CHAPTER FIVE

ISOLATION OF THE COMPLEXES AND MAGNETIC STUDIES
Isolation of the metallic complexes of pyridines have been attempted by various methods as mentioned before in Chapter I (Literature survey p. 17-20). However, in most of the studies, the metallic salt is directly treated with the ligand i.e. in the absence of water. Nickel complexes having composition \((\text{Ni L}_4)^{++}\) and even \((\text{Ni L}_6)^{++}\) (when \(L = \) pyridine or substituted pyridines) have been reported. In the present investigation, however, an attempt has been made to isolate the metallic complexes of pyridine and its derivatives from aqueous phase in order to investigate the structural characteristics of the complexes for which the solution stabilities have been studied in the earlier chapters.

**Isolation of the complexes**

(i) Nickel complexes - Concentrated equimolar solutions of nickel nitrate and ligands were mixed in the ratio of 1:2 (ligand being a bit in excess). Wherever nickel precipitated as nickel hydroxide, the solution was filtered and then refluxed for three hours. It was allowed to stand for two hours. No hydroxide was precipitated, indicating the absence of free nickel ions. The solution was evaporated to one fourth of its original volume and was kept in the vacuum desiccator for four hours. Blue crystals were obtained. The supernatant liquid was decanted. The solid was washed with ether several times to remove the unreacted ligand completely. The complexes were then dried at reduced pressure in vacuum desiccator. In case of \(\alpha\)-picoline a pasty mass was obtained which could not be dried in any way. The 2:6-lutidine and
2-amino-4-methylpyridine complexes could not be isolated because the solution could not be made free from the precipitation of nickel hydroxide.

(ii) Cadmium complexes - The concentrated equimolar solutions of cadmium nitrate and ligands were mixed in the ratio of 1:2 (ligand being a bit in excess) giving immediate precipitate. It was filtered and washed for 2-3 times with water containing 20% ligand and then several times with ether to remove the adsorbed and unreacted ligand completely. The complexes thus isolated were dried under reduced pressure in vacuum desiccator.

The lutidines and collidine complexes, however, could not be isolated.

(iii) Magnesium complexes - Magnesium complexes could not be isolated due to the formation of hydroxide on concentration.

Complexes having glycollate and lactate in outer sphere -

Nickel and cadmium complexes having glycollate and lactate ions in outer sphere have also been isolated as stated below:

(1) Nickel complexes - Nickel glycollate and nickel lactate were prepared by refluxing nickel carbonate (in excess) with glycolic and lactic acids respectively for 3-4 hours. The refluxed mixtures were filtered to remove the unreacted nickel carbonate. The filtrate (a clear solution) was concentrated to one fourth of its original volume and then evaporated to dryness at reduced pressure in vacuum desiccator. The compound was recrystallised from water and analysed for nickel. It was found that both nickel glycollate and lactate
are simple salts having compositions \((\text{CH}_2.\text{OH}.\text{COO})_2 \text{ Ni}\) and 
\((\text{CH}_3.\text{CHOH}.\text{COO})_2 \text{ Ni}\) respectively.

Concentrated equimolar aqueous solutions of nickel glycollate and nickel lactate (separately) and ligands (except that of 2-amino-1-methylpyridine which was prepared in 50 % ethanol) were mixed in the ratio of 1:2 with a little excess of the ligand. The solution was filtered wherever there was a precipitate of nickel hydroxide. The filtrate was concentrated and crystallised at reduced pressure in vacuum desiccator. The crystals obtained were washed several times with ether to remove the unreacted ligand. The complexes of α-picoline, lutidines and collidine could not be isolated in pure form as precipitation of nickel hydroxide could not be checked while concentrating the solution.

(ii) Cadmium complexes - Cadmium glycollate and cadmium lactate were prepared in a way similar to nickel glycollate and lactate. The compounds obtained were found to have composition corresponding to \((\text{CH}_2.\text{OH}.\text{COO})_2 \text{ Cd}\) and 
\((\text{CH}_3.\text{CHOH}.\text{COO})_2 \text{ Cd}\).

Concentrated equimolar aqueous solutions of cadmium glycollate and cadmium lactate (separately) and ligands (except that of 2-amino-1-methylpyridine which was prepared in 50 % ethanol) were mixed in the ratio of 1:2 with a little excess of the ligand. The solution was filtered wherever there was a precipitate of cadmium hydroxide. The filtrate was concentrated and crystallised at reduced pressure in vacuum desiccator. The crystals were washed with ether several
times to remove the unreacted ligand. The complexes of α-picoline, lutidines and collidine, however, could not be isolated.

(iii) Magnesium complexes - Magnesium complexes having glycollate and lactate ions in the outer sphere also could not be isolated due to the precipitation of magnesium hydroxide on concentration.

The complexes so isolated were analysed for metal and nitrogen contents. The results of analysis have been presented in Tables V(i), (ii).

Analysis of the compounds corresponds to the formula 
\[
[M \cdot L_2 \cdot (H_2O)_2] \cdot X_2 \quad \text{where} \quad L = \text{ligand}, \quad M = \text{Ni}^{++} \quad \text{or} \quad \text{Cd}^{++} \quad \text{and} \quad X = \text{nitrate, glycollate or lactate.}
\]

In case of nickel complexes the probable structure could be square planar or a tetrahedral arrangement of two pyridine and two water molecules around the central nickel ion. The structure finds support in magnetic susceptibility studies.

**Determination of magnetic moments** -

The magnetic susceptibility of the isolated complexes was determined by Gouy method using a Mettler balance and electromagnet of constant current strength (say three amperes) in all cases.

According to theory -

\[
g \cdot dw = \frac{1}{2} (K_1 - K_2) \cdot H^2 A \quad \ldots \ldots (5.0)
\]

where \( g \) = gravitational constant

\( dw \) = difference in weight keeping specimen in the field or out of the field.
\( K_1 = \text{volume susceptibility of the material} \)
\( K_2 = \text{volume susceptibility of medium i.e. air} \)
\( H = \text{field strength} \)
\( A = \text{area of the cross section} \)

or \( 2 \frac{g \, dw}{H^2 \, A} = x_1 \rho_1 - x_2 \rho_2 \) \( \cdots \) (5.1)

where \( K/d = x_g \)
\( d = \text{density} \)
\( x_1 = \text{mass susceptibility of specimen} \)
\( x_2 = \text{mass susceptibility of medium i.e. air} \)

or \( x_1 \frac{m}{V} = 2 \frac{g \, dw}{H^2 \, A} + x_2 \rho_2 \) \( \cdots \) (5.2)

when \( m = \text{mass} \)
\( V = \text{volume} \)

\[
2 \frac{g \, dw \, V}{H^2 \, A} \quad + \quad x_2 \rho_2 \, V
\]

\[
\therefore \quad x_1 = \frac{2 \frac{g \, dw}{H^2 \, A}}{m} + x_2 \rho_2 \, V \quad \cdots \) (5.3)

\[
= x_g
\]

Since \( g, x_2 \) and \( \rho_2 \) are constants, \( H \) is maintained constant and \( A \) and \( V \) are constants for a particular tube, equation (5.3) becomes

\[
x_g = \frac{a + \beta \, dw}{m} \quad \cdots \) (5.4)

when \( a = x_2 \rho_2 \, V \)

\[
= 0.029 \times V \times 10^{-6}
\]

When susceptibility for air has been taken as \( 24.16 \times 10^{-6} \) and density as \( 12.04 \times 10^{-4} \) the Bohr magneton can be calculated as:
Calibration for magnetic susceptibility measurements -

Although it is possible to use the Gouy method directly for absolute measurements of magnetic susceptibility by measuring $H$, $A$, etc., this is rarely done and instead the apparatus involved is calibrated by making a measurement on a substance of accurately known susceptibility. When such a measurement has been made in a given Gouy tube then the factor $\beta$ can be evaluated and employed to determine the susceptibility of unknown substances packed in that tube.

Calibration of the tubes - Three Pyrex tubes of different lengths (9, 10 and 11 inches) and known weights and volumes but of uniform bore (say 3 mm.) were calibrated at a particular temperature. The tubes were filled with $\text{Hg}[\text{Co(CNS)}_4]$, whose susceptibility ($x_g = 16.44 \times 10^{-6}$) is known, up to one centimeter and were tapped for equal number of times to pack the substance in the tubes closely. The tube constant, $\beta$ was found by taking the weights of the tubes in the magnetic field and outside the field from equation (5.4) as:

$$B.M. = 2.84 \sqrt{x_M} \cdot T \quad \ldots \ldots \quad (5.5)$$

When $x_M = \text{molecular susceptibility of the specimen} = x_g \times \text{molecular weight of the specimen}$

$T = \text{absolute temperature at which the readings have been taken.}$
\[ \beta = \frac{16.14 W - 0.029 V}{dw} \times 10^{-6} \quad \ldots \quad (5.6) \]

where \( W \) = weight of the substance
\( V \) = volume of the tube
dw = difference of weight in the field and weight out of the field + tube
magnetism i.e. diamagnetic correction of the glass tube.

If the values of \( \beta \) in case of all the three tubes did not coincide or did not come in the difference range of \( \pm 0.1 \) the tubes were filled again up to some more height and the above process was repeated till the values of \( \beta \) in all the cases worked out to be the same or within the range of \( \pm 0.1 \). After the constant values were obtained, the tubes were considered to be calibrated up to that height. That point in the tubes was marked and the tubes were filled up to that mark with the substance whose susceptibility was to be determined. The tubes were tapped equal number of times in each case. In this way the three tubes were calibrated and the tube constant, \( \beta \) was calculated from equation (5.6).

Determination of magnetic susceptibility –

For actual measurement of the magnetic susceptibility the compound was first dried thoroughly and was finely powdered. This dry finely powdered compound was filled up in the calibrated tubes (whose \( \beta \) was known) up to the calibration mark with equal number of tappings.

The temperature was noted and the ampereage (three amperes) was fixed in the electromagnet with the help of a rheostat connected with the instrument in series. Then the
tube was suspended in the balance and the weight of the tube + powder was noted before passing the current and after passing the current in the electromagnet. In this way the magnetic susceptibilities of the complexes were determined which are tabulated in Table V([8]).

Some of the nickel complexes as listed below have a tendency to absorb moisture, hence magnetic study could not be done.

Ni-Y-picolinate nitrate
Ni-2:4-lutidinate nitrate
Ni-2:4-lutidinate glycollate
Ni-2-aminopyridinate glycollate
Ni-2-amino-4-methylpyridinate glycollate
Ni-2:4-lutidinate lactate
Ni-2-aminopyridinate lactate
Ni-2-amino-4-methylpyridinate lactate

The magnetic study of cadmium complexes revealed that all these complexes are diamagnetic.
DISCUSSION

The application of the methods of magnetochemistry is most rewarding in dealing with the coordination compounds particularly of transition and inner transition metal ions with incomplete shells having unpaired electrons. The magnetic effects are taken to be of two types:

(i) arising from the motion of electrons regarded as charged particles which gives rise to the phenomenon of diamagnetism,
(ii) arising from the spin and angular momentum of these electrons, which gives rise to paramagnetism and its extensions to ferromagnetism and antiferromagnetism.

The possession of these forms of angular momentum can be regarded as turning an atomic system into a micro magnetic dipole, of moment $\vec{\mu} = (\vec{L} + 2\vec{s})\sigma$ where $\vec{L}$ is the total orbital angular momentum and $\vec{s}$ the total spin angular momentum (in units of $\hbar/2\pi$) of the set of electrons in the atom. The assembly of such a set of magnetic dipoles gives to a paramagnetic substance its characteristic property: it experiences a force towards the stronger part of the magnetic field i.e. the opposite of a diamagnetic substance. It also leads to the Curie-Weiss law for the variation of the susceptibility ($x$) of a paramagnetic substance with temperature, $x \propto 1/T$. It may be noted that since both the spin and orbital angular momenta of the electrons of a filled shell cancel out to zero, such a system can not show paramagnetism but is left with only a diamagnetic effect. That is why paramagnetism is found mainly in transitional and lanthanide ion series.
The spin-only value i.e. the contribution to the moment from only the electron spin effect is given by the equation:

\[ \mu_s = g \sqrt{s(s+1)} \]  \hspace{1cm} (5.7)

where \( \mu_s \) is the spin moment in units of Bohr magnetons (one B.M. = \( \frac{e\hbar}{4\pi mc} \)), \( s \) is the sum of the spin quantum numbers of the electrons and \( g \) is the Lande' splitting factor which is the ratio of the magnetic moment of the electron to the total angular momentum of the electron. For a free electron \( g = 2.00023 \).

For a many electron system the spin-only moment is evaluated from equation (5.7) by employing \( g = 2 \) and the sum of the spin quantum numbers of all the unpaired electrons as the value for \( s \), (e.g. \( 3/2 \) for three unpaired electrons). The sum of the spins of paired electrons equals zero. Using this procedure, the spin-only moments for 1, 2, 3, 4 and 5 unpaired electrons can be calculated. The following equation can also be used for the same.

\[ \mu_s = \sqrt{n(n+2)} \]  \hspace{1cm} (5.8)

where \( n \) is the number of unpaired electrons.

When there is appreciable spin-orbit coupling in a molecule or ion which gives splitting of the ground state that is large compared to \( KT \), there will be an appreciable contribution to the moment from this coupling. This situation prevails for atoms in the gas phase and for most of the rare earth ions. The moment expected when spin-orbit coupling is present, is given by the following equation:
When $J$ is the total angular momentum of the ground state given according to $L S$ coupling, by:

$$|L + S|, \quad |L + S - 1|, \quad \ldots \quad |L - S|.$$  
If the shell is half filled with electrons, the ground state is $|L - S|$; and if it is more than half filled, it is $|L + S|$. For free gaseous atoms, the $g$ factor is given by:

$$g = 1 + \frac{J (J + 1) + S(S + 1) - L (L + 1)}{2 J (J + 1)} \quad \ldots \quad (5.10)$$

Effect of the ligand field on spin-orbit coupling -

The experimental magnetic moments for first row transition metal ions do not agree very well with those calculated by equation (5.9) and (5.10). The moments are often found to be close to those calculated for the spin-only value. The discrepancy between the measured results and those calculated from equations (5.9) and (5.10) arises because the ligands remove the degeneracy of the set of d orbitals. A simple model of spin-orbit coupling involves electron occupation of equivalent degenerate orbitals which enables the electron to revolve about an axis. For example, when rotation occurs by occupation of $d_{xy}$ and $d_{x^2-y^2}$ orbitals, classically this gives the electron an orbital angular momentum about the $Z$ axis. A ligand field splits the degeneracy of the $d_{x^2-y^2}$ and $d_{xy}$ orbitals, and spin-orbit coupling can not occur via this model for this set of orbitals. In an $O_h$ or $T_d$ complex ion, the $e_g$ set of orbitals ($d_{x^2-y^2}$, $d_z^2$) can not be employed by the electrons.
to rotate about an axis, and these orbitals can not contribute to the orbital angular momentum. Secondly, when the $T_{2g}$ set or orbitals in a complex is half filled or filled, rotation involving $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals is not possible, and orbital contributions from this set are quenched. As long as $T_{2g}$ level is not half filled or completely filled, degenerate arrangements of the electrons in these three orbitals provide a mechanism whereby electrons can circulate about the Z axis by occupying the $d_{xz}$ and $d_{yz}$ orbitals.

In an octahedral field $\text{Ni}^{++}$ ($d^8$) has a non-degenerate ground state, $3A_2 (T_{2g}^6 e_g^2)$, and no contribution from spin-orbit coupling is expected. Similar is the case in outer orbital square planar complexes. The measured moments are in the range 2.8 - 3.3 B.M., very close to the spin-only value of 2.83. Values slightly above the spin-only value arise from slight mixing of a multiplet excited state in which spin-orbit coupling is appreciable. Tetrahedral $\text{Ni}(\text{II})$ has a $T_1$ ground state essentially ($e_g^6 T_{2g}^4$), and a large orbital contribution to the moment is expected. As a result, even though both octahedral and tetrahedral $\text{Ni}(\text{II})$ complexes contain two unpaired electrons, tetrahedral have magnetic moment around 4 B.M compared to 3.3 B.M or less for octahedral complexes.

The magnetic moment measurements indicate that the nickel complexes are paramagnetic and have two unpaired electrons. The magnetic moments of the nickel complexes studied are in the range of 2.70 - 3.25 i.e. corresponding
to spin-only value and this indicates the possibility of square planar complexes. In case of complexes with glycollate and lactate ions in the outer sphere, the values of magnetic moment are almost of the same order which indicates the similarity of their structure with the complexes having nitrate as the outer ion. This supports the consideration that glycollate and lactate ions are in the outer sphere.
<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Ni percentage</th>
<th>N percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td>Pyridinate-nitrate</td>
<td>15.58</td>
<td>15.62</td>
</tr>
<tr>
<td>β-picolinate nitrate</td>
<td>14.53</td>
<td>14.42</td>
</tr>
<tr>
<td>γ-picolinate nitrate</td>
<td>14.53</td>
<td>14.89</td>
</tr>
<tr>
<td>2:4-lutidinate nitrate</td>
<td>13.56</td>
<td>13.69</td>
</tr>
<tr>
<td>2:4:6-collidinate nitrate</td>
<td>12.74</td>
<td>12.68</td>
</tr>
<tr>
<td>2-amino-pyridinate nitrate</td>
<td>14.43</td>
<td>13.98</td>
</tr>
<tr>
<td>Pyridinate glycollate</td>
<td>14.50</td>
<td>14.10</td>
</tr>
<tr>
<td>β-picolinate glycollate</td>
<td>13.56</td>
<td>13.06</td>
</tr>
<tr>
<td>γ-picolinate glycollate</td>
<td>13.56</td>
<td>13.02</td>
</tr>
<tr>
<td>2:4-lutidinate glycollate</td>
<td>12.74</td>
<td>13.27</td>
</tr>
<tr>
<td>2:4:6-collidinate glycollate</td>
<td>12.00</td>
<td>12.31</td>
</tr>
<tr>
<td>2-amino-pyridinate glycollate</td>
<td>13.50</td>
<td>13.01</td>
</tr>
<tr>
<td>2-amino-4-methyl pyridinate gly.</td>
<td>12.69</td>
<td>12.17</td>
</tr>
<tr>
<td>Pyridinate lactate</td>
<td>13.53</td>
<td>12.96</td>
</tr>
<tr>
<td>β-picolinate lactate</td>
<td>12.75</td>
<td>12.87</td>
</tr>
<tr>
<td>γ-picolinate lactate</td>
<td>12.75</td>
<td>12.69</td>
</tr>
<tr>
<td>2-amino-pyridinate lactate</td>
<td>12.69</td>
<td>12.16</td>
</tr>
<tr>
<td>2-amino-4-methyl pyridinate lact.</td>
<td>11.96</td>
<td>11.47</td>
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</tbody>
</table>
### Table V (ii)

Percentage of metal and nitrogen in Cd-complexes

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Ni percentage</th>
<th>N percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td>Pyridinate nitrate</td>
<td>26.10</td>
<td>25.61</td>
</tr>
<tr>
<td>β-picolinate nitrate</td>
<td>24.50</td>
<td>24.86</td>
</tr>
<tr>
<td>γ-picolinate nitrate</td>
<td>24.50</td>
<td>24.06</td>
</tr>
<tr>
<td>2-amino-pyridinate nitrate</td>
<td>24.40</td>
<td>25.08</td>
</tr>
<tr>
<td>Pyridinate glycollate</td>
<td>24.50</td>
<td>24.12</td>
</tr>
<tr>
<td>β-picolinate glycollate</td>
<td>23.10</td>
<td>23.62</td>
</tr>
<tr>
<td>γ-picolinate glycollate</td>
<td>23.10</td>
<td>23.56</td>
</tr>
<tr>
<td>2-amino-pyridinate glycollate</td>
<td>23.00</td>
<td>23.23</td>
</tr>
<tr>
<td>Pyridinate lactate</td>
<td>23.10</td>
<td>23.51</td>
</tr>
<tr>
<td>β-picolinate lactate</td>
<td>21.84</td>
<td>22.24</td>
</tr>
<tr>
<td>γ-picolinate lactate</td>
<td>21.84</td>
<td>22.31</td>
</tr>
<tr>
<td>2-amino-pyridinate lactate</td>
<td>21.76</td>
<td>21.16</td>
</tr>
</tbody>
</table>
Table V(iii)

Magnetic susceptibilities for Nickel complexes

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Magnetic susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-pyridinate nitrate</td>
<td>3.238</td>
</tr>
<tr>
<td>Ni-β-picolinate nitrate</td>
<td>2.910</td>
</tr>
<tr>
<td>Ni-2:4:6-collidinate nitrate</td>
<td>2.946</td>
</tr>
<tr>
<td>Ni-2-amino-pyridinate nitrate</td>
<td>3.068</td>
</tr>
<tr>
<td>Ni-pyridinate glycollate</td>
<td>2.870</td>
</tr>
<tr>
<td>Ni-β-picolinate glycollate</td>
<td>2.720</td>
</tr>
<tr>
<td>Ni-Y-picolinate glycollate</td>
<td>2.700</td>
</tr>
<tr>
<td>Ni-2:4:6-collidinate glycollate</td>
<td>3.047</td>
</tr>
<tr>
<td>Ni-pyridinate lactate</td>
<td>2.961</td>
</tr>
<tr>
<td>Ni-β-picolinate lactate</td>
<td>2.760</td>
</tr>
<tr>
<td>Ni-Y-picolinate lactate</td>
<td>3.060</td>
</tr>
</tbody>
</table>
References