Chapter IV

Synthesis and physicochemical studies of new cyanonitrosyl $\{\text{CrNO}\}_5^5$
coordination compounds of Chromium with imidazole, 1-methyl imidazole
and 2–methyl imidazole.
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4.1 Introduction

In chapter III, synthesis and physicochemical studies of some mixed ligand cyanonitrosyl complexes of chromium having configuration \{CrNO\}^5 with some substituted benzothiazoles like 2-amino-5,6-dimethylbenzothiazole and 2-Amino-4-methoxybenzothiazole have been discussed. In continuation of our interest to synthesize and characterize some neutral mixed ligand cyanonitrosyl complexes of monovalent chromium, studies have been extended using some substituted imidazoles.

In last few years, a great deal of interest has been shown to the study of neutral mixed-ligand cyanonitrosyl complexes of monovalent chromium (4–8,10–14). Few attempts have been made by Maurya and coworkers to isolate some mixed ligand
cyanonitrosyl complexes of chromium having \(\{\text{CrNO}\}^5\) electronic configuration with heterocyclic bases with one and two possible donor sites. It was, therefore, thought worthwhile to synthesize and characterize cyanonitrosyl complexes having \(\{\text{CrNO}\}^5\) electronic configuration with some new heterocyclic compounds having more than one donor site like. Since this chapter involves the use of imidazole, 1-methyl imidazole and 2-methyl imidazole as a ligand so it will be better to discuss some important physico-chemical properties of imidazole derivatives.

Debus (176), the discoverer of the parent compound, prepared it from glyoxal and ammonia and, to indicate its source, proposed the name glyoxaline. This name is still used in the modern literature especially by British workers. The name imidazole, used in the present monograph is due to Hantzsch(177). He classified as azoles the five membered polyheteroatomic ring system containing at least one tertiary nitrogen. The term imidazole implies a five membered, heterocyclic ring system containing in addition to a tertiary nitrogen, an imino group; just as the names oxazole and thiazole designate five membered ring systems containing in addition to a tertiary nitrogen an oxygen or sulfur atom.

\[
\text{Imidazole}
\]

The correct numbering of the imidazole ring is shown above.

The imino nitrogen receives position 1, and the numbering follows
around the ring so as to assign the smallest possible number to the tertiary nitrogen, which is designated as position 3. The substituted nitrogen represents the starting point for the numbering of the N-substituted imidazoles. The designation of a substituent in position 2 offers no problem because of the symmetrical location with respect to the nitrogens. The naming becomes somewhat more complex, however, when a substituent is introduced into the 4- or 5- position. Depending upon the position of the imino hydrogen such a compound must be designated as either a 4- or a 5-monosubstituted imidazole, the tautomeric character of the imidazoles precluding a definite assignment of structure. Such compounds are designated as 4(or 5)-monosubstituted imidazoles.

The presence in the imidazole structure of an acidic pyrrole nitrogen and a basic pyridine nitrogen explains the amphoteric nature of these compounds. Qualitatively, the imidazoles may be regarded as a “cross” between a pyridine and a pyrrole. Thus one could expect a deactivating influence toward electrophilic reagents caused by the pyridine nitrogen, which to a certain degree is offset by the electron-releasing properties of the pyrrole nitrogen. The chemical behavior of the imidazoles is in agreement with this admittedly crude picture.

The consideration of structure must be based on physical as well as chemical properties. It thus seems logical to summarize first the physical properties of the imidazoles. Whenever possible, this done from the point of view of comparison, since pertinent
(i) **Boiling Point**

**TABLE I.**

**Boiling Points Of A Number Of Five-Membered Heterocyclic compounds**

<table>
<thead>
<tr>
<th>COMPOUNDS</th>
<th>B.p., °C. (760mm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furan</td>
<td>32</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>131</td>
</tr>
<tr>
<td>Pyrazole</td>
<td>187</td>
</tr>
<tr>
<td>Imidazole</td>
<td>256</td>
</tr>
</tbody>
</table>
Table I summarizes the boiling points of a number of five
membered heterocyclic compounds and illustrates the unusually
high boiling points of imidazole. Pyrazole also boils rather high in
comparison with furan, and pyrrole, although it does not differ
significantly from them in molecular weight.

The boiling point of imidazole is strikingly lowered by the
introduction of a methyl group in to the 1-position, but is not
significantly affected by the introduction of a methyl group in to
the 4(or 5) -position. Even the introduction of an amyl group,
which doubles the molecular weight, results in a substance boiling
lower than the parent ring system. These results demonstrate that
the free imino hydrogen is, to a certain degree, responsible for the
observed high boiling points of imidazoles (table II)
## Effect of substituents on the boiling point of imidazole

<table>
<thead>
<tr>
<th>compounds</th>
<th>B.p., °C.(760mm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole</td>
<td>256</td>
</tr>
<tr>
<td>1-Methyl</td>
<td>198</td>
</tr>
<tr>
<td>4(or 5)Methyl</td>
<td>264</td>
</tr>
<tr>
<td>1-Propyl</td>
<td>223</td>
</tr>
<tr>
<td>1-Amyl</td>
<td>245</td>
</tr>
<tr>
<td>1,2-Dimethyl</td>
<td>205</td>
</tr>
<tr>
<td>1-Ethyl-2-Methyl</td>
<td>211</td>
</tr>
<tr>
<td>1-Methyl-5-Chloro</td>
<td>202</td>
</tr>
<tr>
<td>1-Methyl-4-Chloro</td>
<td>245</td>
</tr>
<tr>
<td>1,4-Dimethyl</td>
<td>200</td>
</tr>
<tr>
<td>1,5-Dimethyl</td>
<td>220</td>
</tr>
<tr>
<td>1-Phenyl</td>
<td>277</td>
</tr>
<tr>
<td>2-Phenyl</td>
<td>340</td>
</tr>
</tbody>
</table>

### 2. Melting points

Table III summarizes the melting points of a number of imidazoles. Here again it will be noted that the introduction of a substituents into the 1-position of the imidazole ring has a striking lowering effect.
Table III

*Melting points of a number of Imidazole*

<table>
<thead>
<tr>
<th>Compounds</th>
<th>M.p., $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole</td>
<td>90</td>
</tr>
<tr>
<td>1-Methyl</td>
<td>-6</td>
</tr>
<tr>
<td>2-Methyl</td>
<td>140-141</td>
</tr>
<tr>
<td>4(or 5)-Methyl</td>
<td>55-56</td>
</tr>
<tr>
<td>1-Phenyl</td>
<td>13</td>
</tr>
<tr>
<td>2-Phenyl</td>
<td>148-149</td>
</tr>
<tr>
<td>4(or 5)-phenyl</td>
<td>133-134</td>
</tr>
<tr>
<td>1-Benzyl</td>
<td>71-72</td>
</tr>
<tr>
<td>2-Benzyl</td>
<td>125-126</td>
</tr>
<tr>
<td>4(or 5)-Benzyl</td>
<td>82-84</td>
</tr>
<tr>
<td>4,5-Diphenyl</td>
<td>228</td>
</tr>
<tr>
<td>2-Methyl-4,5-diphenyl</td>
<td>240</td>
</tr>
<tr>
<td>1-Methyl-4,5-diphenyl</td>
<td>158</td>
</tr>
</tbody>
</table>
3. **Solubility**

The solubility of imidazole is high in polar and low in non-polar solvents. At room temperature it is so extremely soluble in water that quantitative data on its solubility have not been obtained. The base is somewhat soluble in benzene; however, at room temp. its solubility in this solvent is rather limited. Cyclohexane is poor solvent. 4(or 5)-Methylimidazole exhibits good solubility in benzene. The N-substituted imidazoles are in general much more soluble in non-polar solvents than are the imidazoles with a free imino hydrogen. Quantitative figures on the solubilities of imidazole in benzene and in dioxane, and of 4(or 5)-methyl imidazole in benzene are given in table IV and V.
Table IV:

*Solubility of Imidazole in Benzene and in Dioxane (3)*

<table>
<thead>
<tr>
<th>Benzene</th>
<th>Dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp., °C,</strong></td>
<td><strong>Molality</strong></td>
</tr>
<tr>
<td>36.7</td>
<td>0.198</td>
</tr>
<tr>
<td>41.0</td>
<td>0.258</td>
</tr>
<tr>
<td>42.2</td>
<td>0.486</td>
</tr>
<tr>
<td>42.8</td>
<td>0.688</td>
</tr>
<tr>
<td>44.8</td>
<td>1.195</td>
</tr>
<tr>
<td>45.7</td>
<td>1.524</td>
</tr>
<tr>
<td>17.8</td>
<td>2.38</td>
</tr>
<tr>
<td>49.0</td>
<td>3.00</td>
</tr>
<tr>
<td>51.2</td>
<td>4.63</td>
</tr>
</tbody>
</table>
Solubility of 4(or 5)-Methylimidazole in Benzene (3)

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Molality</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>4.57</td>
</tr>
<tr>
<td>16.8</td>
<td>6.07</td>
</tr>
<tr>
<td>21.1</td>
<td>6.87</td>
</tr>
<tr>
<td>25.4</td>
<td>7.44</td>
</tr>
<tr>
<td>29.3</td>
<td>8.24</td>
</tr>
<tr>
<td>31.4</td>
<td>8.54</td>
</tr>
</tbody>
</table>
4. Molecular Weight and Degree of Association

Ebulliometric molecular weight determinations in boiling benzene also yield abnormal results. For example, 4(or 5)-methylimidazole at a concentration of 0.4 m exhibits an apparent molecular weight of 190, which is approximately twice the formula weight. Imidazole is also appreciably associated in boiling benzene, since at a concentration of 0.4 m a molecular weight of 250 is observed (approximately four times the formula weight). It is of interest to note that imidazole in aqueous solution exhibits a normal molecular weight which changes little with increasing concentration.

All these finding points to a high degree of association of the imidazoles in non polar solvents; that the association is dependent on the presence of a free imino hydrogen is evidenced by the low degree of association of the N-substituted imidazoles and benzimidazoles.

5. Viscosity

The specific viscosity of benzene solutions of imidazole and 4 (or 5)-methylimidazole are given in table-VI. Solution of pyrazole in benzene have approximately the same viscosity as the pure solvent, and negligible variation of the specific viscosity with increasing concentration is observed. This suggests little association. The specific viscosity of solution of imidazole and 4 (or 5) -methylimidazole, on the other hand, increases with increasing concentration (see table VI), a behavior pointing to the presence of long chain aggregates.
**Viscosity of Benzene Solution of Imidazole and 4(or 5)-Methylimidazole**

<table>
<thead>
<tr>
<th>Compound (temp., °C.)</th>
<th>Molality</th>
<th>Specific viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole (30 °C)....</td>
<td>0.036</td>
<td>0.0106</td>
</tr>
<tr>
<td></td>
<td>0.073</td>
<td>0.0248</td>
</tr>
<tr>
<td></td>
<td>0.146</td>
<td>0.0549</td>
</tr>
<tr>
<td></td>
<td>0.146</td>
<td>0.0410</td>
</tr>
<tr>
<td></td>
<td>0.461</td>
<td>0.1500</td>
</tr>
<tr>
<td></td>
<td>0.463</td>
<td>0.1686</td>
</tr>
<tr>
<td>4(or 5)-Methylimidazole (30 °C)....</td>
<td>0.040</td>
<td>0.0071</td>
</tr>
<tr>
<td></td>
<td>0.080</td>
<td>0.0354</td>
</tr>
<tr>
<td></td>
<td>0.242</td>
<td>0.1187</td>
</tr>
<tr>
<td></td>
<td>0.249</td>
<td>0.1277</td>
</tr>
<tr>
<td></td>
<td>0.475</td>
<td>0.2925</td>
</tr>
<tr>
<td></td>
<td>0.493</td>
<td>0.3262</td>
</tr>
<tr>
<td></td>
<td>0.607</td>
<td>0.4113</td>
</tr>
<tr>
<td></td>
<td>1.075</td>
<td>0.7801</td>
</tr>
<tr>
<td></td>
<td>1.362</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>2.068</td>
<td>1.6524</td>
</tr>
<tr>
<td></td>
<td>2.848</td>
<td>2.3138</td>
</tr>
<tr>
<td></td>
<td>3.738</td>
<td>3.1560</td>
</tr>
<tr>
<td>4 (or 5)-Methylimidazole (50 °C)....</td>
<td>0.242</td>
<td>0.0910</td>
</tr>
<tr>
<td></td>
<td>0.249</td>
<td>0.0930</td>
</tr>
<tr>
<td></td>
<td>0.475</td>
<td>0.2140</td>
</tr>
<tr>
<td></td>
<td>0.493</td>
<td>0.2370</td>
</tr>
</tbody>
</table>
Most valuable information on the fine structure of organic molecules may be gained from an exact knowledge of their dielectric properties, since the magnitude of the dipole moments is indicative of the charge distribution within their structures. Unfortunately the experimental material on imidazoles is rather limited, dipole moments being available only for imidazole, 4(or 5)-methylimidazole, 1-methylimidazole, and benzimidazole. The results are summarized in table VII.

### Table VII.

*Dipole Moment in Debye Units of Some Imidazoles in Different Solvents (3,7)*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Naphthalene</th>
<th>Benzene</th>
<th>Dioxane</th>
<th>Carbon tetra chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole</td>
<td>5.7 ((97 °)</td>
<td>6.2(70 °)</td>
<td>4.8 (30 °)</td>
<td>-</td>
</tr>
<tr>
<td>4(or 5)-Methyl......</td>
<td>-</td>
<td>6.2(70 °)</td>
<td>5.1(20 °)</td>
<td>5.8(18 °)</td>
</tr>
<tr>
<td>1-Methyl............</td>
<td>-</td>
<td>3.6(20 °)</td>
<td>3.8(20 °)</td>
<td>-</td>
</tr>
<tr>
<td>Imidazole*...........</td>
<td>-</td>
<td>3.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Infinite dilution.*

Again the high degree of association of the imidazoles containing a free imino group in nonpolar solvents reflects itself in the dipole moments. Thus the moment of 1-methylimidazole when measured in benzene solution is little dependent on the concentration, in contrast to that of imidazole which varies to a considerable extent as illustrated in table VIII.
Variation (with Concentration) of the Dipole Moment of

Imidazole in Benzene (7)

<table>
<thead>
<tr>
<th>Mole fraction of solute</th>
<th>Dipole moment, Debye unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005951</td>
<td>5.62</td>
</tr>
<tr>
<td>0.001140</td>
<td>4.42</td>
</tr>
<tr>
<td>0.000233</td>
<td>3.93</td>
</tr>
</tbody>
</table>

7. Spectroscopic Properties

(a) Ultraviolet Absorption Spectra

The simple imidazoles fail to exhibit selective absorption in the ultraviolet region (8,9). Selective absorption is observed in imidazoles in which imidazole ring is conjugated with a carbonyl group, such as in the imidazolecarboxaldehydes and imidazolecarboxylic acids. Also certain functional derivatives such as the imidazolethiones exhibits characteristics absorption maxima in the ultraviolet region. The spectra of these compounds will be found in the appropriate sections.

(b) Raman Spectra

The Raman spectra of various imidazoles have been investigated, and the reader is referred to the original literature on this subject (10).

(c) Chemiluminescence

A number of arylimidazoles exhibit chemiluminescence when exposed to the action of an oxidizing reagent in alkaline medium. This interesting phenomenon was first observed by
Hoffmann (11) who found that a solution of 2,4,5-triphenylimidazole (lophine) in potassium hydroxide emitted light when it was shaken with air. He was struck by the intense light production and described his observation as follows: “the phenomenon becomes rather spectacular on a large scale; I employed 100 g. of lophine and 300 g. of potassium hydroxide in alcohol for my experiments. The development of light was so intense that it was possible to see the faces of the observers at a distance of two or three feet and at a distance of two and one half to five cm. the numbers and hands of a pocket watch could be recognized”.

The addition of an oxidizing agent to a solution of lophine in an alkali brings about a marked increase of the chemiluminescence. Optimal effects are obtained when a solution of lophine in ethanol, methanol, acetone or dioxane is treated with an oxidizing reagent such as hypohalite, potassium ferricyanide, hydrogen peroxide, or hemoglobin (12-15). A variety of substituted aryl imidazoles such as 2,4,5-tri(p-methylphenyl)-, 2,4,5-tri(p-methoxyphenyl)-, and 2,4,5-tris (p-chlorophenyl)-imidazole, or substances like 4,5-diphenyl-2-methyl-, 4,5-diphenyl-2-ethyl-, 4,5-diphenyl-2-isopropyl-, and 4,5-diphenyl-2-(p-methoxyphenyl)-imidazole exhibit chemiluminescence under the above mentioned conditions (16). Amarine (2,4,5-triphenyl-2-imidazoline) behaves similarly (14). Imidazole exhibits a weak degree of chemiluminescence upon exposure to hydrogen peroxide (12).

The emitted light exhibits a continuous spectrum ranging from 4800-6000 A, with a maximum at 5300 A.
8. Miscellaneous Physical Properties

Information on refractive indexes, densities, molar refractivities, surface tensions, heat of fusion, and heats of solution of imidazole and 4(or 5)-methylimidazole is summarized in table IX, X.
Table IX. Surface Tension of Imidazole and 4(or 5)-Methylimidazole (3)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature, °C.</th>
<th>Surface tension, dynes/cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole ...........</td>
<td>110.0</td>
<td>36.82</td>
</tr>
<tr>
<td></td>
<td>150.0</td>
<td>33.85</td>
</tr>
<tr>
<td></td>
<td>205.0</td>
<td>30.05</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>38.70</td>
</tr>
<tr>
<td></td>
<td>56.0</td>
<td>36.21</td>
</tr>
<tr>
<td></td>
<td>110.0</td>
<td>32.36</td>
</tr>
<tr>
<td></td>
<td>153.0</td>
<td>29.28</td>
</tr>
<tr>
<td>4(or 5)-Methyl-...........</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table X.

Heat Of Fusion And Heat Of Solution In Benzene At Varying Concentration

<table>
<thead>
<tr>
<th>Molality</th>
<th>Heat of solution, cal./mole ($21^0$)</th>
<th>Heat of fusion, cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>-3210</td>
<td>-2840</td>
</tr>
<tr>
<td>0.22</td>
<td>-2170</td>
<td>-</td>
</tr>
</tbody>
</table>

Concentration Of 4(Or 5)-Methyl, Imidazole (3)
Chemical Properties

1. Basic Strength

Imidazole is a monoacidic base have the ability to form crystalline salts with acids. The melting points of a number of characteristic imidazolium salts are listed in table XI. The basic nature of the imidazoles is due to the ability of the pyridine nitrogen to accept a proton.

Substituents influence the basic strength of imidazole in the manner illustrated in table XII. The introduction of methyl groups into the imidazole ring increases its basic strength. This is applicable in terms of the electron-releasing properties of the methyl group, which tends to increase the electron density about the pyridine nitrogen. The situation parallels that observed in the pyridine series, where the basic strength of α-picoline is also higher than that of the parent ring system (33). This increase in basic strength has been attributed to combine inductive and resonance effect (hyperconjugation).

methylimidazole, where hyperconjugated states of the type depicted below are indicated. The introduction of a methyl group into the 4(or 5)-position of the imidazole ring also increases the basic strength, but the effect is less pronounced than that of the 2-methyl group symmetry considerations might offer an explanation for this difference. The 2-methylimidazolium ion represents a highly symmetrical structure with two equivalent contributions, in contrast to the 4(or 5)-methylimidazolium ion with two non-equivalent contributions. The introduction of a methyl group into both the 2- and the 4(or 5)-position causes a further increase in basic strength.
Electron-attracting groups such as the phenyl group, the nitro group, or a halogen, decrease the basic strength. A few qualitative observation on the basic strength of N-alkyl nitroimidazoles are of interest. A comparison of 1-methyl-5-nitroimidazole and 1,2-dimethyl-5-nitroimidazole with their respective 4-nitro derivatives indicates that the 5-nitro compounds are the stronger bases (178, 179). It seems logical that the structure in which the nitro group is located in close proximity to the electron-donor system (pyridine nitrogen) should represent the weaker base.
Basic strength of a number of imidazoles (30,32,32a)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole</td>
<td>6.95; 6.89&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>1-methyl</td>
<td>7.25</td>
</tr>
<tr>
<td>2-methyl</td>
<td>7.86</td>
</tr>
<tr>
<td>4(or 5)-methyl</td>
<td>7.52</td>
</tr>
<tr>
<td>2,4(or 2,5)-dimethyl-</td>
<td>8.36</td>
</tr>
<tr>
<td>2,4,5-trimethyl-</td>
<td>8.86&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2-phenyl-</td>
<td>6.39</td>
</tr>
<tr>
<td>4(or 5)-phenyl-</td>
<td>6.00</td>
</tr>
<tr>
<td>4(or 5)-hydroxymethyl-</td>
<td>6.38</td>
</tr>
<tr>
<td>4(or 5)-carboxy-</td>
<td>6.08&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>4(or 5)-carbethoxy</td>
<td>3.66&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>4(or 5)-bromo-</td>
<td>3.60&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Histamine</td>
<td>5.98&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
2. Pseudoacidic Character

In addition to its basic nature, imidazole also exhibits weakly acidic(pseudoacidic) properties. It forms salts with metals of the general structure shown below. Most important among the salts is the sparingly soluble silver salt, which is precipitated when imidazole is brought into contact with ammoniacal silver solutions. In the presence of ammonia, in soluble salts with cobalt and zinc are also obtained (180, 181). The reaction of imidazole with a Grignard reagent results in the formation of an imidazole magnesium halide (182, 183).

The pseudoacidic nature of imidazole depends upon the presence of the unsubstituted imino group, and imidazoles having this structural requirement form sparingly soluble silver salts in the presence of ammoniacal silver solutions. Many imidazoles form insoluble salts with cuprous ion in the presence of ammonia (184). Imidazole dissolves in liquid ammonia, forming a clear solution from which it is regenerated on evaporation of the solvent. The addition metals or of metal amides to such a solution result in salt formation. The sodaum, potassium, calcium, and magnesium salts obtained in this manner. These salts are unstable in the presence of water and hydrolyze with the formation of imidazole and metallic hydroxides (185). A comparison of the conductance of liquid ammonia solutions of imidazole and of pyrrole demonstrates the former compounds to represent the stronger acid. Electronegative substituents increase the acidic properties of the imidazoles by decreasing the electron density about the pyrrole nitrogen.

Lophine is a stronger acid than imidazole. Like imidazole, lophine forms salts upon treatment with metals or metal amides in liquid ammonia solution (186).
2,4,5-tribromoimidazole is strong enough acid to dissolve in aqueous sodium carbonate solution (187).

3. Chemical Stability And Aromatic Character

Although a detailed discussion of the chemical behaviour of the imidazoles will represent the subject of later chapters, it seems pertinent to summarize briefly a number of their key properties prior to consideration of structure.

Outstanding is the pronounced chemical stability of the imidazoles. They are resistant to the most drastic treatments with acids and bases. Exposers of imidazoles to the action of the iodide at temperatures up to 300° has little effect, and the imidazole ring resist catalytic hydrogenation to a remarkable degree. A number of benzimidazoles, such as 2-methyl, 2-ethyl, and 1,2-dimethylbenzimidazole, in the presence of Adams catalyst and glacial acetic acid undergo hydrogenation in the benzene portion with the formation of the corresponding tetrahydro derivatives. The imidazole portion remains unaffected.

Imidazole is stable toward chromium trioxide (187), but is readily attacked by potassium permagnate and hydrogen peroxide with the formation of oxamide (188, 189). Benzoyl peroxide in chloroform solution also attacks imidazole readily with formation of urea and ammonia (190).

4.2 EXPERIMENTAL

(a) Materials employed:

Imidazole and 1-methyl imidazole and 2-methyl imidazole were obtained from Aldrich Chemical Company,
Hydroxylaminehydrochloride and Chromic acid were supplied by SD Fine Mumbai. Potassium Cyanide was procured from May and Baker Limited, Dagenham. Distilled water was used in all the operations.

(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 (4000-450 cm⁻¹) of the uncoordinated ligands and synthesized complexes were recorded in nujol mulls supported between KBr pellets on PerkinElmer (RXI) spectrometer (at sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow).

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

4.3 PREPARATION OF THE PARENT COMPOUND

Potassium pentacyanonitroycylchromate(I) monohydrate $K_3[Cr(NO)(CN)_3].H_2O$ was again used as the parent compound for synthesizing the complexes under this investigation.

4.4 PREPARATION OF COMPLEXES

(a) Preparation of $[Cr(NO)(CN)_2(IMD)_2(H_2O)]$

To a filtered aqueous solution (40 ml., 0.02M) of potassium salt of the pentacyanonitroycylchromate(I) monohydrate, an aqueous acetic acid solution (10 ml, 1:1) of the imidazole 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 CO$_2$ 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 $[Cr(NO)(CN)_2(1\text{--M Imd})_2(H_2O)]$

To a filtered aqueous solution (40 ml., 0.02M) of potassium salt of the pentacyanonitroycylchromate(I) monohydrate, an aqueous acetic acid solution (10 ml, 1:1) of
the 1-methyl imidazole (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.

(c) Preparation of [Cr(NO)(CN)₂(2-M Imd)₂(H₂O)]

To a filtered aqueous solution (40 ml., 0.02M) of potassium salt of the pentacyanonitrocylchromate(I) monohydrate, an aqueous acetic acid solution (10 ml, 1:1) of the 2-methyl imidazole (0.02M) was added with shaking. When a yellowish-brown 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).

\[
K_3[Cr(NO)(CN)_5].H_2O + 2L \xrightarrow{AcOH} [Cr(NO)(CN)_5(L)_2(H_2O)] + 3KOAC + 3HCN + H_2O
\]

Where \( L = \) Imidazole, 1-methyl imidazole and 2-methyl imidazole

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 pentacyanonitrosylchromate(I) \( [Cr(NO)(CN)_5]^3+ \) to attain \( [Cr(NO)(CN)_2(H_2O)_3] \) favour the above reaction scheme.

Compounds were characterized by on the basis of following results:
(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 important IR spectral bands of the synthesized complexes containing coordinated Imidazole, 1-methyl imidazole and 2–methyl imidazole with other ligands are presented in table 4.8 respectively.

The ligand imidazole, 1-methyl imidazole and 2–methyl imidazole possess 2 possible donor sites; two cyclic nitrogen ring system. Further that the cyclic nitrogen atom involved in coordination through the N atom. The IR frequency of tertiary cyclic nitrogen ring is and essentially changed, thereby, suggesting the cyclic nitrogen of this ligand participate in the coordination.
Coordination through the ring nitrogen present in the imidazole ring causes an increase in the ring v(CN) and imidazole ring breathing mode. In the uncoordinated ligand, the imidazole ring breathing mode appears at 1329 cm\(^{-1}\). The significant positive shift for imidazole ring breathing mode in the synthesized complex with imidazole indicates conclusively that coordination of the ligand takes place through imidazole ring nitrogen only.

Both the synthesized complexes exhibit a broad band in the region 3580–3550 cm\(^{-1}\) indicating the presence of v(OH) of the coordinated water. The synthesized complexes also show a strong band in the region 2120-2150 cm\(^{-1}\) which may be assigned for v(CN), which is in accordance with assignment made for other reported complexes.

The analytical data and all the evidences presented above suggest the formulation of these complexes as [Cr(NO) (CN)\(_2\) (L)\(_2\)(H\(_2\)O)]. Since all these complexes show one CN stretching band and one NO stretching band it is reasonable to propose an octahedral structure (10) where CN is trans to CN and L ligands are trans to each other in equatorial position, whereas NO is trans to water in axial position.

4.7 SUMMARY

The novel mixed-ligand hexacoordinated cyanonitrosyl complexes of monovalent chromium of the general formula [Cr(NO)(CN)\(_2\)(L)\(_2\)(H\(_2\)O)] (where L = imidazole, 1-methly imidazole and 2-methyl imidazole)
have been prepared by the interaction of potassium pentacyanonorrosylchromate(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 \( \{\text{CrNO}\}^5 \) electron configuration.

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

(v) All of them give pink colour with Griess Reagent.
Proposed octahedral structure of $[\text{Cr(NO)} (\text{CN})_2 (\text{L})_2(\text{H}_2\text{O})]$  
(where $\text{L} = \text{imidazole, 1-methyl imidazole and 2-methyl imidazole}$)
1H-imidazole

1-methyl-1H-imidazole

2-methyl-1H-imidazole
**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(Imd)₂(H₂O)]</td>
<td>Aquadicyanobis (imidazole)-nitrosylchromium (I)</td>
<td>{CrNO}⁵</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₂(1-M Imd)₂(H₂O)]</td>
<td>Aquadicyanobis (1-methyl imidazole)-nitrosylchromium (I)</td>
<td>{CrNO}⁵</td>
</tr>
<tr>
<td>3.</td>
<td>[Cr(NO)(CN)₂(2-M Imd)₂(H₂O)]</td>
<td>Aquadicyanobis (2-methyl imidazole)-nitrosylchromium (I)</td>
<td>{CrNO}⁵</td>
</tr>
</tbody>
</table>

166
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>[Cr(NO)(CN)₂(Imd)₂(H₂O)]</td>
<td>16.54 (16.65)</td>
<td>38.40 (38.47)</td>
<td>3.21 (3.23)</td>
<td>31.29 (31.40)</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₂(1-M Imd)₂(H₂O)]</td>
<td>16.37 (16.44)</td>
<td>37.89 (37.98)</td>
<td>4.41 (4.46)</td>
<td>30.80 (31.01)</td>
</tr>
<tr>
<td>3.</td>
<td>[Cr(NO)(CN)₂(2-M Imd)₂(H₂O)]</td>
<td></td>
<td></td>
<td></td>
<td></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(Imd)₂(H₂O)]</td>
<td>Brownish green</td>
<td>260</td>
<td>55</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₂(1-M Imd)₂(H₂O)]</td>
<td>Greenish yellow</td>
<td>265</td>
<td>45</td>
</tr>
<tr>
<td>3.</td>
<td>[Cr(NO)(CN)₂(2-M Imd)₂(H₂O)]</td>
<td>Yellowish brown</td>
<td>268</td>
<td>50</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(Imd)₂(H₂O)]</td>
<td>60%</td>
<td>65%</td>
<td>35%</td>
<td>20%</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₂(1-M Imd)₂(H₂O)]</td>
<td>55%</td>
<td>60%</td>
<td>30%</td>
<td>15%</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>3.</td>
<td>[Cr(NO)(CN)₂(2-M Imd)₂(H₂O)]</td>
<td>50%</td>
<td>45%</td>
<td>25%</td>
<td>15%</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>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)₂(Imd)₃(H₂O)]</td>
<td>115</td>
<td></td>
<td>311.21</td>
<td>312.23</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)₂(1-M Imd)₂(H₂O)]</td>
<td>112</td>
<td></td>
<td>315.02</td>
<td>316.26</td>
</tr>
<tr>
<td>3.</td>
<td>[Cr(NO)(CN)₂(2-M Imd)₂(H₂O)]</td>
<td>112</td>
<td></td>
<td>315.02</td>
<td>316.26</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>$\mu_{\text{eff}}$</th>
<th>'g'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$[\text{Cr(NO)(CN)}_2(\text{Imd})_2(\text{H}_2\text{O})]$</td>
<td>1.72</td>
<td>1.984</td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{Cr(NO)(CN)}_2(1-\text{M Imd})_2(\text{H}_2\text{O})]$</td>
<td>1.74</td>
<td>1.985</td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{Cr(NO)(CN)}_2(2-\text{M Imd})_2(\text{H}_2\text{O})]$</td>
<td>1.74</td>
<td>1.985</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>$v_{(NO)}$</th>
<th>$v_{(CN)}$</th>
<th>$v_{(N\text{ cyclic})}$</th>
<th>$v_{(OH)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Cr(NO)(CN)$_2$(Imd)$_2$(H$_2$O)]</td>
<td>1720</td>
<td>2150</td>
<td>1375</td>
<td>3580(br)</td>
</tr>
<tr>
<td>2.</td>
<td>[Cr(NO)(CN)$_2$(1-M Imd)$_2$(H$_2$O)]</td>
<td>1700</td>
<td>2160</td>
<td>1370</td>
<td>3575(br)</td>
</tr>
<tr>
<td>3.</td>
<td>[Cr(NO)(CN)$_2$(2-M Imd)$_2$(H$_2$O)]</td>
<td>1710</td>
<td>2155</td>
<td>1370</td>
<td>3580(br)</td>
</tr>
</tbody>
</table>
04/01/08 11:12 AH, CODE- M
X: 4 scans, 4.0cm⁻¹, flat, smooth, abex
SPF NO - 6809

COORDINATION COMPOUND WITH
IMIDAZOLE
04/01/08 10:54 AH, CODE-E
X: 4 scans, 4.0cm⁻¹, flat, smooth, abex
SALF NO-6809

COORDINATION COMPOUND WITH
1-METHYL IMIDAZOLE
04/01/08 10:55 AH, CODE - F
X: 4 scans, 4.0 cm⁻¹, flat, smooth, abex
SAIF NO - 6809

COORDINATION COMPOUND WITH
2-METHYL IMIDAZOLE
COORDINATION COMPOUND WITH IMIDAZOLE

INTEGRAL: 1.223

ppm: 1.000, 1.609, 1.7740, 0.568

MRS NO. 6809
COORDINATION COMPOUND WITH 1-METHYL IMIDAZOLE