The lanthanides and actinides constitute a quarter of all of the known chemical elements. These two series of transition elements are continuing to occupy positions of increasing importance in the areas of fundamental science and practical applications. From glazes to lasers to high temperature superconductors, the lanthanides have numerous practical applications. From power sources to smoke alarms to biomedical applications, the actinides have many practical applications. When nuclear waste disposal problems are solved, these nuclear fuels have the potential of providing unlimited renewable energy sources for many centuries to come. Fundamental studies of the lanthanide and actinide series of elements will continue to provide insight into the basic nature of matter and its arrangement in the Periodic Table.

The present work deals with the synthesis and characterization of the compounds of lanthanides and two most prominent actinides thorium and uranium with some non-fused biheterocyclic ligands as well as their solvent extraction behaviour with some chelating extractants.

The thesis is divided broadly into ten chapters.
Chapter - I:

The first chapter is an introduction chapter showing its aim and objectives. It includes a brief discussion about the chemistry of lanthanides and actinides (with special references to uranium and thorium) and also of the ligands. A precise coverage of the developments in this field is also given.

Chapter - II:

This chapter covers the methods of the preparation of the ligands and the analytical methods employed for the chemical analyses of the complexes.

Chapter - III:

This chapter describes lanthanide(III) complexes of bidentate biheterocycles 2-(2'-pyridyl) benzimidazole (PBH) and 1-methyl 2-(2'-pyridyl) benzimidazole (MPB). These ligands form a series of stable complexes of stoichiometry \([\text{Ln(NCS)}_3(\text{PBH})_2]\) and \([\text{Ln(NCS)}_3(\text{MPB})_2]\) (where \(\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd, Dy and Y}\)).
The complexes were characterized by various physico-chemical techniques such as conductance and thermogravimetric studies, electronic, IR, NMR ($^1\text{H}$ & $^{13}\text{C}$), EPR, CV and fluorescence spectral investigations. The ν(C=\text{N}) of the thiocyanate group indicates N-coordination in all cases.

**Chapter - IV:**

This chapter describes the lanthanide(III) complexes of bidentate ligands 5-methyl 2-(2'-pyridyl) benzimidazole (\(L\)) and 2-(2'-pyridyl) benzoxazole (\(L'\)). They form complexes of the type $[\text{Ln(NCS)}_2(L)_2]\text{H}_2\text{O}$ and $[\text{Ln(NCS)}_2(L')_2]\text{H}_2\text{O}$ where (\(\text{Ln} = \text{Y}, \text{Pr-Dy}, \text{except Pm}, n = 2 \text{ or } \text{Ln} = \text{Y}, \text{Pr-, Sm, Eu-Dy}, n = 3,1\)). The complexes were characterised by various physico-chemical techniques such as the conductance, thermogravimetric studies, electronic, IR, NMR ($^1\text{H}$ & $^{13}\text{C}$) and fluorescence spectral investigations. It has been found that all the complexes show the luminescence of the ligand. The Sm, Eu, Tb and Dy complexes show the corresponding metal ion luminescence.
Chapter - V :

This chapter presents the isolation and characterisation of dioxouranium(VI) and thorium(IV) complexes with 2,6-bis(benzoxazol-2'-yl) pyridine (bzopxy), a tridentate ligand. The conductance data indicate that the uranium complexes were all non-electrolyte while among the thorium complexes, NCS and I complexes were non-electrolyte, whereas the nitrate complex show 1:2 electrolytic behaviour. The complexes were characterised by IR, thermogravimetric and NMR ($^1H$ & $^{13}C$) spectral studies.

\[ \text{bzopxy} \]

Chapter - VI :

This chapter includes a brief discussion on the theoretical aspects of solvent extraction and extraction by macrocyclic ligands. In view of the complexity of the extraction equilibria in synergistic solvent extraction systems and also due to the limitations of the graphical methods, recourse has been taken to theoretical analysis.
using a computer in the present thesis.

The chelating extractants such as thenoyl trifluoroacetone, dibenzoylmethane, 1-phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5, 3-phenyl-4-benzoyl-5-isoxazolone have been used in the extraction studies. The structure of these extractants as well as the macrocyclic polyethers used are given as follows:

**Thenoyl Trifluoroacetone:**

![](image1)

**Dibenzoylmethane:**

![](image2)

**1-Phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5**

![](image3)
3-Phenyl-4-benzoyl-5-isoxazolone:

Dibenzo-18-crown-6:

Dicyclohexano-18-crown-6:

Benzo-15-crown-5:

18-Crown-6:

15-Crown-5:
Chapter - VII:

This chapter deals with the synergistic extraction of trivalent lanthanides such as Nd, Eu and Tm with mixture of 1-phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5 and 18-crown-6, or dibenzo-18-crown-6, or 15-crown-5 or monobenzo-15-crown-5 (CE) in chloroform. Lanthanides are found to be extracted as \( \text{Ln(PMTFP)}^3 \) with \( \text{HPMTFP} \) alone and in the presence of a crown ether (CE) as \( \text{Ln(PMTFP)}^3 \text{CE} \). The equilibrium constants of the above species are found to increase monotonically with decreasing ionic radii of these metal ions. The addition of a crown ether to the metal chelate system not only enhances the extraction efficiency but also improves the selectivities among these trivalent lanthanides.

Chapter - VIII:

This chapter deals with the synergistic solvent extraction of trivalent lanthanides such as Nd, Eu, and Tm using mixture of 3-phenyl-4-benzoyl-5-isoxazolone and 18-crown-6, 15-crown-5, benzo-15-crown-5, and dibenzo-18-crown-6. The results demonstrated that these trivalent metal ions are extracted into chloroform as \( \text{Ln(PBI)}^3 \) with \( \text{HPBI} \) alone and as \( \text{Ln(PBI)}^3 \text{CE} \) in the presence of a crown ethers (CE). The addition of a crown ether to the metal chelate system significantly enhances the extractibility of these trivalent metal ions. The order of synergism with various crown ether is as follows: \( 18C6 > 15C5 > B15C5 > DB18C6 \). Solid complexes of these metal ions with \( 18C6, \) and \( 15C5 \) have been isolated and characterized by using
Chapter - IX:

This chapter deals with the extraction of uranium(VI) with the mixture of β-diketones (thenoyltrifluoroacetone or dibenzoylethane) and dibenzo-18-crown-6 or dicyclohexano-18-crown-6 or monobenzo-15-crown-5 into chloroform. The uranium is synergistically extracted as an HX-CE adduct (where HX = β-diketones). The stability of the adduct extracted is mainly related to the basicity of the crown ether, the compatibility of the cation and crown cavity size does not seem to be a significant factor in these complexes. Solid complexes extracted were characterized using elemental analysis, IR and NMR spectroscopic techniques.

Chapter - X:

This chapter describes the extraction of thorium(IV) with mixture of 3-phenyl-4-benzoyl-5-isoxazolone and neutral oxodonors such as tri-n-octyl phosphine oxide (TOPO) and tri-n-butyl phosphate (TBP) in xylene. The extraction constant (log \( k_{ex} \)) for the binary organic phase species Th(PBI)\(_4\) was determined to be 8.26 which is by far the largest amongst the corresponding values known for other β-diketones. The overall extraction constant (log \( k_{sym} \)) for the ternary species Th(PBI)\(_4\)TBP and Th(PBI)\(_4\)2TOPO were estimated to be 14.96 and 20.96, respectively. The steric as well as the electronic effects of adduct formation have been discussed. Analytical application of HPBI for the separation of \(^{234}\)Th radiotracer from natural uranium (99.3% U-238) has been suggested.