Synthesis and Characterization of Biologically Active Transition Metal Complexes containing Monobasic Tridentate Schiff Bases

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(Received: January 09, 2011; Accepted: February 18, 2011)

ABSTRACT

The complexes of V(III) and MoO(V) with the ligands like glycine 2,4-dihydroxybenzaldehyde (GDHB), L-alanine 2,4-dihydroxybenzaldehyde (ADHB) and valine 2,4-dihydroxybenzaldehyde (VAIA) have been synthesised and characterised by analytical data, conductivity, magnetic, infrared and electronic spectral data. The analytical data suggested 1:2 (M:L) stoichiometry for all the synthesised complexes. Octahedral geometry has been proposed for all complexes. The ligands and their respective MoO(V) and V(III) complexes have been screened for their antimicrobial activities.

Key words: V(III), MoO(V), ligand, octahedral, antimicrobial activity.

INTRODUCTION

Vanadium and molybdenum are prominent among the transition metals which play important role in biochemical processes. There is heightened interest in the biological chemistry of vanadium due to the discovery of two types vanadium enzymes\(^1,2\), Vanadium nitrogenase and vanadium bromoperoxidase. According to the available report\(^3\), V(III) is at the active site of vanadium nitrogenase. Vanadium is also known to be an essential nutrient in higher life forms\(^4,7\), where it is involved in phospholipid oxidation, sulphur metabolism and cholesterol biosynthesis\(^8\). Apart from this vanadium has been a subject of investigation with regard to its association with insulin and its role in the body\(^5\). Vanadium salts also controls glucose level in plasma\(^6\). Vanadium is better absorbed in the form of an organic matrix\(^6\). In such a case Schiff base V(III) complexes seems to be important to synthesise. Similarly molybdenum(V) complexes have been found to act as simple models for biochemical redox\(^6\) and in nitrogenase enzymes\(^7\).

Keeping these facts in view, an attempt has been made to synthesize and characterize some of the biologically active Schiff base complexes of vanadium(III) and oxomolybdenum(v).
EXPERIMENTAL

All the chemicals used during this research work, various aldehydes and amino acids were of A.R grade or equivalent purity. The ligands as well as the metal complexes were analysed by standard methods. Conductivity measurements were carried out on Philips conductivity Bridge model PR 9500 using 10^{-3} M DMF and DMSO solution at 25°C. The I.R. spectra were recorded by Perkin Elmer FTIR spectrophotometer by using KBr pellets. Electronic spectra were recorded using Beckmann DU Spectrophotometer. The magnetic susceptibility was determined by Gouy's balance using CuSO_4.5H_2O as calibrant.

Preparation of the ligands

The ligands were prepared by the reported standard method.

Preparation of metal complexes

The ethanolic solutions of the respective ligand and corresponding chlorides of V(III) and MoO(V) were refluxed for 4-5h. The precipitate so obtained was cooled, filtered, washed repeatedly with ethanol to remove any excess of metal chloride and/or ligand. Finally it was dried in vacuum.

RESULTS AND DISCUSSION

The analytical data of the metal complexes, along with melting points, magnetic moments and molar conductance is given in Table 1.

The IR spectra of the ligands were compared with those of the corresponding metal complexes to find out the possible coordination sites. The comparison revealed the monobasic tridentate nature of all the three ligands.

The IR spectra of the ligands exhibited a band in the range of 1640-1620 cm^{-1} assignable to ν(C=N). These bands have shown a downward shift of 15-20 cm^{-1} in the IR spectra of the corresponding V(III) and MoO(V) complexes. These shifts suggested the involvement of azomethine nitrogen atom in coordination with the respective metal. It is expected that coordination of nitrogen to the metal atom would reduce the electron density on the azomethine link and thus lower the HC=N absorption. This assignment was further confirmed by the appearance of non-ligand band in the IR spectra of the corresponding metal complexes around 520-550 cm^{-1}, assignable to ν(M-N).

The asymmetric carboxyl stretching v_{asym}(COO^{-}) has shifted to higher frequency while symmetric carboxyl stretching v_{sym}(COO^{-}) has shifted to lower frequency in all the complexes indicating the linkage between metal ion and carboxylate oxygen atom.

The bands appearing in the region of 1535-1515 cm^{-1} may be assigned to ν(C-O) phenolic stretching. These bands have shifted to higher frequency in the IR spectra of the complexes, suggesting coordination through phenolic oxygen with the metal ion. It was further supported by the appearance of non-ligand band in the far IR region of the spectra of the complexes at 440-400 cm^{-1} attributable to ν(M-O) vibrations.

In the IR spectra of oxomolybdenum (V) complexes, some new bands have appeared in the region of 3400-3250 cm^{-1} due to ν(OH) vibrations of coordinated water molecules and 800-750 cm^{-1}, 720-700 cm^{-1} due to rocking and wagging modes of water molecules respectively.

The IR spectra of the oxomolybdenum complexes also exhibited another new band in the 890-920 cm^{-1} due to the presence of Mo=O moiety.

As expected, all the vanadium (III) and oxomolybdenum (V) complexes are paramagnetic in nature (values in table-1) with two unpaired electrons in V(III) and one unpaired electron in the case of MoO(V). Conductivity for the complexes measured at 25°C and 10^{-3}M dilution suggested 1:1 and 1:2 electrolytic nature for V(III) and MoO(V) complexes respectively.

The electronic spectra of oxomolybdenum (V) complexes are similar to each other, thereby suggesting a uniform structure for all of them. The complexes may be considered as octahedral with strong distortion resulting from molybdenum - oxygen bond (Mo=O). The complexes exhibit three distinct absorption bands in the ligand field region.
Table 1: Characterisation of complexes prepared

<table>
<thead>
<tr>
<th>S. NO.</th>
<th>Complex</th>
<th>Molecular Formula</th>
<th>M.Pt. (In °C)</th>
<th>Elemental analyses</th>
<th>Magnetic Moment (B.M.)</th>
<th>MOLAR Conductance Values (ohm⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DMSO</td>
<td>DMF</td>
</tr>
<tr>
<td>1</td>
<td>bis(Glycine 2,4 di hydroxy benzaldehyde) vanadium(III) chloride</td>
<td>$[V(C_9H_8NO_4)_2]Cl$</td>
<td>295</td>
<td>10.74 (10.65)</td>
<td>45.53 (45.50)</td>
<td>3.37 (3.30)</td>
</tr>
<tr>
<td>2</td>
<td>Diaquo-Glycine 2,4-di hydroxy benzaldehyde oxomolybdenum (V) chloride</td>
<td>$[MoO(C_9H_8NO_4)(H_2O)]_2Cl$</td>
<td>305</td>
<td>27.11 (27.00)</td>
<td>26.15 (26.10)</td>
<td>2.91 (2.85)</td>
</tr>
<tr>
<td>3</td>
<td>bis(alanine 2,4 di hydroxy benzaldehyde) vanadium (III) chloride</td>
<td>$[V(C_{10}H_{10}NO_4)_2]Cl$</td>
<td>275</td>
<td>10.14 (10.10)</td>
<td>47.77 (47.68)</td>
<td>3.98 (3.90)</td>
</tr>
<tr>
<td>4</td>
<td>Diaquo alanine 2,4-di hydroxy benzaldehyde oxomolybdenum (V) chloride</td>
<td>$[MoO(C_{10}H_{10}NO_4)(H_2O)]_2Cl$</td>
<td>300</td>
<td>26.22 (20.68)</td>
<td>28.10 (29.82)</td>
<td>3.27 (2.10)</td>
</tr>
<tr>
<td>5</td>
<td>bis(valine 2,4 di hydroxy benzaldehyde) vanadium (III) chloride</td>
<td>$[V(C_{12}H_{14}NO_4)_2]Cl$</td>
<td>280</td>
<td>9.60 (9.68)</td>
<td>54.29 (54.69)</td>
<td>5.27 (5.49)</td>
</tr>
<tr>
<td>6</td>
<td>Diaquo valine 2,4-di hydroxy benzaldehyde oxomolybdenum (V) chloride</td>
<td>$[MoO(C_{12}H_{14}NO_4)(H_2O)]_2Cl$</td>
<td>310</td>
<td>24.60 (19.41)</td>
<td>31.65 (29.16)</td>
<td>3.95 (2.83)</td>
</tr>
</tbody>
</table>
The low intensity bands spread over Ca 13000-14000 cm\(^{-1}\) region may be due to \(^{2}B_2 \rightarrow ^{2}E\) (\(d_{xy} \rightarrow d_{xz}, d_{yz}\)). The second band appeared at Ca 19000-20000 cm\(^{-1}\) due to the transition, \(^{2}B_2 \rightarrow ^{2}B_1\) (\(d_{xy} \rightarrow dx^2-y^2\)). The third peak lies at Ca 30000-22000 cm\(^{-1}\) and may be due to \(^{2}B_2 \rightarrow ^{2}A_1\) (\(d_{xy} \rightarrow dz^2\)).

The electronic spectra of vanadium(III) complexes exhibited bands at 16700 cm\(^{-1}\) with a shoulder at 21000-21500 cm\(^{-1}\). The low energy band may be assigned to 3T\(_1\)g3T\(_2\)g while the high energy band to 3T\(_1\)g3T\(_1\)g(p) transitions respectively. These are characteristic of octahedral geometry\(^{17}\).

Based on these studies octahedral geometry may be suggested for all these complexes with distortion in the case of oxomolybdenum (V).
All the ligands and their V(III) and MoO(V) complexes were screened for their antimicrobial activity against *E. coli*, *Salmonella typhinurium*, *S. aureus* and *A.niger*. The results revealed that the metal complexes are more potent antimicrobials than their corresponding ligands.

REFERENCES