

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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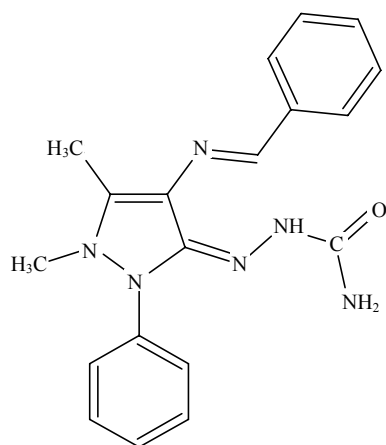
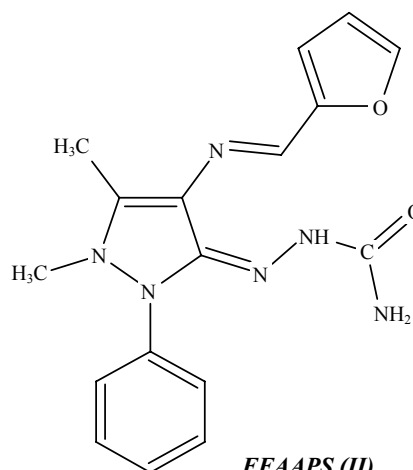
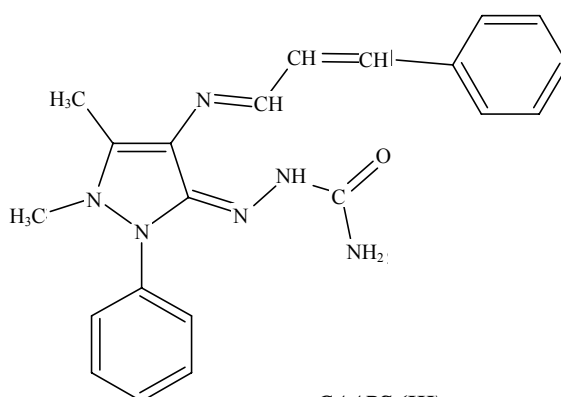
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the lack of strong crystal field effects for the $5f$ electronic configurations as well as from the large ionic radii of these metal ions, which change markedly with either oxidation number, or atomic number for these metal ions. In lighter actinides 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:

**BAAPS (I)****FFAAPS (II)****CAAPS (III)**

EXPERIMENTAL

Th(NO₃)₄·5H₂O (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 desiccator 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-aminoantipyrine, 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 P₄O₁₀. (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 DMSO 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) perchlorate 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 P₄O₁₀ (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 ± 0.01° 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

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

Complex	Yield (%)	Color	Found (Calcd) % Analysis				m.w. found (calcd)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)
			Th	N	S	Anion		
ThCl ₄ (BAAPS)DPSO	75	Yellow	24.93 (25.10)	9.04 (9.09)	3.42 (3.46)	15.26 (15.36)	918 (924)	2.2
ThBr ₄ (BAAPS)DPSO	75	Deep yellow	20.94 (21.05)	7.56 (7.62)	2.87 (2.90)	28.87 (29.03)	1095 (1102)	3.1
ThI ₄ (BAAPS)DPSO	70	Yellowish brown	17.83 (17.98)	6.43 (6.51)	2.44 (2.48)	39.28 (39.37)	427 (1290)	50.1
Th(NCS) ₄ (BAAPS)DPSO	75	Yellow	22.69 (22.87)	13.67 (13.80)	15.69 (15.77)	22.75 (22.87)	1007 (1014)	2.1
Th(NO ₃) ₄ (BAAPS)DPSO	80	Yellow	22.39 (22.52)	13.47 (13.59)	3.06 (3.10)	–	1024 (1030)	1.8
Th(ClO ₄) ₄ 2(BAAPS)DPSO	72	Yellow	15.09 (15.18)	10.89 (10.99)	2.05 (2.09)	25.87 (26.04)	303 (1528)	99.6
ThCl ₄ (FFAAPS)DPSO	78	Light yellow	25.23 (25.38)	9.13 (9.19)	3.45 (3.50)	15.42 (15.53)	908 (914)	2.1
ThBr ₄ (FFAAPS)DPSO	75	Deep yellow	21.12 (21.24)	7.65 (7.69)	2.88 (2.93)	29.19 (29.30)	1086 (1092)	2.7
ThI ₄ (FFAAPS)DPSO	70	Brownish yellow	18.01 (18.12)	6.51 (6.56)	2.46 (2.50)	39.57 (39.68)	423 (1280)	51.3
Th(NCS) ₄ (FFAAPS)DPSO	75	Yellow	22.95 (23.10)	13.84 (13.94)	15.86 (15.93)	22.96 (23.10)	998 (1004)	51.9
Th(NO ₃) ₄ (FFAAPS)DPSO	80	Yellow	22.62 (22.74)	13.63 (13.72)	3.09 (3.13)	–	1014 (1020)	1.7
Th(ClO ₄) ₄ 2(FFAAPS)DPSO	70	Yellow	15.29 (15.38)	11.07 (11.14)	2.09 (2.12)	26.29 (26.39)	298 (1508)	98.9

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, nitrate and thiocyanato complexes are non-electrolytes, 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 ThI₄(L)DPSO and Th(ClO₄)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

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 [UO₂X₂(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].

Table 2: Analytical Data of $UO_2(IV)$ mixed ligands complexes of semicarbazones and DMSO

Complex	Yield (%)	Color	Found (Calcd) % Analysis				m.w. found (calcd)	Λ_m ($ohm^{-1} cm^2 mole^{-1}$)
			Th	N	S	Anion		
$UO_2Br_2(FFAAPS)DMSO$	70	Brownish Yellow	28.02 (28.13)	9.87 (9.92)	3.70 (3.78)	18.80 (18.91)	839 (846)	2.3
$UO_2I_2(FFAAPS)DMSO$	65	Deep Yellow	25.20 (25.31)	8.87 (8.93)	3.35 (3.40)	26.90 (27.02)	935 (940)	3.3
$UO_2(NCS)_2(FFAAPS)DMSO$	72	Bright Yellow	29.57 (29.67)	13.89 (13.96)	11.85 (11.97)	14.32 (14.46)	798 (802)	3.4
$UO_2(NO_3)_2(FFAAPS)DMSO$	75	Yellow	29.29 (29.38)	13.75 (13.82)	3.89 (3.95)	—	805 (810)	2.1
$UO_2(OAc)_2(FFAAPS)DMSO$	70	Yellow	29.51 (29.60)	10.37 (10.44)	3.93 (3.98)	—	799 (804)	2.9
$UO_2(ClO_4)_2(FFAAPS)_2DMSO$	70	Yellow	19.37 (19.46)	13.66 (13.73)	2.55 (2.61)	16.15 (16.27)	410 (1233)	51.2
$UO_2Br_2(CAAPS)DMSO$	72	Brownish Yellow	26.87 (26.98)	9.47 (9.52)	3.56 (3.62)	18.02 (18.14)	875 (882)	2.4
$UO_2I_2(CAAPS)DMSO$	68	Deep Yellow	24.29 (24.38)	8.56 (8.60)	3.22 (3.27)	25.90 (26.02)	972 (976)	3.1
$UO_2(NCS)_2(CAAPS)DMSO$	70	Light Yellow	28.31 (28.40)	13.27 (13.36)	11.34 (11.45)	13.75 (13.84)	833 (838)	3.3
$UO_2(NO_3)_2(CAAPS)DMSO$	72	Yellow	28.04 (28.13)	13.16 (13.23)	3.73 (3.78)	—	841 (846)	2.2
$UO_2(OAc)_2(CAAPS)DMSO$	70	Yellow	28.24 (28.33)	9.95 (10.00)	3.74 (3.80)	—	835 (840)	2.4
$UO_2(ClO_4)_2(CAAPS)_2DMSO$	70	Yellow	18.29 (18.37)	12.89 (12.97)	2.43 (2.47)	15.28 (15.36)	435 (1295)	50.6

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 $\nu(NH_2)$ 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 $1705\text{-}1700\text{ cm}^{-1}$ region [26]. In these complexes, this band is shifted towards lower energy in the $1650\text{-}1640\text{ cm}^{-1}$ region (Table 3 and 4). The amide-II band in free ligands occurs in $1565\text{-}1560\text{ cm}^{-1}$ region. In all these complexes, this band is also shifted towards lower wave numbers by $\sim 30\text{ cm}^{-1}$ which suggests coordination through the carbonyl oxygen atom. The strong band at $\sim 1605 \pm 3\text{ cm}^{-1}$ in all the semicarbazones apparently has a large contribution from the $\nu(C=N)$ 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 $1620 \pm 5\text{ cm}^{-1}$ 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 $968\text{-}960\text{ cm}^{-1}$ showing coordination of DMSO to $UO_2(VI)$ metal ion *via* lone oxygen atom of sulfoxide, and $1040\text{-}1030\text{ cm}^{-1}$ 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 $\nu(M-N)/\nu(M-O)$ are also observed (Table 3 and 4) [29,30].

In all the perchlorato complexes, the occurrence of two strong bands at 1095 ± 5 and $630\text{-}625\text{ cm}^{-1}$ attributed to ν_3 and ν_4 vibrations of perchlorato ion suggests the presence of perchlorato groups outside the coordination sphere [31,32]. The infrared spectra of the nitrate complexes showed no absorption near 1360 cm^{-1} , where

Table 3: Key infrared bands (cm^{-1}) of thorium(IV) mixed ligand complexes of semicarbazones and DPSO

Compound	$\nu(\text{C}=\text{N})$ (Azomethinic)	$\nu(\text{C}=\text{N})$ (Hydrazinic)	$\nu(\text{C}=\text{O})$			$\nu(\text{S}=\text{O})$	$\nu(\text{Th-N})/$ $\nu(\text{Th-O})$
			I	II	III		
DPSO	—	—	—	—	—	1100 s	—
BAAPS	1610 m	1600 m	1700 s	1565 s	1350 s	—	—
$\text{ThCl}_4(\text{BAAPS})\text{DPSO}$	1505 m	1625 m	1645 s	1535 m	1330 m	1035 s	450 m 385 w
$\text{ThBr}_4(\text{BAAPS})\text{DPSO}$	1580 m	1622 m	1650 s	1532 m	1328 m	1040 s	470 m 390 w
$\text{ThI}_4(\text{BAAPS})\text{DPSO}$	1582 m	1625 m	1652 s	1535 m	1325 m	1037 s	455 m 380 w
$\text{Th}(\text{NCS})_4(\text{BAAPS})\text{DPSO}$	1580 m	1630 m	1645 s	1530 m	1328 m	1040 s	460 m 390 w
$\text{Th}(\text{NO}_3)_4(\text{BAAPS})\text{DPSO}$	1582 m	1630 m	1640 s	1532 m	1320 m	1035 s	465 m 382 w
$\text{Th}(\text{ClO}_4)_4 \cdot 2(\text{BAAPS})\text{DPSO}$	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	—	—
$\text{ThCl}_4(\text{FFAAPS})\text{DPSO}$	1575 m	1635 m	1650 m	1540 m	1325 m	1038 s	465 m 395 w
$\text{ThBr}_4(\text{FFAAPS})\text{DPSO}$	1580 m	1628 m	1652 m	1535 m	1322 m	1035 s	472 m 390 w
$\text{ThI}_4(\text{FFAAPS})\text{DPSO}$	1585 m	1630 m	1650 m	1537 m	1320 m	1040 s	468 m 392 w
$\text{Th}(\text{NCS})_4(\text{FFAAPS})\text{DPSO}$	1572 m	1625 m	1645 m	1540 m	1325 m	1035 s	470 m 385 w
$\text{Th}(\text{NO}_3)_4(\text{FFAAPS})\text{DPSO}$	1582 m	1632 m	1652 m	1535 m	1322 m	1040 s	465 m 380 w
$\text{Th}(\text{ClO}_4)_4 \cdot 2(\text{FFAAPS})\text{DPSO}$	1580 m	1630 m	1645 m	1532 m	1330 m	1038 s	475 m 382 w

the free nitrate ion is known to absorb. In all the nitrate 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 ($\sim 1510, 1285, 1030, 1015, 825, 740$ and 725 cm^{-1} as $\nu_1, \nu_4, \nu_2, \nu_6, \nu_3$ and ν_5 respectively) as in $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ [33] and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ [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 nitrate ion, the acetate ion is also a potentially bidentate ligand towards uranyl acetate with neutral monodentate ligands like TPPO, TPA₂O, 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 $[\text{UO}_2(\text{CH}_3\text{COO})_2(\text{L})\text{DMSO}]$ are monomeric in nature and the infrared spectra of these complexes

show two bands in $1550 - 1465 \text{ cm}^{-1}$ region attributed to the asymmetric and symmetric stretching vibrations of $-\text{COO}^-$ respectively [38]. In $[\text{Th}(\text{NCS})_4(\text{L})\text{DPSO}]$ and $[\text{UO}_2(\text{NCS})_2(\text{L})\text{DMSO}]$ complexes, the (C—N) stretching frequency (ν_1) appears in $2070-2060 \text{ cm}^{-1}$ 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 (ν_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 $\nu(\text{U}=\text{O})$ in all complexes has been assigned to $932-920$ and $840-825 \text{ cm}^{-1}$ region [3,6].

Table 4: Key infrared bands (cm^{-1}) of $\text{UO}_2(\text{VI})$ mixed ligands complexes of semicarbazones and DMSO

Compounds	$\nu(\text{C}=\text{N})$ (Azomethinic)	$\nu(\text{C}=\text{N})$ (Hydrazinic)	$\nu(\text{C}=\text{O})$			$\nu(\text{S}=\text{O})$	$\nu(\text{U}-\text{N})/$ $\nu(\text{U}-\text{O})$
			I	II	III		
DMSO	—	—	—	—	—	1020 s	—
FFAAPS	1615 s	1602 m	1700 s	1565 s	1340 s	—	—
$\text{UO}_2\text{Br}_2(\text{FFAAPS})\text{DMSO}$	1590 s	1625 m	1645 s	1530 m	13430 s	960 m	468m, 370 w
$\text{UO}_2\text{I}_2(\text{FFAAPS})\text{DMSO}$	1588 s	1628 m	1648 s	1535 m	1328 m	962 m	460 m, 378 w
$\text{UO}_2(\text{NCS})_2(\text{FFAAPS})\text{DMSO}$	1585 s	1630 m	1650 s	1540 m	1325 m	965 m	472 m, 370 w
$\text{UO}_2(\text{NO}_3)_2(\text{FFAAPS})\text{DMSO}$	1582 s	1625 m	1645 s	1542 m	1323 m	960 m	468 m, 370 m
$\text{UO}_2(\text{OAc})_2(\text{FFAAPS})\text{DMSO}$	1587 s	1628 m	1650 s	1545 m	1325 m	965 m	465 m, 370 w
$\text{UO}_2(\text{ClO}_4)_2(\text{FFAAPS})_2\text{DMSO}$	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	—	—
$\text{UO}_2\text{Br}_2(\text{CAAPS})\text{DMSO}$	1585 s	1630 m	1642 s	1538 m	1322 m	962 m	472 m, 375 w
$\text{UO}_2\text{I}_2(\text{CAAPS})\text{DMSO}$	1582 s	1628 m	1645 s	1535 m	1325 m	960 m	480 m, 382 w
$\text{UO}_2(\text{NCS})_2(\text{CAAPS})\text{DMSO}$	1590 s	1622 m	1648 s	1537 m	1327 m	965 m	482 m, 385 w
$\text{UO}_2(\text{NO}_3)_2(\text{CAAPS})\text{DMSO}$	1585 s	1625 m	1645 s	1528 m	1320 m	968 m	485 m, 382 w
$\text{UO}_2(\text{OAc})_2(\text{CAAPS})\text{DMSO}$	1588 s	1630 m	1642 s	1533 m	1322 m	965 m	482 m, 375 w
$\text{UO}_2(\text{ClO}_4)_2(\text{CAAPS})_2\text{DMSO}$	1582 s	1632 m	1640 s	1535 m	1325 m	960 m	480 m, 370 w

Complexation Effects on Uranyl Ion Spectra

In the present studies of mixed ligand complexes or uranyl ions, it has been observed that the ν_1 mode of the uranyl ion appears as the weak intensity and the ν_3 mode with the strong intensity in the infrared spectra (Table 5). From X-ray studies, Zachariassen [41] had predicted that the U—O bond distance varies from 1.60 Å in $\text{Na}[\text{UO}_2(\text{CH}_3\text{COO})_3]$ to 1.92 Å on MgU_2O_7 . 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 bond-lengths 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 (ν_1) [47]. Another observation is that a plot of ($\nu_1 + \nu_3$) 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 to the interaction between the bonds have also 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).

Table 5: Various force constants (m dynes/Å), U—O bond distances (Å) and frequencies (cm⁻¹) of ν_1 and ν_3 of UO₂(VI) mixed ligands complexes of semicarbazones and DMSO

Complex	U—O Force Constant	Force Constant due to interaction between bonds	U—O Bond Distance	ν_1	ν_3
UO ₂ Br ₂ (FFAAPS)DMSO	6.7242	-0.3085	1.7423	825	920
UO ₂ I ₂ (FFAAPS)DMSO	6.8025	-0.2302	1.7402	835	920
UO ₂ (NCS) ₂ (FFAAPS)DMSO	6.7242	-0.3085	1.7423	825	920
UO ₂ (NO ₃) ₂ (FFAAPS)DMSO	6.8166	-0.3698	1.7399	827	930
UO ₂ (OAc) ₂ (FFAAPS)DMSO	6.8793	-0.2302	1.7402	835	930
UO ₂ (ClO ₄) ₂ (FFAAPS) ₂ DMSO	6.8557	-0.3307	1.7384	832	930
UO ₂ Br ₂ (CAAPS)DMSO	6.8796	-0.2759	1.7378	837	928
UO ₂ I ₂ (CAAPS)DMSO	6.8016	-0.3078	1.7405	830	925
UO ₂ (NCS) ₂ (CAAPS)DMSO	6.7779	-0.3622	1.7408	825	927
UO ₂ (NO ₃) ₂ (CAAPS)DMSO	6.9188	-0.2676	1.7369	840	930
UO ₂ (OAc) ₂ (CAAPS)DMSO	6.8556	-0.3618	1.7384	830	932
UO ₂ (ClO ₄) ₂ (CAAPS) ₂ DMSO	6.8796	-0.2759	1.7378	837	928

X-Ray Powder diffraction studies

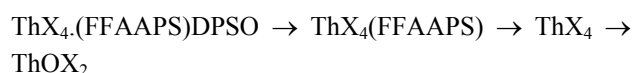
Comparatively less studies have been performed on crystal structure of actinide complexes. Crystal structure of thorium nitrate complexes of tetramethyl urea was determined by Rickard [48]. He inferred that the crystal belongs to monoclinic system with $a = 13.954(1)$; $b = 20.334(2)$; $c = 14.138(a)\text{Å}$ and $\beta = 98.06(3)^\circ$. 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 $c = 11.0715(6)\text{Å}$ 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 $c = 12.0715(4)\text{Å}$ 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

careful analysis of TG-curves of all the complexes 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 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)₂DPSO, 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:



(X = Cl, Br or NCS)

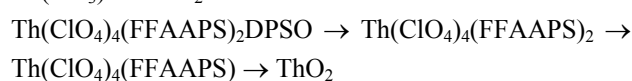
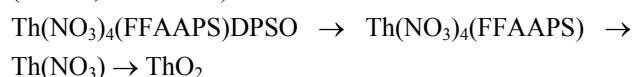


Table 6: X-ray diffraction data for $\text{Th}(\text{NO}_3)_4(\text{FFAAPS})(\text{DPSO})$

$2\theta_{\text{obs}}$	I/I ₀	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 7: X-Ray diffraction data for $\text{Th}(\text{NCS})_4(\text{BAAPS})(\text{DPSO})$

$2\theta_{\text{obs}}$	I/I ₀	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

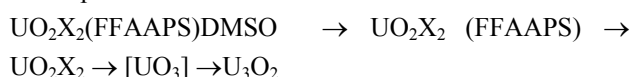
Table 8: Thermal analysis data of mixed ligand complexes of thorium(IV) with FFAAPS and DPSO

Complex	Decomposition temp (°C)		Decomposition product	Weight loss (%)	
	Initial	Final		Theor	Exp
$\text{ThCl}_4(\text{FFAAPS})\text{DPSO}$	140	180	$\text{ThCl}_4(\text{FFAAPS})$	22.10	21.90
	230	280	ThCl_4	59.08	58.83
	400	435	ThOCl_2	65.09	64.92
$\text{ThBr}_4(\text{FFAAPS})\text{DPSO}$	145	185	$\text{ThBr}_4(\text{FFAAPS})$	18.49	17.92
	240	285	ThBr_4	49.45	49.18
	410	440	ThOBr_2	62.63	62.43
$\text{Th}(\text{NCS})_4(\text{FFAAPS})\text{DPSO}$	145	185	$\text{Th}(\text{NCS})_4(\text{FFAAPS})$	20.11	19.89
	240	280	$\text{Th}(\text{NCS})_4$	53.78	53.46
	410	450	$\text{ThO}(\text{NCS})_2$	63.74	63.35
$\text{Th}(\text{NO}_3)_4(\text{FFAAPS})\text{DPSO}$	140	185	$\text{Th}(\text{NO}_3)_4(\text{FFAAPS})$	19.80	19.62
	250	300	$\text{Th}(\text{NO}_3)_4$	52.94	52.36
	440	510	ThO_2	76.07	75.87
$\text{Th}(\text{ClO}_4)_4(\text{FFAAPS})\text{DPSO}$	140	180	$\text{Th}(\text{ClO}_4)_4(\text{FFAAPS})$	13.39	13.19
	210	260	$\text{Th}(\text{ClO}_4)_4(\text{FFAAPS})$	35.80	35.63
	290	500	ThO_2	83.81	83.59

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

Complex	Sample weight (mg)	Residual mass (mg)	Ligand mass loss (%)				Residual (%) ~ 640 ^o C	
			~ 140 ^o C		250-380 ^o C		Theor ^c	Exp
			Theor ^a	Exp	Theor ^b	Exp		
UO ₂ Br ₂ (FFAAPS)DMSO	30.20	10.26	9.22	9.38	49.20	50.12	33.17	33.98
UO ₂ (NCS) ₂ (FFAAPS)DMSO	26.10	9.34	9.72	9.92	51.87	52.38	34.99	35.82
UO ₂ (NO ₃) ₂ (FFAAPS)DMSO	23.30	8.21	9.62	9.83	51.35	51.98	34.65	35.26
UO ₂ (OAc) ₂ (FFAAPS)DMSO	20.80	7.38	9.70	9.86	51.74	52.34	34.90	35.48

The thermal results of [UO₂X₂(FFAAPS)DMSO] (X = Br, NCS, NO₃ or CH₃COO) 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 ~ 140^oC, which corresponds to the evaporation of DMSO molecule from the complexes. The break in the curves in 250-380^oC region indicates that at this stage, one molecule of FFAAPS has been lost. Finally at ~ 640^oC, the oxide U₃O₈ is formed via the formation of UO₃: with no subsequent measurable change in weight [52]. The analysis of the thermogram of [UO₂X₂(FFAAPS)DMSO] indicate the following decomposition scheme.



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(NO₃)₄.5H₂O that the nitrate groups are linked to thorium through two oxygen atoms, each nitrate group functioning as a bidentate ligand [33]. In the Th(NO₃)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 [UO₂(L)₂DMSO](ClO₄)₂ both the perchlorato groups are ionic in nature, thus, in these complexes, a coordination number nine is suggested for U(VI). The infrared data of [UO₂(L)DMSO(NO₃)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.

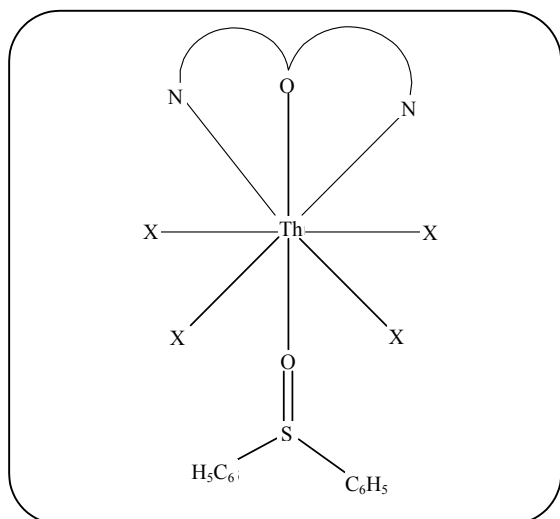


Fig. 1: $[ThX_4(L)DPSO]$; X = Cl, Br or NCS; L = BAAPS or FFAAPS

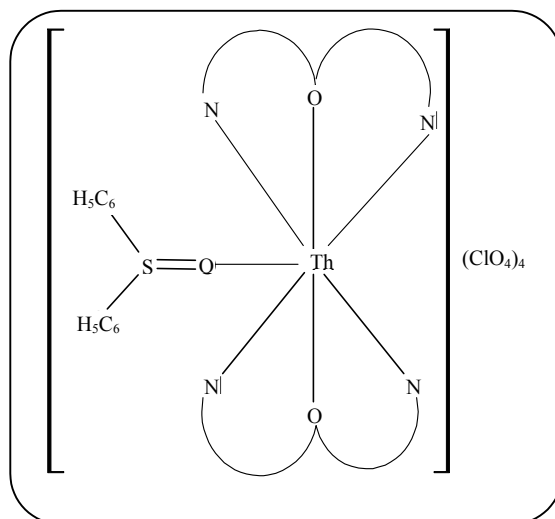


Fig. 4: $[Th(L)_2DPSO](ClO_4)_4$; L = BAAPS or FFAAPS

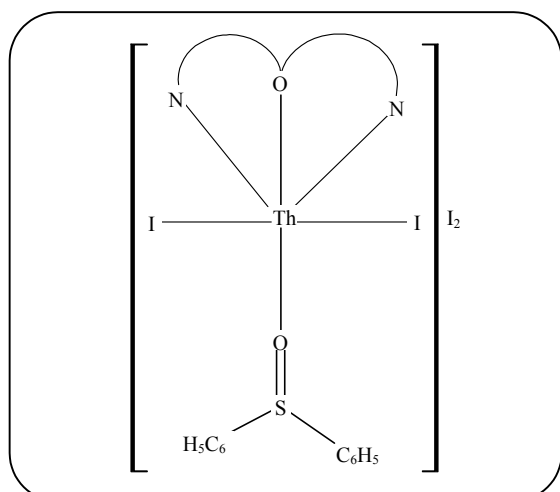


Fig. 2: $[ThI_2(L)DPSO]I_2$; L = BAAPS or FFAAPS

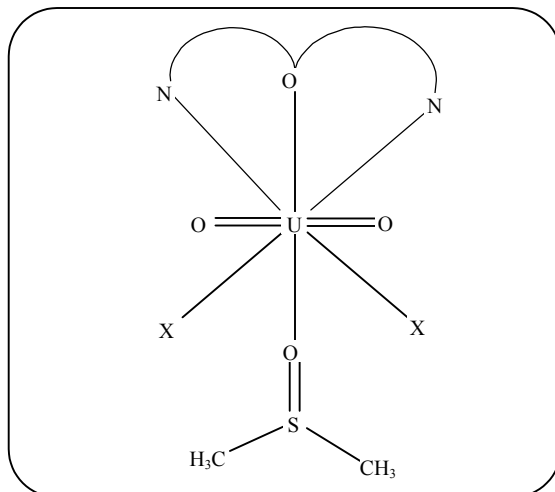


Fig. 5: $[UO_2X_2(L)DMSO]$; X = Br, I or NCS; L = FFAAPS or CAAPS

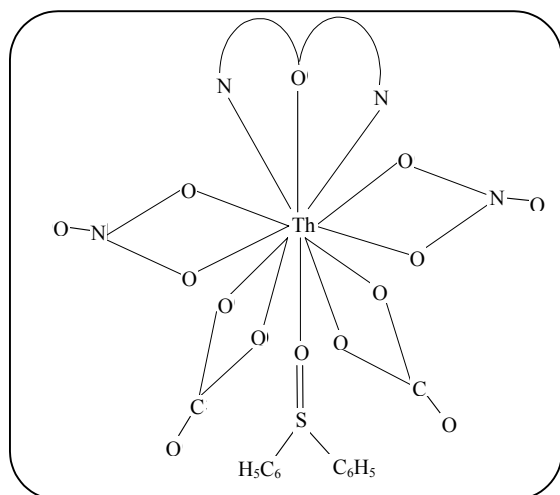


Fig. 3: $[Th(NO_3)_4(L)DPSO]$; L = BAAPS or FFAAPS

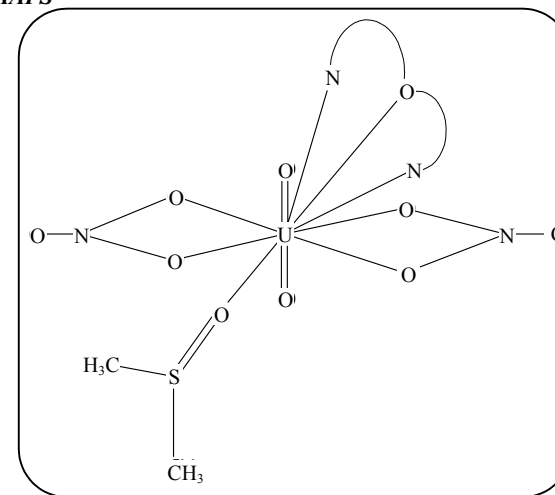


Fig. 6: $[UO_2(NO_3)(L)DMSO]$; L = FFAAPS or CAAPS

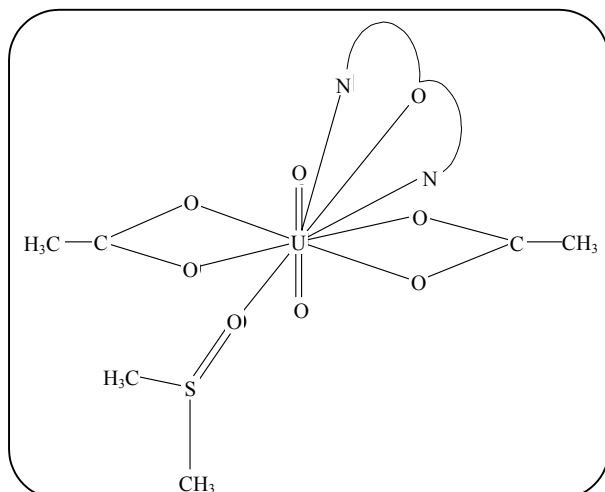


Fig. 7: $[UO_2(CH_3COO)_2(L)DMSO]$; L = FFAAPS or CAAPS

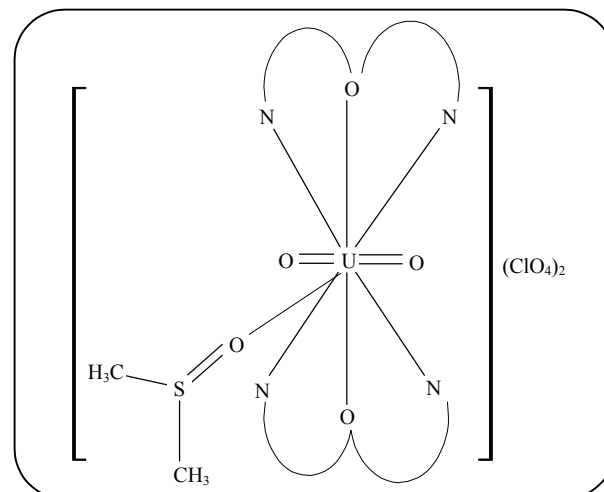


Fig. 8: $[UO_2(L)_2(L)DMSO]/(ClO_4)_2$; L = FFAAPS or CAAPS

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