SYNTHESIS, CHARACTERIZATION AND COORDINATION CHEMISTRY OF HARD AND SOFT DONOR LIGANDS WITH LANTHANIDES AND ACTINIDES

by

SADHAN BIJOY DEB
CHEM012008040010

Bhabha Atomic Research Centre,
Mumbai 400085, India

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Guide / Convener – Dr. S. Kannan	6. 4. 2016 Date
External Examiner: Dr. Prasenjit Ghosh	6/4/16 Date
Member 1 – Dr. V.K.Jain	6/4/2016 Date
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I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

(Sadhan Bijoy Deb)

Dedicated to . . .

My Mother and Wife

List of Publications

1. Coordination and separation studies of uranyl ion with iso-butyramide based ligands. Synthesis and structures of $[UO_2(NO_3)_2({}^{i}C_3H_7CON\{{}^{i}C_4H_9\}_2)_2]$ and $[UO_2(C_6H_5COCHCO\ C_6H_5)_2\ {}^{i}C_3H_7CON\{{}^{i}C_3H_7\}_2]$. Kannan, S.; Deb, S. B.; Gamare, J. S.; Drew, M. G. B., Polyhedron 27 (2008) 2557-2562

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Government of India
Bhabha Atomic Research Centre
HUMAN RESOURCE DEVELOPMENT DIVISION
HRD CENTRE, SOUTH SITE, TROMBAY, MUMBAI 400085.

Sub : Marks in Courses Undertaken during 2007-2008
at BARC Training School, Trombay

Name of Candidate : Sadhan Bijoy Deb

S.No.	SUBJECT	MAXIMUM MARKS	MARKS OBTAINED
1	Actinide Chemistry	**100**	**90**
2	Molecular & Bio-Organic Chemistry	**100**	**87**

Place : Mumbai

September 2008

(M.Ramanamurthi)
Head, OCES PI Section, HRDD

Ravinder Puri
(R.R.Puri)
Head, HRDD

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Abbreviations

Ac = Actinide

ACAC = Acetylacetonates

AHWR = Advanced heavy water reactor

BTBP = Bis-triazinyl bipyridine

BTP = Bis-triazinyl pyridine

CMP = Carbamoyl methyl phosphonates

CMPO = Carbamoyl methyl phosphine oxides

CyMe4-BTBP = 6,6′-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2′-bipyridine

DBM = Dibenzoyl methane

DBM = Dibenzoyl methanate

DIAMEX = Diamide Extraction

DMDOHEMA = N,N′-dimethyl-N,N′-dioctylhexylethoxymalonamide

DTA = Differential thermal analysis

ESIMS = Elctrospray ionization mass spectrometry

GANEX = Group Actinide Extraction

Ln = Lanthanide

NMR = Nuclear magnetic resonance

ORTEP = Oak Ridge Thermal Ellipsoid Plot

PUREX = Plutonium uranium extraction

RE = Rare earth

SANEX = Selective actinide extraction

SNF = Spent nuclear fuel

TALSPEAK = Trivalent actinide lanthanide separation by phosphorus reagent extraction from aqueous complexes

TBP = Tri-butyl phosphate

TG = Thermogravimetry

THF = Tetrhydofuran

TODGA = Tetraoctyldiglycolamide

TOPO = Tri octyl phosphine oxide

TRUEX = Trans uranic extraction

TTA = Triflurotheonyl acetone

XRD = X-ray diffraction

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Synopsis

The coordination chemistry of lanthanide and actinide ions is very important for the development of new extractants for the separation and purification of these ions from the irradiated nuclear fuel and also for the technology concerning the storage of highly radioactive waste materials [1]. The coordination chemistry of uranium has been growing rapidly in the last ten years due to the presence of new synthetic methods available and also the interesting properties such as selective ion-exchange, mixed valency, ionic conductivity, enhanced fluorescence, magnetic ordering and non linear optical properties exhibited by its complexes [2]. The selective separation of uranium-233 from the mixture of thorium and other fission products is an important step in the advanced water reactor (AHWR) technology of the Indian Atomic Energy programme [3] . Many new extractants have been studied for the selective recognition and separation of uranyl ion from various media in recent years [4]. Neutral N-cyclohexyl, 2-pyrrolidone ligand shows selective precipitation of uranium (VI) ion (up to 75%) from the mixture containing various other ions.

Of late the incinerable organic amide based extractants have shown excellent and promising result in the process chemistry of lanthanides and actinides from the nitric acid medium [5]. It is reported that the N, N', 2-ethylhexyl *iso*-butyramide shows selective extraction property for the uranium(VI) ion from nitric acid medium containing thorium(IV) and lanthanide ions [6]. However, no report on the structural aspects of nature complex formed between the *iso*-butyramide ligands with uranyl ion to understand the reason for their selectivity. The strong complexing ability of *iso*-butyramide based ligand with uranyl ion promoted us to study their complexing behavior towards the uranyl, thorium, lanthanum nitrates and uranyl *bis* (β-diketonate) to see the feasibility for using these ligands for the selective separation by precipitation method instead of solvent extraction process, thereby reducing the number of steps involved during separation process. We have carried out the systematic structural studies on *iso*-butyramide uranyl complexes and explained the stability and selectivity on the basis of strong bonding between the amide oxygen and uranyl group. The observed bond distances between the uranium and oxygen atom of amide group [~ 2.35 Å] are much short in lengths as compared to those of other reported U-O(amide) bond distances and comparable to those U-O (phosphine oxide) distances.

Tri-functional diglycolamide ligands show excellent extraction properties for trivalent actinide metal ions over the tetra or hexavalent actinide ions and extensive solvent extraction studies have been reported over the last 10 years [7]. The coordination chemistry of these ligands with lanthanide and actinide ions is reported recently and it shows that the ligand acts as a tridentate chelating ligand and bonds through both the carbamoyl oxygen and ethereal oxygen atoms to the metal centre [8]. The replacement of ethereal oxygen by the CH_2 group in the glutaramide ligand shows extraction for the hexavalent and tetravalent ions but not for the trivalent ions [9]. The coordination chemistry of glutaramide shows that it acts as a monodentate ligand and bridges uranyl nitrate in the solid state to form a linear polymeric chain arrangement [10]. The solvent extraction studies on tri-functional ligands having the ‘‘thio” group in place of the oxygen atom in diglycolamide (called thiodiglycolamide), reported by Sasaki et al. shows extraction for hexavalent, tetravalent and trivalent actinides and lanthanides from the perchloric acid medium [11-13]. The observed distribution data show that its extraction properties are much superior to those of malanomides but poorer than those of diglycolamides. Sasaki et al. had proposed a tridentate mode of bonding for these ligands with the metal ion similar to those of diglycolamide ligands. However, no structural work is reported to support their proposal. Since, the perchloric acid is no where used in the nuclear fuel reprocessing cycle, it is more relevant to carry out the extraction studies from nitric acid medium rather than that of perchloric acid. Tri-functional ligands such as: diglycolamide [14] , 2,6-*bis* [*bis*(alkyl)phosphino)methyl] pyridine trioxide [P(O)N(O)P(O)] [15], 2,6-*bis*(N-alkyl acetamide) pyridine-N-oxide [C(O)N(O)C(O)] [16], and *bis* (carbamoyl methyl) sulfoxide [BCMSO] [17] show excellent extraction properties for trivalent actinides as compared to that of tetra or hexavalent actinides. There is no report on the structural studies of the *bis* (carbomyl methyl) sulfoxide with lanthanides or actinide ions. Similarly, there are no reports on the coordination chemistry of bis(carbomyl methyl) sulfone with any lanthanide or actinide ions so far. We report herein the synthesis and characterization some new *bis*-(carbomyl methyl) sulfide, sulfoxide and sulfone ligands and study their coordination chemistry with the uranyl and lanthanide ions.

There are several reports on 3d–5f complexes [18-25], however there no reports on the complexes chemistry of of 1,1'-bis(diphenylphosphine oxide) ferrocene with any of the 5f metal ions, though this ligand has a 3d metal center iron(II) with two potential phosphine oxide groups. The phosphine oxide group is well known for its strong complexing ability towards the lanthanide and actinide ions. The 1,1'-bis(diphenylphosphine oxide) ferrocene ligand shows a wide variety of coordination geometries with transition metal ions with the bite angles varied in the range from $154^0$to 90^0. Here in, we report the synthesis and structural studies of 1,1'-bis(diphenylphosphine oxide) ferrocene with uranyl nitrate and uranyl di chloride.

The thesis consists of four chapters and the details are given below.

Chapter 1

Introduction

This chapter deals with a brief introduction to coordination chemistry of lanthanide and actinide ions and the factors affects the coordination number and geometry around the metal ions. It also deals with different types of ligands used in the different stages of the nuclear fuel cycle and the structural studies relevant uranyl and lanthanide ions with these ligands with latest literature information. A brief discussion on the characterization techniques like infrared spectroscopy (IR), nuclear magnetic resonance (NMR) and single crystal X-ray diffraction (XRD) employed in this work is also presented. Finally, the scope of the present work is discussed.

Chapter 2

Synthesis, coordination, structural and separation studies of *iso*-butyramide based ligands with uranyl ion

This chapter deals with the synthesis, coordination, structural and separation studies of iso-butyramide based ligands with uranyl ion. A brief discussion on various incinerable amide based extractants used in nuclear industry relevant to present work is included. The complex and structural chemistry of these amide based ligands with uranyl and lanthanide ions are discussed in details.

2.1 Synthesis of ligands

The general reaction for the synthesis of ligands can be represented by the following equation.

$$ {}^{i}C_3H_7COCl + R_2NH + (C_2H_5)_3N \xrightarrow{EtOH} {}^{i}C_3H_7CO\,N\,R_2 + (C_2H_5)_3NHCl $$

$R = {}^{i}C_3H_7,\ {}^{i}C_4H_9,\ C_4H_9$

2.2 Synthesis of compounds

These ligands have been used for the synthesis of uranyl complexes and reaction are given below :

$$ 2\,{}^{i}C_3H_7CONR_2 + UO_2(NO_3)_2\,.6H2O \xrightarrow{CHCl_3} UO_2(NO_3)_2({}^{i}C_3H_7CONR_2)_2] $$

$$ UO_2(OO)_2.2H_2O + {}^{i}C_3H_7CONR_2 \xrightarrow{CHCl_3} UO_2(OO)_2({}^{i}C_3H_7CONR_2) $$

$R = {}^{i}C_3H_7,\ {}^{i}C_4H_9,\ C_4H_9$

$OO = C_4H_3SCOCHCOCF_3,\ C_6H_5COCHCOCF_3,\ C_6H_5COCHCOC_6H_5$

2.3 Results and discussion

All ligands and their compounds with uranyl ion were characterized for C, N, H, analysis followed by IR and NMR techniques. The IR spectra show that ν_{CO} in compounds are about 50-80 cm^{-1} lower in values as compared to that of free ligands indicating a strong bonding between the carbamoyl group and uranyl ion. The observed ^{1}H NMR of all compounds show that the CH proton is deshielded by ca ; 0.5 -0.6 ppm w.r.t to free ligands, indicating that the bonding persist in solution also. The structures for two compounds [$UO_2(NO_3)_2\{{}^{i}C_4H_9CON({}^{i}C_4H_9)_2\}_2$] and [$UO_2(C_6H_5COCHCOC_6H_5)_2\{{}^{i}C_3H_7CON({}^{i}C_3H_7)_2\}$] were characterized by single crystal XRD. The molecular structures of the compounds are shown in the Fig. 1 and Fig. 2 and

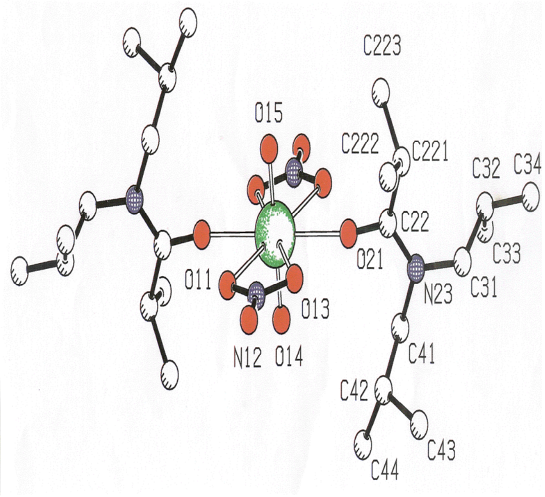


Fig. 1. Molecular Structure of [$UO_2(NO_3)_2.^iPrCON^iBu_2$]

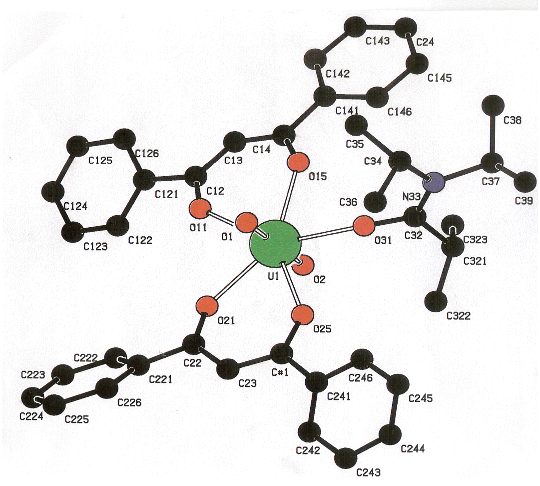


Fig. 2. Molecular Structure of$UO_2(C_6H_5COCHCOC_6H_5)_2$ {$^iC_3H_7CON(^iC_3H_7)_2$}]

they confirm the spectral observations.

The structure of bis N, N’, *iso*-butyl, *iso*-butyramide-uranyl(VI) nitrate contains a crystallographic center of symmetry with uranium atom surrounded by oxygen atoms in a hexagonal bi-pyramidal geometry. On the other hand uranyl(VI) *bis* (dibenzoyl methane)- N,N’di-*iso*-propyl butyramide complex has a pentagonal bi-pyramidal geometry. It forms 1:2 complex with [$UO_2(NO_3)_2$] and 1:1 complex with [$UO_2(OO)_2$]. The observed U-O (amide) bond length is much shorter in length as compared to those of earlier reported uranyl-amide compounds. The short bond lengths may be due to a strong π bonding interaction between the filled p orbitals of oxygen with those of vacant d/f orbitals of uranyl ion.

Separation studies were carried out by taking a solution containing $Th(NO_3)_4.6H_2O$, $La(NO_3)_3.6H_2O$ and $UO_2(NO_3)_26H_2O$ in nitric acid medium and layered with $^iC_3H_7CON(^iC_4H_9)_2$ .This process deposited yellow crystalline solid material. The initial solution, supernatant and the solution of yellow solid in ethanol were analyzed by X-ray fluorescence (XRF) technique. The spectra show that more than 98% of uranium is precipitated selectively from the mixture, whereas thorium and lanthanum remain back in the solution. Thermal studies show that these ligands are completely incinerable.

2.4. Conclusions

iso-butyramide ligands of the type $^{i}C_3H_7CO\ NR_2$ (where R = $^{i}C_3H_7$, $^{i}C_4H_9$, C_4H_9) and complexes of the types $[UO_2(NO_3)_2(^{i}C_3H_7CONR_2)_2]$ and $UO_2(OO)_2(^{i}C_3H_7CONR_2)$ (where OO = $C_4H_3SCOCHCOCF_3$, $C_6H_5COCHCOCF_3$, $C_6H_5COCHCOC_6H_5$) were synthesized and characterized. The ligands form 1:2 Complex with uranyl nitrate and 1:1 complex with uranyl *bis*(β-diketonates). The structural studies reveal that the ligand acts in a monodentate fashion. The geometries around uranium(VI) are hexagonal bi-pyramidal and pentagonal bi-pyramidal respectively in uranyl nitrate and uranyl bis (β-diketonates). The observed U-O (amide) bond lengths are much shorter in length as compared to those of earlier reported uranyl-amide compounds.Thermal studies shows that the ligands are completely incinerable. The ligand selectively precipitates uranyl ion from the solution having bulk of thorium and lanthanide ions.

Chapter 3

Synthesis, structural and complexation studies of bis (N, N'-Di-alkyl carbomyl methyl) sulfide, sulfoxide and sulfone with uranyl and lanthanide ions.

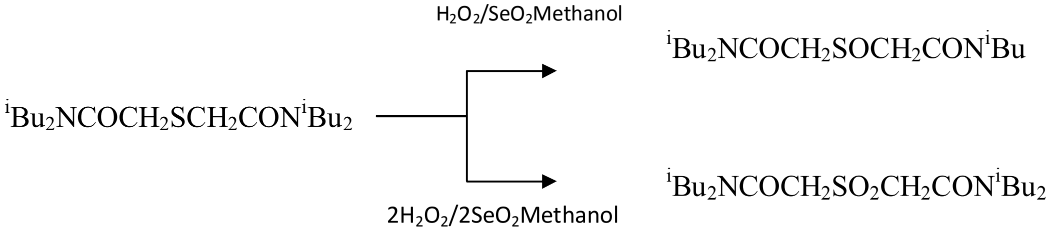
This chapter deals with the synthesis and complexation studies of with bis (N, N'-Di-alkyl carbomyl methyl) sulfide, sulfoxide and sulfone based ligands with uranyl and lanthanide ions.

3.1 Synthesis of ligands

The general reaction for the synthesis of ligands can be represented by the following equation.

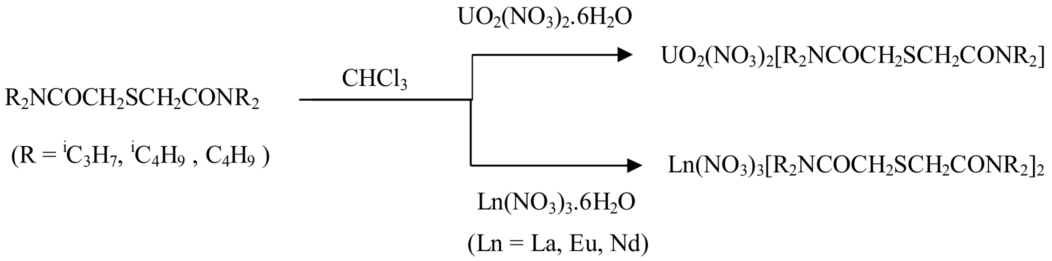
$$2\ R_2NCOCH_2Cl + Na_2S.\ 9\ H_2O \xrightarrow{EtOH} R_2NCOCH_2SCH_2CONR_2 + NaCl$$

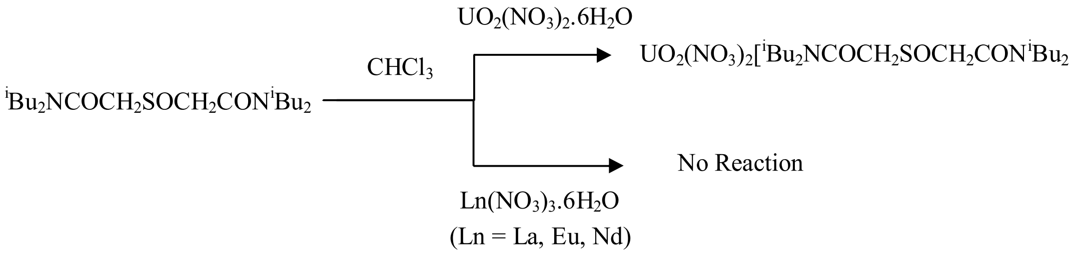
$(R = {}^iC_3H_7,\ {}^iC_4H_9\ ,\ C_4H_9\ )$

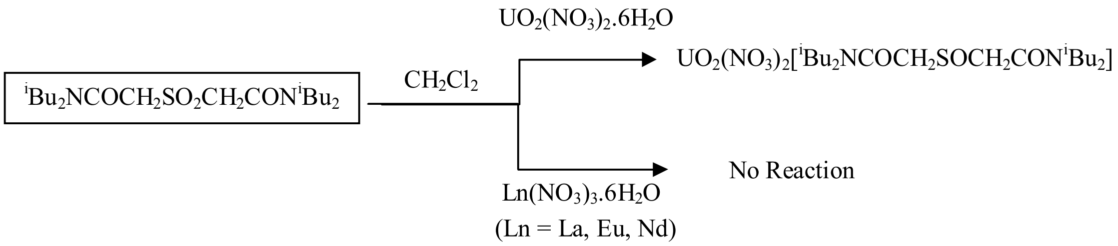


3.2 Synthesis of uranyl and lanthanide complexes

The synthesis of metal complexes are given in the following reactions.







3.3 Results and discussion

The ligands and their compounds of uranyl and lanthanide ions were characterized by, CHN analysis, IR and NMR techniques. The sulfoxide and sulfone ligands did not react with lanthanide nitrate under the conditions studied. Some of these compounds were characterized by XRD and their molecular structures are represented below.

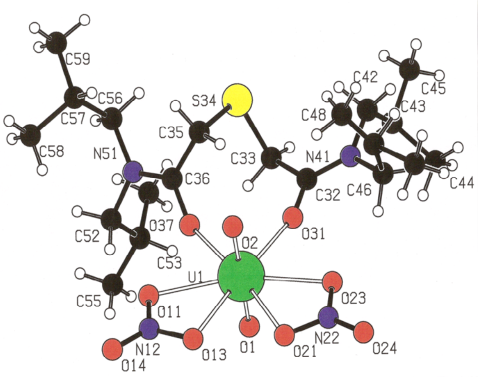


Fig. 3. Molecular structure of

$UO_2(NO_3)_2[^iBu_2NCOCH_2SCH_2CON^iBu_2]$

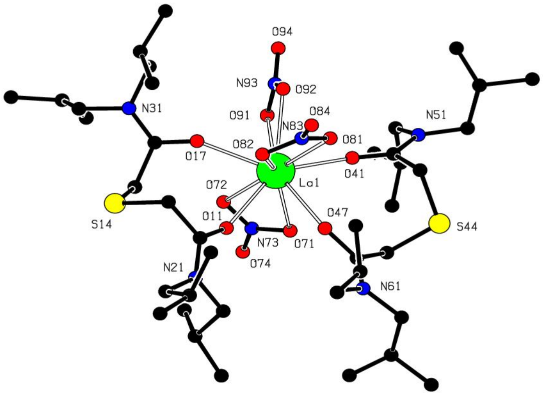


Fig. 4. Molecular structure of

$La(NO_3)_3[^iBu_2NCOCH_2SCH_2CON^iBu_2]_2$

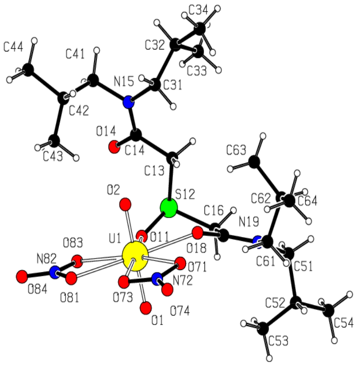


Fig. 5. Molecular structure of

$UO_2(NO_3)_2[^iBu_2NCOCH_2SOCH_2CON^iBu_2$

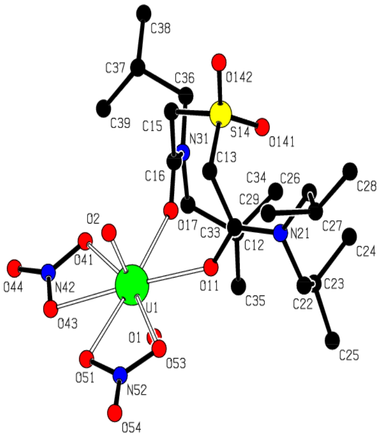


Fig. 6. Molecular structure of

$UO_2(NO_3)_2[^iBu_2NCOCH_2SO_2CH_2CON^iBu_2]$

The structures of thiodiglycolamide with uranyl and lanthanum nitrates are shown in figures 4 and 5. The structures show that the thiodiglycolamide ligands bond to uranyl and lanthanum nitrates in a bidentate chelating fashion through the carbamoyl oxygen atoms and the thioether group is un-coordinated. These structures are very similar to that of the uranyl nitrate–malonamide compounds. The coordination number around uranium(VI) is eight and the geometry is hexagonal bi-pyramidal whereas for lanthanum(III) it is ten and the geometry is a distorted bi-capped square-anti-prism. The NMR spectra reveal that the thioglycolamide ligands are weakly bonded to the lanthanum nitrate in solution. The distribution ratio studies for uranium and americium from 3M HNO_3 with thio-glycolamide ligand in different diluents such as, chloroform, toluene, n-decanol and nitrobenzene show an appreciable extraction for uranium in both chloroform and toluene and poor extraction in decanol and nitrobenzene. However, it further show negligible extraction for Am(III) in all solvents. Solvent extraction studies show that thio-diglycoamide behaves very similarly to those of glutaramide based ligands in solution.

The structure of *bis* (carbamoyl methyl) sulfoxide, uranyl nitrate is shown in Fig. 5. It shows that the ligand bonds to metal ion in a bidentate chelating fashion through the carbamoyl and sulfoxo oxygen atoms. It shows further that one carbamoyl oxygen atom is uncoordinated. The coordination number around uranium(VI) is eight and the geometry is hexagonal bipyramid.. The structure bis (carbamoylmethyl) sulfone, uranyl nitrate is shown in Fig. 6. It shows that the bis (carbamoylmethyl) sulfone ligand bonds to uranyl nitrate in a bidentate chelating fashion through both the carbamoyl oxygen atoms. It shows further that the sulfone group is uncoordinated. This may be due to the fact that the sulfone group is a poor donor towards the metal centre compared to that of the amide group and therefore the coordination of both the carbamoyl groups to the uranyl ion is observed. The coordination number around uranium(VI) is eight and the geometry is hexagonal bipyramidal. Thermal studies on all complexes show that the ligands are completely incinerable.

3.4 Conclusions

The complex chemistry of *bis* (N, N',di-alkyl carbomyl methyl) sulfide, sulfoxide and sulfone with uranyl nitrate was studied. The structural studies reveal that the ligands act in a bidentate chelating mode and bond through the carbamoyl groups to uranyl ion in both sulfide and sulfone cases and bond through one of the carbamoyl and sulfoxo groups in sulfoxide case. However, in lanthanum case the sulfide ligands form 2:1 complexes and bond through both the carbamoyl groups in a bidentate chelating fashion. The reaction of sulfone and sulfoxide ligands with lanthanum nitrate did not yielded the desired products. Thermal studies of all compounds show that the ligands are completely incinerable.

Chapter 4

Synthesis and structural studies of 1,1'-bis(diphenylphosphine oxide) ferrocene - uranyl complexes

This chapter deals with the synthesis and structural studies of 11,1'-bis(diphenylphosphine oxide) ferrocene omplexes of uranyl nitrate and uranyl dichloride.

4.1 Synthesis of ligand

The ligand was synthesized according to following reaction.

$$.(C_6H_5)_2P(C_5H_4)Fe(C_5H_4)P(C_6H_5)_2 \xrightarrow{30\%\ H_2O_2} (C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2$$

4.2 Synthesis of metal complexes

The metal complexes were synthesized by following reactions.

$$[UO_2(NO_3)_2.\{^iC_3H_7CON(^iC_4H_9)_2\}_2]+(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2] \xrightarrow{MeOH}$$

$$[UO_2(NO_3)_2.(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2]$$

$$trans\text{-}[UO_2Cl_2\{iC_3H_7CON(^iC_4H_9)_2\}]+(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2] \xrightarrow{MeOH}$$

$$cis\text{-}[UO_2Cl_2.(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2]$$

4.3 Results and discussion

These compounds were characterized by CHN analysis, IR, NMR and XRD techniques. .

Their molecular structures for both the compounds are represented below.

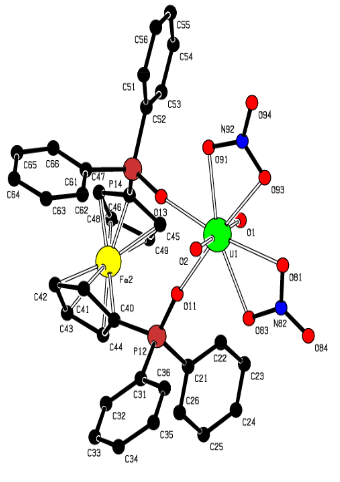


Fig. 7. Molecular structure of

$[UO_2(NO_3)_2.(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2]$

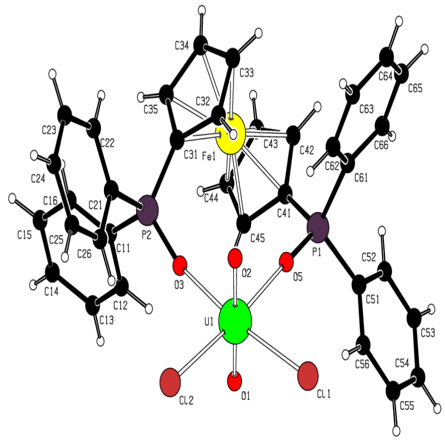


Fig. 8. Molecular structure of cis-UO_2Cl_2.

$(C_6H_5)_2 P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2]$

The molecular structure of [$UO_2(NO_3)_2$DPPOF] is shown in Fig. 7. The structure shows that the uranium atom is surrounded by eight oxygen atoms in a hexagonal bi-pyramidal geometry. The four oxygen atoms of nitrate groups and two oxygen atoms of DPPOF form a planar hexagon. The ligand acts as a bidentate chelating ligand and bonds through both the phosphine oxide oxygen atoms to uranyl group. It is interesting to note that the bite angle between the two P(O) oxygen atoms is 71.56° and is much smaller in value compared to any of the DPPOF metal complexes reported so far.

The molecular structure of [UO_2Cl_2 DPPOF] is shown in Fig. 8. The ligand binds to uranium in a bidentate chelating mode and uranium (VI) ion is surrounded by four oxygen and two chlorine atoms in an octahedral geometry. The two chlorine atoms and two oxygen atoms of the DPPOF ligand form the equatorial square plane The U-Cl bond distance 2.634 Å is comparable in magnitude with those of earlier reported uranyl dihalide compounds. The bite angle between the two P(O) oxygen atoms is 82.90°. The chlorides are mutually cis with a Cl-U-Cl angle of 97.75°.

4.4 Conclusions

1,1'-bis(diphenylphosphine oxide) ferrocene (DPPOF) complexes of uranyl ion [$UO_2(NO_3)_2$DPPOF] and *cis*[UO_2Cl_2DPPOF] were synthesized and characterized. The structures of the compounds show that it acts as a bidentate chelating ligand and the bite angles between two PO groups are 71.56° and 82.90° respectively in uranyl nitrate and uranyl chloride.

CHAPTER 1

Introduction

CHAPTER – 1

1.1 Introduction

Research on the chemistry of actinide elements started with the isolation of uranium from pitchblende in 1789 [1] and thorium from thorite in 1829 [2]. The chemistry of these elements were not clearly known until the discovery of radioactive decay in 1895 by Becquerel [3]. Further development in the chemistry started with the discovery of artificial radioactivity in 1934 [4] and also the research on the discovery of man made elements. The coordination chemistry played a vital role during the discovery research. The discovery of nuclear fission in 1938 provides an important bath for the further development of coordination chemistry of these elements. The separation and purification of plutonium from the fission products by using various new extractants and the separation ^{235}U from ^{238}U by using suitable volatile organo-metallic uranium compounds further extended the coordination chemistry of these elements. Of late, the coordination and structural studies of actinides complexes are not only very important for the development of new technology concerning the safe processing of irradiated nuclear fuel but also the storage of high level active wastes [5].

The lanthanides were first discovered in 1787 when an unusual black mineral was found in Ytterby, Sweden. This mineral, now known as Gadolinite, was later separated into the various lanthanide elements. In 1794, Gadolin obtained yttria, an impure form of yttrium oxide, from this mineral. In 1803, Berzelius and Klaproth secluded the first cerium compound. Later, Moseley used X-ray spectra of the elements to prove that there were fourteen elements between lanthanum and hafnium. Rest of the elements were later separated from the same mineral. These elements were first classified as ‘rare earth’ due to the fact that obtained by reasonably rare minerals. However, this is misleading since the lanthanide elements have a practically unlimited abundance. The term lanthanides was adopted, originating from the first element of the series, lanthanum [6]

1.2 Chemical properties of actinide elements

The actinide metal ions are considered to be relatively hard lewis acid and therefore more likely to make strong complexes with the hard donor ligands. The actinide ions are affected by actinide contraction along the series, resulting in a decrease of ionic radius and an increasing reluctance to exhibit higher oxidation state beyond plutonium. Though, most of the metal ions are paramagnetic, the favorable electron spin- nuclear spin relaxation times are often permit to observe the NMR spectra for most of the complexes. However, the relaxation times are unfavorable to observe ESR spectra at room temperature and need very low temperature close to liquid helium.

The actinide elements show more diversity in their chemistry compared to that of their lanthanide counter parts. The greater radial extent and energetic availability of 5f and 6d orbitals results in increased interaction with ligand orbitals compared those of 4f and 5d orbitals of lanthanides. In the electronic spectra, the actinide complexes often impacted by the ligand filed effects compared to those of lanthanides, where upon, the spin–orbit and electron–electron interactions predominate [7-8]. Due the availability of energetically favorable electrons, the earlier actinides display a much wide range of oxidation states (Table 1.1) and the bonding in their complexes is often described to be more covalent than that of lanthanide ions [9]. Since, the earlier actinides (Th-Pu) are much more readily available, either from natural ores or as products of nuclear materials, and also as they show variable oxidation states, most of the coordination and structural studied were reported for these elements.

Table 1.1 Different oxidation states of the actinide elements

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
4	3	3	3	3	2	3	3	2	2	2	2	2	3
	4	4	4	4	3	4	4	3	3	3	3	3	
	5	5	5	5	4			4					
		6	6	6	5								
			7	7	6								
					7								

1.3 Coordination numbers and geometries of actinide complexes

Since, the ligand field effect on 5f orbitals is very small, the complexes of actinides will not have a well defined coordination number and geometry for a given metal ion as compared to that of the analogous transition metal ions. The coordination number and geometry around a metal ion will be decided mainly by the charge and size of the metal ion and size of the ligands. Actinide ions display relatively large ionic radii and therefore support higher coordination numbers [7] of 8 to 10 and often12 to 14 (Table 1.2), which are not seen in the transition metal ions. The highest coordination number of fourteen is reported in the complexes of [Th$(BH_4)_4$] [10] (Fig. 1.1) and [U$(BH_4)_4$.$(OR_2)_2$] (R = CH_3 or C_2H_5) [11] and the lowest coordination number of three is reported in [Pu(N$\{SiMe_2\}_3$] [12] and [U(N$\{SiMe_2\}_3$] [13].

Table 1.2 Frequently observed coordination geometries in the actinide compounds [7]

C. N	Coordination geometries	Complex
3	Pyramidal	$[U(N\{SiMe_2\}_3]$
4	Tetrahedral	$U(O\text{-}2,\ 6\text{-}Bu_2C_6H_3)_4$
5	Distorted trigonal Pyramidal	$[U(NEt_2)_4]_2$
6	Octahedral	$[MO_2X_2L_2]$ (M = U, Np, Pu), $[MX_4L_2]$ (M=Th,U,Pu)
7	Pentagonal bipyramidal	$[MO_2(\beta\text{-diketonate})_2.L]$ (M=U, Np, Pu)
8	Cubic	MO_2 (M = Th, U, Np, Pu)
8	Square antiprism	ThI_4
8	Hexagonal bipyramidal	$[MO_2(NO_3)_2L_2]$,$[MO_2(OAc)_2.L_2]$ (M = U, Np, Pu)
8	Bicapped trigonal prism	$PuBr_3$
9	Tricapped trigonal Prism	$[Pu(H_2O)_9](CF_3SO_3)_3$, $[Th(TTA)_4.TOPO]$
9	Monocapped square antiprism	$[Th(Tropolonate)_4]$
10	Bicapped square antiprism	$K_4[Th(C_2O_4)_4]$
10	Dodecahedron	$[Th(NO_3)_4.(OPPh_3)_2]$
11	All-capped trigonal prism	$[Th(NO_3)_4.3H_2O]$
12	Icosahedron	$[M(NO_3)_6]^{2-}$ (M= Th, Pu)
14	Bicapped hexagonal antiprism	$[Th(BH_4)_4]$, $[U(BH_4)_4.\ (OR_2)_2]$

X = Halides, L = H_2O, OPR_3, Amides,

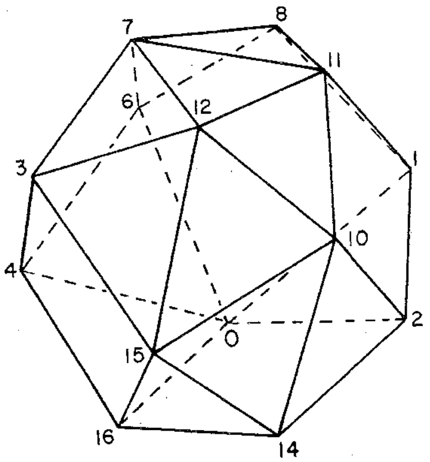


Fig. 1.1 The coordination geometry around thorium in [$Th(BH_4)_4$] (CN=14)

1.4 Structural studies on the compounds of actinide elements

1.4.1 Oxide compounds

Most of the elements are present in the form of MO_2 (M = Th, U, Np, or Pu) having CaF_2 structure in the solid state and used in the nuclear reactor as a fuel. In this structure, the metal (IV) ions are surrounded by eight oxygen atoms in a cubic geometry. Uranium is also present in the forms of UO_3 and U_3O_8 and the oxidation state of uranium in the former is six and in the later is a mixture of four and six. Americium is present in the form of Am_2O_3 in which the oxidation state of americium is three. The coordination number around the metal ion varies from seven to eight in this compound.

1.4.2 Nitrate compounds

The complexes of actinide nitrate are very important for the understanding of their separation from the irradiated nuclear fuel. All actinide metal ions form nitrate complexes and the number of nitrate molecules bonded to the metal ion depends on the oxidation state of metal ion involved. There are no stable trivalent actinide metal nitrate compounds for Th, U, Np and Pu which have been isolated and characterized due to the oxidation of trivalent to tetravalent state in solution. Numbers of stable tetravalent nitrate compounds are reported and show different coordination numbers and geometries. Thorium nitrate complex [$Th(NO_3)_4.5H_2O$] [14] shows coordination number of eleven around the metal ion with four bidentate nitrate and three monodentate water molecules in the primary coordination sphere to give all-capped trigonal prismatic geometry (Fig 1.2). Number of nitrate compounds of tetravalent metal ions of the type [$M(NO_3)_4.2L$] (where M = Th or U, L = phosphine oxide, phosphate) [15-16] are also reported and the coordination number around the metal ion is ten with bi-capped square anti-prismatic geometry.

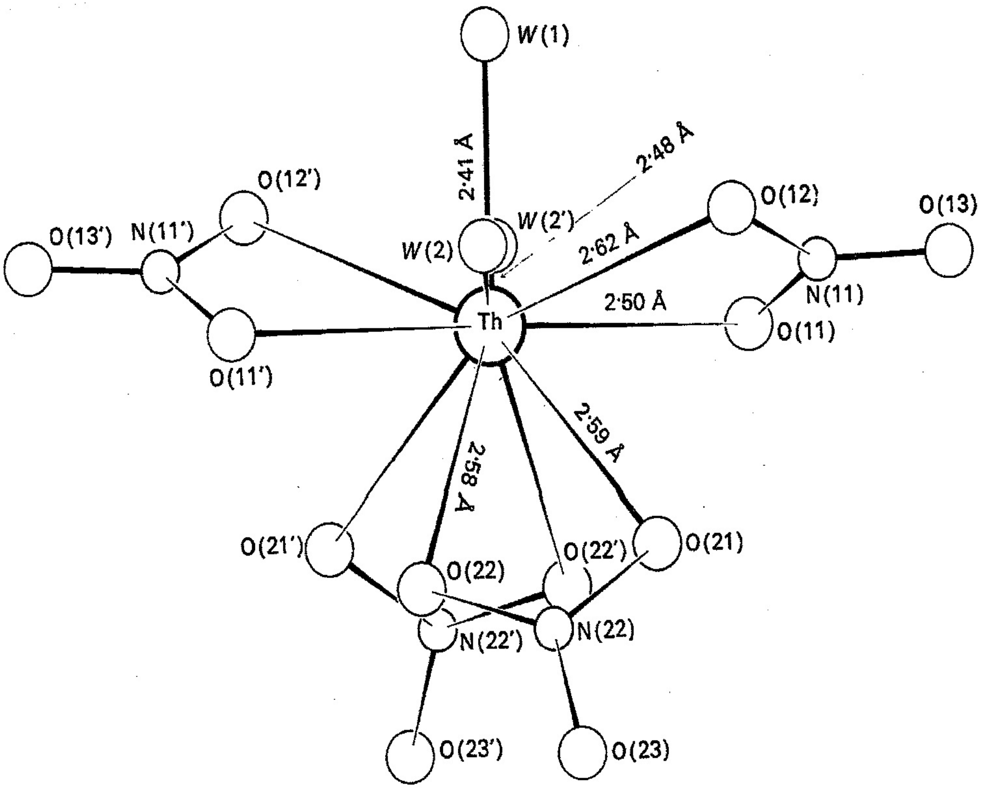


Fig.1.2 Structure of [$Th(NO_3)_4.3H_2O$]

Number of addition compounds of the tetravalent actinide ions of the type $A_2[M (NO_3)_6]$. xH_2O (M = U or Pu ; A = Na, K, Rb or Cs) [17-18] are also reported and the geometry around the metal ion is icosahedron with coordination number of twelve (Fig. 1.3).

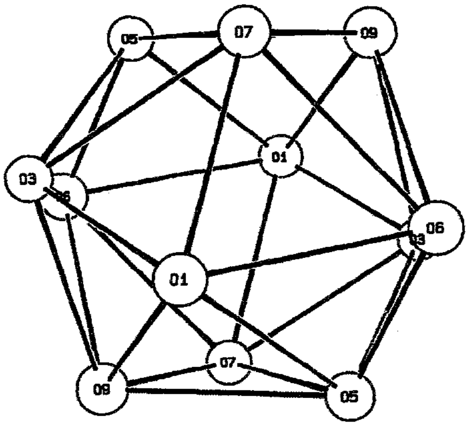


Fig. 1.3 Geometry around metal ion in a twelve coordinated complexes

The hexavalent actinide nitrate complexes of the type $[MO_2(NO_3)_2.2L]$ (M= U, Np, Pu; L = H_2O, phosphine oxide, amides, N-oxides) are reported and the structures show that the uranium(VI) atom is surrounded by eight oxygen atoms (four from two bidentate nitrate groups , two from two neutral molecules and two from uranyl oxygen atoms) in a hexagonal bi-pyramidal geometry [19]. The addition compounds of the type $A_2[MO_2(NO_3)_3]$ (M = U, Np or Pu ; A= Na, K, Rb, or Cs) are also reported, in which the metal ion is surrounded by three bidentate nitrate groups and two uranyl oxygen atoms in hexagonal bi-pyramidal geometry. The U-O bond distances varies from 1.77-1.79 Å (for U=O) to 2.45-2.52 Å {U-O(NO_3)} in all these compounds.

1.4.3 Sulphate compounds

The sulphate forms stable trivalent metal ion complexes and many of the complexes are structurally characterized. The compounds $K_3[U(SO_4)_3]$, $NH_4[U(SO_4)_2.4H_2O]$,

$NH_4[Pu(SO_4)_2.4H_2O]$, [20-22] and $[Am_2(SO_4)_3.8H_2O]$ [23] are some of the examples of trivalent actinide sulfates. The coordination number around U(III) in $NH_4[U(SO_4)_2.4H_2O]$ is nine with tricapped trigonal prismatic geometry and Am(III) in $[Am_2(SO_4)_3.8H_2O]$ is eight with square anti prismatic arrangement. Sulphate has high affinity for the tetravalent actinides and forms complexes of the type $[M(SO_4)_n]^{4-2n}$ (n = 2 to 4). The hydrated $[M(SO_4)_2.4H_2O]$ (M = Th, U or Pu) compounds are obtained in pure crystalline form from sulfuric acid medium [24-26] . These compounds are iso-structural with coordination geometry of bi-capped square anti-prismatic arrangement (coordination number of ten). The hexavalent actinide sulphate complexes of the type $[UO_2 (SO_4).xH_2O]$ and $[UO_2 (SO_4)_2.xH_2O]^{2-}$ are also known, in which the uranium atom is surrounded by seven oxygen atoms in a pentagonal bi-pyramidal geometry [27].

1.4.4 Oxalates, carbonates and carboxylates

Oxalate or carbonate precipitation method is a very important step during the purification and separation of various actinides from the other rare earth and transition metal impurities. Number of oxalate complexes have been reported and structurally characterized. The structure of $A_4[M(C_2O_4)_4]$ (where A = Na, K, NH_4; M = Th, Pu) [28] shows that the metal ion is surrounded by five oxalate groups in a bi-capped square anti prismatic geometry (Fig. 1.4).

Structure for number of carbonate complexes have also been characterized in the solid state. In $[Pu(CO_3)_5]^{6-}$ the plutonium(IV) ion is surrounded by five carbonate anions in a bi-capped square antiprismatic geometry with coordination number of ten [29] . This compound is iso-structural with the analogous thorium compound. Numbers of acetate complexes are also known and the coordination properties of acetate ion are very similar to that of nitrate ion.

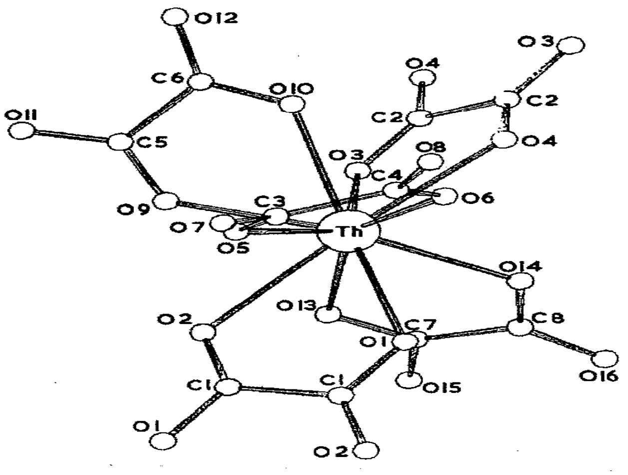


Fig. 1.4 Coordination around $[Th(C_2O_4)_5]$ in $K_4[Th(C_2O_4)_4]$

1.4.5 Organometallic chemistry of actinide elements.

The organometallic chemistry of actinide elements started during Manhattan project to prepare volatile uranium complexes for the isotopic separation ^{235}U from natural uranium. The first organometallic actinide $[(C_5H_5)_3UCl]$ tris-cyclopentadienyl uranium(IV) chloride [30] was reported in 1956 and later on all other actinide complexes of the formula $[(C_5H_5)_3MX]$ (Where M = Th; X = Cl, Br) [31] have also been reported . The structure of first organometallic uranium shows that the uranium (IV) is boned to three cyclopentadienyl anions and one chloride ion (Fig .1.5)

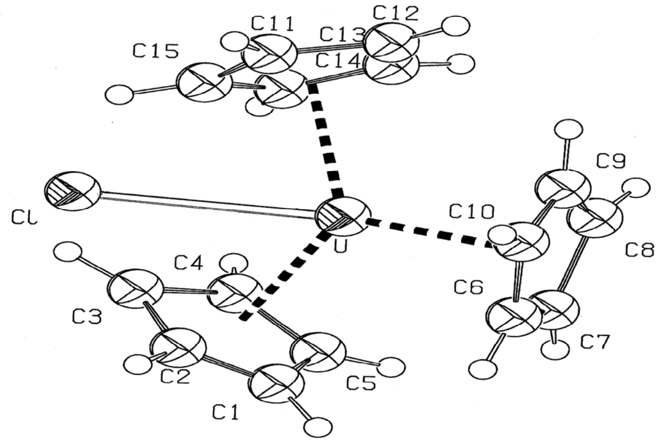


Fig. 1.5 First organo-actinide complex $[U(C_5H_5)_3Cl]$

Number of sandwich compounds of actinide ions are reported and the first one i.e., uranocene [32] was reported in 1968. The structure of the complex shows that the uranium(IV) ion is sandwiched between two of the cyclo-octatetraene (Fig. 1.6). These complexes are highly unstable towards oxygen and air (actinides are hard metals and hard donors which will react with oxygen available from air and water) and should be prepared and stored in dry and inert atmosphere. The stabilities of these complexes can be explained purely on the basis of π back bonding from the filled 5f/6d orbitals to the soft carbon based ligands. These compounds show high catalytic activity towards the hydrogenation of olefins.

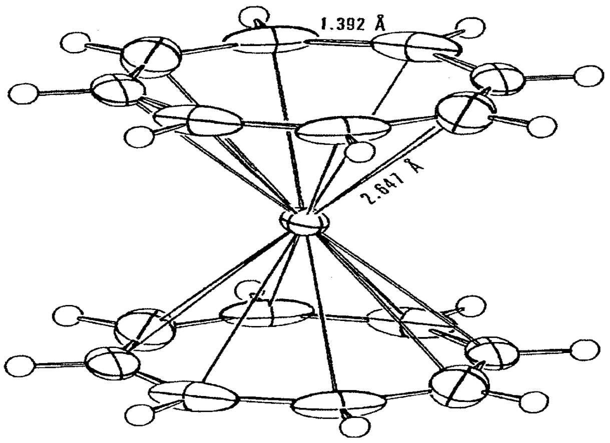


Fig. 1.6 The first actinide sandwich complex Uranocene

1.5 Coordination complexes related to separation studies

Separation of actinides particularly uranium and plutonium from the irradiated nuclear fuel and americium from high level waste solution by using variety of neutral extractants such as, phosphine oxides [33], phosphates [34] and amides [35] were well reported. Various types of neutral extractants having different donor groups have been studied and they were classified according to the number of donor centers present in the molecule, such as mono-functional, bi-functional, tri-functional etc. The coordination, extraction and structural properties of these extractants are completely different from each other and giving interesting geometries around the metal ions.

1.5.1 Neutral mono-functional extractants

Tri-n-butylphosphate is used as an extractant for the separation of uranium and plutonium from the irradiated nuclear fuel in PUREX process [36-37]. Studies on the extraction of uranium, plutonium and neptunium from nitric acid medium using neutral mono-functional extractants such as phosphine oxide [33], phosphates [34, 38] and amides [35, 39-40] have been reported. In all these process, the extraction mechanism could be written as the following:

$[MO_2(NO_3)_2.\ 2H_2O] + 2\ L \rightarrow [\ MO_2(NO_3)_2.\ 2L\ ] + 2H_2O$ (M = U , Np or Pu)

$[M(NO_3)_4.\ nH_2O] + 2\ L \rightarrow [M(NO_3)_4.2L] + 2H_2O$

(M = Th , U or Pu, n = 2 for Pu or U, n = 3 for Th)

L = phosphine oxides, phosphates, N-oxide or amides

These reactions are basically inorganic substitution reactions, in which the water molecules from the primary coordination sphere are replaced by the neutral donor ligands. For many of the extraction reactions, the species responsible for the same are isolated in the solid state and characterized by using IR, ^1H NMR spectroscopy and single crystal X-ray diffraction methods.

The IR spectra of the complexes show the disappearance of the ν_{OH} peak around 3000-3500 cm^{-1} due the presence of the coordinated water molecules in the starting complexes $[MO_2(NO_3)_2.\ 2H_2O]$ and $[M(NO_3)_4.\ 2H_2O]$. The spectra further show that the ligands are bonded through the functional groups such as P=O and C=O, respectively for the phosphine oxides, phosphates and amides to the metal centers (there will be a decrease in frequency of P=O and C=O groups compared to that of free ligands after complexing and the O=U=O frequency appears around 850- 950 cm^{-1} in all uranyl complexes).

The structures for the complexes $[UO_2(NO_3)_2(OPBu_3)_2]$ and $[MO_2(NO_3)_2(OPPh_3)_2]$ (M = U, Np,) [41-42] show that the metal ion is surrounded by two nitrate groups, two mono-functional neutral extractants and two uranyl oxygen atoms in hexagonal bi-pyramidal geometry. Four oxygen atoms from the two nitrate groups (2.48-2.51Å) and two oxygen atoms (1.77 – 1.79 Å) from the two neutral ligands form the planar hexagon and two oxygen atoms (O=M=O) occupies the axial positions.

The structures for the tetravalent nitrate complexes $[M(NO_3)_4(OPPh_3)_2]$ (M= Th , U) [43] show that the metal (VI) ion is surrounded by four nitrate and two phosphine oxide groups giving the coordination number of ten with dodecahedron geometry. Similar coordination geometry has been observed for other tetravalent nitrate-neutral ligand complexes.

1.5.2 Neutral bi and tri- functional extractants.

Bi-functional extractants, such as carbamoyl methyl phosphonates (CMP), carbamoyl methyl phosphine oxides (CMPO), malonamides and bis(diaklyl phosphine oxide) methane and tri-functional ligands such as tetraoctyl diglycolamides show excellent extraction properties for the trivalent actinides in addition to that of tetra and hexavalent actinide ions [39, 44-49]. The complexes responsible for the extraction process were prepared by reacting the respective metal nitrates with these ligands in a required ratio and the final products were characterized by using the IR, ^{1}H, ^{31}P (only for phosphorus containing ligands) NMR spectroscopy. The ^{31}P NMR spectra of the complexes show that the ^{31}P resonance in these complexes are deshielded by ~ 5-10 ppm with respect to the free ligand [50-51]. This result confirms the coordination of phosphine oxide group with the metal centre. The ^{1}H NMR spectra show that all protons are deshielded with respect to free ligand and in particularly the CH_2 protons are deshielded much more (0.5 to 1 ppm) as compared to those of other protons (CH_2 bridging the PO and CO in CMP and CMPO or CO and CO in malonamides) [50-53]. These observations further support the coordination of ligands to the metal ion in solution. The IR spectra further support that the ligands are bonded through both the carbamoyl and phosphine oxide groups to the metal centre in the solid state. The structure of complexes [$UO_2(NO_3)_2$.CMPO] [50] (Fig.1.7) [$UO_2(NO_3)_2$CMP] [54], [$UO_2(NO_3)_2$. malonamide] [55] and [$UO_2(NO_3)_2$.(bis-phophine oxide)] [56] show that the uranyl group is bonded to two nitrates and one neutral bi-functional ligands to give a hexagonal bi-pyramidal geometry.

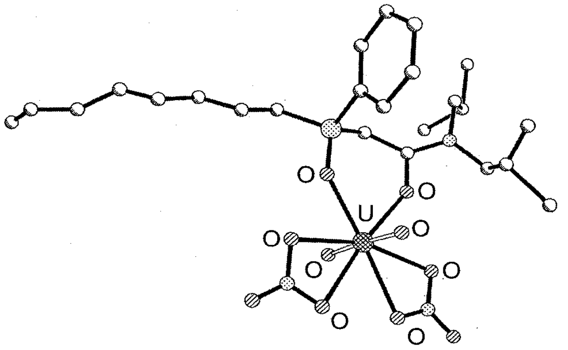


Fig .1.7 Structure of [$UO_2(NO_3)_2$.CMPO]

The structure for the tetravalent nitrate ion complex [$Th(NO_3)_4(CMP)_2$] [57] shows that the thorium (IV) ion is surrounded by four nitrates and two CMP ligands in a icosahedron geometry. Both the nitrate and CMP groups act as bidentate chelating ligands to give coordination number of twelve.

The structure of uranyl nitrate digylcolamide (Fig. 1.8) shows that the uranyl group is bonded to two nitrates and one diglycolamide ligand [58-59]. The diglycolamide ligand acts as a tridentate chelating ligand and bonds through both the carbamoyl and ethereal oxygen atoms to the uranyl group.

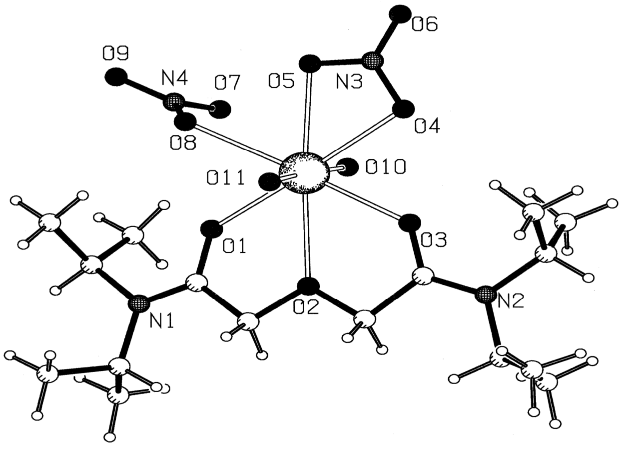


Fig 1.8 Structure of $[UO_2(NO_3)_2 L]$ (L = diglycolamide)

The structure of a symmetrical Neptunyl(V) - diglycolamide compound is also reported and shows that the $[NpO_2]^+$ group is bonded to two of the diglycolamide ligands in a symmetrical fashion to give hexagonal bi-pyramidal geometry around the metal ion [60]. The positive charge on the complex is satisfied by the non-coordinating counter ion ClO_4^-. The tri-functional soft nitrogen containing ligands show better separation factors for the trivalent actinides over those of trivalent lanthanides. The structure of the complex $[U(2, 2',6, 2'terpyridine)_3]^{3+}$ [61] shows that the ligands are bonded through all the nitrogen atoms to the metal nitrates in a tridentate fashion.

1.5.3 Crown ether Complexes

The crown ethers are very important class of extractants for the separation of actinide ions from their mixture. The nature of the complexes formed between the crown ether and metal ion is mainly decided by the experimental conditions employed during separation. The crown ethers form inclusion compounds (Fig. 1.9) with metal ions in presence of non coordinating anions such as: $ClO_4^-$and $CF_3SO_3^-$ [62]. The 18-crown-6 selectively extracts NpO_2^+ or UO_2^{2+} from the perchloric acid medium and the structure of the isolated compound revealed that the NpO_2^+ or UO_2^{2+} ion is selectively encapsulated in the cavity of the crown ether. However, in presence of coordinating anions such as: nitrate, sulphate etc, they form second sphere coordination complexes, in which the crown ether is hydrogen bonded to the water molecules, which are in the primary coordination sphere [63].

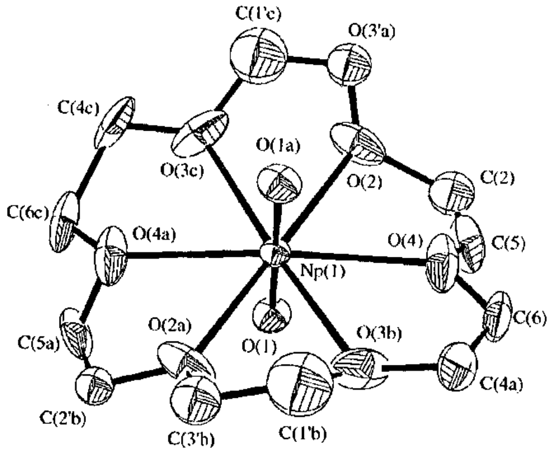


Fig.1.9 Structure of $[NpO_2(18C6)] (ClO_4^-)$

1.5.4 Complexes of actinide ions with β-diketonates

Numbers of acidic extractants were employed for the separation of actinide ions from the acidic media and the well studied extractants are β-diketones [64-65]. These extractants are having ionisable protons and could be easily dissociated to form complexes with the metal ions. These complexes are organic soluble and could be extracted in to the organic phases. Complexes responsible for the extraction in many of the cases were isolated in the solid state and characterized by using the well known spectroscopic techniques, like IR, ^1H, ^{19}F NMR. The structure of $[UO_2(TTA)_2.2H_2O]$ [66] (Fig. 1.10) shows that the uranyl group is bonded to two of the TTA units and one of the water molecule in the primary coordination sphere. The coordination number and geometry around the uranium(VI) is seven and pentagonal bi-pyramidal. The second water molecule is present in the second coordination sphere and hydrogen bonded to the first water molecule. The structures for the tetravalent metal β-diketonate complexes [M(OO)$_4$] (M = Th, U or Pu) (OO = β-diketonate anion) [67] show that the metal ion is surrounded by four β-diketonate anions in a square anti-prismatic geometry.

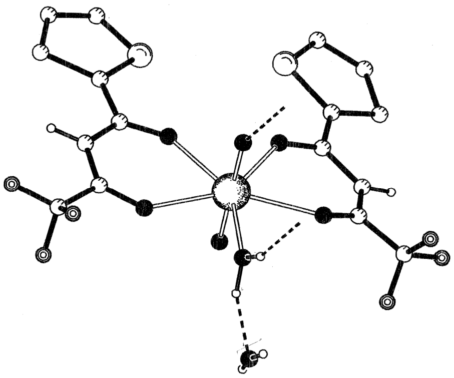


Fig. 1.10 The Structure of [$UO_2(TTA)_2.2H_2O$]

1.5.5 Synergistic extraction of actinide ions using the mixture of β-diketones and neutral extractants

The synergistic extraction of actinide ions from the acid media by using the mixture of β-diketones and neutral extractants is a well established method [68-70]. The increase in extraction was due to the formation of more organic soluble metal complex with both the β-diketones and neutral extractants. A large numbers of complexes of actinide ions with the combination of β-diketonates and neutral extractants have been prepared in the solid state and characterized.

The structures of all complexes shows that the uranyl group [71]is bonded to two of the β-diketonate anions and one neutral extractant (Fig 1.11) to give pentagonal bi-pyramidal geometry around the metal ion.

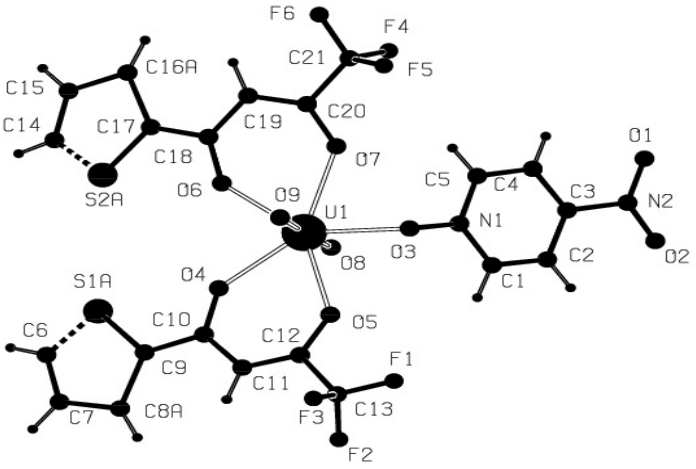


Fig. 1.11 Structure of [$UO_2(TTA)_2$ p-NO_2-C_5H_5NO] [71]

The structure of [$Th(TTA)_4$.TOPO] complex [72] shows that the Th(IV) ion is surrounded by four TTA anions and one TOPO molecule in a tri-capped trigonal prismatic geometry. The β-diketonate acts as a bidentate chelating ligand and the TOPO acts as a monodentate ligand. Similar types of structures have been proposed for the other M(IV) ion –β-diketonate- neutral ligand complexes.

1.6 Chemical properties of lanthanide elements

The lanthanide metals are hard lewis acids and form complexes with hard donors. The effect of the 4f orbitals on the chemistry of the lanthanides is profound and is the factor that distinguishes them from the transition metals. The 4f orbitals penetrate the [Xe] core and are isolated and do not participate in bonding. As a result, the nature of bonding between metal and ligand is purely ionic (electrostatic). The 4f orbitals are unaffected by the crystal field effects and therefore do not form π bonds with the ligands. As there are seven 4f orbitals, the number of unpaired electrons can be as high as 7 which give rise to the large magnetic moments observed for lanthanide compounds. Measuring the magnetic moment can be used to investigate the 4f electron configuration and this is a useful tool in providing an insight into the chemical bonding. The lanthanide contraction, the reduction in size of the Ln^{3+} ion from La^{3+}(0.103 Å)- Lu^{3+}(0.0861Å) is often explained by the poor shielding of the 5s and 5p electrons by the 4f electrons [72].

The chemistry of the lanthanides is dominated by the +3 oxidation state with the configuration of [Xe]4f^{m} . In addition, cerium exits in +4 state, europium and ytterbium in +2 states due to f^{0}, f^{7} and f^{14} configurations (Table 1.3).

Table 1.3 Different oxidation states of the lanthanide elements

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
					2	2						2	2	
3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4					4	4					

1.6.1 Coordination number and geometry of lanthanide complexes

The low probability of the 4f electrons existing at the outer region of the atom or ion permits little effective overlap between the orbitals of a lanthanide ion and any binding ligand. Thus lanthanide complexes typically have little or no covalent character and are not influenced by orbital geometries. The lack of orbital interaction also means that varying the metal typically has little effect on the complex (other than size), especially, when compared to transition metals. Complexes are held together by weaker electrostatic forces and thus the ligands alone dictate the symmetry and coordination of complexes. Steric factors therefore dominate, with coordinative saturation of the metal being balanced against inter-ligand repulsion. This results in a diverse range of coordination geometries, many of which are irregular [73-74] and also manifests itself in the highly fluxional nature of the complexes. As there is no energetic reason to be locked into a single geometry, rapid intra-molecular and inter-molecular ligand exchange will take place, which typically results in complexes which will rapidly fluctuate between all possible configurations. The coordination numbers in most of the lanthanide complexes vary between 8 to 12 and very often 8 to 10 (Table 1.3). The highest coordination number of 12 is reported in many complexes of the type $[Ln(NO_3)_6]^{3-}$ [75] and the lowest coordination number of 3 is reported in $[Ln\{N(SiMe_2)_2\}_3]$ [76].

The trivalent lanthanides mostly form ionic salts. The trivalent ions are hard acceptors and form more stable complexes with oxygen-donor ligands than with nitrogen-donor ligands. The larger ions are 9-coordinate in aqueous solution, $[Ln(H_2O)_9]^{3+}$ but the smaller ions are 8-coordinate, $[Ln(H_2O)_8]^{3+}$ [77]. Complexation with monodentate ligands is generally weak because it is difficult to displace water molecules from the first coordination sphere. Stronger complexes are formed with chelating ligands because of the chelate effect, and many such complexes are reported.

Since the coordination chemistry of trivalent actinides is very similar to that of trivalent lanthanides, the structural studies relevant to separation studies alone will be presented here.

1.7 Structural studies on the compounds of lanthanides relevant to separation process.

1.7.1 Nitrate compounds

Lanthanide nitrates dissolve easily in polar solvents such as water, alcohols, esters or nitriles. Lanthanide nitrates usually have the formula $[RE(NO_3)_3 \cdot nH_2O]$, where $n = 6$ for the lighter rare earth nitrates (lanthanum to neodymium) and $n = 5$ for the heavier rare earth nitrate (europium to lutetium) and this is caused by lanthanide contraction. In lanthanide nitrates, the nitrate groups usually behaves as a bidentate chelating ligand similar to reported in $[Ce(NO_3)_3(C_5H_7N_2CH_2CONBu_2)_2]$ [78] .

1.7.2 Monodentate neutral ligand lanthanide nitrate compounds

Lanthanide nitrates from weak complexes with monoamides, sulfoxides and phosphates [40, 79-80]. In general, these ligands show very poor extractions for lanthanides from HNO_3 medium due to poor complexing ability of these ligands with lanthanide ions. However, the phosphine oxides show appreciable extraction for these ions from nitric acid medium [81] and larger number of phosphine oxide compounds are isolated in solid state and structurally characterized. The phosphine oxides form either $[Ln(NO_3)_3(OPR_3)_3]$ [82] or $[Ln(NO_3)_3(OPR_3)_4]$ [83] types of complexes with coordination number varies between 9 and 10.

1.7.3 Bidentate neutral ligand lanthanide nitrate compounds

Many bi-functional ligands such as carbamoyl methyl phosphonates, carbamoyl methyl phosphine oxides, carbamoyl methyl sulfoxide ligands show excellent extraction for lanthanide and actinide ions from nitric acid medium [84-87]. Number of compounds are isolated in solid state and are structurally characterized. All these ligands form 2:1 complexes with lanthanide nitrates with the formula $[Ln(NO_3)_3.2L]$ (where L = malonamides, carbamoyl methyl phosphonates, carbamoyl methyl phosphine oxides, carbamoyl methyl sulfoxide). In all cases, the ligands act as bidentate chelating ligands and bond through both the donor groups (Fig. 1.12). The coordination number and geometry are 10 and bi-capped square antiprism, respectively.

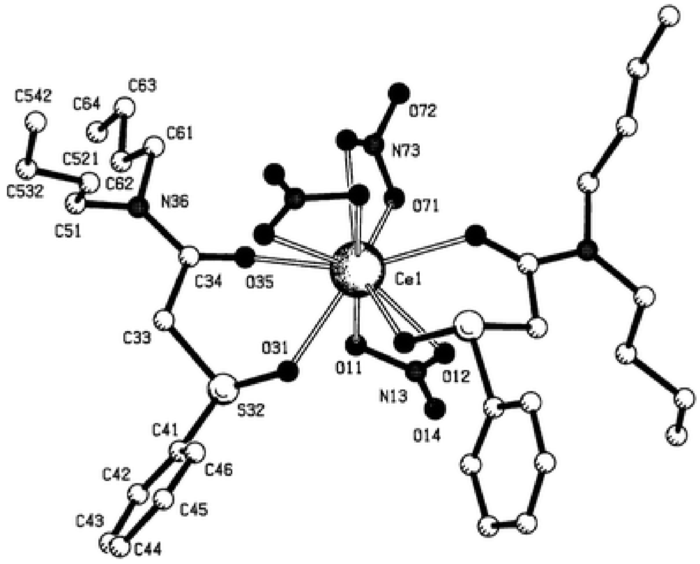


Fig. 1.12 Structure of [Ce $(NO_3)_3(PhSOCH_2CON^iBu_2)_2$]

1.7.4 Tridentate neutral ligand lanthanide nitrate compounds

In recent years, tri-functional chelating ligands of diglycolamide type show excellent extractions for the trivalent lanthanides and actinides from nitric acid medium [58]. For some of the cases, the lanthanide complexes are isolated and structurally characterized. In all cases, the ligand act as tridentate chelating ligand and bond through both the carbamoyl and ethereal oxygen atoms to the metal centre. These ligand form 3:1 complexes of the formula [$LnL_3](NO_3)_3$ with lanthanide nitrates, in which the nitrate ions are outside the coordination sphere [59].

Tri-functional ligands containing nitrogen donor centre are also show good extraction for trivalent actinide ions over lanthanide ions [61, 88] and for some of cases, the species responsible for the separation have been structurally characterized [61]. In most of the cases, the ligand act as tridentate ligands and bond through all nitrogen atoms to metal centre (Fig .1.13).

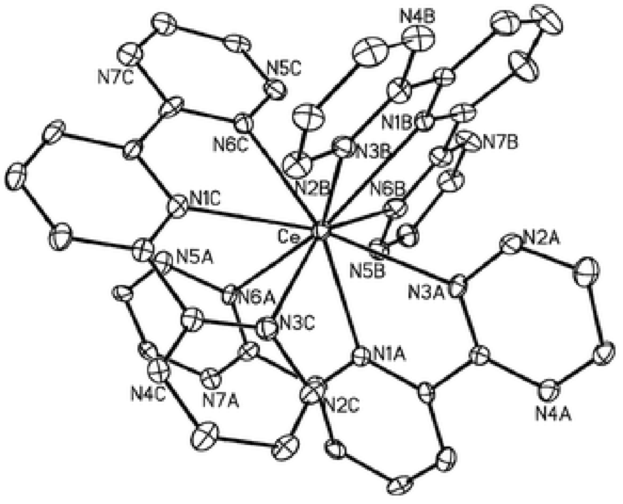


Fig. 1.13 Structure of $[Ce(Mebtp)_3]^{3+}$

1.7.5 Sulphate Compounds

Lanthanide sulphates have the general formula $[RE_2(SO_4)_3\cdot nH_2O]$ where n = 3, 4, 5, 6, 8, and 9. The most common is n = 9 for lanthanum and cerium and n = 8 for praseodymium to lutetium and yttrium. The $[La_2(SO_4)_3\cdot 9H_2O]$ structure consists of an infinitive network. In this structure, one of the lanthanum ions (La1) is coordinated to 12 oxygen atoms from six bidentate sulfate groups, while the other lanthanum ion (La2) shows coordination number of nine with six oxygen atoms from six water molecules and remaining three from monohapto sulfate groups [89] **.** The coordination polyhedron has a tri-capped triangular prism configuration. The rest of the water molecules exist in the network through hydrogen bonds connected to oxygen atoms. Therefore, the formula may be represented as $\{[La_2(SO_4)_3\cdot 6H_2O]\cdot 3H_2O\}_n$. In $[Pr_2(SO_4)_3\cdot 8H_2O]$, the coordination number of praseodymium is eight, among which four of the oxygen atoms come from four water molecules and the rest come from four monohapto sulfate groups. The coordination polyhedron takes on a square antiprism configuration. In this molecule, the sulfate groups adopt two different coordination modes to coordinate to the central ions and they are present as bidentate and tridentate bridges [89].

1.7.6 Crown ether compounds

Lanthanides do not form crown ether inclusion complexes readily in aqueous solution, due to the considerable hydration energy of the Ln^{3+} ion. These complexes are, however, readily synthesized by operating in non-aqueous solvents. Because many studies have been made with lanthanide nitrate complexes, coordination numbers are often high. Thus 12-coordination is found in $[La(NO_3)_3$(18-crown-6)], 11 in $[La(NO_3)_3$(15-crown-5)], and 10 in $[La(NO_3)_3$(12-crown-4)] [90]. Other complexes isolated include [Nd(18-crown-6)$_{0.75}(NO_3)_3]$, which is in fact [{Nd(18-crown-6)$(NO_3)_2\}^+]_3$ $[Nd(NO_3)_6]$. Small crown ethers like 12-crown-4 give 2:1 complexes with lanthanide perchlorates, though the 2:1 complexes are not obtained with lanthanide nitrates, where the anion can readily coordinate. Lanthanide chloride complexes often include water in the co-ordination sphere; thus the complex with the formula $[ErCl_3$(12-crown-4)$.5H_2O]$ actually contains 9-coordinate [Er(12-crown-4)$(H_2O)_5]^{3+}$ cations whilst $[NdCl_3$(18-crown-6)$.4H_2O]$ is [Nd(18-crown-6)$Cl_2(H_2O)2]^+(Cl^-).2H_2O$. On reaction in MeCN/MeOH, 15-crown-5 reacts with neodymium chloride to form complexes with $[Nd(OH_2)_9]^{3+}$ and $[NdCl_2(OH_2)_6]^+$ ions hydrogen-bonded to the crown ether without any direct Nd–crown ether bonds. By carrying out electrocrystallization, the water-free [Nd(15-crown-5)C_{l3}] is obtained. Lanthanides also complexes with noncyclic linear polyethers such as glyme and other macrocycles such as the calixarenes.

1.7.7 Compounds of lanthanides with β-Diketonates

These are an important class of compounds with a general formula [Ln(R^1COCHCO.R^2)$_3$]. The acetylacetonates, Ln(ACAC)$_3$ (R^1 = R^2 = CH_3) can readily be made from a lanthanide salt and acetylactone by adding sodium hydroxide:

$LnX_3 + 3$ Na(acac)→Ln(acac)$_3$ + 3 NaX

They crystallize as hydrates like [Ln(ACAC)$_3$.(H_2O)$_2$] (Ln = La to Ho and Y) and [Yb(ACAC)$_3$.(H_2O)]. These compounds are difficult to dehydrate, even in vacuum as they decompose on heating, and on dehydration at room temperature tend to oligomerize to nonvolatile materials. They form lewis base adducts like [Ln(ACAC)$_3$.(Ph_3PO)] and [Ln(ACAC)$_3$.(phen)] (7- and 8-coordinate, respectively). Using bulkier alkyl groups (for example R^1 and R^2 = CMe_3) affords more congested diketonate complexes like [Ln(Me_3.CO.CH.CO.CMe_3)$_3$] that are more tractable, monomers in solution and sublime in vacuum at 100–200 ◦C. In the solid state, they are dimers for Ln = La to Dy (CN 7) and monomers for Dy to Lu (CN 6) and have trigonal prismatic coordination. They tend to hydrate readily, forming adducts [e.g. capped trigonal prismatic [Ln(DBM)$_3$(H_2O)]] [91-92].

Complexes of fluorinated diketones (R^1 =CF_3, R^2=CH_3; R^1 =R^2 =CF_3; R^1 = C_4H_3S, R^2 = CF_3; R^1 = $CF_3CF_2CF_2$, R^2 = CMe_3) are also important. Again, the initial complexes obtained in synthesis are hydrates that can be dehydrated in vacuo. 2-Thenoyltrifluoroacetone complexes [Ln(TTA)$_3$.2H_2O] are important in solvent extraction. Addition of phosphine oxides gives a synergistic improvement in extraction owing to the formation of phosphine oxide complexes.

1.8 Recent advances in separation of actinides from lanthanides

Immense efforts have been made recently to develop advanced separation methodologies in order to maximize fuel resources and reduce the impact of nuclear waste while providing a proliferation-resistant fuel cycle (i.e., no pure plutonium is isolated) [93-96]. This is a part of the "Partitioning and Transmutation" strategy, where it is proposed that all of the actinides in spent nuclear fuel (SNF), including the minor actinides, can be separated and recycled as nuclear fuel. An alternate option is to "burn" the separated actinides, which will also result in conversion to short-lived fission product nuclides but without nuclear energy production for public consumption. This provides the added benefit of converting most of the long lived actinides in SNF to shorter-lived fission product nuclides compared to current spent fuel management options. As a result, the "Partitioning and Transmutation" strategy can significantly reduce the time it takes for SNF to decay to radioactivity levels of natural uranium and therefore the necessary design lifetime of any nuclear waste repository [97-100].

One of the major separation challenges that need to be overcome for this strategy to be successful is the separation of americium and curium from the lanthanide fission products. This is because the high neutron absorption cross sections of some of the lanthanide ions present in SNF both decrease the flux in a reactor and create more activation products, thereby making transmutation a less attractive option if the lanthanides cannot be separated from the actinides [99]. Achieving this separation is extremely difficult because of the chemical similarities between americium, curium, and the lanthanides, which all most commonly exist in the 3+ oxidation state in solution [101]. Consequently, organic molecules that can selectively extract actinides, in particular Am^{3+} and Cm^{3+}, over the Ln^{3+} ions are of great interest, as is evident by the number of different ligand systems and processes that have been developed by various groups in the field of partitioning. [95, 97-101, 102-111]. Examples include the TALSPEAK (trivalent actinide lanthanide separation by phosphorus reagent extraction from aqueous complexes) process, which uses diethylene-triamine-pentaacetic acid in a lactic acid solution to hold back Am $^{3+}$ and Cm $^{3+}$ in the aqueous phase while the lanthanide ions are extracted into the organic phase containing di(2-ethylhexyl)phosphoric acid, and the TRUEX (trans uranic extraction) process, where the addition of N,N-diisobutyl carboylmethyl phosphine oxide to the organic phase in the core PUREX process allows Am $^{3+}$ and Cm $^{3+}$ to be extracted alongside $\{UO_2\}^{2+}$ and Pu^{4+}, leaving the lanthanide ions and other fission products in the aqueous phase [105-106].

The SANEX (selective actinide extraction) solvent extraction process aims to separate the americium and curium from the lanthanide fission products remaining after plutonium and uranium removal by PUREX and fission product separation (except the lanthanides) by DIAMEX (diamide extraction) using only carbon, hydrogen, oxygen, and nitrogen containing compounds as extractants, diluents, or phase modifiers. A class of molecules that showed early promise for the selective extraction of An^{3+} over Ln^{3+} in a SANEX process were the tridentate 2,6-bis(5,6-dialkyl-1,2,4- triazin-3-yl)pyridines (BTPs) [97,108]. However, many of these extractant molecules suffered problems that precluded them from use in plant-scale extractions including poor stability, slow extraction kinetics, and inefficient back-extraction due to high An^{3+} affinities. Further developments in the use of triazinyl-based N-donor extractants for actinide/lanthanide separations have led to the tetradentate ligand 6,6′-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2′-bipyridine (CyMe4-BTBP), which exhibits significant potential for use in SANEX separations, with separation factors for Am $^{3+}$ over Eu^{3+} found to be ∼150 [97,109-110]. The CyMe4-BTBP extractant has been successfully tested for the extraction of genuine actinide/lanthanide feed through a 16-stage centrifugal contactor setup with excellent recoveries for americium and curium (>99.9%) but has been shown to undergo radiolytic degradation at doses that will be encountered at the high minor actinide loadings obtained in the reprocessing of, for example, fast reactor fuels. The kinetics for actinides extraction with CyMe4-BTBP are still relatively slow, so the addition of a phase-transfer catalyst is necessary [e.g., N,N′-dimethyl-N,N′-dioctyl hexylethoxy malonamide (DMDOHEMA)] if this extractant is to be used for large scale partitioning [110-111]. In an attempt to improve the kinetics of extraction with these tetradentate N-donor extractants, greater conformational rigidity was enforced in the ligand backbone with the synthesis of 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline (CyMe4-BTPhen [112]. This rigid ligand displays very high separation factors for Am^{3+} over Eu^{3+} (up to 400), predominantly due to high Am^{3+} distribution ratios, with significantly faster kinetics of extraction compared to those found for CyMe4-BTBP, thereby eliminating the need for a phase-transfer catalyst. The high Am^{3+} distribution ratios even at low acidities for the aqueous phase may prove problematic during back-extractions, [97] but the use of alternative diluents has shown that efficient back-extractions may be achievable when using the CyMe4-BTPhen extractant [112]. An alternative concept being considered in Europe for the recovery of actinides from SNF is the GANEX (Group Actinide Extraction) process, which is proposed to consist of two cycles [107,113]. Most of the uranium is removed in the first cycle, while the second cycle recovers all of the remaining actinides, mainly the transuranics neptunium through curium, concurrently in varying oxidation states (III−VI) from the fission products found in spent fuel, including the lanthanides. The GANEX process is aimed for generation IV nuclear fuel cycles, where plutonium is likely to exist in higher concentrations during partitioning processes compared to those found in the processing of SNF in current cycles [113]. The major novelty with GANEX compared to most other more technologically mature separation processes is that the plutonium is routed with the minor actinides rather than with the majority of the uranium. The separation of Am $^{3+}$ and Cm $^{3+}$ from the lanthanide ions in a SANEX process is already considered extremely challenging, so performing the same separation in addition to partitioning neptunium, plutonium, and any remaining uranium from all of the fission products in the second stage of the GANEX process is even more difficult. A single extractant in the organic phase is unlikely to achieve the group separation of multiple actinides in variable oxidation states with appropriate efficiencies. Consequently, the performance of multiple extractants in the organic phase, typically already established from other separation processes, has been explored for use in a GANEX process [107, 113-114]. A number of different extractant combinations have been shown to have potential including N,N,N′,N′-tetra-octyl diglycolamide (TODGA; used in DIAMEX) with DMDOHEMA, TODGA with TBP, and CyMe4-BTBP with TBP [107, 113-114].

1.9 Materials and methods

1.9.1 Glassware

Glassware fitted with interchangeable standard ground joints were used. Special types of glassware with appropriate joints were used for synthesis and storage of compounds. Precipitates formed during the reaction were filtered through G-3 and G-2 sintered disks. All the glassware were immersed overnight in an alkali bath [5% NaOH in ethanol-water (1:1 v/v) mixture], washed thoroughly with water, rinsed with distilled water followed by acetone and dried at 120-130 ^{0}C overnight prior to experiment. Hot apparatus were kept in a desiccator containing fused $CaCl_2$ for cooling.

1.9.2 Solvents and Chemicals

All solvents used were of AR grade and dried by standard procedures [115] followed by distillation under inert atmosphere. Benzene (80 ^{0}C) and Toluene (110 ^{0}C) were dehydrated and purified by refluxing them with sodium metal pieces and benzophenone, followed by distillation in an inert atmosphere. Dichloromethane (40 ^{0}C) was dried over calcium chloride followed by decantation and distillation. Methanol (65 ^{0}C) was refluxed over magnesium methoxide (prepared from magnesium turnings and methanol in presence of catalytic amount of iodine) for 2 h and distilled under nitrogen atmosphere. The starting compounds $[UO_2(NO_3)_2.6H_2O]$ was prepared from U_3O_8 and , $[Th(NO_3)_4.9H_2O]$ and lanthanide nitrates were obtained from Indian Rare Earths Ltd, Mumbai.

1.10 Experimental and analytical techniques

1.10.1 Infrared Spectroscopy

The IR spectra were recorded as Nujol mulls between CsI (200-4000 cm^{-1})/KBr (400-400 cm^{-1}) plates on a Jasco (model FT-IR-6100) FT-IR spectrometer with a resolution of 4 cm^{-1}. The spectra were calibrated using a polystyrene film.

1.10.2 Nuclear magnetic spectroscopy

The ^{1}H, ^{13}C and ^{31} P NMR spectra were recorded on a Bruker 500 and 300MHz NMR spectrometer. Chemical shifts are reported in ppm from internal chloroform peak at δ

7.26 ppm for ^{1}H, δ 77.0 ppm for ^{13}C and external 85% H_3PO_4 for ^{31} P. unless otherwise stated, all the spectra were recorded at room temperature.

1.10.3 X-Ray Crystallography

The single crystal X-ray structure analysis of the synthesized compounds were carried out on an Oxford diffraction XcaliberS using Mo – Kα radiation. The crystals were directly mounted on diffractometer after examining the quality of the crystal under polarizing microscope. Sometimes crystals were cut to the desired size before mounting. All the crystals were mounted at ambient temperature. The crystals were positioned at 50 mm from the Image Plate. Three hundred and twenty-one frames were measured with a counting time of 10 s. Data analysis was carried out with the CRYSALIS program [116]. The structures were solved using direct methods with the SHELXS97 program [117]. All non-hydrogen atoms in these structures were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in the geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they attached. Empirical absorption corrections were carried out using the ABSPACK program [118]. The structures were refined to convergence on F^2 using SHELXL97 [119].

1.10.4 Thermogravimetry and Differential Thermal Analysis

The TG/DTA for the compounds was recorded on a Mettler TGA-851E instrument under the flow of an air. The samples were heated up to 800 °C at the rate of 10 °C min^{-1} in an alumina crucible in dynamic air with a flow rate of 50 ml min^{-1}. The thermoanalyzer was calibrated using the thermal decomposition of $CaC_2O_4 \cdot H_2O$ to CaO from 25°C to 1000 °C in air. All the weight changes were corrected for buoyancy corrections.

1.10.5 Total Reflection X-Ray Fluorescence analysis

Elemental compositions in some of the selected compounds and supernatant solutions were analyzed via an ITAL-TXRF instrument. An ITAL Structures TXRF spectrometer TX 2000 having Mo–W dual target X-ray tube was used for all TXRF measurements. The X-ray generator was operated at 50 kV and 10 mA. The W–C multilayer having a 2θ value of 49.4 A° was used to select the desired narrow energy part of the continuum of the tube spectrum (with an intensity maxima at around 30 keV) for efficient excitation. The desired energy band was selected by changing the incidence angle of the primary beam on the multilayer and the total reflection condition on the quartz sample support was obtained by adjusting the X-ray tube housing inclination in such a manner that the narrow energy band of X-rays from the multilayer fall at sample support at an angel less than the critical angel for the support. While doing this adjustment for TXRF conditions, the angle between multilayer and X-ray beam incident on it was kept constant in the earlier optimized position. All the necessary multilayer and tube inclination movements were done by motors controlled by TXRF32 program, provided with the instrument. The ful-filment of the TXRF condition was checked by measuring the intensity of characteristic X-ray line of a suitable single element standard (e.g. Ga) at different inclination values of tube housing. The tube housing inclination giving maximum intensity of the single element standard X-ray line indicates that the TXRF conditions are satisfied. This position is used for TXRF measurements. The X-rays were detected and measured using a Si(Li) detector having a resolution of 139 eV (FWHM) at Mn Kα (5.9 keV). For TXRF measurements, a life time of 1000 was used.

1.10.6 Electrospray ionization mass spectrometric analysis

ESI–MS detection of positive ions was recorded in CH_2Cl_2/CH_3OH/CH_3CN using a

Micromass-Q-TOFMICRO instrument. The sample was introduced into the source with a syringe pump. Nitrogen was employed as both the drying and spraying gas with a source temperature of 90^0C. The cone voltage was set to 30 V, the voltage applied on the capillary was 1162 kV and the sample solution flow rate was 5 mL min^{-1}. Spectrum was recorded from m/z of 100–1000.

1.11 Scope of the present work

The above discussion on the coordination chemistry of actinides and lanthanides clearly reflects that there are various active areas of research and their chemistry has many promising trends for further research. The coordination chemistry of actinides and lanthanides are evolving enormously in recent times. The selective separation of uranium-233 from the mixture of thorium and other fission products is an important step in the advanced water reactor (AHWR) technology of the Indian Atomic Energy programme and many new extractants have been studied for the selective recognition and separation of uranyl ion from various media in recent years. One of the major separation challenges that need to be overcome for reducing the lifetime of long lived fission products is the successful separation of americium and curium from the lanthanide fission products. This is because the high neutron absorption cross sections of some of the lanthanide ions present in spent nuclear fuel (SNF) both decrease the flux in a reactor and create more activation products, thereby making transmutation a less attractive option if the lanthanides cannot be separated from the actinides. Organic molecules that can selectively extract actinides, in particular Am^{3+} and Cm^{3+}, over the Ln^{3+} ions, from the SNF, are of great interest, as is evident by the number of different ligand systems and processes that have been developed by various groups in the field of partitioning.

With this view, new ligands containing both soft and hard donor groups were synthesized and their coordination chemistry with the lanthanides and actinides has been carried out. All the complexes prepared during present investigation have characterized by elemental analysis, IR, NMR (^{1}H, ^{13}C and ^{31}P) spectroscopy. Selected complexes whose crystals could be grown were structurally characterized by single crystal XRD. For clarity the present work is subdivided as follows:

a) Synthesis, coordination, structural and separation studies of *iso*-butyramide based ligands with uranyl ion.

b) Synthesis, structural and complexation studies of bis (N, N’-Di-alkyl carbomyl methyl) sulfide, sulfoxide and sulfone with uranyl and lanthanide ions.

c) Synthesis and structural studies of 1,1' bis(diphenylphosphino oxide) ferrocene-uranyl complexes.

1.12 References

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CHAPTER 2

Synthesis, coordination, structural and separation studies of iso-butyramide based ligands with uranyl ion

CHAPTER-2

2.1 Introduction

Actinide coordination chemistry is very important for the development of new technology concerning the safe processing and storage of irradiated nuclear fuel materials [1–3]. The selective separation of uranium-233 from the mixture of thorium and other fission products is an important step [4] in the advanced heavy water reactor (AHWR) technology [5] of the Indian atomic energy program, where upon the thorium oxide is used as a fuel material. In recent years, incinerable organic amide based extractants have proved to be of particular interest in the process chemistry of lanthanides and actinides from the nitric acid medium [6-12]. It is reported that the N,N'-2-ethylhexyl iso-butyramide shows selective extraction property for the uranium(VI) ion from a mixture containing thorium(IV) or plutonium(IV) ion [13-15]. The solvent extraction method needs many steps such as: extraction, stripping, precipitation and purification during the reprocessing of fuel materials. The neutral N-cyclohexyl-2-pyrrolidone ligand shows selective precipitation of uranium(VI) ion (up to 68%) from the mixture containing various other ions [16] and with this ligand only two steps are required namely precipitation and purification. It has also been reported recently that iso-butyramide based amide ligands show an excellent coordination property towards the uranyl group and form air and moisture stable halide and thiolato complexes [17-18]. The stability of these complexes was explained on the basis of very strong bonding between the amide and uranyl group. The observed bond distances in these complexes are much shorter in length compared to those of any of the uranyl-amide [19–21], uranyl-phosphine oxide [22-26] and uranyl-pyrrolidone [27-28] complexes reported. The strong complexing ability of the iso-butyramide based ligand promoted us to study their complexing behavior towards uranyl nitrate, thorium nitrate, lanthanum nitrate and uranyl bis(β-diketonate) to investigate whether it was feasible to use these ligands for separation purposes and the results of these studies are reported herein.

2.2 Experimental

2.2.1 General Considerations

All the amides [17] and uranyl bis(β- diketonates) were prepared according to the reported methods [29].

2.2.2 Synthesis of the Compounds

2.2.2.1 Synthesis of $[UO_2(NO_3)_2\{^iC_3H_7CON(^iC_3H_7)_2\}_2]$ *(compound* **1***)*

To a solution of $^iC_3H_7CON(^iC_3H_7)_2$ (450 mg, 2.6 mmol) in $CHCl_3$, solid $[UO_2(NO_3)_2.6H_2O]$ (502 mg, 1.0 mmol) was added and stirred for few minutes until all $[UO_2(NO_3)_2.6H_2O]$ dissolves to give a clear solution. This solution was filtered and layered with iso-octane. The solution on slow evaporation deposited a yellow crystalline solid, which was filtered, washed with hexane and dried. Yield: 700 mg (95%).Elemental Analysis Calculated for $[UO_2(NO_3)_2(^iC_3H_7CON\{^iC_3H_7\}_2)_2]$, $C_{20}H_{42}N_4O_{10}U$ (%): Expected: C=32.6; H=5.7; N=7.6. Found: C= 32.3; H=5.5; N= 7.5. IR (Nujol, ν/cm^{-1}) : 1570 (CO), 930 (O=U=O). ^1H NMR (25 °C, $CDCl_3$, δ in ppm): 1.40 (d, 7 Hz, 12H, CH_3, $N^iC_3H_7$), 1.57 (d,7 Hz, 6H, CH_3, $^iC_3H_7$), 3.29 (br, 1H, CH, $^iC_3H_7$), 4.26 (br, 2H, CH, $N^iC_3H_7$).

2.2.2.2 Synthesis of $[UO_2(NO_3)_2\{^iC_3H_7CON(C_4H_9)_2\}_2]$ *(compound* **2***)*

Compound **2** was prepared in a similar way as compound **1** by taking $^iC_3H_7CON(C_4H_9)_2$ (460 mg, 2.31 mmol) and $[UO_2(NO_3)_2.6H_2O]$ (450 mg, 0.89 mmol). Yield: 730 mg

(92%). Elemental Analysis Calculated for $[UO_2(NO_3)_2\{^iC_3H_7CON(C_4H_9)_2\}_2]$, $C_{24}H_{50}N_4O_{10}U$ (%): Expected: C=36.4; H=6.3; N=7.1. Found: C=36.1; H=6.1; N=7.0. IR (Nujol mull, ν/cm^{-1}): 1571 (CO), 932 (O=U=O). ^{1}H NMR (25 °C, $CDCl_3$, δ in ppm): 0.67 (t, 7 Hz, 3H, CH_3, NC_4H_9), 0.97 (m, 2H, CH_2, NC_4H_9), 1.07 (t, 7 Hz, 3H, CH_3, NC_4H_9), 1.43 (d, 6H, CH_3, $^iC_3H_7$), 1.53 (m, 2H, CH_2, NC_4H_9), 1.67 (m, 2H, CH_2, NC_4H_9), 1.86 (m, 2H, CH_2, NC_4H_9), 3.25 (br, 1H, CH, $^iC_3H_7$), 3.63 (m, 4H, NCH_2, NC_4H_9).

*2.2.2.3 Synthesis of $[UO_2(NO_3)_2\{^iC_3H_7CON(^iC_4H_9)_2\}_2]$ (compound **3**)*

Compound **3** was prepared similarly as compound **1** by taking $^iC_3H_7CON(^iC_4H_9)_2$ (454 mg, 2.28 mmol) and $[UO_2(NO_3)_2.6H_2O]$ (502 mg, 1.0 mmol). Yield: 725 mg (91.5%). Elemental Analysis Calculated for $[UO_2(NO_3)_2\{^iC_3H_7\text{-}CON(^iC_4H_9)_2\}_2]$, $C_{24}H_{50}N_4O_{10}$ U (%): Expected: C=36.4; H=6.3; N=7.1. Found: C=36.3; H=6.2; N=7.0. IR (Nujol mull, ν/cm^{-1}): 1571 (CO), 931 (O=U=O). ^{1}H NMR (25 °C, $CDCl_3$, δ in ppm): 0.73 (d, 7 Hz, 6H, CH_3, $N^iC_4H_9$), 1.29 (d, 7 Hz, 6H, CH_3, $N^iC_4H_9$), 1.43 (d, 7 Hz, 6H, CH_3,$^iC_3H_7$), 2.23 (m, 2H, CH, $N^iC_4H_9$), 3.34 (br, 1H, CH, $^iC_3H_7$), 3.5 (m, 4H, CH_2, $N^iC_4H_9$).

*2.2.2.4 Synthesis of $[UO_2(C_4H_3SCOCHCOCF_3)_2\{^iC_3H_7CON(^iC_3H_7)_2\}]$ (compound **4**)*

To a chloroform solution of $[UO_2(C_4H_3SCOCHCOCF_3)_2.2H_2O]$ (500 mg, 0.66 mmol), $^iC_3H_7CON(^iC_3H_7)_2$ (120 mg, 0.70 mmol) was added and refluxed for 30 min. The resultant solution was filtered and layered with iso-octane. The solution on slow evaporation yielded an orange colored product. This was filtered, washed with hexane and dried. Yield: 550 mg (93%). Elemental Analysis Calculated for $[UO_2(C_4H_3SCOCHCOCF_3)_2\{^iC_3H_7CON(^iC_3H_7)_2\}]$, $C_{26}H_{29}NO_7S_2F_6U$ (%): Expected: C=35.3; H=3.3; N=1.6. Found: C=35.0; H=3.5%; N=1.2. IR (Nujol, ν/cm^{-1}):1565 (CO,

${}^{i}C_3H_7CON({}^{i}C_3H_7)_2$), 1600–1630 (CO, $C_4H_3SCOCH\text{-}COCF_3$), 919 (O=U=O). ${}^{1}H$ NMR (25 °C, $CDCl_3$, δ in ppm): 1.43 (br, CH_3, $N{}^{i}C_3H_7$), 1.56 (br, CH_3, ${}^{i}C_3H_7$), 3.32 (br, CH, ${}^{i}C_3H_7$), 4.36 (br, NCH, $N{}^{i}C_3H_7$), 6.77, 6.81 (s, CH, $C_4H_3SCOCHCOCF_3$), 7.17–7.33, 7.77– 7.85, 8.25–8.30 (m, C_4H_3S, $C_4H_3SCOCHCOCF_3$).

2.2.2.5 Synthesis of $[UO_2(C_4H_3SCOCHCOCF_3)_2\{{}^{i}C_3H_7CON({}^{i}C_4H_9)_2\}]$(compound **5***)*

Compound **5** was prepared similarly as compound **4** by taking $[UO_2(C_4H_3SCOCHCOCF_3)_2 . 2H_2O]$ (500 mg, 0.66 mmol) and ${}^{i}C_3H_7CON({}^{i}C_4H_9)_2$ (140 mg, 0.70 mmol). Yield: 580 mg (95%). Elemental Analysis Calculated for $[UO_2(C_4H_3SCOCHCOCF_3)_2\{{}^{i}C_3H_7CON({}^{i}C_4H_9)_2\}]$, $C_{28}H_{33}NO_7S_2F_6U$: Expected (%): C=36.9; H=3.6; N=1.5. Found: C=36.7; H=3.4; N=1.1. IR (Nujol, ν/cm^{-1}): 1571 (CO, ${}^{i}C_3H_7CON({}^{i}C_4H_9)_2$), 1600– 1630 (CO, $C_4H_3SCOCHCO\ CF_3$), 916 (O=U=O). ${}^{1}H$ NMR (25 °C, $CDCl_3$, δ in ppm): 0. 72 (d, CH_3, $N{}^{i}C_4H_9$), 1.17 (d, CH_3, $N{}^{i}C_4H_9$), 1.47 (d, CH_3, ${}^{i}C_3H_7$), 2.24 (m, CH, $N{}^{i}C_4H_9$), 3.34 (br, CH, ${}^{i}C_3H_7$), 3.5–3.6 (m, NCH_2, $N{}^{i}C_4H_9$), 6.77, 6.82 (s, CH, $C_4H_3SCOCHCOCF_3$), 7.33, 7.50– 7.85, 8.25–8.29 (m, $C_4H_3SC_4H_3SCOCHCO\ CF_3$).

2.2.2.6 Synthesis of $[UO_2(C_6H_5COCHCOCF_3)_2\{{}^{i}C_3H_7CON({}^{i}C_3H_7)_2\}]$ (compound **6***)*

Compound **6** was prepared similarly as compound **4** by taking $[UO_2(C_6H_5COCHCOCF_3)_2 .2H_2O]$ (450 mg, 0.611 mmol) and ${}^{i}C_3H_7CON({}^{i}C_3H_7)_2$ (110 mg, 0.64 mmol).Yield: 490 mg (92%). Elemental Analysis Calculated for $[UO_2(C_6H_5COCHCOCF_3)_2\ \{{}^{i}C_3H_7CON({}^{i}C_3H_7)_2\}]$, $C_{30}H_{33}NO_7F_6U$ (%): Expected: C=41.3; H=3.8; N=1.6. Found: C=41.0; H=3.5; N=1.2. IR (Nujol, ν/cm^{-1}) : 1565 (CO, ${}^{i}C_3H_7CON({}^{i}C_3H_7)_2$), 1604–1630 (CO, $C_6H_5COCHCOCF_3$), 918 (O=U=O).${}^{1}H$ NMR (25 °C, $CDCl_3$, δ in ppm): 1.34 (br, CH_3, $N{}^{i}C_3H_7$), 1.64 (br, CH_3, ${}^{i}C_3H_7$), 3.32 (br, CH,

$^iC_3H_7$), 4.36 (br, NCH, N$^iC_3H_7$), 6.98, 7.01 (s, CH, C_6H_5COCH-$COCF_3$), 7.60–7.72, 8.57–8.37 (m, C_6H_5, $C_6H_5COCHCOCF_3$).

2.2.2.7 Synthesis of [$UO_2(C_6H_5COCHCOCF_3)_2\{^iC_3H_7CON(^iC_4H_9)_2\}$] (compound **7***)*

Compound **7** was prepared similarly as compound **4** by taking [UO_2-($C_6H_5COCHCOCF_3)_2$.$2H_2O$] (450 mg, 0.61 mmol) and $^iC_3H_7$-$CON(^iC_4H_9)_2$ (125 mg, 0.63 mmol). Yield: 505 mg (92%). Elemental Analysis Calculated for [$UO_2(C_6H_5COCHCOCF_3)_2\{^iC_3H_7CON(^iC_4H_9)_2\}$], $C_{32}H_{37}NO_7F_6U$ (%): Expected: C=42.7; H=4.1; N=1.6. Found: C=42.5; H=4.4; N, 1.4. IR (Nujol, ν/cm^{-1}): 1570 (CO, $^iC_3H_7CON(^iC_4H_9)_2$), 1603– 1630 (CO, $C_6H_5COCHCOCF_3$), 915 (O=U=O). ^1H NMR (25 °C, $CDCl_3$, δ in ppm): 0.74 (d, CH_3, N$^iC_4H_9$), 1.18 (d, CH_3, N$^iC_4H_9$), 1.50 (d, CH_3, $^iC_3H_7$), 2.25 (m, CH, N$^iC_4H_9$), 3.38 (br, CH, $^iC_3H_7$), 3.5–3.7 (m, NCH_2, N$^iC_4H_9$), 6.99 (s, CH, $C_6H_5COCHCOCF_3$), 7.59–7.77, 8.57– 8.60 (m, C_6H_5, $C_6H_5COCHCOCF_3$).

2.2.2.8 Synthesis of [$UO_2(C_6H_5COCHCOC_6H_5)_2\{^iC_3H_7CON(^iC_3H_7)_2\}$] (compound **8***)*

Compound **8** was prepared in a similar way as compound **4** by taking [$UO_2(C_6H_5COCHCOC_6H_5)_2$.$2H_2O$] (400 mg, 0.532 mmol) and $^iC_3H_7$-$CON(^iC_3H_7)_2$ (95 mg, 0.55 mmol). Yield: 440 mg (93%). Elemental Analysis Calculated for [$UO_2(C_6H_5COCHCOC_6H_5)_2\{^iC_3H_7CON(^iC_3H_7)_2\}$], $C_{40}H_{43}NO_7U$ (%): Expected: C=54.1; H=4.8; N=1.6. Found: C=54.0; H=4.6; N=1.4.IR (Nujol, ν/cm^{-1}) : 1591 (CO, $C_6H_5COCHCOC_6H_5$), 1572 (CO, $^iC_3H_7CON(^iC_3H_7)_2$), 921 (O=U=O). ^1H NMR (25 °C, $CDCl_3$, δ in ppm): 1.38 (br, CH_3, N$^iC_3H_7$), 1.56 (br, CH_3, $^iC_3H_7$), 3.27 (br, CH, $^iC_3H_7$), 4.35 (br, NCH, N$^iC_3H_7$), 7.40 (s, CH, $C_6H_5COCHCOC_6H_5$), 7.50–7.7, 8.42–8.60 (m, C_6H_5, $C_6H_5COCHCOC_6H_5$).

2.2.2.9 Synthesis of $[UO_2(C_6H_5COCHCOC_6H_5)_2\{{}^iC_3H_7CON({}^iC_4H_9)_2\}]$ (compound ***9****)*

Compound **9** was prepared similarly as **4** by taking $[UO_2(C_6H_5COCHCOC_6H_5)_2 .2H_2O]$ (400 mg, 0.532 mmol) and ${}^iC_3H_7$-$CON({}^iC_3H_7)_2$ (110 mg, 0.55 mmol). Yield: 420 mg (86%). Elemental Analysis Calculated for $[UO_2(C_6H_5COCHCOC_6F_5)_2\{{}^iC_3H_7CON({}^iC_3H_7)_2\}]$, $C_{40}H_{43}NO_7U$ (%): Expected: C=54.1; H=4.8; N=1.6. Found: C=54.0; H=4.6; N=1.4. IR (Nujol, ν/cm^{-1}): 1580 (CO, ${}^iC_3H_7CON({}^iC_3H_7)_2$), 1591 (CO, $C_6H_5COCHCOC_6H_5$), 922 (O=U=O).${}^1H$ NMR (25 °C, $CDCl_3$, δ in ppm): 0. 72 (d, CH_3, $N^iC_4H_9$), 1.32 (d, CH_3, $N^iC_4H_9$), 1.45 (d, CH_3, ${}^iC_3H_7$), 2.22 (m, CH, $N^iC_4H_9$), 3.32 (br, CH, ${}^iC_3H_7$), 3.4–3.6 (m, NCH_2, $N^iC_4H_9$), 7.41 (s, CH, $C_6H_5COCHCOC_6H_5$), 7.52–7.7, 8.40–8.60 (m, C_6H_5, $C_6H_5COCHCOC_6H_5$).

2.2.3 Reaction of N, N-di-isobutyl butyramide with $[Th(NO_3)_4 .6H_2O]$

To a solution of ${}^iC_3H_7CON({}^iC_4H_9)_2$ (500 mg, 2.5 mmol) in $CHCl_3$, solid $[Th(NO_3)_4 .6H_2O]$ (600 mg, 1.02 mmol) was added and stirred for 12 h. No reaction between the amide and $[Th(NO_3)_4 .6H_2O]$ was observed due to the presence of an insoluble starting material. Ten millilitres of methanol was added to the solution and stirred for another 6 h. The clear solution was evaporated to dryness and the hygroscopic material was subjected to IR spectral analysis. IR (Nujol, ν/cm^{-1}): 1640 (CO), 3600–3200 (br, H_2O).

2.2.4 Reaction of N, N-di-isobutyl butyramide with $[La(NO_3)_3 .6H_2O]$

This reaction was performed similarly as above by taking the amide (650 mg, 3.27 mmol) and $[La(NO_3)_3 .6H_2O]$ (450 mg, 1.03 mmol). The resultant hygroscopic material was subjected to the IR spectral studies. IR (Nujol, ν/cm^{-1}): 1639 (CO), 3600–3200 (br, H_2O).

2.2.5 Solvent extraction studies

Distribution studies were performed by using a solution of N, N-di-isobutyl butyramide in toluene (0.2 M) with the required aqueous phase spiked with ^{233}U or ^{239}Pu tracers in a thermostat water bath for 1 h at 25 ± 0.1 °C. Assay of organic and aqueous phases were done in duplicate by alpha counting using a dioxane based liquid scintillator for ^{233}U and ^{239}Pu. The distribution ratio (D) is defined as the ratio of the concentration of uranium in the organic phase to that of the aqueous phase.

2.2.6 Separation studies

Stock solutions containing 5g of [$Th(NO_3)_4 . 6H_2O$], 300 mg of [$La(NO_3)_3 .6H_2O$] and 500 mg of [$UO_2(NO_3)_2 .6H_2O$] were prepared in 10 ml of 1, 2, 3 and 6 M HNO_3. This solution was layered with 1 g of N, N-di-isobutyl butyramide and allowed to stand for overnight. This process deposited yellow crystalline solid material (Fig. 2.1), which was filtered, washed with water and then with hexane and dried. The supernatants and the solutions of yellow solid in ethanol were used for the elemental analysis using the total reflection X-ray fluorescence (TXRF) method.

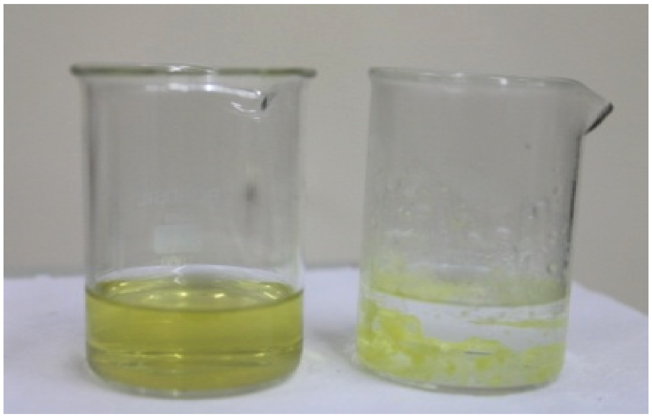

Fig.2.1 Stock solution of La, Th and U layered without and with the ligand

2.2.7 X-ray diffraction studies of compounds 3 and 8.

Selected crystallographic data for compounds **3** and **8** are summarized in Table 2.1

Table 2.1 Crystallographic data for compounds **3** and **8**

	3	**8**
Empirical formula	$C_{24}H_{50}N_4O_{10}U$	$C_{40}H_{43}NO_7U$
Formula weight	792.71	933.85
Crystal system	triclinic	orthorhombic
Space group	P1	Pbca
a (Å)	9.4263(13)	16.2338(7)
b (Å)	9.5422(13)	20.988(4)
c(Å)	10.1230(11)	23.5467(16)
a (°)	75.567(10)	90
b (°)	81.956(10)	90
c(°)	69.296(13)	90
Volume (Å^3)	823.51(18)	8022.8(17)
Z (formula unit)	1	8
Calculated density (g/cm^3)	1.598	1.546
Reflections collected/unique	5695/4591	41448/11 663
Final R_1 indices [$I > 2\sigma(I)$]	0.0750	0.0509
wR_2 indices (all data)	0.1883	0.1544

$w = 1/[\sigma^2(F_o^2) + (0.1579P)^2 + 0.000P]$ for **3**, $w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 0.000P]$ for **8** where $P = (F_o^2 + 2F_c^2)/3$

2.3 Results and discussion

2.3.1 Complexation study of iso-butyramide ligands with the uranyl nitrate.

The complexing ability of $^{i}C_3H_7CON(^{i}C_3H_7)_2$, $^{i}C_3H_7CON(C_4H_9)_2$ and $^{i}C_3H_7CON(iC_4H_9)_2$ with uranyl nitrate was studied by using elemental analysis, IR and NMR spectroscopic techniques. The reaction of $[UO_2(NO_3)_2 .6H_2O]$ with the iso-butyramide ligands yielded the compounds **1** to **3**. The C, H and N analysis revealed that the ratio of ligand to uranyl nitrate is 2:1 in all these compounds.

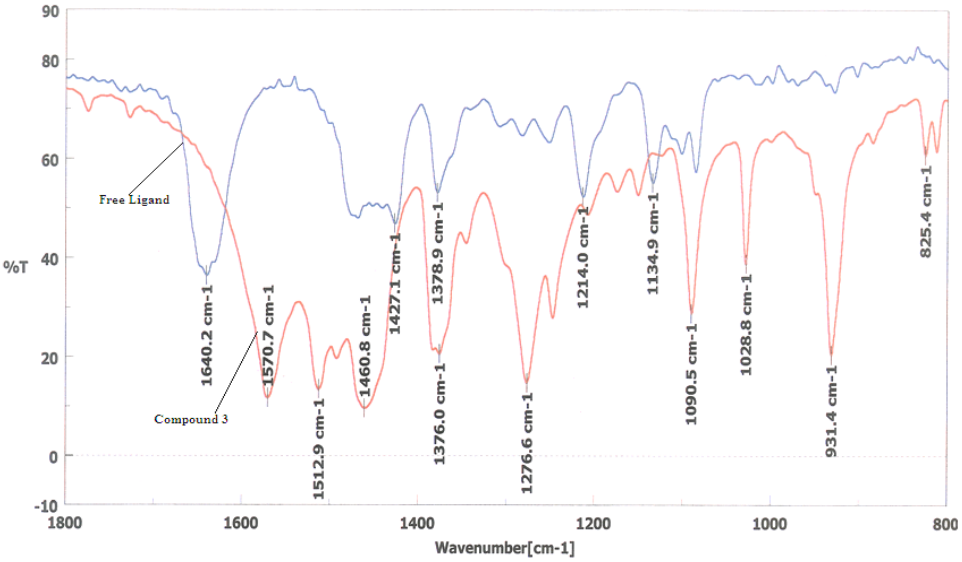

Fig. 2.2 IR spectra of the free ligand and compound **3**

The IR spectra of the compounds **1–3** show that the water molecules from the starting compound $[UO_2(NO_3)_2 . 6H_2O]$ are completely replaced by the ligand and that the ligand is bonded through the carbamoyl oxygen atom to the uranyl group (Fig. 2.2). The observed frequency differences for a carbamoyl ($\Delta\nu_{(CO)}$ = 68–70 cm^{-1}, where $\Delta\nu_{(CO)} = \nu_{(CO)}$ (free ligand) - $\nu_{(CO)}$ (coordinated) group are consistent with the supposition that the carbamoyl group is bonded to the uranyl group directly in the reported compounds.

These differences are comparable in magnitude with those of the $[UO_2Cl_2({}^{i}C_3H_7CON\{{}^{i}C_3H_7\}_2)_2]$, $[UO_2Br_2({}^{i}C_3H_7CON\{{}^{sec}C_4H_9\}_2)_2]$ [17], $[UO_2(C_6H_3Cl_2S)_2\ ({}^{i}C_3H_7CON\{{}^{i}C_4H_9\}_2)_2]$ [18], $[UO_2(NO_3)_2$(N-cyclohexyl,2-pyrrolidone$)_2]$ [27] and $[UO_2(NO_3)_2$ (1,3-dimethyl,2-imidazolidone$)_2]$ [28] complexes and much higher in magnitude compared to those observed in other amides or malonamides uranyl complexes [6-12,30].

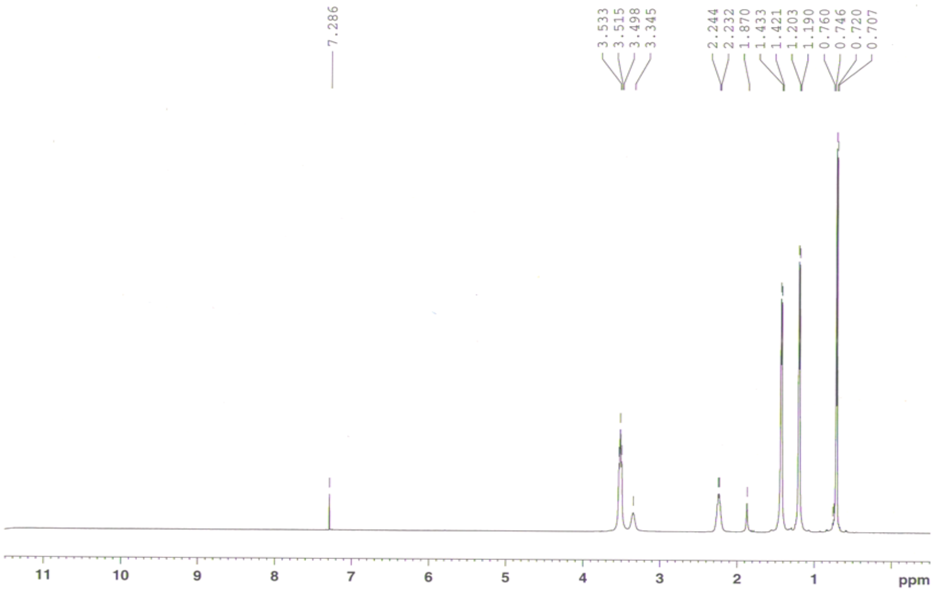

Fig. 2.3 ^{1}HNMR Spectra of compound **3**

The ^{1}H NMR spectra of the compounds **1–3** show that the CH proton of the iso-propyl group is deshielded by ca. 0.5–0.6 ppm with respect to the free ligand (Fig 2.3.), indicating that the ligand is coordinated to the uranyl group in solution also. It is apparent from the elemental analysis and IR spectral results that ligands are acting as monodentate ligand in compounds **1–3** in the solid state to give similar structures to those observed in the compounds of pyrrolidone [27,28] or other monodentate amides [19–21] with the uranyl nitrate. Interestingly, all these complexes are air and moisture stable crystalline solids, having good solubility in $CHCl_3$ and CH_2Cl_2, and can be used as a starting compound for further reactions. The structure of **3** has been determined by single crystal X-ray diffraction methods, which confirms the IR and elemental analysis results.

2.3.2 Molecular structure of compound 3

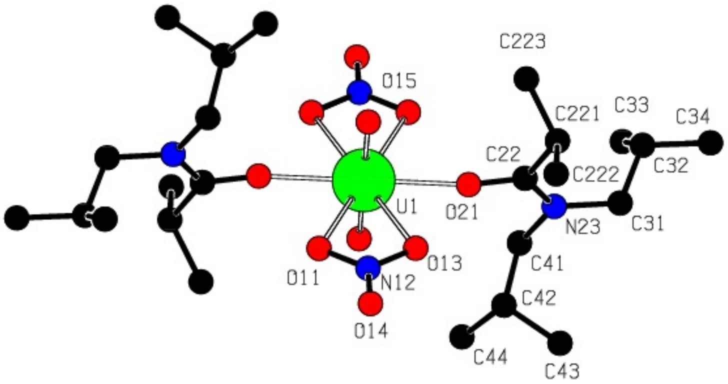

Fig. 2.4 Molecular structure of compound **3** (hydrogen atoms omitted for the clarity)

The molecular structure of the compound **3** is shown in Fig.2.4 and the selected interatomic bond distances and angles for are given in Table 2.2. The structure contains a crystallographic center of symmetry with the uranium atom surrounded by eight oxygen atoms in a hexagonal bi-pyramidal geometry. Two uranyl oxygen atoms occupy the axial positions. There are two bidentate nitrate ligands in the hexagonal equatorial plane together with two carbamoyl oxygen atoms from the two monodentate iso-butyramide ligands. These six oxygen atoms are approximately coplanar to within an r.m.s. of 0.042 Å.

This type of co-ordination is similar to that observed in the compounds of the mono-functional ligands, phosphine oxide, phosphates and amides or pyrrolidones with uranyl nitrate such as: $[UO_2(NO_3)_2(OPPh_3)_2]$ [22], $[UO_2(NO_3)_2(OP\{OEt\}_3)_2]$ [23], $[UO_2(NO_3)_2(OPBu_3)_2]$ [24], $[UO_2(NO_3)_2(TPPPO)_2]$ [25], $[UO_2(NO_3)_2(OP\{OCH_3\}_3)_2]$ [26], $[UO_2(NO_3)_2(DMF)_2]$ [19], $[UO_2(NO_3)_2$(N-cyclohexyl,2-pyrrolidone)$_2]$ [27] and $[UO_2(NO_3)_2$(1,3,dimethyl, 2-imidazo lidone)$_2]$ [28]. The U–O(amide) distance (2.349(1) Å) in 3 is much shorter in length compared to those of earlier reported uranyl nitrate–amide compounds such as: $[UO_2(NO_3)(DMF)_2]$ (2.397(6) Å) [19], $[UO_2(NO_3)_2$(tetrabutylglutaramide)$_2]$ (2.378(6) Å) [20], $[UO_2$ $(NO_3)_2$(dibutyl decanamide)$_2]$ (2.37(2) Å) [21] and $[UO_2(NO_3)_2$ $(^iC_3H_7)_2NCOCH_2$ CON $(^iC_3H_7)_2]$ (2.41(2) Å) [30] and comparable in magnitude with those of $[UO_2(NO_3)_2$(N-cyclohexyl,2-pyrrolidone)$_2]$ (2.347(4) Å) [27] and $[UO_2(NO_3)_2(OPBu_3)_2]$ (2.347(6) Å) [24]. The observed average U–O (NO_3) bond distance 2.531(1) Å is normal [19–28]. The angles subtended at the metal atom show that the uranium atom has a slightly distorted hexagonal bi-pyramidal geometry.

The shorter bond lengths observed in this compound can be explained on the basis of a strong p bonding interaction between the filled ‘p’ orbitals of oxygen atom with those of the vacant d/f orbitals of the uranyl group, which lead to the opening of the U–O–C bond angle from 130° to 140° (normally observed in number of metal– amide compounds [31]) to 171.2(6)°. The observed bond lengths and the U–O–C bond angles are compatible with the earlier reported correlation diagram for the uranyl nitrate–amide compounds [28]. In particular, the characteristic of shorter bond distances and wider bond angles are reported for the iso-butyramide based ligands in the compounds of $[Th(NCS)_4(^iC_3H_7CO\text{-}N\{^iC_3H_7\}_2)_3]$ [32], $[UO_2Cl_2(^iC_3H_7CON\{^iC_3H_7\}_2)_2]$, $[UO_2Br_2(^iC_3H_7CON\{^{sec}C_4H_9\}_2)_2]$ [17] and $[UO_2(C_6H_3Cl_2S)_2$ $(^iC_3H_7CON\{^iC_4H_9\}_2)_2]$ [18].

Table 2.2 Important bond distances (Å) and angles (°) for the compound **3**

U1–O11	2.527(7)	U1–O13	2.535(8)
U1–O15	1.756(6)	U1–O21	2.349(6)
N12–O11	1.264(11)	N12–O13	1.276(11)
N12–O14	1.229(12)	C22–O21	1.264(9)
O11–U1–O13	50.4(2)	O11–U1–O15	90.1(3)
O11–U1–O21	114.9(2)	O13–U1–O15	88.3(3)
O13–U1–O21	64.6(2)	O15–U1–O21	91.4(3)
U1–O21–C22	171.2(6)		

2.3.3 Complexation study of iso-butyramide with the uranyl bis(β-diketonates)

The reaction of ${}^{i}C_3H_7CON({}^{i}C_3H_7)_2$ and ${}^{i}C_3H_7CON({}^{i}C_4H_9)_2$ with $[UO_2(OO)_2 .2H_2O]$ (OO = TTA, BTA or DBM) yielded the compounds **4** to **9**. The C, H, N analyses revealed that the ratio of ligand to metal is 1:1 in all these compounds. The IR spectra of all these compounds show that the water molecules from the starting compounds $[UO_2(OO)_2 .2H_2O]$ are replaced completely by the ligands (Fig. 2.5). The spectra show further that the ligands are bonded through the carbamoyl oxygen atoms to the metal ion ($\Delta\nu_{(CO)}$ = 70–77 cm^{-1}, where $\Delta\nu_{(CO)} = \nu_{(CO)}$ (free ligand) - $\nu_{(CO)}$ (coordinated). The ^{1}H NMR of the compounds (Fig.2.6) show that CH protons of the iso-propyl group is deshielded (ca. 0.5–0.6 ppm) with respect to the free ligand, indicating that the ligand is bonded to the uranyl bis(β-diketonate) in solution also.

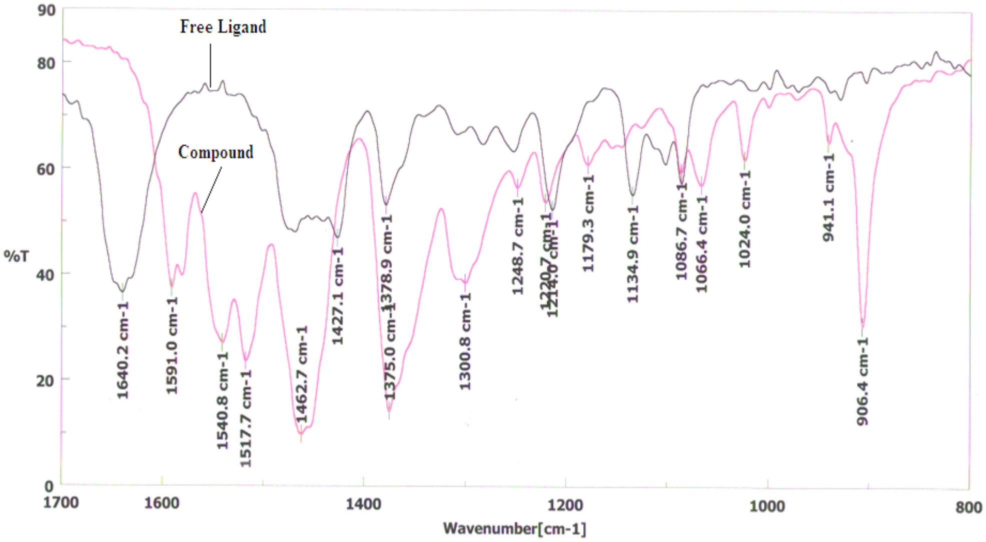

Fig.2.5 IR spectra of free ligand and the compound **8**

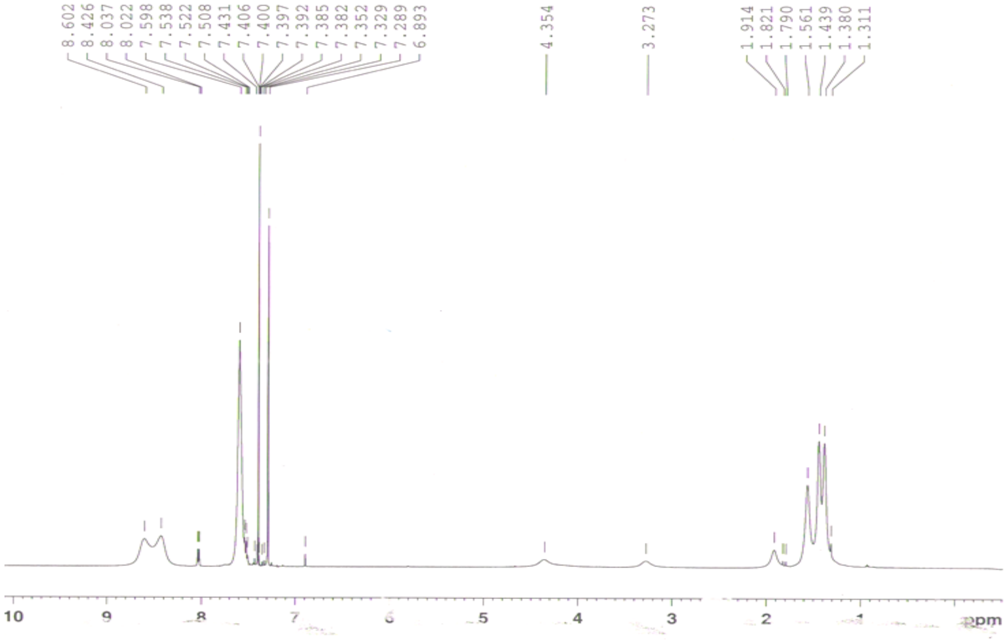

Fig.2. 6 ^{1}HNMR Spectra of compound **8**

The structure of compound $[UO_2(C_6H_5COCHCOC_6H_5)_2\{^iC_3H_7CON(^iC_3H_7)_2\}]$ has been determined by single crystal X-ray diffraction methods, which confirms the spectral and analyses results.

2.3.4 Molecular structure of compound **8**

The molecular structure of the compound **8** is shown in Fig.2.7 together with the numbering scheme and selected interatomic bond distances and angles are given in Table 2.3. There is a disordered toluene molecule refined with 50% occupancy in the asymmetric unit which is not shown. The structure shows that the uranyl group is bonded to two $C_6H_5COCHCOC_6H_5$ groups and an amide group to give a coordination number of seven. The amide ligand acts as a monodentate ligand and is bonded through the carbamoyl oxygen atoms to the uranyl bis(β -diketonates). Four oxygen atoms from two $C_6H_5COCHCOC_6H_5$ groups, one oxygen atom from the amide ligand and two oxygen atoms of uranyl group form a pentagonal bi-pyramidal geometry around the uranium(VI) ion.

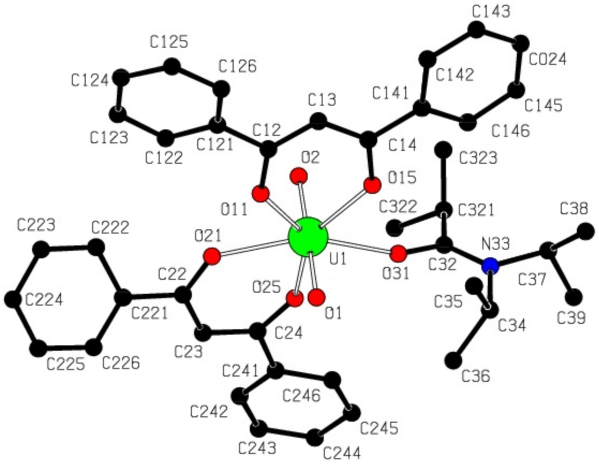

Fig.2.7 The molecular structure of compound **8** (hydrogen atoms omitted for the clarity)

Table 2.3 Important bond distances (Å) and angles (°) for compound **8**

U1–O1	1.770(5)	U1–O2	1.776(5)
U1–O11	2.361(5)	U1–O15	2.352(5)
U1–O21	2.359(5)	U1–O25	2.333(5)
U1–O31	2.379(5)	O31–C32	1.273(8)
O1–U1–O2	179.0(2)	O1–U1–O11	88.6(2)
O1–U1–O15	92.8(2)	O1–U1–O21	90.4(2)
O1–U1–O25	86.7(2)	O1–U1–O31	89.3(2)
U1–O31–C32	159.8(5)		

The five contributing oxygen atoms in the equatorial plane show an r.m.s. deviation of 0.062 Å. Similar structures are also observed in the compounds of phosphine oxide, sulfoxide, N-oxide, ketones and amides with the uranyl bis(β-diketonates) viz; $[UO_2(DBM)_2(OPPh_3)]$ [33], $[UO_2(DBM)_2(C_6H_5SOCH_3)]$ [34], $[UO_2(TTA)_2(C_5H_5NO)]$ [35], $[UO_2(DBM)_2$ (camphor)] [36] and $[UO_2(DBM)_2\{C_4H_9CON(C_5H_{11})(C_4H_9)\}]$ [37]. The observed metal to amide oxygen distance in compound **8** (2.379(5) Å) is shorter in length compared to those value reported in $[UO_2(DBM)_2\{C_4H_9CON(C_5H_{11})(C_4H_9)\}]$ (2.42 Å) [37]. The shortest bond distance observed in compound **8** compared to those observed in $[UO_2(DBM)_2\ \{C_4H_9CON(C_5H_{11})(C_4H_9)\}]$ can be explained once again on the basis of strong interaction between the amide oxygen and uranyl group, which results in opening of U–O–C bond angle to 159.8(5)°. The longer bond distances in **8** compared to those in the compound **3** can be explained on the basis of a bulkier phenyl group of the β-diketonate units, which may not allow the donor group to come closer to uranyl group compared to those of the less bulky nitrate groups.

2.3.5 Complexation study of $^{i}C_3H_7CON(^{i}C_4H_9)_2$ *with* $[Th(NO_3)_4 .6H_2O]$ *and* $[La(NO_3)_3\ 6H_2O]$

The IR spectra of the product obtained from the reaction between $^{i}C_3H_7CON(^{i}C_4H_9)_2$ and $[Th(NO_3)_4 .6H_2O]$ or $[La(NO_3)_3.6H_2O]$ show the presence of an uncoordinated carbonyl group (1639 cm^{-1}) and water molecules (3600–3200 cm^{-1}). This shows clearly that there is no reaction between the amide ligand and metal nitrates. However, the uranyl nitrate forms a strong complex with the same amide under identical conditions.

2.3.6 Thermal studies of the compound **3**

Thermogravimetric (TG), Differential Thermogravimetry (DTG) and differential thermal analyses (DTA) of the compound **3** (Fig.2.8) were carried out to see whether the bonded ligands can be destroyed completely on heating. These compounds decompose in two steps to give U_3O_8 as a final product without any other impurities as revealed by the powder X-ray diffraction methods.

2.3.7 Extraction studies of U(VI) and Pu(IV) with $^{i}C_3H_7CON(^{i}C_4H_9)_2$ *from nitric acid*

The extraction studies were carried out by using the ligand $^{i}C_3H_7CON(^{i}C_4H_9)_2$ in toluene with the U(VI) and Pu(IV) ions in tracer level (using the ^{233}U and ^{239}Pu) from nitric acid medium to assess the feasibility of using this ligand (0.2 M for both the U(VI) and Pu(IV)) for the extraction purpose. Distribution ratios (D) for U(VI) and Pu(IV) as a function of nitric acid concentrations (Fig.2.9) shows clearly that observed distribution values are very low for both the U(VI) and Pu(IV) under the acid concentrations of 1–10 M. However, under any acid concentration, the D for Pu(IV) is much smaller than those of U(VI). This observation is completely contradictory to the data reported for any of the extractants (either mono-functional or bi-functional) with that of Pu(IV) ($D_{Pu(IV)}$ >>

$D_{U(IV)}$ always) [6-9] and agrees well with the result reported for the iso-butyramide based extractant [13-15]. This shows clearly that the uranium can be selectively separated from plutonium or vice versa.

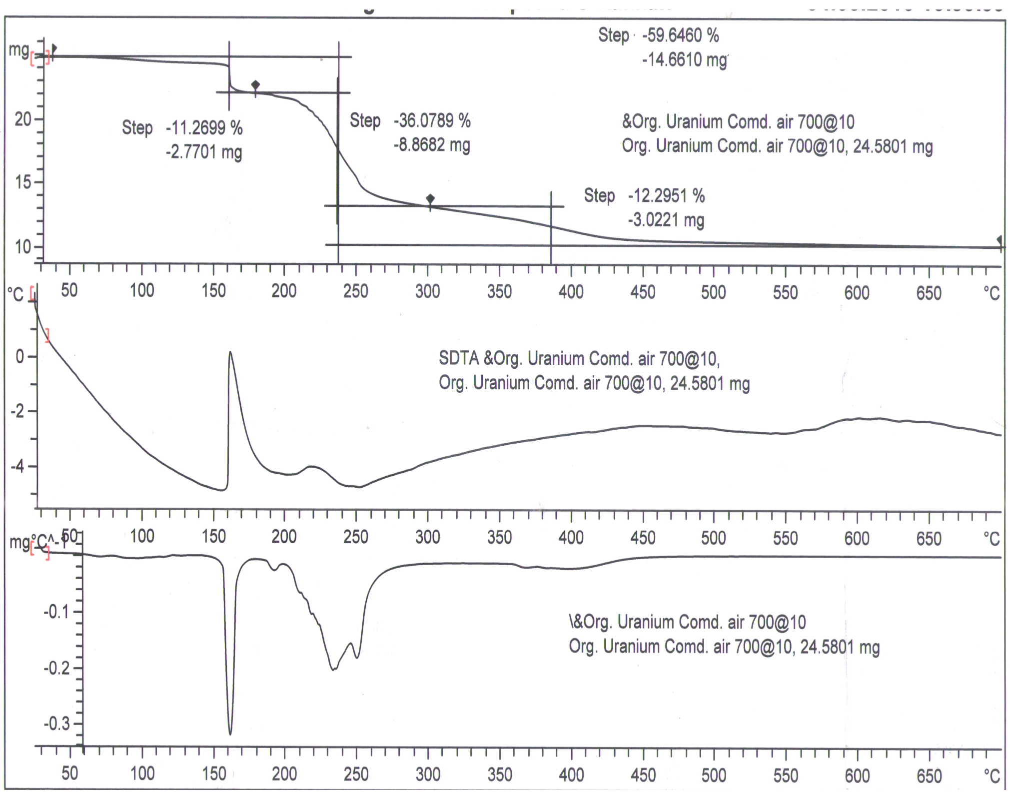

Fig. 2.8 TG, DTG and DTA of compound **3**

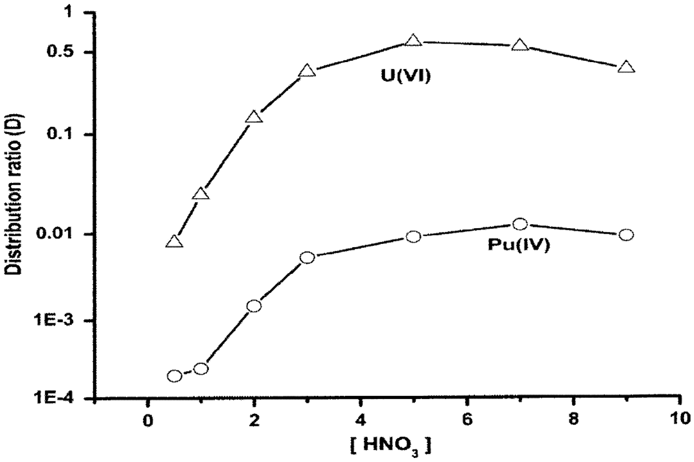

Fig. 2. 9 Variation of distribution ratio for U(VI) and Pu(IV) with HNO_3

2.3.8 Selective separation of uranium from thorium by using $^{i}C_3H_7CON(^{i}C_4H_9)_2$

The total reflection X-ray fluorescence (TXRF) spectrum of the stock and supernatant (Fig.2.10-2.11) clearly shows that more than 98% of the uranium is precipitated from a mixture of thorium, lanthanum and uranium. The TXRF spectrum of the ethanolic solution of the precipitated product shows (Fig.2.12) clearly that the precipitate contains more than 98% of uranium and less than 0.2% of thorium and 0% La. It confirms that the uranium is selectively precipitated as its nitrate complex from the solution leaving the thorium and lanthanum ions. This study clearly demonstrates that the uranium can be selectively separated from the mixture of thorium and lanthanum in an equivalent manner to that of the N-cyclohexyl-2-pyrrolidone type of ligands.

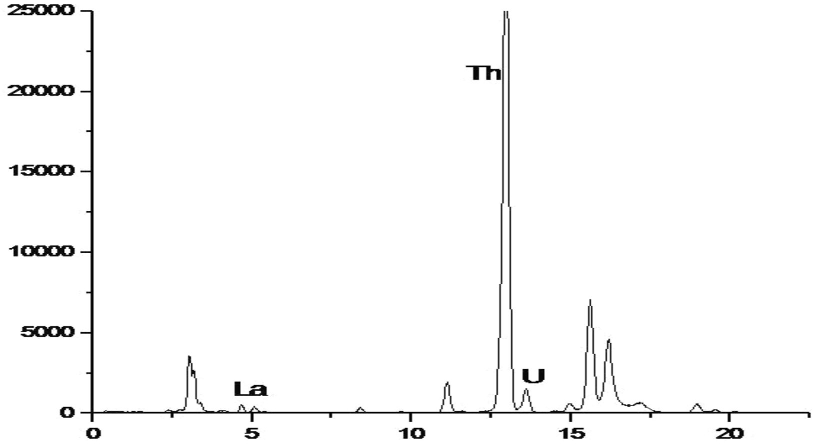

Fig. 2.10 TXRF Spectrum of stock solution

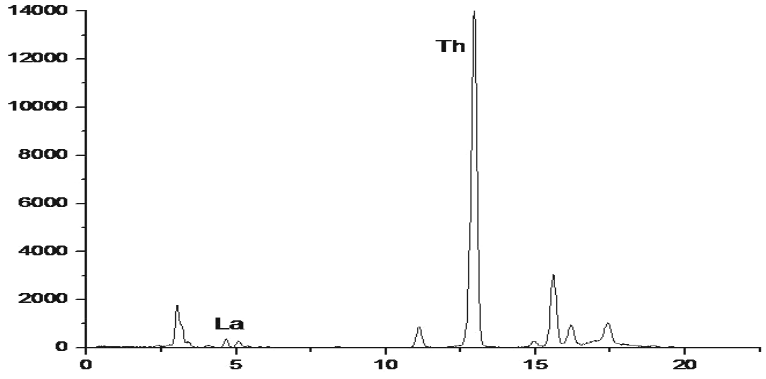

Fig. 2.11 TXRF Spectrum of supernatant solution

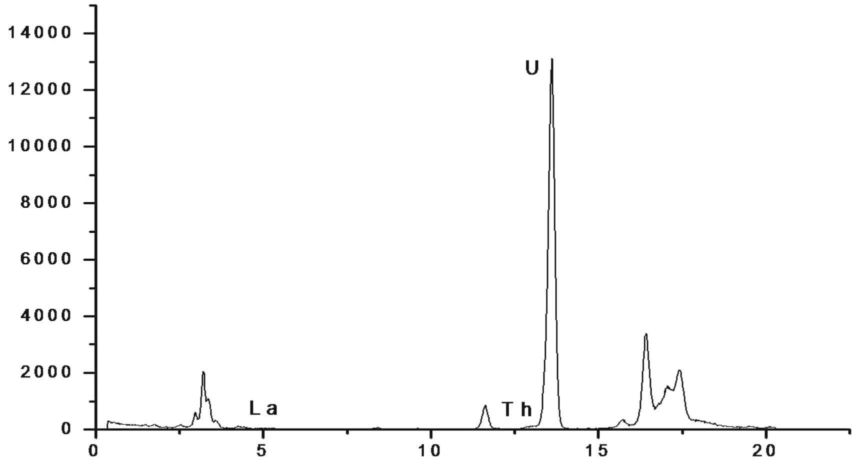

Fig.2.12 TXRF Spectrum of the precipitate in ethanol

2. 4 Conclusions

Studies on the coordination ability of the iso-butyramide based ligands with the uranyl (VI) nitrate show that the ligands act as monodentate ligand and form 1:2 complexes. The studies further show that the ligands are un-reactive towards the thorium (IV) and lanthanum(III) nitrates. Precipitation studies show that the U(VI) can be selectively separated as an uranyl nitrate amide complex from the solution containing the mixture of U(VI), Th(IV) and La(III) ions. TG/DTA experiments show that the uranyl nitrate–amide compound can be completely converted in to U_3O_8 without any other impurities.

2.5 References

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CHAPTER 3

Synthesis, structural and complexation studies of bis (N, N'-di-alkyl carbamoyl methyl) sulfide, sulfoxide and sulfone with uranyl and lanthanide ions

CHAPTER-3

3.1 Introduction

Tri-functional ligands such as diglycolamide (Fig.3.1a), 2,6-bis [bis(alkyl)phosphino)methyl] pyridine N,P,P' trioxide [P(O)N(O)P(O)] (Fig. 3.1b), 2,6-bis(N-alkyl acetamide) pyridine-N-oxide [C(O)N(O)C(O)] (Fig. 3.1c), and bis(carbamoyl methyl) sulfoxide [BCMSO] (Fig. 3.1d) show excellent extraction properties for trivalent actinides over tetra or hexavalent actinides and extensive solvent extraction studies have been reported over the last 10 years [1-4]. The coordination chemistry of diglycolamide with lanthanide and actinide ions has been reported recently [5-7] and shows that the ligand acts in a tridentate chelating fashion and bonds through both the carbamoyl and ethereal oxygens to the metal centre. The coordination chemistry of 2,6-bis[bis(alkyl) phosphino)methyl] pyridine N,P,P' trioxide and 2,6-bis(N-alkyl acetamide) pyridine-N-oxide shows that they can act either as tridentate chelating, bridging, or bidentate chelating ligands [8-9]. The replacement of etheral oxygen atom of diglycolamide by the CH_2 group in the glutaramide ligand (Fig. 3.1e) shows extraction for the hexavalent and tetravalent ions but not for the trivalent ions [10]. The coordination chemistry of glutaramide shows that it acts as a monodentate ligand and bridges uranyl nitrate in the solid state to form a linear polymeric chain arrangement [11]. The solvent extraction studies on tri-functional ligands having the ‘‘thio” group in place of the oxygen atom in diglycolamide (called thio-diglycolamide, (Fig. 3.1f) reported by Sasaki et al. show extraction for hexavalent, tetravalent and trivalent actinides and lanthanides from the perchloric acid medium [12-14]. The observed distribution data show that its extraction properties are much superior to those of malanomides but poorer than those of diglycolamides. Sasaki et al. have proposed a tridentate chelating mode of bonding for these ligands with the metal ion similar to those of diglycolamide ligands [14]. However, no structural work is reported to support their proposal. Since perchloric acid is no where used in the nuclear fuel reprocessing cycle, it is more relevant to carry out the extraction and complexation studies from nitric acid medium rather than that of perchloric acid.

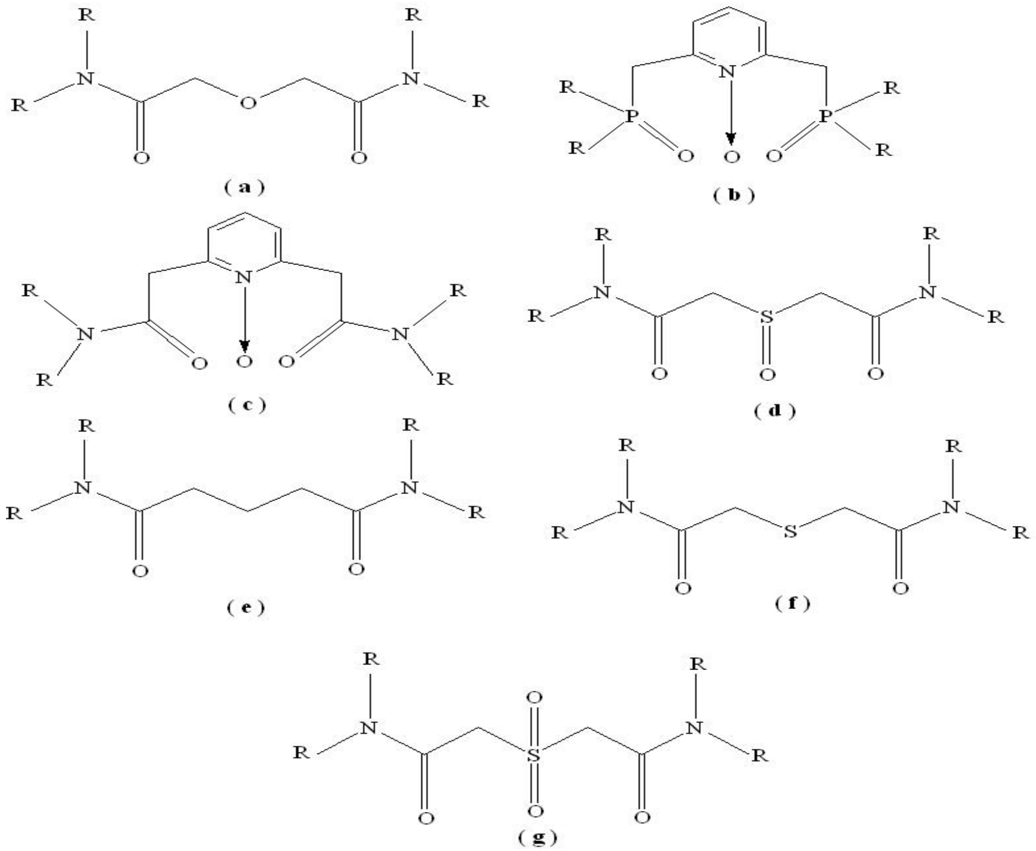

Fig.3.1 Different ligands studied for the separation of actinides from acid media.

Therefore, a systematic work on the synthesis, coordination and extraction chemistry of some new thio-diglycolamide, ligands with uranyl and lanthanum (III) nitrates are investigated in the present work.

The complex chemistry of bis(carbamoyl methyl) sulfoxide (Fig.3.1d) and bis(carbamoyl methyl) sulfone (Fig.3.1g) with any of the actinide or lanthanide has not been reported so far in the literature. Therefore, the synthesis and coordination chemistry of some new bis(carbamoyl methyl) sulfoxide and bis(carbamoyl methyl) sulfone ligands with uranyl and lanthanum(III) nitrates were also studied for the comparison purpose.

3.2 Experimental

3.2.1 Synthesis of thioglycolamide ligands and their uranyl and lanthanide nitrate complexes

3.2.1.1 Synthesis of $[(^iC_3H_7)_2NCOCH_2SCH_2CON\{(^iC_3H_7)_2]$ *(***10***)*

N, N'- di-isopropyl chloroacetamide (50 g, 0.279 mol) and $Na_2S.9H_2O$ (34 g, 0.14 mol) in ethanol (100 mL) were refluxed for 24 h. The volume of the solution was reduced (50 mL) and ca. 300 mL of water was added. The viscous organic residue obtained was extracted with 100 mL of chloroform, dried over anhydrous sodium sulfate and filtered. Removal of the solvent yielded a pasty solid which was re-dissolved in hot hexane and filtered. The solution on slow evaporation yielded a pale yellow solid, which was filtered and washed with cold hexane and dried. Yield: 25 g (57%). Elemental Analysis Calculated for $[(^iC_3H_7)_2NCOCH_2SCH_2CON(^iC_3H_7)_2]$; $C_{16}H_{32}N_2O_2S$ (%): C=60.7; H=10.1; N=8.8. Found: C=60.6; H=9.9; N=8.9. IR (Nujol, ν/cm^{-1}): 1643 (CO). ^1H NMR (25 °C, $CDCl_3$, δ in ppm): 1.20 (d, 7.2 Hz, 12H, CH_3), 1.38 (d, 6.9 Hz, 12H, CH_3),(s, 4H, SCH_2), 3.97 (m, 4H, CH).

3.2.1.2 Synthesis of $[(^iC_4H_9)_2NCOCH_2SCH_2CON(^iC_4H_9)_2]$ *(***11***)*

This was prepared in a way similar as compound **10** by taking $^iBu_2NCOCH_2Cl$ (10 g, 0.0486 mol) and $Na_2S.\ 9H_2O$ (5.5 g, 0.0229 mol). Yield: 95%. Elemental Analysis

Calculated for $[(^iC_4H_9)_2NCOCH_2SCH_2CON(^iC_4H_9)_2]$; $C_{20}H_{40}N_2O_2S$ (%): C=64.5; H= 10.7; N=7.5. Found: C=64.1; H=10.4; N=8.0. IR (Nujol, ν/cm^{-1}): 1640 (CO). ^{1}H NMR (25 °C, $CDCl_3$, δ in ppm): 0.89 (d, 6.5 Hz, 12H, CH_3), 0.92 (d, 7 Hz, 12H, CH_3), 1.91 (m, 2H, CH), 2.02 (m, 2H, CH), 3.14 (d, 8 Hz, 4H, NCH_2), 3.20 (d, 7.5 Hz, 4H, NCH_2), 3.52 (s, 4H, SCH_2).

*3.2.1.3 Synthesis of $[(^nC_4H_9)_2NCOCH_2SCH_2CON\{(^nC_4H_9)_2]$ (**12**)*

This was prepared in a similar way as compound **10** by taking Bu_2NCOCH_2Cl (25 g, 0.1216 mol) and $Na_2S\ 9H_2O$ (14.5 g, 0.0604 mol).Yield: 89%. Elemental Analysis Calculated for $[(^nC_4H_9)_2NCOCH_2SCH_2CON(^nC_4H_9)_2]$, $C_{20}H_{40}N_2O_2S$ (%): C=64.5; H=10.7; N=7.5. Found: C=64.2; H=11.0; N=7.7.IR (Nujol, ν/cm$^{-1)}$: 1639 (CO). ^{1}H NMR (25 °C, $CDCl_3$, δ in ppm): 0.91 (t, 7.5 Hz, 6H, CH_3), 0.94 (t, 7.5 Hz, 6H, CH_3), 1.31 (m, 8H, CH_2), 1.52 (m, 8H, CH_2), 3.27 (m, 8H, CH_2), 3.48 (s, 4H, SCH_2).

*3.2.1.4 Synthesis of $[UO_2(NO_3)_2[(^iC_3H_7)_2NCOCH_2SCH_2CON\{(^iC_3H_7)_2]$ (compound **13**)*

To a solution of $(^iC_3H_7)_2NCOCH_2SCH_2CON(^iC_3H_7)_2$ (691 mg, 2.18 mmol) in chloroform, solid $[UO_2(NO_3)_2 .6H_2O]$ (502 mg,1 mmol) was added and stirred for few minutes until all uranyl nitrate dissolves to give a clear solution. The solution was filtered and layered with iso-octane. The solution on slow evaporation deposited a pasty solid which was washed in di-isopropyl ether to re-move the excess ligand and yield a fine yellow powder. The solution was filtered and the solid residue was washed in isopropyl ether, hexane and dried. This crude product was crystallized from dichloromethane/isooctane mixture as a yellow crystalline solid. Yield: 714 mg (92%). Elemental Analysis Calculated for $[UO_2(NO_3)_2(^iC_3H_7)_2N\text{-}COCH_2SCH_2CON\ (^iC_3H_7)_2]$;

$C_{16}H_{32}N_4O_{10}SU$ (%): C=27.0; H=4.5; N=7.9. Found: C=27.5; H=4.9; N=8.0. IR (Nujol, ν/cm^{-1}): 1610, 1577 (CO), 927 (O=U=O). ^1H NMR (25 °C, $CDCl_3$, δ in ppm): 1.51 (d, 6.5 Hz, 24H, CH_3), 3.74 (br, 4H, SCH_2), 4.14 (m, 4H, CH).

3.2.1.5 Synthesis of $[UO_2(NO_3)_2[(^iC_4H_9)_2NCOCH_2SCH_2C)N\{(^iC_4H_9)_2]$ (compound **14***)*

This compound was prepared in a way similar to compound **13,** by taking $[(^iC_4H_9)_2NCOCH_2]_2S$ (750 mg, 2.016 mmol) and $[UO_2(NO_3)_2 .6H_2O]$ (502 mg, 1 mmol). The crude product was crystallized from chloroform/ dodecane mixture as a yellow crystalline solid. Yield: 738 mg (95.5%). Elemental Analysis Calculated for $[UO_2(NO_3)_2(^iC_4H_9)_2NCOCH_2SCH_2.CON(^iC_4H_9)_2]$; $C_{20}H_{40}N_4O_{10}SU$ (%): C=31.3; H=5.2; N=7.3. Found: C=30.9; H=4.9; N, 7.1. IR (Nujol, ν/cm^{-1}): 1610, 1579 (CO), 936 (O=U=O).^1H NMR (25 °C, $CDCl_3$, δ in ppm): 1.01 (d, 7 Hz, 12H, CH_3), 1.10 (d, 6.5 Hz, 12H, CH_3), 2.17 (m, 2H, CH), 2.29 (m, 2H, CH), 3.45 (d, 7.5 Hz, 4H, NCH_2), 3.88 (s, 4H, SCH_2), 3.97 (d, 6.5 Hz, 4H, NCH_2).

3.2.1.6 Synthesis of $[UO_2(NO_3)_2[(^nC_4H_9)_2NCOCH_2SCH_2CON(^nC_4H_9)_2]$ (compound **15***)*

This was prepared in a similar way as compound **13** by taking $[(^nC_4H_9)_2NC(O)CH_2]_2S$ (760 mg, 2.04 mmol) and $[UO_2(NO_3)_2 .6H_2O]$ (502 mg, 1 mmol). The crude product was crystallized from chloroform/iso-octane mixture as a yellow solid. Yield: 718 mg (93%). Elemental Analysis Calculated for $[UO_2(NO_3)_2(C_4H_9)_2NCOCH_2SCH_2.CON(^nC_4H_9)_2]$; $C_{20}H_{40}N_4O_{10}SU$ (%): C=31.3; H=5.2; N=7.3. Found: C=31.7; H=5.5; N=7.3. IR (Nujol, ν/cm^{-1}): 1610, 1579 (CO), 929(O=U=O). ^1H NMR (25 °C, $CDCl_3$, δ in ppm): 0.88 (t, 7.5 Hz, 6H, CH_3), 1.06 (t, 7.5 Hz, 6H, CH_3), 1.40 (br, 4H, CH_2), 1.49 (br, 4H, CH_2), 1.81 (br, 8H, CH_2), 3.57 (br, 4H, NCH_2), 3.80 (br, 4H, NCH_2), 3.98 (br, 4H, SCH_2).

*3.2.1.7 Synthesis of $[La(NO_3)_3\{(^iC_3H_7)_2NCOCH_2SCH_2CON\{(^iC_3H_7)_2\}_2]$ (compound **16**)*

To a chloroform solution of $[(^iC_3H_7)_2NC(O)CH_2]_2S$ (1.053 g, 3.33 mmol), $[La(NO_3)_3 .6H_2O]$(476 mg, 1.09 mmol) was added and stirred till a clear solution is obtained. The solution was filtered and layered with isooctane. The solution on slow evaporation yielded a white solid. This was washed with di-isopropyl ether, filtered, washed with hexane and finally dried to get a white powder. This powder was dissolved in hot ethanol and allowed to evaporate slowly at room temperature to give a white crystalline compound. Yield: 989 mg (93%). Elemental Analysis Calculated for $[La(NO_3)_3\{(^iC_3H_7)_2N\text{-}COCH_2SCH_2CON(^iC_3H_7)_2\}_2\ H_2O]$; $C_{32}H_{66}\ N_7O_{14}S_2La$ (%): C=39.4; H=6.8; N=10.0. Found: C=40.1; H=6.7; N=10.3.IR (Nujol, ν/cm^{-1}): 3534 (H_2O), 1610–1577 (br) (CO).^{1}H NMR (25 °C, $CDCl_3$, δ in ppm): 1.26 (d, 7 Hz, 12H, CH_3), 1.41 (d, 6.5 Hz, 12H, CH_3), 1.64 (s, 4H, SCH_2), 3.99 (m, 4H, NCH).

*3.2.1.8 Synthesis of $[La(NO_3)_3\{(^iC_4H_9)_2NCOCH_2SCH_2CON(^iC_4H_9)_2\}_2]$ (compound **17**)*

This was prepared similarly as compound **16**, by taking $[(^iC_4H_9)_2NCOCH_2]_2S$ (684 mg, 1.83 mmol) and $[La(NO_3)_3 .6H_2O]$ (265 mg, 0.612 mmol).Yield: 622 mg (95%). Elemental Analysis Calculated for $[La(NO_3)_3\{(^iC_4H_9)_2N\text{-}COCH_2SCH_2CON(^iC_4H_9)_2\}_2]$; $C_{40}H_{80}\ N_7O_{13}\ S_2La$ (%): C=44.9; H=7.4; N=9.2. Found: C=44.7; H=7.9; N=9.1. IR (Nujol, ν/cm^{-1}): 1601–1580 (br) (CO). ^{1}H NMR (25 °C, $CDCl_3$, δ in ppm): 0.92 (d, 6.5 Hz, 12H, CH_3), 0.95 (d, 6.5 Hz, 12H, CH_3), 1.95 (m, 2H, CH), 2.04 (m, 2H, CH), 3.13 (d, 7.5 Hz, 4H, NCH_2), 3.22 (d, 7.5 Hz, 4H, NCH_2), 3.54 (s, 4H, SCH_2).

3.2.1.9 Synthesis of [La(NO$_3$)$_3${(^{n}C$_4$H$_9$)$_2$NC(O)CH$_2$SCH$_2$C(O)N {(^{n}C$_4$H$_9$)$_2$}$_2$] (compound **18***)*

This was prepared in a similar way as compound **16,** by taking [(^{n}C$_4$H$_9$)$_2$NCOCH$_2$]$_2$S (1130 mg, 3.04 mmol) and [La(NO$_3$)$_3$ .6H$_2$O] (438 mg, 1.01 mmol).Yield: 985 mg (91%). Elemental Analysis Calculated for [La(NO$_3$)$_3${(^{n}C$_4$H$_9$)$_2$N-COCH$_2$SCH$_2$CON(^{n}C$_4$H$_9$)$_2$}$_2$]; $C_{40}H_{80}N_7O_{13}S_2La$ (%): C=44.9; H=7.4; N=9.2. Found: C=44.8; H=7.6; N=9.1.IR (Nujol, ν/cm^{-1}): 1602–1580 (br) (CO).^{1}H NMR (25 °C, CDCl$_3$, δ in ppm): 0.95 (m, 12H, CH$_3$), 1.33 (m, 8H, CH$_2$), 1.57 (m, 8H, CH$_2$), 3.29 (m, 8H, CH$_2$), 3.49 (s, 4H, SCH$_2$).

3.2.2 Synthesis of N, N, N', N'-tetra-isobutyl-3-sulfoxo- diglycolamide and its uranyl complex

*3.2.2.1 Synthesis of [(^{i}C$_4$H$_9$)$_2$NCOCH$_2$SOCH$_2$CON(^{i}C$_4$H$_9$)$_2$] (***19***)*

To a solution of [(^{i}C$_4$H$_9$)$_2$NCOCH$_2$SCH$_2$CON(^{i}C$_4$H$_9$)$_2$] (15 g, 0.04 mol) in methanol (50 mL) a solution of 4.6 mL of 30% H_2O_2 (1.37 g, 0.04 mol) and SeO_2 (4.47 g, 0.04 mol) in methanol (50 mL) was added slowly with stirring. The solution was stirred for about 30 min and then 400 mL 10% NaCl solution was added. The viscous organic residue obtained was extracted with 100 mL of chloroform, dried over anhydrous sodium sulfate, and filtered. Removal of the solvent yielded a pasty solid which was redissolved in hot hexane and filtered. The solution on slow evaporation yielded a white solid, which was filtered and washed with cold hexane and dried. Yield: 9.5 g (61%).Elemental Analysis Calculated for [(^{i}C$_4$H$_9$)$_2$NCOCH$_2$SOCH$_2$CON(^{i}C$_4$H$_9$)$_2$]; $C_{20}H_{40}N_2O_3S$ (%): C=61.9; H=10.4; N=7.2. Found: C=61.2; H=9.9; N=6.9.IR (Nujol, ν/cm^{-1}): 1654, 1625 (CO), 1049 (SO). ^{1}H NMR (25 °C, CDCl$_3$, δ in ppm): 0.90 (d, 6 Hz, 12H, CH$_3$), 0.93 (d, 6 Hz, 12H, CH_3), 1.93 (m, 6 Hz, 2H, CH), 2.04 (m, 6 Hz, 2H, CH), 3.00–3.23 (m, 8H, NCH_2), 3.8 (d, 2H, S(O)–CH_2–CO), 4.1 (d, 2H, S(O)–CH_2– CO).

3.2.2.2 Synthesis of $[UO_2(NO_3)_2\{(^iC_4H_9)_2NCOCH_2SOCH_2CON(^iC_4H_9)_2\}]$ *(compound* **20***)*

To a solution of $(^iC_4H_9)_2NCOCH_2SOCH_2CON(^iC_4H_9)_2$ (600 mg, 1.54 mmol) in chloroform, solid $[UO_2(NO_3)_2.6H_2O]$ (502 mg, 1 mmol) was added and stirred for a few minutes until all uranyl nitrate dissolved to give a clear solution. The solution was filtered and layered with iso-octane. The solution on slow evaporation deposited a pasty solid, which was washed in di-isopropyl ether to remove excess ligand and yield a fine yellow powder. The solution was filtered and the solid residue was washed in isopropyl ether, hexane and dried. This crude product was crystallized from dichloromethane/ isooctane mixture as a yellow crystalline solid. Yield: 630 mg (81%). Elemental Analysis Calculated for $[UO_2(NO_3)_2(^iC_4H_9)_2NCOCH_2SOCH_2CON(^iC_4H_9)_2]$; $C_{20}H_{40}N_4O_{11}SU$ (%): C=30.7; H=5.1; N=7.2. Found: C=29.9; H=4.8; N=6.9. IR (Nujol, ν/cm^{-1}): 1656, 1591 (CO), 983 (SO), 943 (O=U=O). ^1H NMR (25 °C, $CDCl_3$, δ in ppm): 0.95–1.12 (m, 2H, CH_3), 1.87–2.18 (m, 4H, CH), 3.21–3.77 (m, 8H, NCH_2), 4.79 (q, 4H, S(O)–CH_2–CO).

3.2.3 Synthesis of N, N, N', N'-tetra-isobutyl-3-sulfone diglycolamide and its uranyl complex

3.2.3.1 Synthesis of $[(^iC_4H_9)_2NCOCH_2SO_2CH_2CON(^iC_4H_9)_2]$ *(***21***)*

The ligand $[(^iC_4H_9)_2NCOCH_2SO_2CH_2CON(\ ^iC_4H_9)_2]$ was prepared by the reaction of bis(carbamoylmethyl) sulfide $[(^iC_4H_9)_2NCOCH_2\text{-}SCH_2CON(\ ^iC_4H_9)_2]$ (15 g,0.04 mol) with 9.2 mL of 30% H_2O_2 (2.8 g, 0.08 mol) and SeO_2 (9.0 g, 0.08 mol) in 100 ml methanol. The solution was stirred for about an hour and then, 400 mL 10% NaCl solution was added. The viscous organic residue obtained was extracted with 100 mL of chloroform, dried over anhydrous sodium sulphate and filtered. Removal of the solvent yielded a pasty solid which was redissolved in hot hexane. The hot solution on cooling yielded a white solid, which was filtered and washed with cold hexane and dried. Yield: 9.8 g (64%). Elemental Analysis Calculated for $[(^iC_4H_9)_2NCOCH_2SO_2CH_2CON(^iC_4H_9)_2]$; $C_{20}H_{40}N_2O_4S$ (%): C=59.4; H=9.9; N=6.9. Found: C=60.1; H=9.7; N=6.8. IR (Nujol, ν/cm^{-1}): 1654, 1626 (CO), 1147, 1110 (SO_2). ^1H NMR (25°C, $CDCl_3$, δ in ppm): 0.93 (d, 6 Hz, 12H, CH_3), 0.95 (d, 6 Hz, 12H, CH_3), 1.90 (m, 6 Hz, 2H, CH), 2.04 (m, 6 Hz, 2H, CH), 3.12 (d, 4H, NCH_2) 3.23 (d, 4H, NCH_2),, 4.5 (s, 4H, $SO_2–CH_2–$ CO).

*3.2.3.2 Synthesis of $UO_2(NO_3)_2[(^iC_4H_9)_2NCOCH_2SO_2CH_2CON(^iC_4H_9)_2)]$ (compound **22**)*

The compound $[UO_2(NO_3)_2\ [(^iC_4H_9)_2NCOCH_2SO_2CH_2CON\ (^iC_4H_9)_2)]$ was prepared by the reaction of $[(^iC_4H_9)_2NCOCH_2SO_2CH_2CON(^iC_4H_9)_2]$ (600 mg, 1.48 mmol) with solid $[UO_2(NO_3)_2.6H_2O]$ (502 mg, 1 mmol) in 25 ml of dichloromethane. The solution was stirred for few minutes until all uranyl nitrate dissolved to give a clear solution which was then filtered and dried under vacuum. The residue obtained was washed with di-isopropyl ether to remove the unreacted ligand. The residue was then dissolved in dichloromethane and filtered. The filtrate on slow evaporation yielded yellow colored crystalline product. Yield: (78%). Elemental Analysis Calculated for $[UO_2(NO_3)_2(^iC_4H_9)_2NCOCH_2SO_2CH_2CON(^iC_4H_9)_2]$; $C_{20}H_{40}N_4O_{12}SU$ (%): C=30.1; H=5.0; N=7.0. Found: C=29.8; H=4.9; N=6.8. IR (Nujol, ν/cm^{-1}): 1620, 1591 (CO), 1570 (NO_3) 1145, 1110 (SO_2), 945 (O=U=O).^{1}H NMR (25 °C, $CDCl_3$, δ in ppm): 1.05 (br, 24H, CH_3), 2.13 (br, 2H, CH), 2.35 (br, 2H, CH), 3.62 (br, 4H, NCH_2), 4.08(br, 4H, NCH_2), 4.73 (s, 4H, SO_2–CH_2–CO).

3.2.4 Solvent extraction studies

Distribution studies were performed by using a (0.2 M) solution of $[(^iC_4H_9)_2NCOCH_2SCH_2N(^iC_4H_9)_2]$ in chloroform, toluene or nitrobenzene with the 1 M HNO_3 as an aqueous phase spiked with ^{233}U or ^{241}Am tracers in a thermostated water bath for 1 h at 25 ± 0.1 C. Assay of organic and aqueous phases were done in duplicate by alpha counting using a dioxane based liquid scintillator for ^{233}U and gamma counting directly for the ^{241}Am. The distribution ratio (D) is defined as the ratio of the concentration of uranium in the organic phase to that of the aqueous phase.

3.2.5 X-ray crystallography

Selected crystallographic data for the compounds **13, 14, 16, 17, 20** and **22** are summarized in Tables 3.1 and 3.2.

Table 3.1 Crystal and structural refinement details for the compounds **13, 14, 16** and **17**

	13	**14**	**16**	**17**
Empirical formula	$C_{16}H_{32}N_4O_{10}SU$	$C_{20}H_{40}N_4O_{10}SU$	$C_{64}H_{132}N_{14}O_{27}S_4La_2$	$C_{40}H_{80}N_7O_{13}S_2La$
Formula weight	710.55	766.65	1947.91	1070.14
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	8.3175(3)	12.7013(5)	12.668(3)	9.8210(10)
b (Å)	16.9316(6)	12.6657(8)	23.760(3)	42.685(7)
c (Å)	18.8682(11)	10.3432(4)	15.163(3)	12.7543(19)
β (°)	94.159(5)	102.525(4)	90.241(17)	99.956(11)
Volume (Å^3)	2650.2(2)	2906.78(19)	4564.1(15)	5266.2(13)
Z (formula unit)	4	4	4	4
Calculated density (g cm^3)	1.781	1.752	1.417	1.350
Reflections collected/unique	16990/7609	18926/8418	32098/13168	34477/15208
Data/restraints/ parameters	7690/0/279	8418/6/333	13168/0/522	15208/6/584
Goodness-of-fit (GOF) on F^2	1.105	1.126	0.779	1.223
Final R indices [I > 2σ(I)]	0.0577	0.0735	0.0544	0.1280
R indices (all data)	0.0826	0.0990	0.1544	0.1899

$W = 1/[\sigma^2(F^2_o) + (0.0405P)^2 + 17.8536P]$ for compound **13**, $W = 1/[\sigma^2(F^2_o) + (0.0319P)^2 + 48.2087P]$ for **14**, $W = 1/[\sigma^2(F^2_o) + (0.0343P)^2 + 0.0000P]$ for **16**, $W = 1/[\sigma^2(F^2_o) + (0.0409P)^2 + 66.2805P]$ for the compound **17**, where $P = (F_o^2 + 2F_c^2)/3$.

Table 3.2 Crystal and structural refinement details for **20** and **22**

	20	**22**
Empirical formula	$C_{20}H_{40}N_4O_{11}SU$	C_{20} H_{40} N_4 O_{12} S U
Formula weight	782.65	798.65
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	8.8749(4)	16.5466(9)
b(Å)	25.8255(14)	11.6185(5)
c(Å)	13.1206(7)	16.6063(11)
β (°)	99.961(5)	103.347(6)
Volume ($Å^3$),	2961.9(3),	3106.3(3)
Z	4	4
Calculated density (g cm^{-3})	1.755	1.708
Reflections collected/Unique	8553/5217	9004/5168
Data/restraints/parameters	8553/0/342	9004/0/351
Goodness-of-fit on F^2	1.059	0.780
Final R indices [I> 2σ(I)]	0.0724	0.0437
R indices (all data)	0.1268	0.0908

$W = 1/[\sigma^2(F^2_o) + (0.0405P)^2 + 17.8536P]$ for **20** and $W = 1/[\sigma^2(F^2_o) + (0.0210P)^2 + 0.0000P]$ for **22** where $P = (F_o^2 + 2F_c^2)/3$

3.3 Results and discussion

3.3.1 Chemistry of thiodiglycolamide ligands

3.3.1.1 Synthesis of thio-diglycolamide ligands

Reaction of carbamoyl methyl chloride with sodium sulfide in ethanol yielded the corresponding thiodiglycolamide ligands (**10** to **12)** The IR spectra of all ligands (Fig.3.2) show the presence of the carbamoyl group in the synthesized compounds. The ^{1}HNMR spectra (Fig.3.3) show the expected peak multiplicities and integration. The CH_2 proton resonance appears at slightly upfield (δ = 3.52 ppm) with respect to the starting R_2NCOCH_2Cl (δ = 4.01 ppm) and the analogous diglycolamide $R_2NCOCH_2OCH_2CONR_2$ (δ = 5.7 ppm) [5], thereby showing that the more electronegative chloride or oxygen is replaced by the less electronegative sulfur atom. The C, H, N analysis supports the expected stoichiometry for the compounds.

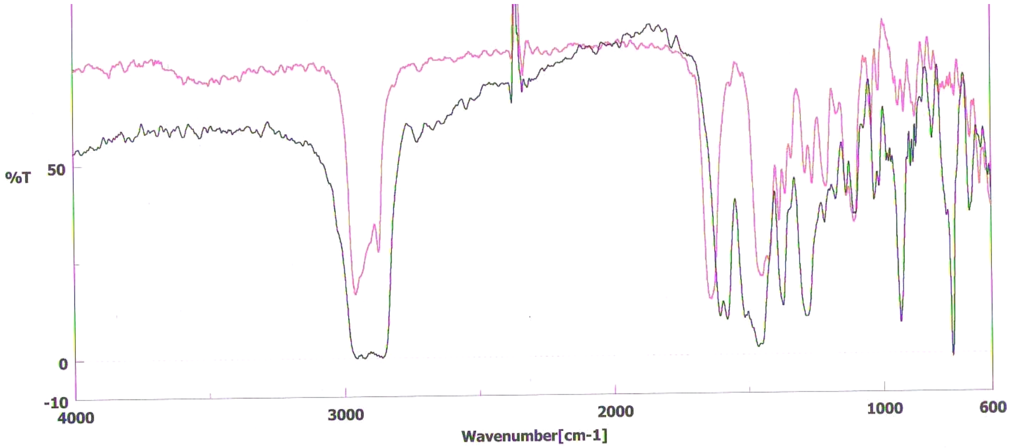

Fig. 3.2 IR spectra of ligand **11 (**red color) and compound **14**

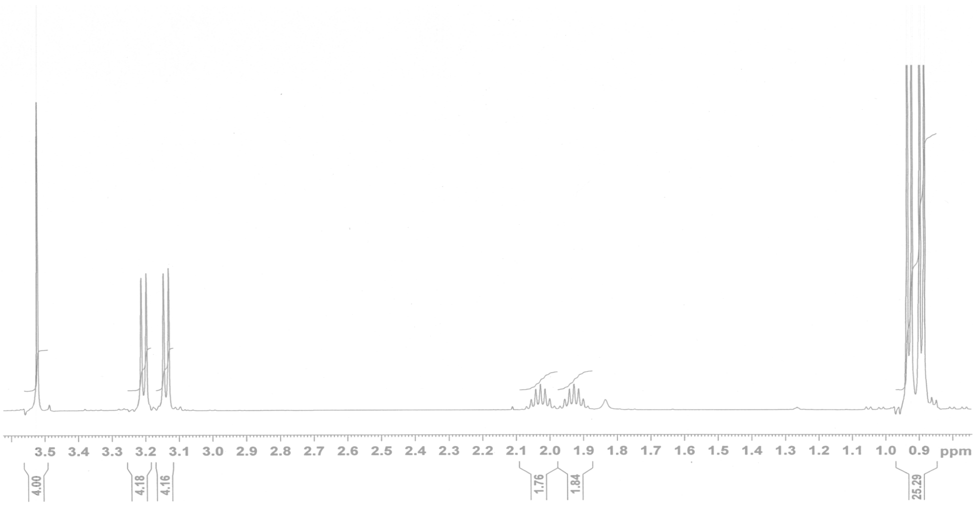

Fig. 3.3 ^{1}HNMR spectra of ligand **11**

3.3.1.2 Synthesis and structural studies of thioglycolamide uranyl complexes

Reaction of $[UO_2(NO_3)_2\ 6H_2O]$ with the thio-glycolamide ligand in dichloromethane yielded compounds of the type $[UO_2\ (NO_3)_2(R_2NCOCH_2SCH_2CONR_2)]$. The IR spectra (Fig. 3.2) of compounds **13 to 15** show that the water molecules from the starting compound $[UO_2\ (NO_3)_2\ 6H_2O]$ are completely replaced by the thio-glycolamide ligand and that the ligand is bonded through both carbamoyl groups to the metal centre. The observed frequency differences for the carbamoyl groups ($\Delta\nu_{CO}$ = 30-60 cm^{-1}, where $\Delta\nu_{CO} = \nu_{CO(free\ ligand)}\ \nu_{CO(complex)}$) are consistent with the supposition that the carbamoyl group is bonded to the uranyl group directly in the reported compounds. Similar differences are also observed in the compounds of amides with uranyl nitrate such as: $[UO_2\ (NO_3)_2\ ({}^{i}C_3H_7CON\{{}^{i}C_4H_9\}_2)_2]$ [15] and $[UO_2(NO_3)_2({}^{i}C_3H_7)_2NCOCH_2\text{-}CON({}^{i}C_3H_7)_2]$ [16]. The ^{1}H NMR (Fig. 3.4) of the compounds shows that the CH_2 protons are deshielded by 0.3–0.4 ppm with respect to the free ligands. This shows clearly that ligands are also bonded to the metal centre in solution. The C, H and N analysis revealed that the metal to ligand ratio is 1:1 in all the compounds. Structures for the compounds $[UO_2(NO_3)_2[({}^{i}Pr_2NCOCH_2SCH_2CON{}^{i}Pr_2)]$ and $[UO_2(NO_3)_2\ ({}^{i}Bu_2NCOCH_2SCH_2CON{}^{i}Bu_2)]$ were determined using X-ray diffraction methods and confirm the spectral and analysis results. The structures of the compounds $[UO_2(NO_3)_2[({}^{i}Pr_2NCOCH_2\text{-}SCH_2CON{}^{i}Pr_2)]$ and $[UO_2(NO_3)_2[({}^{i}Bu_2NCOCH_2SCH_2CON{}^{i}Bu_2)]$ are shown in Fig. 3.5 and 3.6 respectively and the relevant bond lengths and angles are given in Table 3.3. These structures show that the thio-diglycolamide ligand bonds to uranyl nitrate in a bidentate chelating fashion through the carbamoyl oxygen atoms. They show further that the thioether group is un-coordinated in both these structures (U– S = 4.8 Å). These structures are very similar to that of the uranyl nitrate–malonamide compound $[UO_2(NO_3)_2({}^{i}C_3H_7)_2\text{-}$

$\mathrm{NCOCH_2CON(^{i}C_3H_7)_2]}$ [16], in which the malonamide acts as a bidentate chelating ligand and bonds through both carbomoyl oxygen atoms. The coordination number around uranium(VI) is eight and the geometry is hexagonal bi-pyramidal. Four oxygen atoms from two nitrates and two oxygen atoms from the organic ligand form the planar hexagon. The two uranyl oxygen atoms occupy the axial positions. The observed U–O(amide) bond distances 2.352(4) and 2.374(5) Å in compound **13** and 2.358(6) and 2.385(5) Å in compound **14** are slightly shorter than the values observed in $\mathrm{[UO_2(NO_3)_2(^{i}C_3H_7)_2NCOCH_2CON(^{i}C_3H_7)_2]}$ (2.41(2) Å) [16], $\mathrm{[UO_2(NO_3)_2Ph\{EtO\}POCH_2CONEt_2]}$ (2.426(8)Å), $\mathrm{[UO_2(NO_3)_2Ph_2POCH_2\text{-}CONEt_2]}$ (2.404(5)Å) [17] and $\mathrm{[UO_2(NO_3)_2C_6H_5SOCH_2CON(C_4H_9)_2]}$ (2.442(9)Å) [18] and comparable in magnitude with those observed in $\mathrm{[UO_2(NO_3)_2(C_5H_7N_2CH_2CO^{i}Bu_2]}$ (2.364(7)–2.377(9) Å) [19], $\mathrm{[UO_2(NO_3)_2(tetrabutylglutaramide)]_n}$ (2.37(2)Å) [11] and $\mathrm{[UO_2(NO_3)_2\ (^{i}C_3H_7CON\{^{i}C_4H_9\}_2)_2]}$ (2.349(5) Å) [15]. The average U=O (1.757(5)–1.767(5) Å) and U–O($\mathrm{NO_3}$) (2.507(7)–2.526(7) Å) [11,15–19] bond distances are normal and agree well with the earlier reported uranyl nitrate neutral ligand compounds.

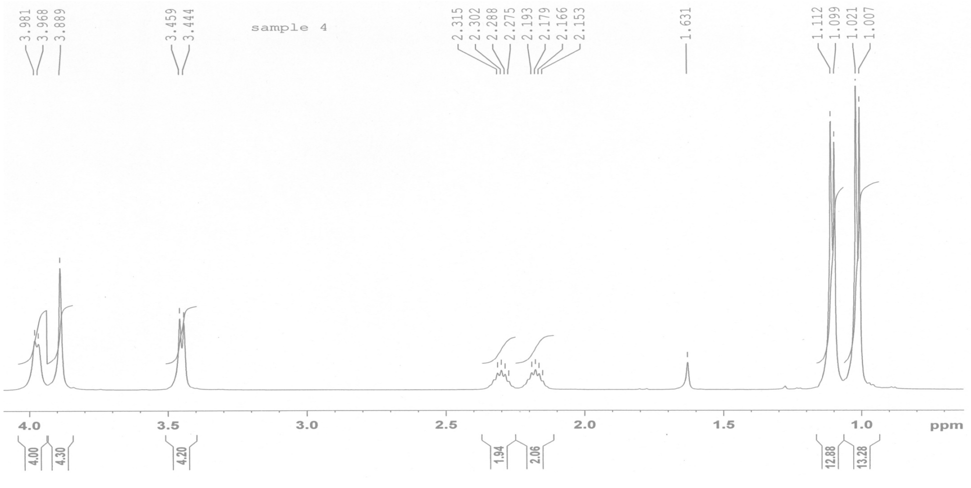

Fig. 3.4 ^{1}HNMR spectra of compound **14**

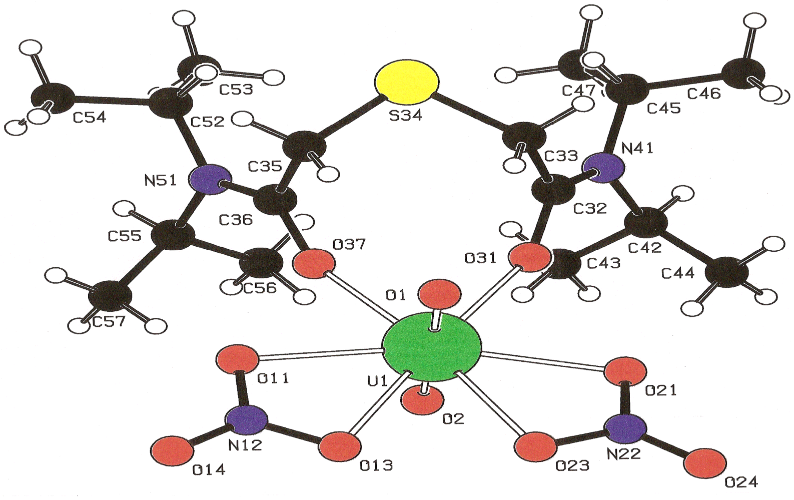

Fig. 3.5 Molecular structure of compound**13** (hydrogen atoms omitted for clarity)

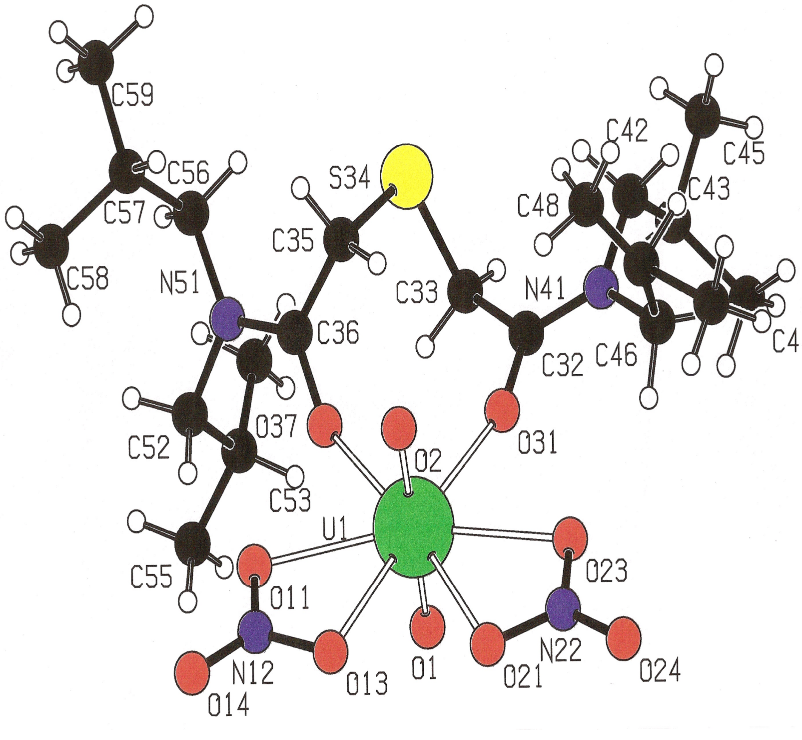

Fig. 3.6 Molecular structure of compound **14** (hydrogen atoms omitted for clarity)

Table 3.3 Important bond distances (Å) and angles (°) for compounds **13** and **14**

		13	
U(1)–O(1)	1.757(5)	U(1)–O(2)	1.758(4)
U(1)–O(11)	2.554(5)	U(1)–O(13)	2.484(5)
U(1)–O(21)	2.497(5)	U(1)–O(23)	2.496(5)
U(1)–O(31)	2.352(4)	U(1)–O(37)	2.374(5)
O(1)–U(1)–O(2)	179.1(2)	O(11)–U(1)–O(13)	50.32(15)
O(21)–U(1)–O(23)	51.03(17)	O(31)–U(1)–O(37)	70.95(17)
O(11)–U(1)–O(37)	63.49(17)	O(21)–U(1)–O(31)	65.40(16)
		14	
U(1)–O(1)	1.765(6)	U(1)–O(2)	1.770(6)
U(1)–O(11)	2.546(7)	U(1)–O(13)	2.515(7)
U(1)–O(21)	2.518(7)	U(1)–O(23)	2.527(7)
U(1)–O(31)	2.358(6)	U(1)–O(37)	2.385(5)
O(1)–U(1)–O(2)	178.7(3)	O(11)–U(1)–O(13)	50.3(2)
O(21)–U(1)–O(23)	50.5(2)	O(31)–U(1)–O(37)	72.3(2)
O(11)–U(1)–O(37)	62.5(2)	O(23)–U(1)–O(31)	65.7(2)

The interesting feature of the structure is that the thio-glycolamide ligand acts as a bidentate chelating ligand, indeed the carbamoyl groups are connected by a three atom bridge CH$_2$–S–CH$_2$. However, the structure of the analogous glutaramide complex of uranyl nitrate [UO$_2$(NO$_3$)$_2$(glutaramide)]$_n$ shows the bridging bidentate mode of bonding for the ligand, though the carbamoyl groups are also connected by a three atom bridge CH$_2$–CH$_2$–CH$_2$ [11]. The structure of the analogous diglycolamide ligand shows the tridentate chelating mode of bonding with the uranyl nitrate [5]. The structural studies clearly revealed that the nature of the complexes formed between the uranyl nitrate and bi-functional amide ligands is decided by the groups bridging the two carbamoyl (amide) groups. The eight-membered metallocyclic ring has the boat conformation with M–S distance of 4.8–4.9 Å in both structures. The structural studies revealed that the thio-glycolamide ligand behaves in a similar fashion to the malonamides in regards to its coordination behavior and not to the diglycolamides.

3.3.1.3 Synthesis and structural studies of lanthanum complexes

Reaction of $[La(NO_3)_3.6H_2O]$ with the thio-glycolamide ligand in ethanol yielded compounds of the type $[La(NO_3)_3[(R_2NCOCH_2SCH_2.CONR_2)_2]$. The IR spectra (Fig.3.7) of the compounds **16** to **18** show that the ligands are bonded through both the carbamoyl groups to the metal centre ($\Delta\nu_{CO}$ = 30 cm^{-1}, $\Delta\nu_{CO} = \nu_{CO(free\ ligand)} - \nu_{CO(complex)}$). The ^1H NMR spectra of the compounds **16** to **18** show the expected peak multiplicities and integrations. The spectra (Fig.3. 8) are very similar to those of free ligands without any deshielding of CH_2 protons, indicating that the ligands are weakly bonded to the metal nitrate in solution. This is further supported by the ESIMS of compounds **16** and **17** which show peaks corresponding to the free ligands (LH^+, 100%) at 317.19 and 373.29 (Fig. 3.9 and 3.10), respectively for the compounds **11 and 12** and no peak corresponding to the compounds **16** and **17**. This shows that the compounds are dissociated in solution. The C, H and N analysis revealed that the metal to ligand ratio is 1:2 in the compounds in the solid state.

The structures for the compounds $[La(NO_3)_3(^iPr_2NCOCH_2SCH_2CON^iPr_2)_2(H_2O)]$ and $[La(NO_3)_3(^iBu_2NCOCH_2SCH_2CON^iBu_2)]$ were determined using X-ray diffraction methods and confirm the IR spectral analysis results. The structures of the compounds $[La(NO_3)_3(^iPr_2NCOCH_2SCH_2CON^iPr_2)_2]$ and $[La(NO_3)_3[(^iBu_2NCOCH_2SCH_2CON^iBu_2)_2]$ are shown in Fig. 3.11 and 3.12, respectively and the relevant bond distances and angles are given in Table 3.4. These structures show that the thio-diglycolamide ligand bonds to lanthanum (III) nitrate in a bidentate chelating fashion through the carbamoyl oxygen atoms. They show further that the thioether group is uncoordinated. These structures are very similar to those of lanthanide nitrate–malonamide compounds reported in the literature [20-21]. The coordination number around lanthanum (III) is ten and the geometry is a distorted bicapped square-antiprism. The average La–O(NO_3) (2.642(3) Å in compound **16** and 2.636(7) Å in compound **17**) [20-22] and La–O(amide) (2.537(3) Å in **16** and 2.500(8) Å in compound **17**) [20-21] bond distances are normal and comparable to those of the reported values. The structural studies revealed that the thio-glycolamide ligand behaves in a similar fashion to the malonamide ligands in its coordination behavior. The eight member metallocyclic ring has a boat conformation with La–S distances of 5.05–5.07 Å.

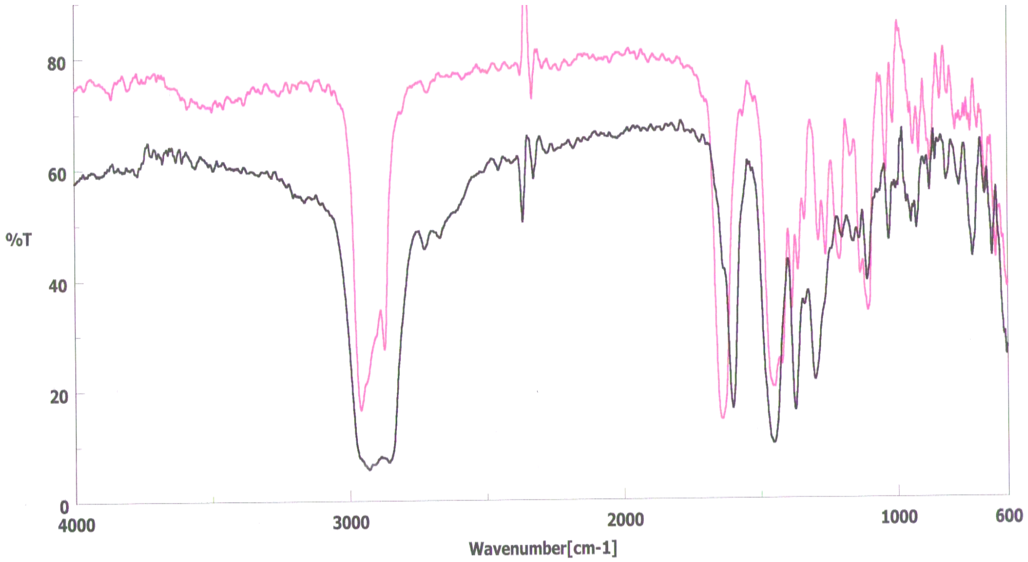

Fig. 3.7 IR spectra of ligand **11** (red color) and the compound **17**

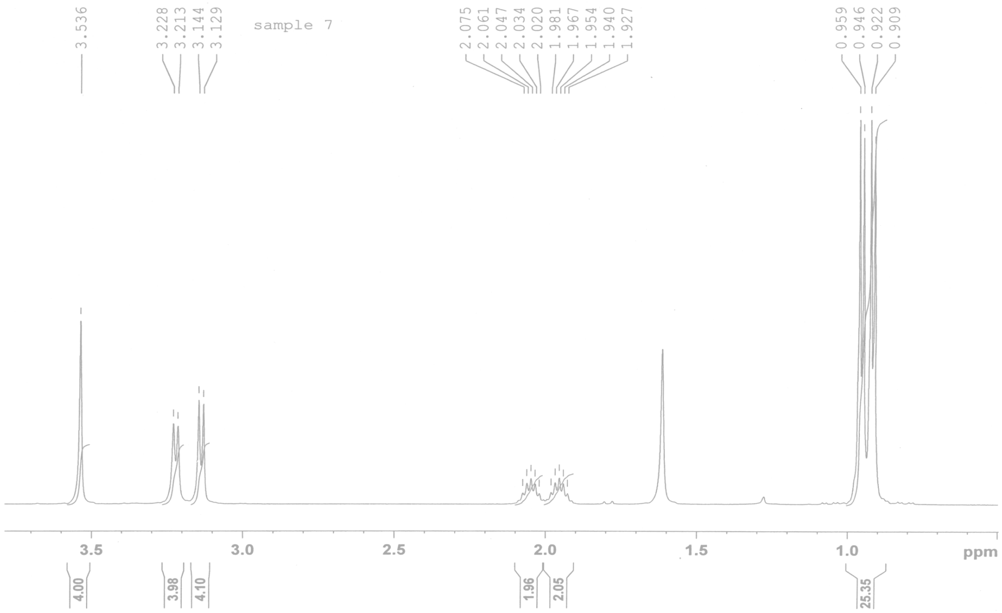

Fig. 3.8 ^{1}HNMR spectra of compound **17**

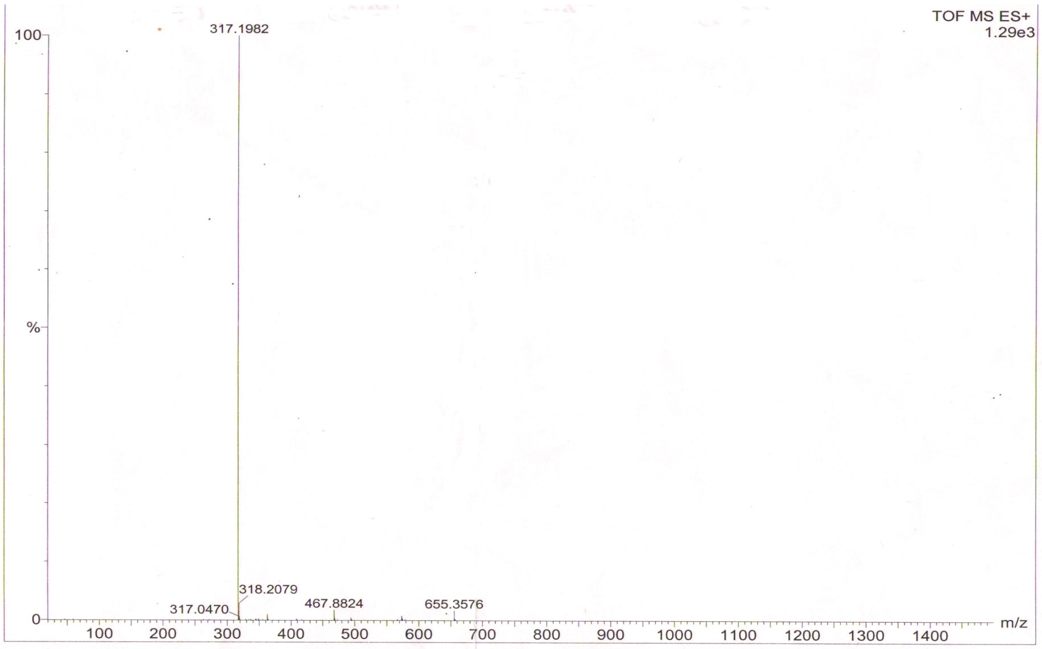

Fig. 3.9 ESI-MS spectrum of compound **16**

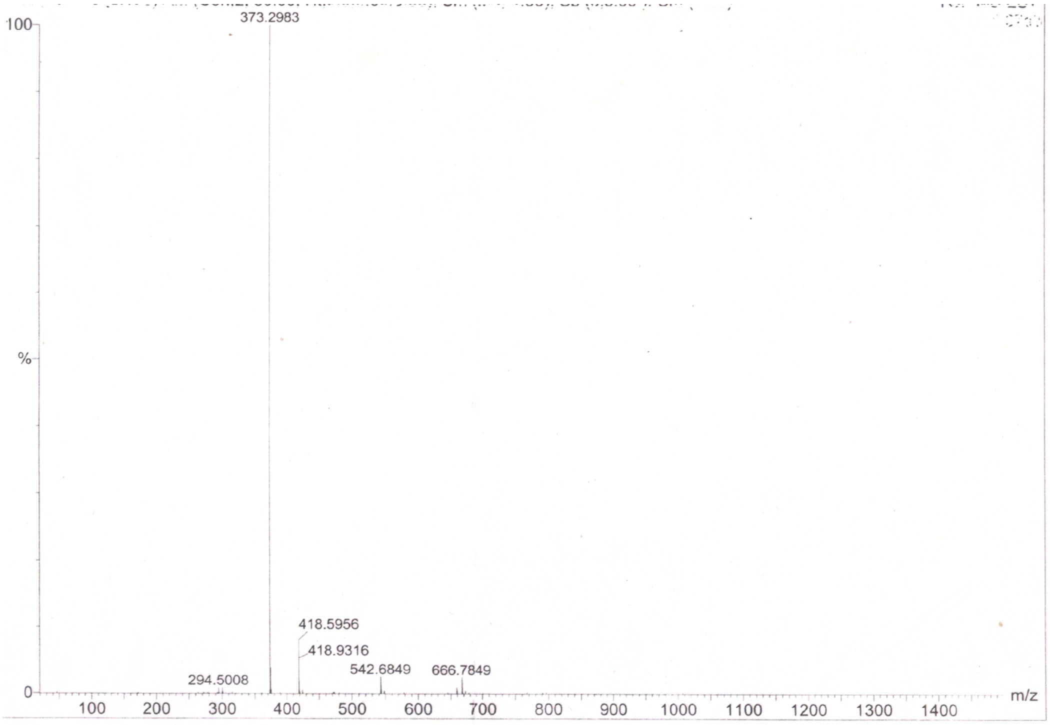

Fig.3.10 ESI-MS spectra of compound **17**

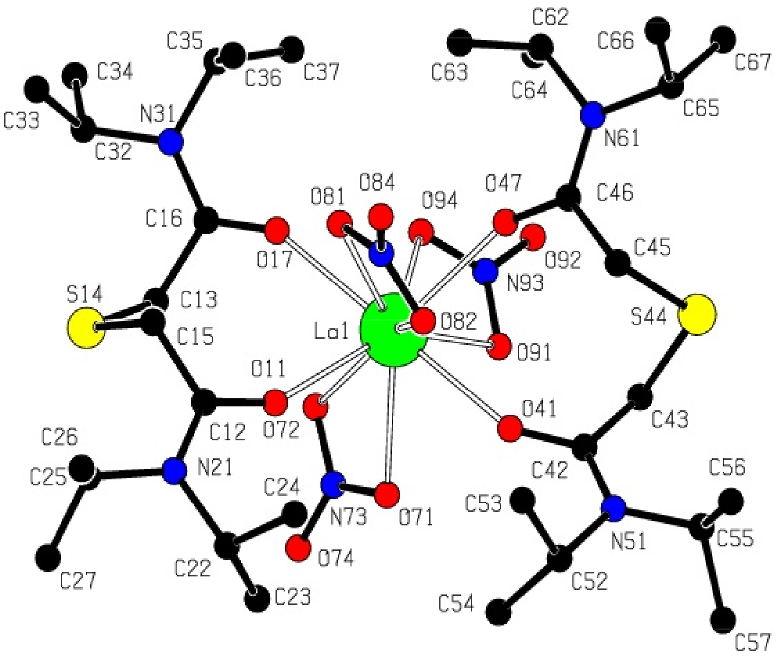

Fig. 3.11 Molecular structure of compound **16** (hydrogen atoms omitted for clarity)

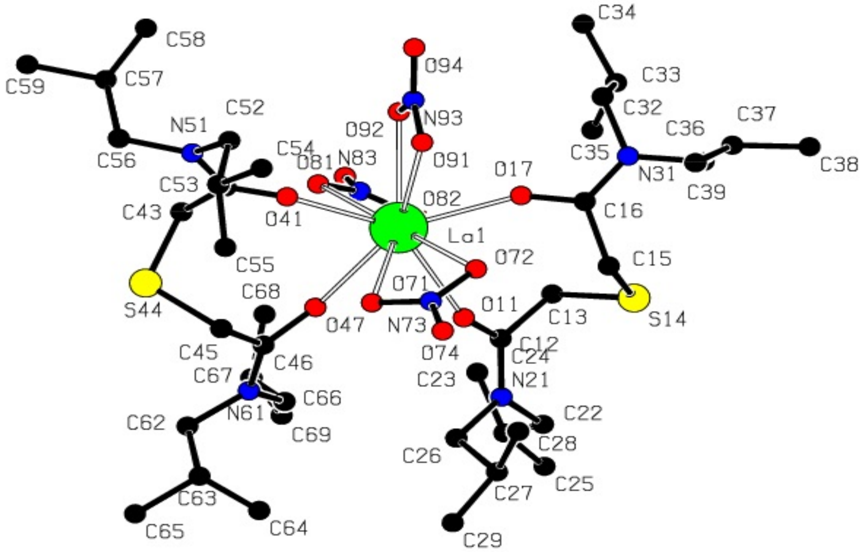

Fig. 3.12 Molecular structure of compound **17** (hydrogen atoms omitted for clarity)

3.3.1.4 Solvent extraction studies

The distribution ratio for uranium and americium was determined with thioglycolamide ligand **11** (0.2 M) in different diluents such as, chloroform, toluene, decanol and nitrobenzene from 1 M HNO_3 (Table.3. 5). These data indicate that the thio-glycolamide ligand shows an appreciable extraction for uranium in both chloroform and toluene and poor extraction in decanol and nitrobenzene. It indicates clearly that the thio-diglycolamide is bonded to uranyl nitrate in solution (chloroform or toluene) and is responsible for the extraction. This is supported by the observed ^{1}H NMR spectrum of the compound **14**, which shows a downfield shift for the CH_2 protons adjacent to the donor centres. The ligand did not show any extraction capability for Am(III) in all for diluents studied. It indicates that there is no bonding or only very week interaction between metal and ligand in all diluents studied. The ^{1}H NMR and ESI-MS data for the chemically similar lanthanum compound **17** in chloroform supports this observation. The observed distribution data for uranyl and Am(III) from nitric acid medium in all the diluents clearly indicate that the thio-glycolamide behaves similar to that of glutaramide in its extraction behavior [10].

Table 3.4 Important bond distances (Å) and angles (L) for compounds **16** and **17**

	16		
La(1)–O(11)	2.518(3)	La(1)–O(17)	2.554(3)
La(1)–O(81)	2.643(3)	La(1)–O(82)	2.678(3)
La(1)–O(91)	2.628(3)	La(1)–O(94)	2.611(3)
La(1)–O(71)	2.662(3)	La(1)–O(72)	2.632(3)
La(1)–O(41)	2.570(3)	La(1)–O(47)	2.509(3)
O(11)–La(1)–O(17)	77.89(10)	O(41)–La(1)–O(47)	77.38(9)
O(71)–La(1)–O(72)	48.80(10)	O(81)–La(1)–O(82)	47.84(9)
O(91)–La(1)–O(94)	48.94(10)	O(17)–La(1)–O(41)	176.68(10)
	17		
La(1)–O(11)	2.500(8)	La(1)–O(17)	2.494(6)
La(1)–O(81)	2.678(6)	La(1)–O(82)	2.610(7)
La(1)–O(91)	2.651(7)	La(1)–O(92)	2.588(7)
La(1)–O(71)	2.628(8)	La(1)–O(72)	2.661(7)
La(1)–O(41)	2.478(7)	La(1)–O(47)	2.528(7)
O(11)–La(1)–O(17)	73.3(2)	O(41)–La(1)–O(47)	76.1(2)
O(71)–La(1)–O(72)	48.1(2)	O(81)–La(1)–O(82)	47.8(2)
O(91)–La(1)–O(92)	49.2(2)	O(72)–La(1)–O(81)	178.0(2)

Table 3.5 Distribution ratio (D) for U(VI) and Am(III) with compound **11** in different diluents

Metal ion	Chloroform	Toluene	Decanol	Nitrobenzene
U(VI)	2.0	1.4	0.2	negligible
Am(III)	5.2×10^{-4}	$3.1\text{x}10^{-4}$	$4.8\text{x}10^{-3}$	negligible

Aqueous phase = 1 M HNO_3

Our observed distribution data for Am(III) from nitric acid medium is completely different to those data reported by Sasaki et al. for a similar type of ligand, when the extraction was carried out from an non-complexing perchloric acid medium [12–14]. The observed extraction for Am(III) or Ln(III) from perchloric acid may be due the presence of strong bonding between thio-glycolamide and Am(III) in solution in the absence of the strongly complexing nitrate ion.

3.3.2 Chemistry of N, N, N’, N’-tetra -isobutyl-3-sulfoxo -diglycolamide ligand

3.3.2.1 Synthesis of $[(^{i}C_4H_9)_2NCOCH_2SOCH_2CON(^{i}C_4H_9)_2]$ *(compound* **19***)*

Reaction of $[(^{i}C_4H_9)_2NCOCH_2SCH_2CON(^{i}C_4H_9)_2]$ with H_2O_2/SeO_2 in methanol yielded the corresponding N, N,N’,N’-tetraisobutyl-3-sulfoxide pentanediamide quantitatively. The IR spectrum (Fig.3.13) shows the presence of both the carbamoyl (ν_{CO}= 1654, 1625 cm^{-1}) and sulfoxo (ν_{SO}= 1049 cm^{-1}) groups in the synthesized ligand. The ^{1}HNMR (Fig.3.14) spectrum shows the expected peak multiplicities and integration. The SO–CH$_2$–CO protons show two doublets due to their diastereotropic nature in agreement with the earlier reported results [4, 18]. C, H, and N analyses support the expected stoichiometry for the ligand.

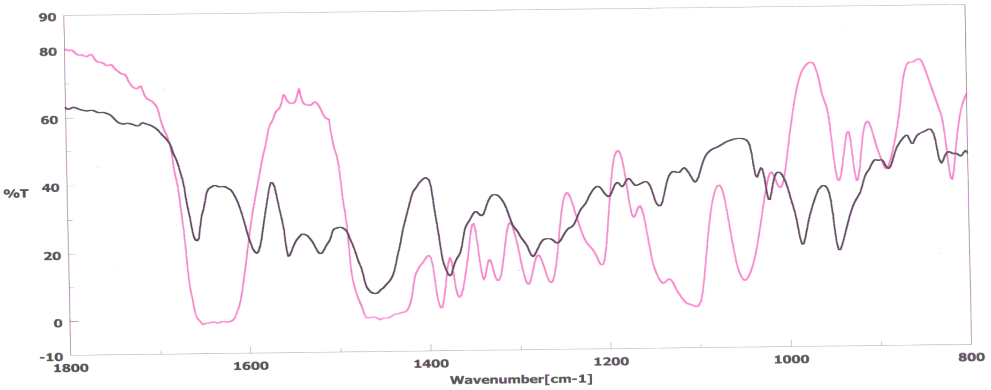

Fig.3.13 IR spectra of ligand **11 (**red color) and compound **19**

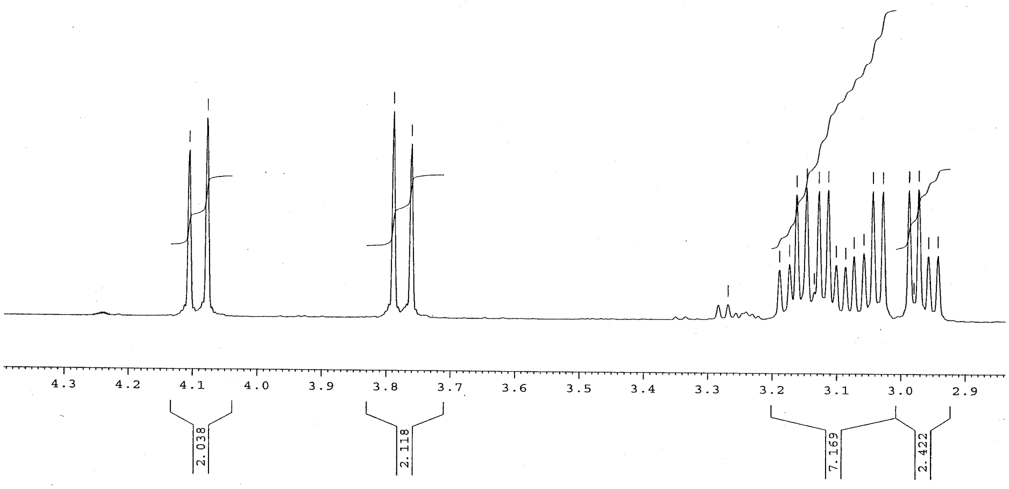

Fig. 3.14 ^{1}HNMR spectra of ligand **19**

3.3.2.2 Synthesis of [$UO_2(NO_3)_2\{(^iC_4H_9)_2NCOCH_2SOCH_2CON(^iC_4H_9)_2\}$]

(compound **20***)*

Reaction of [$UO_2(NO_3)_2.6H_2O$] with the [$(^iC_4H_9)_2NCOCH_2SCH_2CON(^iC_4H_9)_2$] in CH_2Cl_2 yielded [$UO_2(NO_3)_2\{(^iC_4H_9)_2NCOCH_2SOCH_2CON(^iC_4H_9)_2\}$]). The IR spectrum (Fig. 3.13) of compound **20** shows the observed frequency differences for the sulfoxo ($\Delta\nu_{SO}$= 66 cm^{-1}, where $\Delta\nu_{SO} = \nu_{SO(\text{free ligand})} - \nu_{SO(\text{complex})}$) and carbamoyl groups ($\Delta\nu_{CO}$ = 30–50 cm^{-1}, where $\Delta_{CO} = \nu_{CO(\text{free ligand})} - \nu_{CO(\text{complex})}$) are consistent with direct bonding of sulfoxo and carbamoyl to uranyl. Similar differences are also observed in compounds of sulfoxides or amides with uranyl nitrate such as [$UO_2(NO_3)_2C_6H_5SOCH_2CON(C_4H_9)_2$] [18], [$UO_2(NO_3)_2$ $(^iPrO)_2POCH_2SO$ (p-MeC_6H_4)] [23] [$UO_2(NO_3)_2(^iC_3H_7CON$ $\{^iC_4H_9\}_2)_2$] [24], and [$UO_2(NO_3)_2(^iC_3H_7)_2$ $NCOCH_2$ $CON(^iC_3H_7)_2$] [25]. ^{1}H NMR of compound **20** (Fig.3.15) shows that the CH_2 protons are deshielded by 0.5–1.0 ppm with respect to the free ligand, indicating that the ligand is bonded to the metal center in solution also. C, H, and N analyses revealed that the metal to ligand ratio is 1:1. The structure of [$UO_2(NO_3)_2(^iBu_2NCOCH_2SOCH_2CON^iBu_2)$] was determined using X-ray diffraction methods and confirms the spectral and analysis results.

The structure of compound **20** is shown in Fig.3.16 and selected interatomic bond distances are given in Table.3.6. The structure shows that bis(carbamoyl methyl) sulfoxide bonds to uranyl nitrate in a bidentate chelating fashion through the carbamoyl and sulfoxo oxygens. It shows further that one carbamoyl O(14) is uncoordinated. This structure is very similar to that reported for the uranyl nitrate–carbamoylmethyl sulfoxide compound $[UO_2(NO_3)_2(C_6H_5SOCH_2CON(C_4H_9)_2]$ [4], in which the carbamoylmethyl sulfoxide is bidentate chelating, bonding through both the carbomoyl and sulfoxo oxygens.

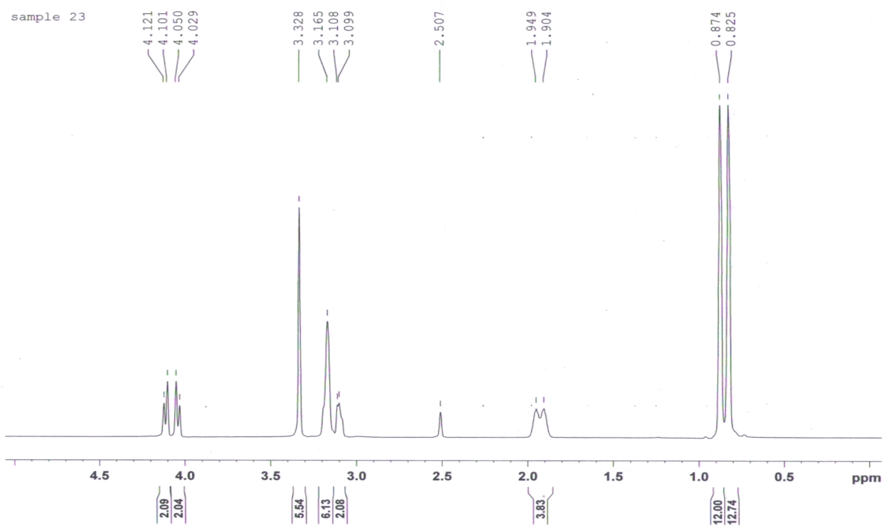

Fig. 3.15 ^{1}HNMR spectra of compound **20**

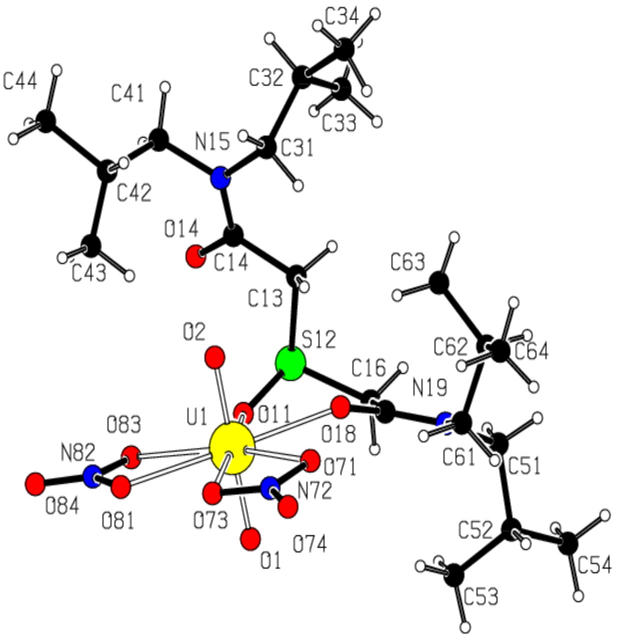

Fig. 3.16 Molecular structure of compound **20**

Table 3.6 Important bond distances (Å) and angles (°) for compound **20**

U(1)–O(11)	2.399(5)	U(1)–O(18)	2.397(6)
U(1)–O(71)	2.522(5)	U(1)–O(73)	2.539(5)
U(1)–O(81)	2.501(6)	U(1)–O(83)	2.517(6)
U(1)–O(1)	1.717(7)	U(1)–O(2)	1.716(7)
O(2)–U(1)–O(1)	179.3(2)	O(81)–U(1)–O(83)	50.9(2)
O(2)–U(1)–O(18)	87.5(2)	O(18)–U(1)–O(71)	64.7(2)
O(18)–U(1)–O(11)	69.7(2)	O(81)–U(1)–O(73)	60.6(2)
O(11)–U(1)–O(83)	64.1(2)	O(71)–U(1)–O(73)	50.3(2)

The coordination number around uranium (VI) in compound **20** is eight in a hexagonal bipyramid. Four oxygen atoms from two nitrates and two oxygen atoms from bis(carbamoyl methyl) sulfoxide form the planar hexagon. The two uranyl oxygen atoms occupy the axial positions. The r.m.s of the six fitted atoms is 0.0579 Å with the metal atom 0.023(3) Å from the plane.

The observed bond distance of 2.399(5) Å between uranium and sulfoxo O(11) is slightly shorter than those reported in [$UO_2(NO_3)_2C_6H_5SOCH_2CON(C_4H_9)_2$] [2.442(9)Å] [4] and [$UO_2(DBM)_2$PhSOPh)] [2.427(4)Å] [26], but longer than those reported in [$UO_2(NO_3)_2$(iPrO)$_2$POCH$_2$SO(p-MeC$_6$H$_4$)] [2.36(2)Å] [23] and [UO_2(DBM)$_2$ PhCH$_2$SOCH$_3$)] [2.375(6) Å] [27]. The observed U–O(amide) bond distance U–O(18) of 2.397(6) Å is slightly shorter than the distances of 2.41(2) Å in [$UO_2(NO_3)_2(iC_3H_7)_2$ NCOCH$_2$CON(iC$_3$H$_7$)$_2$] [28], 2.426(8) Å in [$UO_2(NO_3)_2$Ph{EtO}POCH$_2$CONEt$_2$], 2.404(5) Å in [$UO_2(NO_3)_2Ph_2POCH_2CONEt_2$] [17], 2.442(9)Å in [$UO_2(NO_3)_2$ $C_6H_5SOCH_2CON(C_4H_9)_2$] [4] and comparable in magnitude with the values of 2.364(7)–2.377(9) Å observed in [$UO_2(NO_3)_2(C_5H_7N_2CH_2CO^iBu_2)$] [29]. The average U=O and U–O(NO$_3$) bond distances of 1.717(7) Å and 2.501(6)–2.539(5) Å , respectively, agree well with those found in previously reported uranyl nitrate compounds [4, 15,17, 20-21, 26-27]. As is apparent from figure 3.16, some isopropyl groups show high anisotropy, although no disorder model was found to be appropriate. There are no intermolecular distances less than the sum of vanderwaal's radii.

3.3.2.3 Thermal studies

Thermogravimetric (TG) and differential thermal analyses (DTA) of the compound **20** were carried out to find out the product of the decomposition reaction. This compound decomposes in three steps to give U_3O_8 as the final product (identified from the powder X-ray diffraction pattern of the decomposition product) without any impurities. However, the decomposition product of phosphine oxide compounds of uranyl nitrate yielded the corresponding uranyl phosphate as a final product [30]. This observation clearly shows that the bis(carbamoyl methyl) sulfoxide ligands can be completely destroyed on incineration, as indeed can the amide ligands [28,29].

3.3.2.4. Electrospray ionization *mass spectrometric study*

Electrospray ionization mass spectrum (ESI–MS) of compound **20** was measured in methylene chloride (CH_2Cl_2) to establish the nature of compound formed in solution. The spectrum (Fig.3.17) shows many peaks and some of the peaks could be identified without any doubt. The peaks at the m/z values of 726.12, 717.6 (100%), 523.42 and 389.3 are assigned to the species $[UO_2(NO_3)_2L\text{-}C_4H_9+H]^+$, $[UO_2(NO_3)_2L\text{-}C_4H_9\text{-}NO_3+3H_2O]^+$, $[UO_2L_2]^{2+}$, and $[LH]^+$ (where L = $({}^iC_4H_9)_2NCOCH_2SOCH_2CON({}^iC_4H_9)_2$, respectively. This study shows clearly that the ligand retains its bonding with the metal ion in solution [4].

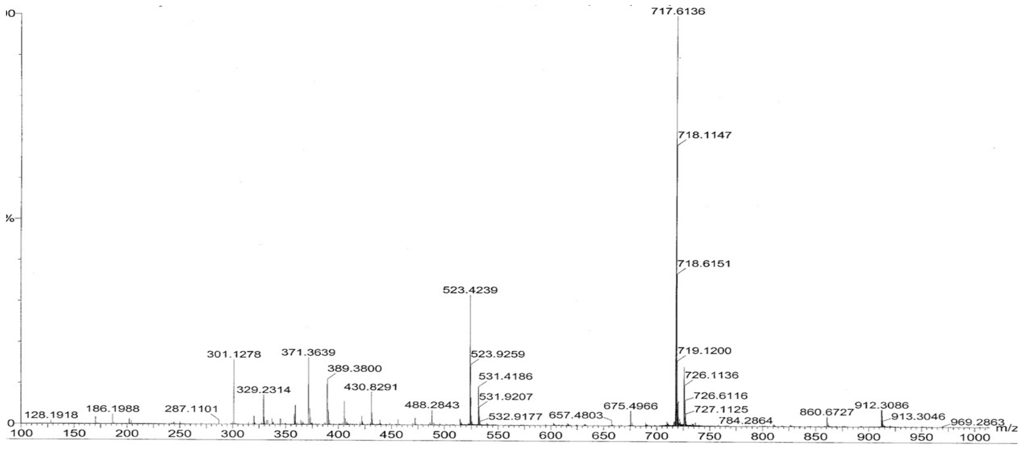

Fig. 3.17 ESI-MS spectra of compound **20**

3.3.3 Chemistry of N, N, N', N'-tetraalkyl-3-sulfone - diglycolamide ligand

3.3.3.1 Synthesis of $[({}^iC_4H_9)_2NCOCH_2SO_2CH_2CON({}^iC_4H_9)_2]$ *(* **21** *)*

Reaction of $[({}^iC_4H_9)_2NCOCH_2SCH_2CON({}^iC_4H_9)_2]$ with two equivalent of H_2O_2/SeO_2 in methanol yielded the corresponding bis(carbamoyl methyl) sulfone [$^iC_4H_9NCOCH_2SO_2$ $CH_2CON^iC_4H_9$], quantitatively. The IR spectrum (Fig. 3.18) of the ligand shows the presence of both the carbamoyl (ν_{CO} =1654, 1626 cm^{-1}) and sulfone (ν_{SO2} =1147, 1110 cm^{-1}) groups in the synthesized ligand. The ^{1}HNMR spectrum (Fig. 3.19) shows the expected peak multiplicities and integration. The SO_2–CH_2–CO protons showed a singlet at δ 4.50 ppm, indicating that the compound is pure and different from the starting sulfide or the intermediate sulfoxide [31-32]. The C, H, N analysis supports the expected stoichiometry for the ligand.

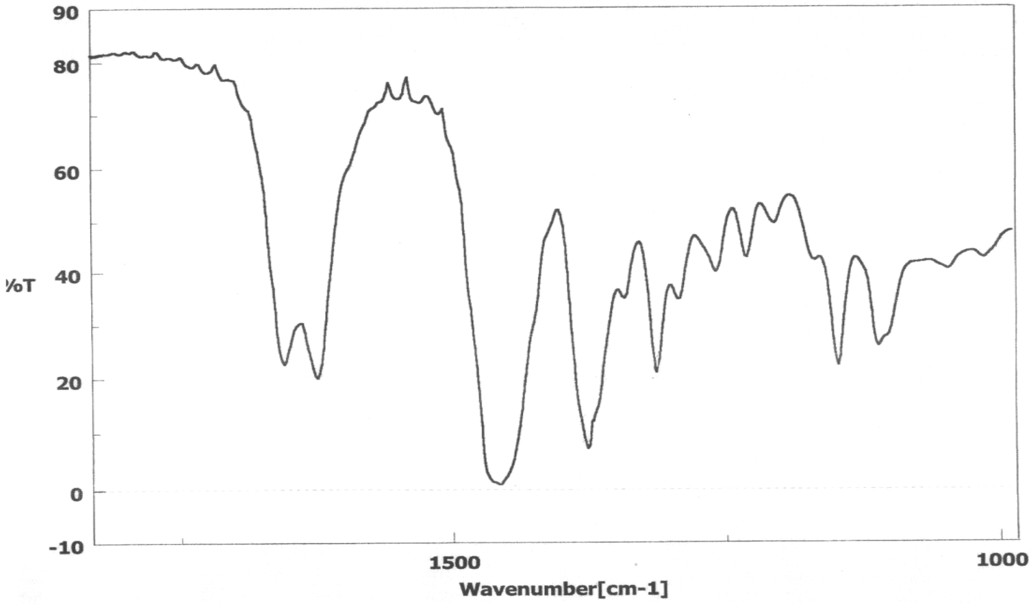

Fig. 3.18 IR spectrum of ligand **21**

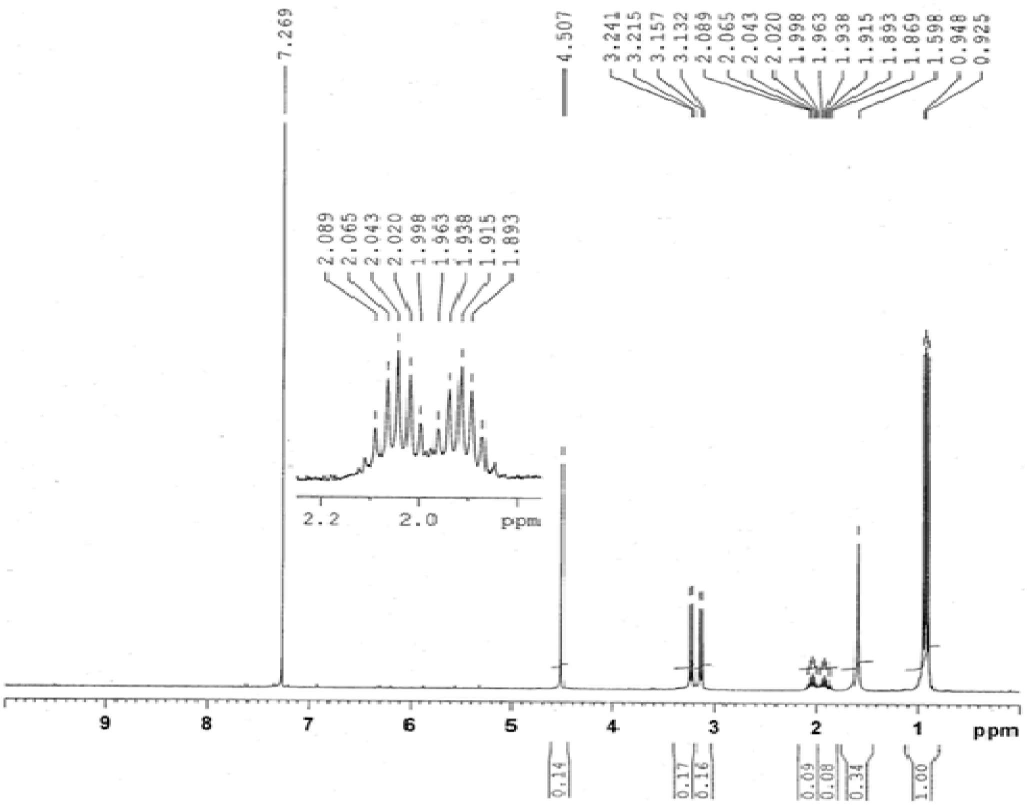

Fig. 3.19 ^{1}HNMR spectrum of ligand **21**

3.3.3.2 .Synthesis and structural studies of $[UO_2(NO_3)_2\{(^iC_4H_9)_2NCOCH_2SO_2CH_2CON(^iC_4H_9)_2\}]$ (compound **22***)*

Reaction of bis (carbamoyl mehyl) sulfone with uranyl nitrate yielded the compound **22** in good yield. The IR spectrum (Fig. 3.20) of the compound **22** shows that the water molecules from the starting compound $[UO_2(NO_3)_2.6H_2O]$ are completely replaced by the bis (carbamoyl methyl) sulfone ligand and that the ligand is bonded through the carbamoyl groups to the metal centre. The observed frequency difference for the carbamoyl group ($\Delta\nu_{CO}$ =30 cm^{-1}, where $\Delta\nu_{CO} = \nu_{CO(\text{free ligand})} - \nu_{CO(\text{complex})}$) is consistent with the fact that the carbamoyl group is bonded directly to the uranyl group. Similar differences are also observed in compounds of amides with uranyl nitrate such as; $[UO_2(NO_3)_2(^iC_3H_7)_2NCOCH_2CON(^iC_3H_7)_2]$ [16] and $[UO_2(NO_3)_2.(^iC_3H_7CON$

$\{^iC_4H_9\}_2)_2]$ [15]. The ^{1}H NMR spectrum (Fig. 3.21) of the compound **22** shows the expected peaks and multiplicities. The SO_2–CH_2–CO protons are deshielded by ca. 0.23 ppm with respect free ligand indicating that the bonding between metal and ligand in solution. The C, H and N analysis revealed that the metal to ligand ratio is 1:1 in the reported compound. The structure of the compound **22** was determined using X-ray diffraction [33-35] methods and confirms the spectral and analysis results.

The structure of the compound **22** is shown in Fig. 3.22and selected interatomic bond distances and angles are given in Table.3.7. The structure shows that the bis (carbamoylmethyl) sulfone ligand bonds to uranyl nitrate in a bidentate chelating fashion through both the carbamoyl oxygen atoms. It shows further that the sulfone group is uncoordinated. This may be due to the fact that the sulfone group is a poor donor towards the metal centre compared to that of the amide group and therefore the coordination of both the carbamoyl groups to the uranyl ion is observed in compound **22.** In addition that the sulfoxide group is a better donor towards the metal centre compared to that of sulfone group and therefore the coordination of sulfoxide and carbamoyl groups to uranyl ion is seen with ligand (Fig.1e) [32].

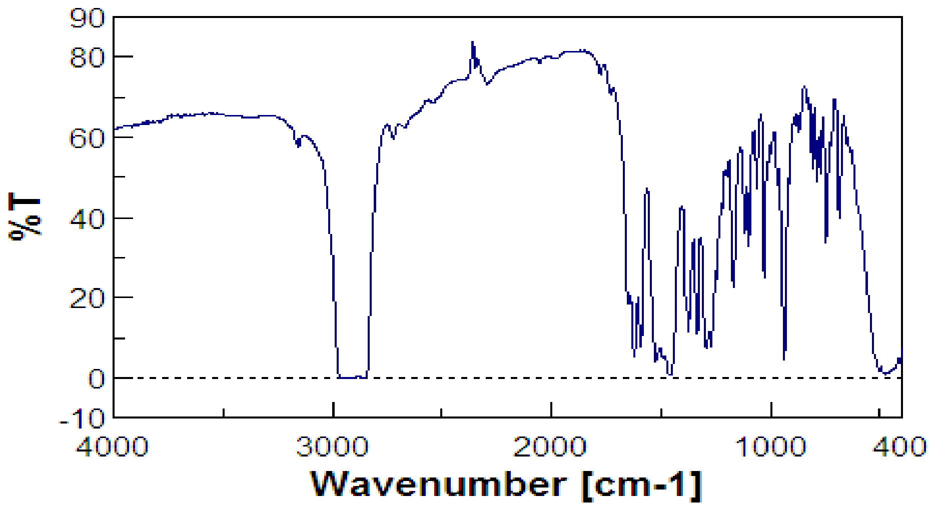

Fig. 3.20 IR spectrum of compound **22**

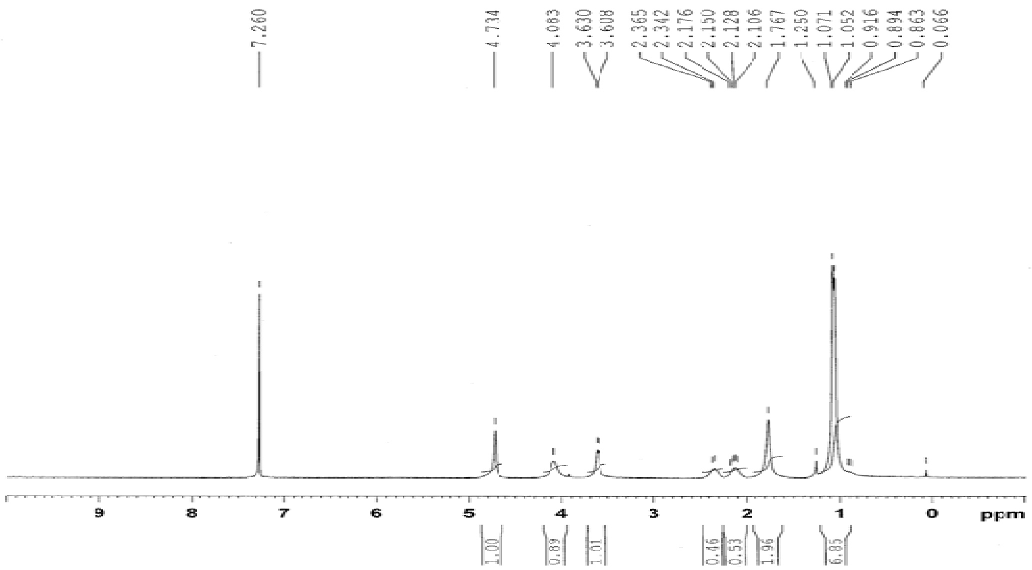

Fig. 3.21 ^{1}HNMR spectrum of compound **22**

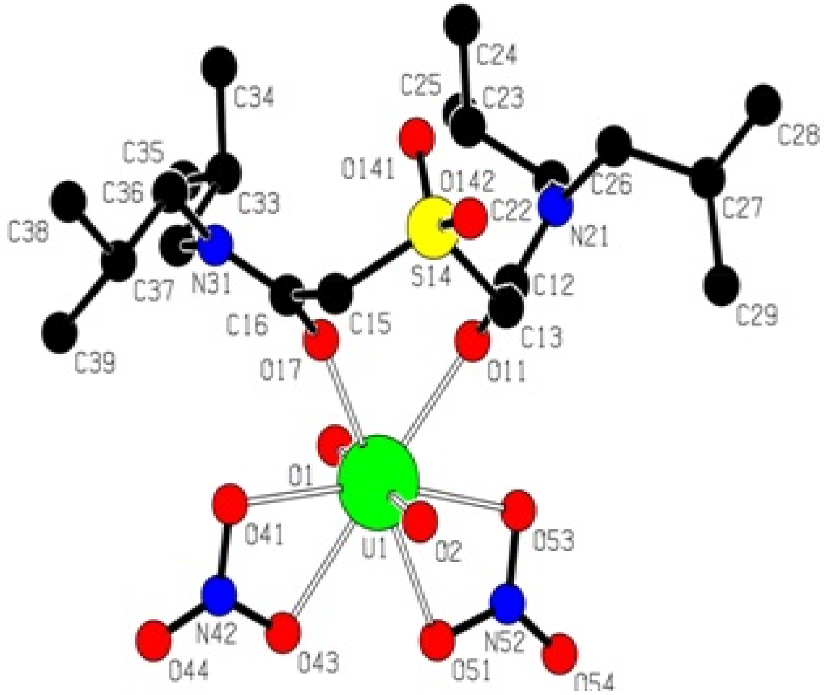

Fig. 3.22 Molecular structure of compound **22** (hydrogen atoms are not shown for clarity).

Table 3.7 Important bond distances (Å) and angles (°) for compound **22**

U(1)–O(41)	2.510(4)	U(1)–O(11)	2.405(3)
U(1)–O(43)	2.505(3)	U(1)–O(17)	2.363(3)
U(1)–O(51)	2.507(3)	U(1)–O(53)	2.520(3)
U(1)–O(1)	1.747(3)	U(1)–O(2)	1.753(3)
O(2)–U(1)–O(1)	179.23(16)	O(17)–U(1)–O(41)	64.99(12)
O(2)–U(1)–O(11)	90.63(14)	O(11)–U(1)–O(53)	64.94(11)
O(17)–U(1)–O(11)	66.60(12)	O(51)–U(1)–O(53)	50.59(11)
O(43)–U(1)–O(51)	62.35(12)	O(41)–U(1)–O(43)	50.85(12)

The structure of compound **22** is very similar to that reported for the uranyl nitrate–malanoamide complex $[UO_2(NO_3)_2(^iC_3H_7)_2NCOCH_2CON(^iC_3H_7)_2]$ [16] and the bis(carbamoylmethyl) sulfide complex $[UO_2(NO_3)_2\ (^iBu_2NCOCH_2SCH_2CON^iBu_2)]$ [31], in which the malonamide or bis (carbamoylmethyl) sulfide acts as a bidentate chelating ligand and bonds through both the carbomoyl oxygen atoms to the uranyl nitrate. The coordination number around uranium (VI) in 1 is eight and the geometry is hexagonal bipyramidal. Four oxygen atoms from two nitrates and two oxygen atoms from the bis(carbamoylmethyl) sulfone ligand form the planar hexagon. The two uranyl oxygen atoms occupy the axial positions. The r. m. s of the six fitted atoms is 0.065 Å with the metal atom 0.004(2)Å from the plane. The observed average U–O(amide) bond distance 2.384(3)Å) is slightly shorter than the distances of 2.41(2)Å in $[UO_2(NO_3)_2(^iC_3H_7)_2NCOCH_2CON(^iC_3H_7)_2]$ [16], 2.426(8)Å in $[UO_2(NO_3)_2Ph\{EtOPOCH_2CONEt_2]$,2.404(5)Å in $[UO_2(NO_3)_2Ph_2POCH_2CONEt_2]$ [17] , 2.442(9)Å in $[UO_2(NO_3)_2C_6H_5\ SOCH_2CON(C_4H_9)_2]$ [18] and comparable in magnitude with values of 2.364(7)–2.377(9)Å observed in $[UO_2(NO_3)_2(C_5H_7N_2CH_2CO^iBu_2]$ [29]. The average U=O and U–O(NO_3) bond distances of 1.750(3) and 2.510(4)Å respectively are normal and agreeing well with those found in previously reported uranyl nitrate neutral ligand compounds [5, 10, 15-16, 17-18, 29, 32].

3.3.3.3 Thermal studies

The simultaneous thermogravimetry (TGA) and differential thermal analyses (DTA) for compound **22** were recorded on Mettler TG/DTA instrument under a flow of air at the heating rate of 10 °C/min. This compound decomposes in three steps to give U_3O_8 as a final product (identified from the powder X-ray diffraction pattern of the decomposition product) without any other impurities. This observation clearly shows that the bis (carbamoyl methyl) sulfone ligands can be completely destroyed on incineration, as indeed can the amide ligands [15-16, 36].

3.3.3.4 Electrospray ionization *mass spectrometric study*

Electrospray ionization mass spectrometric detection of positive ions for the compound **22** in CH_2Cl_2 shows (Fig.3.23) many peaks and some of the peaks could be unambiguously identified. The peaks at the m/z values of 1141.03, 741.1(100%), 736.57, 539.48 and 405.4 are assigned to the species $[UO_2(NO_3)L_2+H]^+$, $[UO_2(NO_3)_2L–C_4H_9]^+$, $[UO_2(NO_3)L]^+$, $[UO_2L_2]^{2+}$ and $[LH]^+$ (where L= $^iC_4H_9NCOCH_2SO_2CH_2CON^iC_4H_9$) respectively. This study shows clearly that the ligand retains its bonding with the metal ion in solution and also that the compound undergoes disproportionation to give a mixture of 1:1 and 1:2 complexes [18].

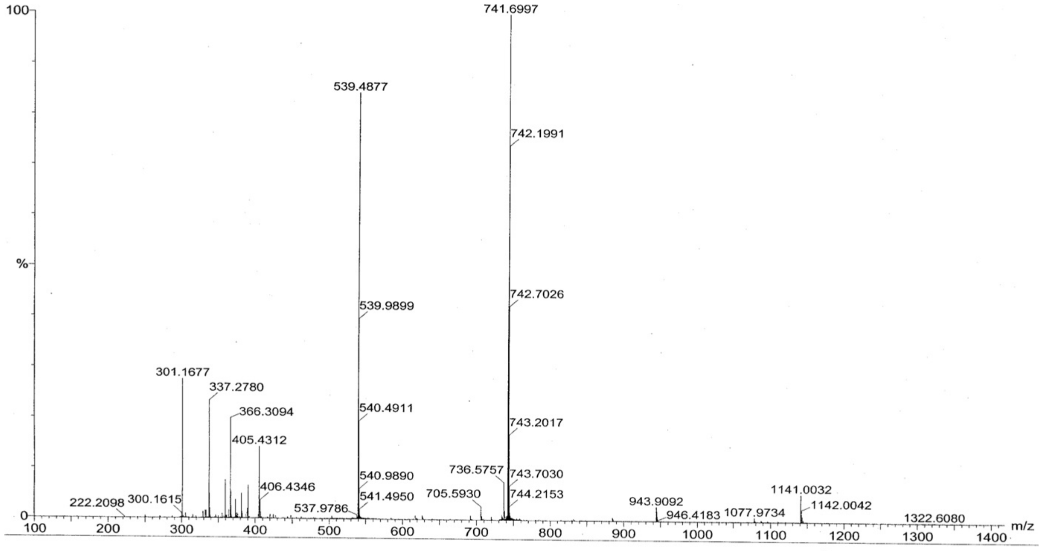

Fig.3.23 ESI-MS spectra of compound **22**

3.4 Conclusions

3.4.1 Chemistry of thiodiglycolamide ligands

New class of tri-functional ligands thiodiglycolamide have been synthesized and their coordination chemistry with the uranyl and lanthanum(III) nitrates is studied using IR, ^{1}H NMR spectroscopy and elemental analysis methods. The structural studies reveled that the ligands behave similarly to those of malonamides in solid state. In all cases, these ligands act as bidentate chelating ligand and bond through both the carbamoyl oxygen atoms to metal centre. The solvent extraction studies from nitric acid medium show that thio-diglycolamide ligand behaves very similarly to those of glutaramide ligand in solution. This ligand extract U(VI) and Pu(IV) from nitric acid medium and show negligible extraction for Am(III) from the same medium.

3.4.2 Chemistry of N, N, N’, N’-tetra-isobutyl-3-sulfoxo-diglycolamide ligand

The coordination chemistry of a new tri-functional ligand, bis(carbamoylmethyl) sulfoxide with uranyl nitrate shows that it acts as a bidentate chelating ligand and bonds through sulfoxo and one of carbamoyl oxygen atoms to uranyl group. The ESI-MS study in CH_2Cl_2 revealed that the ligand retains its bonding with uranyl ion in solution. The TG/DTA study shows that the ligand is completely incinerable on heating.

3.4.3 Chemistry of N, N, N', N'-tetra-isobutyl-3-sulfone-diglycolamide ligand

The coordination chemistry of new tri-functional ligand, bis (carbamoylmethyl) sulfone with uranyl nitrate shows that it acts as a bidentate chelating ligand and bonds through both the carbamoyl oxygen atoms to metal centre. The electrospray mass spectrometric study in CH_2Cl_2 revealed that the ligand retains its bonding with uranyl ion in solution also. The TG/DTA study shows that the ligand is completely incinerable on heating.

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CHAPTER 4

Synthesis and structural studies of 1,1'-bis (diphenylphosphine oxide) ferrocene uranyl complexes

CHAPTER 4

4.1 Introduction

In recent years, considerable research interests in the 3d-4f and 3d-5f bimetallic complexes due to their catalytic, semi-conductive and magnetic properties [1-5]. There are several reports on the 3d -5f metal ion complexes [6-14], however, no report on the complex chemistry of 1,1'-bis(diphenylphosphine oxide) ferrocene with any of the 5f metal ions in literature and only one report on the 4f metal ions [15], though this ligand has a 3d metal centre (Fe(II)) with two potential phosphine oxide groups. The phosphine oxide group is well known for its strong complexing ability towards the lanthanide [15-17] and actinide [18-23] ions. Uranyl dihalide complexes of the type $UO_2X_2L_2$ (where L is $OPPh_3$ or iso-butyramide; X = Cl or Br) [21-24] were used as precursors in the uranyl complex chemistry and having an octahedral geometry. These complexes normally exist in the *trans* isomeric form with a linear X-M-X bonds. There are few structurally characterized uranyl dihalide complexes, where the two halides situated at an equatorial site with an X-M-X bond angle more than 90° [25-29]. The reaction of bidentate chelating ligands with the uranyl dihalides forms binuclear complexes containing both bridging and terminal halides [30], instead of mononuclear complexes. The reason for the same may be due to the fact that a simple bidentate chelating ligand might not coordinatively satisfy a larger uranyl centre that often accommodates five donor groups in the equatorial plane. The 1,1'-bis (diphenylphosphine oxide) ferrocene ligand shows a wide variety of coordination geometries with the transition metals [31-35], lanthanide [15] ions, with the bite angles ranging from 71.5°- 154°. Due this unique property, the 1,1'-bis(diphenylphosphine oxide) ferrocene ligand is expected to form a mononuclear *cis*-uranyl dihalide complex, without any solvent participation or dimerization, by suitably adjusting the bite angle.

A systematic work on the complex chemistry of 1,1'-bis(diphenylphosphine oxide) ferrocene (DPPOF) with uranyl nitrate and uranyl chloride is carried out in the present investigation and the results are reported herein.

4.2 Experimental

4.2.1 Synthesis of $[(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2.2H_2O]$ (DPPOF.2H$_2$O)

To a clear solution of 1,1'-bis(diphenylphosphine) ferrocene (DPPF) (5 g, 9.02 mol) in benzene (100 mol), H_2O_2 (5 mL of 30% H_2O_2) was added with stirring slowly. The solution precipitated orange colored powder on stirring about 10 min. The solution was allowed to stir for another 30 min and the solid was filtered, washed with benzene and dried. The product was crystallized from ethanol (95%) as a yellow crystalline solid (yield, 4.6 g, 92%). Elemental Analysis Calculated for $C_{34}H_{28}P_2O_2Fe.2H_2O$ (%): C=65.5; H=5.2. Found: C=65.3; H=5.7. IR (Nujol mull, ν/ cm^{-1}): 3519, 3194 (OH of H_2O); 1153 (PO). ^1H NMR ($CDCl_3$, δ ppm): 4.29 (d, ^3J (HH) = 6 Hz, 4H, CpH_α); 4.74 (d, ^3J (HH) = 6 Hz, 4H, CpH_β); 7.36–7.47 (m, 10H, C_6H_5), 7.59–7.63 (m, 10H, C_6H_5). $^{31}P\{^1H\}$($CDCl_3$, δ ppm): 28.2 (s).

4.2.2 Synthesis of $[UO_2(NO_3)_2$ DPPOF] (compound **23***)*

To a methanolic solution of $[UO_2(NO_3)_2.(^iC_3H_7CON\{^iC_4H_9\}_2)_2]$ (300 mg, 0.378 mmol), methanolic solution of DPPOF (222 mg, 0. 378 mmol) was added slowly from the side. The solution was kept aside for overnight without disturbing. This process deposited brownish colored crystalline product, which was filtered, washed with methanol and dried (yield, 320 mg, 86%). Elemental Analysis Calculated for $C_{34}H_{28}P_2O_{10}N_2FeU$ (%): C=41.6; H=2.9; N=2.9. Found: C=40.8; H=3.1; N=2.6 IR (Nujol mull, ν/ cm^{-1}): 1523, 1294, 1272 (NO_3); 1133 (PO); 923 (O=U=O). ^1H NMR (CD_3CN, δ ppm): 4.25 (br, 4H,

CpH_α); 4.71 (br, 4H, CpH_β); 7.30-7.80 (d, 20H, C_6H_5). $^{31}P\ \{^1H\}$ (DMSO-d_6, δ ppm): 25.2 (s)

*4.2.3 Synthesis of cis-[UO_2Cl_2 DPPOF] (compound **24**)*

To a methanolic solution of $[UO_2Cl_2(^iC_3H_7CON\{^iC_4H_9\}_2)_2]$ (400 mg, 0.541 mmol), a solution of DPPOF (320 mg, 0. 546 mmol) in methanol was added slowly. The solution was kept undisturbed overnight. This process deposited brownish colored crystalline product, which was filtered, washed with cold methanol and dried. (Yield, 475 mg, 95%). Elemental Analysis Calculated for $C_{34}H_{28}P_2O_4Cl_2FeU$ (%): C=44.0; H=3.0. Found. C=44.1; H=2.9. IR(Nujol mull, ν/ cm^{-1}) : 1130 (PO); 916(O=U=O). $^{31}P\{^1H\}$(DMSO-d_6, δ ppm): 28.1 (s). ^1H NMR (CD_3CN, δ ppm) : 4.40(br, 4H, C_5H_4), 4.65(br, 4H, C_5H_4), 7.40-7.60 (d, 20H, C_6H_5).

4.2.4 X-ray crystallography

Selected crystallographic data for the compounds **23** and **24** are summarized in Table 4.1.

4.3 Results and discussion

4.3.1 Synthesis and structural studies of 1, 1'-bis(diphenylphosphine oxide) ferrocene-uranyl nitrate complex.

The reaction of N,N'-di-butyl isobutyramide uranyl(VI) nitrate with 1,1'-bis(diphenylphosphine oxide) ferrocene (DPPOF) in methanol yielded the compound $[UO_2(NO_3)_2(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2]$. The IR spectrum of the compound shows (Fig.4.1) that the amide molecules from the starting compound

$[UO_2(NO_3)_2\,({}^iC_3H_7CON\,\{{}^iC_4H_9\}_2)_2]$ are replaced completely by the DPPOF ligand. It suggests further, that the ligand coordinates through both the phosphine oxide oxygen atoms to the uranyl group ($\Delta\nu_{PO}$ = 58 cm^{-1}). The $^{31}P\ \{^1H\}$ NMR spectrum (Fig.4. 2) shows a single resonance at 25.2 ppm for the compound and is different from that of the free ligand. This shows clearly that both PO groups are bonded to the metal center in the compound. The ^1H NMR spectrum (Fig.4.3) shows the expected peaks and multiplicities for the C_5H_4 and C_6H_5 protons of the DPPOF in the ligand and the compound. The carbon, hydrogen and nitrogen analysis revealed that the ratio of $UO_2(NO_3)_2$ to DPPOF is 1:1 in the compound. The structure of compound was determined by X-ray diffraction methods and confirms the chelating mode of coordination for this ligand.

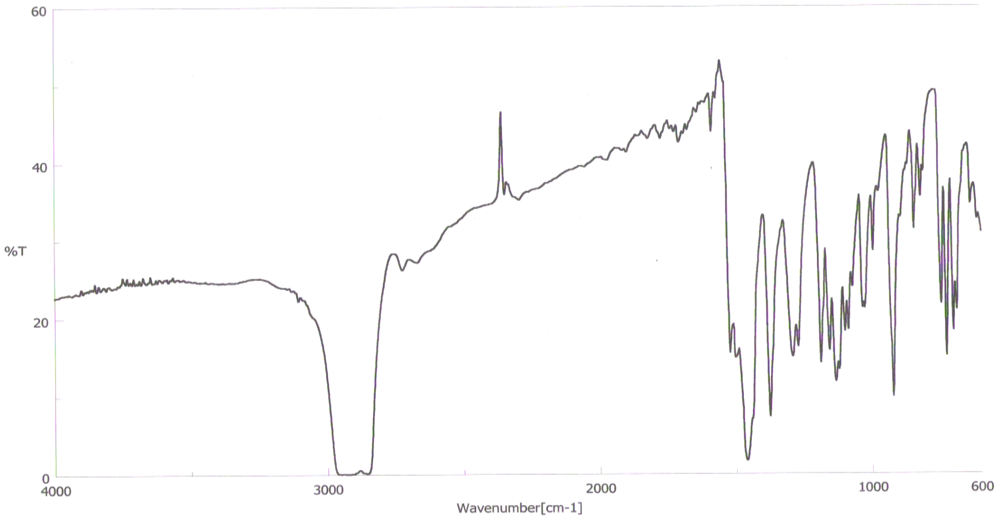

Fig. 4.1 IR spectrum of the compound **23**

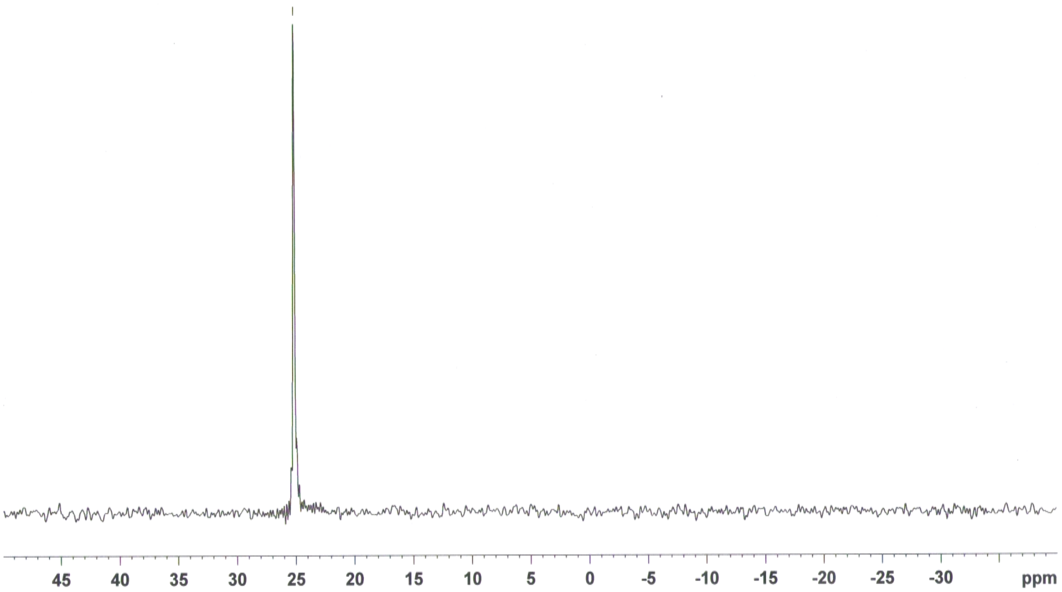

Fig.4.2 ^{31}P- NMR spectrum of the compound **23**

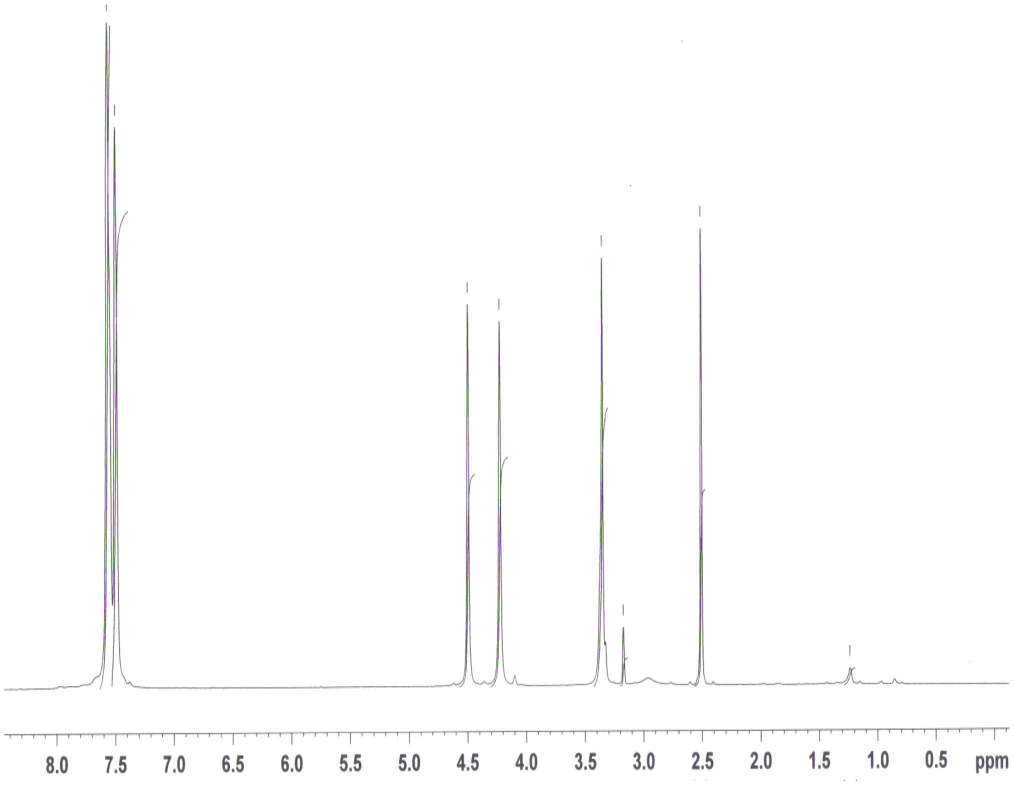

Fig.4. 3 ^{1}HNMR spectrum of the compound **23**

4.3.2 Molecular structure of uranyl (VI) nitrate bis(diphenylphosphine oxide) ferrocene

The molecular structure of $[UO_2(NO_3)_2$. DPPOF] is shown in Fig. 4.4 together with the numbering scheme and important bond distances and angles are given in Table 4.1 and Table 4.2. The structure shows that the uranium atom is surrounded by eight oxygen atoms in a hexagonal bi-pyramidal geometry. The four oxygen atoms of nitrate groups and two oxygen atoms of DPPOF forms a planar hexagon and these six oxygen atoms show a r.m.s deviation of 0.103 Å with the metal 0.006(1) Å from the plane. The observed (average) bond distances between $U–O_{(uranyl)}$ (1.751(2) Å), $U–O_{(nitrate)}$ (2.537(3) Å) and U—O(DPPOF) (2.352(2) Å) agree well the earlier reported uranyl nitrate, phosphine oxide compounds $[UO_2(NO_3)_2$(DPPOM)] [20], $[UO_2(NO_3)_2(PPh_3O)_2]$ [23]. It is interesting to note that the bite angle between the two P(O) oxygen atoms is 71.56(8)° and is much smaller in value compared to any of the DPPOF metal complexes reported so far. For example in $[PdCl_2$(DPPOF)] [33], the bite angle is 104.3(3)°, [Cu(DPPF)(DPPOF)]PF_6 [31], 102.1(6)°, $[Cu(DPPOF)_2](BF_4)_2]$, 154.0(4)°, 152.8(4)°, $[Cu(DPPOF)_2(EtOH)]-(BF_4)_2]$ [32], 90.1(3)°, 95.7(3)° and $[CoI_2$(DPPOF)] [35] 108.4(2)°. It is interesting to note that the geometry around the metal ions in all reported transition metal DPPOF complexes varies from tetrahedral, square planar to square pyramidal and this reflects in the bite angle between the two oxygen atoms of DPPOF. However, in present complex the geometry around uranium atom is hexagonal bi-pyramidal and the bite angle between two oxygen atoms of DPPOF is expected to be lesser than 90° and more than 60°. The observed bite angle of 71.5(8)° is very close to the value (71.5(4)°) observed in analogous DPPOM compound $[UO_2(NO_3)_2$(DPPOM)] [20]. Thus it is clear that the DPPOF ligand can adjust the bite angle from 71.5° to 154.0° by simple rotation of $(C_5H_4)C–P$ bonds depending upon the coordination geometry around the metal ion. All other bond lengths and angles for the DPPOF parts are normal and agree well with the reported results.

It is interesting to note that the compound [$UO_2(NO_3)_2$DPPOF] is the first DPPOF compound of any of the 5f metal ions. The direct reaction of [$UO_2(NO_3)_2.6H_2O$] with DPPOF gives product immediately as a precipitate and is insoluble in common organic solvents except DMSO and therefore the method was modified using different starting compound [$UO_2(NO_3)_2(^iC_3H_7CON\text{-}\{^iC_4H_9\}_2)_2$] to get the crystalline product.

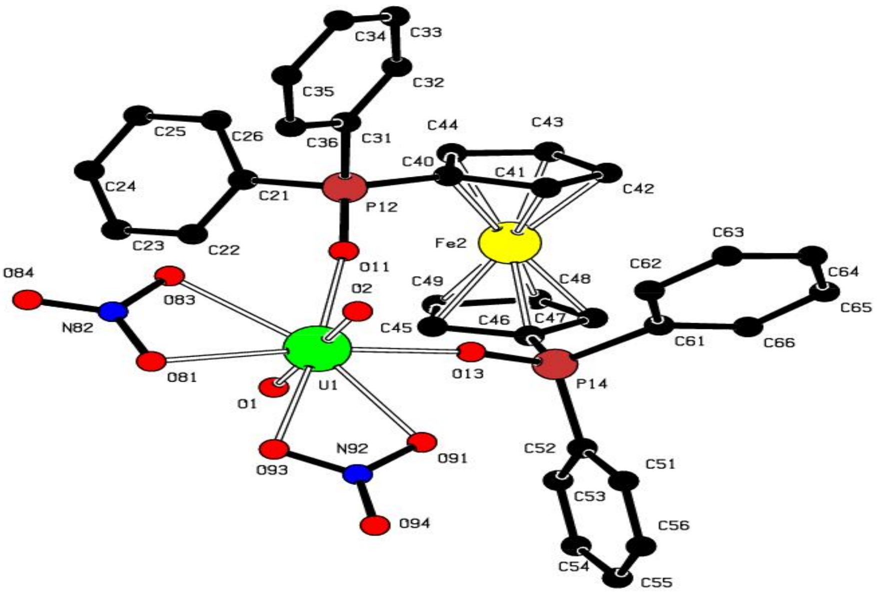

Fig. 4.4 Molecular structure of compound **23**

Table 4.1 Crystal and structural refinement details for the compounds **23** and **24**

	23	**24**
Empirical formula	$C_{34}H_{28}P_2O_{10}N_2FeU$	$C_{34}H_{28}P_2O_4Cl_2FeU$
Formula weight	980.40	927.28
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.5254(3)	12.4489(5)
b(Å)	21.5314(4)	21.0884(10)
c(Å)	13.4802(3)	13.1108(5)
β (°)	111.871(3)	111.385(5)
Volume ($Å^3$),	3373.80(14)	3205.0(2)
Z	4	4
Calculated density (g cm^{-3})	1.930	1.9218
Reflections collected/Unique	9795 /6517	8734/6019
Data/restraints/parameters	9795 /0/451	8734/0/397
Goodness-of-fit on F^2	0.824	0.931
Final R indices [$I > 2\sigma(I)$]	0.0348	0.0578
R indices (all data)	0.0617	0.0923

$W = 1/[\sigma^2(F^2_o) + (0.0179P)^2 + 0.000P]$ for **23** and $W = 1/[\sigma^2(F^2_o) + (0.0171P)^2 + 0.000P]$ for **24** where $P = (F_o^2 + 2F_c^2)/3$

Table 4.2 Important bond distances (Å) and angles (°) for compounds **23** and **24**

		23	
U(1)–O(1)	1.749(2)	U(1)–O(2)	1.752(3)
U(1)–O(11)	2.361(2)	U(1)–O(13)	2.344(2)
U(1)–O(81)	2.547(3)	U(1)–O(83)	2.552(3)
U(1)–O(91)	2.526(3)	U(1)–O(93)	2.523(3)
O(1)–U(1)–O(2)	177.89(12)	O(11)–U(1)–O(13)	71.56(8)
O(81)–U(1)–O(83)	49.68(9)	O(91)–U(1)–O(93)	50.08(9)
P(12)–O(11)–U(1)	171.40(15)	P(14)–O(13)–U(1)	164.00(16)
		24	
U(1)–O(1)	1.764(4)	U(1)–O(2)	1.760(4)
U(1)–O(3)	2.316(4)	U(1)–O(5)	2.309(5)
U(1)–Cl(1)	2.6321(18)	U(1)–Cl(2)	2.637(2)
O(1)–U(1)–O(2)	176.9(2)	O(3)–U(1)–O(5)	82.90(16)
O(3)–U(1)–Cl(2)	91.64(13)	O(5)–U(1)–Cl(1)	87.73(12)
Cl(1)–U(1)–Cl(2)	97.75(7)	O(2)–U(1)–O(5)	89.2(2)
O(2)–U(1)–O(3)	89.50(18)	O(1)–U(1)–O(5)	88.9(2)
O(1)–U(1)–O(3)	87.82(18)	O(2)–U(1)–Cl(2)	90.34(19)

4.3.3 Synthesis and structural studies of cis-uranyl (VI) dichloride – 1, 1'-bis(diphenyl phosphine oxide) ferrocene complex

The reaction of trans-$[UO_2Cl_2({}^iC_3H_7CON\{{}^iC_4H_9\}_2)_2]$ with $[(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2.2H_2O]$ in methanol yielded cis-$[UO_2Cl_2.(C_6H_5)_2P(O)(C_5H_4)Fe(C_5H_4)P(O)(C_6H_5)_2]$. This compound is insoluble in chloroform, methylene dichloride, 1,2-dichloroethane, benzene, toluene, diethyl ether, di-isopropyl ether, tetrahydofurane and acetone. It is sparingly soluble in dimethyl sulfoxide, dimethyl formamide and acetonitrile on warming. The IR spectrum of the compound (Fig.4.5) shows that the amide molecules from the starting compound trans-$[UO_2Cl_2({}^iC_3H_7CON\{{}^iC_4H_9\}_2)_2]$ are replaced completely by the DPPOF ligand. It shows further, that the ligand coordinates through both the phosphine oxide oxygen atoms to the uranyl group ($\Delta\nu_{PO}$ = 63 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum (Fig.4.6) shows a single resonance at δ 28.09 ppm and is ca. 6 ppm down field shift compared to that of the free ligand (δ 22.1 ppm). This indicates clearly that both the PO groups are bonded to the metal center in the reported compound. The ^1H NMR spectrum (Fig.4.7) shows the expected peaks and multiplicities for the C_5H_4 and C_6H_5 protons of the DPPOF in the ligand and the compound. The C,H analyses revealed that the ligand to metal ratio is 1:1 in the compound. The structure of the compound was determined by X-ray diffraction methods and confirms the chelating mode of coordination for this ligand around the uranyl group.

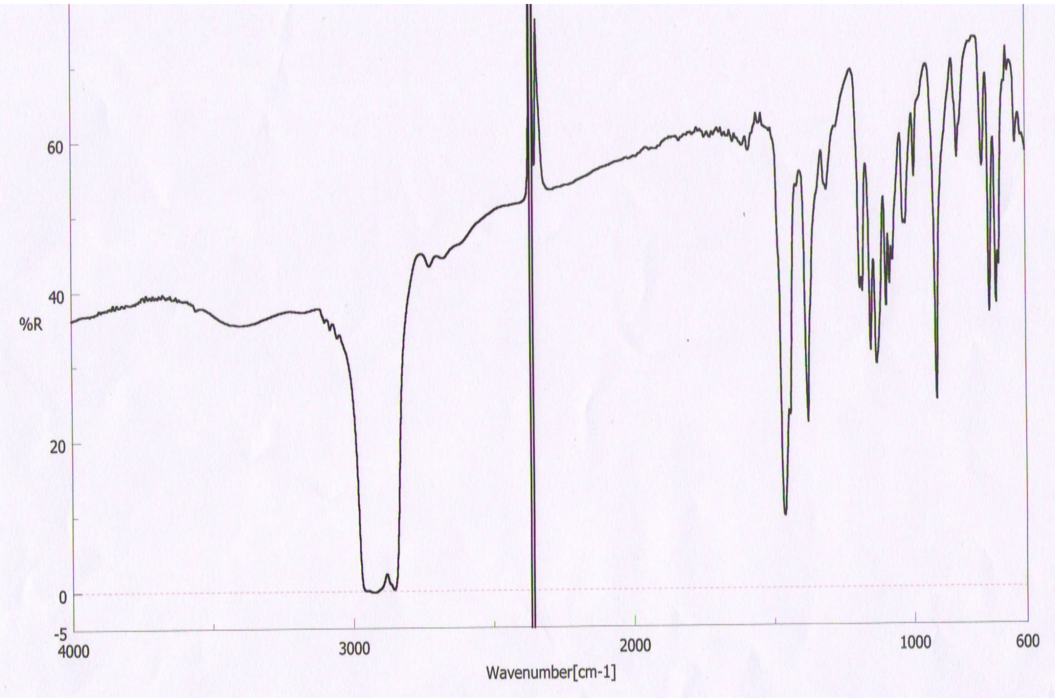

Fig. 4.5 IR spectrum of compound **24**

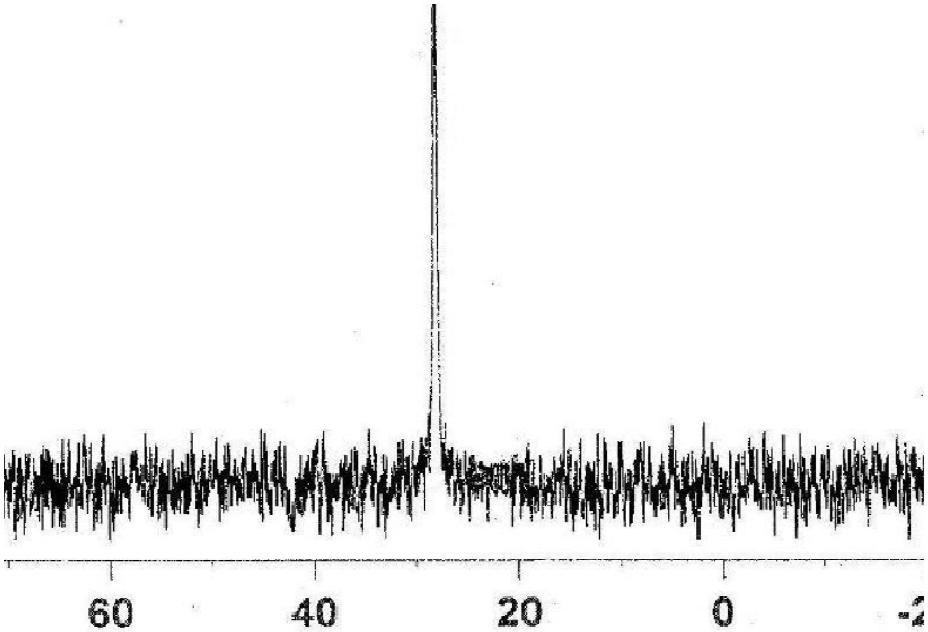

Fig. 4.6 ^{31}P-NMR spectrum of compound **24**

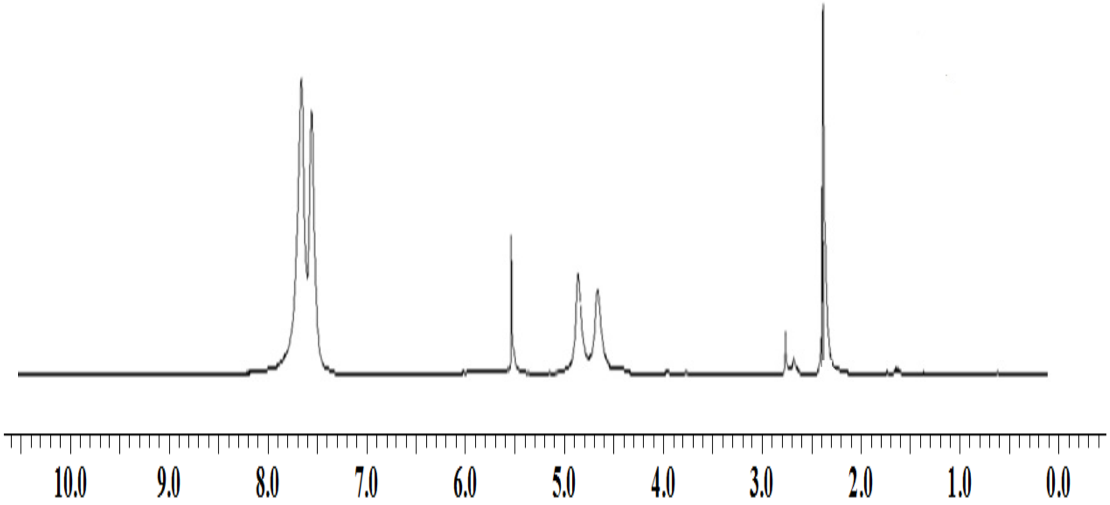

Fig. 4.7 ^{1}H NMR of compound **24**

4.3.4 Molecular structure of cis- uranyl (VI) dichloride-1, 1'-bis(diphenyl phosphine oxide) ferrocene

The molecular structure of [UO_2Cl_2 DPPOF] is shown in Fig.4.8 together with the numbering scheme and important bond distances and angles are given in Table 4.1 and

Table 4.2. The structure shows that the uranium (VI) ion is surrounded by four oxygen and two chlorine atoms in an octahedral geometry. The two chlorine atoms and two oxygen atoms of the DPPOF ligand form the equatorial square plane and these atoms show an r.m.s deviation of 0.019 Å with the metal and 0.011(2) Å from the plane. The observed (average) bond distances for U-O(uranyl) (1.762(4) Å), and U-O(DPPOM) (2.312(5) Å) agree well with those of previously reported uranyl-phosphine oxide compounds such as, [$UO_2(NO_3)_2$ DPPOF], [$UO_2(NO_3)_2$(DPPOM)] [20], [$UO_2Cl_2(OPPh_3)_2$] [21-22] and [$UO_2(NO_3)_2$ ($PPh_3O)_2$] [23]. The chlorine atoms are cis to each other with a Cl-U-Cl bond angle of 97.69(7)$^\circ$. However, the analogous bi-functional DPPOM compound of the uranyl dihalide is dimeric in nature with the bridging and terminal halides [30].

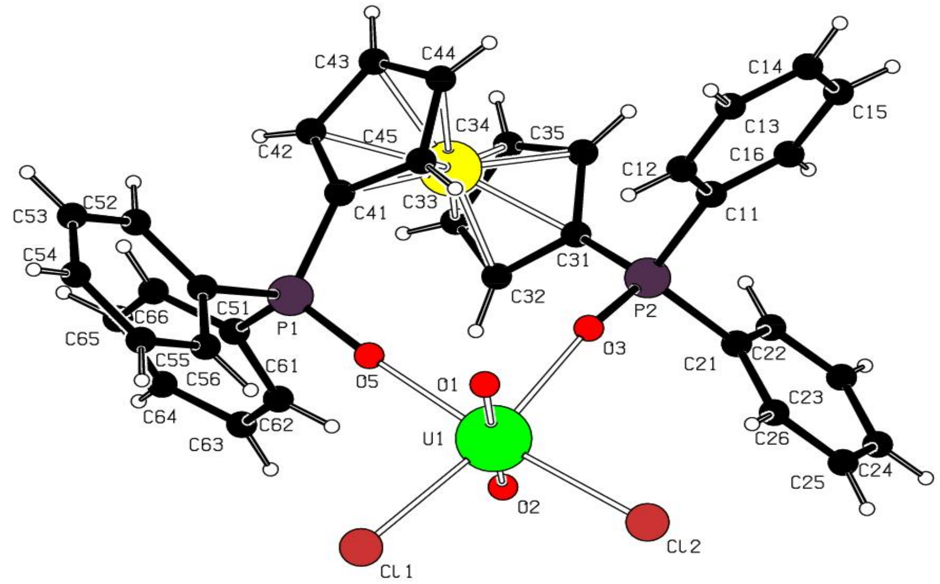

Fig.4. 8 Molecular Structure of compound **24**

The U-Cl bond distance 2.634(2) Å is comparable in magnitude with those of earlier reported uranyl dihalide compounds such as, [$UO_2Cl_2(OPPh_3)_2$] [21,22] and [$UO_2Cl_2(^iC_3H_7CON\{^iC_4H_9\}_2)_2$] [24]. It is interesting to note that the bite angle between the two P(O) oxygen atoms is 82.90(16)° and is smaller in value compared to those reported in [$PdCl_2$(DPPOF)], 104.3(3) ° [33], [Cu(DPPF) (DPPOF)]PF_6, 102.1(6) ° [31], [$Cu(DPPOF)_2](BF_4)_2$], 154.0(4)°, 152.8(4)° [32], [$Cu(DPPOF)_2(EtOH)](BF_4)_2$], 90.1(3)°, 95.7 (3)° [32], [$NiCl_2(DPPOF)_2$], 92.12(16)°, 91.19(16)° [34], [$Fe(DPPOF)_2Cl_2]ClO_4$, 92.20(11)°, 91.92(11)° [33], [$MnCl_2$(DPPOF)], 104.60(7)° [34], [$ZnCl_2$(DPPOF)], 102.07(15)° and [CoI_2(DPPOF)], 108.4(2)° [35] and larger in value compared to that observed in [$UO_2(NO_3)_2$ DPPOF], 71.5(8)°. Thus, it is clear that the $DPPFO_2$ ligand can adjust the bite angle from 71.5 to 154.0° by simple rotation of (C_5H_4) C-P bond depending upon the coordination geometry required around the metal ion. All other bond lengths and angles for the DPPOF part are normal and agree well with the reported results.

4.4 Conclusions

4.4.1 Chemistry of uranyl(VI) nitrate-1,1'- bis(diphenylphosphine oxide) ferrocene.

The first structurally characterized 1,1'-bis(diphenylphosphine oxide) ferrocene 5f element compound shows that it acts as a bidentate chelating ligand with the uranyl nitrate and the observed bite angle of 71.5° is much smaller in value compare to previously reported values for this ligand.

4.4.2 Chemistry of cis-uranyl(VI) dichloride-1,1'-bis(diphenyl phosphine oxide) ferrocene

The structure of 1,1'-bis(diphenylphosphine oxide) ferrocene compound of uranyl (VI) dichloride shows that the ligand acts as a bidentate chelating ligand with a bite angle of 82.90(16)°. The chlorides are mutually cis with a Cl-U-Cl angle of 97.75(7) °. This study further shows clearly that the DPPOF ligand can adjust the bite angle according to the coordination geometry around the metal centre.

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