3.1. Introduction

Vanadium is a pervasive element of biological systems, being widely distributed across the food supply. It has been estimated to comprise about 136 ppm of the earth’s crustal rocks. It is the fifth most abundant transition metal after Fe, Ti, Mn and Zr. This element 23, first claimed to have been discovered by A.M. del Rio in 1801, then rediscovered by N.G. Sefström in 1830, was named vanadium after Vanadis, the Scandinavian goddess of beauty, because of the richness and variety of colors in its compounds. While vanadium is widely spread with a natural abundance of ~0.014% there are few concentrated deposits and pure vanadium is rare due to its reactivity towards oxygen. Although vanadium can possess formal oxidation states from +5 to -1, the most stable under normal conditions is +4, with +3 and +2 states also having many well-characterized compounds.

The +4 oxidation state is most notable for the uniquely stable VO$^{2+}$ (vanadyl) ion which retains its identity throughout a wide variety of reactions and forms many complexes. Many of compounds containing the VO$^{2+}$ unit
are blue to green, form stable complexes with $F$, $Cl$, $O$, and $N$ donor semicarbazones and can be cationic, neutral, or anionic. Most often, these compounds are 5 coordinate and are almost always square pyramidal while in the case of hexacoordinated complexes octahedral geometry predominates.

Recent studies indicate that vanadium, which is proposed to be one of essential trace elements in animals and humans, relates to both glucose and lipid metabolisms. Oxidovanadium(IV) and vanadate(V) are the main species present in solution under physiological conditions. The physiological effects are in many cases a consequence of good complexation behavior of $\text{VO}^{2+}$, and the chemical similarity of phosphate and vanadate. The coordination chemistry of vanadium has received considerable attention since the discovery of vanadium in enzymes like bromoperoxidases and azotobactervinelandii [1].

Medicinal applications of vanadium compounds have focused on their in vitro and in vivo activity in the treatment of insulin deficiency [2]. Vanadium complexes of semicarbazones of low molecular weight could in principle be useful as potential biomimetic drugs. Vanadium coordination compounds are much safer as antidiabetic agents than inorganic vanadium salts [3]. Besides the antidiabetic effects for which it is now so well known, vanadium compounds also exhibit a number of therapeutic effects including antitumor [2-5], anti-inflammatory [3] and antibacterial [6] activities.

This chapter deals with the syntheses and spectral characterization of mononuclear and binuclear oxidovanadium(IV) complexes with two new ONO donor semicarbazones, 2-hydroxy-4-methoxyacetophenone-$N^4$-phenylsemicarbazone ($\text{H}_2\text{ASC}$), 2-hydroxy-4-methoxybenzophenone-$N^4$-phenylsemicarbazone ($\text{H}_2\text{BSC}$) and some heterocyclic compounds like 1,10-
phenanthroline, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine and 4-picoline as coligands.

3.2. Experimental

3.2.1. Materials

2-Hydroxy-4-methoxyacetophenone (Sigma-Aldrich), 2-hydroxy-4-methoxybenzophenone (Sigma-Aldrich), N^4-phenylsemicarbazide (Sigma-Aldrich), vanadyl sulphate monohydrate (Aldrich), 1,10-phenanthroline (Ranchem), 2,2'-bipyridine (Qualigens), 4,4'-dimethyl-2,2'-bipyridine (Qualigens), and 4-picoline (BDH) were of analar grade and were used as received. Solvent used was methanol.

3.2.2. Syntheses of semicarbazones

2-Hydroxy-4-methoxyacetophenone-N^4-phenylsemicarbazone monohydrate (H₂ASC·H₂O) and 2-hydroxy-4-methoxybenzophenone-N^4-phenylsemicarbazone (H₂BSC) were synthesized as described in Chapter 2.

3.2.3. Syntheses of VO(IV) complexes of 2-hydroxy-4-methoxyacetophenone-N^4-phenylsemicarbazone (H₂ASC)

3.2.3.1. [VO(ASC)]₂·2H₂O (I)

The complex 1 was prepared by refluxing a methanolic solution of H₂ASC·H₂O (0.317 g, 1 mmol) and an aqueous solution of vanadyl sulfate (0.163 g, 1 mmol) for 5 h. The resulting solution was allowed to evaporate at room temperature and the yellow colored product formed was filtered, washed with methanol, followed by ether and dried over P₄O₁₀ in vacuo.

Elemental Anal. Found (Calcd.) (%): C: 49.91 (50.27); H: 4.60 (4.48); N: 10.70 (10.99)
3.2.3.2. [VO(ASC)(bipy)]·2H₂O (2)

An aqueous solution of vanadyl sulfate (0.163 g, 1 mmol) was added to a hot methanolic solution of H₂ASC·H₂O (0.317 g, 1 mmol) and 2,2′-bipyridine (0.156 g, 1 mmol) and refluxed for 4 h. The reddish brown solution was allowed to stand at room temperature and after slow evaporation the yellowish brown complex formed was filtered, washed with methanol and then ether and dried over P₄O₁₀ in vacuo.

Elemental Anal. Found (Calcd.) (%): C: 56.70 (56.12); H: 4.90 (4.89); N: 12.3 (12.59)

3.2.3.3. [VO(ASC)(dmbipy)]·3H₂O (3)

The complex 3 was synthesized by adding an aqueous solution of vanadyl sulfate (0.163 g, 1 mmol) to a hot methanolic solution of H₂ASC·H₂O (0.317 g, 1 mmol) and the base 4,4′-dimethyl-2,2′-bipyridine (0.156 g, 1 mmol) and refluxing the solution for 6 h. The complex formed was collected, washed with methanol and ether and dried over P₄O₁₀ in vacuo.

Elemental Anal. Found (Calcd.) (%): C: 55.22 (55.81); H: 4.90 (5.52); N: 11.30 (11.62)

3.2.4. Syntheses of VO(IV) complexes of 2-hydroxy-4-methoxybenzophenone-N⁴-phenylsemicarbazone

3.2.4.1. [VO(BSC)]₂·2H₂O (4)

A hot solution of H₂BSC (0.361 g, 1 mmol) in 20 ml of methanol was treated with an aqueous solution of vanadyl sulfate (0.163 g, 1 mmol) and was refluxed for 5 h. The resulting brown solution was allowed to stand at room temperature and after slow evaporation the yellow complex was separated out.
It was filtered, washed with methanol followed by ether and dried over $P_4O_{10}$ in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 55.01 (54.55); H: 4.56 (4.58); N: 9.03 (9.09)

\textbf{3.2.4.2. $[\text{VO(BSC)(phen)}] \cdot 2\text{H}_2\text{O}$ (5)}

Methanolic solutions of $H_2\text{BSC}$ (0.361 g, 1 mmol) and 1,10-phenanthroline (0.198 g, 1 mmol) and an aqueous solution of vanadyl sulfate (0.163 g, 1 mmol) were mixed and the resulting mixture was refluxed for 4 h. The dark yellow colored complex separated out was filtered, washed with methanol followed by ether and dried over $P_4O_{10}$ in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 61.78 (61.68); H: 4.80 (4.55); N: 10.75 (10.90)

\textbf{3.2.4.3. $[\text{VO(BSC)(dmbipy)}] \cdot 2\text{H}_2\text{O}$ (6)}

To a methanolic solution of $H_2\text{BSC}$ (0.361 g, 1 mmol), an aqueous solution of vanadyl sulfate (0.163 g, 1 mmol) was added. 4,4′-Dimethyl-2,2′-bipyridine (0.184 g, 1 mmol) was also added to it. The resulting mixture was refluxed for 4 h. The complex formed was green in color. It was filtered, washed with methanol, followed by ether and dried over $P_4O_{10}$ in \textit{vacuo}.

Elemental Anal. Found (Calcd.) (%): C: 61.82 (61.30); H: 4.73 (5.14); N: 10.53 (10.83)

\textbf{3.2.4.4. $[\text{VO(BSC)(pic)}] \cdot 0.5\text{H}_2\text{O}$ (7)}

A hot methanolic solution of $H_2\text{BSC}$ (0.361 g, 1 mmol) was mixed with 4-picoline (0.186 g, 1 mmol) and an aqueous solution of vanadyl sulfate (0.163 g, 1 mmol) was added to it. The resulting mixture was refluxed for 4 h.
The yellow product formed was filtered, washed with methanol followed by ether and dried over P4O10 in vacuo.

Elemental Anal. Found (Caled.) (%): C: 61.63 (61.37); H: 5.20 (4.77); N: 10.56 (10.60)

3.3. Results and discussion

The oxidovanadium(IV) complexes of N4-phenylsemicarbazones 1 and 4 were synthesized by refluxing methanolic solutions of the respective semicarbazone and vanadyl sulphate monohydrate in 1:1 ratio. The complexes 2, 3, 5, 6 and 7 were synthesized by refluxing the methanolic solution of semicarbazone, vanadyl sulfate monohydrate and heterocyclic bases in 1:1:1 ratio. Out of the seven complexes prepared complexes 1 and 4 are binuclear, while the remaining five are mononuclear metal chelates. All the complexes are yellow in color except 6, which is green in color. They are soluble in solvents like DMSO, DMF and CH3CN. In all the complexes synthesized the semicarbazones coordinated to the metal centre in the iminol form and act as dideprotonated tridentate semicarbazones. The synthesized compounds are characterized by the following physico-chemical methods.

3.3.1. Elemental analyses

Elemental (C, H, N) analyses of all complexes were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India and the values were given in Sections 3.2.3 and 3.2.4.

3.3.2. Molar conductivity

The conductivity measurements were made at 298 K with a systronic model 303 direct reading conductivity bridge in DMF (10⁻³ M) solutions and
the observed values were found to be less than 12 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) which is very much less than the value of 65-90 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) reported for a 1:1 electrolyte in the same solvent [7]. This confirmed the nonelectrolytic nature of the complexes.

### 3.3.3. Magnetic susceptibility

Magnetic moments of the complexes were calculated from the magnetic susceptibility measurements at room temperature. Complexes 1 and 4 showed \(\mu_{\text{eff}}\) 1.20 BM and 1.27 BM respectively and this subnormal values are due to the strong antiferromagnetic exchange, suggesting dimeric nature to these complexes [8]. All other complexes exhibited magnetic moments having slight deviations from the spin only value for a \(d^1\) system. All the complexes contain the VO\(^{2+}\) unit in which vanadium is in +4 oxidation state. The magnetic moment and molar conductivity values of the complexes are given in Table 3.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_m^*)</th>
<th>(\mu_{\text{eff}}) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[VO(ASC)](\cdot)2H(_2)O (1)</td>
<td>8</td>
<td>1.20</td>
</tr>
<tr>
<td>[VO(ASC)(bipy)](\cdot)2H(_2)O (2)</td>
<td>11</td>
<td>1.67</td>
</tr>
<tr>
<td>[VO(ASC)(dmbipy)](\cdot)3H(_2)O (3)</td>
<td>6.5</td>
<td>1.77</td>
</tr>
<tr>
<td>[VO(BSC)](\cdot)3H(_2)O (4)</td>
<td>2.8</td>
<td>1.27</td>
</tr>
<tr>
<td>[VO(BSC)(phen)](\cdot)2H(_2)O (5)</td>
<td>4.5</td>
<td>1.65</td>
</tr>
<tr>
<td>[VO(BSC)(dmbipy)](\cdot)2H(_2)O (6)</td>
<td>3.0</td>
<td>1.74</td>
</tr>
<tr>
<td>[VO(BSC)(pic)](\cdot)0.5H(_2)O (7)</td>
<td>9</td>
<td>1.78</td>
</tr>
</tbody>
</table>

\(^*\)Molar conductivity (in mho cm\(^2\) mol\(^{-1}\)) taken in 10\(^{-3}\) M DMF solution.
3.3.4. Infrared spectra

The IR spectra of the seven vanadium complexes were recorded in the 4000-400 cm\(^{-1}\) range with KBr pellets. The shift of characteristic IR bands of the complexes from the metal free phenyl semicarbazones provide significant indications regarding the ligating behavior to the metal centre. By coordination, shifts of the \(\nu(C=N)\), \(\nu(C=O)\) and the phenolic \(\nu(C-O)\) bands were observed for the complexes. They are consistent with the tridentate coordination of the phenyl semicarbazones through the enolic oxygen atom, the azomethine nitrogen atom and the phenolic oxygen atom [9]. Some IR spectra are shown in Figs. 3.1-3.3.

The bands at 3295 and 3145 cm\(^{-1}\) due to \(\nu(N^2H)\), 1692 and 1662 cm\(^{-1}\) due to \(\nu(C=O)\) for the semicarbazones \(H_2ASC\cdot H_2O\) and \(H_2BSC\) respectively disappeared on complexation indicating the involvement of the carbonyl oxygen in bonding as enolate form. The presence of a new band in the region 1540-1571 cm\(^{-1}\) due to the newly formed \(\nu(C=N)\) bond confirms this statement. The shift of \(\nu(C=N)\) of the semicarbazones at 1619 and 1631 cm\(^{-1}\) to lower wavenumbers in the metal complexes in the region (1574-1615 cm\(^{-1}\)) indicates the coordination of azomethine nitrogen to the metal [10]. The positive shift of the characteristic ligand bands due to \(\nu(N-N)\) in the spectra of complexes in the range 1055-1109 cm\(^{-1}\) is owing to the increase in double bond character, counterbalancing the electron density via donation to the metal [11]. The azomethine nitrogen coordination is further evidenced by the presence of new bands in the range 415-440 cm\(^{-1}\) assignable to \(\nu(V-N)\) for the complexes [12]. The sharp bands at 3535 and 3316 cm\(^{-1}\) for \(H_2ASC\cdot H_2O\) and \(H_2BSC\) respectively assigned to the phenolic –OH groups disappeared and it gives evidence for the coordination in its deprotonated form [13]. This causes \(\nu(C-O)\) to shift to lower
frequencies and a new band in the range 510-550 cm\(^{-1}\), assigned to \(\nu(V-O)\) is found in complexes [14]. Furthermore, the compounds containing the vanadyl unit have a characteristic strong V=O stretching band. For these complexes a strong band is observed in the range 935-965 cm\(^{-1}\) due to terminal V=O stretching and this is close to the usual range (960 \(\pm\) 50 cm\(^{-1}\)) observed for the majority of oxidovanadium (IV) complexes [15]. In addition to this a prominent band is observed at \(ca.\) 896 and at 846 cm\(^{-1}\) for the binuclear complexes 1 and 4 respectively due to the V–O–V bridge vibrations [16,17]. Since IR spectra are rich with bands tentative assignments of vibrational bands were made and are listed in Table 3.2.

Fig. 3.1. IR spectrum of [VO(ASC)]\(_2\)2H\(_2\)O (1).
Fig. 3.2. IR spectrum of [VO(BSC)(phen)]·2H₂O (5).

Fig. 3.3. IR spectrum of [VO(BSC)(pic)]·0.5H₂O (7).
### Table 3.2 Selected IR bands (cm\(^{-1}\)) with tentative assignments of VO(IV) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(\text{C=O}))</th>
<th>(v(\text{C=N}))</th>
<th>(v(\text{C=N})^a)</th>
<th>(v(\text{N=N}))</th>
<th>(v(\text{C=O}))</th>
<th>(v(\text{N=H}))</th>
<th>(v(\text{V=O}))</th>
<th>(v(\text{V-O}))</th>
<th>(v(\text{V-N}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{ASC} \cdot \text{H}_2\text{O})</td>
<td>1692</td>
<td>1619</td>
<td>----</td>
<td>1020</td>
<td>1270</td>
<td>3295</td>
<td>----</td>
<td>432</td>
<td></td>
</tr>
<tr>
<td>([\text{VO(ASC)}]_2 \cdot 2\text{H}_2\text{O} (1))</td>
<td>----</td>
<td>1591</td>
<td>1542</td>
<td>1055</td>
<td>1255</td>
<td>----</td>
<td>944</td>
<td>550</td>
<td>433</td>
</tr>
<tr>
<td>([\text{VO(ASC)(bipy)}]_2 \cdot 2\text{H}_2\text{O} (2))</td>
<td>----</td>
<td>1604</td>
<td>1530</td>
<td>1089</td>
<td>1263</td>
<td>----</td>
<td>965</td>
<td>545</td>
<td>439</td>
</tr>
<tr>
<td>([\text{VO(ASC)(dmbipy)}]_2 \cdot 3\text{H}_2\text{O} (3))</td>
<td>----</td>
<td>1574</td>
<td>1540</td>
<td>1109</td>
<td>1246</td>
<td>----</td>
<td>956</td>
<td>548</td>
<td>439</td>
</tr>
<tr>
<td>(\text{H}_2\text{BSC})</td>
<td>1662</td>
<td>1631</td>
<td>----</td>
<td>1059</td>
<td>1292</td>
<td>3145</td>
<td>----</td>
<td>415</td>
<td></td>
</tr>
<tr>
<td>([\text{VO(BSC)}]_2 \cdot 2\text{H}_2\text{O} (4))</td>
<td>----</td>
<td>1615</td>
<td>1539</td>
<td>1065</td>
<td>1226</td>
<td>----</td>
<td>932</td>
<td>510</td>
<td>418</td>
</tr>
<tr>
<td>([\text{VO(BSC)(phen)}]_2 \cdot 2\text{H}_2\text{O} (5))</td>
<td>----</td>
<td>1598</td>
<td>1563</td>
<td>1082</td>
<td>1245</td>
<td>----</td>
<td>962</td>
<td>514</td>
<td>418</td>
</tr>
<tr>
<td>([\text{VO(BSC)(dmbipy)}]_2 \cdot 2\text{H}_2\text{O} (6))</td>
<td>----</td>
<td>1602</td>
<td>1566</td>
<td>1090</td>
<td>1244</td>
<td>----</td>
<td>953</td>
<td>518</td>
<td>422</td>
</tr>
<tr>
<td>([\text{VO(BSC)(pic)}]_2 \cdot 0.5\text{H}_2\text{O} (7))</td>
<td>----</td>
<td>1609</td>
<td>1571</td>
<td>1065</td>
<td>1210</td>
<td>----</td>
<td>935</td>
<td>515</td>
<td>429</td>
</tr>
</tbody>
</table>

*a* Newly formed C=N
3.3.5. Electronic spectra

The electronic spectral bands of H₂ASC and H₂BSC and their vanadyl complexes are presented in Table 3.3. For complexes 1, 3, 4, 5 and 7 spectra were recorded in acetonitrile solutions and for complexes 2 and 6 in DMF solutions. The bands in the range 41750-31330 cm⁻¹ attributed to the n-π* and π-π* transitions for semicarbazones suffered some shift upon complexation and they are observed in between 31050-44230 cm⁻¹. The high energy bands in the region 27630-24750 cm⁻¹ are attributed to ligand to metal charge transfer (LMCT) transitions and their broadness can be explained due to the combination of O→V and N→V LMCT transitions [18]. The UV spectra of all the complexes are given in Figs. 3.4-3.7, along with the spectra of corresponding semicarbazones.

![UV spectra of H₂ASC, [VO(ASC)]₂, and [VO(ASC)(dmbipy)].](image-url)
### Table 3.3. Electronic spectral assignments (cm\(^{-1}\)) of N\(^4\)-phenylsemicarbazones and their VO(IV) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Intraligand transitions</th>
<th>LMCT</th>
<th>d-d</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)ASC</td>
<td>CH(_3)CN</td>
<td>31780, 34540, 35600(sh), 41750</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>H(_2)ASC</td>
<td>DMF</td>
<td>31590, 34250, 35300</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[VO(ASC)](_2)(2)H(_2)O (1)</td>
<td>CH(_3)CN</td>
<td>31050(sh), 34080(sh), 35670, 41610</td>
<td>27630</td>
<td>18600</td>
</tr>
<tr>
<td>[VO(ASC)(bipy)](2)H(_2)O (2)</td>
<td>DMF</td>
<td>33610(sh), 34550(sh), 37220</td>
<td>26790</td>
<td>----</td>
</tr>
<tr>
<td>[VO(ASC)(dmbipy)](3)H(_2)O (3)</td>
<td>CH(_3)CN</td>
<td>32260(sh), 34270, 35770(sh), 41380</td>
<td>26740</td>
<td>16280</td>
</tr>
<tr>
<td>H(_2)BSC</td>
<td>CH(_3)CN</td>
<td>31330, 33820, 35030, 41680</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>H(_2)BSC</td>
<td>DMF</td>
<td>31030, 32070 (sh), 33610, 34890</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[VO(BSC)](_2)(2)H(_2)O (4)</td>
<td>CH(_3)CN</td>
<td>31780(sh), 32310(sh), 34300, 41180</td>
<td>26810</td>
<td>17550</td>
</tr>
<tr>
<td>[VO(BSC)(phen)](2)H(_2)O (5)</td>
<td>CH(_3)CN</td>
<td>31100(sh), 34230(sh), 37050, 44230</td>
<td>24750</td>
<td>18800</td>
</tr>
<tr>
<td>[VO(BSC)(dmbipy)](2)H(_2)O (6)</td>
<td>DMF</td>
<td>31080, 33640, 34870, 37810</td>
<td>25840</td>
<td>----</td>
</tr>
<tr>
<td>[VO(BSC)(pic)](0.5)H(_2)O (7)</td>
<td>CH(_3)CN</td>
<td>31430, 33860, 34950(sh), 40780</td>
<td>25780</td>
<td>----</td>
</tr>
</tbody>
</table>

sh = shoulder
Fig. 3.5. UV spectra of H$_2$ASC and [VO(ASC)(bipy)].

Fig. 3.6. UV spectra of H$_2$BSC, [VO(BSC)]$_2$, [VO(BSC)(phen)] and [VO(BSC)(pic)].
Ballhausen and Gray (BG scheme) have provided a convenient energy level scheme for VO(IV) type complexes. In general most of the oxidovanadium complexes show three low intensity bands in the 12000-24000 cm⁻¹ range. In the visible region, with various semicarbazones 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, assigned to \( ^2E \leftarrow ^2B_2 (\nu_1) \) \((d_{xy} \rightarrow d_{xz}, d_{yz})\), \(^2B_1 \leftarrow ^2B_2 (\nu_2) \) \((d_{xy} \rightarrow d_{x^2-y^2})\), \(^2A_1 \leftarrow ^2B_2 (\nu_3) \) \((d_{xy} \rightarrow d_{z^2})\) [19]. Since the \(^2E\) and \(^2B_1\) levels are very close in energy and may cross and result a weak broad band. In our present investigation complexes 1, 4 and 5 showed two weak \(d\)-\(d\) bands, while in compound 3 two distinct \(d\)-\(d\) bands due to \(\nu_1\) and \(\nu_2\) are observed. Generally the third band is not observed and is thought to be buried beneath the low energy tail of the much more intense charge transfer bands [20].

The two bands at 11600 and 18600 cm⁻¹ for the complex 1 are due to the \(\nu_1\) and \(\nu_2\) transitions, while in 4 these transitions are observed at 12500 and
Chapter 3

17550 cm\(^{-1}\) respectively. In compound 3 the distinct energy bands at 12250 and 16280 cm\(^{-1}\) are corresponding to \(\nu_1\) and \(\nu_2\) transitions. In complex 5 these \(d-d\) bands are at \textit{ca.} 18800 and 12000 cm\(^{-1}\) [21]. In all other complexes the expected \(d-d\) bands are not observed and are probably obscured by the intense LMCT absorptions. The observed electronic spectra of the complexes in DMF, in the region 22000-11000 cm\(^{-1}\) are presented in Figs. 3.8.1-3.8.4.

Fig. 3.8.1. [VO(ASC)]\(_2\)  
Fig. 3.8.2. [VO(ASC)(dmbipy)]  
Fig. 3.8.3. [VO(BSC)]\(_2\)  
Fig. 3.8.4. [VO(BSC)(phen)]  

Fig. 3.8. Visible spectra of VO(IV) complexes.
3.3.6. Electron paramagnetic resonance spectra

Electron paramagnetic resonance is a branch of absorption spectroscopy in which radiation of microwave frequency is absorbed by a molecule or ion having unpaired electron(s). Thus it is a convenient and effective way to probe the electronic structure of paramagnetic molecules.

The oxidation state of the central vanadium atom in the complexes was confirmed by the measurements of EPR spectroscopy. In vanadyl complexes vanadium is in +4 oxidation state with $d^1$ configuration and they are EPR active. Complexes containing the VO$_2^+$ unit in which vanadium is in +5 oxidation state with $d^0$ configuration are EPR silent. All seven complexes synthesized were EPR active and contain VO$_2^+$ unit. For the case of vanadium(IV) the nuclear spin $I = 7/2$ and eight and fifteen hyperfine lines are expected for mononuclear and binuclear complexes respectively, separated by the hyperfine coupling constant, $A$.

EPR spectra of all the oxidovanadium complexes were recorded in polycrystalline state at 298 K and in DMF solution at 77 K using TCNE as the standard with 100 kHz modulation frequency, modulation amplitude 1 G and 9.4 GHz microwave frequency. The spectral parameters are summarized in Table 3.4. The EPR spectra of complexes (2-5) in the solid state at 298 K are isotropic in nature and hence only one $g$ value, arising due to dipolar interactions and enhanced spin-lattice relaxation. Compounds 1, 6 and 7 gave axial spectra in the polycrystalline state in which that of 7 is poorly resolved and difficult to interpret. $A_{||}$ complexes in DMF solution at 77 K displayed well resolved axial anisotropy with two sets of eight line pattern with $g_{||} < g_{\perp}$ and $A_{||} > A_{\perp}$ relationship, characteristic of an axially compressed
$d_{xy}^1$ configuration [22,23]. The absence of any ligand nitrogen superhyperfine lines on the vanadium line is an explicit indication of the sole electron lying in the $d_{xy}$ orbital $^2B_2$ ground state, localized on metal, thus excluding the possibility of its direct interaction with the semicarbazones [24,25].

Some of the EPR spectra are simulated and the experimental and simulated best fits are presented. The spectrum of the compound 1 is axial both in polycrystalline state at 298 K and in frozen DMF at 77 K. The spectrum in polycrystalline state is presented in Fig. 3.9.

![EPR spectrum](image)

**Fig. 3.9.** The EPR spectrum of [VO(ASC)]$_2$·2H$_2$O (1) in polycrystalline state at 298 K.

It exhibits well resolved axial anisotropy with two sets of eight line pattern, characteristic of an unpaired electron being coupled to the vanadium nuclear spin ($^{51}$V, $I$=7/2) with anisotropic hyperfine parameters $g_\parallel$ =1.962 and $g_\perp$ =1.980 and $A_\parallel$ = $169\times10^{-4}$ cm$^{-1}$, $A_\perp$ = $55\times10^{-4}$ cm$^{-1}$. In the case of
binuclear complexes, a half field signal is expected due to forbidden $\Delta M_s = \pm 2$ transition. But in this compound half field is absent, indicating that the spin-spin interaction of this compound is not so significant such that each unpaired electron virtually interact with only one vanadium centre [26]. The spectrum in frozen DMF at 77 K is presented in Fig. 3.10. Here also the spectrum displays well resolved axial anisotropy with $g_\parallel = 1.951$ and $g_\perp = 1.980$ and $A_\parallel = 164 \times 10^{-4}$ cm$^{-1}$, $A_\perp = 52 \times 10^{-4}$ cm$^{-1}$.

![EPR spectrum of [VO(ASC)]$_2$ in DMF at 77 K.](image)

The spectrum of compound 2 in polycrystalline state is isotropic with $g_{iso} = 1.977$ (Fig. 3.11) and in frozen DMF at 77 K it displays a well resolved axial anisotropy (Fig. 3.12) with two sets of eight-line pattern with anisotropic hyperfine parameters $g_\parallel = 1.914$ and $g_\perp = 1.975$ and $A_\parallel = 171 \times 10^{-4}$ cm$^{-1}$, $A_\perp = 68 \times 10^{-4}$ cm$^{-1}$.
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Fig. 3.11. EPR spectrum of [VO(ASC)(bipy)]·2H₂O (2) in polycrystalline state at 298 K.

Fig. 3.12. EPR spectrum of [VO(ASC)(bipy)] in DMF 77 K.

Compound 3 exhibits an isotropic spectrum, with $g_{\text{iso}} = 1.975$ (Fig. 3.13). The anisotropic EPR spectrum obtained for this compound in frozen DMF is depicted in Fig. 3.14. For this compound $g_{\parallel} = 1.945$ and $g_{\perp} = 1.979$, $A_{\parallel} = 152 \times 10^{-4}$ cm$^{-1}$ and $A_{\perp} = 52 \times 10^{-4}$ cm$^{-1}$. The $g_{\parallel} < g_{\perp}$ and $A_{\parallel} > A_{\perp}$ relationships are consistent
with an axially compressed octahedral geometry around the vanadium(IV) centre with the unpaired electron in the $d_{xy}$ orbital.

Fig. 3.13. EPR spectrum of $[\text{VO(ASC)(dmbipy)}] \cdot 3\text{H}_2\text{O} \ (3)$ in polycrystalline state at 298 K.

Fig. 3.14. EPR spectrum of $[\text{VO(ASC)(dmbipy)}]$ in DMF at 77 K.

The X-band EPR spectrum of compound 4 in polycrystalline state at 298 K exhibits an isotropic spectrum with $g_{\text{iso}}$ 1.976 (Fig. 3.15) and its spectrum in DMF is depicted in Fig. 3.16. Here also it exhibits well resolved
axial anisotropy with two sets of eight-line pattern with \( g_\parallel = 1.945 \) and \( g_\perp = 1.984 \), \( A_\parallel = 153 \times 10^{-4} \) cm\(^{-1}\) and \( A_\perp = 50 \times 10^{-4} \) cm\(^{-1}\). Though the compound 4 is a binuclear complex, the expected half field signal due to \( \Delta M_s = \pm 2 \) transition is not observed. It is probably due to insignificant spin-spin interaction [26].

Fig. 3.15. EPR spectrum of \([\text{VO(BSC)}]_2 \cdot 2\text{H}_2\text{O}\) (4) in polycrystalline state at 298 K.

Fig. 3.16. EPR spectrum of \([\text{VO(BSC)}]_2\) in DMF at 77 K.
The compound [VO(BSC)(phen)]·2H₂O (5) in polycrystalline state at 298 K displayed an isotropic spectrum with g_{iso} 1.978 (Fig. 3.17) and in DMF at 77 K an axial spectrum with two sets of g and A values is observed and is depicted in Fig. 3.18.

Fig. 3.17. EPR spectrum of [VO(BSC)(phen)]·2H₂O (5) in polycrystalline state at 298 K.

In polycrystalline state at 298 K, EPR spectrum of compound 6 is axial with $g_{||} = 1.945$ and $g_{\perp} = 1.987$ (Fig. 3.19). The spectrum shows two sets of eight-line pattern, but not well resolved.

Fig. 3.18. EPR spectrum of [VO(BSC)(phen)] in DMF at 77 K.
But a well resolved axial spectrum is obtained in frozen DMF at 77 K. The calculated anisotropic hyperfine parameters are as follows, $g \parallel = 1.955$ and $g \perp = 1.987$, $A \parallel = 147 \times 10^{-4}$ cm$^{-1}$ and $A \perp = 51 \times 10^{-4}$ cm$^{-1}$ (Fig. 3.20).
The EPR spectrum of the complex 7 in polycrystalline state is poorly resolved and was difficult to interpret. But the solution spectrum in frozen DMF shows well resolved axial anisotropy (Fig. 3.20) with hyperfine parameters $g_\parallel = 1.945$ and $g_\perp = 1.988$, $A_\parallel = 156 \times 10^{-4} \text{ cm}^{-1}$ and $A_\perp = 58 \times 10^{-4} \text{ cm}^{-1}$.

In all these complexes the anisotropic parameters are related with isotropic parameters by the equations, $A_{av} = \frac{1}{3} (A_\parallel + 2A_\perp)$ and $g_{av} = \frac{1}{3} (g_\parallel + 2g_\perp)$ [27]. The values obtained for $g_{av}$ are near to the $g_{iso}$ values obtained from the polycrystalline spectra, suggest that the molecules retain their structural identity in solution.

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 $\alpha^2$ and $\beta^2$ for the complexes by using the following equations:
\[ \alpha^2 = \frac{(2.0023 - g_\parallel)E_{d-d}}{8\lambda\beta^2} \]

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

where \( P = 128 \times 10^{-4} \text{ cm}^{-1} \), \( \lambda = 135 \text{ cm}^{-1} \) and \( E_{d-d} \) is the energy of \( d-d \) transition.

A less than unity value of \( \alpha^2 \) is an indication of increasing covalency, while that of \( \beta^2 \) does not found to vary significantly, from the most often observed value of 1.0 for most of the complexes. This is expected as the bonding ability of the ligand decreases with increasing distortion from the planar geometry [28]. EPR spectral data for VO(IV) complexes are presented in Table 3.4.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Polycrystalline state (298 K)</th>
<th>DMF solution (77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g_{\text{iso}}) (g_{|})</td>
<td>(g_{\perp}) (g_{\alpha})</td>
</tr>
<tr>
<td>[VO(ASC)](2)2H(2)O (1)</td>
<td>1.962/1.980</td>
<td>1.951</td>
</tr>
<tr>
<td></td>
<td>(g_{|}, g_{\perp})</td>
<td></td>
</tr>
<tr>
<td>[VO(ASC)(bipy)]2H(2)O (2)</td>
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<td>1.914</td>
</tr>
<tr>
<td>[VO(ASC)(dmbipy)]3H(2)O (3)</td>
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<td>1.945</td>
</tr>
<tr>
<td>[VO(BSC)23H(2)O (4)</td>
<td>1.976</td>
<td>1.945</td>
</tr>
<tr>
<td>[VO(BSC)(phen)]2H(2)O (5)</td>
<td>1.978</td>
<td>1.955</td>
</tr>
<tr>
<td>[VO(BSC)(dmbipy)]2H(2)O (6)</td>
<td>1.945/1.987</td>
<td>1.955</td>
</tr>
<tr>
<td></td>
<td>(g_{|}, g_{\perp})</td>
<td></td>
</tr>
<tr>
<td>[VO(BSC)(pic)]0.5H(2)O (7)</td>
<td>-----</td>
<td>1.945</td>
</tr>
</tbody>
</table>

* Expressed in units of cm\(^{-1}\) multiplied by a factor of 10\(^{16}\).*
3.3.7. Thermogravimetric analyses

Thermal methods are based upon the measurement of the dynamic relationship between temperature and some property of a system such as mass, heat of reaction or volume. In thermogravimetric analysis, the mass of sample is recorded continuously as its temperature is increased linearly from ambient to as high as 1200 °C. A plot of mass as a function of temperature (a thermogram) provides both qualitative and quantitative information.

The thermal behavior of all the complexes was investigated by TG-DTG measurements. Decomposition was carried out by heating the sample from 50 °C to 1000 °C with a heating rate of 10 °C/min. in an inert atmosphere of nitrogen. It was observed that the hydrated complexes lose water molecules of hydration in the first step, followed by decomposition of ligand molecules in the subsequent steps. Analyses show that the weight losses for lattice water are observed below 200 °C [29] and weight losses due to coordinated water molecules are in the range of 200-350 °C [30]. In all the complexes the weight loss is observed between 60-190 °C suggesting the presence of water molecules outside the coordination sphere. The weight loss data in % composition with temperature was recorded and some thermograms are presented in Figs. 3.22-3.24. The decomposition was not seen to be completed even upto 1000 °C and vanadium pentoxide has been inferred to be the ultimate pyrolysis product [31].

The TGA curve for the complex 5 displays the first stage of decomposition in the temperature range of 60-190 °C in two steps due to the loss of two molecules of water with 2.6% of the total weight of the complex (calcd. 2.97%). The weight losses due to the decomposition of ligand and the heterocyclic base, phenanthroline were found to take place over 250 °C.
In compound 6 a weight loss of 4.9% is observed at about 125 °C (calcd 5.5%) due to the loss of two molecules of water from its lattice. Further degradation of the complex takes place in three steps over 200 °C.

Fig. 3.23. Thermogram of the compound [VO(BSC)(dmbipy)]·2H₂O (6).
Fig. 3.24. Thermogram of the compound [VO(BSC)(pic)]·0.5H₂O (7).

In compound 7 the first stage of decomposition is observed in the range 90 -160 °C which is due to the loss of 0.5 molecule of water with 1.88% of the total weight of the complex (calcd. 1.70%) and it confirms the presence of lattice water. Beyond 200 °C a gradual weight loss occurs due to the thermal degradation of the ligand and heterocyclic base.

Based on the above physico-chemical methods, proposed structures for some compounds are given below. Water molecules are omitted. Out of the seven oxidovanadium complexes prepared two are dimers and the remaining five are mixed ligand metal chelates incorporating heterocyclic bases. In all the complexes semicarbazones exist in iminol form and act as dideprotonated ONO donor semicarbazones.
Syntheses and spectral characterization of oxidovanadium(IV) complexes of $N^4$-phenylsemicarbazones

$[\text{VO(ASC)}]_2\cdot2\text{H}_2\text{O} \ (1)$

$[\text{VO(ASC)(bipy)}]\cdot2\text{H}_2\text{O} \ (2)$

$[\text{VO(BSC)(phen)}]\cdot2\text{H}_2\text{O} \ (5)$
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