Chapter III

Synthesis and Structural characterization of some novel mixed-ligand cyanonitrosyl $[\text{CrNO}]^5$ complexes of chromium with Glutamic acid and Aspartic acid
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Synthesis and characterization of some novel mixed-ligand cyanonitrosyl \( \{\text{CrNO}\}^5 \) complexes of chromium with Glutamic acid and Aspartic acid.

3.1 Introduction

In chapter II, synthesis and physiochemical studies of some mixed ligand cyanonitrosyl \( \{\text{CrNO}\}^5 \) complexes of chromium with L-Alanine and L-Lysine. As a part of our programme to synthesize and characterize some neutral mixed ligand cyanonitrosyl complexes of monovalent chromium, studies have been extended using Glutamic acid and Aspartic acid.

3.2 EXPERIMENTAL

(a) Materials used:

Glutamic acid and Aspartic acid were used as such as supplied by Sisco Research Laboratories Pvt. Ltd. Mumbai. Analysis of the constituent elements:
(i) Carbon, hydrogen and nitrogen were estimated micro-analytically.

(ii) Estimation of chromium

For the estimation of the chromium as chromic oxide \((\text{Cr}_2\text{O}_3)\), the compounds were decomposed by heating with alkali followed by dissolving in nitric acid. Chromium was precipitated as chromic hydroxide by means of dil. ammonium hydroxide. Chromic hydroxide, when ignited, was converted into \(\text{Cr}_2\text{O}_3\). Repeated heating, cooling and weighing were carried out until constant weight obtained.

(c) Physical Methods:

(i) Conductance Measurements

Conductances were measured in analytical grade dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) using dip type cell on Toshniwal Conductivity Bridge at the department of chemistry, Atarra P.G. College, Atarra.
(ii) Magnetic measurements:

Room temperature magnetic susceptibility measurements of the investigated complexes were made by Gouy's method. Cobalt mercury thiocyanate was used as a calibrant.

(iii) Infrared spectra measurements:

Infrared spectra (4000-4500 cm\(^{-1}\)) of the uncoordinated ligands and synthesized complexes were recorded in nujol mulls supported between KBr pellets on Perkin Elmer (RXI) spectrometer (at Sophisticated Analytical Instrument Facility).

(iv) UV-VIS spectral measurements

UV-VIS spectra of the uncoordinated ligands and synthesized complexes were recorded on Perkin Elmer lambda 15 UV-VIS spectrophotometer ranging from (260-700 nm) (at sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow).
(v) NMR measurements

NMR spectra of the uncoordinated ligands and synthesized complexes were recorded on Brucker DRX-300MHz FT NMR using DMSO as solvent.

(vi) Molecular weight determination

Molecular weight determination of the synthesized complexes were made by Rast’s method.

3.3 PREPARATION OF THE PARENT COMPOUND

Potassium pentacyanonitrosylchromate(I) monohydrate was prepared by the method reported by Wilkinson et. al. as follows:

Chromium trioxide (CrO₃) (7 gm.) was added to a cold saturated solution of KOH (20 gm.) with ice cooling. Saturated aqueous KCN (35 gm.) was then added and the mixture filtered. NH₂OH.HCl (8 gm.) was added to the filtrate and the solution was heated on steam both for two hours, and then filtered and cooled, and the filtrate poured with stirring into ethanol (95%, 25 ml.). The precipitate was dissolved in minimum quantity of water and the compound again precipitated with ethanol; on
crystallization from water gave bright crystals. Compound was characterized by elemental analysis and IR spectroscopy.

The observed results are as follows:

<table>
<thead>
<tr>
<th></th>
<th>K (in %)</th>
<th>Cr (in %)</th>
<th>C (in %)</th>
<th>N (in %)</th>
<th>H₂O (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>33.8</td>
<td>15.8</td>
<td>18.05</td>
<td>24.5</td>
<td>5.1</td>
</tr>
<tr>
<td>Calculated</td>
<td>33.8</td>
<td>15.1</td>
<td>18.03</td>
<td>24.2</td>
<td>5.2</td>
</tr>
</tbody>
</table>

I.R.; \(\nu(\text{NO})^+\) \(\nu(\text{CN})\)

| Found (reported) | 1645 vs (1645 vs) | 2135 (2135 s) | 2192 (2195 s) |

3.4 PREPARATION OF COMPLEXES

(a) Preparation of \([\text{Cr(}\text{NO})(\text{CN})_2(\text{Glutamic acid}) (\text{H}_2\text{O})]\)

To a filtered aqueous solution of potassium salt of the pentacyanonitrosylchromate(I) monohydrate (0.1M, 50 ml.), an aqueous acetic acid solution (10 ml, 1:1) of the Glutamic acid ligand (0.02M) was added with shaking. A coloured solid was precipitated on heating
the mixture for 20 minutes over a hot plate at 80°C. The resulting yellow-brown mixture was freed from the liberated HCN by passing a current of CO₂ for few hours. The precipitate was suction filtered, washed several times with 10% acetic acid and finally with water and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in table 3.2.

(b) Preparation of \([\text{Cr(NO)(CN)}_2(\text{Aspartic acid})(\text{H}_2\text{O})]\)

To a filtered aqueous solution of potassium salt of the pentacyanonitrosylchromate(I) monohydrate (0.1M, 50 ml.), an aqueous acetic acid solution (10 ml, 1:1) of the Aspartic acid ligand (0.02M) was added with shaking. A coloured solid was precipitated on heating the mixture for 20 minutes over a hot plate at 80°C. The resulting greenish-brown mixture was freed from the liberated HCN by passing a current of CO₂ for few hours. The precipitate was suction filtered, washed several times with 10% acetic acid and finally with water and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in table 3.2.
3.5 PROPERTIES OF COMPLEXES

All the complexes are coloured solids (see Table 3.3 for colours). They are stable in air. Solubilities of these complexes in different solvents are given in Table 3.4. The complexes are thermally stable and do not melt or decompose upto 300°C (Table 3.4). They decompose in dil. acids and alkalis only on heating. Both complexes after decomposition with KOH followed by acidifying with acetic acid give a pink coloured with few drops of Griess reagent (29). This reaction indicates the presence of NO group in the synthesized complexes. The probable reaction scheme for the Griess reagent is summarized as below.
PROBABLE REACTION SCHEME FOR THE GRIESS REAGENT

\[
\begin{align*}
\text{[Cr(NO)(CN)_2(L)(H_2O)]} & \xrightarrow{\text{KOH, H_2O, Decomposition}} \text{NO}_2^- + \text{Chromium oxide} \\
\text{NO}_2^- + H^+ & \rightarrow \text{HNO}_2
\end{align*}
\]

Sulphanilic Acid

(A component of Griess Reagent)

Naphthylamine

(Another component of Griess reagent)

Pink coloured dye + CH_3COOH
3.6 RESULTS AND DISCUSSION

The mixed-ligand cyanonitrosyl complexes (see Table 3.1 for ligand names) were prepared according to equation

\[ K_3[Cr(NO)(CN)_5].H_2O + L \xrightarrow{AcOH \text{ to } H_2O} [Cr(NO)(CN)_5(L)(H_2O)] + 3KAc + 3HCN + H_2O \]

Where \( L = \) Glutamic acid, Aspartic acid

The partial replacement of cyano groups in the parent complex, \( K_3[Cr(NO)\ (CN)_5].H_2O \) by two molecules of ligand, \( L \), is facilitated by the trans effect of the NO group. Raynor and co-workers* studied the stepwise aquation of \([Cr(NO)(CN)_5]^{3^-}\) and obtained the tris (aqua) species, \([Cr(NO)(CN)_5(H_2O)]^3\) which is consistent with equation (1).

Compounds were characterized by on the basis of following results:

However, the more common mode of coordination is as a bidentate chelate through the N and O-atoms, which gives rise to a thermodynamically stable five membered ring for the \( \alpha \)-amino acids. The formation constant of some of the
major species are shown in table-2. The constant refer to the formation reactions. Because of the wide range of conditions and method employed. It is important also to realise that since the species concentration will be pH dependent a large numerical value for the formation constant does not necessarily mean that the species will be of major significance.

The conclusion that Freeman made are still valid, namely (1) the average dimensions of free and complexed peptides are very similar, except for the peptide C-O bond, which lengthens upon coordination, and the C-N bond, which shortens; (2) the peptide group remains very close to planar; (3) protonated N(peptide) never coordinates to a metal ion (presumably the tetrahedral geometry required would be energetically and geometrically unfavourable); (4) when a metal ion is bonded to three donor groups of a peptide molecule, the central one of which is a peptide N, then the three donor atoms and the metal must be coplanar.

Taking into account factor (3) then factor (1) can be explained in terms of the canonical forms in equation (18). The displacement of the peptide hydrogen by a metal ion requires a considerable lowering of the peptide pKa. Values compiled by Sigel and Martin, relating to the equilibrium
reactions (19-21), are given in Table 10. These are in keeping with the general observation that the N-chelated NiII peptides require a higher pH for their formation than do the CuII analogues. For the divalent metal ions most commonly studied the ability to displace a peptide proton follows the order Pd(2)>Cu(4)>Ni(8)>Co(10), with the approximate pKa values given in parentheses ZnII is unable to promote peptide ionization in the measurable pH range. The kinetically inert CoIII and PtII appear to be as effective as PdII. As an illustration of the pH dependence CuII and triglycine (Gly-Gly-Gly) solutions at low pH are green-blue, consistent with bidentate N(amone), O(peptide) chelation. However, on raising the pH the solution turns violet as the Cu displaces the peptide protons to give a tridentate N(amine), 2N(peptide) chelate. This UV shift of the d-d absorption band reflects the greater ligand field associated with N(peptide) donation. The inert CoIII complexes also allow the study of the reverse protonation process. Thus, for [Co(GlyGlyO)2]− the successive protonation constants (log values) are 1.46 and 0.10, the protonation occurring at the peptide oxygen atoms.
(a) Conductance Measurements

The molar conductance values measured in $10^{-3}$M dimethylsulphoxide as well as in dimethylformamide solutions. The conductance data are in agreement with the non-electrolytic nature (8) of these complexes.

(b) Magnetic Measurements

The magnetic moment values of the synthesized complexes at room temperature are presented in Table 3.6. An observation of the table shows that the magnetic moment values of the complexes are closed to the spin only values for one unpaired electron (1.73 B.M.)

(c) Infrared Measurements

The IR spectra are some of the reported complexes and substituted amino acids, coordinated NO and synthesized complexes are presented in the Table 3.7.

A comparision of the infrared spectra of the parent compound, $K_3[(Cr(NO)(CN)_5]).H_2O$ and of the synthesized complexes suggests that the appearance of a very strong bonds in the region 1700-1705 cm$^{-1}$ in these complexes, is of coordinated NO$^+$ stretching. The positive shift of approximately 50 cm$^{-1}$ in these
complexes compared to the parent compound is perhaps due to the non-electrolytic nature of these complexes.

All the compounds reported here show a strong band in the region 2140-2160 cm\(^{-1}\). This band is assigned for \(v(\text{CN})\), which is in accordance with the assignment made for other reported complexes. Broad bands in the region 3540-3580 cm\(^{-1}\) and 3350-3400 cm\(^{-1}\) in both complexes are assigned to \(v(\text{OH})\) of the coordinated water. The appearance of broad band in the range 3100-3050 cm\(^{-1}\) and 1550-1485 cm\(^{-1}\) in both complexes may be assigned to \(\text{NH}_3^+\) group of amino acid. The absorption bands in the 1600-1590 cm\(^{-1}\) regions are assigned to the carboxylate ion of coordinated amino acid.

The ligand L-glutamic and L-aspartic possess only two donor sites; amino and carboxylate ion group. The IR frequency of amino group (3100 cm\(^{-1}\)) undergoes a shift of 30 cm\(^{-1}\), thereby, suggesting that the amino group of these ligands are involved in the coordination. Further the coordination through carboxylate ion of the
amino acid invariably results in an increase in v(COO\textsuperscript{-}) by at least 25 cm\textsuperscript{-1}.

### 3.7 SUMMARY

The novel mixed-ligand hexacoordinated cyanonitrosyl complexes of monovalent chromium of the general formula [Cr(NO)(CN)\textsubscript{2}(L)(H\textsubscript{2}O)] (where L = Glutamic acid and Aspartic acid) have been prepared by the interaction of potassium pentacyanonitrosylchromate (I) monohydrate with the said ligands. The complexes, which have been characterized by elemental analysis, magnetic measurements, conductance studies, molecular weight determinations, infrared spectral studies; UV-VIS spectral analysis and NMR studies, contain chromium(I) in a low spin \{CrNO\}\textsuperscript{5} electron configuration.

A suitable octahedral structure where CN is \textit{trans} to CN and L is \textit{trans} to L, and NO is \textit{trans} to water is proposed for all the complexes. It is observed that –

(i) All the complexes are air stable coloured solids.
(ii) They are soluble in DMF, DMSO, ethanol and methanol but insoluble in nitrobenzene and ethyl acetate.

(iv) All the complexes contain $\{\text{CrNO}\}^5$ electron configuration.

(v) All the compounds are thermally stable upto $300^\circ C$.

(vi) All of them give pink colour with Griess Reagent.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>I.U.P.A.C. Name</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)₂(Glutamic Acid)(H₂O)]</td>
<td>aquadicyano glutamic acid nitrosylchromium(I)</td>
<td>(CrNO)⁵</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₂(Aspartic Acid)(H₂O)]</td>
<td>aquadicyano aspartic acid nitrosylchromium(I)</td>
<td>(CrNO)⁵</td>
</tr>
</tbody>
</table>
Table 3.2

Analytical Data of the Complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>% Cr Found (Calc.)</th>
<th>% C Found (Calc.)</th>
<th>% H Found (Calc.)</th>
<th>% N Found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)$_2$(Glutamic Acid)(H$_2$O)]</td>
<td>17.00 (17.39)</td>
<td>27.50 (28.09)</td>
<td>3.60 (3.67)</td>
<td>18.02 (18.73)</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)$_2$(Aspartic Acid)(H$_2$O)]</td>
<td>17.50 (18.24)</td>
<td>24.76 (25.26)</td>
<td>3.01 (3.15)</td>
<td>18.84 (19.64)</td>
</tr>
</tbody>
</table>
Table 3.3
Colour, Decomposition Temperature and % Yield of the Complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>Colour</th>
<th>Decomposition Temperature (°C)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>([\text{Cr(NO)}(\text{CN})_3(\text{Glutamic Acid})(\text{H}_2\text{O})])</td>
<td>Light-Brown</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>2.</td>
<td>([\text{Cr(NO)}(\text{CN})_3(\text{Aspartic Acid})(\text{H}_2\text{O})])</td>
<td>Greenish brown</td>
<td>300</td>
<td>53</td>
</tr>
</tbody>
</table>
Table 3.4

Solubilities of the Complexes in different Solvents

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>DMF</th>
<th>DMSO</th>
<th>EtOH</th>
<th>MeOH</th>
<th>Nitrobenzene</th>
<th>Ethylacetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)₆(Glutamic Acid)(H₂O)]</td>
<td>50%</td>
<td>60%</td>
<td>32%</td>
<td>25%</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₆(Aspartic Acid)(H₂O)]</td>
<td>45%</td>
<td>55%</td>
<td>30%</td>
<td>20%</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>Dehydration temperature (°C)</th>
<th>(molecular weight)</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)₆(Glutamic Acid)(H₂O)]</td>
<td>300</td>
<td></td>
<td>297</td>
<td>299</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₆(Aspartic Acid)(H₂O)]</td>
<td>300</td>
<td></td>
<td>282</td>
<td>285</td>
</tr>
</tbody>
</table>
Table 3.6

Magnetic and ESR data of the Complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ (M.)</th>
<th>'g'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)$_2$(Glutamic Acid)(H$_2$O)]</td>
<td>1.75</td>
<td>1.980</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)$_2$(Aspartic Acid)(H$_2$O)]</td>
<td>1.71</td>
<td>1.986</td>
</tr>
</tbody>
</table>
Table 3.7

Important IR spectral bands and their assignments

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>$v_{(NO)}$</th>
<th>$v_{(CN)}$</th>
<th>$v_{(NH\cdots)}$ cm$^{-1}$</th>
<th>$v_{(OH)}$</th>
<th>$v_{(COOH)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)$_3$(Glutamic Acid)(H$_2$O)]</td>
<td>1715</td>
<td>2155</td>
<td>3050 1510</td>
<td>3575</td>
<td>1598</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)$_3$(Aspartic Acid)(H$_2$O)]</td>
<td>1730</td>
<td>2185</td>
<td>3100 1545</td>
<td>3579</td>
<td>1595</td>
</tr>
</tbody>
</table>
Glutamic acid

Aspartic acid