CHAPTER-II

MATERIALS AND METHODS
2.1 The metal salts

Hydrated lanthanides nitrate (Indian Rare Earths Ltd. Udyogmandal, Kerala, 99.99% Pure) were used as such. Methanolic solutions of metal thiocyanate were obtained by metathesis of the respective metal nitrates with stochiometric amounts of KNCS [156].

Hydrated UO$_2$Cl$_2$, UO$_2$(NO$_3$)$_2$, UO$_2$(CH$_3$COO)$_2$, UO$_2$SO$_4$ and Th(NO$_3$)$_4$ were B.D.H. reagent grade and were used as supplied.

Methanolic solution of UO$_2$L$_2$ [156] was obtained by mixing a solution of uranyl nitrate hexahydrated (0.5 gm, 1 mmol) in 3 mL of methanol with KI (0.34 gms, 2 mmol) in 5 mL of methanol. The insoluble metal nitrate was filtered off. The filtrate was somewhat concentrated by slow evaporation and used as such. UO$_2$(NCS)$_2$ [157] was also prepared similarly by metathesis of UO$_2$(NO$_3$)$_2$ .6H$_2$O with KNCS in methanol.

Alcoholic solutions of ThI$_4$ [158] and Th(NCS)$_4$ [157] were prepared similarly from Th(NO$_3$)$_4$ .6H$_2$O and KI or KNCS, respectively.

Anhydrous UO$_2$Cl$_2$.2THF was obtained as a free flowing solid by refluxing UO$_2$Cl$_2$.2H$_2$O in dry THF for several hours, filtering the insoluble and removing the solvent in vacuo.
2.2. The ligands:

(a) Synthesis of 2-(2'-pyridyl) benzimidazole (PBH).

The ligand pyridyl benzimidazole (PBH) was synthesised by a modification of literature procedure [159]. An intimate mixture of o-phenylene diamine (2.3947 gm, ~20 mmoL) and picolinic acid (2.1527 gm, ~20 mmoL) was added to excess viscous polyphosphoric acid (PPA) in a conical flask. The flask was heated at 200-210 °C for about 6h, cooled to about 120 °C and poured in a thin stream into a large volume of rapidly stirred water. The insoluble residue was collected by filtration, washed with a small amount of water. The filtrate was made alkaline by addition of 8% NaOH. The crude product obtained was filtered and washed thoroughly with water, dried and recrystallized from ethanol-water mixture (1:1).

Yield = 2.1 gm, m.p = 220 °C (lit 221 °C) [160].

Found: C, 73.6; H, 4.8; N, 21.4;
Calc. for PBH C₁₂H₉N₃: C, 73.8; H, 4.6 N, 21.5 %, m/z 195 in Mass spectra.

(b) Synthesis of 1-methyl 2-(2'-pyridyl) benzimidazole (MPB).

1.5 mL (15 mmoL) of dimethyl sulphate (DMS) was added dropwise to a well stirred suspension of 2.357 gm ( ~ 60 mmoL) of powdered NaOH, 1.95 gm (10 mmoL) of PBH and 0.190 gm ( ~ 4 mmoL %) of tetrabutyl ammonium bromide (TBAB) (used as phase transfer catalyst) in 25 mL of dioxane. Stirring at room temperature was continued for 30 min and the reaction monitored
by TLC. The mixture was filtered, washed with ethylacetate and the combined washing and filtrate was treated with 1:1 NH$_4$OH solution to remove excess DMS. The volume of the resultant solution was reduced to 10-15 mL and was stored at 4 °C for about 2h. The orange red oily liquid was washed with hexane and the light yellow washings cooled perfectly. It was filtered washed with little hexane and air-dried.

Yield: 1.01 gm, m.p = 62 °C (Lit. 64-65 °C) [161].

Found: C, 74.35; H, 5.23; N, 19.95;
Calc. for MPB. $\text{C}_{13}\text{H}_{11}\text{N}_3$ : C, 74.6; H, 5.3; N, 20.1 %; m/z 209 in Mass spectra.

(c) 2-(2'-pyridyl) benzoxazole (PBOX).

Powdered mixture of 1.1 gm of 1-amino phenol and 1.23 gm of picolinic acid was heated with freshly prepared polyphosphoric acid (8.8 gm, P$_2$O$_5$ and 3.5 mL of orthophosphoric acid in an oil bath at ~ 200 °C for 4h. The temperature was brought down to 120 °C and the syrupy liquid was added to rapidly stirred water. Filtered and filtrate was neutralized with aqueous NaOH solution. The brown coloured solid was filtered, washed repeatedly with hot water and dried in air oven at 100 °C. Recrystallisation from hot hexane gave orange-yellow crystals.

Yield : 0.8 gm, m.p = 110 °C.

Found: C, 74.3; H, 3.8; N, 13.4;
Calc. for PBOX $\text{C}_{12}\text{H}_8\text{N}_2\text{O}$ : C, 74.5; H, 4.1; N, 13.3%; m/z 196 in Mass spectra.
(d) 5-Methyl-2-(2'-pyridyl) benzimidazole (MePBH).

The ligand (MePBH) was prepared by slight modification of procedure reported in ref. [159]. An intimate mixture of 3,4 diamino toluene 1.22 g (\(\approx\) 10 mmol) and picolinic acid 1.23g (\(\approx\) 10 mmol) was added to an excess viscous polyphosphoric acid (PPA) in a conical flask. The flask was heated on a oil bath, at 200-220 °C for 6h. Then it was added to rapidly stirred water in a beaker. The solution was then filtered. The filtrate was made alkaline with NaOH solution and kept over night. The precipitate obtained was filtered and washed with water several times and recrystallized from ethanol-water mixture (1:1).

Yield: 1.5 g, m.p = 153-158 °C.

Found: C, 74.5; H, 5.3; N, 20.8;
Calc. for MePBH \(C_{13}H_{11}N_3:\) C, 74.6; H, 5.3; N, 20.1 %) m/z 209 in Mass spectra.

(e) Synthesis of 2,6-bis(benzoazol-2-yl) pyridine (bzopxy).

The ligand bnzopxy was synthesised by a modification of the method of Addison and Burke [162]. An intimate mixture of 2,6 pyridine dicarboxylic acid (0.668 gm, \(\approx\) 4 mmol) and 1-amino phenol (1.01 g, \(\approx\) 8 mmol) was added to an excess polyphosphoric acid (PPA) in a conical flask. The flask was heated at 220 °C for about 4h, cooled to about 120 °C and poured in a thin stream of rapidly stirred water. Filtered and filtrate was neutralized with aqueous NaOH solution. The brown coloured solid was filtered, washed repeatedly with hot water, and dried in air. Recrystallization from hot benzene gave white shining crystals.
Yield: 1 gm, m.p. = 280-185 °C.

Found: C, 72.9; H, 3.5; N, 13.4.

Calc. for bzopxy $C_{19}H_{11}N_3O_2$: C, 72.1; H, 3.4; N, 13.7; m/z 313 in Mass spectra.

2.3 **Characterization of complexes:**

2.3.1 **Analytical methods:**

(A) **Estimation of Lanthanides:** [163]

The lanthanide contents of the complexes were determined either complexometrically using xylenol orange as indicator [163] or by gravimetrically.

**Gravimetric determination of lanthanides by oxalateoxide method:**

A known amount of the complex (~ 0.2 gm) was treated with conc $\text{HNO}_3$ (20 mL) and the resultant solution was evaporated to dryness on a water bath. The residue obtained was dissolved in conc $\text{HCl}$ (20 mL), and resulting solution was again evaporated to dryness. This residue (lanthanide chloride) was dissolved in water (50 mL) and the pH of the solution was adjusted to unity by adding conc. $\text{HCl}$. The solution was heated to boiling, and a saturated solution of oxalic acid was added to it with stirring. A curdy white precipitate initially formed would quickly change to crystalline precipitate. The precipitate was allowed to stand for 8h with occasional stirring. Then the precipitate (lanthanide oxalate) was filtered through a Whatman 42 filter paper and washed 6-8 times with water containing 2% (w/v) oxalic acid and 1% (v/v)
HCl. The precipitate was ignited in a platinum crucible for 90 min, cooled in a desiccator and weighed as the stable lanthanide oxides are La\(_2\)O\(_3\), Pr\(_6\)O\(_{17}\) Nd\(_2\)O\(_3\), Sm\(_2\)O\(_3\), Gd\(_2\)O\(_3\), Dy\(_2\)O\(_3\) and Y\(_2\)O\(_3\). From the weights of the oxides, the lanthanide contents of the complexes were calculated.

(B) Estimation of Uranium:

Uranium content in the complexes were determined by direct heating the complexes at 800 °C in an electrically controlled muffle furnace and weighed as U\(_3\)O\(_8\) after heating.

In some complexes, uranium content was determined by ignition to U\(_3\)O\(_8\) after complete destruction of weighed sample by repeated treatment with concentrated HNO\(_3\) [164].

(C) Estimation of Thorium:

The Thorium content of all complexes were determined gravimetrically by the following method. Accurately weighed complex was dissolved in dil HCl and then made alkaline with ammonium hydroxide. The precipitated Th(OH)\(_4\) was filtered on a Whatman 41 filter paper, washed with dil NH\(_4\)OH, dried and ignited at 750-850 °C and weighed as ThO\(_2\) after being cooled. Ignition was continued till constant weight [165].

(D) Estimation of Anions:

(i) Estimation of chloride:

The chloride content of the complexes were estimated as AgCl [165] after oxidative fusion of the complex with Na\(_2\)O\(_2\)/NaOH.
(ii) **Estimation of thiocyanate:**

In the absence of halide ions, thiocyanate can be estimated as $\text{AgSCN}$ in the presence of cold dilute $\text{HNO}_3$ [166], when the thiocyanate compound is not soluble in cold dil $\text{HNO}_3$, the compound is fused with sodium hydroxide and sodium peroxide to oxidise sulphur to sulphate. The thiocyanate is weighed as $\text{BaSO}_4$.

(iii) **Estimation of sulphate:**

When the compound is insoluble in water or dil $\text{HCl}$, it is determined as $\text{BaSO}_4$ after oxidative fusion with a mixture of $\text{NaOH}$ and $\text{Na}_2\text{O}_2$ [166].

(iv) **Estimation of nitrogen:**

Nitrogen was estimated in some ligands and complexes synthesized in this work by the Kjeldahl's method [166].

(v) **Estimation of carbon, hydrogen and nitrogen:**

The $\text{C}, \text{H}$ and $\text{N}$ microanalyses were carried out at the Central Drugs Research Institute, Lucknow and Regional Sophisticated Instrumentation Centre, Chandigarh.
2.3.2 Physico-Chemical Methods:

The following methods are employed for the characterisation of the complexes.

(a) Electrical conductivity:

All the conductance measurements were performed at room temperature using freshly distilled solvents such as methanol, acetonitrile, acetone dimethyl sulphoxide etc. in a systronics direct reading digital conductivity meter Model 306 with a dip type cell having cell content 1.0. The molar conductance values of the complexes, in a suitable solvent, were compared with standard value of known electrolytes [167].

(b) Infra red spectra (IR)

The FT-IR spectra of the compounds were recorded as KBr pellets or as Nujol mul in the range of 4000–200 cm\(^{-1}\) on Perkin ELMER FT-IR instrument.

(c) Nuclear Magnetic Resonance Spectra (NMR)

\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of the compounds were recorded using various solvents such as CDCl\(_3\), DMSO-d\(_6\) on a Bruker 200 MHz FT-NMR instruments or on a Bruker 400 MHz AMX equipment.
(d) **Electronic spectra:**

Electronic spectra of the complexes were recorded in dilute solutions \( \sim 10^{-3} \text{ M} \) using different solvents on a Beckmann DU-640B or Beckmann DU-7 spectrophotometer.

(e) **Fluorescence spectra:**

Fluorescence spectra of the compounds were recorded on a Shimadzu spectrofluorophotometer RF-510 or F-3010 Hitachi spectrofluorometer.

(f) **Thermogravimetric measurements:**

Thermal decomposition studies (TG/DTA) were carried out using a Shimadzu DT-40 thermal analyser in static air at a heating rate of 10 °C/min.

(g) **Cyclic Voltammetry and Electron Paramagnetic Resonance spectra:**

The CV and EPR spectra of some complexes were obtained on Polarecord E-506 (Metrohm) and Varian-E-4 spectrometer, respectively.

(h) **Mass spectra:**

El mass spectra of the ligands were recorded on a JEOL D-300 mass spectrophotometer at 70 eV (ionization) and 100 uA (ionization current), 3 KV (accelerating voltage) and 200 °C
ion source temperature. The FAB mass spectra of the complexes were recorded on a JEOL SX 102/DA-6000 mass spectrophotometer using Xenon (6 KV, 10 mA) as the FAB gas. The acceleration voltage was 10 KV and the spectra were recorded at room temperature.