Synthesis and Studies of Spectral and Thermal Properties of Some Mixed Ligand Complexes of Thorium(IV) and Dioxouranium(VI) With Semicarbazones as Primary Ligand and Sulfoxide as Secondary Ligand

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ABSTRACT: The present work describes the studies on the coordination behaviour of 4[N-(benzalidene) amino]antipyrine semicarbazone (BAAPS) (I), 4[N-(furfural)amino]antipyrine semicarbazone (FFAAPS) (II) and 4[N-(cinnamalidene)amino]antipyrine semicarbazone (CAAPS) (III) in presence of dimethyl sulfoxide (DMSO) or diphenyl sulfoxide (DPSO) towards Th^{4+} and UO_2^{2+} salts. All the complexes were isolated in non-aqueous solvents like ethanol or acetone. The mixed ligand complexes have the general composition $ThX_4(L)DPSO$ (X = Cl, Br, I, NCS or NO_3), $Th(ClO_4)_4(L)_2DPSO$ (L = BAAPS or CAAPS), $UO_2X_2(L)DMSO$ ($X = Br, I, NCS, NO_3$ or CH_3COO) and $UO_2(ClO_4)_2(L)_2DMSO$ (L=FFAAPS or CAAPS). The analytical data include elemental analyses, molecular weight determination, conductivity, spectral and thermal studies. XRD-powder diffraction of two representative thorium(IV) complexes have also been reported.In these complexes, the primary ligands behave as neutral tridentate (N, N, O) ligand, while the secondary ligand (DMSO or DPSO) acts as unidentate oxygen donor. Thorium(IV) displays coordination number 6,7,8 or 12, while uranium(VI) ion displays coordination number 8, 9 or 10 depending on the nature of anionic ligand.

KEY WORDS: Thorium(IV), Dioxouranium(IV), Mixed ligand complexes, Semicarbazones, Sulfoxide.

INTRODUCTION

The structural chemistry of the actinide elements has recently undergone considerable development and a wide variety of coordination numbers and geometries have been observed [1-7]. The structural versatility arises from

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the lack of strong crystal field effects for the 5f electronic configurations as well as from the large ionic radii of these metal ions, which change markedly with either oxidation number, or atomic number for these metal ions. In lighter actinides the 5f-orbitals are not completely shielded from the influence of the 6s and 6p electrons, allowing radial expansion of the 5f-orbitals sufficient for overlapping with the ligand orbitals and, as a consequence, they are rather versatile in their oxidation numbers. On going to the right in the actinide series, the increase in nuclear charge causes a contraction of the 5f-orbitals with decreasing metal-ligands overlap and the trivalent oxidation state dominates with an even more highly ionic character in the bonding. However, the only structural evidence for covalent bonding in actinide chemistry is related to the actinyl ions *e.g.*, MO^{2+} and MO_2^{2+} , in which there is clear evidence that both f and d-orbitals participate in the actinyl bond. The predominant ionic character in the bonding in their complexes has in consequence a variety of coordination numbers and ligand arrangements as steric and electrostatic factors become dominant. High coordination numbers, usually in the range of six to twelve are observed in actinide metal coordination compounds [6,7].

In past, a number of researchers have isolated thorium(IV) and dioxouranium(VI) coordination compounds with a variety of Schiff bases including semicarbazones [3,8-11]. There is no report available in literature about the mixed ligand complexes of actinides metal complexes with semicarbazones.

In view of it, we describe here in the preparation and characterization of thorium(IV) and dioxouranium(VI) coordination compounds of semicarbazone as primary ligand, and dimethyl sulfoxide/diphenyl sulfoxide as secondary ligand. The structures (I- III) of semicarbazone ligands used in this study are given as follows:



EXPERIMENTAL

Th(NO₃)₄5H₂O (BDH, AnalaR) was used as received. Thorium(IV) perchlorate was prepared as reported [12]. Thorium(IV) chloride and bromide were prepared by treating thorium(IV) hydroxide with the corresponding halogeno acids and concentrating the solution until crystallization occurred. Thorium(IV) iodide and thorium(IV) thiocyanate were however, prepared as follows: 10% methanolic solutions of Th(NO₃)₄ and KI or KSCN were mixed to give a Th:I or Th:SCN of 1:4. The precipitated KNO₃ was filter off. The filtrate containing ThI₄ was used for the preparation of the complex. Thorium(IV) thiocyanate however, was obtained from the filtrate after concentration by passing dry air through the solution. Being hygroscopic all the thorium(IV) salts were stored in dessicator over conc. sulfuric acid.

Uranyl nitrate and uranyl acetate were used as received from BDH. Uranyl nitrate was dehydrated by keeping it over concentrated sulfuric acid [13]. Uranyl bromide was prepared from uranyl acetate by treating it with HBr in ethanol. After evaporating most of the solvent, the solution was kept over sulphuric acid till yellow crystals were separated out [14]. Uranyl iodide was obtained by treating uranyl nitrate with barium iodide in dry ether [15]. Uranyl thiocyanate was prepared by mixing alcoholic solution of anhydrous uranyl nitrate and potassium thiocyanate [16]. Uranyl perchlorate was prepared by digesting uranyl nitrate with calculated amount of perchloric acid and evaporating the mixture to dryness. Uranyl perchlorate was crystallized until free from nitrate ions [17].

The ligands BAAPS/FFAAPS/CAAPS were synthesized by refluxing an ethanolic solution of 1:1:1 molar ratio of 4-aminoanitpyrine, corresponding aromatic aldehyde and neutralized semicarbazone hydrochloride for ~ 2 h.[18]. On cooling the respective ligand BAAPS/FFAAPS/CAAPS precipitated out. It was filtered, washed with ethanol, ether and finally dried in vacuum desiccator over P_4O_{10} .(Yield 70-75%). Dimethyl sulfoxide and diphenyl sulfoxide were purchased from Aldrich Chemical and used as received. All the solvents used were of AnalaR grade.

All the thorium(IV) complexes were synthesized as follows: ethanolic solutions of the ligands (BAAPS or FFAAPS) and DPSO were mixed with the thorium(IV) salt solution in ethanol in 1:1:1 molar ratio (both the ligands were taken in 10% excess). In case of thorium (IV) perchlorato complexes the ratio was 1:2:1. The mixture was refluxed for about 4 hrs. The resulting solution was concentrated by evaporation on a water bath. It was then washed repeatedly with benzene and then extracted with petroleum ether to get the desired solid complex. The complexes were filtered and dried in *vacuo* over P_4O_{10} (Yield 70-80%).

All the dioxouranium(VI) complexes were prepared by refluxing UO₂X₂ (X = Br, I, NCS, NO₃ or CH₃COO), semicarbazone and DMSO in the molar ratio 1:1:1 in acetone. In case of dioxouranium perchlorate, the ratio taken is 1:2:1 (both the ligands were taken in 10% excess). The reaction mixture is concentrated and extracted with benzene and diethyl ether to get yellow to brown coloured solid complexes (Yield 70-82%).

Analytical Methods

Thorium or uranium content of the complexes was estimated by decomposing the complexes with boiling concentrated nitric acid and precipitating metal hydroxide was filtered on Whatmann filter paper, washed thoroughly with distilled water which were finally ignited and weighed as ThO₂ or U₃O₈. The nitrogen was estimated by Kjeldahl's method. Sulphur content was estimated gravimetrically as BaSO₄. The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer with $\pm 0.01^{\circ}$ C accuracy. The conductivity measurements were carried out using a Toshniwal Conductivity Bridge (Type CL 01/01) and a dip type cell operated at 220 Volts AC. All the measurements were done at room temperature in nitrobenzene. The magnetic measurements were carried out at room temperature with Gouy's balance using [HgCo(SCN)₄] as a calibrant. The infrared spectra of the complexes were recorded on a Perkin Elmer Infrared spectrophotometer model-521 in CsI in the range 4000-200 cm⁻¹. Thermogravimetric analysis was carried out in a Stanton Redcraft thermobalance model PTG-750 product of M/s Stanton Redcraft, U.K., at heating rate 10° C/min.

RESULTS AND DISCUSSION

The elemental analyses of all the present complexes are presented in Table 1 and 2. These complexes are quite stable at room temperature. All are sufficiently soluble in

Complex	Yield			Found (Calcd) % Analysis		m.w.	Λ_m (ohm ⁻¹	
<u>-</u>	(%)	Color	Th	Ν	S	Anion	found (calcd)	cm ² mole ⁻¹)	
ThCL (PAADS)DDSO	75	Vallow	24.93	9.04	3.42	15.26	918	2.2	
Theta (BAAFS) DF SO	75	1 chow	(25.10)	(9.09)	(3.46)	(15.36)	(924)	2.2	
Ther (PAAPS)DPSO	75	Deep vallow	20.94	7.56	2.87	28.87	1095	2.1	
IIIBI4(BAAF 5)DF 50	15	Deep yellow	(21.05)	(7.62)	(2.90)	(29.03)	(1102)	5.1	
ThL/PAAPS)DPSO	70	Vallowish brown	17.83	6.43	2.44	39.28	427	50.1	
IIII4(BAAF 3)DF 50	70	i chowish brown	(17.98)	(6.51)	(2.48)	(39.37)	(1290)	50.1	
THOUCE (PAARS) DRSO	75	Vallow	22.69	13.67	15.69	22.75	1007	2.1	
III(NC3)4(BAAF3)DF30	15	1 chow	(22.87)	(13.80)	(15.77)	(22.87)	(1014)		
THOMA) (PAAPS)DPSO	80	Vallow	22.39	13.47	3.06		1024	1.8	
111(NO ₃) ₄ (BAAPS)DPSO 80	80	1 chow	(22.52)	(13.59)	(3.10)	-	(1030)		
	70	Vallaw	15.09	10.89	2.05	25.87	303	99.6	
III(CIO ₄) ₄ 2(BAAPS)DPSO	12	renow	(15.18)	(10.99)	(2.09)	(26.04)	(1528)		
THEL (TEA A DE) DDEO	70	79 Light vallow	25.23	9.13	3.45	15.42	908	2.1	
THC4(FTAAFS)DF50	/0	Light yellow	(25.38)	(9.19)	(3.50)	(15.53)	(914)	2.1	
The (EEA ADS)DDSO	75	Deen vallevu	21.12	7.65	2.88	29.19	1086	2.7	
11ibi ₄ (FFAAPS)DPSO	73	Deep yellow	(21.24)	(7.69)	(2.93)	(29.30)	(1092)	2.7	
THI (EEA A DE) DDEO	70	Drownigh vollow	18.01	6.51	2.46	39.57	423	51.2	
IIII4(FFAAPS)DPSO	70	Brownish yellow	(18.12)	(6.56)	(2.50)	(39.68)	(1280)	51.3	
THANGEN (EEA A DENDREO	75	Vallaw	22.95	13.84	15.86	22.96	998	51.0	
In(INCS)4(FFAAPS)DPSO	15	renow	(23.10)	(13.94)	(15.93)	(23.10)	(1004)	51.9	
Th(NO ₃) ₄ (FFAAPS)DPSO	20	Yellow	22.62	13.63	3.09		1014	17	
	80		(22.74)	(13.72)	(3.13)	-	(1020)	1./	
TH(CIO.) OFFICA ADOUDDOO	70	X7.11	15.29	11.07	2.09	26.29	298	08.0	
$1 \Pi(CIO_4)_{42}(FFAAPS)DPSO$	/0	Y ellow	(15.38)	(11.14)	(2.12)	(26.39)	(1508)	98.9	

 Table 1: Analytical, conductivity and molecular weight data of mixed ligand complexes of thorium(IV) with
 BAAPS/FFAAPS and DPSO

common organic solvents. Molar conductance values of the complexes were determined in nitrobenzene and the results are presented in table 1 and 2. In case of thorium(IV) complexes it is suggested that the chloro, bromo, nitrato and thiocyanato complexes are nonelectrolytes, while the perchlorato and the iodo complexes are 1:4 and 1:2 electrolytes respectively. Thus all perchlorato groups are ionic in the former set of complexes, whereas only two of the four iodides may be ionic in nature [19]. Molecular weight data of these complexes in freezing nitrobenzene (Table 1) show that the complexes are monomeric in nature.In case of $ThI_4(L)DPSO$ and $Th(ClO_4)_4(L)_2DPSO$, the ratios of experimental and calculated molecular weights are 0.33 and 0.20 respectively. These data further indicate that three species are formed in the case of the iodo complexes and five species are formed in perchlorato complexes.

In case of dioxouranium(VI) complexes, only perchlorato complexes are non-electrolytes in PhNO₂. The molar conductivities of both the perchlorato complexes confirm that these complexes behave as 1:2

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electrolytes. Molecular weight data obtained for the complexes in freezing nitrobenzene are given in Table 1 and 2, along with their formula weights. The ratios of the molecular weights observed for $[UO_2X_2(L)DMSO]$ (X = Br, I, NCS, NO₃ or CH₃COO; L = FFAAPS or CAAPS) to the calculated over are ~ 0.98, which shows that these complexes are monomeric in solution. In case of perchlorato complexes, the ratio of observed molecular weight to the formula weight is found to be 0.33 indicating the formation of three species from these complexes in solution, which further confirms the ionic nature of these complexes as observed by molar conductivity values.

The dioxouranium (VI) complexes are either diamagnetic or weakly paramagnetic depending upon the diamagnetism of other ions and the surrounding ligand field [20]. Their magnetic susceptibilities are independent of field strength and temperature [21]. Since the ground state of dioxouranium(VI) compounds contain no unpaired electron, all these complexes are weakly diamagnetic as observed earlier [22,23].

Complex	Yield	Yield		Found (Calcd) % Analysis				$\Lambda_{\rm m}$ (ohm ⁻¹ cm ² mole ⁻¹	
	(%)	0.00	Th	Ν	S	S Anion		¹)	
UO2Br2(FFAAPS)DMSO	70	Brownish	28.02	9.87	3.70	18.80	839	23	
002612(1111110)61100	70	Yellow	(28.13)	(9.92)	(3.78)	(18.91)	(846)	2.5	
UOAL(FEAAPS)DMSO	65	Deen Vellow	25.20	8.87	3.35	26.90	935	3.3	
00212(1111110)))))	05	Deep renow	(25.31)	(8.93)	(3.40)	(27.02)	(940)	5.5	
LIO-(NICS)-(FEA APS)DMSO	72	Bright Vellow	29.57	13.89	11.85	14.32	798	3.4	
002(11C5)2(11 AAI 5)DW50	12	Diigin Tenow	(29.67)	(13.96)	(11.97)	(14.46)	(802)	5.4	
LIO (NO.) (FEA APS)DMSO	75	Vellow	29.29	13.75	3.89		805	2.1	
002(N03)2(ITAAI 3)DW30	15	TCHOW	(29.38)	(13.82)	(3.95)		(810)	2.1	
	70	Vellow	29.51	10.37	3.93		799	2.9	
$OO_2(OAC)_2(FFAAPS)DMSO$		renow	(29.60)	(10.44)	(3.98)		(804)	2.7	
UO ₂ (ClO ₄) ₂ (FFAAPS) ₂ DMSO 70	70	70 Yellow	19.37	13.66	2.55	16.15	410	51.2	
	70		(19.46)	(13.73)	(2.61	(16.27)	(1233)		
LIO DE (CAADE)DMEO	72	Brownish	26.87	9.47	3.56	18.02	875	2.4	
UO2BI2(CAAPS)DMSU	12	Yellow	(26.98)	(9.52)	(3.62)	(18.14)	(882)	2.4	
LIO L (CAADS)DMSO	60	Deen Vellew	24.29	8.56	3.22	25.90	972	2.1	
UO212(CAAPS)DMSO	08	Deep renow	(24.38)	(8.60)	(3.27)	(26.02)	(976)	5.1	
	70	Lisht Vallass	28.31	13.27	11.34	13.75	833	2.2	
$UU_2(INCS)_2(CAAPS)DMSU$	70	Light renow	(28.40)	(13.36)	(11.45)	(13.84)	(838)	5.5	
	70	V-ll	28.04	13.16	3.73		841	2.2	
UO ₂ (NO ₃) ₂ (CAAPS)DMSO	72	Yellow	(28.13)	(13.23)	(3.78)		(846)	2.2	
	70	V-ll	28.24	9.95	3.74		835	2.4	
$UU_2(UAC)_2(UAAPS)DMSU$	70	Yellow	(28.33)	(10.00)	(3.80)		(840)	2.4	
	70	V-ll	18.29	12.89	2.43	15.28	435	50.0	
$UU_2(UU_4)_2(UAAPS)_2DMSO$	70	Yellow	(18.37)	(12.97)	(2.47)	(15.36)	(1295)	50.6	

Table 2: Analytical Data of UO₂(IV) mixed ligands complexes of semicarbazones and DMSO

Infrared Spectra

The partial infrared spectral data of the free ligands and their Th^{4+} and UO_2^{2+} complexes are given in table 3 and 4. As expected, the v(NH₂) band of the hydrazinic nitrogen of semicarbazide (1622 cm⁻¹) is absent in the infrared spectra of the semicarbazone [24]. It has also been observed that the amide-II band is shifted towards the lower energy side compared to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen [25].

The characteristic absorption of the carbonyl group in BAAPS/FFAAPS/CAAPS is observed in 1705-1700 cm⁻¹ region [26]. In these complexes, this band is shifted towards lower energy in the 1650-1640 cm⁻¹ region (Table 3 and 4). The amide-II band in free ligands occurs in 1565-1560 cm⁻¹ region. In all these complexes, this band is also shifted towards lower wave numbers by ~ 30 cm⁻¹ which suggests coordination through the carbonyl oxygen atom. The strong band at $\sim 1605 \pm 3$ cm⁻¹ in all the semicarbazones apparently has a large contribution from the v(C=N) mode of semicarbazone moiety [27]. This has been observed as a blue shift in the

position of the (C=N) band in all the complexes. Another strong band was observed at 1620 ± 5 cm⁻¹ due to azomethine (C=N) absorption upon complexation this band is shifted towards the lower frequency region, indicating the coordination through the azomethinic-N atom [28].

The strong (S=O) stretching frequency in free DMSO and DPSO appears as a strong absorption at 1020 and 1100 cm⁻¹ respectively, which appears in the region 968-960 cm⁻¹ showing coordination of DMSO to UO₂(VI) metal ion *via* lone oxygen atom of sulfoxide, and 1040-1030 cm⁻¹ in thorium(IV) complexes suggest coordination of DPSO to Th(IV) through lone oxygen atom of sulfoxide [6,7]. In far infrared spectra the bands due to v(M-N)/v(M-O) are also observed (Table 3 and 4) [29,30].

In all the perchlorato complexes, the occurrence of two strong bands at 1095±5 and 630-625 cm⁻¹ attributed to v_3 and v_4 vibrations of perchlorato ion suggests the presence of perchlorato groups outside the coordination sphere [31,32]. The infrared spectra of the nitrato complexes showed no absorption near 1360 cm⁻¹, where

Compound	v(C=N)	v(C=N)		v(C=O)	(S=O)	v(Th-N)/	
compound	(Azomethinic)	(Hydrazinic)	Ι	II	III	V(S=O)	v(Th-O)
DPSO						1100 s	
BAAPS	1610 m	1600 m	1700 s	1565 s	1350 s		
ThCl4(BAAPS)DPSO	1505 m	1625 m	1645 s	1535 m	1330 m	1035 s	450 m 385 w
ThBr4(BAAPS)DPSO	1580 m	1622 m	1650 s	1532 m	1328 m	1040 s	470 m 390 w
ThI4(BAAPS)DPSO	1582 m	1625 m	1652 s	1535 m	1325 m	1037 s	455 m 380 w
Th(NCS) ₄ (BAAPS)DPSO	1580 m	1630 m	1645 s	1530 m	1328 m	1040 s	460 m 390 w
Th(NO ₃) ₄ (BAAPS)DPSO	1582 m	1630 m	1640 s	1532 m	1320 m	1035 s	465 m 382 w
Th(ClO ₄) ₄ 2(BAAPS)DPSO	1585 m	1625 m	1642 s	1530 m	1325 m	1030 s	470 m 390 w
FFAAPS	1620 m	1605 m	1705 s	1570 s	1350 m		
ThCl ₄ (FFAAPS)DPSO	1575 m	1635 m	1650 m	1540 m	1325 m	1038 s	465 m 395 w
ThBr ₄ (FFAAPS)DPSO	1580 m	1628 m	1652 m	1535 m	1322 m	1035 s	472 m 390 w
ThI4(FFAAPS)DPSO	1585 m	1630 m	1650 m	1537 m	1320 m	1040 s	468 m 392 w
Th(NCS)4(FFAAPS)DPSO	1572 m	1625 m	1645 m	1540 m	1325 m	1035 s	470 m 385 w
Th(NO ₃) ₄ (FFAAPS)DPSO	1582 m	1632 m	1652 m	1535 m	1322 m	1040 s	465 m 380 w
Th(ClO ₄) ₄ 2(FFAAPS)DPSO	1580 m	1630 m	1645 m	1532 m	1330 m	1038 s	475 m 382 w

Table 3: Key infrared bands (cm⁻¹) of thorium(IV) mixed ligand complexes of semicarbazones and DPSO

the free nitrate ion is known to absorb. In all the nitrato complexes, the nitrate groups coordinate in a bidentate fashion, since the infrared frequencies due to NO_3^- groups are almost in the same frequency ranges (~1510, 1285, 1030, 1015, 825, 740 and 725 cm⁻¹ as v_1 , v_4 , v_2 , v_6 , v_3 and v_5 respectively) as in Th(NO₃)₄5H₂O [33] and UO₂(NO₃)₂2H₂O [34]. Ueki et al [35] and Taylor [36] established the bidentate character of the nitrate groups in nitrate compounds of actinide by X-ray and neutron diffraction studies. Similar to nitrato ion, the acetato ion is also a potentially bidentate ligand towards uranyl acetate with neutral monodentate ligands like TPPO, TPAsO, HMPA or DPSO as reported in literature [37]. In these complexes acetate ion behaves as covalent bidentate and the coordination number is found to be seven or eight, depending on whether the complexes are monomeric or dimeric. The present complexes [UO₂(CH₃COO)₂(L)DMSO] are monomeric in nature and the infrared spectra of these complexes

show two bands in 1550 - 1465 cm⁻¹ region attributed to the asymmetric and symmetric stretching vibrations of -COO⁻ respectively [38]. In [Th(NCS)₄(L)DPSO] and $[UO_2(NCS)_2(L)DMSO]$ complexes, the (C-N) stretching frequency (v1) appears in 2070-2060 cm⁻¹ region, which lies on the border line for distinguishing between nitrogen or sulphur bonding in the thiocyanate [39], although the high relative intensity of this band in both complexes suggests that the thiocyanate groups are N-bonded [39]. The frequency of the (C-S) stretching vibration (v_3) has also been used to diagnose the bonding mode in thiocyanates [34]. The C-S band identified at 815 and 845 cm⁻¹ in thorium (IV) and dioxouranium (VI) complexes, respectively further confirm that the thiocyanate group is almost N-bonded in these complexes [40]. In the present investigation, the v(U=O) in all complexes has been assigned to 932-920 and 840-825 cm⁻¹ region [3,6].

Compounds	v(C=N)	ν(C=N)		v(C=O)		v(S=0)	v(U-N)/	
Ĩ	(Azomethinic)	(Hydrazinic)	Ι	II	III	v(3-0)	ν(U-O)	
DMSO						1020 s		
FFAAPS	1615 s	1602 m	1700 s	1565 s	1340 s			
UO2Br2(FFAAPS)DMSO	1590 s	1625 m	1645 s	1530 m	13430 s	960 m	468m, 370 w	
UO2I2(FFAAPS)DMSO	1588 s	1628 m	1648 s	1535 m	1328 m	962 m	460 m, 378 w	
UO2(NCS)2(FFAAPS)DMSO	1585 s	1630 m	1650 s	1540 m	1325 m	965 m	472 m, 370 w	
UO2(NO3)2(FFAAPS)DMSO	1582 s	1625 m	1645 s	1542 m	1323 m	960 m	468 m, 370 m	
UO2(OAc)2(FFAAPS)DMSO	1587 s	1628 m	1650 s	1545 m	1325 m	965 m	465 m, 370 w	
UO2(CIO4)2(FFAAPS)2DMSO	1585 s	1625 m	1645 s	1540 m	1320 m	968 m	480 m, 375 w	
CAAPS	1625 s	1608 m	1705 s	1560 m	1340 s			
UO2Br2(CAAPS)DMSO	1585 s	1630 m	1642 s	1538 m	1322 m	962 m	472 m, 375 w	
UO2I2(CAAPS)DMSO	1582 s	1628 m	1645 s	1535 m	1325 m	960 m	480 m, 382 w	
UO2(NCS)2(CAAPS)DMSO	1590 s	1622 m	1648 s	1537 m	1327 m	965 m	482 m, 385 w	
UO2(NO3)2(CAAPS)DMSO	1585 s	1625 m	1645 s	1528 m	1320 m	968 m	485 m, 382 w	
UO2(OAc)2(CAAPS)DMSO	1588 s	1630 m	1642 s	1533 m	1322 m	965 m	482 m, 375 w	
UO2(CIO4)2(CAAPS)2DMSO	1582 s	1632 m	1640 s	1535 m	1325 m	960 m	480 m, 370 w	

Table 4: Key infrared bands (cm⁻¹) of UO₂(VI) mixed ligands complexes of semicarbazones and DMSO

Complexation Effects on Uranyl Ion Spectra

In the present studies of mixed ligand complexes or uranyl ions, it has been observed that the v_1 mode of the uranyl ion appears as the weak intensity and the v_3 mode with the strong intensity in the infrared spectra (Table 5). From X-ray studies, Zachariasen [41] had predicted that the U-O bond distance varies from 1.60 Å in Na[UO₂(CH₃COO)₃] to 1.92 Å on MgU₂O₂. Such a large range of U-O bond distances in different uranyl salts should produce a very large range of uranyl frequencies. Jones [42] has suggested the determination of bondlengths from infrared spectral data and calculation of the force-constants by valence force field. Narasimhan [43] had calculated the various force constants of the uranyl ion in cesium uranyl nitrate using Wilson's GF matrix method [44]. Hoekstra [45] has calculated bond lengths in uranyl fluoride and uranyl carbonate using Badgers rule. A group theoretical consideration [46] shows that a linear and symmetrical triatomic UO_2^{2+} ion possessing $D_{\infty h}$ symmetry gives rise

to three fundamental modes of vibrations. Wilson's GF matrix method [44] has been used to determine the stretching and interaction force constants. The results are in turn use to evaluate U-O bond distances following Badger's formula [45]. The force-constant, bond distances and spectral data used herein are summarized in table 5. It is apparent from table 5, that the bond lengths, decreases with the increase in the value of symmetric stretching frequency (v_1) [47]. Another observation is that a plot of $(v_1 + v_3)$ versus force constant gives a straight line with the increase in the symmetric stretching vibration on complexation. The U-O force constant and the force constant due the interaction between the bonds have also to been found. Further the U-O bond distance of uranyl salts generally varies from 1.60 to 1.92 Å depending on the equatorial ligands [41]. The calculated values of the U-O bond distances of the present complexes are well within the range 1.7378 to 1.7423 Å (Table 5).

Complex	U—O Force Constant	Force Constant due to interaction between bonds	U—O Bond Distance	ν_1	v ₃
UO2Br2(FFAAPS)DMSO	6.7242	-0.3085	1.7423	825	920
UO2I2(FFAAPS)DMSO	6.8025	-0.2302	1.7402	835	920
UO2(NCS)2(FFAAPS)DMSO	6.7242	-0.3085	1.7423	825	920
UO2(NO3)2(FFAAPS)DMSO	6.8166	-0.3698	1.7399	827	930
UO2(OAc)2(FFAAPS)DMSO	6.8793	-0.2302	1.7402	835	930
UO2(ClO4)2(FFAAPS)2DMSO	6.8557	-0.3307	1.7384	832	930
UO2Br2(CAAPS)DMSO	6.8796	-0.2759	1.7378	837	928
UO2I2(CAAPS)DMSO	6.8016	-0.3078	1.7405	830	925
UO2(NCS)2(CAAPS)DMSO	6.7779	-0.3622	1.7408	825	927
UO2(NO3)2(CAAPS)DMSO	6.9188	-0.2676	1.7369	840	930
UO2(OAc)2(CAAPS)DMSO	6.8556	-0.3618	1.7384	830	932
UO2(ClO4)2(CAAPS)2DMSO	6.8796	-0.2759	1.7378	837	928

Table 5: Various force constants (m dynes/Å), U—O bond distances (Å) and frequencies (cm⁻¹) of v_1 and v_3 of UO₂(VI) mixed ligands complexes of semicarbazones and DMSO

X-Ray Powder diffraction studies

Comparatively less studies have been performed on crystal structure of actinide complexes. Crystal structure of thorium nitrato complexes of tetramethyl urea was determined by Rickard [48]. He inferred that the crystal belongs to monoclinic system with a = 13.954(1); b = 20.334(2); c = 14.138(a)Å and β = 98.06(3)°. Th(NCS)₄(depa)₃ and ThCl₄(dmpa)₄ complexes were also examined using X-ray crystallographic studies and both of them were found to be monoclinic[49]. In present investigation, authors have performed X-ray powder diffraction studies on two representative thorium(IV) complexes. Th(NO₃)₄(FFAAPS)(DPSO) belongs to monoclinic system with a = 8.0168(a); b = 10.1384(5)and c = 11.0715(6)Å and $\beta = 82.110^{\circ}$ (Table 6). Th(NCS)₄(BAAPS)(DPSO) also belongs to monoclinic with a = 5.0557(8); b = 9.5276(7) and c = 12.0715(4)Å and $\beta = 79.33^{\circ}$ (Table 7).

Thermogravimetric Analysis

The results of the thermal analysis of thorium (IV) are summarized in Table 8. The TG-curves of the complexes do not show the presence of water molecules either in or out of the coordination sphere. The

suggest that in the first step, DPSO ligand has been evaporated in 140-185°C temperature range; while at ~300°C, the primary ligand (FFAAPS) has been lost. In chloro, bromo and thiocvanato complexes

careful analysis of TG-curves of all the complexes

In chloro, bromo and thiocyanato complexes at ~450°C, formation of oxohalide and oxothiocyanate takes place[50]. In case of nitrate complex at 510° C, ThO₂ is the final product. From the pyrolysis curve of Th(ClO₄)₄ (FAAPS)₂ DPSO, it is revealed that at 180°C, DPSO molecule has been lost. In 210-260°C temperature region, one molecule of FFAAPS has been lost. Finally at 500°C, ThO₂ is the final product [51]. The analysis of the thermogram indicate the following decomposition scheme:

 $\begin{array}{l} {\rm ThX_{4}.(FFAAPS)DPSO} \rightarrow {\rm ThX_{4}(FFAAPS)} \rightarrow {\rm ThX_{4}} \rightarrow \\ {\rm ThOX_{2}} \\ ({\rm X=Cl, Br \ or \ NCS}) \\ {\rm Th(NO_{3})_{4}(FFAAPS)DPSO} \rightarrow {\rm Th(NO_{3})_{4}(FFAAPS)} \rightarrow \\ {\rm Th(NO_{3})} \rightarrow {\rm ThO_{2}} \\ {\rm Th(ClO_{4})_{4}(FFAAPS)_{2}DPSO} \rightarrow {\rm Th(ClO_{4})_{4}(FFAAPS)_{2}} \rightarrow \\ {\rm Th(ClO_{4})_{4}(FFAAPS)} \rightarrow {\rm ThO_{2}} \end{array}$

20 _{obs}	I/I _o	hkl	d _{obs}	d _{cal}
23.78	54	022	3.739	3.738
25.21	42	113	3.530	3.534
27.70	13	031	3.218	3.232
28.16	100	113	3.166	3.182
28.80	05	231	3.097	3.099
32.18	05	140	2.779	2.794
35.70	11	124	2.513	2.521
38.82	04	133	2.318	2.320
41.42	04	315	2.175	2.180
46.23	04	423	1.962	1.965
52.85	05	525	1.731	1.732

Table 6: X-ray diffraction data for Th(NO₃)₄(FFAAPS)(DPSO)

 Table7: X-Ray diffraction data for Th(NCS)₄(BAAPS).(DPSO)

$2\theta_{obs}$	I/I _o	hkl	d_{obs}	d _{cal}
23.80	80	022	3.739	3.739
26.55	99	113	3.355	3.358
29.07	86	031	3.069	3.071
29.89	89	113	2.987	2.989
30.88	91	231	2.893	2.895
31.55	79	140	2.833	2.837
46.19	89	423	1.964	1.966
48.60	74	225	1.872	1.873
53.42	74	535	1.714	1.715

Table 8: Thermal analysis data of mixed ligand complexes of thorium(IV) with FFAAPS and DPSO

Complex	Decomposi	tion temp (°C)	Decomposition product	Weight loss (%)		
	Initial	Final		Theor	Exp	
ThCl₄(FFAAPS)DPSO	140	180	ThCl ₄ (FFAAPS)	22.10	21.90	
	230	280	ThCl ₄	59.08	58.83	
	400	435	ThOCl ₂	65.09	64.92	
ThBr₄(FFAAPS)DPSO	145	185	ThBr ₄ (FFAAPS)	18.49	17.92	
	240	285	ThBr ₄	49.45	49.18	
	410	440	ThOBr ₂	62.63	62.43	
Th(NCS)4(FFAAPS)DPSO	145	185	Th(NCS) ₄ (FFAAPS)	20.11	19.89	
	240	280	Th(NCS) ₄	53.78	53.46	
	410	450	ThO(NCS) ₂	63.74	63.35	
Th(NO ₃) ₄ (FFAAPS)DPSO	140	185	Th(NO ₃) ₄ (FFAAPS)	19.80	19.62	
	250	300	Th(NO ₃) ₄	52.94	52.36	
	440	510	ThO ₂	76.07	75.87	
Th(ClO ₄) ₄ 2(FFAAPS)DPSO	140	180	Th(ClO ₄) ₄ 2(FFAAPS)	13.39	13.19	
	210	260	Th(ClO ₄) ₄ (FFAAPS)	35.80	35.63	
	290	500	ThO ₂	83.81	83.59	

			Ligand mass loss (%)				Residual (%)	
Complex	Sample weight (mg)	Residual mass (mg)	$\sim 140^{\circ}$ C		250-380 [°] C		$\sim 640^{\circ} \mathrm{C}$	
			Theor ^a	Exp	Theor ^b	Exp	Theor ^c	Exp
UO2Br2(FFAAPS)DMSO	30.20	10.26	9.22	9.38	49.20	50.12	33.17	33.98
UO2(NCS)2(FFAAPS)DMSO	26.10	9.34	9.72	9.92	51.87	52.38	34.99	35.82
UO2(NO3)2(FFAAPS)DMSO	23.30	8.21	9.62	9.83	51.35	51.98	34.65	35.26
UO2(OAc)2(FFAAPS)DMSO	20.80	7.38	9.70	9.86	51.74	52.34	34.90	35.48

Table 9: Thermal analysis data on UO₂(VI) mixed ligands complexes of FFAAPS

The thermal results of [UO₂X₂(FFAAPS)DMSO] $(X = Br, NCS, NO_3 \text{ or } CH_3COO)$ are presented in Table 9. The T.G. curves of the complexes clearly indicated the absence of water molecules in these complexes. All the complexes show a weight loss (9.38-9.92%) at $\sim 140^{\circ}$ C, which corresponds to the evaporation of DMSO molecule from the complexes. The break in the curves in 250-380°C region indicates that at this stage, one molecule of FFAAPS has been lost. Finally at ~ 640°C, the oxide U_3O_8 is formed via the formation of UO₃: with no subsequent measurable change in weight [52]. The analysis of the thermogram of $[UO_2X_2(FFAAPS)DMSO]$ indicate the following decomposition scheme.

 $\begin{array}{rcl} UO_2X_2(FFAAPS)DMSO & \rightarrow & UO_2X_2 & (FFAAPS) & \rightarrow \\ UO_2X_2 \rightarrow [UO_3] \rightarrow U_3O_2 \end{array}$

Stereochemistry of the Complexes

The preferred coordination number of thorium (IV) is 6 or 8, but higher coordination numbers have also been observed[53]. It has been found from single crystal x-ray structure determination of $Th(NO_3)_4.5H_2O$ that the nitrate groups are linked to thorium through two oxygen atoms, each nitrate group functioning as a bidentate ligand [33]. In the $Th(NO_3)_4$ (L) DPSO the presence of four bidentate nitrate groups, tridentate semicarbazone and monodentate DPSO produces a coordination number of 12 for the thorium atom. The coordination number is 8 in the chloride, bromide

and thiocyanate complexes. The conductance and molecular weight data indicate that in the iodo complexes, two iodine atoms are present outside the coordination sphere, thus the coordination number 6 has been assigned for these complexes. In case of perchlorato complexes, all the four perchlorate behave as ionic in nature, hence present outside the coordination sphere. Only two semicarbazone molecule and one DPSO molecule are coordinating with thorium(IV) atom and hence a coordination number seven is proposed in these complexes.

In dioxouranium(VI) halo and pseudohalo complexes, both the anions are covalently bonded and the semicarbazones (FFAAP and CAAPS) are tridentate (N, N, O) in nature. In these complexes, DMSO is coordinating via its lone oxygen atom. Thus the present complexes show that the coordination number of U(VI) is eight. In $[UO_2(L)_2DMSO](CIO_4)_2$ both the perchlorato groups are ionic in nature, thus, in these complexes, a coordination number nine is suggested for The infrared U(VI). data of $[UO_2(L)DMSO(NO_3)_2]$ suggest that nitrate groups are bidentate in nature. Thus, in these complexes, U(VI) is surrounded by 8-oxygen atoms and 2-nitrogen atoms and this produce a coordination number ten. Similarly, in [UO₂(L)DMSO(CH₃COO)₂] complexes, a ten-coordination number is assigned to U(VI). The tentative structures of these complexes are given in Fig. 1 - 8.



Fig. 1: $[ThX_4(L)DPSO]$; X = Cl, Br or NCS; L = BAAPS or FFAAPS



Fig. 2: $[ThI_2(L)DPSO]I_2$; L = BAAPS or FFAAPS



Fig. 3: $[Th(NO_3)_4(L)DPSO]$; L = BAAPS or FFAAPS



Fig. 4: $[Th(L)_2DPSO](ClO_4)_4$; L = BAAPS or FFAAPS



Fig. 5: $[UO_2X_2(L)DMSO]$; X = Br, I or NCS; L = FFAAPS or CAAPS ______



Fig. 6: $[UO_2(NO_3)(L)DMSO]$; L = FFAAPS or CAAPS



Fig. 7: $[UO_2(CH_3COO)_2(L)DMSO]$; L = FFAAPS or CAAPS

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REFERENCES

- Cattalini, L., Croatto, U., Degeto, S. and Tondello, E., *Inorg. Chim. Acta Revs.*, 5, 19 (1971).
- [2] Bomberi, G., Inorg. Chim. Acta, 139, 21 (1987).
- [3] Maurya M.R. and Maurya, R.C., *Reviews Inorg. Chem.*, **15**, 1 (1995).
- [4] Bagnall, K.W., Coord. Chem. Revs., 2, 146 (1967).
- [5] Brown, D., Halides of Lanthanide's and Actinides, Wiley, London (1967).
- [6] Arora, K., Goel, R.C., Agarwal, D.D. and Agarwal, R.K., *Reviews Inorg. Chem.*, 18283(1998).
- [7] Agarwal, R.K., Agarwal, H. and Arora, K., *Reviews. Inorg. Chem.*, **20**, 1(2000)
- [8] Agarwal, R.K., J. Indian Chem. Soc., 72263 (1995).
- [9] Agarwal, R.K. and Prakash, J., Polyhedron, 10, 2399 (1991).
- [10] Agarwal, R.K., Tyagi, N. and Chakraborti, I., *Egypt. J. Anal. Chem.*, 7, 127 (1998).
- [11] Rajendran, G. and Kalakumari, C.R., *Asian J. Chem.*, 13, 1084 (2001).
- [12] Ramamurthy, P. and Patel, C.C., J. Inorg. Nucl. Chem., 25, 310 (1963).
- [13] Gatehouse, B.M. and Comyns, A.E., J. Chem. Soc., 3965 (1958).
- [14] Sandhu, S.S. and Sandhu(Jr.), S.S., *Indian J. Chem.*, 11A, 369 (1973).
- [15] Sidgwick, N.V., "The Chemical Elements and their Compounds," Oxford Press (1952).



Fig. 8. $[UO_2(L)_2(L)DMSO]$](ClO₄)₂; L = FFAAPS or CAAPS

- [16] Savant, V.V. and Patel, C.C., J. Inorg. Nucl. Chem., 34, 1462 (1972).
- [17] Ramamurthy, P. and Patel, C.C., *Canad. J. Chem.*, 42, 856 (1964).
- [18] Agarwal, R.K., Agarwal, H. and Manglik, A.K., Synth. React. Inorg. Met.-Org. Chem., 26, 1163 (1996).
- [19] Geary, W.J., Coord. Chem. Rev., 7,110 (1971).
- [20] Sahakari, M.P. and Mukhedar, A.J., J. Inorg. Nucl. Chem., 33, 888 (1971).
- [21] Day, J.P. and Venanzi, L.M., J. Chem. Soc.(A), 1363 (1960).
- [22] Connick, R.E. and Hughes(Jr.), Z.Z., J. Am. Chem. Soc., 746012 (1952).
- [23] Einstein, J.C. and Pryce, M.H.L., Proc. Roy. Soc., A-229, 20 (1955).
- [24] Reed, G. and Cohn, M., J. Biol. Chem., 255, 662 (1970).
- [25] Levanon, H., J. Chem. Phys., 49, 2031 (1968).
- [26] Campbell, M.J.M. and Grzeskowiak, R., J. Inorg. Nucl. Chem., 30, 1865 (1968).
- [27] Dyer, J.F., "Applications of Absorption Spectroscopy of Organic Compounds", (Prentice-Hall, New Delhi) (1984).
- [28] Agarwal, R.K. and Sarin, R.K., Polyhedron, 122411 (1993).
- [29] Agarwal, R.K., Arora, K. and Dutt, P., *Polyhedron*, 13, 957 (1994).
- [30] Agarwal, R.K., Arora, K. and Dutt, P., Synth. & React. Inorg. Met.-Org. Chem., 24, 301 (1994).

- [31] Agarwal, R.K. and Rastogi, S.C., *Thermochim. Acta*, **95**, 279 (1985).
- [32] Agarwal, R.K., Rawat, H.K. and Srivastava, A.K., *Indian J. Chem.*, **27A**, 1105 (1988).
- [33] Ferraro, J.R. and Walker, A., J. Chem. Phys., 45, 550 (1966).
- [34] Topping, G., Spectrochim. Acta, 211745 (1965).
- [35] Ueki, T., Zalkin, A. and Templeton, D., Acta Crystallogr., 20, 836 (1966).
- [36] Taylor, J.C., Mueller, H.M. and Hittermann, R.L., *Acta Crystallogr.*, **20**, 842 (1966).
- [37] Casellato, U., Vigato, P.A. and Vidali, M. Coord. Chem., Revs., 26, 85 (1978).
- [38] Ahuja, I.S., Yadav, C.L. and Tripathi, S., Asian J. Chem., 1, 195 (1989).
- [39] Burmeister, J.L., Coord. Chem. Revs., 1, 205 (1966);
 3, 225 (1968).
- [40] Bailly, R.A., Kozak, S.L., Michelson, T.W. and Mills, W.N., *Coord. Chem. Rev.*, 6, 407 (1971).
- [41] Zacharisen, W.H., Acta Cryst., 8, 743, 847 (1954).
- [42] Jones, L.H., *Spectrochim. Acta*, **10**, 395 (1958).
- [43] Narasimhan, K.V., Indian J. Chem., 35, 282 (1961).
- [44] Wilson, L.E., J. Chem. Phys., 7, 1047 (1939); 9, 76 (1941).
- [45] Badger, R.M., J. Chem. Phys., 2, 128 (1934); 3, 710 (1935).
- [46] Rastogi, V.K., Pandey, A.N., Gupta, S.L. and Saxena, R.C., *Indian J. Pure & Appl. Phys.*, 18, 379 (1980).
- [47] Garg, C.L., Gupta, S.D. and Narasimhan, K.V., *Indian J. Pure & Appl. Phys.*, 8, 108 (1970).
- [48] Rickard, C.E.F. and Woolard, D.C., Austr. J. Chem., 33, 1161 (1980).
- [49] Bombieri, G., Benetollo, F., Croatto, U., Castellani, C.B., Bagnall, K.W. and Li, X.F., *Inorg. Chim. Acta*, 95, 237 (1984).
- [50] Agarwal, R.K., Rawat, H.K. and Singh, G., Synth. React. Inorg. Met.-Org.Chem., 16,801 (1986).
- [51] Srivasatava, A.K., Srivastava, M. and Agarwal, R.K. *Ind. Engg. Chem. Prod. Res. Dev.*, **21**, 135 (1982).
- [52] Wendlandt, W.W., J. Inorg. Nucl. Chem., 5, 118 (1957); 9, 136 (1959).
- [53] Smith, B.C. and Wassef, M.A., J. Chem. Soc.(A) 1817 (1968).