CHAPTER II

EXPERIMENTAL
This chapter describes

Purification of solvents.

Materials employed.

Elemental analyses and

Physico-chemical techniques employed

PURIFICATION OF SOLVENTS

Benzene

Reagent grade benzene (C.P.) was mechanically stirred for 20-30 min with 15ml of concentrated sulphuric acid in a three necked flask. The process was repeated twice or thrice until the acid layer was almost colourless indicating the complete removal of thiophene. The mixture was transferred to a separating funnel and the acid layer was removed and rejected. Benzene was then shaken twice with water and washed once with aqueous sodium carbonate to remove the traces of acid. The benzene was agian washed twice with water to remove the carbonate. Finally, the washed benzene was stored over anhydrous calcium chloride. The dried benzene was distilled and stored over fresh sodium wire. It was freshly distilled whenever required. The fraction distilling at 76-77°C was collected and stored in a glass stoppered bottle.
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. Five grams 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 colour of the solution disappeared. After some time all the magnesium was converted into its ethylate. Nine hundred ml of the absolute alcohol was then added and the mixture was refluxed for about 3 hrs. The alcohol was distilled directly into a dry flask. Adequate precautions were taken to protect the extremely hygroscopic dry alcohol from atmospheric moisture.

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.
Ether

Ether (C.P.) 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 glass apparatus, using calcium chloride tubes to protect the contents from atmospheric moisture. It was stored in an amber coloured bottle over sodium wire and freshly distilled before use. The fraction distilling at 34-35°C was collected.

MATERIALS EMPLOYED

The following metal salts were used for synthesising the various complexes in the present investigation.

1. Cobaltous chloride hexahydrate, LR grade (BDH)
2. Nickel chloride hexahydrate, LR grade (BDH)
3. Cupric chloride dihydrate LR grade (BDH)
4. Niobium pentachloride (Fluka)
5. Lanthanide oxides (Indian rare earths Ltd.)
6. Uranyl acetate, AR grade (Analar)

The following lanthanide oxides were used during the study: La$_2$O$_3$, Pr$_{6.11}$, Nd$_2$O$_3$, Sm$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, Tb$_4$O$_7$, Dy$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$, and Y$_2$O$_3$. For the preparation of Cerium
complexes, Cerium(III) nitrate hexahydrate was used.

**Preparation of lanthanide(III) nitrates**

The nitrate salts of the above lanthanides were prepared from their respective oxides. The lanthanide(III) nitrates were prepared by dissolving a slight excess of the required amount of the oxide in hot 50% (v/v) aqueous nitric acid. The solutions were evaporated to a small volume, diluted with water and evaporated again nearly to dryness. The residues were extracted with water and the process of evaporation was repeated three times to remove the excess acid resulting in crystals of lanthanide(III) nitrates.

**Preparation of uranium(IV) acetate**

A mixture of uranyl acetate (5 g) and zinc amalgam (5 g) in 50 ml glacial acetic acid was refluxed with stirring. On completion of the reduction, the slurry of Zn[U(CH₃COO)₆] in acetic acid was decanted. The complex was precipitated completely by refluxing the decantate with an excess of acetic anhydride 20 ml. The solid was filtered through a sintered glass crucible and washed with dry ether.

The precipitate was refluxed with 20 ml glacial acetic
acid, 20 ml acetic anhydride and 3 ml concentrated hydrochloric acid. Zinc chloride being soluble in acetic acid goes into solution and the $\text{U(CH}_3\text{COO)}_4$ precipitates. It was filtered through a sintered glass crucible and washed 3-4 times with dry ether to remove acetic acid and acetic anhydride. Finally the product was subjected to vacuum to remove last traces of volatile materials and stored in vacuum.

Following chemicals were used during the preparation of various class of ligands in the present investigation.

1. Salicylaldehyde (Merck)
2. Morpholine (Sisco-chem)
3. Piperidine (Sisco-chem)
4. Diethyl malonate (Sisco-chem)
5. Aniline (S.d. fine)
6. o-Vanilline (Sisco-chem)
7. 2-Hydroxy-Naphthaldehyde (Sisco-chem)
8. Glyoxal (Sisco-chem)
9. Biacetyl (Merck)

The following compounds were synthesised and used during the preparation of various class of ligands used in the present investigation.
Preparation of 5-methyl salicylaldehyde

A mixture of glycerol (150 g) and boric acid (35 g) was heated for 30 minutes at 170°C to expel all the water. To this an intimate mixture of p-cresol (25 g) and hexamethylenetetraamine (25 g) was added with vigorous stirring at -160°C. The reactants were stirred at 150-155°C for 15 minutes. The thick brown liquid obtained was cooled to 110°C and then a solution of concentrated sulphuric acid (30 ml) in water (100 ml) was added. The mixture so obtained was subjected to steam distillation. The distillate was cooled and filtered to get 5-methyl salicylaldehyde, M.P. 55°C (lit 56°C) yield 8.0 g.

Preparation of 5-chloro salicylaldehyde

20 g of salicylaldehyde was taken in a 250 ml flat bottomed flask and gently warmed on a water bath. Then dry chlorine gas was bubbled through the aldehyde for about 2 hrs. The solution first turned green and finally to bright yellow. It was then poured into ice-cold water with stirring when white solid of 5-chloro salicylaldehyde separated. It was filtered, washed with water, air dried and recrystallised from aqueous ethanol, M.P. 98°C (lit 99°C) yield 15.0 g.
Preparation of 5-bromo salicylaldehyde

15 g of salicylaldehyde was taken in a 250 ml round bottomed flask containing ~ 50 ml of chloroform. The solution was cooled in ice-water bath and then bromine (~ 12 ml) was added drop wise with constant stirring. The solution was then poured into ice-cold water with stirring when white solid of 5-bromo salicylaldehyde was separated. It was filtered, washed with water, air dried and recrystallised from aqueous ethanol, M.P. 104°C (lit. 105-106°C) yield ~ 8.0 g.

ELEMENTAL ANALYSIS

The Carbon, hydrogen, nitrogen, sulphur, and chloride present in the complexes were determined as explained below.

Estimation of carbon and hydrogen

Carbon and hydrogen was estimated by Liebig's combustion method. A known weight of the substance (0.02 g) was weighed into a small platinum boat and placed in a combustion tube, packed with oxidising filling. It was then subjected to combustion at 800°C in a stream of dry carbon dioxide free oxygen. The evolved water vapour and carbon dioxide were absorbed successively in previously weighed absorption tubes containing anhydrous magnesium perchlorate and soda-lime
respectively. From the increase in the weights of the tubes, the carbon and hydrogen contents of the substance were calculated.

Estimation of nitrogen

Nitrogen was estimated by Dumas method. A known weight of the substance (0.02 g) was weighed and transferred into a combustion tube packed with oxidising filling (cupric oxide). It was then subjected to combustion at about 800°C in an atmosphere of air-free carbon dioxide. The evolved nitrogen was swept out of the heated tube by a stream vessel (nitrometer) over 50% potassium hydroxide solution which absorbs the carrier gas. Any oxides of nitrogen that might have been produced during combustion were reconverted to nitrogen by a heated copper spiral in the combustion tube. From the measured volume of nitrogen gas, reduced to normal temperature and pressure, the amount of nitrogen in the substance was calculated.

% of Nitrogen of 27°C and 700 mm.

\[
\text{Vol. of } N_2 \text{ (in cc)} \times 0.98 \times 273 \times 700 \times 28 \times 100 \\
= \frac{300 \times 760 \times 22,400 \times \text{Wt. of substance}}{}
\]

Apart from the above classical methods of analysis for the estimation of carbon, hydrogen and nitrogen, a modern
Estimation of chloride

The chloride content in the complex was estimated as silver chloride. A known weight (~ 0.15 g) of the complex was digested with 1:1 nitric acid (30 ml) on a water bath for 1 hr. The solution was filtered through whatman filter paper No. 40 to remove insoluble organic part. The filtrate was then diluted with distilled water to 100 ml and treated with silver nitrate (0.1 M) solution. The solution was digested on a water bath and allowed to stand for 2 hrs. for complete coagulation. The process of precipitation and coagulation were performed in subdued light. The precipitate was filtered through a previously weighed sintered glass crucible G₄ and washed with very dilute nitric acid and dried at 130-140°C to constant weight.

Estimation of sulphur

About (0.15g) of complex was accurately weighed and decomposed with mixture of fuming nitric acid and concentrated hydrochloric acid. Heating was continued till the last traces
of nitric acid was removed. It was cooled to room temperature and then diluted with distilled water. To this, warm 5% barium chloride solution was added drop wise with constant stirring. The supernatent liquid was tested with the reagent for complete precipitation and solution was allowed to stand for 4 hrs. (preferably over night). Then it was filtered through whatman filter paper No 40. The precipitate was washed with hot water and then ignited in a previously weighed silica crucible for 10-15 min. The crucible was allowed to cool and the residue was weighed as barium sulphate.

Estimation of cobalt(II)\textsuperscript{26}

Accurately weighed about 0.2g amount of complex was decomposed with concentrated nitric acid (about 10-15 ml) and concentrated hydrochloric acid (about 10 ml). The residue was treated with 5 ml conc. sulphuric acid and heated till the white fumes commenced to evolve. The residue was dissolved in water and treated with 2g of sodium acetate and 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 $G_3$, washed with hot water to remove excess of oxine. The precipitate after drying at $110^\circ C$ was weighed as $\text{Co(C}_9\text{H}_6\text{NO)}_2$.

**Estimation of nickel(II)**

The complex (0.2-0.3g) was decomposed with conc. nitric acid (10-15 ml) and conc. hydrochloric acid (10 ml) and then dissolved in 150 ml of water. The solution was heated to about 70-80°C and treated with a slight excess (15-20 ml) of 1% ethanolic dimethylglyoxime solution followed by ammonia. The precipitate was digested for about 20-30 min on water bath. The supernatent liquid was tested for complete precipitation. The solution was cooled to room temperature and filtered through a previously weighed sintered glass crucible $G_4$. The precipitate was washed with cold water until free from chloride and dried at 110-120°C for about an hour and weighed as $\text{Ni(C}_4\text{H}_7\text{N}_2\text{O}_2)_2$.

**Estimation of copper(II)**

The complex (0.2-0.3g) was decomposed with concentrated nitric acid (10-15 ml) and concentrated hydrochloric acid (10 ml) and then dissolved in about 100 ml of water. The solution
was neutralised with 2N sodium hydroxide till a slight permanent precipitate occurs. The precipitate was dissolved by adding drop by drop dilute acetic acid and treated with slight excess of salicylaldehyde 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 complex was dried at 100-104°C for one hour and weighed as Cu\(\text{C}_7\text{H}_6\text{NO}_2\)_2.

Estimation of niobium(V)\(^{27}\)

Niobium content in the complex was estimated gravimetrically as \(\text{Nb}_2\text{O}_5\). A known weight of complex (0.5 g) was digested with diluted H\(\text{NO}_3\). Metal hydroxide was precipitated by the addition of ammonia with stirring. Ammonium nitrate was added in order to effect the coagulation. Ammonium nitrate was added to accelerate the filtration. In few cases "whatman" filter paper pulp was added. The precipitate was allowed to settle, filtered through a quantitative filter paper No. 42, washed with distilled water, dried and ignited and weighed as metal oxide.
Estimation of lanthanide(III)\textsuperscript{28}

Lanthanide(III) in the metal complexes was estimated volumetrically.

About 0.1 to 0.2 g of the complex was accurately weighed and decomposed by repeated treatment with Conc. HNO\textsubscript{3}. The residue was dissolved in distilled water. The pH of the solution was adjusted to 6 (using hexamine) and then titrated against standard EDTA titration using xylenol orange as indicator.

Estimation of uranium(IV)\textsuperscript{26}

Uranium in the complexes was estimated gravimetrically as U\textsubscript{3}O\textsubscript{8}. About 0.1-0.2 g of the complex was accurately weighed. It was decomposed with conc. nitric acid, cooled and diluted to 150 ml with water. Uranium was then precipitated as hydroxide by adding ammonia. The precipitate was filtered through a whatman filter paper No 41 and washed with water. 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 U\textsubscript{3}O\textsubscript{8}.
The metal content in the complexes were analysed by the following methods.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Element</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon and hydrogen</td>
<td>Liebig's combustion and microanalytical</td>
</tr>
<tr>
<td>2</td>
<td>Nitrogen</td>
<td>Dumas and microanalytical</td>
</tr>
<tr>
<td>3</td>
<td>Chloride</td>
<td>Gravimetry (using AgNO₃)</td>
</tr>
<tr>
<td>4</td>
<td>Sulphur</td>
<td>Gravimetry (using BaCl₂)</td>
</tr>
<tr>
<td>5</td>
<td>Cobalt(II)</td>
<td>Gravimetry (using Oxine)</td>
</tr>
<tr>
<td>6</td>
<td>Nickel(II)</td>
<td>Gravimetry (using DMG)</td>
</tr>
<tr>
<td>7</td>
<td>Copper(II)</td>
<td>Gravimetry (using salicylaldoxine)</td>
</tr>
<tr>
<td>8</td>
<td>Niobium(V)</td>
<td>Gravimetry (using NH₄OH)</td>
</tr>
<tr>
<td>9</td>
<td>Lanthanide(III)</td>
<td>Volumetry (using EDTA)</td>
</tr>
<tr>
<td>10</td>
<td>Uranium(IV)</td>
<td>Gravimetry (using NH₄OH)</td>
</tr>
</tbody>
</table>
Conductivity measurements

The 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 following relation.

\[ \lambda_M = \frac{1000 \times \text{Cell constant} \times \text{Specific conductance}}{\text{Molar concentration}} \]

The measurements were made using an Elico CM-82 conductivity bridge provided with a dip type conductivity cell having platinised Pt electrodes. The cell constant was determined by measuring the resistance of aqueous KCl solutions, the specific conductivities of which were known accurately from literature\(^{29}\). The values of cell constant thus determined was found to be 0.3048 cm\(^{-1}\). For measuring the conductivities of the solution of the complexes under investigation, the solution of \(10^{-3}\) M concentration were employed.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Type of the electrolyte</th>
<th>Molar conductance (Ohm Cm mol⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>1:1</td>
<td>78-85</td>
<td>30, 31, 32</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>140-170</td>
<td>33, 31</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>200-260</td>
<td>34, 31</td>
</tr>
<tr>
<td>DMSO</td>
<td>1:1</td>
<td>37-40</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>70-80</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>110</td>
<td>37, 38</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 complex were interpreted in terms of type of the electrolyte with the help of table I shown above which represents the molar conductivities of various types of electrolytes in DMF and DMSO.

**Magnetic susceptibility**

Magnetic susceptibilities of paramagnetic solid substances were measured at room temperature by the Gouy method at room temperature.
Electronic spectra

The UV-VIS spectra in the region 200-900 nm were measured on a Hitachi model 150-20 spectrophotometer using calibrated silica cells. Weighed samples were dissolved in appropriate solvents and solutions were diluted to the required strength (10^{-3} and 10^{-4} M) and all the measurements were done at room temperature.

Infrared spectra

The IR spectra of ligands and complexes were obtained on a Nicolet impact 410, IR spectrophotometer in the region 4000-400 cm^{-1}. The spectra of a few complexes in the region 4000-200 cm^{-1} were recorded on a perkin Elmer, 783 model spectrophotometer in KBr pellets.

Electron Spin Resonance spectra

The electron spin resonance spectra of copper(II) complexes in polycrystalline state were recorded on Varian E-4, x-band ESR spectrometer using tetracyano ethylene (TCNE) free radical as 'g' marker (g = 2.00277) at room temperature and at liquid nitrogen temperature.
Nuclear Magnetic Resonance spectra

The proton magnetic resonance spectra of a few ligands and complexes in DMSO-\(d_6\) were recorded on 300 MHz VXR 300S Varian supercon NMR spectrometer at room temperature using pre-calibrated sheet and tetramethyl silane as the internal standard.

Thermal studies

TG studies were made on few complexes under study in the range from room temperature to 1000 °C in static air or nitrogen atmosphere on Rigaku TAS-100 model with a heating rate 10 °C/min.

Kinetic studies of decomposition of metal complexes

The thermograms obtained during TG scans were analysed to give the percentage weight loss as a function of temperature. Using Broido’s method, plots of ln(ln 1/y) vs. 1/T (where y is the fraction not yet decomposed) for different stages of the thermal degradation process of the complexes, were drawn. Using the above graph activation energy (Ea), frequency factor (ln A), enthalpy (\(\Delta G^\#\)), entropy (\(\Delta S^\#\)) and free energy (\(\Delta G^\#\)) were calculated using standard equations as

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follows.

\[ Ea = -2.303 \times R \times \text{Slope} \]
\[ -\ln(\ln \frac{1}{y}) = \frac{Ea}{R \cdot T_d} - \ln \frac{A \cdot R}{Ea} \]
\[ \Delta H^\# = \frac{Ea}{R \cdot T_d} \]
\[ \Delta S^\# = \frac{\Delta H}{T} - 4.576 \log \frac{T}{k'} - 47.22 \]
\[ \Delta G^\# = \Delta H - T \cdot \Delta S \]

X-Ray Diffraction Studies

Powder X-ray patterns were recorded on Phillips x-ray diffractometer using CuKa radiation (k = 1.5418 Å).