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 (H2L) which are represented as [VOLphen]·2H2O (1), [VOLbipy] (2), [VOLdmbipy] (3), [VOL]2 (4) and [VO2HL]·CH3OH (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 [VO2HL]·CH3OH, coordination takes place in thione form instead of thiolate sulfur. All the complexes except [VO2HL]·CH3OH 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 VO2+ unit can readily coordinate to four and five donor atoms to form VOL4 and VOL5 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 radical sources.

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 preventive 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
VOSO4·H2O (Sigma–Aldrich), vanadium(IV) oxide acetylacetone, 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 (H2L) has been synthesized as reported by us earlier [5].
2.3. Synthesis of complexes

The complexes [VOLphen·2H2O (1), [VOLbipy (2), [VOLdmmbipy (3) were prepared by refluxing 1 mmol each of VOSO4·H2O in aqueous solution, heterocyclic base (phen/bipy/dmbipy) in solid form and H2L in methanol for 3 h. The complexes [VOL]2 (4), [VO2HL]·CH3OH (5) were prepared by refluxing 1 mmol of VOSO4·H2O for 4 and 1 mmol of vanadium(IV) oxide acetylacetone for 5 in aqueous solution with 1 mmol of H2L in methanol for 3 h. The compounds formed were filtered, washed with methanol and ether and dried in vacuo over P2O5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(C=O)</th>
<th>ν(C=N)</th>
<th>ν(CS)</th>
<th>ν(C=O)</th>
<th>ν(V=O)</th>
<th>ν(V–O)</th>
<th>ν(V–N)</th>
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<tr>
<td>H2L</td>
<td></td>
<td>-</td>
<td>1375, 825</td>
<td>1251</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>[VOLphen·2H2O]</td>
<td>1560</td>
<td>1591</td>
<td>1310, 755</td>
<td>1245</td>
<td>953</td>
<td>503</td>
<td>457</td>
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<td>[VOLbipy]</td>
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<td>1592</td>
<td>1313, 749</td>
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<td>955</td>
<td>502</td>
<td>451</td>
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<tr>
<td>[VOLdmmbipy]</td>
<td>1562</td>
<td>1595</td>
<td>1315, 750</td>
<td>1243</td>
<td>960</td>
<td>515</td>
<td>455</td>
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<td>[VOL]2</td>
<td>1574</td>
<td>1591</td>
<td>1316, 749</td>
<td>1234</td>
<td>953</td>
<td>509</td>
<td>445</td>
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<tr>
<td>[VO2HL]·CH3OH</td>
<td>1571</td>
<td>-</td>
<td>1340, 755</td>
<td>1240</td>
<td>977, 873</td>
<td>506</td>
<td>435</td>
</tr>
</tbody>
</table>

Fig. 1. Tentative structure of the complex [VOL]2 (4).

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. The elemental analyses data are consistent with the general formula [VOLB·2H2O for complex 1, [VOLB for 2 and 3 and [VOL]2 for 4 and [VO2HL]·CH3OH 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. Results and discussion

3.1. Synthesis

The elemental analyses data are consistent with the general formula [VOLB·2H2O for complex 1, [VOLB for 2 and 3 and [VOL]2 for 4 and [VO2HL]·CH3OH 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 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⁻¹ 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 ν(C=O) to shift to lower frequencies and a new band in the range ca. 507 cm⁻¹, assigned to ν(V=O) is found in complexes which confirm the coordination of the ligand via phenolic oxygen [7]. On coordination of azomethine nitrogen, ν(C=N) shifts to lower wavenumbers by 20–30 cm⁻¹, as the band shifts from 1602 cm⁻¹ in the uncomplexed thiosemicarbazone spectrum to ca. 1568 cm⁻¹ 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⁻¹ assignable to ν(N–N) for the complexes [9]. The increase in frequency of ν(N–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⁻¹ due to ν(C=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⁻¹ for 1–4 are assigned to the newly formed (C=N) bond due to enolization, which confirms the coordination via thiolate sulfur [11]. However, in the spectrum of complex 5, this new band is absent and the decrease in stretching frequency of ν(C=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⁻¹, 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⁻¹ [12]. However, a characteristic feature in the form of a prominent band in the region 853 cm⁻¹ 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.

Table 1

Selected IR bands (cm⁻¹) with tentative assignments of vanadium(IV/V) complexes.
of the complexes 1, 2 and 3 display bands characteristic of coordinated heterocyclic bases in the range 1470–1485 cm\(^{-1}\).

### 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 bands. The other bands observed in the complexes are 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 \(g_l = 1.934\) and \(g_z = 1.969\) and compound 4 is isotropic in nature with \(g_{iso} = 1.984\). 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 \(^{51}\)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 \(g_l < g_z\) and \(A_l > A_z\) relationship, characteristic of an axially compressed \(d_{xy}\) configuration [17]. The absence of any ligand hyperfine lines in the \(g_z\) features due to nitrogen indicates that the unpaired electron, for most of the times staying in the \(b_{2u}\) (\(d_{xy}, b_{2g}\) 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

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Intraligand transitions</th>
<th>LMCT</th>
<th>(d-d)</th>
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<tbody>
<tr>
<td>([\text{VOLphen}]) (2\text{H}_2\text{O})</td>
<td>299, 326</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>([\text{VOLbipy}])</td>
<td>275, 330</td>
<td>382</td>
<td>544</td>
</tr>
<tr>
<td>([\text{VOLdmmbipy}])</td>
<td>288, 329</td>
<td>388</td>
<td>547</td>
</tr>
<tr>
<td>([\text{VOL}])</td>
<td>286</td>
<td>346</td>
<td>750</td>
</tr>
<tr>
<td>([\text{VOL}]\cdot\text{CH}_3\text{OH})</td>
<td>296, 316</td>
<td>369</td>
<td>571</td>
</tr>
<tr>
<td>([\text{H}_2\text{L}]\cdot\text{CH}_3\text{OH})</td>
<td>291, 309</td>
<td>349</td>
<td>–</td>
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### Table 3

<table>
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<tr>
<th>Compound</th>
<th>Polycrystalline state (298 K)</th>
<th>DMF solution (77 K)</th>
<th>(g_l)</th>
<th>(g_z)</th>
<th>(A_l) (a)</th>
<th>(A_z) (a)</th>
<th>(\beta^a)</th>
<th>(\alpha^a)</th>
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<tbody>
<tr>
<td>([\text{VOLphen}]) (2\text{H}_2\text{O})</td>
<td>–</td>
<td>1.950</td>
<td>1.980</td>
<td>162.80</td>
<td>52.42</td>
<td>0.963</td>
<td>0.955</td>
<td></td>
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<tr>
<td>([\text{VOLbipy}])</td>
<td>1.934/1.969 ((g_l/g_z))</td>
<td>1.999</td>
<td>1.987</td>
<td>160.71</td>
<td>53.01</td>
<td>0.937</td>
<td>0.834</td>
<td></td>
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<tr>
<td>([\text{VOLdmmbipy}])</td>
<td>–</td>
<td>1.950</td>
<td>1.985</td>
<td>160.66</td>
<td>51.35</td>
<td>0.946</td>
<td>0.720</td>
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<tr>
<td>([\text{VOL}])</td>
<td>1.984 ((g_{iso}))</td>
<td>1.951</td>
<td>1.987</td>
<td>160.21</td>
<td>51.84</td>
<td>0.946</td>
<td>0.929</td>
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</tbody>
</table>

* Expressed in units of \(\text{cm}^{-1}\) multiplied by a factor of \(10^4\).
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.

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 $g_{||}, g_{\perp}, A_{||}$ 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:

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

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

where $P = 128 \times 10^{-4}$ cm$^{-1}$, $\lambda = 135$ 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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References