Synthesis, Physiochemical, Thermal, Catalytic and Electrical Studies of Mn(III) VO(IV), MoO_2(VI) and UO_2(VI) Complexes with Unsymmetrical Schiff Base Ligand

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Abstract: The solid complexes of Mn(III), VO(IV), MoO_2(VI) and UO_2(VI) with unsymmetrical dibasic tetridentate ONNO donor Schiff base derived from the condensation of salicylaldehyde, o-hydroxy acetophenone and ethylene diamine have been synthesized and characterized by elemental analysis, magnetic susceptibility measurements, IR and reflectance spectra. The thermal dehydration and decomposition of these complexes were studied kinetically using the Horowitz-Metzger method. The solid state electrical conductivity of complexes has been measured in the temperature range 313 K ≤ T ≥403 K and the complexes exhibited semiconducting behavior. Scanning electron micrograph has also been reported and suggested homogeneous phase material. Complexes were used for the catalytic oxidation of styrene.

Keywords: Unsymmetrical Schiff base, Tetradentate, Electrical conductivity, Catalytic oxidation

Introduction

Schiff base are an important class of ligands in coordination chemistry and find extensive application in different fields. Schiff bases derived from the salicylaldehyde are well known as polydentate ligands coordinating in neutral forms. Oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to form transition metal complexes with unusual configuration, structural liability and sensitivity to molecular environments. Their metal complexes find wide applications as antibacterial, antiviral, antimalarial agents, homogeneous and heterogeneous catalysts and magnetic materials. A literature survey reveals that the Schiff base derived from salicylaldehyde, o-hydroxyacetophenone and ethylenediamine has not reported so far. In this article, we describe the synthesis and characterization of Mn(III), Vo(IV), MoO_2(VI) and UO_2(VI) complexes of N-(salicylidene)-N’-(o-hydroxyacetophenone)-ethylenediamine.
Experimental
The metal contents in the complexes were analyzed by standard methods. The analysis of Carbon, Hydrogen and Nitrogen were performed on Carlo Erba 1108 elemental analyzer at Central Drug Research Institute (CDRI), Lucknow, India. The infrared spectra of ligand and its complexes were obtained in KBr pellets on Perkin-Elmer spectrophotometer 597 at SAIF, Panjab University, Chandigarh, India. The room temperature magnetic susceptibility measurements of the resulting complexes were measured by Gauy’s method. The paramagnetic susceptibilities were corrected for diamagnetism of ligand and metal ion. Thermograms of the complexes were recorded in the temperature range room temperature to 700 °C at the heating rate of 20 °C /min using a Metzsch STA 409 simultaneous thermal analyzer at IIT Madras, Chennai India. Solid-state electrical conductivity of the complexes was measured in their compressed pellet forms using the conventional two-probe method. Diffuse reflectance spectra of complexes were recorded on Varien Cary 5E UV-NIR spectrophotometer at RSIC, IIT Madras, Chennai. SEM image of complexes were recorded at VNIT, Nagpur, India.

All chemicals used in the present work viz., salicyladehyde, o-hydroxyacetophenone, ethylenediamine, metal salts, solvents, etc., were of A.R. grade. The unsymmetrical Schiff base N-(salicylidene)-N’-(o-hydroxyacetophenone) ethylenediamine (H2L) was obtained by known method11. Manganese(III) acetate dehydrate and dioxomolybdenum diacetate were prepared by known methods12.

Preparation of metal complexes
Ligand is highly soluble in hot DMF (90-100 °C) to increase solubility of ligand; minimum amount of DMF was used. To a hot stirred solution of 2 mmol of ligand in DMF (10 mL) was added a solution of metal salts (2 mmol) (10 mL) in DMF and then reflux for 1 h. Then pH of the solution was adjusted to 7.5 using alcoholic ammonia and resulting solution was further refluxed for about 4 h. The colored solution was concentrated to ca 15 mL and then cooled to room temperature to give colored precipitation of the complex. The complexes thus separated out was filtered, washed with DMF and hot ethanol to give the analytically pure products and dried in desiccators over CaCl2.

Antibacterial and antifungal study
The antibacterial activities of the ligand and the complexes have been carried out against the bacteria Staphalococcus aureus, Bacillus Subtilis, Salmonella typhimurium and Escherichia coli using nutrient agar medium by the disc diffusion method. Solutions of 100, 200 and 300 ppm of the compounds in DMSO were used for the studies. These discs were placed on the already seeded plates and incubated at 35 °C for 24 h. The diameter (mm) of the inhibition zone around each disc was measured after 24 h.

The antifungal activity was evaluated by the same disc diffusion method using potato dextrose agar medium containing starch 20 g. Dextrose 20 g and agar-agar powder 15 g dissolved in 1000 mL distilled water. Same concentrations of compounds were used. The organisms used were Aspergillus oryzae and Fusarium species. The fungicidal activity of the compounds was recorded after 7 days.

Catalytic oxidation study
Catalytic oxidation of styrene to corresponding epoxide by VO(IV) and UO2(VI) complexes tested in presence of an aqueous solution of 30% H2O2 as an oxidant. These catalytic reactions were carried out in 50 mL reaction flask fitted with water condenser. A general
procedure was followed for all reactions. In a typical experiment, styrene (5.2 g, 30 mmol) and 30% H\textsubscript{2}O\textsubscript{2} (1.7 g, 30 mmol) were mixed in 1:1 proportion in 5 mL of acetonitrile and the reaction mixture was heated at 60 °C with continuous stirring. An appropriate catalyst to be tested (0.3 g, 3 mmol) was added to the reaction mixture and heated at 60 °C under constant stirring for 4 h. After the completion of reaction, an organic layer was separated by separating funnel and analyzed using 19091Z.413E Agilent Gas Chromatography with HP-1 column having length 30 m and inner diameter 0.32 mm and FID detector.

**Results and Discussion**

The reaction of the ligand with the metal ions gave desired complexes. The newly synthesized Schiff base complexes are very stable at room temperature in solid state. The complexes are insoluble in common organic solvents and soluble in DMSO. The results of elemental analysis and physical properties of the compounds are presented in Table 1 and are good agreement with the proposed Schiff base complexes. The elemental analysis suggests 1:1 metal: ligand ratio.

**Table 1.** Analytical and spectral data of compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>% of yield</th>
<th>Elemental Analysis (%)</th>
<th>IR cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[H\textsubscript{2}L]</td>
<td>Yellow</td>
<td>90.80</td>
<td>72.30</td>
<td>6.88</td>
</tr>
<tr>
<td>[MnL(OAc)\textsubscript{2}H\textsubscript{2}O]</td>
<td>Brown</td>
<td>59.84</td>
<td>55.08</td>
<td>5.07</td>
</tr>
<tr>
<td>[VOL]</td>
<td>Silver Gray</td>
<td>62.35</td>
<td>58.52</td>
<td>4.59</td>
</tr>
<tr>
<td>[MoO\textsubscript{2}L]</td>
<td>Pale Cream</td>
<td>61.28</td>
<td>49.76</td>
<td>3.90</td>
</tr>
<tr>
<td>[UO\textsubscript{2}L]</td>
<td>Golden Brown</td>
<td>71.43</td>
<td>36.91</td>
<td>2.89</td>
</tr>
</tbody>
</table>

**Electronic spectra**

The Mn(III) ion(d\(^{4}\)) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transitions. The diffuse reflectance spectrum of Mn(III) complex display absorption bands at 818, 609 and 445 nm corresponding to tetragonally distorted octahedral geometry. These bands may be assigned to \(^{5}B\textsubscript{1g} \rightarrow ^{5}A\textsubscript{1g}, ^{5}B\textsubscript{1g} \rightarrow ^{5}B\textsubscript{2g}, \) and \(^{5}B\textsubscript{1g} \rightarrow ^{5}E\textsubscript{g}, \) transitions, respectively\(^{13}\). The VO(IV) complex display absorption bands at 782, 613 and 454 nm corresponding to \(^{2}B\textsubscript{2} \rightarrow ^{2}E\textsubscript{1}, ^{2}B\textsubscript{2} \rightarrow ^{2}B\textsubscript{1}, \) and \(^{2}B\textsubscript{2} \rightarrow ^{2}A\textsubscript{1}, \) transitions respectively for square pyramidal environment around V(IV) ion\(^{14}\). MoO\textsubscript{2}(VI) complex display bands at 445 nm suggesting octahedral geometry\(^{15}\). UO\textsubscript{2}(VI) complex shows bands at 802, 583 and 355 nm consistent with the vibronic structure of the triatomic entity of the UO\textsubscript{2}(VI) group. The UO\textsubscript{2}(VI) complex display weak band at 583 nm assignable to \(^{1}\Sigma_{g}^{+} \rightarrow ^{3}\Pi\textsubscript{u}, \) transitions\(^{16}\).

**Infrared spectra**

The characteristic vibrational frequencies have been identified by comparing the spectra of the complexes with that of the parent ligand and literature value of absorption of simple type of compound (Table 1). The Schiff base exhibits a medium broad band at 3052 cm\(^{-1}\), which
may be due to the presence of intramolecular hydrogen bonding between phenolic hydrogen and azomethine nitrogen atoms\(^\text{17,18}\). The absence of this band in the spectra of complexes indicates the deprotonation of the phenolic group and coordination of the oxygen atom to metal ion. This is further supported by the shift of the \(\nu (C-O)\) (phenolic)\(^\text{19}\) band from 1283 cm\(^{-1}\) of the ligand to 1295-1330 cm\(^{-1}\) in the spectra of complexes, indicating the coordination of phenolic oxygen atom to the metal ion\(^\text{20}\). The strong band observed at 1635 cm\(^{-1}\) due to \(\nu (C=N)\) stretch in ligand spectrum has been shifted to lower frequency by ca. 20-40 cm\(^{-1}\) upon coordination\(^\text{21,22}\). The Mn(III) complex show two bands at 1656 and 1449 cm\(^{-1}\) corresponding to \(\nu_{\text{asym}}(\text{COO}^-)\) and \(\nu_{\text{sym}}(\text{COO}^-)\). The magnitude of the separation \(\Delta \nu_{\text{COO}}\) between the frequencies of \(\nu_{\text{asym}}(\text{COO}^-)\) and \(\nu_{\text{sym}}(\text{COO}^-)\) in Mn(III) complex is much greater (\(\Delta \nu_{\text{COO}} = 207 \text{ cm}^{-1}\)) than the ionic value (\(\Delta \nu_{\text{COO}} = 158 \text{ cm}^{-1}\)). This indicates that acetate ligand coordinated as monodentate ligand\(^\text{23}\). In the oxovanadium complex, strong band at 977 cm\(^{-1}\) is assigned to \(\nu (\text{V=O})\) mode\(^\text{24}\). MoO\(_2\)(VI) complex exhibit \(\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})\) and \(\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})\) bands at 944 and 902 cm\(^{-1}\) respectively in the present compound suggest a cis-MoO\(_2\) structure because dioxomolybdenum(VI) compound having trans-MoO\(_2\) structure is expected to exhibit only the \(\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})\) band since \(\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})\) is IR inactive\(^\text{25}\). The uranyl complex exhibit a strong band at 940 cm\(^{-1}\) and the medium intensity band at 879 cm\(^{-1}\) assignable to \(\nu_{\text{asym}}(\text{O}=\text{U}=\text{O})\) and \(\nu_{\text{sym}}(\text{O}=\text{U}=\text{O})\) mode respectively\(^\text{26}\). The bonding through oxygen and nitrogen is supported by the appearance of new bands in the region 520-585 and 464-491 cm\(^{-1}\) which may be assigned to \(\nu (\text{M-O})\) and \(\nu (\text{M-N})\) vibrations respectively\(^\text{27}\).

**Magnetic properties**

The MoO\(_2\)(VI) and UO\(_2\)(VI) complexes are found to be diamagnetic in nature expected for octahedral geometry\(^\text{15,28}\). The magnetic moment of VO(IV) complex was found to be 1.71 B.M. towards square pyramidal geometry\(^\text{29}\). Mn(III) complex was found to be 4.76 B.M. which is expected for d\(^{4}\) system\(^\text{30}\).

**Thermal properties**

Thermal decomposition studies of complex have been carried out as to corroborate the information obtained from the IR spectral studies about the status of water molecules present in some of these complexes as well as to know their decomposition pattern. An analysis of the thermogram of the complexes of VO(IV), MoO\(_2\)(VI) and UO\(_2\)(VI) indicate that these complexes undergo one step decomposition after dehydration, while Mn(III) complex undergo two step decomposition after dehydration. The complexes of VO(IV), MoO\(_2\)(VI) and UO\(_2\)(VI) show mass loss up to 140 °C indicating the presence of one lattice water molecule (% wt. loss obs/calcld: Mn(III): 4.98/4.18, MoO\(_2\)(VI): 3.96/4.23 and UO\(_2\)(VI): 3.49/3.17). There is further loss in weight up to 280 °C indicating the presence of one coordinated water in Mn(III) complex (% wt. loss obs/calcld: Mn(III): 8.75/8.37). In all the complexes, rapid loss in weight has been observed around 300 °C indicative of decomposition of free part of the coordinated ligand. A gradual increase in temperature above 600 °C was accompanied by degradation of coordinated part of the ligand. The thermogravimetric analysis has proved to be useful analytical technique in evaluating thermodynamic activation parameters of the complexes upon thermal decomposition process, such as activation energy (E\(_a\)), frequency factor (Z), entropy change (-\(\Delta S\)) and free energy change (\(\Delta F\)) by employing Horowitz-Metzger method\(^\text{31}\), which are shown in Table 2.
Table 2. Magnetic, Electrical conductivity and Thermal decomposition data of complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\mu_{\text{eff}}$</th>
<th>Electrical conductivity ($\Omega^{-1}\text{cm}^{-1}$)</th>
<th>Half decomposition temp, oC</th>
<th>Activation energy $E_a$ (kJmol$^{-1}$)</th>
<th>Frequency Factor $Z$ (Sec$^{-1}$)</th>
<th>Entropy change ($-\Delta S$) (Jmol$^{-1}$K$^{-1}$)</th>
<th>Free energy change ($\Delta F$) (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MnL(OAc)H$_2$O]</td>
<td>4.76</td>
<td>1.12x$10^{-8}$</td>
<td>238</td>
<td>15.20</td>
<td>109.42</td>
<td>210.38</td>
<td>65.27</td>
</tr>
<tr>
<td>[VOL]</td>
<td>1.71</td>
<td>8.38x$10^{-6}$</td>
<td>386</td>
<td>34.88</td>
<td>78.32</td>
<td>215.29</td>
<td>117.98</td>
</tr>
<tr>
<td>[MoO$_2$L]</td>
<td>Diamagnetic</td>
<td>1.23x$10^{-9}$</td>
<td>634</td>
<td>21.44</td>
<td>150.89</td>
<td>209.52</td>
<td>154.28</td>
</tr>
<tr>
<td>[UO$_2$L]</td>
<td>Diamagnetic</td>
<td>1.15x$10^{-8}$</td>
<td>301</td>
<td>16.03</td>
<td>141.13</td>
<td>209.25</td>
<td>79.03</td>
</tr>
</tbody>
</table>

**Electrical properties**

The DC electrical conductivity of the ligand and its complexes has been studied in the temperature range 313 K < T < 403 K using the two-probe technique Table 2. The value of the solid-state electrical conductivity of the complexes were found to be in the range of $10^{-9}$ to $10^{-6} \Omega^{-1}\text{cm}^{-1}$ and they are semiconductor in nature, because their conductivity increases with increase in temperature and decreases upon cooling over the studied temperature range. The activation energy-temperature dependence follows the Arrehenius relation

$$\sigma = \sigma_0 \exp \left(-\frac{E_a}{kT}\right)$$

Where $\sigma_0$, $E_a$ and $k$ are conductivity constants, the activation energy and the Boltzmann constant, respectively. The plots of $\log \sigma$ vs. $1000/T$ (Figure 2) for all the compounds are found to be linear over the entire temperature range. The activation energy of the compounds lies in the range 0.199-0.583.

**Figure 1.** $N$-(Salicylidene)-$N^1$-($\alpha$-hydroxyacetophenone)-ethylenediamine (H$_2$L)

**Figure 2.** Plot of $\log \sigma$ vs. $1000/T$

Surface analysis is used in understanding the surface features of the material. The Scanning electron micrograph (SEM) of metal complexes indicates the presence of well-defined crystals free from any shadow of the metal ion on their external surface. The morphology and particle size of the unsymmetrical Schiff base metal complexes have been
illustrated by SEM. Figure 3 depict the SEM photograph of the synthesized VO(IV) complex as representative example. There is a uniform matrix of the synthesized complexes in the pictograph, which leads to dealing with homogeneous phase material. VO(IV) complex is rock like shape morphology with 2-3.5 µm particle size and ~ 2 µm pore size.

Figure 3. Scanning electron micrograph of [VOL]

**Antimicrobial activity**

The Schiff base and its metal complexes were evaluated for antimicrobial activity against two strain gram +ve bacteria (Staphalococcus aureus, Bacillus subtilis), gram –ve bacteria (Salmonella typhimurium, Escherichia coli) and fungi (Aspergillus oryzae, Fusarium species). The antimicrobial screening results are given in Table 3. These observations show that the majority of the compounds are more active than their respective Schiff bases. In some cases, Schiff bases and their complexes have similar activity against bacteria and fungi. Chelation may enhance or suppress the biochemical potential of bioactive organic species. The antibacterial screening shows that compounds [MnL(OAc)H2O] and [UO2L] exhibit the most activity. The fungicidal screening shows that compounds [VOL] and [MoO2L] are most effective against Fusarium species.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Antibacterial Screening Data</th>
<th>Antifungal Screening Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Staphalococcus aureus</td>
<td>Bacillus subtilis</td>
</tr>
<tr>
<td></td>
<td>Concentration in ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 200 300 100 200 300 100 200 300 100 200 300</td>
<td></td>
</tr>
<tr>
<td>LH2</td>
<td>9 17 6 6 8 9 7 7 9 8 12 17</td>
<td>- - - - - - - 6 -</td>
</tr>
<tr>
<td>[MnL(OAc)H2O]</td>
<td>9 20 - 9 11 8 10 13 8 11 19</td>
<td>6 6 7 6</td>
</tr>
<tr>
<td>[VOL]</td>
<td>- - 7 9 12 6 7 10 - 6 8 7</td>
<td>- 8 6 7 - 9</td>
</tr>
<tr>
<td>[MoO2L]</td>
<td>- 6 8 - 8 11 - 7 10 - 7 9</td>
<td>- 7 - 6 8 10</td>
</tr>
<tr>
<td>[UO2L]</td>
<td>- - 7 - 5 6 8 11 - 6 8</td>
<td>- - - 8 10 13</td>
</tr>
</tbody>
</table>

**Catalytic activity**

The catalytic oxidation of organic substrates by transition metal complexes is an area of current interest, in view of this in the present paper the catalytic activity of VO(IV) and UO2(VI) complexes for epoxidation of styrene to corresponding styrene oxide were carried out using H2O2 as an oxidant. These oxidation reaction yielded styrene oxide as a major product with minor amount of phenyl acetaldehyde as side product. Epoxidation of styrene resulted 6.20 and 19.20% conversion and 18.55 and 95.94% Selectivity for VO(IV) and UO2(VI) complexes, respectively of styrene into styrene oxide (Figure 4). No significant side products were identified.
Conclusion

Coordination chemistry of an unsymmetrical Schiff base ligand, obtained from the reaction of salicylaldenyde, o-hydroxy acetophenone and ethylene diamine, is described. Mn(III), VO (IV), MoO2(VI) and UO2(VI)) complexes have been synthesized using above Schiff base ligand and characterized on the basis of analytical, magnetic and spectral data. The Schiff base coordinates through its azomethine nitrogens and phenolic oxygens to the metal ion and act as a tetradentate ligand. All the complexes except VO(IV) complex exhibits regular octahedral geometry. Thermal behavior, electrical conductivity and antimicrobial activity of all the complexes are investigated. All the complexes are semiconducting in nature. SEM image of the VO(IV) complex indicates homogeneous phase material. It has been suggested that chelation/coordination enhance or suppress the biochemical potential of bioactive organic species.

References