6.1 **INTRODUCTION**

Synthesis and structural investigation of some mixed-ligand cyanonitrosyl \( \{\text{CrNO}\}_5 \) complexes of chromium with some potentially monodentate pyridine derivative like 2-picolylichloride and bidentate pyridine derivatives like ethyl 2-pyridylacetate, 2-(2-methylaminoethyl)pyridine, 3-acetoxypyridine and N,N-diethylnicotinamide have been discussed in Chapter-V. In view of our interest to synthesize and characterize some novel mixed-ligand cyanonitrosyl complexes of monovalent chromium, studies have been extended to synthesize and characterize such complexes with some biologically active organic compounds.

Although in recent years there has been a great upsurge in synthesis and characterization of some neutral mixed-ligand
cyanonitrosyl complexes of monovalent chromium, there is only one report by R.C. Maurya (4) on mixed-ligand cyanonitrosyl complexes of monovalent chromium with quinoline. Further, quinoline derivatives have been reported to be of great biological importance (59, 60). It is, therefore, thought of interest to synthesize and characterize some novel mixed-ligand cyanonitrosyl complexes of chromium with quinoline derivatives like lepidine, quinaldine, 4-hydroxymethylquinoline, 4-chloromethylquinoline and 4-mercaptomethylquinoline. The purpose of selecting these quinoline derivatives in synthesis of titled complexes is to get complexes of effective biological activities.

Lepidine
$\text{CH}_3$

Quinaldine
$\text{CH}_3$

$\text{CH}_2\text{OH}$

$\text{CH}_2\text{Cl}$

4-Hydroxymethylquinoline
M.P. = 96-97°C

4-Chloromethylquinoline
M.P. = 55-57°C
6.2 **EXPERIMENTAL**

(a) **Materials used**: 
Lepidine and quinaldine were obtained from Aldrich Chemical Co., USA. The rest three quinoline derivatives - 4-hydroxymethylquinoline, 4-chloromethylquinoline and 4-mercaptopmethylquinoline were synthesized in our laboratory by the method reported by S.R. Ramadas and co-workers (61).

Hydroxylammonium hydrochloride and chromic acid were supplied by SD’s Lab-Chem. Industry, Bombay. Potassium cyanide was procured from May and Baker limited, Dagenham, England. Distilled water was used in all operations.

(b) **Analysis of the constituent elements**:

(i) Carbon, hydrogen and nitrogen were estimated microanalytically.

(ii) **Estimation of chromium**: Chromium contents of the synthesized complexes were estimated according to the procedure given in Chapter-II.
(c) **Physical Methods**:

(i) **Magnetic measurements**: Room temperature magnetic susceptibility measurements of the investigated complexes were made by Gouy method. Cobalt mercury thiocyanate was used as a calibrant.

(ii) **Infrared spectral measurements**: Infrared spectra (4000-660 cm\(^{-1}\)) were recorded in nujol mulls on a Beckman-IR-20 spectrophotometer at the Department of Chemistry, Kurukshetra University, Kurukshetra.

(iii) **Electron spin resonance spectra**: Synthesized complexes were scanned for electron spin resonance spectra at room temperature using powdered sample on a Varian E-3 spectrometer at the University of British Columbia, Vancouver (Canada).

(iv) **Thermogravimetric Analysis**: The t.g. curves were recorded on a G-70 thermoanalyser, SETARAM, Lyon, France, in air at a heating rate 10°C min\(^{-1}\), and upto 800°C.

6.3 **PREPARATION OF STARTING COMPOUNDS**

Potassium pentacyanonitrosylchromate(I) monohydrate prepared by the method of Wilkinson and co-workers (9). was used as the starting compound for the synthesis of complexes mentioned in this chapter.
6.4 PREPARATION OF THE COMPLEXES

(a) Synthesis of $[\text{Cr(NO)(CN)}_2(\text{Lepn})_2(\text{H}_2\text{O})]$ :

To a filtered aqueous solution of potassium pentacynonitrosylchromate(I)monohydrate ($0.01 \text{ M}, 50 \text{ cm}^3$), an 1:1 aqueous acetic acid solution ($10 \text{ cm}^3$) of lepidine was added with shaking. The resulting green solution was heated for 15 minutes with shaking at $80^\circ\text{C}$ over a hot plate cum magnetic stirrer. CO$_2$ was bubbled through the reaction mixture for a few hours to expel hydrocyanic gas, and a coloured solid was precipitated. This was filtered, washed several times with distilled water and finally with ethanol, and dried in a vacuum desiccator over silica gel at room temperature to a constant weight. Analytical data are given in Table 6.2.

(b) Synthesis of $[\text{Cr(NO)(CN)}_2(\text{Quidn})_2(\text{H}_2\text{O})]$ :

This compound was prepared by following an identical procedure described above taking starting compound, $K_3[\text{Cr(NO)-(CN)}_5]$.H$_2$O and quinaldine. The precipitate so obtained was dried in vacuo over silica gel at room temperature to a constant weight.

(c) Synthesis of $[\text{Cr(NO)(CN)}_2(4-\text{Hmeq})_2(\text{H}_2\text{O})]$:

An identical procedure given above was also adopted in synthesis of this compound taking 4-hydroxymethylquinoline
and $K_3[\text{Cr(NO)(CN)}_2].H_2O$. The analytical data are given in Table 6.2.

(d) Synthesis of $[\text{Cr(NO)(CN)}_2(4-\text{Chlmeq})_2(H_2O)]$:

This compound was also prepared by adopting the similar procedure described above taking 4-chloromethylquinoline and the parent compound. The analytical data are given in Table 6.2.

(e) Synthesis of $[\text{Cr(NO)(CN)}_2(4-\text{Mcpmeq})_2(H_2O)]$:

An identical procedure given above was also adopted in synthesis of this compound taking 4-mercaptomethylquinoline and $K_3[\text{Cr(NO)(CN)}_2].H_2O$. The analytical data are given in Table 6.2.

6.5 PROPERTIES OF COMPLEXES

The resulting compound are coloured solids. They are exceptionally stable in air. All the compound after decomposition with KOH followed by acidifying with acetic acid give a pink colour with a few drops of Griess reagent (29). This test shows the presence of NO group in complexes. They are thermally stable and do not melt or decompose below 300°C. All the compounds are insoluble in common organic solvents as well as in water and, therefore, their molar conductivity values and molecular weights could not be measured.
6.6 RESULTS AND DISCUSSION

The mixed-ligand complexes, $[\text{Cr(NO)}(\text{CN})_2(L)_2(\text{H}_2\text{O})]$ were prepared according to the following equation:

$$K_3[\text{Cr(NO)}(\text{CN})_5].\text{H}_2\text{O} + 2L \xrightarrow{\text{CH}_3\text{COOH}} [\text{Cr(NO)}(\text{CN})_2(L)_2(\text{H}_2\text{O})] + 3\text{CH}_3\text{COOK} + 3\text{HCN} \ (g) + \text{H}_2\text{O}$$

Where $L$ = lepidine, quinaldine, 4-hydroxymethylquinoline, 4-chloromethylquinoline and 4-mercaptomethylquinoline.

The partial replacement of the cyano groups in the hexa-coordinated complex, $K_3[\text{Cr(NO)}(\text{CN})_5].\text{H}_2\text{O}$ by two molecule of ligand arises from the trans effect of the NO group. Studies by Raynor and co-workers (35) on the stepwise aquation of the pentacyanonitrosylchromate(I), $[\text{Cr(NO)}(\text{CN})_5]^{3-}$, thereby attaining the third aquated species of composition, $[\text{Cr(NO)}(\text{CN})_2^-(\text{H}_2\text{O})_3]$ favour the above reaction scheme.

Compound were characterised on the basis of the following result:

(i) Infrared spectra:

The important infrared spectral bands of the complexes are presented in Table 6.6. The appearance of a very strong band in 1680–1705 cm$^{-1}$ region and a strong band in 2135–2150 cm$^{-1}$ region are assigned to $\nu$(NO)$^+$ and $\nu$(CN) modes, respectively.
which are in accordance with assignment made for other reported complexes (7,8).

All the ligands used in the present study, Lepn, Quidn, 4-Hymeq, 4-chlmeg and 4-Mcpmeq possess only the ring nitrogen as the donor site. Coordination through the ring nitrogen atom causes an increase in the ring stretching $\nu$(C=C) and $\nu$(C=N) frequencies in the donor molecules similar to quinoline derivatives. The appearance of $\nu$(C=N) and $\nu$(C=C) modes due to ring nitrogen in all the complexes under study around 1600 and 1560 cm$^{-1}$, respectively (as compared to those of the free quinoline derivatives around 1570 and 1540 cm$^{-1}$) is indicative of the coordination of these ligand through the ring nitrogen atom as suggested by Ramana Rao et.al. (62).

All the complexes exhibit the $\nu$(OH) stretching in the region 3575-3580 and 3375-3400 cm$^{-1}$; the occurrence of $\nu$(OH) band is indicative of coordinated water in these complexes (10).

(ii) Thermogravimetric analysis:

The dehydration temperature obtained by T.G.A. are presented in Table 6.4. The weight loss observed at the dehydration temperature for each compound corresponds to the elimination of one molecule of water. This result supports the presence of one molecule of water in each compound. (Vide infrared discussion for coordinated water in these complexes).
(iii) Magnetic and e.s.r. studies:

The magnetic and electron spin resonance data of the complexes are given in Table 6.5. The magnetic moments, 1.70-1.74 B.M., at room temperature and 'g' values, 1.980-1.987 of powdered compounds, which are comparable to the observation made by Manoharan and Gray (36) and Meriwether et al. (37), are consistent with a low-spin d⁵-configuration of chromium(I).

6.7 SUMMARY

Some new mixed-ligand cyanonitrosyl complexes of chromium (I) with the formulation [Cr(NO)(CN)₂(L)₂(H₂O)] where L = Lepn, Quidn, 4-chlmeq, 4-Hymeq, and 4-Mcpmeq have been synthesized by substitution of the cyano groups in K₃[Cr(NO)(CN)₅].H₂O by the above ligands, L. The complexes have been characterized in solid state on the basis of elemental analyses, room temperature magnetic measurements, electron spin resonance and infrared spectral studies. A suitable octahedral structure has been proposed for all the complexes. It is observed that:

(i) All the complexes are coloured solid.

(ii) All the complexes are insoluble in common organic solvents as well as in water and hence their conductance studies and molecular weight determination could not be carried out.
Fig. 6.1: Proposed octahedral structure of 
$[\text{Cr(NO)}(\text{CN})_2(\text{L})_2(\text{H}_2\text{O})]$, where $\text{L = Lepn, Quidn, 4-Hymeq, 4-Chlmeq or 4-Mcpmeq.}$
(iii) All the complexes contain a low-spin $\{\text{CrMo}\}^5$
electron configuration.

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

(v) They all give positive Griess reagent test.
Table - 6.1

Nomenclature and Electron configuration of 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>([\text{Cr(NO)(CN)}_2(\text{Lepn})_2(\text{H}_2\text{O})])</td>
<td>Aquadicyanobis (lepidine)-nitrosylchromium (I)</td>
<td>({\text{CrNO}}_5)</td>
</tr>
<tr>
<td>2.</td>
<td>([\text{Cr(NO)(CN)}_2(\text{Quidn})_2(\text{H}_2\text{O})])</td>
<td>Aquadicyanobis (quinaldine)-nitrosylchromium (I)</td>
<td>({\text{CrNO}}_5)</td>
</tr>
<tr>
<td>3.</td>
<td>([\text{Cr(NO)(CN)}_2(4-\text{Hymeq})_2(\text{H}_2\text{O})])</td>
<td>Aquadicyanobis (4-hydroxymethylquinoline)-nitrosylchromium (I)</td>
<td>({\text{CrNO}}_5)</td>
</tr>
<tr>
<td>4.</td>
<td>([\text{Cr(NO)(CN)}_2(4-\text{Chlmeq})_2(\text{H}_2\text{O})])</td>
<td>Aquadicyanobis (4-chloromethylquinoline)-nitrosylchromium (I)</td>
<td>({\text{CrNO}}_5)</td>
</tr>
<tr>
<td>5.</td>
<td>([\text{Cr(NO)(CN)}_2(4-\text{Mcpmeq})_2(\text{H}_2\text{O})])</td>
<td>Aquadicyanobis (4-mercaptopmethylquinoline)-nitrosylchromium (I)</td>
<td>({\text{CrNO}}_5)</td>
</tr>
</tbody>
</table>

Abbreviation: Lepn = Lepidine; Quidn = Quinaldine; Hymeq = Hydroxymethylquinoline
Chlmeq = Chloromethylquinoline; Mcpmeq = Mercaptopmethylquinoline.
<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}(\text{NO})(\text{CN})_2(\text{Lepn})_2(\text{H}_2\text{O})])</td>
<td>11.62 (11.87)</td>
<td>60.38 (60.27)</td>
<td>4.41 (4.56)</td>
<td>16.12 (15.98)</td>
</tr>
<tr>
<td>2.</td>
<td>([\text{Cr}(\text{NO})(\text{CN})_2(\text{Quidn})_2(\text{H}_2\text{O})])</td>
<td>11.50 (11.87)</td>
<td>60.10 (60.27)</td>
<td>4.69 (4.56)</td>
<td>15.79 (15.98)</td>
</tr>
<tr>
<td>3.</td>
<td>([\text{Cr}(\text{NO})(\text{CN})_2(4-\text{Hymeq})_2(\text{H}_2\text{O})])</td>
<td>11.21 (11.06)</td>
<td>56.28 (56.17)</td>
<td>4.11 (4.25)</td>
<td>14.70 (14.89)</td>
</tr>
<tr>
<td>4.</td>
<td>([\text{Cr}(\text{NO})(\text{CN})_2(4-\text{chlm eq})_2(\text{H}_2\text{O})])</td>
<td>11.12 (11.25)</td>
<td>52.29 (52.07)</td>
<td>3.41 (3.56)</td>
<td>13.61 (13.80)</td>
</tr>
<tr>
<td>5.</td>
<td>([\text{Cr}(\text{NO})(\text{CN})_2(4-\text{Mcpmeq})_2(\text{H}_2\text{O})])</td>
<td>10.31 (10.40)</td>
<td>52.61 (52.80)</td>
<td>3.75 (3.60)</td>
<td>14.20 (14.00)</td>
</tr>
</tbody>
</table>
### Table - 6.3

**Colour, Decomposition Temperature and % Yield of the Complexes**

<table>
<thead>
<tr>
<th>S. NO</th>
<th>Compound</th>
<th>Colour</th>
<th>Decomposition Temp. ( (^\circ C) )</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(\text{Leaph}_2)(\text{H}_2\text{O})])</td>
<td>Greenish Yellow</td>
<td>(&gt;300)</td>
<td>50</td>
</tr>
<tr>
<td>2.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(\text{Quidn}_2)(\text{H}_2\text{O})])</td>
<td>- Do -</td>
<td>(&gt;300)</td>
<td>51</td>
</tr>
<tr>
<td>3.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(4\text{-Hy}meq)_2(\text{H}_2\text{O})])</td>
<td>- do -</td>
<td>(&gt;300)</td>
<td>49</td>
</tr>
<tr>
<td>4.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(4\text{-ch}1\text{meq})_2(\text{H}_2\text{O})])</td>
<td>Brownish Yellow</td>
<td>(&gt;300)</td>
<td>48</td>
</tr>
<tr>
<td>5.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(4\text{-Mep}meq)_2(\text{H}_2\text{O})])</td>
<td>- do -</td>
<td>(&gt;300)</td>
<td>45</td>
</tr>
</tbody>
</table>
### Table 6.4

**Dehydration Temperature of the Complexes**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>Dehydration Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\text{[Cr(NO)}(CN)_2(\text{Lepn})_2(H_2O)]$</td>
<td>115</td>
</tr>
<tr>
<td>2.</td>
<td>$\text{[Cr(NO)}(CN)_2(\text{Quidn})_2(H_2O)]$</td>
<td>112</td>
</tr>
<tr>
<td>3.</td>
<td>$\text{[Cr(NO)}(CN)_2(4-\text{Hymeq})_2(H_2O)]$</td>
<td>118</td>
</tr>
<tr>
<td>4.</td>
<td>$\text{[Cr(NO)}(CN)_2(4 \text{chlmeq})_2(H_2O)]$</td>
<td>105</td>
</tr>
<tr>
<td>5.</td>
<td>$\text{[Cr(NO)}(CN)_2(4 \text{Mepmeq})_2(H_2O)]$</td>
<td>106</td>
</tr>
<tr>
<td>S. NO.</td>
<td>Compound</td>
<td>$\mu_{\text{eff}}$ (B.M.)</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>----------------</td>
</tr>
<tr>
<td>1.</td>
<td>$[\text{Cr(NO)(CN)}_2\text{(Lepn)}_2\text{(H}_2\text{O)}]_2$</td>
<td>1.70</td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{Cr(NO)(CN)}_2\text{(Quidn)}_2\text{(H}_2\text{O)}]_2$</td>
<td>1.71</td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{Cr(NO)(CN)}_2(4\text{-Hymeq})_2\text{(H}_2\text{)}]$</td>
<td>1.71</td>
</tr>
<tr>
<td>4.</td>
<td>$[\text{Cr(NO)(CN)}_2(4\text{-chlmeq})_2\text{(H}_2\text{O)}]$</td>
<td>1.74</td>
</tr>
<tr>
<td>5.</td>
<td>$[\text{Cr(NO)(CN)}_2(4\text{-Mepmeq})_2\text{(H}_2\text{O)}]$</td>
<td>1.72</td>
</tr>
</tbody>
</table>

**Table 6.5**

Magnetic and E.S.R. Data of the Complexes
### Table - 6.6

**Important I.R. bands and their assignments**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compounds</th>
<th>$\nu$(NO)$^+$</th>
<th>$\nu$(CN)</th>
<th>$\nu$(OH)</th>
<th>$\nu$(C=C)$^+$ modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)$_2$(Lepn)$_2$(H$_2$O)]</td>
<td>1680</td>
<td>2150</td>
<td>3580 (br)</td>
<td>3400 (br) 1600,1550</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)$_2$(Quidn)$_2$(H$_2$O)]</td>
<td>1700</td>
<td>2140</td>
<td>3580 (br)</td>
<td>3380 (br) 1605,1560</td>
</tr>
<tr>
<td>3.</td>
<td>[Cr(NO)(CN)$_2$(4-Hymeq)$_2$(H$_2$O)]</td>
<td>1690</td>
<td>2135</td>
<td>3575 (br)</td>
<td>3400 (br) 1600,1550</td>
</tr>
<tr>
<td>4.</td>
<td>[Cr(NO)(CN)$_2$(4-Chlmeq)$_2$(H$_2$O)]</td>
<td>1705</td>
<td>2140</td>
<td>3580 (br)</td>
<td>3400 (br) 1610,1560</td>
</tr>
<tr>
<td>5.</td>
<td>[Cr(NO)(CN)$_2$(4-Mepmeq)$_2$(H$_2$O)]</td>
<td>1700</td>
<td>2145</td>
<td>3580 (br)</td>
<td>3375 (br) 1605,1565</td>
</tr>
</tbody>
</table>
IR SPECTRUM OF
\[ \text{Cr(II)} \left( \text{CN})_2 (\text{Lepr})_2 (\text{H}_2\text{O}) \right] \]
(4000 - 1600 cm\(^{-1}\))
IR SPECTRUM OF

\[ [\text{Cr(NO)}(\text{CN})_2(\text{Lepn})_2\text{H}_2\text{O})] \]

(1600-600 cm\(^{-1}\))
IR SPECTRUM OF
\[ \text{Cr(NO)}_2(\text{CN})_2(\text{Hymeq})_2(\text{H}_2\text{O}) ] \\
(4000 - 1600 \text{ cm}^{-1})
IR SPECTRUM OF

\[ [\text{Cr(NO)(CN)\textsubscript{2}(4-\text{Hymeq})\textsubscript{2}(H\textsubscript{2}O)}] \]

\((1600-600 \text{ cm}^{-1})\)
IR SPECTRUM OF

\[
\text{[Cr(NO)(CN)_2(4-Mcpmcg)_2(H_2O)]}
\]

(4000 - 1600 cm\(^{-1}\))
IR SPECTRUM OF
\[
[\text{Cr}^2(\text{NO})_2(\text{CN})_2(4-\text{Mcpmeq})_2(\text{H}_2\text{O})]
\]
(1600 - 600 cm\(^{-1}\))
E.S.R. SPECTRUM OF
\[ \text{[Cr(NO)CN]}_2(\text{Lepr})_2(\text{H}_2\text{O})] \]

SCAN RANGE

2500 3000 3500 4000
E.S.R. SPECTRUM OF
\[ \text{Cr(NO)(CN)}_2 (4-\text{chlmeq})(\text{H}_2\text{O}) \]