

Synthesis, Spectral and Thermal Investigations of Some Mixed Ligand Complexes of Thorium(IV) Derived from Semicarbazones and Diphenyl Sulfoxide

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In the present work, the authors describe the synthesis of some mixed ligand complexes of thorium(IV) derived from 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrine semicarbazone (HNAAPS) or 4[N-(cinnamalidene)amino]antipyrinesemicarbazone (CAAPS) as primary ligand and diphenyl sulfoxide (DPSO) as secondary ligand with the general composition $\text{ThX}_4 \cdot n(\text{L}) \cdot \text{DPSO}$ ($n = 1$, $\text{X} = \text{Cl}$, Br , NCS or NO_3 ; $n = 2$, $\text{X} = \text{I}$ or ClO_4 , $\text{L} = \text{HNAAPS}$ or CAAPS). All the compounds were characterized through elemental analysis, molar conductance, molecular weight, infrared data and thermogravimetric analysis. The infrared studies reveal that the semicarbazones behave as neutral tridentate (N,N,O) while DPSO coordinates through its oxygen atom. The nitrates are bicovalently bonded, while thiocyanates are N-coordinated in these compounds. In conclusion, the coordination number of the central metal ion displays coordination number 7, 8, 9 or 12 depending on the nature of the anionic ligands.

Keywords: Mixed ligand, Complexes, Thorium, Semicarbazone, Diphenyl sulfoxide

INTRODUCTION

Thorium(IV) chemistry presents an excellent area of research, because of its possibility of formation of compounds with high coordination number, a feature sparingly observed in transition metal chemistry. The coordination chemistry of thorium(IV) has been less extensively investigated [1-3]. Th(IV) with an ionic radius 0.99 Å and a charge of 4+ fulfills the optimum conditions required for a high coordination. In view of the variations in stoichiometry from ligand to ligand [2,3] observed for various thorium(IV) complexes, it was considered worthwhile to study some mixed ligand complexes of thorium(IV) derived from 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinesemicarbazone (HNAAPS) (Fig. 1) and 4[N-(cinnamalidene)amino]antipyrinesemicarbazone

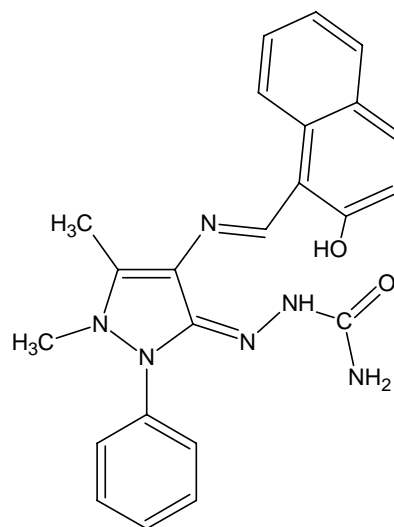


Fig. 1. 4[N-(2'-Hydroxy-1'-naphthalidene)amino]antipyrinesemicarbazone.

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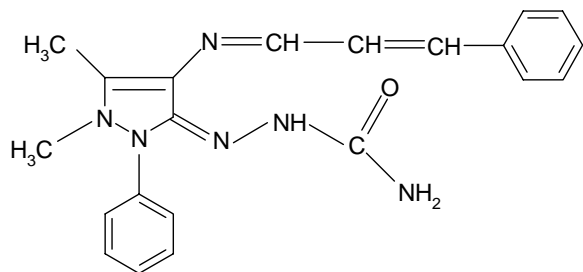


Fig. 2. 4[N-(cinnamalidene)amino]antipyrinesemicarbazone

(CAAPS) (Fig. 2) as primary ligand and diphenyl sulfoxide (DPSO) as secondary ligand. Semicarbazones are reported to possess versatile structural features and good antifungal and antibacterial properties [4-6]. Recently, we published our work [7] on thorium(IV) complexes of semicarbazones. In continuation of our work on thorium(IV), we report here the synthesis, spectral and thermal properties of some mixed ligand complexes of thorium(IV) derived from semicarbazones and DPSO.

EXPERIMENTAL

Thorium(IV) nitrate was obtained from BDH. Thorium(IV) perchlorate was prepared as reported in literature [8]. Crystals of ThX_4 ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ or NCS^-) were prepared by known methods [9]. The ligands HNAAPS and CAAPS were synthesized by known methods [7].

All the thorium(IV) complexes were synthesized by the following general method: A hot methanolic solution of the ligand (HNAAPS or CAAPS) 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) perchlorate and iodo complexes, the ratio was 1:2:1. The mixture was refluxed for ~3 h. The resulting solution was concentrated by evaporation on a water bath. The reaction mixture was then kept in an ice bath to get the desired solid complexes. All the complexes were filtered and dried in vacuo over P_4O_{10} . (Yield ~65-70%).

Analytical Methods

Thorium contents of the complexes was estimated by decomposing the complexes with boiling concentrated nitric

acid and precipitating as thorium hydroxide, which was filtered on Whatmann filter paper, washed thoroughly with distilled water and finally ignited and weighed as ThO_2 . The nitrogen was estimated by Kjeldahl's method. Sulphur content was estimated gravimetrically as BaSO_4 . The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of ± 0.01 °C accuracy. The conductivity measurements were carried out using a Conductivity Bridge and a dip type cell. All the measurements were done at room temperature in nitrobenzene. The infrared spectra of the complexes were recorded on a Perkin Elmer Infrared spectrophotometer model Spectrum 1000 in nujol. Thermogravimetric analysis was carried out on a Stanton Redcraft thermobalance model PTG-750 at a heating rate of 10 °C min^{-1} .

RESULTS and DISCUSSION

The interaction of thorium(IV) salts with HNAAPS/CAAPS in the presence of DPSO results in the formation of $\text{ThX}_{4.n}(\text{L})\text{DPSO}$ ($n = 1$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{NCS}^-$ or NO_3^- ; $n = 2$; $\text{X} = \text{I}^-$ or ClO_4^- ; $\text{L} = \text{HNAAPS}$ or CAAPS). The analytical data of these complexes are given in Table 1. The complexes are anhydrous, which is evident from the analytical, infrared and thermal studies. All of the complexes are quite stable and can be stored for long periods except for the thorium(IV) iodide complexes, which decompose slowly at room temperature with the evolution of iodine vapors. All of the complexes are generally soluble in common organic solvents. Among the thorium(IV) complexes, the chloro, bromo and thiocyanato complexes are non-electrolytes (Table 1) in nitrobenzene, whereas the iodo and perchlorato complexes dissociate in this solvent. The iodo complexes appear to be a 1:2, while the perchlorato complexes are 1:4 electrolytes. Data on the molecular weight of the complexes in freezing nitrobenzene are presented in Table 1, along with values calculated on the basis of the established formula of the complexes. The ratio of molecular weight observed for $\text{ThX}_4(\text{L})\text{DPSO}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{NCS}^-$ or NO_3^- ; $\text{L} = \text{HNAAPS}$ or CAAPS) to that calculated is ~0.98, which shows that the complexes are monomeric in solution. In the case of $[\text{ThI}_2(\text{L})_2\text{DPSO}]\text{I}_2$ and $[\text{Th}(\text{L})_2\text{DPSO}](\text{ClO}_4)_4$, the ratios are ~0.33 and ~0.20, respectively. These data further support that

Some Mixed Ligand Complexes of Thorium(IV)

Table 1. Analytical, Conductivity and Molecular Weight Data of Mixed Ligand Complexes of Thorium(IV) with HNAAPS/CAAPS and DPSO

| Complex | Found (Calcd.) Analysis (%) | | | | $\wedge m$ (ohm \cdot cm 2 mol $^{-1}$) | Mol. Wt. found (Calcd.) |
|------------------------------------|-----------------------------|------------------|----------------|------------------|---|-------------------------|
| | Th | N | S | Anion | | |
| ThCl $_4$ (HNAAPS).DPSO | 23.29 (23.43) | 8.42 (8.48) | 3.20 (3.23) | 14.26 (14.34) | 2.0 | 985 (990) |
| ThBr $_4$ (HNAAPS).DPSO | 19.75 (19.86) | 7.12 (7.19) | 2.71 (2.73) | 27.29 (27.39) | 2.7 | 1162 (1168) |
| ThI $_4$.2(HNAAPS).DPSO | 13.01 (13.10) | 9.40 (9.49) | 1.78 (1.80) | 28.58 (28.70) | 50.1 | 583 (1770) |
| Th(NCS) $_4$ (HNAAPS).DPSO | 21.38 (21.48) | 12.83 (12.96) | 2.94 (2.96) | 21.36 (21.48) | 2.1 | 1076 (1080) |
| Th(NO $_3$) $_4$ (HNAAPS).DPSO | 21.05 (21.16) | 12.67 (12.77) | 2.87 (2.91) | - | 1.8 | 1092 (1096) |
| Th(ClO $_4$) $_4$.2(HNAAPS).DPSO | 14.65 (14.77) | 10.61 (10.70) | 1.99 (2.03) | 19.52 (19.61) | 99.6 | 322 (1570) |
| ThCl $_4$ (CAAPS).DPSO | 24.30 (24.42) | 8.79 (8.84) | 3.32 (3.36) | 14.82 (14.94) | 2.1 | 947 (950) |
| ThBr $_4$ (CAAPS).DPSO | 20.44 (20.56) | 7.39 (7.44) | 2.79 (2.83) | 28.24 (28.36) | 2.7 | 1125 (1128) |
| ThI $_4$.2(CAAPS).DPSO | 13.62 (13.72) | 9.88 (9.94) | 1.86 (1.89) | 29.95 (30.05) | 51.3 | 560 (1690) |
| Th(NCS) $_4$ (CAAPS).DPSO | 22.19 (22.30) | 13.38 (13.46) | 3.04 (3.07) | 22.22 (22.30) | 51.9 | 1036 (1040) |
| Th(NO $_3$) $_4$ (CAAPS).DPSO | 21.84 (21.96) | 13.18 (13.25) | 3.00 (3.03) | - | 1.7 | 1052 (1056) |
| Th(ClO $_4$) $_4$.2(CAAPS).DPSO | 15.46 (15.57) | 11.17 (11.25) | 2.11 (2.14) | 20.58 (20.67) | 98.9 | 296 (1490) |

three species are formed in the former complexes and five species are formed in the latter set of the complexes.

Infrared spectra

The infrared spectra of the semicarbazones are too complex to make definite assignments. Empirical assignments by referring to the group frequencies may not be effective since coupling between various modes of vibration are expected as a result of resonance in the pyrazolone ring. The infrared absorption of both semicarbazones have been assigned by a comparison of their spectra with those of antipyrine, 4-aminoantipyrine [10,11] and some previous works on semicarbazones [7,12,13]. The key infrared spectral bands of free ligands and their thorium(IV) complexes are given in Table 2. As expected, the ν (NH_2) band of hydrazinic nitrogen of semicarbazide (1622 cm^{-1}) is absent in the infrared spectra of the semicarbazones [14]. It has also been observed that the amide-II band is shifted towards the lower energy side compared to that of the semicarbazones. The effect is due to the electron density drift from the hydrazinic nitrogen [15]. The characteristic absorption of the carbonyl group in HNAAPS/CAAPS is observed at $\sim 1700\text{ cm}^{-1}$ [7,12,13]. In the present complexes this band is shifted towards lower energy in the $1655\text{-}1640\text{ cm}^{-1}$ region (Table 2). The amide-II band in free ligands occurs in $1572\text{-}1565\text{ cm}^{-1}$ 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 1600 cm^{-1} in both semicarbazones apparently has a large contribution from the ν ($\text{C}=\text{N}$) mode of semicarbazone moiety [12-14]. This has been observed as a blue shift in the position of the ($\text{C}=\text{N}$) band in all the complexes. Another strong band was observed at $\sim 1610\text{ cm}^{-1}$ due to azomethine ($\text{C}=\text{N}$) absorption. On complexation this band is shifted towards the lower frequency region, indicating the coordination through the azomethinic-N atom [7,12,13]. In HNAAPS, the stretching frequency in $3500\text{-}3400\text{ cm}^{-1}$ is attributed to ν (OH). In all the complexes of HNAAPS, hydroxy frequency appears at the same region as in free ligand clearly indicating that the $-\text{OH}$ group is not taking part in coordination.

The strong ($\text{S}=\text{O}$) stretching frequency in free DPSO appears as a strong absorption at 1030 cm^{-1} , but in present complexes it appears in the region $970\text{-}960\text{ cm}^{-1}$ showing

coordination of DPSO to Th(IV) through its oxygen atom of DPSO [3,16]. In far infrared spectra the bands due to ν (Th-N)/ ν (Th-O) have also been identified (Table 2) [7,17,18].

The pseudo halide ion SCN^- ion is very interesting anion for it may coordinate through the sulfur (thio) or through the nitrogen (isothio) or through both these atoms (bridging). Infrared spectroscopy is very useful in elucidation of the type of bonding exists [19-21]. The various criteria proposed for determining the mode of bonding have been discussed by Nakamoto [22]. In general, the bonding depends on (a) the nature of central atom, (b) the nature of other ligands in the coordination sphere and (c) environmental controls and kinetic (mechanistic) controls. Class-A metals form the (M-N) bond, whereas class-B metals form the (M-S) bond [19-21]. The (C-N) stretching frequency in both the thiocyanato complexes of thorium(IV) appears at $\sim 2050\text{ cm}^{-1}$, which lies on the borderline for distinguishing, although the high relative intensity of the band in these cases suggests that the thiocyanato groups are N-bonded [19-22]. The (C-S) band identified at $\sim 830\text{ cm}^{-1}$, further confirms that the thiocyanate group is certainly N-bonded. The δ (N-C-S) (ν_2) is also identified in these complexes.

The infrared spectra of the nitrate complexes showed no absorption near 1360 cm^{-1} , where the free nitrate ion is known to absorb. The occurrence of two strong absorptions at ~ 1525 and 1300 cm^{-1} which are attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate group, respectively, further confirm that all the nitrate groups are present inside the coordination sphere [23,24]. Other absorption bands associated with the covalent nitrate groups are also observed in the spectra of these complexes, *i.e.*, 1035 (ν_2), 810 (ν_6), 742 (ν_3) and 720 cm^{-1} (ν_5). The spectral bands of $[\text{Th}(\text{L})(\text{NO}_3)_4\text{DPSO}]$ ($\text{L} = \text{HNAAPS}$ or CAAPS) were compared with the known bands of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ [25], *i.e.*, 1540 (ν_4), 1290 (ν_1), 1030 (ν_2), 808 (ν_6), 745 (ν_3) and 715 (ν_5) cm^{-1} , in which the bidentate character of the nitrate groups has been established by X-ray [26] and neutron diffraction studies [27]. It is concluded that the nitrate groups in these complexes also behave as bidentate ligands. In $[\text{Th}(\text{L})_2\text{DPSO}](\text{ClO}_4)_4$ ($\text{L} = \text{HNAAPS}$ or CAAPS), the presence of the ν_3 at ~ 1080 and ν_4 at $\sim 620\text{ cm}^{-1}$ indicate that the T_d symmetry of ClO_4^- is maintained in both the complexes. This, therefore suggests the presence of ClO_4^- outside the coordination sphere in the

Some Mixed Ligand Complexes of Thorium(IV)

Table 2. Key Infrared Bands (cm^{-1}) of Thorium(IV) Mixed Ligand Complexes of Semicarbazones and DPSO

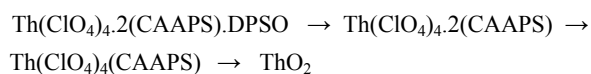
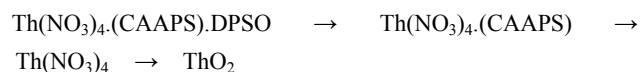
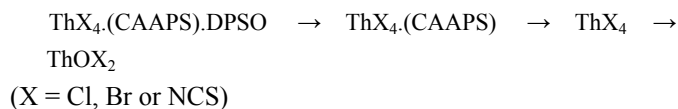
| Compound | ν (C=N) (azomethinic) | ν (C=N) (hydrazinic) | ν (C=O) | | | ν (S=O) | ν (Th-N)/ ν (Th-O) |
|--|------------------------------|-----------------------------|-------------|--------|-------|-------------|-------------------------------|
| | | | I | II | III | | |
| DPSO | - | - | - | - | - | 1030s | - |
| HNAAPS | 1608m | 1600m | 1702s | 1565s | 1342s | - | - |
| ThCl ₄ (HNAAPS).DPSO | 1570m | 1625m | 1645s | 1535m | 1330m | 965s | 455m 380w |
| ThBr ₄ (HNAAPS).DPSO | 1575m | 1628m | 1650s | 1532m | 1328m | 960s | 460m 390w |
| ThI ₄ .2(HNAAPS).DPSO | 1580m | 1625m | 1655s | 1535m | 1325m | 965s | 465m 380w |
| Th(NCS) ₄ (HNAAPS).DPSO | 1578m | 1630m | 1645s | 1530m | 1328m | 970s | 460m 390w |
| Th(NO ₃) ₄ (HNAAPS).DPSO | 1580m | 1630m | 1640s | 1532m | 1320m | 965s | 465m 385w |
| Th(ClO ₄) ₄ .2(HNAAPS).DPSO | 1585m | 1625m | 1645s | 1530m | 1325m | 970s | 470m 390w |
| CAAPS | 1610m | 1600m | 1700s | 1572s | 1350m | - | - |
| ThCl ₄ (CAAPS).DPSO | 1575m | 1635m | 1650m | 1540m | 1325m | 960s | 455m 390w |
| ThBr ₄ (CAAPS).DPSO | 1580m | 1628m | 1655m | 1535m | 1322m | 965s | 470m 390w |
| ThI ₄ .2(CAAPS).DPSO | 1585m | 1630m | 1650m | 1537m | 1320m | 970s | 465m 390w |
| Th(NCS) ₄ (CAAPS).DPSO | 1572m | 1625m | 1645m | 1540m | 1325m | 968s | 470m 385w |
| Th(NO ₃) ₄ (CAAPS).DPSO | 1582 m | 1632 m | 1650m | 1535 m | 1322m | 965s | 465m 380w |
| Th(ClO ₄) ₄ .2(CAAPS).DPSO | 1580 m | 1630 m | 1645m | 1532 m | 1330m | 968s | 475 m 382 w |

complexes [28,29].

Thermal Studies

The thermal results of the Th(IV) complexes of CAAPS and DPSO are presented in Table 3. The thermogravimetric curves of the Th(IV) complexes do not show the presence of water molecules, either in or out of the coordination sphere. The pyrolysis curves of these complexes suggest that in the first step, DPSO ligand has been evaporated in 155-170 °C temperature range. The break in the TG-curves at ~310 °C indicates that the primary ligand (CAAPS) has been lost. In chloro, bromo and thiocyanato complexes at ~455 °C, the oxohalide and oxothiocyanate formation takes place [30]. In case of nitrate complex at 510 °C, ThO₂ is the end product. From the pyrolysis curve of Th(ClO₄)₄2(CAAPS).DPSO, it is revealed that at 170 °C, DPSO molecule has been lost. In 220-250 °C temperature range, one molecule of CAAPS has been lost. Finally, at 550 °C, ThO₂ is the end product [30]. The analyses of the thermograms indicate the following

nitrobenzene solvent. Thus, in the case of [ThX₄(L).DPSO] decomposition scheme:



Stereochemistry of the Complexes

The preferred coordination number of Th(IV) is either 6 or 8, but higher coordination numbers have also been reported [31]. In the chloro, bromo and thiocyanato complexes, the conductance and molecular weight determinations suggest that the complexes are non-ionic in nature and do not dissociate in

Table 3. Thermal Analysis Data of Mixed Ligand Complexes of Thorium(IV) with CAAPS and DPSO

| Complex | Decomposition temp. (°C) | | Decomposition product | Weight loss (%) | |
|--|--------------------------|-------|---|-----------------|-------|
| | Initial | Final | | Theor. | Exp. |
| ThCl ₄ (CAAPS).DPSO | 140 | 180 | ThCl ₄ (CAAPS) | 21.26 | 20.90 |
| | 230 | 280 | ThCl ₄ | 60.63 | 59.83 |
| | 400 | 435 | ThOCl ₂ | 66.42 | 65.22 |
| ThBr ₄ (CAAPS).DPSO | 145 | 185 | ThBr ₄ (CAAPS) | 17.90 | 17.44 |
| | 240 | 285 | ThBr ₄ | 51.06 | 50.78 |
| | 410 | 440 | ThOBr ₂ | 63.82 | 62.43 |
| Th(NCS) ₄ (CAAPS).DPSO | 145 | 185 | Th(NCS) ₄ (CAAPS) | 19.42 | 18.75 |
| | 240 | 280 | Th(NCS) ₄ | 55.38 | 54.12 |
| | 410 | 450 | ThO(NCS) ₂ | 65.00 | 63.98 |
| Th(NO ₃) ₄ (CAAPS).DPSO | 140 | 185 | Th(NO ₃) ₄ (CAAPS) | 19.12 | 18.67 |
| | 250 | 300 | Th(NO ₃) ₄ | 54.54 | 53.65 |
| | 440 | 510 | ThO ₂ | 75.00 | 73.88 |
| Th(ClO ₄) ₄ 2(CAAPS).DPSO | 140 | 180 | Th(ClO ₄) ₄ 2(CAAPS) | 13.55 | 13.10 |
| | 210 | 260 | Th(ClO ₄) ₄ (CAAPS) | 38.65 | 34.78 |
| | 290 | 500 | ThO ₂ | 82.65 | 81.96 |

Some Mixed Ligand Complexes of Thorium(IV)

(X= Cl, Br or NCS; L = HNAAPS or CAAPS), the coordination number of Th(IV) is found to be 8. In the case of iodo complexes, the 1:2 electrolytic nature suggests that two iodine atoms are present outside the coordination sphere and, hence, the coordination number of Th(IV) in $[\text{Th}(\text{L})_2\text{DPSO}\cdot\text{I}_2]$ (L = HNAAPS or CAAPS) is found to be 9. It has been found from a single crystal X-ray structure determination of $\text{Th}(\text{NO}_3)_4\cdot 5\text{H}_2\text{O}$ that each nitrate group is linked to thorium through two oxygen atoms, each nitrate group thus functioning as a bidentate ligand. In $[\text{Th}(\text{NO}_3)_4(\text{L})\text{DPSO}]$ (L = HNAAPS or CAAPS) complexes, the Th(IV) is surrounded by ten oxygens and two nitrogens and thus the products have a coordination number of 12 for the thorium(IV) atom. In $[\text{Th}(\text{L})_2\text{DPSO}](\text{ClO}_4)_4$ (L = HNAAPS or CAAPS), the conductance, molecular weight and infrared studies revealed that all the four perchlorato groups are present outside the coordination sphere, hence suggesting the presence of seven-coordinated Th(IV) in these complexes. The proposed structures of the present thorium (IV) complexes are given in Fig. 3-5.

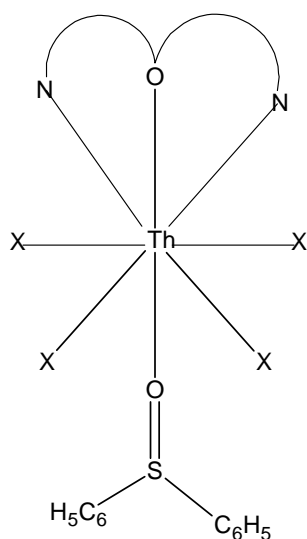


Fig. 3. $[\text{ThX}_4(\text{L})\text{DPSO}]$; X = Cl, Br or NCS; L = HNAAPS or CAAPS.

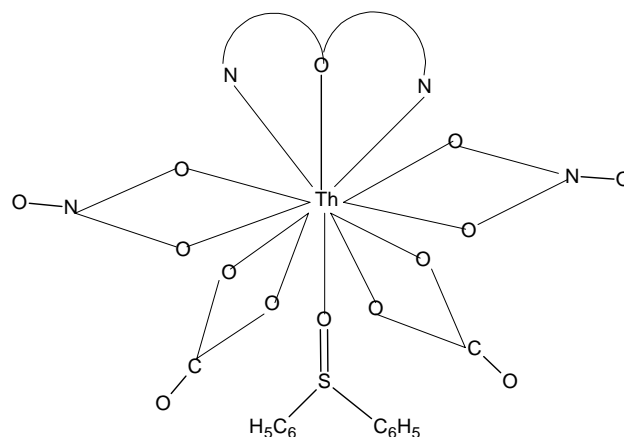


Fig. 4. $[\text{Th}(\text{NO}_3)_4(\text{L})\text{DPSO}]$; L = HNAAPS or CAAPS

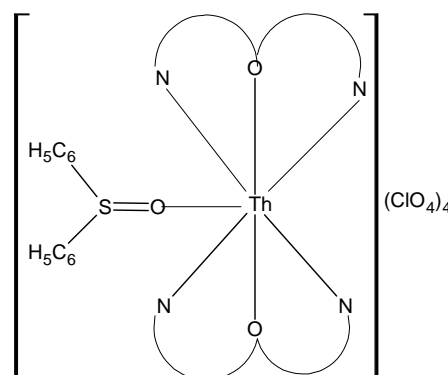


Fig. 5. $[\text{Th}(\text{L})_2\text{DPSO}](\text{ClO}_4)_4$; L = HNAAPS or CAAPS

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