3.1. Introduction

Vanadium is a widespread trace element distributed in nature. Vanadium is an essential trace element of plants and animals and has significant effect on normal growth [1]. In higher animals, once absorbed through the gastrointestinal tract, it is mainly accumulated in bone tissue. In the last decades, vanadium compounds have been widely studied because of their potential therapeutic applications. The pharmacological effects of vanadium include insulin mimetic actions, antineoplastic effects and osteogenic effects [2].

The coordination chemistry of vanadium, in view of the fact that its catalytic activity is of particular importance in the biosphere, has generated a considerable escalation of interest in related investigations in recent years. The broad range of ligands used to synthesize oxovanadium complexes include a wide range of Schiff base-type ligands, which can afford monomeric or dimeric compounds [3]. Oxovanadium(IV) and (V) complexes, especially with bi- and tridentate chelating ligands bound to the metal mainly via oxygen and nitrogen atoms, have being extensively investigated in recent years with respect to their remarkable efficiency as insulin mimetic compounds. Their use as orally active
medicaments would represent an important advance in the treatment of human diabetes mellitus. Other studies involving potential applications of oxovanadium complexes have been also performed, with emphasis, for example, in their antitumor and antibacterial activity [4].

The interaction of simple vanadium species (viz., VO$^{2+}$ and VO$^{3+}$) with ligand groups having pharmacological activity is of growing interest. More detailed physico-chemical characterization of vanadium compounds with pharmacologically important ligands will help in further understanding of pharmacology of vanadium [5]. The discovery of the insulin-like in vitro and in vivo activity of oxovanadates(V) and oxovanadium(IV) complexes has stimulated research on vanadium compounds that may have important application in the treatment of type-1 and type-2 diabetes mellitus [6]. Organic ligands, complexed to vanadium in coordination compounds, provide way in tuning the effects of vanadium, thereby minimizing any adverse effects without sacrificing important benefits [7-9].

Vanadium forms a large number of compounds in which the most important oxidation states are +3, +4 and +5. Vanadium easily switches between the oxidation states +4 and +5. Complexes of vanadium usually adopt five-coordinate square pyramidal and six-coordinate distorted octahedral geometries.

3.2. Experimental

3.2.1. Materials

All the chemicals and solvents used for the syntheses were of analytical grade. Di-2-pyridyl ketone (Aldrich), N(4)-methyl thiosemicarbazide (Aldrich), vanadyl sulphate monohydrate (Aldrich), potassium thiocyanate (E-Merck), ethanol and methanol were used as supplied.
3.2.2. Synthesis of the ligand

The synthesis of the thiosemicarbazone ligand, HDpyMeTsc has been described already in Chapter 2.

3.2.3. Syntheses of oxovanadium(IV) complexes

3.2.3a. Synthesis of $[\text{VO(}\text{DpyMeTsc}\text{)(NCS)}] \ (1)$

HDpyMeTsc (0.271 g, 1 mmol) was dissolved in ethanol by heating. To this, an aqueous solution of KSCN (0.097 g, 1 mmol) and methanolic solution of vanadyl sulfate (0.163 g, 1 mmol) were added and refluxed for 4 hours. The resulting solution was allowed to stand at room temperature and after slow evaporation, the orange precipitate separated out was filtered, washed with ethanol followed by ether and dried over $\text{P}_4\text{O}_{10}$ in vacuo.

$\lambda_{\text{m}}$ (DMF): 31 ohm$^{-1}$ cm$^2$ mol$^{-1}$, Elemental Anal. Found (Calcd.) (%): C: 42.60 (42.53); H: 3.25 (3.06); N: 20.90 (21.26).

3.2.3b. Synthesis of $[\text{VO(}\text{HDpyMeTsc}\text{)(SO}_4\text{)}] \ (2)$

To a solution of the ligand, HDpyMeTsc (0.271 g, 1 mmol) in hot ethanol, was added a methanolic solution of vanadyl sulfate (0.163 g, 1 mmol). The mixture was heated under reflux for 3 hours and cooled. The light green precipitate obtained was filtered, washed with ethanol and then with ether and dried over $\text{P}_4\text{O}_{10}$ in vacuo.

$\lambda_{\text{m}}$ (DMF): 16 ohm$^{-1}$ cm$^2$ mol$^{-1}$, Elemental Anal. Found (Calcd.) (%): C: 34.76 (34.52); H: 2.93 (3.34); N: 15.39 (15.48).

3.3. Results and discussion

Based on the elemental analyses, conductivity measurements and spectral investigations, the complexes were formulated. Both the complexes
contain the VO$^{2+}$ unit, in which vanadium is in +4 oxidation state ($d^1$). The molar conductivity measurements in 10$^{-3}$ M DMF solution indicate that both complexes are non-electrolytic in nature [10]. In complex 1, the thiosemicarbazone deprotonates and chelates in thiolate form as evidenced by the IR spectra, while in complex 2 the ligand coordinates in the thioamido form.

The magnetic moments of the complexes were calculated from the magnetic susceptibility measurements and the value for complex 1 at room temperature is 1.60 B.M. and that for 2 is 1.67 B.M. The values are found to be very close to the spin only value 1.73 B.M., which indicate the presence of one unpaired electron [11]. Both the complexes are EPR active due to this unpaired electron.

### 3.3.1. 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 significant bands observed in the IR spectrum of the ligand and its complexes along with their tentative assignments are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu(C=\text{N})$</th>
<th>$\nu(C=\text{N})^a$</th>
<th>$\nu(\delta(C-S))$</th>
<th>$\nu(N-N)$</th>
<th>$py(ip)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDpyMeTsc</td>
<td>1588</td>
<td>...</td>
<td>1431, 800</td>
<td>1110</td>
<td>618</td>
</tr>
<tr>
<td><a href="1">VO(DpyMeTsc)(NCS)</a></td>
<td>1513</td>
<td>1545</td>
<td>1390, 788</td>
<td>1168</td>
<td>649</td>
</tr>
<tr>
<td><a href="2">VO(HDpyMeTsc)(SO$_4$)</a></td>
<td>1580</td>
<td>...</td>
<td>1326, 793</td>
<td>1183</td>
<td>646</td>
</tr>
</tbody>
</table>

$^a$Newly formed C=N

The $\nu(C=\text{N})$ band of thiosemicarbazone is found to be shifted to lower frequencies in both complexes representing the coordination via the azomethine
nitrogen [12]. The increase for the $\nu$(N–N) frequency in the spectra of the complexes is probably due to enhanced double bond character through chelation, thus offsetting the loss of electron density via donation to the metal atom, and is supportive of azomethine nitrogen coordination. For complex 1, a new band at 1545 cm$^{-1}$ due to the newly formed $\mathbf{\text{C}=\text{N}}$ moiety is observed. This indicates that the ligand enolizes and coordinates in the thiolate form [13]. Coordination via thiolate sulfur is also indicated by the downward shift of frequencies of $\nu$/$\delta$(C–S) bands found at 1431 and 800 cm$^{-1}$ [14]. The in-plane bending vibrations of the pyridine ring in uncomplexed ligand at 618 cm$^{-1}$ shift to higher frequencies on complexation, conforming the coordination of the ligand to the metal via the pyridine nitrogen.

Further, the intense bands observed at 974 cm$^{-1}$ for complex 1 and 981 cm$^{-1}$ for complex 2 correspond to the terminal V=O stretching band [15]. Thiocyanato complex 1 has a very strong and sharp band at 2084 cm$^{-1}$ and a medium band at 740 cm$^{-1}$ corresponding to $\nu$(CN) and $\nu$(CS) modes of the NCS group. The intensities and positions of these bands indicate the unidentate coordination of the thiocyanate group through the nitrogen atom [16].

It was found that the sulfato complex 2 exhibits four fundamental vibrations. Bands at $\sim$980 cm$^{-1}$ due to $\nu_1$ and medium bands around 460 cm$^{-1}$ due to $\nu_2$, strong bands at 1278, 1191 and 1017 cm$^{-1}$ corresponding to $\nu_3$ and band at 727 cm$^{-1}$ due to $\nu_4$. These bands are attributed to a chelating bidentate sulfato group [17]. IR spectra of complexes are presented in Figs. 3.1 and 3.2.
3.3.2. Electronic spectra

The electronic spectral assignments for the free ligand (HDpyMeTsc) and their V(IV) complexes are summarized in Table 3.2. The ligand exhibits intraligand transitions at 35890 and 29280 cm$^{-1}$ assignable to $\pi \rightarrow \pi^*$ transitions of the pyridyl ring and thiosemicarbazone moiety [18]. These bands suffer considerable shifts on coordination. In addition to these intra-ligand bands,
new bands at 23340 cm\(^{-1}\) are observed in the spectra of complexes. This band can safely be assigned to ligand→metal charge-transfer bands.

### Table 3.2. Electronic spectral data (cm\(^{-1}\)) of vanadium(IV) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV absorption bands (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDpyMeTsc</td>
<td>35890 29280</td>
</tr>
<tr>
<td>[VO(DpyMeTsc)(NCS)]([\text{I}])</td>
<td>35680 29750 23340 17270 14600</td>
</tr>
<tr>
<td>[VO(HDpyMeTsc)(SO(_4))]([\text{I}])</td>
<td>37250 29560 23340 18450</td>
</tr>
</tbody>
</table>

Interpretation of the electronic spectra of oxovanadium(IV) complexes is the subject of continuing investigation and discussion. Following the energy level scheme derived by Ballhausen and Gray for oxovanadium(IV) complexes, the energy of the molecular orbitals are ordered as \(B_2 (d_{xy}) < E (d_{xz}, d_{yz}) < B_1 (d_{z^2}) < A_1 (2d_z)\). Thus the spectral bands at 13,000-14,000, 15,400-16,300 and 22,000-24,600 cm\(^{-1}\) can be assigned to \(^2E \leftrightarrow ^2B_2\) (\(d_{xy} \rightarrow d_{xz}, d_{yz}\)), \(^2B_1 \leftrightarrow ^2B_2\) (\(d_{xy} \rightarrow d_{z^2}\)) and \(^2A_1 \leftrightarrow ^2B_2\) (\(d_{xy} \rightarrow d_z\)) transitions [19]. Most of the oxovanadium complexes show three prominent bands in the electronic spectral region. However, we can locate only two weak bands for complex 1 and one band for complex 2, probably due to the masking by high intensity charge transfer bands. The electronic spectra of complexes are given in Figs. 3.3–3.5.
Fig. 3.3. Electronic spectrum of [VO(DpyMeTsc)(NCS)](1)

Fig. 3.4. Electronic spectrum of [VO(DpyMeTsc)(NCS)](1) in the visible region
3.3.3. Electron paramagnetic resonance spectra

All the compounds are EPR active due to the presence of an unpaired electron. The oxidation state of the central vanadium atom in the complexes was confirmed by the measurements of EPR spectroscopy. EPR spectra of both the complexes were recorded in polycrystalline state at 298 K and in frozen DMF at 77 K. EPR spectral parameters of oxovanadium(IV) complexes are summarized in Table 3.3.

In polycrystalline state at 298 K, the two complexes are isotropic in nature with $g_{iso} = 1.956$ and 1.968 respectively (Figs. 3.6 & 3.7). In frozen DMF at 77 K both the complexes show 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 ($I = 7/2$), characteristic of mononuclear oxovanadium complexes (Figs. 3.8 & 3.9). The anisotropic hyperfine parameters were also calculated. The $g_{||} < g_{\perp}$ and $A_{||} > A_{\perp}$
relationship, characteristic of an axially compressed system with unpaired electron in $d_{xy}$ orbital [20]. The absence of superhyperfine splittings in the spectra also indicate the unpaired electron to be in $d_{xy}$ orbital localized on metal, thus excluding the possibility of its direct interaction with the ligand [21,22].

The EPR parameters $g_{||}$, $g_{\perp}$, $A_{||}$ and $A_{\perp}$ and energies of $d$-$d$ transitions were used to evaluate the molecular orbital coefficients $\alpha^2$ and $\beta^2$ for the complexes by using the following equations [23]

$$\alpha^2 = \frac{(2.00277 - g_{||})E_{d-d}}{8\lambda\beta^3}$$

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

Where $P = 128 \times 10^{-4}$ cm$^{-1}$, $\lambda = 135$ cm$^{-1}$ and $E_{d-d}$ 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.

**Table 3.3.** EPR spectral data of vanadium (IV) complexes in the polycrystalline state at 298 K and in frozen DMF at 77 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>Polycrystalline (298 K)</th>
<th>DMF Solution (77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_{iso}$</td>
<td>$g_{</td>
</tr>
<tr>
<td>[VO(DpyMeTsc)(NCS)]$\text{[1]}$</td>
<td>1.956</td>
<td>1.950</td>
</tr>
<tr>
<td>[VO(HDpyMeTsc)(SO$_4$)]$\text{[2]}$</td>
<td>1.968</td>
<td>1.964</td>
</tr>
</tbody>
</table>

$^a$ values in $10^{-4}$ cm$^{-1}$
Fig. 3.6. EPR spectrum of $[\text{VO(DpyMeTsc}_2\text{NCS}]$ (1) in polycrystalline state at 298 K

Fig. 3.7. EPR spectrum of $[\text{VO(HDpyMeTsc}_2\text{SO}_4]$ (2) in polycrystalline state at 298 K
Fig. 3.8. EPR spectrum of [VO(DpyMeTsc)(NCS)](1) in DMF at 77 K

Fig. 3.9. EPR spectrum of [VO(HDpyMeTsc)(SO₄)](2) in DMF at 77 K
References


