Studies On Some Novel Mixed Ligand Complexes Of Cobalt(II)-Imidazol-Amino Acids.
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Abstract: Imidazolate anion is known to act as a bridging ligand in certain metalloenzymes, hence it is interesting to study about its chelation behaviour. Also Amino acids- the most common classes of substances present in biological systems and having two principal potentially active sites are of prime importance, and hence study of their mixed ligand metal complexes have been our main area of interest. Hence some mixed ligand complexes of Cobalt(II) salts have been prepared. Ligands used here are Imidazole and Amino Acids like Arginine, Glycine, Histidine and Methionine. All complexes corresponds to a general formulae [Co(imi)(amino acid)].H2O. The structures of Cobalt(II) complexes have been characterized on the basis of their elemental analysis, magnetic properties, conductivity measurements, UV-Vis and IR Spectral studies, their solubilities and melting points have also been observed. Electronic Spectral data for the complexes are in accordance with distorted Octahedral environment around the central Cobalt(II) ion. The Amino acids acts as a bidentate chelating ligands.

Keywords: Imidazole, Amino Acids, Mixed Ligand Complexes.

I. INTRODUCTION
Proteins are essential to all living matter and perform numerous functions as cellular components in the form of enzymes. Some serve as architectural constituents of protoplasm and cell membranes. Most important are the classes of enzymes that are characterized as protein or, protein like compounds because of their polypeptidic structure. Recombinant DNA (rDNA) technology has had a dramatic impact on our ability to produce complex proteins and polypeptides structurally identical with those found in-vivo. They sometimes have exhibited neurotransmitter and hormonal properties that regulate numerous important physiological processes.
Amino acids have two principal potentially active sites in the formation of complexes, the acid carboxyl group and the basic amino group. However natural amino acids can also include other functional groups in the chain during the peptide bond formation with sites for chemical activity in the peptide chains.
Imidazole also plays an important role in biological systems. It is because the imidazole moiety of the histidyl residue in a large number of metalloproteins form all or, part of the binding site of many transition metal ions. In bovine superoxide dismutase bridge formation has been observed between Cu and Zn. In Bovine thus imidazolate anion acts as a bridging ligand. Here, we report the preparation, Chemical Characterization of the mono nuclear mixed ligand complex, [Co(imi)(amino acid)2(H2O)]
Amino Acid = Arginine, Glycine, Histidine & Methionine.
imi = Imidazole.

II. EXPERIMENTAL
All experiments were carried out in an open air. Amino Acids (Glycine, Arginine, Histidine & Methionine), Imidazole and Cobalt (II) Chloride were purchased from Merk. All chemicals were of high purity and were used as purchased without further purification. Nano pure-quality water and the ethanol of Merk were used throughout this work.
The metal complexes were decomposed with fuming nitric acid and the metal content was determined with the method reported in the literature. C, H & N were analysed and was received from CDRI Lucknow. The analytical data are reported in table-1. Magnetic moment measurements were carried out at room temperature by Gouy’s Method. The magnetic moment data were made available to us at University PG Deptt. of Chemistry, L.N.M.U Darbhanga. The conductivities of the complexes were determined with the help of Systronics Conductivity meter bridge (Model-304) in 10^-3 M DMF solution. Melting points were measured in open capillaries and are uncorrected. Purity of the complexes were ascertained by TLC measurements too.
Electronic spectra of the complexes were recorded in Deptt. of Chemistry, IIT Kharagpur and CDRI Lucknow. Infrared spectra of the ligand and metal complexes were recorded in KBr pellets on a Perkin Elmer Model 22 Spectrophotometer, in the range of 4000-400 Cm^-1 in the IIT Kharagpur and CDRI Lucknow.
Preparation of Complexes [Co(imi)₄(H₂O)₂]Cl₂:
01 mmol of CoCl₂ (0.130 gm) was dissolved in 5ml of water. Now solution containing 1mmol (0.068gm) of imidazole in 2 ml ethanol was added. After one day the deep grey precipitate was formed (yield 50%).

\[ \text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{imi} \rightarrow [\text{Co(imi)}_4(\text{H}_2\text{O})_2]\text{Cl}_2 \]

Preparation of Complexes [Co(amino acid)₂(H₂O)₂]:
01 mmol (0.130 gm) of CoCl₂ in 2ml water was dissolved. Now 1mmol of respective amino acids (Glycine, Arginine, Methionine and Histidine) in 2ml water was prepared. Both were mixed and the reaction mixture was continuously stirred for 2h on a water bath at 40-45°C. The resulting solution was filtered off and was washed to remove any impurities and it was now allowed to stand at room temperature for days. After six days greyish precipitate was formed. It was filtered, washed and dried in dessicator.

Preparation of Complexes [Co(imi)(amino acid)₂(H₂O)₂]:
The mixed ligand amino acid-imidazol complexes of Co(II) were prepared by reacting the solutions of above two complexes. Suitable amount 1mmol of amino acids (1-4) dissolved in water were added separately to [Co(imi)₂(H₂O)₂] solutions. Now Mixtures were stirred continuously for 4-6 hours on water bath at 50°C. Complexes of greyish shades were obtained. These were washed with a 1:1 mixture of “ethanol+water”. The product was dried at room temperature.

All complexes are air-stable and are soluble in water at room temperature too.

Table 1:

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>Color</th>
<th>( \mu \text{cm}^2\text{OH}^{-1})</th>
<th>( A_m ) (ohm cm² mol⁻¹)</th>
<th>% Analysis [Found(Calc)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co(imi)(arg)₂H₂O]</td>
<td>Deep grey</td>
<td>4.95</td>
<td>11.9</td>
<td>36.61(36.51) 6.95(6.89) 28.46(28.39) 12.01(11.94)</td>
</tr>
<tr>
<td>2</td>
<td>[Co(imi)(gly)₂H₂O]</td>
<td>Light grey</td>
<td>4.97</td>
<td>11.2</td>
<td>28.63(28.47) 5.51(5.42) 19.03(18.97) 20.05(20.01)</td>
</tr>
<tr>
<td>3</td>
<td>[Co(imi)(met)₂H₂O]</td>
<td>Grey</td>
<td>5.10</td>
<td>12.7</td>
<td>35.67(35.21) 6.47(6.32) 12.75(12.64) 13.35(13.31)</td>
</tr>
<tr>
<td>4</td>
<td>[Co(imi)(his)₂H₂O]</td>
<td>Deep grey</td>
<td>5.05</td>
<td>12.5</td>
<td>40.01(39.56) 5.34(5.27) 24.76(24.61) 13.04(12.95)</td>
</tr>
</tbody>
</table>

III. Results And Discussion

Magnetic moments of Co(II) complexes lie in the range of 4.94-5.15BM. These observations indicate complete orbital contribution. The ground state electronic configuration of Co(II) octahedral complexes is \( ^3T_{1g} \) and next excited state is \( ^4T_{2g} \). Thus complete orbital contribution is characteristic of octahedral stereochemistry. 3

Electronic spectra of Co(II) complexes shows three bands in the range of 10.05-10.7 kK, 16.43-17.23 kK and 26.06-27.62 kK (Table 2) and these bands are quite similar to those observed in the spectrum of Co(en)₃²⁺ species which is octahedral in nature. 9,10

Table 2: Electronic spectra (in solid state) of mixed ligand complexes. [Band Assignments(in kK)]

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>( ^4T_{1g} \leftrightarrow ^4T_{2g}(F) )</th>
<th>( ^4T_{1g} \leftrightarrow ^4A_{2g}(F) )</th>
<th>( ^4T_{1g}(F) \leftrightarrow ^4T_{1g}(P) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co(imi)(arg)₂H₂O]</td>
<td>10.02</td>
<td>16.40</td>
<td>26.08</td>
</tr>
<tr>
<td>2</td>
<td>[Co(imi)(gly)₂H₂O]</td>
<td>10.3</td>
<td>17.02</td>
<td>27.4</td>
</tr>
<tr>
<td>3</td>
<td>[Co(imi)(met)₂H₂O]</td>
<td>10.06</td>
<td>17.21</td>
<td>26.23</td>
</tr>
<tr>
<td>4</td>
<td>[Co(imi)(his)₂H₂O]</td>
<td>10.68</td>
<td>16.89</td>
<td>27.61</td>
</tr>
</tbody>
</table>

Table 3: IR Spectral bands (in cm⁻¹) for Ternary Co(II) Complexes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>( \nu_{\text{OH}} )</th>
<th>( \nu_{\text{CDOS}} )</th>
<th>( \nu_{\text{CDOS}} )</th>
<th>( \nu_{\text{C-O-C}} )</th>
<th>( \nu_{\text{C-N}} )</th>
<th>( \nu_{\text{C=C-O}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co(imi)(arg)₂H₂O]</td>
<td>3228</td>
<td>1635,1670</td>
<td>1395</td>
<td>1296</td>
<td>1485</td>
<td>485</td>
</tr>
<tr>
<td>2</td>
<td>[Co(imi)(gly)₂H₂O]</td>
<td>3303</td>
<td>1636,1672</td>
<td>1412</td>
<td>1285</td>
<td>1487</td>
<td>412</td>
</tr>
<tr>
<td>3</td>
<td>[Co(imi)(met)₂H₂O]</td>
<td>3342</td>
<td>1640,1667</td>
<td>1416</td>
<td>1287</td>
<td>1482</td>
<td>409</td>
</tr>
<tr>
<td>4</td>
<td>[Co(imi)(his)₂H₂O]</td>
<td>3402</td>
<td>1638,1672</td>
<td>1413</td>
<td>1278</td>
<td>1465</td>
<td>413</td>
</tr>
</tbody>
</table>

The IR Spectra of complexes shows the characteristic bands of imidazole and amino acid moieties. Strong and broad bands in the 3400-3230 cm⁻¹ range are attributed to the \( \nu_{\text{OH}} \) and \( \nu_{\text{NH}} \) stretching vibrations respectively. In ternary complexes peaks are weaker and have been replaced to higher wave-number. The peaks at 1055 cm⁻¹ and at 1480 cm⁻¹ attributes to -C-H & -C=N imidazole ring.

A strong and sharp band in 405-490 cm⁻¹ & 700-810 cm⁻¹ range was observed in all Co(II) complexes. No such bands was observed in the free ligand in this range. This band is assigned to Co-N & Co-O stretching frequencies. 11
IV. REFERENCES


V. ACKNOWLEDGEMENTS

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