Chapter IV

Synthesis
and characterization of some novel
hexa coordinated mixed ligand
cyanonitrosyl \( \{\text{CrNO}\}^5 \) complexes of
chromium with tyrosine and arginine.
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4.1 Introduction

In chapter III, synthesis and characterization of some novel mixed ligand cyanonitrosyl \{CrNO\}^5 complexes of chromium with Glutamic acid and Aspartic acid have been discussed. In continuation of our interest to synthesize and characterize some neutral mixed ligand cyanonitrosyl \{CrNO\}^5 complexes of monovalent chromium, studies have been extended using Tyrosine and Arginine.

4.2 EXPERIMENTAL

(a) Materials employed:

Tyrosine and Arginine were obtained from Sisco Research Laboratories Pvt. Ltd. Mumbai.
(b) **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:**

Magnetic susceptibility measurements of the synthesized 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.

4.3 **PREPARATION OF THE PARENT COMPOUND**

Potassium pentacyanonitrosylchromate(II) monohydrate $K_3[Cr(NO)_2(CN)_6].H_2O$ was again used as the parent compound for synthesizing the complexes under this investigation.

4.4 **PREPARATION OF COMPLEXES**

(a) **Preparation of $[Cr(NO)(CN)_2(Tyrosine)(H_2O)]$$^-$**

To a filtered aqueous solution (40 ml, 0.02M) of potassium salt of the pentacyanonitrosylchromate(II) monohydrate, an aqueous acetic acid solution (10 ml, 1:1) of the Tyrosine ligand (0.02M) was added with
shaking. When a brownish-greenish coloured solid was precipitated on warming the mixture for 20 minutes over a hot plate at 80°C., the resulting mixture was freed from the liberated HCN by passing a current of CO₂ for few hours. The precipitate was filtered, washed several times with water and finally with ethanol and ether and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in table 4.2

(b) Preparation of [Cr(NO)(CN)₆(Arginine)(H₂O)]

To a filtered aqueous solution (40 ml., 0.02M) of potassium salt of the pentacynonitrosyl- chromate(I) monohydrate, an aqueous acetic acid solution (10 ml, 1:1) of the Arginine (0.02M) was added with shaking. When a greenish-yellow coloured solid was precipitated on warming the mixture for 20 minutes over a hot plate at 80°C., the resulting mixture was freed from the liberated HCN by passing a current of CO₂ for few hours. The precipitate was filtered, washed several times with water and finally with ethanol and ether and dried in vacuo over silica gel at room
temperature to a constant weight. The analytical data are given in table 4.2.

4.5 PROPERTIES OF COMPLEXES

All the complexes are coloured solids (see Table 4.3 for colours). They are stable in air. Solubilities of these complexes in different solvents are given in Table 4.4. The complexes are thermally stable and do not melt or decompose up to 260°C (Table 4.3). 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.

4.6 RESULTS AND DISCUSSION

The mixed-ligand cyanonitrosyl complexes (see Table 4.1 for ligand names) were synthesized according to equation (1).

\[ \text{K}_2[\text{Cr(NO)(CN)}_2\text{H}_2\text{O} + \text{L}] \xrightarrow{\text{AcOH, H}_2\text{O}} [\text{Cr(NO)(CN)}_2\text{(L)}(\text{H}_2\text{O})] + 3\text{KOAC} + 3\text{HCN} + \text{H}_2\text{O} \]

Where L = Tyrosine, Arginine
The partial replacement of cyano groups in the hexa co-ordinated complexes, \( K_3[Cr(NO)(CN)_5].H_2O \) by two molecules of ligand, \( L \), arises from the trans effect of the NO group. Studies of Raynor and co-workers on stepwise aquation of the pentacyanonirosylchromate(I) \([Cr(NO)(CN)_5]^3-\) to attain \([Cr(NO)(CN)_3(H_2O)_3]\) favour the above reaction scheme.

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(amine), 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 for these complexes are presented in Table 4.5. 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 4.7. 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 spectral studies**

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 $\nu$(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 $\nu$(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 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-lyrosine and L-arginine 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 \(\nu(\text{COO}^-)\) by at least 25 cm\(^{-1}\).

4.7 SUMMARY

The novel mixed-ligand hexacoordinated cyanonitrosyl complexes of monovalent chromium of the general formula \([\text{Cr(NO)}(\text{CN})_2(L)(\text{H}_2\text{O})]\) (where L = Lyrosine and Arginine) 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 \(\{\text{CrNO}\}^5\) 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.

(iii) All the complexes contain \{CrNO\}^5 electron configuration.

(iv) All the compounds are thermally stable upto 300°C.

(v) All of them give pink colour with Griess Reagent.
Table 4.1

I.U.P.A.C. Name and Electron Configuration of the synthesized complexes

<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(Tyrosine)(H₂O)]</td>
<td>aquadicyano tyrosine nitrosylchromium(I)</td>
<td>{CrNO}⁵</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₂(Arginine)(H₂O)]</td>
<td>aquadicyano arginine nitrosylchromium(I)</td>
<td>{CrNO}⁵</td>
</tr>
</tbody>
</table>
### Table 4.2

**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>([\text{Cr(NO)(CN)}_2(\text{Tyrosine})(\text{H}_2\text{O})])</td>
<td>14.98 (15.61)</td>
<td>38.76 (39.63)</td>
<td>3.85 (3.90)</td>
<td>15.76 (16.81)</td>
</tr>
<tr>
<td>2.</td>
<td>([\text{Cr(NO)(CN)}_2(\text{Arginine})(\text{H}_2\text{O})])</td>
<td>15.20 (15.85)</td>
<td>28.76 (29.26)</td>
<td>4.60 (4.87)</td>
<td>29.36 (29.87)</td>
</tr>
</tbody>
</table>
Table 4.3

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>[Cr(NO)(CN)$_2$(Tyrosine)(H$_2$O)]</td>
<td>Greenish brown</td>
<td>270</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>[Cr(NO)(CN)$_2$(Arginine)(H$_2$O)]</td>
<td>Brown</td>
<td>270</td>
<td>45</td>
</tr>
</tbody>
</table>
Table 4.4

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)₂(Tyrosine)(H₂O)]</td>
<td>65%</td>
<td>70%</td>
<td>35%</td>
<td>25%</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₂(Arginine)(H₂O)]</td>
<td>60%</td>
<td>65%</td>
<td>30%</td>
<td>20%</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>
Table 4.6

Dehydration temperature and molecular weight of the Complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>Dehydration temperature</th>
<th>molecular weight</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)(_2)(Tyrosine)(H(_2)O)]</td>
<td>115(^\circ)C</td>
<td>328</td>
<td>333</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)(_2)(Arginine)(H(_2)O)]</td>
<td>120(^\circ)C</td>
<td>322</td>
<td>328</td>
</tr>
</tbody>
</table>
Table 4.7

Magnetic and ESR data of the Complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>'g'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)$_2$(L)(H$_2$O)]</td>
<td>1.72</td>
<td>1.980</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)$_2$(L)(H$_2$O)]</td>
<td>1.75</td>
<td>1.984</td>
</tr>
</tbody>
</table>
Table 4.8

Important IR spectral bands and their assignments

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>$v_{(\text{NO})}$</th>
<th>$v_{(\text{CN})}$</th>
<th>$v_{(\text{N cyclic})}$ $\text{cm}^{-1}$</th>
<th>$v_{(\text{OH})}$</th>
<th>$v_{(\text{M-H})}$ $\text{cm}^{-1}$</th>
<th>$v_{(\text{COOH})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)$_2$(L)(H$_2$O)]</td>
<td>1712</td>
<td>2155</td>
<td>1370</td>
<td>3575</td>
<td>3090</td>
<td>1535</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)$_2$(L)(H$_2$O)]</td>
<td>1725</td>
<td>2189</td>
<td>1375</td>
<td>3578</td>
<td>3080</td>
<td>1510</td>
</tr>
</tbody>
</table>