Chapter 3

SCHIFF BASE OXOVANADIUM (IV) COMPLEXES

Contents

3.1 Introduction
3.2 Materials and Methods
3.3 Synthesis, Results and Discussions
3.1 Introduction

Because of increasing biological and catalytic significance of vanadium, a lot of attention has been focussed on it, over the past decade. Vanadium constitutes 0.015% of earth’s crust which is nearer to abundance of zinc. Biochemical role of vanadium has now become a widely chosen topic of bioinorganic chemistry\(^1\). Though, the requirement of vanadium in mammals is at nano to picomolar level, however, its involvement in promotory and inhibitory biochemical processes\(^2-^5\) viz. enzymes-nitrogenases and haloperoxidases, phosphatase and ATPase inhibitor, lowering of hyperglycemia and hyperlipidemia etc., have enough driving force for intensive research with an approach to establish its role as a micronutrient in human beings.

The coordination chemistry of oxovanadium (IV) with multidentate ligands received attention of researchers due to its growing applications in catalysis\(^6-^7\) and therapeutics\(^8\). Vanadium has multiple biological roles as essentiality in traces, therapeutic effect in small doses and toxicity in excess. Vanadium containing compounds have their utility as insulin mimetic\(^9-^10\) and antiamoebic agent\(^11\). Accumulating evidences from experiments in past decade, suggest that vanadium could be considered as a representative of a new class of non-platinum metal anti-tumour agent\(^12\). The significant correlation between vanadate\(^9\) and phosphate ions at physiological pH in blood plasma has emerged as a point of interest\(^13-^14\).

The Schiff base ligands widely vary in their structural flexibility, electronic nature and the presence of additional donor atoms besides imino nitrogen.\(^15-^17\) The central metal in these complexes act as active sites and thereby successfully catalyse chemical reactions.\(^18\) The design and synthesis of metal chelated multidentate Schiff bases has received attention because of recent development of supra molecular chemistry, where ligand geometry and coordination propensity of the metal ions play a significant role. The Schiff base transition metal complexes are a family of attractive oxidation catalysts.
for a variety of organic substrates because of their cheap and easy synthesis and their chemical and thermal stability.\textsuperscript{19-22}

\textit{V(IV)}-\textit{V(IV)}/\textit{V(IV)}-\textit{V(III)} redox systems are very significant from reactivity view point\textsuperscript{23}. Vanadium compounds have been utilized in various homogenous/heterogeneous catalytic processes\textsuperscript{24-25}, where they exhibited good synthetic potential\textsuperscript{26}. Doped vanadium compounds have been used in synthesizing nanoparticles\textsuperscript{27}. The distortion in geometry of oxovanadium(IV) complexes from trigonal bipyramidal, square pyramidal to octahedral is also a subject of interest for structural studies\textsuperscript{28-36}

Considering the relevance and significance of the work, here the synthesis and characterization of ten novel oxovanadium(IV) Schiff base complexes have been done viz: [VO(cap)\textsubscript{2}], 4H\textsubscript{2}O (I); [VO(dap)\textsubscript{2}], 4H\textsubscript{2}O (II); [VO(hba)\textsubscript{2}], 3H\textsubscript{2}O (III); [VO(hbb)(H\textsubscript{2}O)\textsubscript{2}] (IV); [VO(hbp)]\textsubscript{2} H\textsubscript{2}O (V); [VO(caph)\textsubscript{2}], 2H\textsubscript{2}O (VI); [VO(daph)]. 3H\textsubscript{2}O (VII); [VO(dacp)]. 3H\textsubscript{2}O (VIII); [VO(dapy)].SO\textsubscript{4}. 4H\textsubscript{2}O (IX) and [VO(dcpa)].SO\textsubscript{4}. 3H\textsubscript{2}O (X), where Hcap = 4-chlorobenzylidene-2-amino-4-chlorophenol, Hdap = 4-dimethylaminobenzylidene-2-aminophenol, Hhba = 2-hydroxy-1-naphthylidene-4-bromoaniline, H\textsubscript{2}hbb = N,N' bis (2-hydroxy benzylidene) benzidine; H\textsubscript{2}hbp=N,N' bis (2-hydroxy benzylidene)-1,4-phenylenediamine, Hcaph = cinnamylidene-2-aminophenol, H\textsubscript{2}daph = diphenylglyoxalidene - α, α'-bis (2-aminophenol), H\textsubscript{2}dacp = diphenylgly-oxalidene - α, α'-bis (2-amino-4-chlorophenol), dap = diphenylglyoxalidene-α, α'bis (2-aminopyridine) and dcp = diphenylglyoxalidene - α, α'-4-chloro-1,3-phenylenediamine.

### 3.2 Materials and Methods

Oxovanadium (IV) sulphate pentahydradate, 4-chlorobenzaldehyde, 4-dimethylaminobenzaldehyde, 2-hydroxy-1-naphthaldehyde, salicylaldehyde, cinnamaldehyde, diphenylglyoxal, 2-amino-4-chlorophenol, 2-aminophenol, 4-bromoaniline, benzidine, 1,4-phenylenediamine, 1,3-phenylenediamine and 2-aminopyridine were obtained from Loba chemie (India), BDH, CDH and Fluka. All the chemicals and solvents were of A. R. grade.
Elemental analyses were carried out using a Heraeus Elemental Analyzer and the FAB mass spectra were recorded at room temperature on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas (accelerating voltage 10 kV) at SAIF, CDRI, Lucknow. The complexes were analysed for vanadium and sulphate contents by the standard methods. Magnetic measurement was made by Gouy's method. Electronic spectra (in MeOH) were recorded on Perkin Elmer Lambda-2B-spectrophotometer. Molar conductance ($10^3 M$ in Methanol) was measured on Elico-CM82 -conductivity bridge at room temperature. FT-IR spectra (in KBr disc) were recorded on Perkin Elmer RX-I spectrophotometer and X-ray diffraction powder diffractogram (Cu$\alpha$-1.5406Å) were recorded at SAIF, Panjab university Chandigarh. X-band EPR spectra were recorded at room temperature in a Varian E-112 spectrophotometer using TCNE (g = 2.0027) as the standard at SAIF, IIT Mumbai. The solid state AC-electrical conductivity have been measured by impedance spectroscopic method using HIOKI 3532-50 LCR Hitester at room temperature.

3.3 Synthesis, Results and Discussion

(A) Oxovanadium (IV) complexes with the schiff bases viz. 4-chlorobenzylidene-2-amino-4-chlorophenol(cap),4-dimethy minobenzylidene-2-aminophenol (dap) and 2-hydroxy-1-napht- hylidene-4-bromoaniline (hba)

Synthesis of schiff bases (ligands)

The three Schiff bases (Hcap, Hdap and Hhba) have been synthesized by adding the methanolic solution of 4-Chlorobenzaldehyde/4-dimethylaminobenzaldehyde/2-hydroxy-1-naphthaldehyde (0.01 mole) with methanolic solution of 2-amino-4-chlorophenol/2-aminophenol /4-bromoaniline (0.01 mole) in equimolar ratio. The reaction mixture was then refluxed on a waterbath for about 5-6 hours. The condensation product was filtered thoroughly washed with ethanol and ether, re-crystallized and dried in vacuo. The purity of the synthesized compounds was monitored by TLC using silica gel (yield % : 58-70%).
Structure of Schiff bases

[Chemical structures of Hcap, Hdap, and Hhba]

Preparation of Oxovanadium(IV) complexes

The VO(IV)-complexes have been prepared by mixing the methanolic solution of VOSO₄.5H₂O (0.01 mole) to the methanolic solution of Schiff bases (Hcap/Hdap/Hhba) (0.02 mole) in 1:2 molar ratio. The resulting mixture was refluxed on water bath for 7-8 hours. A coloured product appeared on standing and cooling the above solution. The complex was filtered, washed with ether and dried under reduced pressure over anhydrous CaCl₂ in a dessicator. It was further dried in an electric oven at 50-70°C.

Results and Discussion

All the metal chelates are coloured solids, stable towards air and moisture, decompose at high temperature and more or less soluble in common organic solvents. The analytical data of the complexes are consistent with proposed molecular formulae (Table 1A). All the metal chelates have 1:2 (metal : ligand) stoichiometry. Low molar conductance values of the complexes in methanol (10⁻³ M) suggest their non-electrolytic nature. All the complexes have a general composition [ML₂]. x H₂O.
Table-1A: Analytical and physical data of Oxovanadium(IV) Schiff base complexes

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compounds (Mol. Formula)</th>
<th>Mol. Wt.</th>
<th>Colour</th>
<th>Yield</th>
<th>M.P./Dec. (°C)</th>
<th>Found (Cal.) %</th>
<th>$\lambda_{m}$ S cm$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-I</td>
<td>$C_{13}H_8NCl_2O$ (Hcaph)</td>
<td>266</td>
<td>Light brown</td>
<td>60</td>
<td>240</td>
<td>58.12 (58.64)</td>
<td>3.17 (3.38) 5.15 (5.26)</td>
</tr>
<tr>
<td>I</td>
<td>[VO($C_{13}H_8NCl_2O$)$_2$].4H$_2$O</td>
<td>669</td>
<td>Black</td>
<td>80</td>
<td>310</td>
<td>46.72 (46.50)</td>
<td>3.62 (3.58) 4.15 (4.17)</td>
</tr>
<tr>
<td>SB-II</td>
<td>$C_{15}H_{16}N_2O$ (Hdap)</td>
<td>240</td>
<td>Dark brown</td>
<td>70</td>
<td>250</td>
<td>75.18 (75.00)</td>
<td>6.50 (6.66) 11.58 (11.66)</td>
</tr>
<tr>
<td>II</td>
<td>[VO($C_{15}H_{13}N_2O$)$_2$].4H$_2$O</td>
<td>617</td>
<td>Black</td>
<td>65</td>
<td>&gt;320</td>
<td>54.52 (54.13)</td>
<td>5.82 (5.71) 8.38 (8.42)</td>
</tr>
<tr>
<td>SB-III</td>
<td>$C_{17}H_{12}NBrO$ (Hhba)</td>
<td>326</td>
<td>Yellow</td>
<td>58</td>
<td>255</td>
<td>62.16 (62.57)</td>
<td>3.51 (3.68) 4.21 (4.29)</td>
</tr>
<tr>
<td>III</td>
<td>[VO($C_{17}H_{11}NBrO$)$_2$].3H$_2$O</td>
<td>771</td>
<td>Yellowish green</td>
<td>70</td>
<td>&gt;320</td>
<td>52.62 (52.78)</td>
<td>4.22 (4.16) 3.59 (3.62)</td>
</tr>
</tbody>
</table>
FAB mass

The FAB mass spectrum of \([\text{VO(hba)}_2]\) \(3\text{H}_2\text{O}\) complex has been studied as one of the representative case. The peaks of appreciable intensity have been observed at m/z values 766, 714, 391, 326 and 107 suggesting the fragmentation pattern. The m/z value 766 corresponds to nearest composition \(\text{VOL}_2.3\text{H}_2\text{O}\); 714 to \(\text{VOL}_2\), 391 to \(\text{VOL}\); 326 to ligand alone and 107 to VO with chelated O & N ligand moiety. This further indicates that oxovanadium (IV) at the center of the complex is coordinated with two units of anionic bidentate Schiff base ligand and the resulting complex is monomeric in nature\(^{39}\) (Fig. 3A.1).

Scheme-1 : FAB mass Fragmentation Pattern of Complex III,obs. (cal.)m/z values

\[
\begin{align*}
[\text{VO(hba)}_2].3\text{H}_2\text{O} & \rightarrow [\text{VO(hba)}_2] \rightarrow [\text{VO(hba)}] \rightarrow \text{VO-some chelated O and N ligand moiety} \\
766 (771) & \rightarrow 714 (717) \rightarrow 391 (391) \rightarrow 107 (99)
\end{align*}
\]

Reactivity

The solution of complexes was made in methanol (99%) to check the reactivity and substitution behaviour against ammine, chloro, aquo, thiocyanato and hydroxo ligands. Reaction was monitored by observing change in colour or precipitation.\(^{40}\)

Reaction with dilute aqueous \(\text{NH}_3\) : VO-cap complex does not react with dil aq. ammonia on keeping for 1 h, at room temperature but VO-dap and VO-hba complexes react slowly. All the three complexes react poorly on heating.

Reaction with dilute aqueous \(\text{HCl}\) : VO-dap and VO-hba complexes do not react with dil. HCl, even on retaining for 1 hr. at room temperature but VO-cap complex reacts slowly under similar conditions. On heating, the complexes react appreciably.

Reaction with \(\text{H}_2\text{O}\) : VO-cap and VO-dap complexes react slowly while VO-hba complex reacts rapidly on addition of slight amount of water at room temperature. All the three complexes decompose on heating with water.
Reaction with dilute aqueous KSCN: All the three complexes react slowly on keeping for an hour at room temperature; however, all the three complexes react to sufficient extent on heating.

Reaction with dilute aqueous NaOH: VO-cap complex reacts slowly but VO-dap and VO-hba complexes react fast at room temperature (1 h). All the three complexes react well on heating.

Infrared Spectrum

A careful comparison of ligand and complex spectra resulted following information regarding various groups\(^{41}\) (Table-2A). The IR spectra of Schiff base ligands (Hcap, Hdap & Hhba) give medium intensity band at about 1620 ± 15 due to \(\nu_{C-N}\) (azomethine) group. This band shifts down by 30-50 cm\(^{-1}\) in complexes, suggesting coordination through azomethine nitrogen\(^{16}\). A strong band in ligand spectrum at 1370 ± 20 cm\(^{-1}\) due to phenolic -OH (deformation) has been found absent in complexes. This suggests deprotonation of phenolic -OH. The chelation of phenolic oxygen is supported by upward shift of \(\nu_{C-O}\) (phenolic; 1260 ± 20 cm\(^{-1}\)) in complexes. The appearance of broad band around 3200-3400 cm\(^{-1}\) in the spectra of complexes may be due to associated lattice water molecules. A characteristic non-ligand sharp band in the spectra of complexes at 980 – 985 cm\(^{-1}\), has been assigned to \(\nu_{V-O}\). Some new bands\(^{42}\) of low intensity in the region 400 – 550 cm\(^{-1}\) in the spectra of complexes have been attributed to \(\nu_{V-O}\) and \(\nu_{V-N}\) (Fig. 3A.2-3A.7).

Table 2A: Selected IR frequencies (cm\(^{-1}\)) of ligands and their VO (IV) complexes

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compounds (Abbr. Name)</th>
<th>(\nu_{(C=N)}) azomethine</th>
<th>(\nu_{(O-H)}) phenolic</th>
<th>(\nu_{(C-O)}) phenolic</th>
<th>(\nu_{(V=O)})</th>
<th>(\nu_{(V-O)})</th>
<th>(\nu_{(V-N)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-I</td>
<td>Hcap</td>
<td>1620</td>
<td>1375</td>
<td>1260</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>I</td>
<td>[VO(cap)(_2)] . 4H(_2)O</td>
<td>1590</td>
<td>-</td>
<td>1287</td>
<td>984</td>
<td>500</td>
<td>475</td>
</tr>
<tr>
<td>SB-II</td>
<td>Hdap</td>
<td>1615</td>
<td>1370</td>
<td>1265</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>[VO(dap)(_2)] . 4H(_2)O</td>
<td>1593</td>
<td>-</td>
<td>1290</td>
<td>985</td>
<td>510</td>
<td>490</td>
</tr>
<tr>
<td>SB-III</td>
<td>Hhba</td>
<td>1616</td>
<td>1385</td>
<td>1268</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III</td>
<td>[VO(hba)(_2)] . 3H(_2)O</td>
<td>1575</td>
<td>-</td>
<td>1292</td>
<td>981</td>
<td>514</td>
<td>493</td>
</tr>
</tbody>
</table>
Electronic Spectra and Magnetic Moment

Room temperature magnetic moments of the VO(IV)-complexes lie in range 1.70-1.76 BM. The values are well suited for oxovanadium (IV) -monomeric chelates with one unpaired electron. The electronic spectra (in methanol) of [VO(cap)_2], [VO(dap)_2] and [VO(hba)_2] complexes exhibit bands in the regions 13790-14285, 19100-20000 and 23150-24000 cm⁻¹, the transitions have been assigned to be due to \(^2\!B_2\!\rightarrow\!^2\!E\), \(^2\!B_2\!\rightarrow\!^2\!B_1\) and \(^2\!B_2\!\rightarrow\!^2\!A_1\), respectively (Table-3A). The geometry of these neutral five coordinated mononuclear complexes (I, II & III) can be described in terms of a trigonal bipyramid distorted towards a tetragonal pyramid or square pyramidal\(^{43-45}\) (Fig. 3A.8-3A.10).

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Complexes (Abbr. Name)</th>
<th>Transitions/Band (cm⁻¹)</th>
<th>(\mu_{eff}) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>[VO(cap)_2].4H₂O</td>
<td>(^2!B_2!\rightarrow!^2!E)</td>
<td>13790 19100 23150</td>
</tr>
<tr>
<td>II</td>
<td>[VO(dap)_2].4H₂O</td>
<td>(^2!B_2!\rightarrow!^2!B_1)</td>
<td>13950 19500 23250</td>
</tr>
<tr>
<td>III</td>
<td>[VO(hba)_2].3H₂O</td>
<td>(^2!B_2!\rightarrow!^2!A_1)</td>
<td>14285 20000 24000</td>
</tr>
</tbody>
</table>

Electron Spin Resonance

The X-band EPR spectra of oxovanadium (IV) \((d^1; ^{51}V, I = 7/2)\) complexes are not so resolved at room temperature to exhibit all the eight hyperfine lines. The calculated values of \(g_{ll}\), \(g_\perp\), \(g_{av}\) and \(\Delta g\) for all the three complexes have been given in Table-4A. Here \(g_{av} = 1/3 [2g_\perp + g_{ll}]\). The values are typical of the spectra displayed by square pyramidal VO(IV) complexes with one unpaired electron in an orbital of mostly \(d_{xy}\) character. The \(g\) average values determined from the spectra are nearer to spin only value; a slight variation may be accounted to spin-orbit coupling. In square pyramidal complexes with \(C_{4v}\) symmetry, the V=O bond is along \(z\) and the other four donor atoms (O₂N₂) are along the \(x, y\) axes so, an anisotropic EPR spectrum\(^{45-47}\) is expected, exhibiting two \(g\) (\(g_z = g_{ll} < g_\perp = g_x = g_y\)) (Fig 3A.11-3A.15).
Table 4A : ESR parameters of the VO (IV)-Schiff base complexes

| Comp. No. | Complexes                  | $g_{||}$ | $g_{\perp}$ | $g_{av}$ | $\Delta g$ |
|-----------|----------------------------|----------|-------------|----------|------------|
| I         | [VO (cap)$_2$.4H$_2$O]     | 1.8973   | 1.9783      | 1.9513   | 0.081      |
| II        | [VO(dap)$_2$.4H$_2$O]      | 1.8863   | 1.9813      | 1.9496   | 0.095      |
| III       | [VO (hba)$_2$.3H$_2$O]     | 1.9486   | 1.9783      | 1.9684   | 0.0297     |

X-Ray

X-ray powder diffractograms of [VO(cap)$_2$.4H$_2$O and [VO(dap)$_2$.4H$_2$O complexes were recorded using CuKα as source in the range 5.01 – 59.87° (2θ). The important X-ray diffraction data have been presented in the Table-5A & 6A. X-ray crystal system has been worked out by trial and error method$^{48}$, for finding the best fit between observed and calculated $\sin^2 \theta$ values. Both the complexes have crystallized in tetragonal system. Crystal data for [VO(cap)$_2$.4H$_2$O ; $a = b = 9.37$ Å, $c = 34.44$ Å, $V = 3027.82$ Å$^3$, $Z = 4$ Dobs. = 1.4717 g cm$^{-1}$, Dcal. = 1.5883 g cm$^{-1}$ and for [VO(dap)$_2$.4H$_2$O ; $a = b = 9.34$ Å, $c = 22.23$ Å, $V = 1940.32$ Å$^3$, $Z = 3$, Dobs. = 1.5890 g cm$^{-1}$, Dcal. = 1.4118 g cm$^{-1}$ . The calculated and experimental values of density of complex show good agreement and are within the experimental error limits.$^{49}$ (Fig. 3A.14-3A.15).

Thermal

The Table-7A gives account of thermal degradation behaviour of the complexes heated in muffle furnace for 30-35 minutes at four temperatures (100°; 300°, 400° and 600°C); the resulting weight was measured. The remaining weight at 100°C corresponds to loss of lattice water molecules from complexes. The weight measured after heating at 300°C indicates almost no change in weight of complexes suggesting them as appreciably thermally stable chelates. On heating at 400°C, the remaining weight corresponds to loss of parts of ligand moiety almost equal to one ligand. The weight of pyrolysis product after heating at 600°C correspond to vanadium-oxide (V$_2$O$_5$); at this temperature both the ligands degrade.
### Table 5A: X-ray (powder diffraction) data of [VO(cap)$_2$].4H$_2$O complex

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>d spacing</th>
<th>Relative Intensity (%)</th>
<th>sin$^2$θ</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Obs.</td>
<td>Cal.</td>
</tr>
<tr>
<td>1</td>
<td>9.1912</td>
<td>56.2</td>
<td>0.0070</td>
<td>0.0070</td>
</tr>
<tr>
<td>2</td>
<td>7.1843</td>
<td>54.2</td>
<td>0.0115</td>
<td>0.0115</td>
</tr>
<tr>
<td>3</td>
<td>6.3229</td>
<td>22.3</td>
<td>0.0148</td>
<td>0.0150</td>
</tr>
<tr>
<td>4</td>
<td>5.8491</td>
<td>40.8</td>
<td>0.0173</td>
<td>0.0175</td>
</tr>
<tr>
<td>5</td>
<td>5.5520</td>
<td>50.2</td>
<td>0.0192</td>
<td>0.0195</td>
</tr>
<tr>
<td>6</td>
<td>5.1962</td>
<td>32.3</td>
<td>0.0220</td>
<td>0.0220</td>
</tr>
<tr>
<td>7</td>
<td>4.8244</td>
<td>63.5</td>
<td>0.0255</td>
<td>0.0255</td>
</tr>
<tr>
<td>8</td>
<td>4.6035</td>
<td>43.7</td>
<td>0.0279</td>
<td>0.0280</td>
</tr>
<tr>
<td>9</td>
<td>4.2947</td>
<td>100</td>
<td>0.0321</td>
<td>0.0320</td>
</tr>
<tr>
<td>10</td>
<td>4.0046</td>
<td>47.9</td>
<td>0.0370</td>
<td>0.0370</td>
</tr>
<tr>
<td>11</td>
<td>3.7148</td>
<td>54.6</td>
<td>0.0430</td>
<td>0.0430</td>
</tr>
<tr>
<td>12</td>
<td>3.5730</td>
<td>63.3</td>
<td>0.0464</td>
<td>0.0465</td>
</tr>
<tr>
<td>13</td>
<td>3.3336</td>
<td>73.6</td>
<td>0.0534</td>
<td>0.0535</td>
</tr>
<tr>
<td>14</td>
<td>3.1986</td>
<td>44.6</td>
<td>0.0580</td>
<td>0.0580</td>
</tr>
<tr>
<td>15</td>
<td>3.0661</td>
<td>22.2</td>
<td>0.0631</td>
<td>0.0630</td>
</tr>
<tr>
<td>16</td>
<td>3.0569</td>
<td>49.2</td>
<td>0.0635</td>
<td>0.0635</td>
</tr>
<tr>
<td>17</td>
<td>3.0148</td>
<td>31.2</td>
<td>0.0676</td>
<td>0.0675</td>
</tr>
<tr>
<td>18</td>
<td>2.2237</td>
<td>15.4</td>
<td>0.1200</td>
<td>0.1200</td>
</tr>
</tbody>
</table>

*Hcap = 4-chlorobenzylidene-2-amino-4-chlorophenol*

Crystal system - Tetragonal

A = B = 0.0035, C = 0.0005

a = b = 9.37 Å, c = 34.44 Å

V = 3027.82 Å$^3$, Z = 4

Dobs. = 1.4700 g cm$^{-3}$, Dcal. = 1.5883 g cm$^{-3}$
### Table 6A: X-ray (powder diffraction) data of [VO(dap)₂]. 4H₂O Complex

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>d spacing</th>
<th>Relative Intensity (%)</th>
<th>( \sin^2 \theta ) Obs.</th>
<th>( \sin^2 \theta ) Cal.</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.3267</td>
<td>15.3</td>
<td>0.0068</td>
<td>0.0068</td>
<td>(100)</td>
</tr>
<tr>
<td>2</td>
<td>6.7477</td>
<td>74.1</td>
<td>0.0130</td>
<td>0.0136</td>
<td>(110)</td>
</tr>
<tr>
<td>3</td>
<td>6.3297</td>
<td>18.2</td>
<td>0.0148</td>
<td>0.0148</td>
<td>(111)</td>
</tr>
<tr>
<td>4</td>
<td>5.8511</td>
<td>58.6</td>
<td>0.0173</td>
<td>0.0176</td>
<td>(103)</td>
</tr>
<tr>
<td>5</td>
<td>5.5607</td>
<td>38.1</td>
<td>0.0191</td>
<td>0.0184</td>
<td>(112)</td>
</tr>
<tr>
<td>6</td>
<td>4.9350</td>
<td>50.8</td>
<td>0.0243</td>
<td>0.0244</td>
<td>(113)</td>
</tr>
<tr>
<td>7</td>
<td>4.7027</td>
<td>83.4</td>
<td>0.0268</td>
<td>0.0272</td>
<td>(200)</td>
</tr>
<tr>
<td>8</td>
<td>4.6047</td>
<td>78.7</td>
<td>0.0279</td>
<td>0.0284</td>
<td>(201)</td>
</tr>
<tr>
<td>9</td>
<td>4.2896</td>
<td>50.8</td>
<td>0.0322</td>
<td>0.0320</td>
<td>(202)</td>
</tr>
<tr>
<td>10</td>
<td>3.9450</td>
<td>77.1</td>
<td>0.0381</td>
<td>0.0388</td>
<td>(212)</td>
</tr>
<tr>
<td>11</td>
<td>3.6966</td>
<td>74.1</td>
<td>0.0434</td>
<td>0.0448</td>
<td>(213)</td>
</tr>
<tr>
<td>12</td>
<td>3.5794</td>
<td>100</td>
<td>0.0463</td>
<td>0.0464</td>
<td>(204)</td>
</tr>
<tr>
<td>13</td>
<td>3.2878</td>
<td>93.2</td>
<td>0.0548</td>
<td>0.0544</td>
<td>(220)</td>
</tr>
<tr>
<td>14</td>
<td>3.2242</td>
<td>65.4</td>
<td>0.0570</td>
<td>0.0556</td>
<td>(221)</td>
</tr>
<tr>
<td>15</td>
<td>3.1675</td>
<td>37.1</td>
<td>0.0591</td>
<td>0.0592</td>
<td>(222)</td>
</tr>
<tr>
<td>16</td>
<td>3.0765</td>
<td>47.2</td>
<td>0.0626</td>
<td>0.0624</td>
<td>(301)</td>
</tr>
<tr>
<td>17</td>
<td>2.9767</td>
<td>21.2</td>
<td>0.0667</td>
<td>0.0660</td>
<td>(302)</td>
</tr>
<tr>
<td>18</td>
<td>2.9267</td>
<td>25.4</td>
<td>0.0692</td>
<td>0.0692</td>
<td>(311)</td>
</tr>
<tr>
<td>19</td>
<td>2.2021</td>
<td>9.8</td>
<td>0.1223</td>
<td>0.1224</td>
<td>(330)</td>
</tr>
</tbody>
</table>

Hdap = 4-dimethylaminobenzylidene-2-aminophenol

Crystal system = Tetragonal

\[ a = b = 9.34 \, \text{Å}, \quad c = 22.23 \, \text{Å} \]

\[ V = 1940.32 \, \text{Å}^3, \quad Z = 3 \]

\[ \text{Dobs.} = 1.5890 \, \text{g cm}^{-3}, \quad \text{Dcal.} = 1.4118 \, \text{g cm}^{-3} \]
Table 7A: Composition and % weight obs. (cal.) (Based on heating)

<table>
<thead>
<tr>
<th>Complexes (Room temp., 35°C)</th>
<th>100-300°C*</th>
<th>400°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[VO(cap)₂].4H₂O 100 (100)</td>
<td>[VO(cap)₂]</td>
<td>VO-chelated ligand moiety</td>
<td>V₂O₅</td>
</tr>
<tr>
<td></td>
<td>88.12 (89.27)</td>
<td>53.64 (49.63)</td>
<td>16.21 (13.56)</td>
</tr>
<tr>
<td>[VO(dap)₂].4H₂O 100 (100)</td>
<td>[VO(dap)₂]</td>
<td>VO-chelated ligand moiety</td>
<td>V₂O₅</td>
</tr>
<tr>
<td></td>
<td>86.87 (88.37)</td>
<td>56.27 (49.60)</td>
<td>16.34 (14.70)</td>
</tr>
<tr>
<td>[VO(hba)₂].3H₂O 100 (100)</td>
<td>[VO(hba)₂]</td>
<td>VO-chelated ligand moiety</td>
<td>V₂O₅</td>
</tr>
<tr>
<td></td>
<td>91.27 (93.02)</td>
<td>58.37 (50.84)</td>
<td>15.54 (11.78)</td>
</tr>
</tbody>
</table>

*No change in weight

Solid State Conductivity

The solid state A.C. electrical conductivity of the synthesized complexes in compressed pellet form (3 tonn.cm⁻²) at room temperature (40°C) has been measured. The A.C. electrical conductivity value in the room temperature are as :

[VO(cap)₂].4H₂O = 1.62 x 10⁻⁴ S cm⁻¹;
[VO(dap)₂].4H₂O = 2.48 x 10⁻⁵ S cm⁻¹;
[VO(hba)₂].3H₂O = 6.83 x 10⁻⁴ S cm⁻¹

The values fall in semiconductor region⁴⁹⁻⁵⁰. The A.C. electrical conductivity of chelates follow the order:

[VO(hba)₂] 3H₂O > [VO(cap)₂] 4H₂O > [VO(dap)₂] 4H₂O.
Structure of Oxovanadium(IV)-Schiff base Complexes

I

\[
\begin{array}{c}
\text{Cl} \\
\text{H-C} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{V} \\
\text{N} \\
\text{C-H} \\
\text{Cl} \\
\text{Cl}
\end{array}
\]

\[.4\text{H}_2\text{O}\]

II

\[
\begin{array}{c}
\text{NMe}_2 \\
\text{H-C} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{V} \\
\text{N} \\
\text{C-H} \\
\text{NMe}_2
\end{array}
\]

\[.4\text{H}_2\text{O}\]

III

\[
\begin{array}{c}
\text{Br} \\
\text{H-C} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{V} \\
\text{N} \\
\text{C-H} \\
\text{Br}
\end{array}
\]

\[.3\text{H}_2\text{O}\]
Fig 3A.1: FAB mass spectrum of 2-hydroxy-1-naphthyldiene-4-bromoaniline (hba) Oxovanadium(IV) complex

Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.)
Fig. 3A. 3 (I) : Infrared spectrum of 4-chlorbenzylidene-2-amino-4-chlorophenol(cap) oxovanadium(IV) complex
Fig. 3A.4 (SB-II) : Infrared spectrum of 4-dimethylaminobenzylidene-2-aminophenol(Hdap) ligand
Fig. 3A.5 (II): Infrared spectrum of 4-dimethylaminobenzylidene-2-aminophenol(dap) oxovanadium (IV) complex
Fig. 3A.6 (SB-III): Infrared spectrum of 2-hydroxy-1-naphthylidene-4-bromoaniline (Hhba) ligand
Fig. 3A.7 (III) : Infrared spectrum of 2-hydrxy-1-naphthylidne-4-bromoaniline(hba) oxovanadium(IV) complex
Fig. 3A.8 (I): Electronic spectra of 4-chlorobenzylidene-2-amino-4-chlorophenol (cap) oxovanadium(IV) complex

Fig. 3A.9 (II): Electronic spectra of 4-dimethylamino benzylidene-2-amino phenol (dap) oxovanadium(IV) complex

Fig. 3A.10 (III): Electronic spectra of 2-hydroxy-1-naphthylidene-4-bromoaniline (hba) oxovanadium(IV) complex
Fig. 3A.11 (I): ESR spectra of 4-chlorobenzylidene-2-amino-4-chlorophenol (cap) oxovanadium complex

Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.)
Fig. 3A.12 (II) : E S R spectra of 4-dimethylaminobenzylidene-2-aminophenol (dap) oxovanadium(IV) complex
Fig. 3A.13 (III) : E S R spectra of 2-hydroxy-1-naphthylidene-4-bromoaniline (hba) oxovanadium(IV) complex

Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.)
Fig. 3A.14 (I): X-ray diffractogram of 4-chlorobenzylidene-2-amino-4-chlorophenol (cap) oxovanadium(IV) complex
Fig. 3A.15 (II) : X-ray diffractogram of 4-dimethylaminobenzylidene-2-aminophenol (dap) oxovanadium(IV) complex
(B) Complexes of Oxovanadium (IV) with Schiff bases viz. N,N' bis (2-hydroxy benzylidene) benzidine (hbb), N,N' bis 2- hydroxy benzylidene)-1,4-phenylenediamine (hbp) and cinnamylidene-2-aminophenol (caph)

Synthesis of Schiff bases (Ligands):

Two Schiff bases (H₂hbb and H₂hbp) have been synthesized by adding methanolic solution of salicylaldehyde (0.02 mole) with methanolic solution of benzidine/1,4-phenylenediamine (0.01 mole) in 2:1 molar ratio. The third Schiff base (Hcaph) has been synthesized by condensing cinnamaldehyde (0.01 mole) with 2-aminophenol (0.01 mole, methanolic solution). The reaction mixture was then refluxed on a waterbath for about 5-6 hours. The condensation product was filtered, thoroughly washed with ethanol and ether, re-crystallized with ethanol and dried under the reduced pressure over anhydrous CaCl₂. The purity of the synthesized compounds was monitored by TLC using silica gel (yield % : 60-70).
Preparation of Oxovanadium(IV) Schiff base complexes:

The VO(IV) (hbb and hbp) complexes have been prepared by mixing the methanolic solution of VOSO₄·5H₂O (0.01 mole) to the methanolic solution of Schiff bases (hbb and hbp) (0.01 mole) in equimolar ratio. The VO(IV)-caph complex has been synthesized by mixing methanolic solution of VOSO₄·5H₂O (0.01 mole) with Schiff base caph (0.02 mole) in 1:2 molar ratio. The resulting mixture was refluxed on waterbath for 7-8 hours. A coloured product appeared on standing and cooling the refluxate. The precipitated complex was filtered and washed repeatedly with ether. The complexes were recrystallized twice with ethanol, finally washed with diethyl ether and dried under reduced pressure over anhydrous CaCl₂ in a desiccator. The complexes were further dried in an electric oven at 50-70°C.

Results and Discussion

All the metal complexes are coloured solids, stable towards air and moisture at room temperature, decompose at high temperature and more or less soluble in common organic solvents. The analytical data of the complexes are consistent with proposed molecular formulae shown in Table-1B. The metal complexes exhibit 1:1 (VO-hbb), 2:2 (VO-hbp) and 1:2 (VO-caph) (metal : Schiff base ligand) stoichiometry. Low molar conductance values of the complexes in methanol (10⁻³ M) suggest their non-electrolytic nature³⁸.

FAB mass

The FAB mass spectra of [VO(hbb)(H₂O)₂] and [VO(hbp)]₂H₂O complexes have been studied. The peaks of appreciable intensity have been observed for [VO(hbb)(H₂O)₂] at m/z values 498, 482, 460, 391 and 106 which indicate the fragmentation pattern³⁹. The m/z value 498 corresponds to nearest composition [VO(hbb)(H₂O)₂]; while 482 to [VO(hbb)(H₂O)]; 460 to [VO(hbb)] and 391 to ligand (hbb) alone. The value 106 corresponds to VO with chelated O and N donors as ligand moiety. The m/z values for [VO(hbp)]₂H₂O appear at 778, 759, 391, 314 and 107. The m/z value 778 corresponds to the nearest dimeric composition [VO(hbp)]₂H₂O; 759 to [VO(hbp)]₂; 391 to monomeric [VO(hbp)]; 314 to ligand (hbp) alone and 107 to VO with chelated O and N donors of ligand moiety (Fig. 3B.1-3B.2).
### Table-2A: Analytical, physical and conductance data of Oxovanadium(IV) Schiff base complexes

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compounds (Mol. Formula)</th>
<th>Mol. Wt.</th>
<th>Colour</th>
<th>Yield</th>
<th>M.P./Dec. (°C)</th>
<th>Found (Cal.) %</th>
<th>$\lambda_m$ S cm$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>SB-IV</td>
<td>$C_{26}H_{20}N_2O_2$ (H$_2$hbb)</td>
<td>392</td>
<td>Cream</td>
<td>65</td>
<td>260</td>
<td>80.00 (79.59)</td>
<td>5.16 (5.10)</td>
</tr>
<tr>
<td>IV</td>
<td>[VO($C_{26}H_{18}N_2O_2$)(H$_2$O)$_2$]</td>
<td>493</td>
<td>Light brown</td>
<td>80</td>
<td>310</td>
<td>62.59 (63.03)</td>
<td>4.12 (4.44)</td>
</tr>
<tr>
<td>SB-V</td>
<td>$C_{20}H_{16}N_2O_2$ (H$_2$hbb)</td>
<td>316</td>
<td>Golden</td>
<td>70</td>
<td>245</td>
<td>76.12 (75.94)</td>
<td>5.00 (5.06)</td>
</tr>
<tr>
<td>V</td>
<td>[VO($C_{20}H_{14}N_2O_2$)$_2$.H$_2$O]</td>
<td>780</td>
<td>Black</td>
<td>85</td>
<td>290</td>
<td>60.45 (61.22)</td>
<td>3.49 (3.82)</td>
</tr>
<tr>
<td>SB-VI</td>
<td>$C_{15}H_{13}NO$ (Hcaph)</td>
<td>223</td>
<td>Brown</td>
<td>60</td>
<td>250</td>
<td>80.56 (80.71)</td>
<td>5.65 (5.82)</td>
</tr>
<tr>
<td>VI</td>
<td>[VO($C_{15}H_{12}NO$)$_2$.2H$_2$O]</td>
<td>547</td>
<td>Black</td>
<td>75</td>
<td>300</td>
<td>65.57 (66.12)</td>
<td>4.37 (4.52)</td>
</tr>
</tbody>
</table>

*Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.)*
FAB mass Fragmentation Pattern of Complexes IV & V, obs. (cal.) m/z value of fragments

**Scheme-1B**

\[
\begin{align*}
[\text{VO (hbb) (H}_2\text{O)}_2] & \\ 498 (495) & \xrightarrow{-\text{H}_2\text{O}} [\text{VO (hbb) (H}_2\text{O)}] & 482 (477) \\
\left[\text{VO-Some chelated} \right. & -\text{hbb} \\
\left. \text{ligand moiety} \right] & 106 (99) & \xrightarrow{-\text{H}_2\text{O}} [\text{VO (hbb)}] & 460 (459) \\
391 (392) & 
\end{align*}
\]

**Scheme-2B**

\[
\begin{align*}
[\text{VO (hbp)}]_2 \cdot \text{H}_2\text{O} & \\ 778 (784) & \xrightarrow{-\text{H}_2\text{O}} [\text{VO (hbp)}]_2 & 759 (766) \\
\left[\text{VO-Some chelated} \right. & -\text{hbp} \\
\left. \text{ligand moiety} \right] & 107 (113) & \xrightarrow{-\text{H}_2\text{O}} [\text{VO (hbp)}] & 391 (383) \\
314 (316) & 
\end{align*}
\]

**Reactivity**

The solution of complexes were made in methanol (99%) to check the reactivity and substitution behaviour against hydroxo, aquo, ammine, chloro and thiocyanato ligands. Reaction was monitored by observing change in color or precipitation.\(^\text{40}\)

*Reaction with dilute NH\(_3\) (aq.)*: VO-(hbb and hbp) complexes react very slowly on keeping for one hour at room temperature but VO-caph complex reacts fast. All the complexes react appreciably on heating the reactants indicating substitution.

*Reaction with dilute HCl*: VO-hbb complex does not react at room temperature while VO-hbp complex reacts rapidly. VO-caph complex react
very slowly on keeping the reactants mixed together for an hour at room temperature. All the complexes react well on heating the reaction mixture except VO-hbb complex.

Reaction with dilute NaOH: VO-(hbb and hbp) complexes react slowly while VO-caph complex reacts quickly at room temperature (kept for an hour). All three complexes react appreciably on heating.

Reaction with dilute KSCN: VO-(hbb and caph) complexes react rapidly but VO-hbp complex react slowly at room temperature. All of the complexes react well on heating.

Reaction with H₂O: VO-(hbb and hbp) complexes do not react with H₂O but VO-caph complex reacts slowly. On heating too, these complexes exhibit poor reactivity with water.

Infrared Spectrum

A careful comparison of the spectra of ligands and complexes resulted following information regarding coordination through various groups⁴¹. The IR spectra of Schiff base ligands (H₂hbb, H₂hbp and Hcaph) exhibit medium intensity band at 1620±15 cm⁻¹ due to νC-N (azomethine) group. This band shift to lower energy region by 30-50 cm⁻¹ in VO-hbp and VO-caph complexes (V&VI) suggesting chelation through azomethine nitrogen (except VO-hbb complex). The azomethine band did not shift in VO-hbb (IV) complex, ruling out its possibility of coordination. A strong band in ligand spectra at 1370±20 cm⁻¹ due to phenolic –OH has been found absent in complexes. This indicates the deprotonation of phenolic –OH on coordination with metal. The chelation of phenolic oxygen is supported by upward shift of ν(C-O) (phenolic;1263±15 cm⁻¹) in complexes. The appearance of broad band around 3200-3400 cm⁻¹ in the spectra of complexes (V&VI) has tentatively been assigned to associated water molecules. A medium intensity band in the IR spectrum of complex VO-hbb (IV) at 745 cm⁻¹, is assignable to rocking mode due to coordinated water molecules. A characteristic non-ligand sharp band at 974-985 cm⁻¹ in the
spectra of complexes is due to \( v_{\nu=O} \). Some new bands of weaker intensity in the region 400-550 cm\(^{-1}\) in complexes give inferences about V-O and V-N bonding.\(^2\) (Fig. 3B.3-3B.6).

**Table 2B : Selected I R frequencies (cm\(^{-1}\)) of ligands and their VO (IV) complexes**

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compounds (Abbrev. Name)</th>
<th>( v(C=\text{N}) ) azomethine</th>
<th>( v(OH) ) phenolic</th>
<th>( v(C-O) ) phenolic</th>
<th>( v(\text{V=O}) ) rocking</th>
<th>( v(\text{H}_2\text{O}) )</th>
<th>( v(\text{V}=\text{O}) )</th>
<th>( v(\text{V-N}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-4</td>
<td>H(_2)hbb</td>
<td>1618</td>
<td>1365</td>
<td>1281</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>[VO(hbb)(H(_2)O)(_2)]</td>
<td>1617</td>
<td>-</td>
<td>1290</td>
<td>979</td>
<td>745</td>
<td>521</td>
<td>490</td>
</tr>
<tr>
<td>SB-5</td>
<td>H(_2)hbp</td>
<td>1615</td>
<td>1362</td>
<td>1283</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>[VO(hbp)](_2).H(_2)O</td>
<td>1585</td>
<td>-</td>
<td>1299</td>
<td>975</td>
<td>-</td>
<td>500</td>
<td>475</td>
</tr>
<tr>
<td>SB-6</td>
<td>Hcaph</td>
<td>1622</td>
<td>1368</td>
<td>1280</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>[VO(caph)](_2).H(_2)O</td>
<td>1590</td>
<td>-</td>
<td>1297</td>
<td>977</td>
<td>-</td>
<td>515</td>
<td>495</td>
</tr>
</tbody>
</table>

**Cyclic Voltammetry**

The electrochemical behaviour\(^1\) of [VO(hbp)]\(_2\).H\(_2\)O complex has been studied by C V. The cyclic voltammogram (scan range 1000 to 1500 mV ) of H\(_2\)hbp ligand and their VO(IV) complex has been recorded and compared. The voltammogram of the H\(_2\)hbp ligand exhibit two well separable cathodic peaks with Ep = -750 mV and -1200 mV, may be due to presence of reducible two azomethine (C=N ) groups. The VO(IV)-hbp complex exhibit only one cathodic peak at Ep = -800 mV; this corresponds to one electron transfer process. The shift in peak potential and change in the peak pattern may be accounted to coordination of C=N group with oxovanadium(IV) ion. The electrode process is quasi-reversible. Thus the C.V.support the coordination of oxovanadium(IV) ion with ligand H\(_2\)hbp (Fig. 3B.7-3B.8).

**Electronic Spectra and Magnetic Moment**

Room temperature magnetic moment values of VO(IV)- complexes lie in the range 1.70-1.80 B.M. The values are suited for oxovanadium (IV) monomeric and dimeric complexes with one unpaired electron. The electronic spectra (in methanol) of [VO(hbb)(H\(_2\)O)\(_2\)], [VO(hbp)]\(_2\).H\(_2\)O and [VO(caph)]\(_2\).2H\(_2\)O complexes exhibit bands in regions : 13790-14285, 16806-
20000 and 23150-24000 cm\(^{-1}\); the transitions have been assigned to be due to \(^2\text{B}_2 \rightarrow ^2\text{E}, \ ^2\text{B}_2 \rightarrow ^2\text{B}_1\) and \(^2\text{B}_2 \rightarrow ^2\text{A}_1\) respectively (Table-3B). At least minimum two bands have been observed clearly in complexes. The geometry of these neutral five coordinated mononuclear and binuclear complexes (IV, V& VI) can be described in terms of a trigonal bipyramidal, distorted towards a tetragonal pyramidal or square pyramidal\(^{43-45}\) (Fig. 3B.9-3B.11).

Table 3B: Electronic spectral and magnetic moment data of VO (IV) complexes

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Complexes (Abbr. Name)</th>
<th>Transitions/Band (cm(^{-1}))</th>
<th>(\mu_{\text{eff}}) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>[VO(hbb)(H(_2)O)(_2)]</td>
<td>(^2\text{B}_2\rightarrow^2\text{E})</td>
<td>14285 19000 23550</td>
</tr>
<tr>
<td>V</td>
<td>[VO(hbp)](_2)H(_2)O</td>
<td>(^2\text{B}_2\rightarrow^2\text{B}_1)</td>
<td>14100 16806 24000</td>
</tr>
<tr>
<td>VI</td>
<td>[VO(caph)](_2)H(_2)O</td>
<td>(^2\text{B}_2\rightarrow^2\text{A}_1)</td>
<td>13790 20000 23150</td>
</tr>
</tbody>
</table>

Electron Spin Resonance

The X-band EPR spectra\(^{45-47}\) of oxovanadium (IV) (d\(^1\), \(^{51}\)V.I = 7/2) complexes are not so resolved at room temperature to exhibit all the eight hyperfine lines. The calculated values of \(g_{\parallel}, \ g_{\perp}, \ g_{\text{av}}\) and \(\Delta g\) for complexes IV & V are given in Table 4B. Here \(g_{\text{av}} = 1/3[2g_{\perp}+g_{\parallel}]\). The values are typical of the spectra displayed by tcp or sp VO(IV) complexes with the one unpaired electron in an orbital of mostly \(d_{xy}\) character. The \(g_{\text{av}}\) values determined from the spectra are nearer to spin only; a slight variation may be accounted to spin-orbital coupling. In square pyramidal complexes with \(C_4\) symmetry, the V=O bond is along z and the other four donor atoms (O\(_4\) or O\(_2\)N\(_2\)) are along the x,y axes. An anisotropic EPR spectrum is expected, exhibiting two g values (\(g_z = g_{\parallel} < g_{\perp} = g_x = g_y\)) (Fig. 3B.13-3B.14).

Table 4B: ESR parameter of VO(IV)-Schiff base complexes

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Complexes</th>
<th>(g_{\parallel})</th>
<th>(g_{\perp})</th>
<th>(g_{\text{av}})</th>
<th>(\Delta g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>[VO(hbb)(H(_2)O)(_2)]</td>
<td>1.9198</td>
<td>1.9753</td>
<td>1.9568</td>
<td>0.0555</td>
</tr>
<tr>
<td>V</td>
<td>[VO(hbp)](_2)H(_2)O</td>
<td>1.8754</td>
<td>1.9783</td>
<td>1.9440</td>
<td>0.1029</td>
</tr>
</tbody>
</table>
Thermal

The thermal degradation behaviour of the complexes have been noted on heating (30 minutes) in muffle furnace at four temperatures (100°, 290°, 400° and 600°C) in air. The weight after each heating was measured. The percentage remaining weight and approximate composition corresponding to each temperature are given in Table 5B. The complexes are stable (w.r.t. Schiff base) chelate in general upto 290°C; above this temperature some part of the chelated Schiff base starts decomposing. The ultimate pyrolysis product (600°C) in oxygenated atmosphere for all the cases is vanadium pentaoxide.\textsuperscript{51}

Table-5 B : Composition and % weight obs. (cal.) ( Based on heating)

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Complexes (Room Temp.)</th>
<th>100°C</th>
<th>290°C</th>
<th>400°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>[VO(C\textsubscript{2}H\textsubscript{3}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]\textsubscript{2}</td>
<td>98.45(100)</td>
<td>89.21(92.72)</td>
<td>VO-chelated ligand moiety 50.49(56.36)</td>
<td>V\textsubscript{2}O\textsubscript{5} 17.75(18.38)</td>
</tr>
<tr>
<td>V</td>
<td>[VO(C\textsubscript{2}H\textsubscript{3}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}]\textsubscript{2}H\textsubscript{2}O</td>
<td>95.23(97.70)</td>
<td>94.21(97.70)</td>
<td>VO-chelated ligand moiety 68.63 (71.17)</td>
<td>V\textsubscript{2}O\textsubscript{2} 22.52 (23.21)</td>
</tr>
<tr>
<td>VI</td>
<td>[VO(C\textsubscript{2}H\textsubscript{3}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}]2H\textsubscript{2}O</td>
<td>91.26 (93.44)</td>
<td>90.27 (93.44)</td>
<td>VO-chelated ligand moiety 50.56 (52.82)</td>
<td>V\textsubscript{2}O\textsubscript{3} 15.26 (16.57)</td>
</tr>
</tbody>
</table>

Solid State Electrical Conductivity

The solid state AC electrical conductivity of the synthesized complexes in compressed pellet form (3 ton cm\textsuperscript{-2}) have been measured at room temperature (35°C). The AC electrical conductivity value in the room temperature are as :

\[
[\text{VO(hbb)}(\text{H}_2\text{O})_2] = 5.23 \times 10^{-4} \text{ S cm}^{-1}
\]

\[
[\text{VO(hbp)}]_2 \cdot \text{H}_2\text{O} = 8.26 \times 10^{-4} \text{ S cm}^{-1}
\]

\[
[\text{VO(caph)}]_2 \cdot 2\text{H}_2\text{O} = 1.49 \times 10^{-4} \text{ S cm}^{-1}
\]

The values fall in semiconductor range. The AC electrical conductivity of chelates follow the order.\textsuperscript{49-51} :

\[
[\text{VO(hbp)}]_2 \cdot \text{H}_2\text{O} > [\text{VO(hbb)} (\text{H}_2\text{O})_2] > [\text{VO(caph)}]_2 \cdot 2\text{H}_2\text{O}
\]
Structure of Schiff base Oxovanadium(IV) complexes

(IV)

(V)

(VI)
Synthesis and Physico-chemical studies of Oxovanadium(IV) complexes

Fig 3B.1: FAB mass spectrum of $N,N'$-bis (2-hydroxy benzylidene) benzidine (hbb) Oxovanadium(IV) complex

Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.)
Fig. 3B.2: FAB mass spectrum of $N,N'$-bis (2-hydroxy benzylidene)-1,4-phenylenediamine (hbp)
Oxovanadium(IV) complexes

Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.)
Fig. 3B.3 (SB-IV) : Infrared spectrum of $N,N'$-bis (2-hydroxybenzylidene) benzidine ($H_2hbb$) ligand
Fig. 3B.4 (IV): Infrared spectrum of \( N,N' \)-bis (2-hydroxybenzylidene) benzidine (hbb) oxovanadium (IV) complex
Fig. 3B.5 (SB-V): Infrared spectrum of \(N,N^\prime\)-bis (2-hydroxybenzylidene)-1,4-phenylenediamine (H\(_2\)hbp) ligand
Fig. 3B.6 (V) : Infrared spectrum of N,N'-bis (2-hydroxybenzylidene)-p-phenylenediamine (hbp) oxovanadium (IV) complex
Fig. 3B.7: Cyclic voltammogram of N,N'-bis (2-hydroxy benzylidene)-1,4-phenylenediamine (hbp) ligand

![Graph showing cyclic voltammogram data]

Fig. 3B.8: Cyclic voltammogram of N,N'-bis (2-hydroxy benzylidene)-1,4-phenylenediamine (hbp) Oxovanadium(IV) complex

![Graph showing cyclic voltammogram data]
Fig. 3B.9 (IV) : Electronic spectra of 4,4'-bis (2-hydroxy-benzylidene) benzine (hbb) oxovanadium(IV) complex

Fig. 3B.10 (V) : Electronic spectra of 1,4-bis (2-hydroxy-benzylidene) phenyleldiamine (hbp) oxovanadium(IV) complex

Fig. 3B.11 (VI) : Electronic spectra of cinnamidene-2-amino phenol (caph) oxovanadium(IV) complex
Fig. 3B.13 (IV) : ESR spectra of N,N'-bis(2-hydroxybenzylidene) benzidine (hbb) oxovanadium(IV) complex
Fig. 3B.14 (V) : E S R spectra of N,N'-bis(2-hydroxybenzylidene) benzidine (hbp) oxovanadium(IV) complex
(C) : Complexes of oxovanadium(IV) with the Schiff bases viz. diphenylglyoxaldinedene-α,α'-bis (2-aminophenol) (daph), diphenylglyoxaldinedene-α,α'-bis(2-amino-4-chlorophenol) (dacp), diphenylglyoxaldinedene-α,α'-bis (2-aminopyridine) (dapy) and diphenylgly-oxaldinedene-α,α'-4-chloro-1,3-phenylenediamine (dcpa)

Synthesis of Schiff bases (Ligands)

The Schiff bases (H₂daph/H₂dacp/dapy/dcpa) have been synthesized by adding the methanolic solution of diphenylglyoxal (0.01 mole) with the methanolic solution of 2-aminophenol/2-amino-4-chlorophenol/2-aminopyridine/4-chloro-1,3-phenylenediamine (0.02 or 0.01 mole) in 1:2 or 1:1 molar ratio. The reaction mixture was then refluxed on a water bath for about 7-8 hours. The condensation product was filtered, thoroughly washed with ethanol and ether, re-crystallized with ethanol and dried under reduced pressure over anhydrous CaCl₂. The purity of the synthesized compounds was monitored by TLC using silica gel.

Structure of Schiff bases
Preparation of VO (IV)-daph/dacp/dapy Schiff base complexes

The VO(IV)-daph/dacp/dapy complexes have been prepared by mixing the methanolic solution of VOSO$_4$.5H$_2$O (0.01 mole) to the methanolic solution of Schiff bases (H$_2$daph/H$_2$dacp/dapy) (0.01 mole) in equimolar ratio. The resulting mixture was refluxed on water bath for 9-10 hours. A coloured product appeared on standing and cooling the refluxate. The precipitated complexes were filtered and washed repeatedly with ether. The complexes were re-crystallised twice with ethanol, finally washed with diethyl ether and dried under reduced pressure over anhydrous CaCl$_2$ in a dessicator. The complexes were further dried in an electric oven at 50-70$^\circ$C.

Preparation of VO(IV)-dcpa Schiff base complex (by Template method)

Because of poor yield of dcpa Schiff base by simple condensation, the template synthetic method has been used. VO(IV)-dcpa complex has been prepared by mixing the methanolic solution of VOSO$_4$.5H$_2$O (0.01 mole) to the methanolic solution of diphenylglyoxal (0.02 mole) in 1:2 molar ratio. The reaction mixture was then refluxed on a water bath for about 4-5 hours. A change in colour of reaction mixture occurs, then a methanolic solution of 4-chloro-1,3-phenylenediamine (0.02 mole) was added. The resulting mixture was again refluxed on a water bath for about 5-6 hours. A coloured product appeared on standing and cooling the refluxate. The precipitated complex was filtered and washed repeatedly with ether. The complex was re-crystallized twice with ethanol, finally washed with diethyl ether and dried under reduced pressure over anhydrous CaCl$_2$ in a dessicator. The complex was further dried in an electric oven at 50-70$^\circ$C.

Results and Discussion

All the oxovanadium(IV)-Schiff base complexes are coloured solids, stable towards air and moisture at room temperature, decomposes at high temperature and more or less soluble in common organic solvents. The analytical data of the complexes are consistent with proposed molecular formula shown in Table-1C. The metal complexes exhibit 1:1 (VO-daph/dacp/dapy) and 1:2 (VO-dcpa) metal to Schiff base ligand stoichiometry. Molar conductance values show that VO-daph/dacp complexes are non-electrolytes and the VO-dapy/dcpa complexes have 2:2 electrolytic nature$^{38}$.

Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.)
Table-3A: Analytical, physical and conductance data of VO(IV)-Schiff base complexes

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compounds (Mol. formula)</th>
<th>Mol. Wt.</th>
<th>Colour</th>
<th>Yield %</th>
<th>M.P./Dec. (°C)</th>
<th>Found (Cal.) %</th>
<th>( \Lambda_m ) S cm(^2)mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-VII</td>
<td>C(<em>{26})H(</em>{30})O(_2)N(_2) \nH(_2)daph</td>
<td>392</td>
<td>Dark brown</td>
<td>65</td>
<td>240</td>
<td>78.12 (79.59)</td>
<td>4.99 (5.10)</td>
</tr>
<tr>
<td>VII</td>
<td>[VO (C(<em>{26})H(</em>{18})O(_2)N(_2))].3H(_2)O</td>
<td>511</td>
<td>Black</td>
<td>70</td>
<td>280</td>
<td>61.12 (61.05)</td>
<td>4.82 (4.69)</td>
</tr>
<tr>
<td>SB-VIII</td>
<td>C(<em>{26})H(</em>{18})O(_2)N(_2)Cl(_2) \nH(_2)daccp</td>
<td>461</td>
<td>Light brown</td>
<td>62</td>
<td>250</td>
<td>67.12 (67.67)</td>
<td>4.01 (3.90)</td>
</tr>
<tr>
<td>VII</td>
<td>[VO(C(<em>{26})H(</em>{16})O(_2)N(_2)Cl(_2))].3H(_2)O</td>
<td>580</td>
<td>Black</td>
<td>65</td>
<td>290</td>
<td>53.90 (53.79)</td>
<td>3.90 (3.79)</td>
</tr>
<tr>
<td>SB-IX</td>
<td>C(<em>{24})H(</em>{18})N(_4) \ndapy</td>
<td>362</td>
<td>Yellow</td>
<td>60</td>
<td>230</td>
<td>80.12 (79.55)</td>
<td>5.10 (4.97)</td>
</tr>
<tr>
<td>IX</td>
<td>[VO(C(<em>{26})H(</em>{18})N(_4))].SO(_4)4H(_2)O</td>
<td>597</td>
<td>Black</td>
<td>65</td>
<td>285</td>
<td>47.95 (48.24)</td>
<td>4.12 (4.35)</td>
</tr>
<tr>
<td>SB-X</td>
<td>C(<em>{26})H(</em>{18})N(_2)Cl(dcpa)</td>
<td>313.5</td>
<td>Brown</td>
<td>40</td>
<td>245</td>
<td>77.16 (76.55)</td>
<td>3.10 (3.18)</td>
</tr>
<tr>
<td>X</td>
<td>[VO(C(<em>{26})H(</em>{18})N(_2)Cl(_2)]SO(_4)3H(_2)O</td>
<td>844</td>
<td>Black</td>
<td>68</td>
<td>295</td>
<td>56.12 (56.87)</td>
<td>3.16 (3.08)</td>
</tr>
</tbody>
</table>

Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.)
Reactivity

The solution of complexes were made in methanol (99%) to check the reactivity and substitution behaviour against aquo, ammine, chloro, hydroxo and thiocynato ligands. The reaction was monitored by observing change in colour or precipitation.

Reaction with $H_2O$ : VO-daph/dacp/dcpa complexes react slowly while VO-dapy complex reacts rapidly on addition of slight amount of water at room temperature (1 hour). All the complexes decompose on heating with water.

Reaction with dilute $NH_3 (aq.)$ : VO-daph/dacp/dcpa complexes react slowly with dilute aqueous ammonia on keeping for 1 hour at room temperature, but VO-dcpy complex reacts fast. All the complexes react appreciably on heating.

Reaction with dilute $HCl (aq.)$ : VO-daph/dacp/dcpa complexes react slowly but VO-dapy reacts rapidly with dilute hydrochloric acid, on keeping for 1 hour at room temperature. On heating the complexes decompose quickly.

Reaction with dilute $NaOH (aq.)$ : VO-daph/dacp/dcpa complexes react slowly while VO-(dapy/dcpa) complexes react rapidly with dilute alkali at room temperature (1 hour). All the complexes react to sufficient extent on heating.

Reaction with dilute $KSCN (aq.)$ : VO-daph/dacp/dcpa complexes react slow with dilute potassium thiocynate, even on retaining for 1 hour at room temperature but VO-dapy complex react fast under similar conditions. On heating the complexes react appreciably.

Infrared Spectral Studies

A careful comparison of ligand and complex spectra resulted the following information regarding various groups\textsuperscript{41} (Table-2C). The IR spectra of Schiff base ligands (H$_2$daph, H$_2$dacp, dapy and dcpa) give strong intensity band at about 1590±5 cm$^{-1}$ due to $\nu_{c-N}$ (azomethine) group. This band shifts lower side by 20-30 cm$^{-1}$ in complexes, suggesting coordination through azomethine nitrogen. A strong band in H$_2$daph and H$_2$dacp ligand spectrum at
1343 and 1354 cm\(^{-1}\) due to phenolic-OH (deformation) has been found absent in complexes. This suggests deprotonation of phenolic-OH in VO-daph/dacp complexes. The chelation of phenolic oxygen in VO-daph/dacp complexes is supported by upward shift of \(\nu_{c-o}\) (phenolic \(1265 \pm 5 \text{ cm}^{-1}\)). The ligand dapy gives bands at 1578, 1490 and 1449 cm\(^{-1}\) due to \(\nu(c=\cdots c, c=\cdots n)\) (pyridine ring). These bands shift lower side by 15-25 cm\(^{-1}\) in VO-dapy complex indicating chelation with nitrogen of pyridine ring. The appearance of broad band around 3400-3100 cm\(^{-1}\) in the spectra of complexes is due to associated water molecules. A characteristic non-ligand sharp band in the spectra of complexes at 999-984 cm\(^{-1}\), has been assigned to \(\nu_{v-o}\). Some new bands\(^ {42}\) of low intensity in the region 540-465 cm\(^{-1}\) in the spectra of complexes, have been attributed to \(\nu_{v-o}\) and \(\nu_{v-n}\). This indicates that ligands \(\text{H}_2\text{daph}/\text{H}_2\text{dacp}/\text{dapy}\) and \(\text{dcpa}\) behave as tetradentate and bidentate, respectively (Fig. 3C.1-3C.5).

**Table-2C : Selected IR frequencies of ligands and their VO (IV) complexes**

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compounds (Abbr. Name)</th>
<th>(\nu_{(c-n)}) azomethine</th>
<th>(\nu_{(c=\cdots c)}) or (\nu_{(c=\cdots c+ c=\cdots n)})</th>
<th>(\nu_{(o-h)}) phenolic</th>
<th>(\nu_{(c-o)}) phenolic</th>
<th>(\nu_{(v-o)})</th>
<th>(\nu_{(v-d)})</th>
<th>(\nu_{(v-n)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-VII</td>
<td>(\text{H}_2\text{daph})</td>
<td>1587</td>
<td>1570 1475 1450</td>
<td>1343</td>
<td>1263</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VII</td>
<td>([\text{VO(daph)}].3\text{H}_2\text{O})</td>
<td>1565</td>
<td>1568 1492 1449</td>
<td>-</td>
<td>1312</td>
<td>984</td>
<td>540</td>
<td>468</td>
</tr>
<tr>
<td>SB-VIII</td>
<td>(\text{H}_2\text{dacp})</td>
<td>1592</td>
<td>1560 1485 1452</td>
<td>1354</td>
<td>1270</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VIII</td>
<td>([\text{VO(dacp)}].3\text{H}_2\text{O})</td>
<td>1560</td>
<td>1550 1488 1448</td>
<td>-</td>
<td>1323</td>
<td>980</td>
<td>535</td>
<td>465</td>
</tr>
<tr>
<td>SB-IX</td>
<td>(\text{dapy})</td>
<td>1594</td>
<td>1578 1490 1449</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IX</td>
<td>([\text{VO(dapy)}].\text{SO}_4.4\text{H}_2\text{O})</td>
<td>1573</td>
<td>1544 1476 1421</td>
<td>-</td>
<td>-</td>
<td>975</td>
<td>-</td>
<td>509</td>
</tr>
<tr>
<td>SB-X</td>
<td>(\text{dcpa})</td>
<td>1590</td>
<td>1515 1470 1455</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X</td>
<td>([\text{VO(dcpa)}]_2.\text{SO}_4.3\text{H}_2\text{O})</td>
<td>1570</td>
<td>1513 1466 1447</td>
<td>-</td>
<td>-</td>
<td>999</td>
<td>-</td>
<td>502</td>
</tr>
</tbody>
</table>
Magnetic Moment and Electronic Spectra

Room temperature magnetic moment values of oxovanadium (IV) complexes lie in the range 1.74-1.78 B.M. The values are well suited for oxovanadium (IV) monomorphic complexes with one unpaired electron. The electronic spectra (in MeOH) of [VO(daph)].3H₂O, [VO(dacp)].3H₂O, [VO(dapy)]SO₄.4H₂O and [VO(dcpa)]₂SO₄. 3H₂O complexes exhibit bands in the region 13695-14203, 19000-20100, and 23130-24150 cm⁻¹; which are assignable to ²B₂ - ²E, ²B₂ - ²B₁ and ²B₂ - ²A₁, transitions, respectively (Table-3C). The geometry of these five coordinated mononuclear complexes (VII, VIII, IX & X) have been ascribed to be trigonal bipyramidal (tbp) or square pyramidal (sp)⁴³⁻⁴⁵(Fig. 3C.6-3C.9).

Table-3C : Electronic spectral and magnetic moment data of VO(IV)-Schiff base complexes

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Complexes</th>
<th>Transitions/Band (cm⁻¹)</th>
<th>μ_eff B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII</td>
<td>[VO(daph)].3H₂O</td>
<td>13700 19980 24150</td>
<td>1.76</td>
</tr>
<tr>
<td>VIII</td>
<td>[VO(dacp)].3H₂O</td>
<td>13695 19960 24160</td>
<td>1.77</td>
</tr>
<tr>
<td>IX</td>
<td>[VO(dapy)].SO₄.4H₂O</td>
<td>13706 20100 23130</td>
<td>1.74</td>
</tr>
<tr>
<td>X</td>
<td>[VO(dcpa)]SO₄.3H₂O</td>
<td>14203 19000 23250</td>
<td>1.78</td>
</tr>
</tbody>
</table>

Thermal

The thermal degradation behaviour of the complexes have been noted on heating for 30 minutes in a muffle furnace at four temperatures (100⁰, 275⁰, 375⁰ and 600⁰C) in the atmosphere of air. The weight of the complex sample after each heating was recorded. The percentage remaining weight and the approximate nearby composition of the pyrolytic product corresponding to each temperature, have tentatively been given in Table 4C. The complexes are stable (w.r.t. Schiff base) in general upto 275⁰C; above this temperature some part of the chelated Schiff base start decomposing. The ultimate pyrolytic product (600⁰C) in oxygenated atmosphere for all the cases is supposed to be vanadium pentaoxide ⁴⁹.
Table-4C : Composition and % weight obs. (cal.)

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Complexes (Room temp.)</th>
<th>100° - 275°C</th>
<th>400°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII</td>
<td>[VO (C₈H₁₈O₂N₂)₃H₂O]</td>
<td>VO- some chelated ligand moiety 40.12</td>
<td>V₂O₅</td>
<td>17.15</td>
</tr>
<tr>
<td></td>
<td>[VO (C₆H₁₆O₂N₂)]</td>
<td>90.12 (89.43)</td>
<td></td>
<td>(17.80)</td>
</tr>
<tr>
<td>VIII</td>
<td>[VO(C₂H₆O₂N₂Cl₂)].3H₂O</td>
<td>VO- some chelated ligand moiety 42.78</td>
<td>V₂O₅</td>
<td>15.20</td>
</tr>
<tr>
<td></td>
<td>[VO(C₂H₆O₂N₂Cl₂)]</td>
<td>91.26 (90.68)</td>
<td></td>
<td>(15.68)</td>
</tr>
<tr>
<td>IX</td>
<td>[VO(C₂H₆N₄)] SO₄.4H₂O</td>
<td>VO- some chelated ligand moiety 44.12</td>
<td>V₂O₅</td>
<td>15.02</td>
</tr>
<tr>
<td></td>
<td>[VO(C₂H₆N₄)]SO₄</td>
<td>86.76 (87.93)</td>
<td></td>
<td>(15.24)</td>
</tr>
<tr>
<td>X</td>
<td>[VO(C₃H₁₀N₂Cl₂)] SO₄.3H₂O</td>
<td>VO- some chelated ligand moiety 45.79</td>
<td>V₂O₅</td>
<td>10.10</td>
</tr>
<tr>
<td></td>
<td>[VO(C₃H₁₀N₂Cl₂)] S</td>
<td>94.56 (93.60)</td>
<td></td>
<td>(10.78)</td>
</tr>
</tbody>
</table>

Solid State Electrical Conductivity

The solid state AC-electrical conductivity of the synthesized complexes in compressed pellet form (3 ton cm⁻²) at room temperature (35°C) has been measured. The AC-electrical conductivity values are as :

[VO(daph)].3H₂O = 2.23 x 10⁻⁵ S cm⁻¹
[VO (dapr)].3H₂O = 2.17 x 10⁻⁵ S cm⁻¹,
[VO(dapy)] SO₄ 4H₂O = 9.17 x 10⁻⁴ S cm⁻¹
[VO (dcpa)₂]SO₄.3H₂O = 8.96 x 10⁻⁴ S cm⁻¹

These values corresponds to semiconducting nature⁴⁹-⁵⁰. The AC-electrical conductivity of chelates follow the order :

[VO(dapy)] SO₄ 4H₂O > [VO (dcpa)₂]SO₄.3H₂O
> [VO(daph)].3H₂O > [VO (dapr)].3H₂O
Structure of VO(IV)-Schiff base Complexes

(VII) \[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{C} \\
\text{O} \\
\text{V} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{O} \\
\end{array}
\]
\[0.3H_2O\]

(VIII) \[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{N} \\
\text{C} \\
\text{C} \\
\end{array}
\]
\[0.3H_2O\]

(IX) \[
\begin{array}{c}
\text{O} \\
\text{V} \\
\text{N} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}
\]
\[0.4SO_4\cdot4H_2O\]

(X) \[
\begin{array}{c}
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]
\[0.3SO_4\cdot3H_2O\]
Fig. 3C.1 (SB-VII): Infrared spectrum of diphenyloxalidene-α,α'-bis(2-aminophenol) (H₂daph) ligand
Fig. 3C.2 (VII) : Infrared spectrum diphenylglyoxalidene-α,α'-bis (2-aminophenol) (daph) oxovanadium (IV) complex
Fig. 3C.3 (SB-IX) : Infrared spectrum of diphenylglyoxalidene-α,α'- (2-aminopyridine) (dapy) ligand
Fig. 3C.4 (IX): Infrared spectrum of diphenylglyoxalidene-α,α'-(2-aminopyridine) (dapy) oxovanadium (IV) complex
Fig. 3C.5 (X) : Infrared spectrum of diphenylglyoxalidene-\(\alpha,\alpha'-1,3\)-phenylenediamine (dcpa) oxovanadium(IV) complex
Fig. 3C.6 (VII) : Electronic spectra of diphenylglyoxalidene-$\alpha,\alpha'$-bis (2-aminophenol) (daph) oxovanadium(IV) complex

Fig. 3C.7 (VIII) : Electronic spectra of diphenylglyoxalidene-$\alpha,\alpha'$-bis (2-amino-4-chlorophenol) (daczp) oxovanadium(IV) complex
Fig. 3C.8 (IX) : Electronic spectra of diphenylglyoxalidene-α,α'-bis (2-aminopyridine) (dapy) oxovanadium(IV) complex

Fig. 3C.9 (X) : Electronic spectra of diphenylglyoxalidene-α,α'-4-chloro-1,3-phenylenediamine (dcpa) oxovanadium(IV) complex
Fig. 3C.9 (X): Infrared spectrum of diphenylglyoxalidene-α,α'-1,3-phenylenediamine (dcpa) oxovanadium(IV) complex
Fig. 3A.2 (SB-I) : Infrared spectrum of 4-chlorobenzylidene-2-amino-4-chlorophenol(Hcap) ligand
References:


