5.1 INTRODUCTION

In chapter IV, synthesis and characterization of some novel hexa-coordinated mixed-ligand cyanonitrosyl \( \{\text{CrNO}\}^5 \) complexes of chromium with some heterocyclic esters such as nicotinic acid methyl ester, isonicotinic acid methyl ester, picolinic acid methyl ester and nicotinic acid phenyl ester, heterocyclic ketone like 2-pyridyl ethyl ketone and heterocyclic alkanol like 2-pyridinepropanol have been discussed. In continuation of our interest to synthesize and characterize some neutral mixed-ligand cyanonitrosyl complexes of monovalent chromium, attempts are being made to synthesize such complexes involving some new potentially mono- and bidentate pyridine based organic compounds.
Although considerable importance has been shown to the study of the neutral mixed-ligand cyanoitrosyl complexes of chromium(I) (4-8,10-14), cyanoitrosyl complexes of chromium(I) with ethyl 2-pyridyl acetate, 2-(2-methylaminoethyl)pyridine, 2-picolyllchloride, 3-acetoxypyridine and N,N-diethyl-nicotinamide, have not been described hitherto. We, therefore report here the first synthesis of neutral cyanoitrosyl complexes of monovalent chromium with the aforesaid ligands, and the present chapter described the results of this study.

![Ethyl 2-pyridylacetate](image1)

Ethyl 2-pyridylacetate

\[ \text{d} = 1.084 \]

![2-(2-Methylaminoethyl)pyridine](image2)

2-(2-Methylaminoethyl)pyridine

\[ \text{d} = 0.984 \]

![2-Picolyllchloride hydrochloride](image3)

2-Picolyllchloride hydrochloride

M.P. = 125-127°C

![3-Acetoxypyridine](image4)

3-Acetoxypyridine

\[ \text{d} = 1.141 \]

![N,N-Diethylnicotinamide](image5)

N,N-Diethylnicotinamide
5.2 EXPERIMENTAL

(a) Material used:

N,N-Diethyl nicotinamide (Tokyo chemical industry Co.Ltd., Japan), ethyl 2-pyridylacetate, 2-(2-methylaminoethyl)pyridine, picolylichloride hydrochloride and 3-acetoxypyridine (Aldrich Chemical Co., USA) were used as supplied. Distilled water was used in all operations.

(b) Analysis of the constituent elements:

Carbon, hydrogen and nitrogen were estimated micro-analytically. Chromium was estimated according to the procedure given in chapter II.

(c) Physical methods:

(i) Magnetic measurements:

Magnetic susceptibility measurements of the synthesized complexes were made by Gouy method at room temperature. Cobalt mercury thiocyanate, Hg[Co(NCS)_4] was used as a calibrant. Magnetic moments were calculated using the equation:

\[ \mu_{\text{eff}} = 2.84 \left( x^\text{corr.}_M T \right)^{1/2} \]

(ii) Infrared spectral measurements:

Infrared spectra of the uncoordinated ligands and of the complexes were recorded in nujol mulls on a Beckman IR-20-spectrophotometer at the Department of chemistry, Kurukshetra University, Kurukshetra. Spectra were recorded in the range 4000-600 cm\(^{-1}\).
(iii) **Electron spin resonance**:  
Electron spin resonance spectra were recorded for 'g' values at room temperature using the powdered sample on a Varian E-3 spectrometer at the University of British Columbia, Vancouver (Canada). Spectra were recorded at the microwave frequency 9.53 GHz and 'g' values were calculated using the equation.

\[
g = \frac{7.14.44 \times \sqrt{n(GHz)}}{H(G)}
\]

(iv) **Thermogravimetric analysis**:

The t.g. curves were recorded on a G-70 thermoanalyser, SETARAM, Lyon, France, in air at a heating rate of 10°C min\(^{-1}\), and up to 800°C.

5.3 **PREPARATION OF THE PARENT COMPOUND**

Potassium pentacyanonitrosylchromate(I) monohydrate prepared by the method reported by Wilkinson and co-workers(9), was used as the starting compound for the preparation of complexes mentioned in this chapter.

5.4 **PREPARATION OF THE COMPLEXES WITH SOME POTENTIALLY MONODENTATE PYRIDINE BASED ORGANIC COMPOUNDS**

(a) **Synthesis of \([\text{Cr(NO)(CN)}_2(2-\text{Pic})_2(\text{H}_2\text{O})]\)**:

To a filtered aqueous solution of \(K_3[\text{Cr(NO)(CN)}_5]\centerdot\text{H}_2\text{O}\) (0.01 M, 50 cm\(^3\)), an 1:1 water-acetic acid solution (10 cm\(^3\)) of 2-picolylic chloride hydrochloride (0.02 M) was added with shaking.
A coloured solid precipitated on heating the mixture for 20-25 minutes on a hot plate at 80°C. The resulting mixture was freed from the liberated HCN by passing a current of CO₂ through the mixture for a few hrs. The precipitate was suction filtered, washed several times with water and finally with ethanol and then dried in vacuo at room temperature to a constant weight. The analytical data are given in Table 5.2

5.5 PREPARATION OF THE COMPLEXES WITH SOME POTENTIALLY BIDENTATE PYRIDINE BASED ORGANIC COMPOUND

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

To a filtered aqueous solution of potassium pentacyanonoitrosylchromate(I) monohydrate (0.01 M), an aqueous acetic acid (1:1) solution of ethyl-2-pyridylacetate (0.02 M) was added with shaking when an yellow coloured solid was precipitated on warming the mixture for 20 minutes. The resulting mixture was freed from the liberated HCN by passing a current of CO₂ through the mixture for approximately 2-3 hours. The precipitate was filtered, washed several times with water and finally with ethanol and dried over silica gel in a desiccator at room temperature to a constant weight. The analytical results are given in Table 5.2.

(b) Synthesis of \([\text{Cr(NO)(CN)}_2(2-\text{MAEP})_2(\text{H}_2\text{O})]\):

The complex was prepared taking 2-(2-methylaminoethyl)-pyridine in place of ethyl-2-pyridyl acetate adopting similar method. The analytical data are given in Table 5.2.
(c) Synthesis of \([\text{Cr(NO)}(\text{CN})_2(3-\text{APY})_2(\text{H}_2\text{O})]\) :

This compound was also prepared by following an identical procedure described above taking starting compound and 3-acetoxyphosphine.

(d) Synthesis of \([\text{Cr(NO)}(\text{CN})_2(\text{DENICAM})_2(\text{H}_2\text{O})]\) :

An identical method as above was used in the preparation of this compound taking N,N-diethylphosphinamide and \(K_3[\text{CrNO(CN)}_5]\). \(\text{H}_2\text{O}\). The analytical data are given in Table 5.2.

### 5.6 PROPERTIES OF COMPLEXES

All the compounds are coloured solids (Table 5.3) and stable in air. All the compounds after decomposition with KOH followed by acidifying with acetic acid give a pink colour with few drops of Griess reagent (29). They are thermally stable and do not melt or decompose below 300°C. All these complexes are insoluble in common solvents as well as in water and, therefore, their molar conductivity values and molecular weights could not be measured.

### 5.7 RESULTS AND DISCUSSION

The mixed-ligand complexes, \([\text{CrNO(CN)}_2(L)_2(\text{H}_2\text{O})]\) were prepared according to the following equation:

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

Where \(L = \text{EPYA, 2-MAEP, 2-PIC, 3-APY or DENICAM.} \)
The partial replacement of the cyano groups in the parent complex by two molecules of ligand, L, is facilitated by the trans effect of the NO group. Raynor et al. (35) studied the stepwise aquation of $[\text{Cr(NO)}(\text{CN})_5]^{3-}$ and obtained the tris (aqua) species, $[\text{Cr(NO)}(\text{CN})_2(\text{H}_2\text{O})_3]$, which is consistent with equation (1).

Compounds were characterized on the basis of following result.

(i) **Magnetic and E.S.R. studies**:

The magnetic and electron spin resonance data of the complexes are given in Table 5.5. The magnetic moments, 1.71-1.75 B.M. at room temperature and 'g' values, 1.981-1.988 of powdered compounds, which are comparable to the observation made by Manoharan and Gray and Meriwether et al. (36,37), are consistent with a low-spin $\{\text{CrNO}\}_5$ electron configuration of chromium(I).

(ii) **Thermogravimetric Analysis**:

The dehydration temperature obtained by T.G.A. for all the compounds are presented in Table 5.4. The weight loss observed at the dehydration temperature for each compound corresponds to the elimination of one molecule of water (34). This result supports the presence of one molecule of water in each compounds (Vide Infrared discussion for coordinated water in these complexes).
(iii) **Infrared spectra:**

The important infrared spectral bands of the complexes are present in Table 5.6. The appearance of a very strong band in the region 1695-1710 cm\(^{-1}\) and a strong band in the region 2140-2160 cm\(^{-1}\) are assigned to \(\tilde{\nu}(\text{NO})\) and \(\tilde{\nu}(\text{C\equiv N})\), respectively, which are in agreement with the reported results (4,8).

All the ligands (except 2-PIC) used in the present study, EPYA, 2-MAEP, 3-APY and DENICAM, possess two potential donor sites:

(i) Pyridine ring nitrogen, and (ii) carbonyl oxygen in EPYA, 3-APY and DENICAM or amino nitrogen in 2-MAEP. 2-PIC possesses only the pyridine ring as the donor site. In carbonyl donors (40), a significant negative shift of the carbonyl frequency takes place because of the coordination through the carbonyl oxygen. The coordination of amino nitrogen is inferred by lowering in \(\tilde{\nu}(\text{NH})\). The \(\tilde{\nu}(\text{CO})\) in free EPYA, 3-APY and DENICAM remain either unchanged or undergo slight positive shift in their respective complexes. This feature clearly indicate that carbonyl oxygen in EPYA, 3-APY and DENICAM is inert towards coordination in these complexes. Similarly, no change in \(\tilde{\nu}(\text{NH})\) of free 2,MAEP after complexation, concludes the inertness of amino nitrogen of 2-MAEP. Further, the pyridine ring breathing vibration occurring at \(\sim 1000\) cm\(^{-1}\) in all the free ligands undergoes a significant positive shift
in all the complexes indicating conclusively that co-ordination takes place via the pyridine ring nitrogen atoms only (58).

All the complexes exhibit the $\tilde{\nu}$(OH) stretching in the region 3570-3580 and 3380-3400 cm$^{-1}$; the occurrence of $\tilde{\nu}$(OH) band is indicative of co-ordinated water in these complexes(10).

5.8 SUMMARY

Five novel mixed-ligand hexa-coordinated cyanonitrosyl complexes of monovalent chromium of the general formula, 
$[\text{Cr(NO)(CN)}_2(L)_2(H_2O)]$ (where $L =$ ethyl-2-pyridylacetate, 2-(2-methylaminoethyl)pyridine, 2-picolylchloride, 3-acetoxy-pyridine or N,N-diethylnicotinamide, have been prepared by the interaction of potassium pentacyanonitrosylchromate(I) monohydrate, $K_3[\text{Cr(NO)(CN)}_5].H_2O$ with the said heterocyclic bases, $L$. The complexes, which have been characterized by elemental analysis, magnetic measurement, electron spin resonance and infrared spectral studies, contain chromium(I) in a low-spin $d^5$ configuration. An octahedral structure, where CN is trans to CN and $L$ is trans to $L$ in equatorial positions, and NO is trans to water at axial position, has been proposed for the complexes. It is observed that :-

(i) Synthesized complexes are coloured solids.

(ii) All the compounds have magnetic moment values close to spin only value for one unpaired electron (1.73 B.M.).
Fig.5.1: Proposed octahedral structure of
\[ \text{[Cr(NO)(CN)\textsubscript{2}(L)\textsubscript{2}(H\textsubscript{2}O)]} \], Where L =
EPYA, 2-MAEP, 2-PIC, 3-APY or
DENICAM
(iii) All the compounds are insoluble in common solvents as well as water.

(iv) All the compounds give positive Griess Reagent test.

(v) An octahedral structure has been proposed for all the complexes.

(vi) All the compound have a low-spin \(\{\text{CrNO}\}^5\) electron configuration.

(vii) Ligand like ethyl-2-pyridylacetate, 2-(2-methylaminoethyl) pyridine, 3-acetoxypyridine and N,N-diethylnicotinamide are although potentially bidentate, but they all behave as monodentate in complexation by co-ordination through pyridine ring nitrogen only.
# Table - 5.1

**Nomenclature and Electron configuration of the synthesized complexes**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>I.U.P.A.C.</th>
<th>Electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$[\text{Cr(NO)(CN)}_2(\text{EPYA})_2(\text{H}_2\text{O})]$</td>
<td>Aquadicyanobis (ethyl 2-pyridyl acetate) nitrosyl-chromium(I)</td>
<td>$\text{CrNO}^5$</td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{Cr(NO)(CN)}_2(2-\text{MAEP})_2(\text{H}_2\text{O})]$</td>
<td>Aquadicyanobis (2-(2-methylamino-ethyl) pyridine) nitrosylchromium (I)</td>
<td>$\text{CrNO}^5$</td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{Cr(NO)(CN)}_2(2-\text{PIC})_2(\text{H}_2\text{O})]$</td>
<td>Aquadicyanobis (2-picolylchloride) nitrosyl chromium(I)</td>
<td>$\text{CrNO}^5$</td>
</tr>
<tr>
<td>4.</td>
<td>$[\text{Cr(NO)(CN)}_2(3-\text{APY})_2(\text{H}_2\text{O})]$</td>
<td>Aquadicyanobis (3-Acetoxypyridine) nitrosylchromium (I)</td>
<td>$\text{CrNO}^5$</td>
</tr>
<tr>
<td>5.</td>
<td>$[\text{Cr(NO)(CN)}_2(\text{DENICAM})_2(\text{H}_2\text{O})]$</td>
<td>Aquadicyanobis (N,N-diethyl- nicotinamide) nitrosylchromium (I)</td>
<td>$\text{CrNO}^5$</td>
</tr>
</tbody>
</table>

**Abbreviation:** EPYA = Ethyl 2-pyridylacetate; 2-MAEP = 2-(2-methylaminoethyl)-pyridine; 2-PIC = 2-picolyl chloride; 3-APY = 3-acetoxypyridine; DENICAM = N,N-diethylnicotinamide.
### Table 5.2

**Analytual Data of the Symtjesozed 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)}(\text{CN})_2(\text{EPY})_2(\text{H}_2\text{O})])</td>
<td>10.61 (10.78)</td>
<td>49.51 (49.79)</td>
<td>5.12 (4.97)</td>
<td>14.65 (14.52)</td>
</tr>
<tr>
<td>2.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(2\text{-MAEP})_2(\text{H}_2\text{O})])</td>
<td>12.38 (12.26)</td>
<td>50.79 (50.94)</td>
<td>6.0 (6.13)</td>
<td>23.28 (23.11)</td>
</tr>
<tr>
<td>3.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(2\text{-PIC})_2(\text{H}_2\text{O})])</td>
<td>12.50 (12.77)</td>
<td>41.39 (41.27)</td>
<td>3.21 (3.43)</td>
<td>17.28 (17.19)</td>
</tr>
<tr>
<td>4.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(3\text{-APY})_2(\text{H}_2\text{O})])</td>
<td>12.38 (12.20)</td>
<td>44.89 (45.07)</td>
<td>3.60 (3.75)</td>
<td>16.57 (16.43)</td>
</tr>
<tr>
<td>5.</td>
<td>([\text{Cr(NO)}(\text{CN})_2(\text{DENICAM})_2(\text{H}_2\text{O})])</td>
<td>10.41 (10.23)</td>
<td>51.78 (51.96)</td>
<td>6.15 (5.90)</td>
<td>19.38 (19.29)</td>
</tr>
</tbody>
</table>
Table 5.3  
Colour, Decomposition Temperature and % Yield

<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>$[\text{Cr(NO)(CN)}_2(\text{EPYA})_2(\text{H}_2\text{O})]$</td>
<td>Brownish Yellow</td>
<td>$&gt;270$</td>
<td>48</td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{Cr(NO)(CN)}_2(2\text{-MAEP})_2(\text{H}_2\text{O})]$</td>
<td>Yellow</td>
<td>$&gt;280$</td>
<td>50</td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{Cr(NO)(CN)}_2(2\text{-PIC})_2(\text{H}_2\text{O})]$</td>
<td>Yellow</td>
<td>$&gt;290$</td>
<td>48</td>
</tr>
<tr>
<td>4.</td>
<td>$[\text{Cr(NO)(CN)}_2(3\text{-APY})_2(\text{H}_2\text{O})]$</td>
<td>Yellow</td>
<td>$&gt;290$</td>
<td>52</td>
</tr>
<tr>
<td>5.</td>
<td>$[\text{Cr(NO)(CN)}_2(\text{DENICAM})_2(\text{H}_2\text{O})]$</td>
<td>Brownish Yellow</td>
<td>$&gt;280$</td>
<td>54</td>
</tr>
<tr>
<td>S.No.</td>
<td>Compound</td>
<td>Dehydration Temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>----------------------------------------------</td>
<td>-------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>$[\text{Cr(NO)(CN)}_2\text{EPYA}_2\text{H}_2\text{O}]$</td>
<td>114</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{Cr(NO)(CN)}_2\text{2-MAEP}_2\text{H}_2\text{O}]$</td>
<td>118</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{Cr(NO)(CN)}_2\text{2-PIC}_2\text{H}_2\text{O}]$</td>
<td>112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>$[\text{Cr(NO)(CN)}_2\text{3-APY}_2\text{H}_2\text{O}]$</td>
<td>116</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>$[\text{Cr(NO)(CN)}_2\text{DENICAM}_2\text{H}_2\text{O}]$</td>
<td>109</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table - 5.5

Magnetic and E.S.R. Data of the Complexes

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>$\mu_{\text{eff}}$</th>
<th>'g'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$[\text{Cr(NO)(CN)}_2(\text{EPY})_2(\text{H}_2\text{O})]$</td>
<td>1.72</td>
<td>1.981</td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{Cr(NO)(CN)}_2(2-\text{MAEP})_2(\text{H}_2\text{O})]$</td>
<td>1.75</td>
<td>1.987</td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{Cr(NO)(CN)}_2(2-\text{PIC})_2(\text{H}_2\text{O})]$</td>
<td>1.71</td>
<td>1.986</td>
</tr>
<tr>
<td>4.</td>
<td>$[\text{Cr(NO)(CN)}_2(3-\text{APY})_2(\text{H}_2\text{O})]$</td>
<td>1.74</td>
<td>1.988</td>
</tr>
<tr>
<td>5.</td>
<td>$[\text{Cr(NO)(CN)}_2(\text{DENICAM})_2(\text{H}_2\text{O})]$</td>
<td>1.74</td>
<td>1.982</td>
</tr>
<tr>
<td>S.No.</td>
<td>Compound</td>
<td>$\gamma$(NO)$^+$</td>
<td>$\gamma$(CN)</td>
</tr>
<tr>
<td>-------</td>
<td>----------------------------------------------</td>
<td>------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>1.</td>
<td>$[\text{Cr(NO)(CN)}_2(\text{EPYA})_2(\text{H}_2\text{O})]$</td>
<td>1705 (vs)</td>
<td>2150 (s)</td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{Cr(NO)(CN)}_2(2-\text{MAEP})_2(\text{H}_2\text{O})]$</td>
<td>1700 (vs)</td>
<td>2160 (s)</td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{Cr(NO)(CN)}_2(2-\text{PIC})_2(\text{H}_2\text{O})]$</td>
<td>1705 (vs)</td>
<td>2140 (s)</td>
</tr>
<tr>
<td>4.</td>
<td>$[\text{Cr(NO)(CN)}_2(3-\text{APY})_2(\text{H}_2\text{O})]$</td>
<td>1695 (vs)</td>
<td>2160 (s)</td>
</tr>
<tr>
<td>5.</td>
<td>$[\text{Cr(NO)(CN)}_2(\text{DENICAM})_2(\text{H}_2\text{O})]$</td>
<td>1710 (vs)</td>
<td>2150 (s)</td>
</tr>
</tbody>
</table>
IR SPECTRUM OF

\[ [\text{G} \text{ (NO)} \text{ (CN)}_2 \text{(EPYA)}_2 \text{(H}_2\text{O})] \]

\((4000 - 1800 \text{ cm}^{-1})\)
IR SPECTRUM OF
[Cr(NO)(CN)₂(CPYA)(H₂O)]
(1800 - 600 cm⁻¹)

PERCENT TRANSMISSION
IR SPECTRUM OF
\([\text{Cr} \text{(NO)} \text{(CN)}_2(2-\text{pic})_2\text{(H}_2\text{O})]\)

\((4000-1800 \text{ cm}^{-1})\)
IR SPECTRUM OF

\[(\text{G-CNO})(\text{CN})_2(\text{2-PIC})_2(\text{H}_2\text{O})]\]

\[(1800 - 600 \text{ cm}^{-1})\]
IR SPECTRUM OF
\[ \text{C}_{\text{r}}(\text{NO})(\text{CN})_{2}(-\text{DENICAM})_{2}(\text{H}_{2}\text{O}) \]
(4000 - 1800 cm\(^{-1}\))
IR SPECTRUM OF
\[
\left[ \text{Cu(NO)}(\text{CN})_2(\text{DENICAM})_2(\text{H}_2\text{O}) \right]
\]
(1800 - 600 cm\(^{-1}\))
E.S.R. SPECTRUM OF

\[ \text{[Cu(NO)(CN)_2(3-APY)_2(H_2O)]} \]