Purification of solvents, preparation of the ligands and their metal complexes, elemental analyses and the various physico-chemical techniques employed are described in this Chapter.

I. Purification of solvents

a) Dry benzene

Reagent grade benzene (C.P.) was mechanically stirred for half an hour with 15% of its volume of concentrated sulphuric acid in a three necked flask. The process was repeated until the acid layer was almost colourless, indicating the complete removal of thiophene. Then the mixture was transferred to a separating funnel and acid layer was removed and rejected. Thus obtained thiophene free benzene was then shaken twice with water, followed by aqueous sodium carbonate to remove the traces of acid. Once again benzene was washed twice with water to remove excess carbonate. Finally the washed benzene was stored over anhydrous calcium chloride. Thus dried benzene was distilled and stored over sodium wire. It was finally distilled when required in an all glass apparatus. The fraction distilling at 77-78°C was collected and used for the preparation of bimetallic complexes.
b) **Dry chloroform**

Chloroform (C.P.) was shaken 5-6 times with half its volume of water to remove alcohol added as a stabiliser and aqueous layer was rejected. The chloroform was stored over anhydrous calcium chloride for several hours. It was then distilled using an all glass apparatus under anhydrous conditions. The fraction distilling at 57-58°C was collected which was used for the preparation of bimetallic complexes.

c) **Dry ethyl alcohol**

About 75 ml of distilled absolute alcohol was placed in a two-litre, ground glass joint round bottom flask, provided with a double walled reflux condenser and calcium chloride tube. 5 gms of clean magnesium turnings and 0.5 gms of iodine were added to the flask and heated on a heating mantle. The evolution of hydrogen started with the disappearance of the colour of the solution. After magnesium was converted into its ethylate, 900 ml of absolute alcohol was added and was refluxed for thirty minutes. Then the alcohol to be dried was added and refluxation of the mixture was continued for another thirty minutes. The alcohol was then directly distilled into a clean dry flask. Adequate precautions were taken to keep the extremely hygroscopic dry alcohol free from atmospheric moisture.
d) **Methanol**

This was purified in a similar manner as ethyl alcohol by treatment with magnesium activated iodine. The fraction distilling at 61-62°C was collected.

e) **Dimethyl sulfoxide (DMSO)**

Reagent grade dimethyl sulfoxide was allowed to stand over ignited calcium oxide for two days and was distilled under reduced pressure (10 mm.). The middle fraction boiling in the range 65-70°C was collected.

f) **Dimethyl formamide (DMF)**

B.D.H. make DMF was kept over potassium hydroxide for 2-3 days in a stoppered bottle and distilled under pressure just before use in an all glass apparatus (b.p. 58-59°C/25 mm.).

II. **Materials employed**

a) **Amines**

1) Ethylenediamine (Fluka grade)
2) Propylenediamine (Fluka grade)
3) o-Phenylenediamine (Kosch-light grade)

b) **Aldehyde**

Salicylaldehyde (Bush grade) was distilled before use.

c) **Ketone**

Acetylacetone was of Reidel grade and was distilled before use (B.P. 134-136°C).

d) **Aldoxime**

Pyridine-2-aldoxime used was of Aldrich grade,
III. Preparation of ligand

a) Schiff bases derived from diamines

0.1 mole of diamine and 0.2 mole of aldehyde were mixed thoroughly in methanol and the mixture was refluxed on a water bath for 30 minutes. After cooling, crystals of Schiff base were separated and recrystallised from methanol.

b) 3-Formylsalicylic acid

3-Formylsalicylic acid was prepared by the known standard method and was purified.

IV. Preparation of soft ligand

The nickel, copper and cobalt complexes which were utilised for the preparation of bimetallic complexes were prepared as mentioned below.

a) Nickel(II) Schiff base

0.2 moles of salicylaldehyde in ethyl alcohol was heated on water bath and 0.1 mole of nickel(II) chloride in ethyl alcohol was added to the aldehyde solution in hot condition.

The refluxation was carried out for 15 minutes and 0.1 mole of sodium hydroxide in 10 ml of aqueous alcohol was added. The separated green coloured aldehyde complex was
filtered and dried, 0.2 moles of this complex was dissolved in alcohol and 0.1 mole of ethylenediamine in hot ethyl alcohol was added and the contents were refluxed for 30 minutes. The separated complex was filtered and dried in a vacuum desiccator.

For propylenediamine and o-phenylenediamine the following method was adopted.

0.2 moles of salicylaldehyde, 0.1 mole of respective diamine and 0.1 mole of nickel(II) chloride were taken in a 500 ml round bottom flask fitted with reflux condenser in alcoholic medium. The mixture was refluxed for 45 minutes and nickel(II) Schiff base complexes were separated after cooling. The bright coloured complexes were filtered, washed with alcohol and dried over calcium chloride.

b) **Pyridine-2-aldoximates of copper(II), nickel(II) and cobalt(II)**

0.2 mole of pyridine-2-aldoxime in ethanol was refluxed with 0.1 mole of copper chloride or nickel chloride in the same solvent for about 30 minutes. The greenish coloured salts formed were cooled and filtered. They were recrystallised in ethanol and finally dried over phosphorus pentoxide, but in the preparation of the cobalt complex, acetone was used as a solvent. The cobalt(II) pyridine-2-aldoximate has pinkish colour.
c) Ethylenediamine-3-formylsalicylic acid M(II) soft ligand, where $M = \text{Nickel, cobalt and copper}$

Metal complex is prepared in accordance with the standard procedure$^2$.

d) M(II) acetylacetonates, where $M = \text{nickel, cobalt and copper}$

The preparation of the soft ligands viz. nickel(II), cobalt(II) and copper(II) acetylacetonates is in accordance with the published standard method$^3$.

V. Preparation of the bimetallic complexes

The following metal salts were used for the preparation of complexes.

- Nickel(II) Chloride (B.D.H. Analar Grade)
- Nickel(II) acetate (B.D.H. Analar Grade)
- Cobalt(II) Chloride (B.D.H. Analar Grade)
- Cobalt(II) acetate (B.D.H. Analar Grade)
- Copper(II) Chloride (B.D.H. Analar Grade)
- Copper(II) acetate (B.D.H. Analar Grade)
- Silicon(IV) Chloride (Reidel Grade)
- Tin(IV) Chloride (Reidel Grade)
- Selenium(IV) Chloride (B.D.H. Analar Grade)
- Tellurium(IV) Chloride (B.D.H. Analar Grade)
- Zirconium(IV) Chloride (S. Merck Grade)
- Titanium(IV) Chloride (Reidel Grade)
a) **Preparation of bimetallic complexes involving acetyl-acetonates**

Nickel(II), cobalt(II) and copper(II) acetylacetonates, which were used as soft ligands were taken (0.01 mole) in dry chloroform to which silicon(IV) chloride (0.01 mole), tin(IV) chloride (0.01 mole), selenium(IV) chloride (0.01 mole) and tellurium(IV) chloride (0.01 mole) in the same medium were added with constant shaking. The separated complexes were allowed to settle and kept over-night. They were filtered, washed with dry chloroform and dried in vacuum over phosphorus pentoxide. The complexes were always stored in perfectly anhydrous conditions.

b) **Preparation of bimetallic complexes from nickel(II) tetradentate Schiff base and tetravalent metal ions**

The soft ligand, nickel(II) Schiff base complex was taken in dry benzene and treated with tin(IV) chloride, selenium(IV) chloride, tellurium(IV) chloride and zirconium(IV) chloride in the same solvent in 1:1 molar ratio. The flask was then kept aside for several hours with occasional shaking. The bright coloured complexes were filtered, repeatedly washed with dry benzene and finally dried over phosphorus pentoxide. The complexes were always stored in perfectly anhydrous conditions.
c) Bimetallic complexes obtained from M(II) 3-formylsalicylic acid diamine schiff bases

The soft ligands obtained by the reaction between the transition metal ions such as nickel(II), cobalt(II), copper(II) and ethylenediamine-3-formylsalicylic acid (H₂fsaen) were taken in super dry benzene (0.01 mole). To this tetravalent metal ions, namely, silicon(IV) chloride, tin(IV) chloride, tellurium(IV) chloride and titanium(IV) chloride were added in the same molar ratio. The flasks were occasionally shaken and kept aside for several hours. The bright coloured complexes were filtered and dried in vacuum over phosphorus pentoxide. The complexes were stored in a moisture free condition.

d) Bimetallic complexes employing nickel(II), cobalt(II), copper(II), pyridine-2-aldoximates and tetravalent metal ions

The transition metal pyridine-2-aldoximates were taken in dry benzene. Silicon(IV) chloride, tin(IV) chloride, tellurium(IV) chloride and titanium(IV) chloride were added in the same medium and in the ratio of 1:1. The flasks were shaken from time to time and the separated bright coloured complexes were allowed to settle overnight. They were filtered and dried in vacuum over phosphorus pentoxide. The complexes were always stored in perfectly anhydrous condition.
VI. Elemental analyses

All the determinations and estimations were carried out in accordance with the standard methods of analyses published in literature.

In the complexes containing silicon, tin, titanium, zirconium, direct ignition was carried out and the metal content was weighed as their respective oxide.

Cobalt and copper were estimated as their pyridine thiocyanate salt and nickel was estimated as dimethylglyoximate.

Selenium and tellurium were estimated by the established thiourea method.

Chloride in the complexes was determined as silver chloride by gravimetric method.

Nitrogen present in the complexes was estimated by the micro kjeldahl's method.

VII. Physico-chemical techniques employed

a) Magnetic susceptibility measurements

Magnetic susceptibility measurements of the paramagnetic complexes were made at room temperature by the Gouy method. The Gouy tube was packed uniformly with the
complex, without leaving space for the air gaps, upto the mark. The tube was suspended vertically by means of an aluminium chain connected to the pan of a single pan Mettler balance. The length of the chain was adjusted, so that bottom of the tube was exactly at the centre of the pole faces. The magnetic poles used have the following specifications.

1) Pole gap = 3.5 cms
2) Diameter of the pole faces = 9 cms
3) Field applied = 10,000 gauss.

Under the magnetic field, the complex in the cylindrical shape experiences a magnetic gradient. This will naturally cause variations in the weight of the sample. Readings were noted, with and without the magnetic field and the observation was repeated. The mean of the observations is employed to determine the apparent change in the weight (F). From this, the total pull (F') on the sample was calculated using the equation,

\[ F' = F - \delta \]

where, \( \delta \) is the pull (a negative quantity) on the Gouy tube. The gram susceptibility \( \chi_g \) of the sample was derived using the relation,

\[ \chi_g = \frac{\alpha L \beta F'}{W} \]
where, \( \alpha \) and \( \beta \) are constants for a particular Gouy tube.

\[
\alpha = 0.029 \times \text{specimen volume} \\
\beta = \text{tube calibration constant} \\
W = \text{weight of the sample taken.}
\]

The product of gram susceptibility and the molecular weight of the sample yields the molar susceptibility \( (X_M) \), which is used to calculate the magnetic moments.

The molar susceptibility was corrected for diamagnetism of the constituents of the complex using Pascal's constants. The effective magnetic moment \( \mu_{\text{eff}} \) (B.M) was calculated using the derivation,

\[
\mu_{\text{eff}} = 2.84 \sqrt{X_M'} \times T
\]

where,

\[
X_M' = \text{corrected molar susceptibility} \\
T = \text{absolute temperature at which the values were recorded}
\]

b) Electrical conductivity

Conductance measurements of the complexes in solution were made to verify the ionic formulation of the complexes. The molar conductivity of a solution was obtained from the derivation,
\[ \lambda = \frac{1000 \times \text{cell constant} \times \text{sp. conductance}}{\text{Molar concentration}} \]

The measurements were made using an ELICO CM-82 conductivity bridge provided with a dip-type conductivity cell having platinised platinum electrodes. The cell constant was determined by measuring the resistances of aqueous KCl solutions, the specific conductivities of which were known accurately from literature\(^7\). The value of the cell constant thus determined was found to be \(0.829 \text{ cm}^{-1}\). For measuring the conductivities of the solutions under consideration, the solutions of \(10^{-3}\text{M}\) concentration were employed.

Thus, value of the molar conductivity of an electrolyte in a particular solvent depends upon several factors like viscosity, polarity, mobility, etc, of the solvent. To assist the interpretation of the experimental molar conductivity of the coordination compounds, the molar conductivities of various types of electrolytes in a number of common solvents are given in the Table 1.

c) Ultraviolet-visible spectra

Ultraviolet-visible spectra of all the complexes were scanned on CARL-ZEISS SPECORD, UNICAM SP. 800 and SHIMADZU -200 S in the region 50,000-12,000 cm\(^{-1}\) (200-850 nm) using 1 cm quartz cells in appropriate solvents and the
solution was diluted to the required strength \((10^{-5}\text{ M})\). All these measurements were made at room temperature.

d) **Infrared spectra**

Infrared spectra were scanned using the following instruments:

i) CARL-ZIESS UR-10 Spectrophotometer in the region 4000-400 \(\text{cm}^{-1}\) in KBr pellets and also in Nujol mull.

ii) BECKMANN Infrared Spectrophotometer, in the region 4000-200 \(\text{cm}^{-1}\) in KBr pellets.

iii) PERKIN-ELMER 4397-5000 Infracord in the region 4000-200 \(\text{cm}^{-1}\) using KBr and CsI pellets.

iv) PERKIN-ELMER 397 Infracord in the region 4000-200 \(\text{cm}^{-1}\) using KBr pellets and also nujol mull.

v) POLYTEC-FIR-30 Spectrophotometer in the far IR region 650-100 \(\text{cm}^{-1}\), in KBr pellets.

vi) PERKIN-ELMER-257 Spectrophotometer in the region 4000-600 \(\text{cm}^{-1}\) in KBr discs and nujol mull.
Table 1
Molar conductance of the electrolytes in some common organic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molar conductance</th>
<th>Type of the electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{m} ) ohm(^{-1}) cm(^2)mole(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>85, 200</td>
<td>1:1, 1:2</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>150-160, 210-290, 410-480</td>
<td>1:1, 1:2, 1:3</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>75-85, 140-170, 200-260</td>
<td>1:1, 1:2, 1:3</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>37-43, 70-80, 110</td>
<td>1:1, 1:2, 1:3</td>
</tr>
</tbody>
</table>
References


