Chapter II

This chapter describes the analysis of the constituent elements and the procedures for the preparation of complexes followed by their properties.
EXPERIMENTAL

A- ANALYSIS OF THE CONSTITUENT ELEMENTS:

Nitrogen:

When the compound contained thiocyanate group or ligands like o-phenanthroline, dipyridyl, etc., when a tertiary nitrogen was a member of the ring, the nitrogen content was determined microanalytically by Dubois's method.

Carbon and Hydrogen:

Carbon and hydrogen present in the sample were estimated microanalytically.

Estimation of Chromium:

For the estimation of chromium as chromic oxide, the compounds were decomposed by heating with alkali followed by dissolving in nitric acid. Chromium was precipitated as chromic hydroxide by means of the slightest possible excess of dilute NH₄OH. The chromic hydroxide when ignited was converted into Cr₂O₃. Repeated heating, cooling and weighing were carried out until weight became constant.

Estimation of Sulphur:

An aqueous suspension of the chromium complex containing sulphur was treated with bromine water and the solution was heated on a water bath for complete oxidation. Digestion was continued till the solution after evaporation of the excess bromine became perfectly colourless. The solution was then acidified with dilute HCl and the sulphate produced was precipitated by addition of BaCl₂ solution and estimated as usual.
PREPARATION AND PROPERTIES OF THE COMPLEXES:

Reagents:

Reagents used for example, chromium trioxide, hydroxylaminehydrogenchloride, potassium hydroxide, potassium cyanide and ligands were of analytical grade. Deaerated water was used in all operations.

Preparation of potassium pentacyanonitrosylchromate(I)-hydrate, \( K_3[CrCN(CN)_5] \cdot H_2O \):

Potassium salt of pentacyanonitrosylchromate(I)-monohydrate was prepared according to the procedure of Griffith, Lewis and Wilkinson and was characterized by elemental analyses and infrared spectroscopy.

Found:

\[ K, 33.8; Cr, 15.1; C, 18.05; N, 24.2; H_2O, 5.1\% . \]

\( K_3[CrCN(CN)_5] \cdot H_2O \) requires \( K, 33.8; Cr, 15.1 \;\%

\[ C, 17.3; N, 24.2; H_2O, 5.2\% . \]

Preparation of dicyanodipryidylnitrosylchromium(I), \([CrNC(CN)_2(dipy)]\):

Into a filtered aqueous solution (20 ml.) of potassium salt of pentacyanonitrosylchromate(I)hydrate (1.5 g), a solution of dipyridyl (0.75 g) in acetic acid-water (1:1, 10 ml.) was added. The resulting solution was warmed for 10 min. and diluted with 30 ml. of water when a greenish yellow solid precipitated. The resulting mixture was freed from liberated
hydrocyanic acid by passing a current of \( \text{Cl}_2 \) through the mixture for an hour and the precipitate was filtered off, washed with water, alcohol and ether and dried in vacuum to a constant weight and analysed. The yield based on pentacyanonitrosylchromate(I) was 80%.

\textbf{Found:}

\[ \text{Cr}, \ 16.1; \ N, \ 24.2; \ C, \ 49.6; \ H, \ 2.6\% \]

\[ [\text{Cr}(\text{CN})_2(\text{dipy})] \text{ requires Cr, 17.9; N, 24.1; C, 49.7; H, 2.76\%}. \]

Preparation of dicyanomethylene-phenanthroline-nitrosylchromium(I), \( [\text{Cr}(\text{CN})_2(\text{o-phen})] \):

A filtered aqueous solution (20 ml.) of potassium salt of pentacyanonitrosylchromate(I) hydrate (1.5 g) was added slowly into an aqueous-acetic acid (1:1, 10 ml.) of o-phenanthroline (1.0 g) with shaking when immediate greenish yellow solid started to precipitate. After the total addition, the liberated hydrocyanic acid was driven off in identical fashion as described earlier, and the precipitate was filtered off, washed with water, alcohol, ether and dried in vacuo.

\textbf{Found:}

\[ \text{Cr}, \ 16.7; \ N, \ 22.3; \ C, \ 53.5; \ H, \ 2.7\% \]

\[ [\text{Cr}(\text{CN})_2(\text{o-phen})] \text{ requires Cr, 16.6; N, 22.3; C, 53.5; H, 2.5\%}. \]
Preparation of dicyanodi(pyridine)nitröxychromium(II),
\[ \text{CrCl}_2(\text{CN})_2(\text{py})_2 \]:—

A filtered aqueous solution (25 ml.) of potassium salt of pentacyanoni-trosylchromate(I)hydrate (2.00 g) was added into an aqueous-acetic acid (1:1, 15 ml.) of pyridine (2.5 ml.). The resulting green solution was immediately diluted with air free water (100 ml.) and the mixture was kept in warm condition. Carbon dioxide was allowed to bubble through the solution to chase the liberated hydrocyanic acid when a yellow solid was started to precipitate. After two hrs. the precipitation was completed, which was filtered washed with water, alcohol and ether and dried in vacuo.

Found:
Cr, 17.8; N, 24.1; C, 48.9; H, 3.6%

\[ \text{CrCl}_2(\text{CN})_2(\text{py})_2 \] requires Cr, 17.8; N, 24.0; C, 49.3; H, 3.4%.

Preparation of dicyanobis(quinoline)nitröxychromium(II).
\[ \text{CrCl}_2(\text{CN})_2(\text{qu})_2 \]:—

The complex was prepared by following an identical procedure described in the preparation of the corresponding pyridine complex just by replacing pyridine with quinoline and the passing of Cu₂ was continued for a period of 6 hrs. to get the yellow coloured complex.
Found:

\[ \text{Cr, 13.1; N, 11.7; C, 61.0; H, 3.6\%} \]

\[ \text{[CrCl(CN)_2(Qu)]_2 requires Cr, 13.3; N, 17.9; C, 61.2; H, 3.6\%} \]

Preparation of dicyanodi(\(\beta\)-picoline)nitrosylchromium(I),

\[ \text{Cr(NH}_2\text{CN})_2 (\beta\text{-picoline})_2 \text{ :-} \]

A somewhat identical procedure was followed as described earlier for the preparation of this complex replacing pyridine by \(\beta\)-picoline.

Found:

\[ \text{Cr, 16.2; C, 52.4; N, 21.8; H, 4.3\%} \]

\[ \text{[Cr(NH}_2\text{CN})_2(\beta\text{-picoline})_2 \text{ requires Cr, 16.3; C, 52.5; N, 21.9; H, 4.4\%} \]

Preparation of dicyanodi(\(\gamma\)-picoline)nitrosylchromium(I),

\[ \text{[CrCl(CN)_2(\gamma\text{-picoline})_2 \text{ :-} \]}

This complex was also prepared by following an identical procedure described in the preparation of the corresponding pyridine complex just by replacing pyridine by \(\gamma\)-picoline.

Found:

\[ \text{Cr, 16.2; C, 52.3; N, 21.7; H, 4.3\%} \]

\[ \text{[CrCl(CN)_2(\gamma\text{-picoline})_2 \text{ requires Cr, 16.3; C, 52.5; N, 21.9; H, 4.4\%} \}

Properties of the cyano substituted complexes,

\[ \text{[CrCl(CN)_2 L}_2 \text{ :-} \]

All the cyano substituted complexes are obtained as yellow highly dispersed solids having slight green tinges. They are exceptionally stable in
air and remain almost unattacked in dilute acids or alkalis and decomposed only on warming. Thermally they are also stable and do not show any melting or decomposition up to a temperature of 250°C (Table-11). All these complexes are slightly soluble in acetoni-trile being insoluble in other common solvents. Ligands of good donor capacity like pyridine, dipyridyl or triphenylphosphine could not be accommodated in the sixth position even under drastic sealed tube reaction.

\[
\text{[Cr}_\text{II}^\text{(CN)}_2\text{L}_2\text{]} + \text{excess py sealed tube } \xrightarrow{\Delta} \text{ no change.}
\]

\[
\text{[Cr}_\text{III}^\text{(CN)}_2\text{L}_2\text{]} + \text{excess dipy sealed tube } \xrightarrow{\Delta} \text{ no change.}
\]

\[
\text{[Cr}_\text{III}^\text{(CN)}_2\text{L}_2\text{]} + \text{excess pph}_3 \text{ sealed tube } \xrightarrow{\Delta} \text{ no change.}
\]

Attempts to methylate the cyano groups in the cyano substituted compounds using \((\text{CH}_3)_2\text{S}_2\text{N}_4\) or \(\text{CH}_3\text{I}\) in sealed tube were unsuccessful.

\[
\text{[Cr}_\text{III}^\text{(CN)}_2\text{L}_2\text{]} + \text{CH}_3\text{I sealed tube } \xrightarrow{\Delta} \text{ no change.}
\]

\[
\text{[Cr}_\text{III}^\text{(CN)}_2\text{L}_2\text{]} + (\text{CH}_3)_2\text{S}_2\text{N}_4 \text{ sealed tube } \xrightarrow{\Delta} \text{ no change.}
\]

Methylation reaction was also found to be unsuccessful when it was carried out using \(\text{CH}_3\text{I}\) with \(\text{HgI}_2\) in sealed tube. Though the products isolated in these reactions showed the presence of methylisocyanide retaining nitrosyl group yet they appeared to contain some decomposed product or unreacted starting compound.
\[ \text{CrM} \cdot (\text{Cr})_2 \cdot \text{I}_2 + \text{CH}_3 \text{I} + \text{MgI}_2 \rightarrow \text{sealed tube} \]
\[ \text{partial decomposition with no change.} \]

The mol. z conductance values of practically saturated anhydrous methanol solution \(10^{-4} \text{M}\) of these cyanometal complexes (Table-11) suggest their non-electrolytic nature.

\[ \text{No-2 : preparation of bis(acetylacetonato)nitrosylchromium(I), } \]
\[ \text{[Cr}^{\neq} \text{(acac)}_2]^- \]

The complex was prepared by refluxing a mixture of \(K_2\text{[Cr}^{\neq} \text{(Cr)}_2 \cdot \text{I}_2\) (2.0 g) and excess acetylacetonate (6 ml.) in an air tight compartment with an intermittent removal of the liberated hydrogen cyanide by passing dry carbon dioxide. After refluxing for 8 hrs., the excess acetylacetonate was distilled off and the resultant mixture was cooled in vacuo over solid KOH. Traces of free acetylacetone were removed from the cooled brown mass by repeated using with petroleum ether and brown crust was extracted with acetone. In evaporation of acetone, the solution gave brown crystals which were washed with petroleum ether. The crystallization process was repeated thrice. The crystals thus obtained were dried and analysed.

**Found:**

\[ \text{Cr, 10.6; N, 5.0; C, 42.9; H, 5.32\%;} \]
\[ \text{[Cr}^{\neq} \text{(acac)}_2] \text{ requires Cr, 10.6; N, 5.0; } \]
\[ \text{H, 6.23\%;} \]
Properties:

This non-electrolytic monomeric complex (Table-11) is soluble in most of the common non-polar organic solvents but insoluble in water. Its stability is comparable to that of Cr(acac)$_3$ as it remains unaffected by concentrated alkalies or mineral acids in cold and decomposes only on prolonged boiling. This complex does not show any interaction with ethanol suggesting that solvation does not take place at the sixth position. But when it is refluxed with traces of pyridine in ethanol, pyridine shows interaction at the sixth position and this has been demonstrated by e.s.r. spectroscopy (due in?re).

D-3 Preparation of aquochloro(dimethyl ditiancarbamate) nitrosyl hexacyanoferrate(I), [CrCl$_2$(DTC)$_2$(H$_2$O)$_2$, ]$^-$

1.5 g of potassium pentacyan cittosyl chromate(I) dichloride was dissolved in 30 ml. of water and into it an aqueous solution of dimethyl ditian carbamate (1.0 g) was added. Into the mixed solution 10 ml. of (1:1) dilute acetic acid was slowly added with stirring and the issuing gas was chased by a current of carbon dioxide, whereby, reddish brown precipitate appeared which was filtered under suction, washed several times with water. This precipitate is now extracted with acetone and the red
brown compound was precipitated by adding petroleum ether, washed with petroleum ether, dried and analysed. The yield was approximately 35%.

Found:

\[ \text{C}_x13.2; \text{ C}, 30.1; \text{ N}, 10.5; \text{ H}, 5.5\% \]

\[ \text{C}_{\text{XII}}(\text{BTC})_2(\text{H}_2\text{O}) \text{ requires } \text{C} 13.1; \text{ C}, 30.3; \]

\[ \text{N}, 10.6; \text{ H}, 5.5\% \]

Properties:

This complex is soluble in alcohol, acetone and acetonitrile to impart orange red colour and in methanol the complex is found to be non-electrolytic in nature (Table-11).

1-4 Preparation of diaminotriazene-dipyridyl nitrosylchromium(III), \[ \text{C}_{\text{XII}}(\text{BTC})_2(\text{dipy}) \]:

1.0 g of potassium chromate and 3.0 g of potassium thiocyanate was taken in a beaker and 40 ml. of water was added to dissolve the mixture. 1.0 g hydrazinohydrogenchloride was slowly added into the solution with stirring. A vigorous reaction sets in and addition of hydrazinohydrogenchloride was cautiously done to control the temperature (further addition leads to the expulsion of N\(_2\)). After the addition of hydrazinohydrogenchloride the reaction mixture was stirred at room temperature for an hr. and any grey colour precipitate was allowed to
Table 11
physical properties

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>$\Lambda$ $\mu$m$^{-1}$ cm$^{-2}$ mole$^{-1}$</th>
<th>m.p. $^\circ$C</th>
<th>Pol. U.L.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CuN}(CN)_2(dip)]$</td>
<td>Greenish yellow</td>
<td>16.2</td>
<td>$&gt;250^\circ$C</td>
<td></td>
</tr>
<tr>
<td>$[\text{CuN}(CN)_2(o\text{-phen})]$</td>
<td>Greenish yellow</td>
<td>13.5</td>
<td>$&gt;250^\circ$C</td>
<td></td>
</tr>
<tr>
<td>$[\text{CuN}(CN)_2(py)_2]$</td>
<td>Yellow</td>
<td>15.2</td>
<td>$&gt;250^\circ$C</td>
<td></td>
</tr>
<tr>
<td>$[\text{CuN}(CN)_2(Qu)_2]$</td>
<td>Brownish yellow</td>
<td>8.2</td>
<td>$&gt;250^\circ$C</td>
<td></td>
</tr>
<tr>
<td>$[\text{CuN}(CN)_2(\beta\text{-picoline})_2]$</td>
<td>Greenish yellow</td>
<td>13.2</td>
<td>$&gt;250^\circ$C</td>
<td></td>
</tr>
<tr>
<td>$[\text{CuN}(CN)_2(\gamma\text{-picoline})_2]$</td>
<td>Greenish yellow</td>
<td>14.3</td>
<td>$&gt;250^\circ$C</td>
<td></td>
</tr>
<tr>
<td>$[\text{CuN}(acac)_2]$</td>
<td>Brown</td>
<td>13.2</td>
<td>206$^\circ$C</td>
<td>300</td>
</tr>
<tr>
<td>$[\text{CuN}(BTC)_2(H_2O)]$</td>
<td>Reddish brown</td>
<td>17.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
dissolve by adding dropwise dilute acetic acid. To the filtered green solution, 0.18 g of dipyrizidyl dissolved in dilute acetic acid was added, a khaki colour precipitate appeared which was stirred for an hr. at a temperature around 90° and filtered. The precipitate was washed several times with dilute acetic acid, finally washed with water, dried in air and recrystallised from methanol-petroleum ether. The yield was approximately 45%.

**Found:**

Cr, 14.6; C, 40.5; N, 15.7; H, 2.1; S, 10.1%

\[\text{Cr} (\text{NCS})_2 (\text{dipy})\] requires Cr, 14.7; C, 40.7;

N, 19.0; H, 2.2; S, 10.0%.

iso

Preparation of 1-thiocyanato-9,10-phenanthroline-
1-nitrosochromium(II), \[\text{Cr} (\text{NCS})_2 (\text{o-phen})\]:-

The corresponding o-phenanthroline complex was prepared analogously as described above just by replacing dipyrizidyl with o-phenanthroline. The olive green recrystallised compound was analysed.

**Found:**

Cr, 13.6; C, 44.2; N, 16.3; H, 2.1; S, 15.3%

\[\text{Cr} (\text{NCS})_2 (\text{o-phen})\] requires Cr, 13.0; C, 44.4;

N, 18.5; H, 2.1; S, 16.8%.
Preparation of dithiocyanodipyridylpyridinonitrosochromium(I), \([\text{CrI}(NCS)_2(\text{dipy})(\text{py})]\) :-

About 0.5 g of dithiocyanodipyridylpyridinonitrosochromium(I) was dissolved in 15 ml. of acetone and 1 ml. of pyridine was added into it. The solution was refluxed for about 2 hrs. on a water bath with positive pressure of the inside solvent vapour (using a pool of mercury) and the resultant solution was vacuum concentrated. The product was isolated from the solution by adding petrolatum ether as yellow solid which was recrystallised from acetonepetroleum ether mixture. The yield was approximately 75%.

Found:

Cr, 11.5; C, 47.0; H, 15.2; N, 2.9; S, 14.6%  

\([\text{CrI}(NCS)_2(\text{dipy})(\text{py})]\) requires Cr, 12.0; C, 47.1; 
N, 19.4; H, 3.0; S, 14.0%.

Preparation of dithiocyanatoortho-phenanthroline-
pyridinonitrosochromium(I), \([\text{CrI}(NCS)_2(o-\text{phen})(\text{py})]\) :-

The o-phenanthroline analogue of the previous compound was prepared analogously just by taking dithiocyanato-ortho-phenanthroline nitrosochromium(I) instead of dithiocyanodipyridylpyridinonitrosochromium(I) as described earlier. The yellow xeroprecipitated compound from acetone-petroleum ether mixture was dried and analysed.
Found:

Cr: 11.3; C, 49.8; N, 18.2; H, 2.7; S, 13.9%

$[\text{Cr(NCS)}_2(\text{c-phen})(\text{py})]$ requires Cr, 11.4;
C, 49.9; N, 16.4; H, 2.8; S, 14.0%.

Properties of thiocyanato substituted complexes:

The thiocyanato substituted complexes are greenish yellow to yellow in colour and are highly soluble in alcohol and acetone. Alcoholic or acetone solution of these complexes impart greenish yellow colour and addition of manganic silver nitrate does not give any immediate precipitation but on standing silver is deposited. The molar conductivity of $[\text{Cr(NCS)}_2(\text{dipy})]$ and $[\text{Cr(NCS)}_2(\text{c-phen})]$ are found to be 15.3 and 12.7 $\Omega^{-1}\text{cm.}^2\text{ mole}^{-1}$ respectively suggesting that the complexes are non-electrolytic in nature. The other complexes are also non-electrolytic in nature (Table-12).

It is interesting to note that complexes of (CrIII) moiety with S- or O-donor are coloured reddish brown whereas when the donor is only nitrogen the colour is predominantly yellow. For mixed carbon-nitrogen donor sites, colour is green.

All the complexes described here are somewhat stable in acids but on treatment with alkali the complexes decompose and the coordinated nitrosyl group changes to NO$^-$, which can be tested by using Griess
<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>$\lambda_{\text{fi}}$ cm$^{-1}$ cm$^2$ mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CnMo(NCS)}_2(\text{dipy})]$</td>
<td>Khaki</td>
<td>15.3</td>
</tr>
<tr>
<td>$[\text{CnMo(NCS)}_2(\text{o-phen})]$</td>
<td>Olive green</td>
<td>12.7</td>
</tr>
<tr>
<td>$[\text{CnMo(NCS)}_2(\text{dipy})(\text{py})]$</td>
<td>Yellow</td>
<td>13.6</td>
</tr>
<tr>
<td>$[\text{CnMo(NCS)}_2(\text{o-phen})(\text{py})]$</td>
<td>Yellow</td>
<td>12.9</td>
</tr>
</tbody>
</table>
reagent. This suggests that though the well known complex, $K_3[CrN_2(C\equiv N)_5]$, $K_2L$ has been isolated in strong alkali medium, yet depending on the nature of co-ligands the same $(CrN_2)^{2+}$ moiety is attacked by alkali with the concomitant conversion of coordinated nitric oxide to $N_2\equiv$ as known for intrapustide anion (vide-supra).

The physico-chemical aspects of these complexes have been discussed in the chapter of structural chemistry of the complexes.