CHAPTER -II

Experimental
This chapter describes the following details

I : Methods of purification of solvents
II : Materials employed
III : Synthesis of ligands
IV : Synthesis of metal complexes
V : Methods of elemental analyses and
VI : Various physicochemical techniques employed in the present investigations.

I. METHODS OF PURIFICATION OF SOLVENTS

1. Super Dry Ethyl Alcohol

About 50-75 ml of distilled commercial absolute alcohol was placed in a two-litre ground glass joint round bottom flask, provided with a double walled reflux condenser and calcium chloride tubes. 5g of clean dry magnesium turnings and 0.5 g of Iodine were added to the flask and heated on a heating mantle. The evolution of hydrogen commenced and color of the solution disappeared. After some time all magnesium was converted into its ethylate. 900 ml of the absolute alcohol was then added and the mixture was refluxed for 30 min. The alcohol was distilled directly into a clean glass flask. Adequate precautions were taken to protect the extremely hygroscopic dry alcohol from atmospheric moisture.

2. Methanol

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

3. Dimethyl Formamide (DMF)

BDH reagent grade DMF was kept over potassium hydroxide pellets for two days in a stoppered bottle and distilled under reduced pressure (just before use) using an all cleaned glass apparatus (b.p.58-59 °C/25 mm).
4. Dimethyl Sulphoxide (DMSO)

Water white dimethyl sulphoxide was allowed to stand over ignited calcium oxide for two days and then distilled under reduced pressure. The middle fraction boiling in the range of 65–70 °C (~ 10mm) was collected in a cleaned dry bottle.

5. Chloroform

Chloroform was shaken 5-6 times with half of its volume of water to remove the alcohol added as a stabilizer and the aqueous layer was rejected. The chloroform was then 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 and stored in an amber colored glass stoppered bottle.

6. Ether

Ether was shaken thoroughly with 15% ferrous sulphate solution (to remove peroxide) and the aqueous layer was drawn off. Ether was then stored over anhydrous calcium chloride and distilled, after several hours of standing in an all glass apparatus, using calcium chloride guard tube. It was stored in an amber colored bottle over sodium wire and freshly distilled before use. The fraction distilling at 34-35 °C was collected.

II. MATERIALS EMPLOYED

The chemicals used for preparing the Schiff bases were of reagent grade. Salicylaldehyde was distilled before use.

1. Preparation of Thio carb ohydrazide

Thiocarb ohydrazide was prepared by the known method \[^{[Z]}\]. Carbodiisulphide (1 mol) was added slowly to hydrazine hydrate (2 mol) in 150 ml of water with constant shaking. The reaction mixture was refluxed for 30 min and cooled to 0 °C for 30 min. The precipitated thiocarb ohydrazide was filtered and washed thoroughly with water and then recrystallized in distilled water. Yield: 67 g; m.p. 169 °C (lit. 171 °C).
2. Preparation of Substituted Salicylaldehydes

Substituted salicylaldehydes were prepared by Duff's method [7]. A mixture of 300 g glycerol and 70 g boric acid was heated in a 2 L beaker with stirring until the temperature reached 165 °C. The mixture was allowed to stand at that temperature in order to expel the considerable amount of water. An intimate mixture of 50 g of the phenol and 50 g of hexamethylenetetramine was prepared by grinding the materials together thoroughly. The mixture was then added with vigorous stirring to the glyceroboric acid solution. Previously cooled to 150 °C. The reactants were stirred for 20 min during which the temperature maintained between 150 °C and 165 °C. Finally, the reaction mixture was allowed to cool to 115 °C and was then acidified with a mixture of 50 ml of concentrated sulphuric acid and 150 ml of water. The mixture was subjected to steam distillation. The distillate was cooled and filtered to get the aldehydes. In the case of solid aldehydes the distillate was cooled and filtered to get the aldehydes. In the case of liquid aldehydes the aldehydes were separated by extraction with ether.

3. Synthesis of 3-Substituted-4-Amino-5-Mercapto-1,2,4-Triazoles

3-substituted-4-amino-5-mercapto-1,2,4-triazoles were prepared by the reported methods [7,4].

A mixture of thio-carbohydrazide (10 g) and aliphatic carboxylic acid (60 ml) was refluxed for 4-5 hrs; within an hour of refluxion, the solid started separating from the clear solution. The triazoles thus obtained were recrystallized from alcohol into shining yellow crystals. The m.p. of these tally well with the reported ones [7,4].

<table>
<thead>
<tr>
<th>Acid</th>
<th>Triazole</th>
<th>M.P. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic</td>
<td>-H</td>
<td>97 – 98</td>
</tr>
<tr>
<td>Acetic</td>
<td>- CH₃</td>
<td>218 – 219</td>
</tr>
<tr>
<td>Propionic</td>
<td>- C₂H₅</td>
<td>140 – 141</td>
</tr>
<tr>
<td>Butyric</td>
<td>- C₃H₇</td>
<td>72 – 74</td>
</tr>
</tbody>
</table>

Table – 1
4. Synthesis of Bis-(4-Amino-5-Mercapto-1,2,4-Triazol-3-yl)Alkanes

Thiocarbohydrazide (0.2 mol) was treated with 0.1 mol of dicarboxylic acid in 4N HCl. The reaction mixture was refluxed for about 6 h and set aside overnight for cooling. The bis-triazole was precipitated by basifying the reaction mixture with ammonia. It was filtered, washed with water and recrystallized from ethanol. Purity of the sample was verified by elemental analyses.

5. Synthesis of 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazoles

A mixture of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and hydrazinehydrate (N₂H₄·H₂O) in 1:1 molar proportions in ethanol was refluxed for 4-5 h on a water bath. The reaction mixture was cooled at room temperature, within an hour the compound separated from the clear solution. It was filtered, washed and recrystallized from ethanol.

6. Preparation of 2,6-Diformyl-4-Methylphenol

Preparation of 2,6-diformyl-4-methyl phenol was described earlier [5-6] was prepared by a completely different way. To a solution of p-cresol (10.8g; 0.1mol) in acetic acid (50cm³) were added hexamethylenetetramine (28.2 g; 0.2 mol) and para formaldehyde (30 g; 1.0 mol). The system was stirred until a light brown viscous solution was formed and then heated (70-90°C) for 2h. The solution was formed cooled to room temperature and conc. H₂SO₄ (10 cm³) carefully added. The resulting solution was refluxed again for 0.5 h and then on treatment with distilled water (400 cm³) resulted in the formation of a light yellow precipitate, which was stored at 4°C overnight. The yellow product was isolated by filtration and washed with a small amount of cold CH₃OH. A purest product was obtained by means of recrystallization from toluene. Yield; 5.7 g (35%), mp 130-134°C (lit.133.5 °C). Skin contact with 2,6-diformyl-4-methyl-phenol causes persistent deep yellow stains.
7. Preparation of Diethyl Ester of Terephthalic Acid

Terephthalic acid (1.6 g) in super dry ethanol containing 2-3 drops of conc. \( \text{H}_2\text{SO}_4 \) (AR) was refluxed till it dissolves. Then, the reaction mixture was poured on to ice cold water, immediately a solid started separating from the clear solution. To this a solution of sodium bicarbonate was added till the effervescence seizes. The ester thus obtained was filtered and washed with water for several times (mp. 44 °C).

8. Preparation of Dihydrazide of Terephthalic Acid

A mixture of diethyl ester of terephthalic acid hydrazide (2.22 g) and hydrazine hydrate (2 cc) in ethanol was refluxed for 4-5 h. The reaction mixture was allowed to cool to room temperature then, the cooled solution was poured on to ice cold water. The dihydrazide of terephthalic acid thus obtained was filtered and recrystallized from ethanol.

III. SYNTHESIS OF SCHIFF BASES

1. 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole Schiff Bases

A mixture of 3-substituted-4-amino-5-hydrazino-1,2,4-triazole (0.1 mol) and substituted salicylaldehyde (0.2 mol) in alcohol was refluxed for 3-4 h in presence of a few drops of concentrated hydrochloric acid. The product separated on evaporation of the alcohol and was recrystallized from ethanol. Yield (60-70%).

2. Synthesis of Bis-(4-Amino-5-Mercapto-1,2,4-Triazol-3-yl)Alkanes

Macrocyclic Schiff Bases

2,6-Diformyl-4-methylphenol (2 mmol) in ethanol (20 ml) was added to an ethanolic solution of bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes (2 mmol, 30 ml) containing a few drops of concentrated HCl. The reaction mixture was refluxed for 3 h. The mixture was cooled to room temperature and the solvent removed under reduced pressure until a solid product was formed that was washed with cold ethanol and dried under vacuuo. mp. 235-230 °C, yield (70-75%).
3. Synthesis of 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole Macrocyclic (20-Membered) Schiff Bases

2,6-Diformyl-4-methylphenol (2 mmol) in ethanol (20 ml) was added to a ethanolic solution of 3-substituted-4-amino-5-hydrazino-1,2,4-triazole (2 mmol, 30 ml) containing few drops of concentrated HCl. The reaction mixture was refluxed for 3 h. The mixture was cooled to room temperature and the solvent removed under reduced pressure until a solid product was formed that was washed with cold ethanol and dried under vacuum. mp. 252-299 °C, yield (60-65%).

4. Preparation of Terephthalic Acid Disydrazones

The ligands were synthesized by refluxing (0.01 mol) terephthalic acid dihydrazide in ethanol with an alcoholic solution of (0.02 mol) substituted salicylaldehyde containing a few drops of concentrated HCl for about 2-3 h on a water bath. On cooling, the product was separated and was filtered and washed with ethanol, dried and recrystallized from ethanol.

5. Synthesis of 3-Substituted-4-Amino-5-Mercapto-1,2,4-Triazole Schiff Bases

A mixture of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and indole-3-aldehyde in 1:1 molar proportions in an alcoholic medium containing a few drops of concentrated HCl were refluxed for 3-4 h. The products separated on evaporation of the alcohol and were recrystallized from ethanol.

6. Thiocarbohydrazone

Thiocarbohydrazone (0.1 mol) was treated with thiophene-2-aldehyde (0.2 mol) in alcoholic medium and a few drops of concentrated hydrochloric acid were added. The resulting reaction mixture was refluxed for 3 h. The product separated on cooling was filtered and washed thoroughly with ethanol. The thiocarbohydrazone thus obtained was purified by recrystallization.
IV. PREPARATION OF METAL COMPLEXES

The following metal salts were used to prepare various complexes.

1. Cobaltous chloride hexahydrate [BDH make]
2. Nickel chloride hexahydrate [BDH make]
3. Cupric chloride dihydrate [BDH make]
4. Lanthanum nitrate [Fluka make]
5. Thorium nitrate [BDH make]

1. Synthesis of Co(II), Ni(II) and Cu(II) Complexes with Schiff Bases Derived from 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole and Substituted Salicylaldehydes and Synthesis of Ni(II) Complexes with Terephthalic Acid Hydrazones

Metal (II) chloride (0.01 mol) was treated with ligand (0.01 mol) in an ethanol. The reaction mixture was refluxed for about an hour. Then the reaction mixture was added 2g of sodium acetate (0.02 mol) in water and refluxion was continued for about 3 h. The metal (II) complex separated was filtered and washed free of reagent with distilled water containing small quantity of ethanol and dried in vacuo over fused CaCl₂.

2. Synthesis of Co(II), Ni(II) and Cu(II) Complexes of Schiff Bases Derived from Bis-(4-Amino-5-Mercapto-1,2,4-Triazol-3-yl)Alkanes/3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole and 2,6-Diformyl-4-Methylphenol

Co(II), Ni(II) and Cu(II) complexes of Schiff bases, were prepared by adopting template method owing to the insolubility of the ligands in common organic solvents. 2,6-diformyl-4-methylphenol (2 mmol), bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes/3-substituted-4-amino-5-hydrazino-1,2,4-triazoles (2 m mol) and respective metal chloride (2 mmol) in ethanol were refluxed for 2-3h. The separated complexes were collected by filtration, washed with hot ethanol and dried in a vacuum desiccators over P₂O₅ (yield 60-70%).
3. Synthesis of Co(II), Ni(II) and Cu(II) Complexes of Schiff Bases Derived from 3-Substituted-4-Amino-5-Mercapto-1,2,4-Triazole and Indole-3-Aldehyde

A mixture of ligand (0.02 mol) and metal chloride (0.01 mol) was refluxed for an hour in alcohol. To the reaction mixture sodium acetate (0.02 mol) in water was added and the reflux was continued for 2 hours. Adding water precipitated the complex by adding distilled water. The complex separated was filtered, washed with water, then with alcohol and finally dried in vacuum over fused CaCl₂.

4. Lanthanum(III) Complexes of Schiff Bases Derived from 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole and Substituted Salicylaldehydes/Bis(thiophene-2-Aldehyde)-N,N'-Thiocarbohydrazone/Schiff Bases Derived from Bis-(4-Amino-5-Mercapto-1,2,4-Triazol-3-yl) Alkanes and 2,6-Diformyl-4-Methylphenol

A solution of lanthanum(III) nitrate (0.01 mol) in super dry alcohol was treated with (0.01 mol) Schiff base in super dry alcohol. The reaction mixture was refluxed for about 2-3 h. Then, the reaction mixture was cooled; the precipitation of the complex was initiated by adding distilled water containing liquor ammonia. The precipitated complex was filtered and washed thoroughly with distilled water, alcohol then with ether. The complex was dried under reduced pressure over fused calcium chloride.

5. Thorium(IV) Complexes of Bis-(Thiophene-2-Aldehyde)-N,N'-Thiocarbohydrazone/Schiff Bases Derived from Bis-(4-Amino-5-Mercapto-1,2,4-Triazol-3-yl) Alkanes and 2,6-Diformyl-4-Methylphenol

Thorium (IV) nitrate (0.01 mol) was refluxed with ligand (0.01 mol) in an ethanol for about 3 h. The precipitation of the complex was initiated by adding distilled water containing liquor ammonia. The precipitated complex was filtered and washed thoroughly with distilled water, alcohol then with ether. The complex was dried under reduced pressure over fused calcium chloride.
V. METHODS OF ELEMENTAL ANALYSES

1. **Estimation of cobalt(II)** [7]

   Accurately weighed (0.2 g) of the complex was decomposed with concentrated nitric acid (15 ml) and concentrated hydrochloric acid (10 ml). Then the residue was dissolved in water and treated with 2 g of sodium acetate and the solution was heated to 70 °C and cobalt was precipitated from warm solution by treating with 10-15 ml of 2% ethanolic oxine solution with constant stirring. The precipitate was boiled gently for a few minutes. Light brown cobalt oxinate was filtered through a previously weighed sintered glass crucible G3, washed with hot water to remove excess oxine. The precipitate was dried at 100 °C and weighed as Co(C₉H₆NO)₂.2H₂O.

2. **Estimation of Nickel(II)** [7]

   Accurately weighed (0.2 g) complex was decomposed with concentrated nitric acid (15 ml) and concentrated hydrochloric acid (10 ml). The residue was treated with 5 ml of concentrated sulphuric acid and heated till the white fumes commenced to evolve. The residue was dissolved in about 150 ml of water. The solution was heated to about 70-80 °C and treated with a slight excess (15 to 20 ml) of 1% ethanolic dimethyl glyoxime solution followed by dilute ammonia. The precipitate was digested for 30 min on a water bath. The supernatant liquid was tested for complete precipitation. The solution was cooled to room temperature and filtered through a previously weighed sintered glass crucible. The precipitate was washed free of chloride with water and dried at 110-120 °C for about 2 h and weighed as Ni(C₄H₇N₂O₂)₂.

3. **Estimation of Copper(II)** [7]

   The accurately weighed 0.2 g of metal complex was decomposed with concentrated nitric acid (15 ml) and concentrated hydrochloric acid (10 ml). The residue obtained was dissolved in 100 ml of water and treated with 2N sodium hydroxide until a slight permanent precipitate was formed. The precipitate was dissolved by adding drop by drop dilute acetic acid and treated...
with slight excess of salicylaldoxime reagent at room temperature with constant stirring. The precipitate was allowed to settle and filtered through a previously weighed sintered glass crucible and washed with water until the washings gave no colour with ferric chloride. The precipitate was dried at 100-105 °C for 2 h and weighed as Cu(C7H6N02)2.

4. Estimation of Lanthanum(III) [7]

Lanthanum in the complexes was estimated volumetrically as follows: Accurately weighed 0.2 g of the complex was decomposed by repeated treatment with concentrated nitric acid. The residue was dissolved in distilled water. The pH of the solution was adjusted to 5 by the addition of hexamine and then titrated against standard EDTA solution using xylenol orange as indicator.

5. Estimation of Thorium(IV) [7]

Accurately weighed 0.2 g of the complex was decomposed with concentrated nitric acid, cooled and diluted to 150 ml with water. Thorium was then precipitated as hydroxide by adding ammonia. The precipitate was filtered through whatman filter paper No. 41 and washed with water. Then the filter paper along with the precipitate was placed in a previously weighed silica crucible and ignited for an hour. The residue was then weighed as ThO2.


Nitrogen in ligands and metal complexes was estimated by Duma’s method.


Accurately weighed complex (0.2 g) was evaporated repeatedly with aqueous ammonia to affect hydrolysis and finally boiled with aqueous ammonia. The precipitate was coagulated with about 5 g of ammonium nitrate and filtered. The precipitate was thoroughly washed with water and washings were collected in the same beaker. The filtrate was acidified with concentrated
nitric acid and heated to boiling and the solution was treated with 0.1N silver nitrate. The precipitate was digested on water bath for a while and allowed to settle. The precipitate was filtered through a previously weighed sintered glass crucible, washed thoroughly with water, finally with alcohol and dried at 120 °C and weighed as AgCl.

8. Estimation of Sulphur

About 0.15 g of complex was accurately weighed and decomposed with mixture of fuming nitric acid and concentrated hydrochloric acid. Heating was continued till the last trace of nitric acid was removed. The resultant solution was cooled to room temperature and diluted to 200 ml. The solution was heated to boiling and treated with warm 5% barium chloride solution with constant stirring till the precipitation was complete. The supernatant liquid was tested with the reagent for complete precipitation and solution was allowed to stand for 4 h. Then it was filtered through whatman filter paper No. 40. The precipitate was washed with hot water and was ignited in a previously weighed silica crucible at red heat for 10-15 min. The crucible was allowed to cool and the residue was weighed as BaSO₄.

VI. PHYSICOCHEMICAL TECHNIQUES

1. Electrical Conductivity

Conductivity measurements of the complexes in solutions were made to verify the ionic formulation of the complexes. The molar conductivity of a solution was obtained from a following relation.

\[ \Lambda_M = \frac{1000 \times \text{Cell Constant} \times \text{Specific Conductance}}{\text{Molar Concentration}} \]

The measurements were made by 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 resistance of aqueous KCl solutions, the specific conductivities of which were known accurately from literature. The value of the cell constant thus determined
was found to be 0.51 cm\(^{-1}\). For measuring the conductivities of the solutions of the complexes under investigation, the solutions of 10\(^{-3}\) M concentration were employed.

Table – 2 Molar Conductance of Electrolytes in Some Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Type of the Electrolyte</th>
<th>Molar Conductance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ohm(^{-1}) Cm(^{2}) Mole(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Dimethyl Formamide</td>
<td>1 : 1</td>
<td>78 - 85</td>
<td>9, 10, 11</td>
</tr>
<tr>
<td></td>
<td>1 : 2</td>
<td>140 - 170</td>
<td>12, 13, 14, 15</td>
</tr>
<tr>
<td></td>
<td>1 : 3</td>
<td>200 – 260</td>
<td>15, 16, 17</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide</td>
<td>1 : 1</td>
<td>37 – 43</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1 : 2</td>
<td>70 – 80</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>1 : 3</td>
<td>110</td>
<td>16, 17</td>
</tr>
</tbody>
</table>

The observed molar conductivity of a substance (electrolyte) in a particular solvent depends upon various factors like viscosity, polarity, mobility etc., of the solvent. The observed molar conductivities of the complexes were interpreted in terms of type of the electrolyte with the help of Table-2 shown above; which represents the molar conductivities of various types of electrolytes in dimethyl formamide and dimethyl sulfoxide.

2. Magnetic Susceptibility Measurements

Magnetic susceptibilities of paramagnetic solid substances were measured at room temperature using the Gouy method. The Gouy tube was filled uniformly with the powdered sample upto a mark, previously adjusted (where magnetic field was found to be negligible) and was suspended vertically by means of an aluminium chain from the pan of a semi-micro one pan Mettler balance in such a way that, the bottom of the tube was at the centre of the pole faces, (Pole gap is about 3.5 cm and the diameter of the pole faces is about 8 cm; the field is about 10,000 gauss). Under this condition when, the magnetic field is applied the cylindrical tube experiences a magnetic gradient. This will cause a change in the weight of the sample. The process of recording the weight field off and on was repeated and the mean of at least three observations
is used to obtain the apparent change in the weight (F). From the apparent change in the weight (F) the total pull (F') on the sample was calculated as

$$F' = F - \delta$$

Where, "\(\delta\)" is the pull (a negative quantity) on the Gouy tube. The gram susceptibility \(X_g\) of the sample was given by

$$X_g = \left(\alpha + \beta + F'\right) / w$$

Where \(\alpha\) and \(\beta\) are constants for a particular Gouy tube

\[\alpha = 0.029 \times \text{Specimen volume}\]
\[\beta = \text{Tube calibration constant}\]

(For the tube used in the present investigation: \(\beta = 1532\))

"w" is the weight of the sample.

In evaluating the magnetic moment, the quantity used is molar magnetic susceptibility \(X_M\).

$$X_M = X_g \times \text{Molecular weight of the sample.}$$

The molar susceptibility was corrected for the diamagnetism of the constituents of the complex using Pascal’s constants \([\mu \beta]\). The effective magnetic moment \(\mu_{\text{eff}}\) (B.M.) was calculated by using the following equation.

$$\mu_{\text{eff}} = 2.84 \sqrt{X_{M_{\text{corr}}} \times T}$$

Where, \(X_{M_{\text{corr}}}\) = Corrected molar susceptibility

\(T = \text{Absolute temperature at which the measurement is made.}\)

3. Uv–Visible Spectra

The Uv-Visible spectra in the region 200-1100 nm were measured on VARIANCARY Bio-50 model spectrophotometer using calibrated silica cells. Weighed samples were dissolved in appropriate solvents and solutions were diluted to the required strength \([10^{-3} \text{ and } 10^{-4} \text{ M.}]\). All the measurements were done at room temperature.
4. Infrared Spectra

The Spectra of some ligands and the complexes were obtained on a Nicolet 5700 spectrophotometer, in the region 4000-350 cm\(^{-1}\).

5. Electron Spin Resonance Spectra

The ESR spectra of a few copper (II) complexes in polycrystalline state were recorded at LNT using varian E-4 x-band ESR spectrometer with cylindrical quartz sample tube operating at microwave frequency ~ 9.1GHz. Field calibration was checked using tetracyanoethylene (TCNE) free radical for which \(g=2.00277\) at room temperature.

6. Nuclear Magnetic Resonance Spectral Measurements

The magnetic resonance spectra of few ligands and their complexes in DMSO-\(d_6\)/CDCl\(_3\) were recorded on BRUKER-300 MHz NMR spectrometer by using tetramethyl silane (TMS) as an internal standard.

7. Fluorescence Study

The fluorescence studies of few Schiff bases and their metal complexes were carried out on fluorescence spectrophotometer model HITACHI F-2000.

8. FAB-Mass Spectra

The FAB-mass spectra of few ligands and their complexes were recorded on a JEOL Sx102 / DA-6000 mass spectrometer using Argon / Xenon as the FAB gas.

9. Thermal Studies

There are various thermal analytical techniques; amongst, the most widely used techniques are thermogravimetric analyses (TGA), differential thermal analyses (DTA), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC).
In the present investigation, thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) techniques have been used to study the thermal behaviour of the complexes. Thermoanalytical method involves the measurement of various properties of compounds subject to dynamically changing environment under predetermined continuous change of heating rate, temperature range and gaseous atmosphere or vacuum.

Thermogravimetry deals with the change in the mass of the substance continuously monitored as a function of temperature or time when it is heated or cooled at a predetermined rate. It provides information on the thermal stability of the substance at different temperatures.

The apparatus used is called thermobalance and it consists of recording balance, furnace, temperature programmer and recorder.

In the present investigations the complexes are placed in a platinum crucible and subjected to a thermal treatment in presence of nitrogen against an inert substance Al₂O₃ as reference. The thermograms were recorded from ambient temperature to 1000 °C at a heating rate of 10 °C / min. The percentage weight loss was recorded at the various stages for each complex and the data was interpreted in terms of loss of ligand molecules and/or decomposition to the metal oxide by trial and error method.

The instrument employed was Perkin Elmer Diamond THERMAL ANALYSER with computer.

**Cyclic Voltammetric Studies of Some of Schiff Bases and their Metal Complexes**

Cyclic voltammetry is a powerful and sensitive analytical tool and widely used for both qualitative and quantitative analysis. It is used in all fields of chemistry as a means of studying redox states. The electrode potential at which a metal ion or complex, drug or other compounds undergo either reduction (acceptance of electrons) or oxidation (removal of electrons) can be rapidly located by cyclic voltammetry (CV). A very important aspect of CV is
its ability to generate a new redox species during the first potential scan and probe the species fate on the second and subsequent scans. Therefore, the CV is a powerful kinetic probe monitoring relative species. Since the rate of potential scan is variable, both fast and slow reaction can be followed [18A].

The theory of CV is any atom, molecule or other assembly of atoms can be oxidized or reduced if sufficient energy can be provided, such molecules are said to be electrochemically active. The important parameters of cyclic voltammogram are the magnitudes of the anodic peak current (ipa), the cathodic peak current (ipc), the anodic peak potential (Epa) and cathodic peak potential (Epc). The voltammogram is a display of current (vertical axis) versus potential. Because the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. The reducing or oxidizing strength of the electrode is precisely controlled by the applied potential. Scanning the potential in the negative direction makes the electrode a stronger reductant, whereas scanning the potential in the positive direction makes it a better oxidant.

Cyclic voltammetric methods have been found to extensive applications for numerous basic studies of electrochemical systems and analytical purposes especially powerful tools in the study of electrode reaction mechanisms and adsorbed species [18B,18C]. Extensive applications for evaluation of thermodynamics (n, k, S and G) and mass transport (D) phenomenon of a number of redox reactions and associated chemical reactions. Applications of CV are extensive and include the analysis of solids as well as solutions, media with or without added supporting electrolytes, emulsions and suspensions, frozen solutions, polymers membrane and liquid/liquid systems and biological systems such as enzyme or cultures of bacteria. The CV studies in rat brain [18D,18E], in vivo studies in animals [18F], bacteria [18G] and even plants are picking up [18H]. With the introduction of newer electrode material of very small size, these methods of chemical analyses in living systems might grow even faster.
The primary objective of developing these CV techniques was analytical, both qualitative as well as quantitative. Hence, this method can be used for the estimation of a number of inorganic, organic and organometallic compounds. Voltammetric detectors may also find increasing applications in chromatography [181,18J]. The electrochemical behavior of Schiff bases and their Cu(II) complexes were examined on CHI110A-electrochemical (HCH Instruments) analyzer (Made in U.S.A) by employing glassy carbon as working electrode, Ag/AgCl as reference electrode and platinum wire as auxiliary electrode. The working media consisted of DMF and n-Bu₄NCIO₄ as supporting electrolyte. The cyclic voltammogram of Cu(II) complexes in 10⁻³ M solution were recorded at room temperature in the potential range -5.0V to + 5.0V with a scan rate 100mV s⁻¹.
PART - A

TRANSITION METAL COMPLEXES