CHAPTER 2

EXPERIMENTAL SECTION

The analytical procedures and physicochemical techniques used in the present investigations are given in this chapter in brief.

2.1 MATERIALS

Commercially available chemicals (Analar or equivalent grade) were used as such. The solvents were distilled before use. Thioglycolic acid, thiomalic acid, thiobenzoic acid and 5-sulphosalicylic acid were received from Fluka /Sigma. All other chemicals are easily available with commercial grades.

2.2 ANALYTICAL METHODS

The analytical methods include the quantitative estimation of hydrazine and metal ions such as cobalt, nickel, copper, zinc, cadmium, mercury, lead, lanthanum, praseodymium, neodymium, samarium and gadolinium.

2.2.1 Estimation of Hydrazine

The hydrazine content of the complexes was determined volumetrically using a standard KIO₃(0.025 M) solution under Andrews conditions (Vogel 1975).

\[
\text{IO}_3^- + \text{N}_2\text{H}_4 + 2\text{H}^+ + \text{Cl}^- \rightarrow \text{ICl} + \text{N}_2 + 3\text{H}_2\text{O}
\] (2.1)
1 mL of 0.025 M KIO$_3$ $\equiv$ 0.0008013 g of hydrazine.

In an iodometric flask, the mixture of 100 mg of the sample dissolved in mixture of conc. HCl (30 mL) and distilled water (20 mL) along with 5 mL of CCl$_4$ or CHCl$_3$ was taken. It was titrated against standard KIO$_3$ solution from the burette. The solution was shaken well after the addition of each mL of KIO$_3$ solution. The end point is the disappearance of the violet colour in the organic layer.

### 2.2.2 Estimation of Metal Ions

The metal content in the complexes was determined by EDTA complexometric titrations (Vogel 1975) after decomposing a known weight of the sample with nitric acid and making it to a standard volume. A standard solution of EDTA was prepared directly by weighing the disodium salt of EDTA (1.8614 g in 500 mL, 0.01 M) and dissolving in distilled water. The standardization of this solution was done with standard zinc sulphate solution.

#### 2.2.2.1 Zinc

The content of zinc was estimated by titrating the sample solution maintained at pH 10 by adding ammonium chloride and ammonia solution against EDTA solution using Eriochrome Black T as the indicator. The end point is the colour change from wine red to steel blue.

#### 2.2.2.2 Cobalt and Cadmium

To a known volume of sample solution, 3 drops of xylenol orange were added, followed by very dilute sulphuric acid until the colour changes from red to yellow. The pH of the solution was increased by adding powered hexamine, which acts
as a buffer to pH 6. This solution was titrated against EDTA until the colour changes from red to yellowish orange. The cobalt containing solution was heated to 40 °C before titrating with EDTA.

2.2.2.3 Nickel

To the sample solution, 50 mg of the murexide (Ammonium purpurate) indicator was added. The pH of the solution was increased to 10 by the addition of \( \text{NH}_4\text{Cl} \) and \( \text{NH}_3 \) buffer solution. The yellow coloured solution was titrated against EDTA until the colour changes from yellow to wine red.

2.2.2.4 Copper

To a known volume of sample solution \( \text{NH}_4\text{OH} \) was added till a faint permanent precipitate appeared. Then a little acetic acid was added in drops to make the solution clear. A spatula of solid KI was added to the solution and titrated against a standard thiosulphate solution. When the brown colour of the solution became straw yellow, 3 mL of starch indicator was added and the titration was continued till the blue colour changed to dirty white.

Ammonium thiocyanate was added with the starch indicator to liberate \( \text{I}_2 \) absorbed by the cuprous iodide.

2.2.2.5 Mercury

The sample solution was added with HCl till acidic and saturated with hydrogen sulphide. The black precipitate formed was washed with water followed by alcohol and ether mixture to avoid sulphur precipitation. Then it was filtered through sintered crucible and weighed as \( \text{HgS} \), after drying at 105 - 110 °C.
2.2.2.6  Lanthanides Estimation (La, Pr, Nd, Sm and Gd)

A known volume of the solution was pipette out into a titration flask and a few drops of 1:1 ammonia were added to precipitate the metal ion as hydroxide. The precipitate was dissolved with a few drops of dilute nitric acid so that a clear solution was obtained. Approximately 10 – 15 ml of buffer solution (sodium acetate in acetic acid) was then added to the titration flask to maintain a pH of 5. A few drops of pyridine and 4 drops of xylenol orange indicator were added. The red solution was titrated with 0.01M EDTA until the colour of the solution changed to yellow. Another drop of pyridine was added. If the pH of the solution dropped too much, the red colour would reappear. The titration was completed to a permanent yellow end point.

2.3  PHYSICO-CHEMICAL TECHNIQUES

The instrumental techniques employed in the present study are, elemental analysis, melting point measurements, the spectroscopic techniques like infrared and electronic spectra, magnetic susceptibility measurements thermal analysis techniques like differential thermal analysis (DTA) and thermogravimetry (TG), X-ray diffraction techniques and SEM analysis.

2.3.1  Elemental Analysis and Melting Point Measurements

Elemental analysis was performed on Perkin Elmer – 240B CHN analyzer. Melting points were determined on Sigma melting point apparatus.
2.3.2 Spectroscopic Techniques

2.3.2.1 Infrared spectra

The infrared spectra of the solid samples in the range 4000-400 cm\(^{-1}\) were recorded on a Shimadzu FTIR 8000 spectrophotometer using KBr pellets.

2.3.2.2 Electronic spectra

The solid state absorption spectra of the samples were recorded on a Jasco V 530 UV-visible spectrophotometer by dispersing the solid samples in nujol mull.

2.3.2.3 NMR spectra

The NMR spectra for the samples were recorded using Bruker Avance III 500 MHz(AV 500) with 11.7 tesla superconducting long hold magnet built in cryo-shims(34 channel) at room temperature.

2.3.3 Magnetic Susceptibility Measurements

The magnetic susceptibility of the complexes was measured using a vibrating sample magnetometer, VSM EG & G model 155.

2.3.4 Thermal Analysis

Thermal analysis is a group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substances are subjected to a controlled temperature programme. The thermal
analysis techniques include thermogravimetry (TG), derivative thermogravimetry, differential thermal analysis, and differential scanning calorimetry (DSC). In many cases the use of a single thermal analysis technique may not provide sufficient information and hence the use of other thermal analytical techniques either by independent or simultaneous for complementary or supplementary information becomes necessary. For example, it is fairly to complement DTA or DSC data with thermogravimetry (TG) for the present study, simultaneous TG-DTA measurements are mostly used in addition to DSC and DTG.

The important factors that affect both DTA and TG curves have been discussed in detail in literature (Keatch and Dollimore 1975, Mackenzie and Mitchell 1970, Ravindran and Sundaram 1979 and Wendlandt 1986). Some of them are nature and shape of the container, sample weight and its preparation, particle size and packing density of the sample, heating rate employed and the surrounding atmosphere etc.

2.3.4.1 Differential thermal analysis

It is a thermal technique in which the temperature of a sample, compared with the temperature of a thermally inert molecule, is recorded as a function of the sample, inert material or furnace temperature as the sample is heated or cooled at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic enthalpic transitions or reactions such as those caused by phase change, fusion, crystalline structure inversions, boiling, sublimation and vaporization, dehydration reactions, dissociation or decomposition reactions, oxidation and reduction reactions, destruction of crystalline lattice structure and other chemical reactions. Generally phase transitions, dehydration, reduction and some decomposition reactions produce endothermic effects whereas crystallization, oxidation and decomposition reactions produce exothermic effects.
2.3.4.2 Thermogravimetry

It is the one in which the change in sample mass (loss or gain) is determined as a function of temperature or time. Three modes of thermogravimetry are commonly used. They are isothermal thermogravimetry, quasi-isothermal and dynamic thermogravimetry. Most of the studies refer to dynamic thermogravimetry, which is designated as thermogravimetry, in which the sample is heated in air environment whose temperature is changing in a pre-determined manner. The resulting mass change versus temperature curve provides information concerning the thermal stability and composition of the initial sample, the thermal stability and the composition of the intermediate compounds that may be formed and the composition of residue, if any.

The simultaneous TG-DTA studies were done on a STA 1500 thermal analyzer, NETZSCH- Geratebeau GmbH thermal analyzer and the curves obtained in air using platinum cups as sample holders with 5-10 mg of the samples at the heating rate of 10° C/min. in N₂/air atmosphere up to 700-800 °C.

2.3.5 X-ray Diffraction

It is the most general of all diffraction methods, and, when properly employed, can yield a great deal of structural information about the material under investigation. Basically, powder diffraction method involves the diffraction of monochromatic X-rays by a powder specimen. X-ray powder patterns of the compounds were recorded on a Siemens D-5005 X ray diffractometer and JEOL JDX 8P X-ray diffractometer using Cu-Kα radiation with nickel filters.

The molecular structure, atomic coordinates, bond lengths, bond angles, molecular orientation and packing of molecules in single crystals can be determined by
X-ray crystallography. Single crystal X-ray diffractometer collects intensity data required for structure determination. Single crystal diffraction intensity data for the crystal were measured on a Bruker axs kappa Apex II CCD diffractometer with monochromatic X-ray radiation wavelength, $\lambda = 0.71073$ Å at 293 K.

2.3.6 Scanning Electron Microscopy

It is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a faster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The SEM images of the residual oxides were recorded using a Cambridge Scanning Electron Microscope with EDAX attachment (CF).

2.3.7 Transmission Electron Microscopy

It is microscopic technique where a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed the interaction of the electrons transmitted through the specimen and it is magnified, focused in to an imaging device, such as fluorescent screen, on a layer of photographic film or to be detected by a sensor such as CCD camera. The TEM images of the residual oxides were recorded using a JEOL JEM 2100 High Resolution Transmission Electron Microscope(HRTEM) with EDX attached.
2.3.8 Electrical Conductivity

Conductivities of the complexes have been measured using Zentech 33.5 automatic component analyzer. The instrumental setup is shown in Figure 2.1a and the conductivity cell chamber in Figure 2.1b.

Figure 2.1a The Instrumental Setup

Figure 2.1b Conductivity Cell Chamber