Found (Calcd.) (%): C, 57.79 (57.24); H, 4.06 (4.45); N, 13.32 (12.36).

[VOLbipy] (**2**): Elemental Anal. Found (Calcd.) (%): C, 59.85 (59.29); H, 4.66 (4.18); N, 14.09 (13.83).

[VOLdmbipy] (**3**): Elemental Anal. Found (Calcd.) (%): C, 58.71 (58.69); H, 4.66 (4.93); N, 12.98 (12.67).

[VOL]<sub>2</sub> (**4**): Elemental Anal. Found (Calcd.) (%): C, 50.98 (51.43); H, 4.27 (3.74); N, 11.88 (12.00).

[VO<sub>2</sub>HL]·CH<sub>3</sub>OH (**5**): Elemental Anal. Found (Calcd.) (%): C, 48.40 (48.12); H, 3.86 (4.54); N, 10.80 (10.52).

### 2.4. Physical measurements

Microanalysis of carbon, hydrogen and nitrogen content of the thiosemicarbazone and its complexes were carried out on a Vario EL III CHN elemental analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a JASCO FT/IR-4100 type Infrared Spectrometer using KBr pellets in the range 4000–400 cm<sup>-1</sup>. Electronic spectra were recorded on a Cary 5000 version 1.09 UV–vis–NIR Spectrophotometer from a solution in DMF. EPR spectra of complexes in solid state at 298 K and in frozen DMF at 77 K were recorded on a Varian E-112 spectrometer at X-band, using TCNE with 100 kHz modulation frequency and 9.1 GHz microwave frequency at SAIF, IIT Bombay, India.

## 3. Results and discussion

### 3.1. Synthesis

The elemental analyses data are consistent with the general formula [VOLB]·2H<sub>2</sub>O for complex **1**, [VOLB] for **2** and **3** and [VOL]<sub>2</sub> for **4** and [VO<sub>2</sub>HL]·CH<sub>3</sub>OH for **5**, where L is the doubly deprotonated thiosemicarbazone ligand and B is the bidentate heterocyclic base *viz.*, phen, bipy, dmbipy. However, we could not isolate single crystal of suitable quality for XRD for any of these complexes.

### 3.2. Infrared spectra

The characteristic IR bands of the complexes show significant changes when compared with that of the parent ligand and shift of some of characteristic vibrational frequency of the ligand upon complexation provides evidence for the mode of binding of the ligand to the metal ion. The important IR frequencies of the ligand and

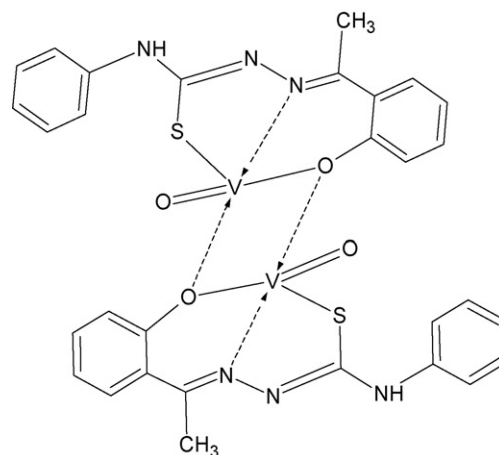


Fig. 1. Tentative structure of the complex [VOL]<sub>2</sub> (**4**).

its complexes along with their relative assignments are presented in Table 1.

The spectrum of the free ligand exhibits a broad band at 3330 cm<sup>-1</sup> which is assigned to the phenolic –OH group. The disappearance of this band is an evidence for the ligand coordination around the metal ion in its deprotonated form [6]. This causes  $\nu(\text{C}=\text{O})$  to shift to lower frequencies and a new band in the range *ca.* 507 cm<sup>-1</sup>, assigned to  $\nu(\text{V}=\text{O})$  is found in complexes which confirm the coordination of the ligand *via* phenolic oxygen [7]. On coordination of azomethine nitrogen,  $\nu(\text{C}=\text{N})$  shifts to lower wavenumbers by 20–30 cm<sup>-1</sup>, as the band shifts from 1602 cm<sup>-1</sup> in the uncomplexed thiosemicarbazone spectrum to *ca.* 1568 cm<sup>-1</sup> in the spectra of complexes [8]. The azomethine nitrogen coordination is further evidenced by the presence of new bands in the range 450–460 cm<sup>-1</sup> assignable to  $\nu(\text{V}=\text{N})$  for the complexes [9]. The increase in frequency of  $\nu(\text{N}=\text{N})$  bands in the complexes due to the increase in bond strength also supports coordination through azomethine nitrogen in all the complexes.

The strong bands at 1375 and 825 cm<sup>-1</sup> due to  $\nu(\text{C}=\text{S})$  stretching and bending vibration of thioamide group, of the free ligand are shifted to lower values, indicating coordination *via* thiolate sulfur [10] in complexes **1–4**. Also strong new bands found at *ca.* 1592 cm<sup>-1</sup> for **1–4** are assigned to the newly formed (C=N) bond due to enolization, which confirms the coordination *via* thiolato sulfur [11]. However, in the spectrum of complex **5**, this new band is absent and the decrease in stretching frequency of  $\nu(\text{C}=\text{S})$  is less compared to the other four complexes. This supports the coordination through the thione form in this complex. The complexes **1–4** exhibit strong bands in the range 950–977 cm<sup>-1</sup>, due to the terminal V=O stretching [11]. In addition, monomeric neutral dioxo complex **5**, displays two strong V=O stretching frequencies at 977 and 873 cm<sup>-1</sup> [12]. However, a characteristic feature in the form of a prominent band in the region 853 cm<sup>-1</sup> is observed for the binuclear complex **4** due to the V–O–V bridging vibrations [13]. Tentative structure of compound **4** is shown in Fig. 1. The IR spectra

Table 1  
Selected IR bands (cm<sup>-1</sup>) with tentative assignments of vanadium(IV/V) complexes.

Compound	$\nu(\text{C}=\text{N})_{\text{azo}}$	$\nu(\text{C}=\text{N})$	$\nu(\text{CS})$	$\nu(\text{C}=\text{O})$	$\nu(\text{V}=\text{O})$	$\nu(\text{V}=\text{O})$	$\nu(\text{V}=\text{N})$
H <sub>2</sub> L	1602	–	1375, 825	1251	–	–	–
[VOLphen]·2H <sub>2</sub> O	1568	1591	1310, 755	1245	953	503	457
[VOLbipy]	1565	1592	1313, 749	1247	955	502	451
[VOLdmbipy]	1562	1595	1315, 750	1243	960	515	455
[VOL] <sub>2</sub>	1574	1591	1316, 749	1234	953	509	445
[VO <sub>2</sub> HL]·CH <sub>3</sub> OH	1571	–	1340, 755	1240	977, 873	506	455

**Table 2**  
Electronic spectral assignments (nm) of vanadium(IV/V) complexes.

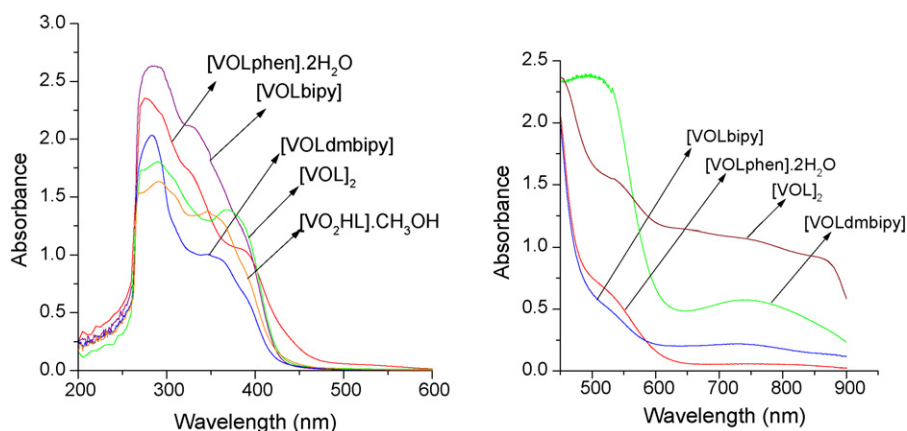
Compound	Intraligand transitions	LMCT	d–d
H <sub>2</sub> L	299, 326	–	–
[VOLphen].2H <sub>2</sub> O	275, 330	382	544
[VOL bipy]	288, 329	388	547
[VOL dmbipy]	286	346	750
[VOL] <sub>2</sub>	294, 316	369	571
[VO <sub>2</sub> HL].CH <sub>3</sub> OH	291, 309	349	–

of the complexes **1**, **2** and **3** display bands characteristic of coordinated heterocyclic bases in the range 1470–1485 cm<sup>-1</sup>.

### 3.3. Electronic spectra

Electronic spectral data of the ligand and complexes in DMF solution are summarized in Table 2. The ligand exhibits intraligand transitions at ~299 nm due to  $\pi \rightarrow \pi^*$  transitions and at ~326 nm due to  $n \rightarrow \pi^*$  transitions. On complexation these bands suffer considerable shifts on coordination. The vanadium(V) complex **5**, displays a band at ~349 nm originating from ligand to metal charge transfer (LMCT) arising from the phenolate oxygen to an empty d orbital of the vanadium(V) center [14]. All the oxovanadium complexes **1–4** exhibit an intense LMCT [PhO  $\rightarrow$  V<sub>(d $\pi$ )</sub>] band in the range 346–388 nm [15].

Usually three absorptions are observed in the spectra of VO<sup>2+</sup> with various ligands arising from the tetragonal compression caused by V=O bond, which results in further splitting of d orbitals and give rise to three spin allowed transitions  ${}^2E \leftarrow {}^2B_2$ ,  ${}^2B_1 \leftarrow {}^2B_2$ ,  ${}^2A_1 \leftarrow {}^2B_2$  [16]. However, we could locate only one band in the complexes, probably due to the masking by high intensity charge transfer bands. The other bands observed in the complexes are due to the intraligand transitions. In complex **5**, no d–d transitions are observed due to the absence of d electrons. Representative spectra of the complexes are presented in Fig. 2.



**Fig. 2.** Electronic spectra of the vanadium(IV/V) complexes.

**Table 3**  
EPR spectral assignments of oxovanadium(IV) complexes in polycrystalline state at 298 K and in frozen DMF at 77 K.

Compound	Polycrystalline state (298 K)	DMF solution (77 K)				$\beta^2$	$\alpha^2$
		$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^a$	$A_{\perp}^a$		
[VOLphen].2H <sub>2</sub> O	–	1.950	1.980	162.80	52.42	0.963	0.959
[VOLbipy]	1.934/1.969 ( $g_{\parallel}/g_{\perp}$ )	1.959	1.987	160.71	53.01	0.937	0.834
[VOLdmbipy]	–	1.950	1.985	160.66	51.35	0.946	0.720
[VOL] <sub>2</sub>	1.984 ( $g_{\text{iso}}$ )	1.951	1.987	160.21	51.84	0.946	0.929

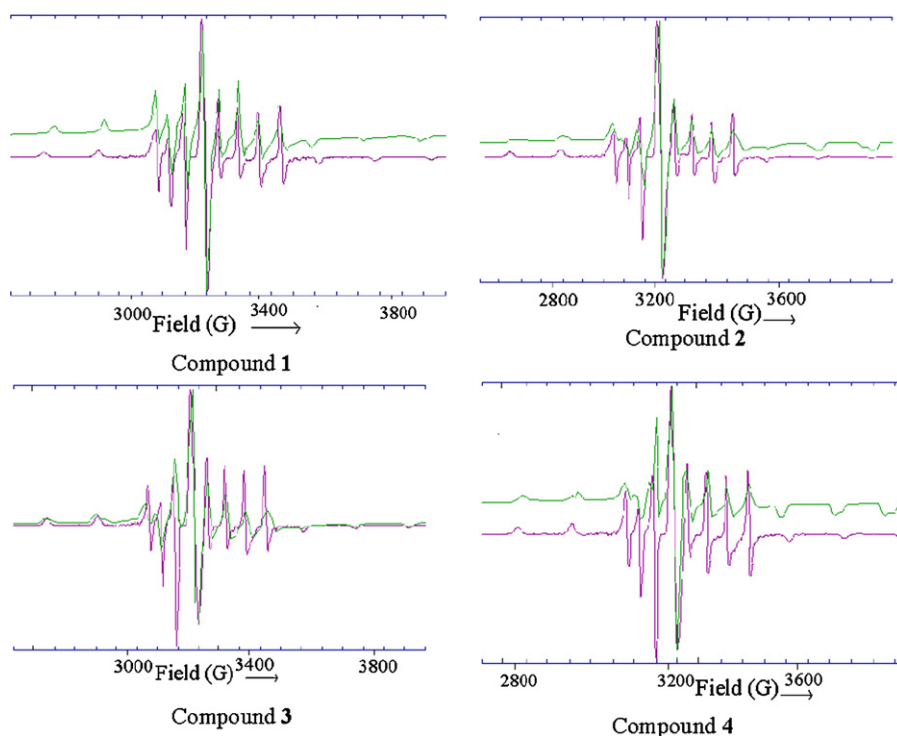
<sup>a</sup> Expressed in units of cm<sup>-1</sup> multiplied by a factor of 10<sup>-4</sup>.

### 3.4. EPR spectra

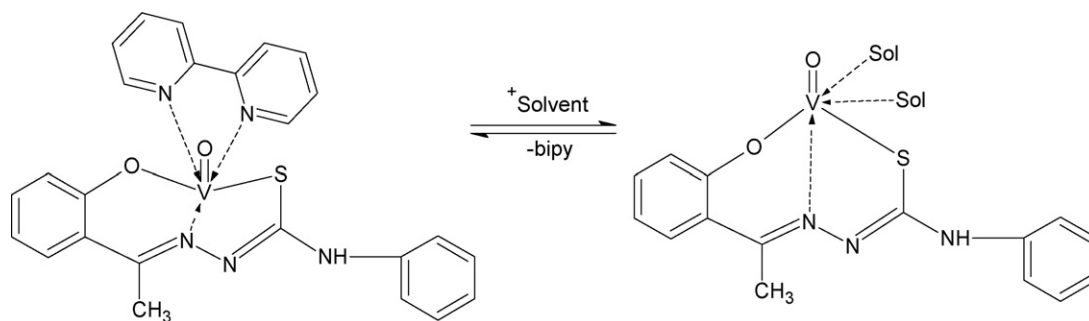
All the compounds except [VO<sub>2</sub>HL].CH<sub>3</sub>OH are EPR active due to the presence of an unpaired electron. EPR spectra of all oxovanadium(IV) complexes **1–4** were recorded in polycrystalline state at 298 K and in frozen DMF at 77 K. In polycrystalline state at 298 K, compound **2** is axial with  $g_{\parallel} = 1.934$  and  $g_{\perp} = 1.969$  and compound **4** is isotropic in nature with  $g_{\text{iso}} = 1.984$ . The EPR spectra of other complexes in polycrystalline state at 298 K were difficult to interpret.

In frozen DMF at 77 K compounds **1–4** showed well resolved axial anisotropy characterized by two sets of eight lines which result from coupling of the electron spin to the spin of the <sup>51</sup>V nucleus ( $I = 7/2$ ). Spectral parameters for **1–4** are collected in Table 3 and the experimental and simulated best fits of EPR spectra of the complexes are given in Fig. 3. All the complexes showed well-resolved axial anisotropy with two sets of eight line pattern with  $g_{\parallel} < g_{\perp}$  and  $A_{\parallel} > A_{\perp}$  relationship, characteristic of an axially compressed  $d_{xy}^1$  configuration [17]. The absence of any ligand hyperfine lines in the  $g_{\parallel}$  features due to nitrogen indicates that the unpaired electron, for most of the times staying in the  $b_{2g}$  ( $d_{xy}$ ,  ${}^2B_2$  ground state) orbital localized on metal, thus excluding the possibility of its direct interaction with the ligand [18,19].

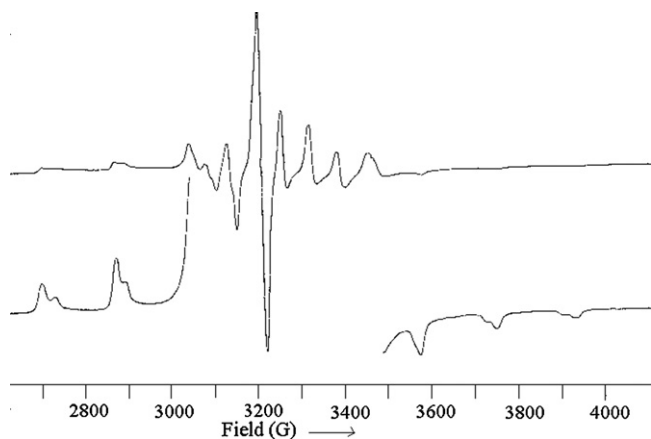
The EPR spectra in frozen DMF (77 K) differ for bipyridine and phenanthroline containing complexes. The  $g$  and  $A$  values are sensitive to the vanadium coordination environment and may be used to distinguish between species with different coordination environment [20]. In the case of bipyridyl and dimethylbipyridyl base adducts, the dissolution of the compound in solution is initiated by the coordination of the solvent and subsequent replacement of the base from the coordination environment (Scheme 1). The EPR spectra of these complexes showed more than one species in solution (Fig. 4), which is assumed to be a partially solvent coordinated oxovanadium(IV) ion. When the DMF replaces the base from the coordination environment the electron delocalization to the ligand is restricted which contributes to a greater residence time for the



**Fig. 3.** Experimental (green) and simulated best fit (purple) of the EPR spectra of complexes 1–4 in frozen DMF at 77 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Scheme 1.**



**Fig. 4.** EPR spectrum of [VOLbipy] in DMF at 77 K.

electron at the nucleus. The EPR spectra of the phenanthroline base adducts at 77 K are, however, not influenced by the solvent and are reasonably stable in the polar solvents, probably due to the lack of proper room at the sixth coordination site of these compounds.

The EPR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  and energies of d–d transitions were used to evaluate the molecular orbital coefficients  $\alpha^2$ ,  $\beta^2$  for the complexes by using the following equations:

$$\alpha^2 = \frac{(2.00277 - g_{\parallel}) E_{d-d}}{8\lambda\beta^2},$$

$$\beta^2 = \frac{7}{6} \left[ \left( \frac{-A_{\parallel}}{P} \right) + \left( \frac{A_{\perp}}{P} \right) + \left( g_{\parallel} - \frac{5}{14g_{\perp}} \right) - \frac{9}{14g_e} \right]$$

where  $P = 128 \times 10^{-4} \text{ cm}^{-1}$ ,  $\lambda = 135 \text{ cm}^{-1}$  and  $E$  is the energy of d–d transition. The lower values for  $\alpha^2$  compared to  $\beta^2$  indicate that in-plane  $\sigma$  bonding is more covalent than in-plane  $\pi$  bonding [21].

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