CHAPTER II

THE EXPERIMENTAL TECHNIQUES AND THE PRINCIPLES
UNDERLYING THE PHYSICOCHEMICAL METHODS EMPLOYED

FOR CHARACTERIZING COMPLEXES
Identification and structure determination of coordination complexes using various physicochemical methods has become an important step in their study. Apart from the routine measurements such as analysis, conductance, and magnetic susceptibility, some modern spectroscopic measurements ranging in the different regions of electromagnetic spectrum are also frequently used. This chapter describes, first the general methods used for the preparation of the complexes and then the techniques as well as the principles underlying the various physicochemical methods used.

MATERIALS:

1. SOLVENTS: B.D.H.(A.R./L.R.) grade solvents were used after purification and dehydration by the standard methods.

2. STARTING MATERIAL

Cobalt(II) and iron(II) oxalates L.R. grade (made in U.S.S.R., Moscow) were used. The latter was kept in a vacuum desiccator to prevent the oxidation of Fe(II) into Fe(III).

3. LIGANDS:

B.D.H.(A.R./L.R.) grade or E.Mercks (G.R.) grade amines were used after distillation. The solid amines were used after repeated crystallizations from suitable solvents.
N-methyl piperazine and N-phenyl piperazine were prepared by well established procedures (122-25). In the Table-1 the abbreviations used in the text for specifying the various amines are given:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amine</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>m-Toluidine</td>
<td>m-tol</td>
</tr>
<tr>
<td>2.</td>
<td>Aniline</td>
<td>an</td>
</tr>
<tr>
<td>3.</td>
<td>Ammonia</td>
<td>amm</td>
</tr>
<tr>
<td>4.</td>
<td>Quinoline</td>
<td>Q</td>
</tr>
<tr>
<td>5.</td>
<td>Pyridine</td>
<td>py</td>
</tr>
<tr>
<td>6.</td>
<td>Piperidine</td>
<td>pip</td>
</tr>
<tr>
<td>7.</td>
<td>Morpholine</td>
<td>morph</td>
</tr>
<tr>
<td>8.</td>
<td>α-picoline</td>
<td>α-pic</td>
</tr>
<tr>
<td>9.</td>
<td>β-picoline</td>
<td>β-pic</td>
</tr>
<tr>
<td>10.</td>
<td>γ-picoline</td>
<td>γ-pic</td>
</tr>
<tr>
<td>11.</td>
<td>o-phenanthroline</td>
<td>phen</td>
</tr>
<tr>
<td>12.</td>
<td>2,2'-dipyridyl</td>
<td>dipy</td>
</tr>
<tr>
<td>13.</td>
<td>Ethylene diamine</td>
<td>en</td>
</tr>
<tr>
<td>14.</td>
<td>o-phenylenediamine</td>
<td>phdi</td>
</tr>
<tr>
<td>15.</td>
<td>N-methyl piperazine</td>
<td>N-mepz</td>
</tr>
<tr>
<td>16.</td>
<td>N-phenyl piperazine</td>
<td>N-phpz</td>
</tr>
<tr>
<td>17.</td>
<td>Nicotinamide</td>
<td>nic</td>
</tr>
</tbody>
</table>
PREPARATION OF THE COMPLEXES:

Coordination compounds described and studied in the present investigation were prepared by direct interaction of metal-oxalates with ligands according to the equation given below:

\[
\text{MC}_2\text{O}_4^- + nL \rightarrow \text{MC}_2\text{O}_4\cdot nL
\]

(where \( M = \text{Fe}^{2+} \) or \( \text{Co}^{2+} \) and \( n = 2 \) or \( 4 \) )

The resulting coordination compounds could be isolated by a variety of methods as under:

METHOD A:

About 5 g. of metal (II) oxalate was dissolved in excess of liquor ammonia and the resulting complex was isolated in crystalline form by addition of acetone. It was then filtered, washed with acetone and dried in an evacuated desiccator over calcium chloride.

METHOD B:

5 g. of metal (II) Oxalate was stirred vigorously with excess of amine in ethanol for 6-20 hours. The reaction mixture was allowed to stand for about 12 hours and the resulting complex was then filtered, washed with ethanol and ether
successively and dried under vacuum.

**METHOD C:**

The metal(II) oxalate was suspended in some suitable solvent like carbon tetrachloride, chloroform or ethanol, depending upon the solubility of amine. The calculated amount of amine was then added and the reaction mixture was refluxed with stirring for eight to twenty hours. The complex thus obtained was allowed to stand overnight and was then filtered, washed and dried as described earlier.

Pyridine complexes of the metals were prepared by the method of Lapiere (126), whereas the complexes of various methyl substituted pyridines were prepared by the methods of Logan and Costa (127).

**CHARACTERIZATION OF COMPLEXES:**

Various techniques described below have been employed for characterization, assignment of the molecular structure, and locating the actual site of bonding of ligand to the metals in the complexes.

The molecular formulae of the complexes were obtained by elemental analysis i.e. estimation of oxalate, metal, carbon, hydrogen and nitrogen, the latter three of which were estimated microanalytically. The metals were estimated after decomposing
a known weight of the complex several times with a mixture of nitric acid and sulphuric acids. Oxalate could be estimated either gravimetrically as calcium oxalate monohydrate or volumetrically also by titrating against potassium permanganate (in the case of cobalt(II) complexes) (128-129).

(I) **CONDUCTIVITY MEASUREMENTS:**

Conductance of the solution depends upon the number of ions present and is expressed in terms of molar conductance represented by \( \lambda \), which is found to increase with dilution and to reach a maximum value at infinite dilution i.e. \( \lambda \propto \).

The measurement of conductance thus provides information regarding the number of ions in solutions. In addition to water some non-aqueous solvents have also been employed for such measurements. The value of \( \lambda \propto \) in these has been found to be less than 1 mho for non-electrolytes but falls between 27-29 mhos for uni-univalent electrolytes, 40-44 mhos for uni-bivalent electrolytes and above 50 mhos for uni-trivalent electrolytes (130).

The molar conductance of the complexes were measured in formamide solution at a concentration of approximately \( 10^{-3} \) M using a conductometric bridge.
(II) **INFRARED SPECTROSCOPY:**

The inorganic molecules which contain a number of atoms linked by covalent bonds, constitute the simplest kinds of vibrating systems, and absorb the infrared radiations (10,000 - 100 cm⁻¹) to obtain enough energy for such vibrations.

In order for a particular vibration to result in the absorption of infrared energy, that vibration must cause a change in dipole moment of the molecule. A nonlinear molecule containing "n" atoms may have 3n-6 fundamental vibration modes, which are responsible for the absorption of infrared light.

The two important vibrations for molecules which are affected on coordination are stretching and bending (deformation) modes occurring at certain quantized frequencies. Several other vibrations may also be observed in the form of absorption bands of reduced intensity, because of overtones or harmonics. Bending vibrations are usually weaker and are found to occur at longer wavelength, because they require less energy. On the other hand the stretching vibrations require more energy and as a result occur at shorter wavelength and are more intense in nature.

The structures of the complexes formed by the amines are interpreted by using a 1:1 model and the important vibra-
tional frequencies are the symmetric and asymmetric N-H strechings, symmetric and asymmetric N-H deformations, C-N stretching and M-N stretches. In addition to these the C=C and ring stretching modes are also important for aromatic amines (131).

(a) **N-H STRETCHING VIBRATION:**

In the region 3570 - 3333 cm\(^{-1}\), occurs this most characteristic vibration, the position, intensity and the shape of which depends upon the structure of the parent molecule. Thus, it is observed as a doublet in primary amines, as a singlet in secondary amines while the tertiary amines do not absorb at all in this region. Coordination almost always causes a negative shift in the position of this band.

(b) **N-H DEFORMATION VIBRATION:**

The deformation vibrations may be observed due to any of the following four modes:

(i) In-plane
(ii) Out-of plane
(iii) Twisting, and
(iv) Scissoring

The spectra of primary amines show the symmetric and asymmetric in-plane deformation vibrations in the 851-805 cm\(^{-1}\)
and 810 - 786 cm\(^{-1}\) regions, respectively (132). Sometimes a weak band is observed in the spectra of secondary aliphatic amines in the region 1650 - 1550 cm\(^{-1}\), whose detection is extremely difficult. The assignment of these bands is also difficult due to complications arising from conjugation effects (133). It is however, found that on complexation these bands shift to higher wave numbers.

(c) **C-N STRETCHING VIBRATION:**

The region 1400 - 1000 cm\(^{-1}\) is usually the range in which the C-N stretching vibrations have been observed. These are specifically seen between the frequency ranges of 1340-1250 cm\(^{-1}\) and 1350 - 1280 cm\(^{-1}\) for primary and secondary aromatic amines respectively (134). In most of the cases these vibrations are coupled with C=C vibrations (135).

It is found that frequencies of these vibrations are significantly lowered on coordination due to the drainage of electrons from the nitrogen atom of the base to the metal.

(d) **AROMATIC C-H STRETCHING AND RING VIBRATIONS:**

The most prominent and in fact the most important bands in the spectra of aromatic amines are present in the region 3100 - 3000 cm\(^{-1}\) and 1600 - 1300 cm\(^{-1}\) which are the C-H and ring stretching vibrations respectively. The latter absorptions are due to stretching and contractions of all the bands
present in the ring and these usually appear as doublets, their nature depending upon the type of substituent present in the ring.

(e) **C-H OUT-OF-PLANE DEFORMATION:**

The out-of-plane bending vibrations of the aromatic and heteroaromatic rings are coupled with the adjacent hydrogens bending in the phase. The positions of these absorptions are, therefore, characteristic of a particular pattern of the hydrogen atoms in the ring. These bands are comparatively more intense than the previous ones, and appear around 720-960 cm\(^{-1}\) region.

Coordination of the aromatic amine to the metal usually causes a positive shift in the position of these bands.

(f) **M-N STRETCHING VIBRATION**

The M-N stretching modes provide valuable information about coordination of nitrogen atom of the ligand to the metal ion. These vibrations are affected by several factors viz.- Oxidation number of the metal, masses of metal and ligand, coordination number of metal, stereochemistry of the coordination complex, basicity of the donor molecule, and ligand field stabilization energy. M-N absorption bands are always observed in far-infrared region, probably due to relatively heavy mass of the metal and the low bond order of the coordinate bond (136,137).
(g) M-O STRETCHING VIBRATION:

In case of the present complexes another important absorption band is the metal-oxygen stretching vibration which occurs as a medium band in the range 350 - 550 cm⁻¹ depending upon the mass of the metal and the bond order. The presence of these bands in the spectra of the complexes is an indication that the oxalate ion is coordinated to the metal.

The i.r. spectra were recorded on a Perkin Elmer spectrophotometer model 621 using KBr and Nujol discs. The following notations have been used to denote the intensity of absorption bands throughout the discussion of i.r. spectra:—

\[ s = \text{strong, } m = \text{medium; } w = \text{weak; } sh = \text{shoulder, } v = \text{very; } \text{br}= \text{broad, and } db = \text{doublet.} \]

The spectra of the individual complexes are given at the end of the thesis.

(iii) MAGNETIC SUSCEPTIBILITY MEASUREMENT:

The measurement of magnetic moments is helpful in making deductions about the bond arrangement and geometries of the complexes. The two important classes of magnetic behaviour associated with the complexes are —

(a) Diamagnetism, and
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(a) Diamagnetism, and
(b) Paramagnetism

The diamagnetic substances when placed in a magnetic field tend to be repelled by the applied field while the paramagnetic compounds are attracted by it.

The experimentally measureable quantity is \( \chi_\text{g} \) or gram-susceptibility which is equal to \( K \rho \), where \( K \) is magnetic permeability per unit volume and \( \rho \) is the density. It is multiplied by molecular weight to give the quantity known as molar susceptibility \( \chi M \). It is necessary to apply a correction to this quantity, called the diamagnetic correction which results from the diamagnetism of the molecule. The magnetic moment in Bohr-Magnetons is then calculated by using the equation.

\[
\mu_{\text{eff}} = 2.84 \sqrt{\chi M_{\text{corr}} x T}
\]

Its value is directly related to the number of unpaired electrons, a knowledge of which helps in deducing the structure of the molecule.

In its divalent state, cobalt has seven 'd' electrons and the value of magnetic moment depends upon the shape of the complex molecule and strength of the ligand. It is thus, found that in the tetra coordinated complexes, the square planar and tetrahedral geometries are characterized by one or three
unpaired electrons respectively, and the magnetic moments fall in the range 1.8 - 2.9 B.M. and 4.20 - 4.60 B.M. The six coordinate complexes are always octahedral, but among these, inner orbital or low spin (d²Sp³) and outer orbital or high spin (Sp³d²) types are also possible and magnetic moments are an important source in distinguishing the two bond types, as the former contain one and the latter three unpaired electrons (138).

Iron(II) with the "d⁶" configuration has been found to give four and six coordinated complexes like cobalt(II), and some distinction as regards their geometries is possible on the basis of magnetic moment values. The tetracoordinated complexes are mostly tetrahedral and in this state these are highly paramagnetic with moments falling around 5.4 B.M. corresponding to four unpaired electrons. In case of octahedral complexes both inner and outer orbital types are known. The former with d²Sp³ hybridisation are diamagnetic and the latter possessing Sp³d² hybridisation are paramagnetic (139,140).

The magnetic measurements were made using Gouy's method. The complexes under investigation were finely powdered and filled in a Gouy tube carefully by tapping, so that no air gaps were left in between. The tube was calibrated with freshly prepared Hg [Co(CNS)₄] and A.R. CuSO₄·5H₂O and was suspended between the two poles of a strong electromagnet, so that its axis was at right angles to the lines of force. The
length of the tube is so adjusted that only its lower and is under the influence of the magnetic field and the upper end is out of it.

During the experiment the empty tube is weighed first with and without the field. The substance whose magnetic moment is to be determined is filled in the tube upto the marked level, and is weighed again with and without the field. The gram susceptibility is calculated by using the formula

\[ \chi_g = \frac{1}{w} (\alpha V + \beta f) \]

where \( \chi_g \) = gram susceptibility; \( w \) = weight of the substance; \( \alpha \) = linear coefficient of air, \( V \) = volume of the tube, \( \beta \) = tube constant and \( f \) = change in pull.

(iv) **ELECTRONIC SPECTROSCOPY:**

As pointed out earlier in chapter 1, under the effect of a ligand field, the degeneracy of the 'd' level is lifted, because of which the transitions of an electron in the molecule from a lower electronic energy level to a higher level is possible. These transitions are responsible for the different colours of the complexes (141).

The cobalt(II) ion has different ground states under different ligand fields. In a weak octahedral ligand field it
is $t_{2g}^6e_{g}^2$ and $t_{2g}^6e_{g}^1$ for stronger fields. A truly regular octahedral complex is theoretically not expected(142), as the $t_{2g}^6e_{g}^1$ configuration is susceptible to Jahn-Teller distortion. An octahedrally coordinated cobalt(II) ion may have three spin allowed d-d transitions from the ground state $4T_1$ (F), to the excited states, $4T_{2g}$, $4A_{2g}$ and $4T_{1g}$ (P). The first and last of these are usually observed around 20.00 and 8.50 kK, while the middle one is weak in intensity and also due to the closeness to the first transition is often not observed in the spectra (143).

The electronic absorption spectra of tetrahedral cobalt(II) complexes are also expected to show three bands due to the three spin allowed transitions, but in practice a large number of bands are observed in the spectra with main centres around 16.40 and 6.30 kK.

The ground state for $d^6$ configuration in a weak octahedral ligand fields is $5T_{2g}$, and the only excited state of the same spin multiplicity is $5E_g$, originating from $5D$. Usually octahedral iron(II) complexes are high spin and their spectra show only one $5T_{2g} \rightarrow 5E_g$ transition (around 10.50 kK). On the other hand, the ground state of tetrahedrally coordinated iron(II) is $5E$ but here also only one absorption band corresponding to $5E \rightarrow 5T_2$ (around 6.80 kK) transition is possible (144).
The electronic spectra of the complexes were obtained on a Cary 14 recording spectrophotometer in the 200 - 2000 nm range in the form of nujol mulls. The spectra of the complexes are attached at the end of the thesis after chapter IV.