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SYNTHESIS, SPECTRAL AND THERMAL PROPERTIES OF SOME HIGH COORDINATED COMPLEXES OF THORIUM(IV) AND DIOXOURANIUM(VI) DERIVED FROM 4[N-(2'-HYDROXY-1'-NAPHTHALIDENE)AMINO] ANTIPYRINETHIOSEMICARBAZONE

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ABSTRACT. In present work, we describe the synthesis of thorium(IV) and dioxouranium(VI) coordination compounds of 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinethiosemicarbazone (HNAAPTS) with the general composition $ThX_4.n(HNAAPTS)$ (X = Cl, Br, I, NCS or ClO_4, n = 2; X = NO_3, n = 1) and $UO_2X_2.n(HNAAPTS)$ (X = Br, I, NCS or ClO_4, n = 2, X = NO_3 or CH_3COO, n = 1). All the coordination compounds were characterized by analytical, molar mass, molar conductance and infrared studies. The infrared spectral studies reveal that the ligand HNAAPTS is coordinated in neutral tridentate (N,N,S) fashion. The coordination number of Th(IV) in these coordination compounds varies from 6, 8, 10 or 11; while for U(VI) the coordination number are 8, 9 or 10. Thermal stabilities of these complexes were investigated through thermogravimetric analysis.

KEY WORDS: Thorium(IV) complexes, Dioxouranium(VI) complexes, 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinethiosemicarbazone

INTRODUCTION

Lippard [1] and Muetterties [2] suggested that for a metal ion to achieve a high coordination numbers, two conditions are to be satisfied, (a) an effective size of the metal ion and (b) a high positive charge resulting from high oxidation state of central metal ion. Actinide ions generally present a high coordination number and the type of polyhedron obtainable is influenced by the nature of the coordinating ligands. Thorium(IV) and uranium(VI) with atomic radii of 1.65 and 1.42 Å, respectively, and a high positive charge fulfils the optimum conditions for formation of coordination compounds with high coordination number. A number of workers have investigated the high coordination compounds of Th(IV) and UO_2(VI) with different Schiff bases [3-11]. Actinide ions form stable complexes with 4-aminoantipyrine and its derivatives. Comparatively less is known about actinide coordination compounds with thiosemicarbazones [12, 13]. Thiosemicarbazones are potential coordinating ligands toward transition metal ions. 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinethiosemicarbazone offers multidenticity towards metal ions. In present studies, it acts as neutral tridentate (N,N,S) donor ligand. We describe some high coordination compounds of Th(IV) with varying coordination number 6, 8,10 or 11 and UO_2(VI) with 8, 9 or 10 coordination number derived from 4[N-(2'-hydroxy-1'-naphthalidene)amino] antipyrinethiosemicarbazone(HNAAPTS) (Figure 1).

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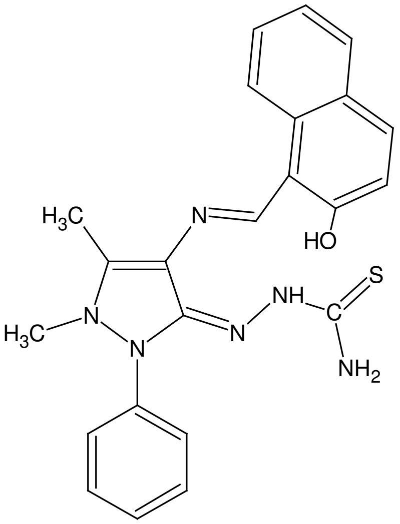


Figure 1. 4[N-(2'-hydroxy-1'-naphthalidene)amino] antipyrinethiosemicarbazone.

EXPERIMENTAL

Materials

$Th(NO_3)_4.5H_2O$ (S.D. Fine Chemicals, India) was used as received. Thorium(IV) perchlorate was prepared by known method [14]. Thorium(IV) chloride and bromide were prepared by treating thorium(IV) hydroxide with the corresponding halo acids and concentrating the solution until crystallization occurred. Thorium(IV) iodide and thiocyanate were prepared as follows: 10% methanolic solution of $Th(NO_3)_4$ and KI or KSCN were mixed so as to give Th:I or Th:NCS in the ratio of 1:4. The precipitated KNO_3 was filtered off. The filtrate containing ThI_4 was used for the preparation of complex. Thorium(IV) thiocyanate was however obtained from the filtrate after concentration by passing dry air through the solution. All the thorium(IV) salts being hygroscopic well stored in a desiccator over concentrated sulfuric acid. Uranyl(VI) nitrate and uranyl(VI) acetate were used as received from S.D. Fine Chemicals (India). Uranyl(VI) nitrate was dehydrated by keeping it over concentrated sulfuric acid [15]. Uranyl(VI) bromide was prepared from uranyl(VI) acetate by treating it with HBr. After evaporating most of the solvent, the solution was kept over sulfuric acid, till yellow crystals were separated out [16]. Uranyl(VI) iodide was obtained by treating uranyl(VI) nitrate with barium iodide in dry ether [17]. Uranyl(VI) thiocyanate was prepared by mixing alcoholic solution of anhydrous uranyl(VI) nitrate and potassium thiocyanate [18]. Uranyl(VI) perchlorate was prepared by digesting uranyl(VI) nitrate with calculated amount of perchloric acid and evaporating the mixture to dryness. It was further crystallized until free from the nitrate ions [19].

The ligand 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinethiosemicarbazone was synthesized in the laboratory by reported method [20]. All the solvents were obtained from standard sources such as E. Merck and S.D. Fine Chemicals. These solvents were used as such or after distillation if felt necessary.

Synthesis of the actinide metal-complexes

All the thorium(IV) and dioxouranium(VI) coordination compounds of HNAAPTS were synthesized by either of the following methods.
(a) The corresponding metal salt and the ligand HNAAPTS were taken in the required molar ratios in hot ethanol and the reaction mixture was refluxed for ~2 h. In each case the solid product was obtained on cooling which was washed with the solvent and finally with diethyl-ether and dried in *vacuo* over P_4O_{10}.
(b) Some of the coordination compounds were synthesized by treating HNAAPTS with the respective metal salt in the required molar ratio in isopropanol and refluxing the resulting mixture for 2-3 h. All the coordination compounds were collected after cooling and were washed with solvent and finally with anhydrous diethyl ether and then dried in *vacuo* over P_4O_{10}.

Techniques

Thorium and uranium were estimated by decomposing the complexes with boiling concentrated nitric acid and precipitating the metal hydroxide. The precipitate was filtered on Whatman filter paper and washed thoroughly with distilled water. It was finally ignited and weighed as ThO_2 or U_3O_8 respectively. The halogens were estimated by Volhard method [21]. The perchlorate was estimated by the method suggested by Kurz *et al.* [22]. Nitrogen was determined in the laboratory by the Kjeldahl method. Sulfur was estimated gravimetrically as $BaSO_4$. The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of accuracy ± 0.01 ^{o}C in the laboratory. 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 mains. All the measurements were done at room temperature in $PhNO_2$. The infrared spectra of the complexes were recorded on a Perkins Elmer infrared spectrophotometer model-521 in KBr. Thermogravimetric analysis of these coordination compounds was carried with a Santon Redcraft Thermobalance Model TG-750 thermobalance in a static air open sample holder at 6 ^{o}C/min heating rate.

RESULTS AND DISCUSSION

The reaction of non-aqueous solutions of thorium(IV) and dioxouranium(VI) with HNAAPTS resulting in formation of the coordination compounds of the general composition ThX_4.n(HNAAPTS) (X = Cl, Br, I, NCS or ClO_4, n = 2; X = NO_3, n = 1) and UO_2X_2.nL (X = Br, I, NCS or ClO_4, n = 2, X = NO_3 or CH_3COO, n = 1). The analytical data of the present coordination compounds are given in Table 1. The coordination compounds are anhydrous in nature, which is evident from their analytical, infrared and thermal studies. All the complexes are quite stable and can be stored for long period except ThI_4.2(HNAAPTS), which decomposes slowly at room temperature with evolution of iodine vapors. The analytical data are presented in Table 1. TG-curves indicated no changes up to 130 ^{o}C suggesting the absence of either coordinated or uncoordinated water molecule in these coordination compounds. The molar conductance values in nitrobenzene (Table 1) of thorium(IV) chloro, bromo, nitrato and isothiocyanato complexes are too low to account any dissociation, hence we consider that these complexes are non-electrolytes. While the iodo and perchlorato complexes dissociate in this solvent. The iodo complex appears to be a 1:2, while the perchlorato complex is 1:4 electrolyte. The uranyl(VI) complexes UO_2X_2.n(HNAAPTS) (X = Br, I, NCS, NO_3 or CH_3COO) are all essentially non-electrolytes in nitrobenzene medium. The conductance value for

$UO_2(ClO_4)_2$.2(HNAAPTS) suggests ionic perchlorato groups in this complex. Data on molecular weight of Th(IV) and UO_2(VI) complexes in nitrobenzene are given in Table 1 along with values calculated on the basis of established formula of the complexes. The ratio of molecular weight observed for ThX_4.2(HNAAPTS) (X = Cl, Br or NCS), $Th(NO_3)_4$.(HNAAPTS), UO_2X_2.2(HNAAPTS) (X = Br, I or NCS) and UO_2X_2(HNAAPTS) (X= NO_3 or CH_3COO) to that calculated is ~0.98 which shows that the complexes are monomeric in solution. In case of ThI_4.2(HNAAPTS), $UO_2(ClO_4)_2$.2(HNAAPTS) and $Th(ClO_4)_4$.2(HNAAPTS), the ratio are 0.33, 0.33 and 0.20, respectively. These data further support that three species are formed in the case of the former two complexes and five species are formed in the latter complex.

Table 1. Analytical, conductivity and molecular weight data of Th(IV) and UO_2(VI) complexes of HNAAPTS.

Compounds	Yield (%)	Colour	Analysis: found (calcd.) %				M.W. found(calc.)	Λ_m (Ohm^{-1} cm^2 mole^{-1})
			Th/U	N	S	Anion		
$ThCl_4$.2(HNAAPTS)	70	Brown yellow	18.60 (18.80)	13.40 (13.61)	5.11 (5.18)	11.39 (11.50)	1229 (1234)	2.9
$ThBr_4$.2(HNAAPTS)	65	Deep yellow	16.25 (16.43)	11.75 (11.89)	4.47 (4.53)	22.49 (22.66)	1407 (1412)	3.2
ThI_4.2(HNAAPTS)	72	Bright yellow	14.33 (14.50)	10.36 (10.50)	3.95 (4.00)	31.54 (31.78)	527 (1600)	58.2
$Th(NCS)_4$.2(HNAAPTS)	75	Yellow	17.38 (17.52)	16.78 (16.91)	14.37 (14.50)	17.30 (17.52)	1318 (1324)	2.8
$Th(NO_3)_4$.(HNAAPTS)	70	Yellow	25.30 (25.49)	15.32 (15.45)	3.45 (3.51)	-	906 (910)	2.3
$Th(ClO_4)_4$.2(HNAAPTS)	70	Yellow	15.38 (15.57)	11.16 (11.27)	4.24 (4.29)	26.58 (26.71)	294 (1490)	98.2
UO_2Br_2.2(HNAAPTS)	72	Brown-yellow	18.50 (18.68)	13.06 (13.18)	4.95 (5.02)	12.41 (12.55)	1269 (1274)	3.1
UO_2I_2.2(HNAAPTS)	68	Deep yellow	17.20 (17.39)	12.17 (12.28)	4.60 (4.67)	18.29 (18.56)	1362 (1368)	3.4
$UO_2(NCS)_2$.2(HNAAPTS)	70	Light yellow	19.16 (19.34)	15.80 (15.93)	10.36 (10.40)	9.23 (9.43)	1224 (1230)	2.9
$UO_2(NO_3)_2$.(HNAAPTS)	72	Yellow	29.30 (29.45)	13.71 (13.86)	3.90 (3.96)	-	804 (808)	2.3
$UO_2(OAc)_2$.(HNAAPTS)	70	Yellow	29.50 (29.67)	10.32 (10.47)	3.92 (3.99)	-	798 (802)	2.2
$UO_2(ClO_4)_2$.2(HNAAPTS)	70	Yellow	17.96 (18.12)	12.66 (12.79)	4.80 (4.87)	14.94 (15.15)	435 (1313)	56.9

Infrared spectra

A study and comparison of infrared spectra of free ligand (HNAAPTS) and its Th(IV) and UO_2(VI) coordination compounds (Table 2) imply that the ligand behaves as neutral tridentate and the metal ions are coordinated through N and N of two azomethine groups and of S of thioketo group. The strong bands observed in 3420-3310 cm^{-1} in free ligand have been assigned to ν(NH) vibrations. Practically no effect on these frequencies after complexation precludes the possibility of metal-coordination at this group.

The absorptions at 1600 cm^{-1} in the free ligand can be attributed to (C=N) stretching vibrations of imine which is in agreement with the observations of previous workers [23, 24]. On complexation this frequency observed to be shifted to lower wavenumber (Table 2). This observation suggests involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the central metal ion.

Table 2. Infrared absorption frequencies (cm^{-1}) of Th^{4+} and UO_2^{2+} complexes of HNAAPTS.

Complex	ν(NH)	ν(C=N)	ν(C=S) + ν(C=N) + ν(C-N)	δ(NCS) + CS-bending	ν(N-N)	ν(C=S)	ν(M-N) + ν(M-S)
HNAAPTS	3420 s 3310 s	1600 vs	1320 s 1195 m	1120 m 1095 m	1060 m	840 s 820 s	-- --
$ThCl_4$.2(HNAAPTS)	3418 s 3310 m	1570 s	1362 s 1240 m	1172 m 1135 m	1072 m	782 s 755 m	380 m 325 w
$ThBr_4$.2(HNAAPTS)	3422 s 3315 m	1565 s	1365 s 1242 m	1170 m 1125 m	1068 m	780 s 762 m	382 m 320 w
ThI_4.2(HNAAPTS)	3420 m 3310 m	1572 s	1370 s 1245 m	1175 m 1132 m	1072 w	770 s 745 m	387 m 315 w
$Th(NCS)_4$.2(HNAAPTS)	3418 m 3312 w	1568 s	1362 s 1242 m	1170 m 1137 m	1070 w	772 s 752 s	380 m 312 w
$Th(NO_3)_4$.(HNAAPTS)	3420 m 3312 m	1570 s	1365 s 1245 m	1175 m 1132 m	1068 m	770 s 750 m	382 w 315 w
$Th(ClO_4)_4$.2(HNAAPTS)	3422 s 3312 m	1572 s	1370 s 1252 m	1170 m 1130 w	1065 m	772 s 752 s	390 m 325 w
UO_2Br_2.2(HNAAPTS)	3418 m 3312 m	1575 s	1365 s 1240 m	1170 m 1130 w	1072 m	772 s 755 s	350 m 320 w
UO_2I_2.2(HNAAPTS)	3422 s 3310 m	1570 s	1362 s 1242 m	1172 m 1125 m	1070 m	770 s 750 s	352 m 322 m
$UO_2(NO_3)_2$.(HNAAPTS)	3418 m 3310 m	1562 s	1362 s 1240 m	1175 m 1130 m	1068 m	771 s 752 s	340 w 315 w
$UO_2(NCS)_2$.2(HNAAPTS)	3415 m 3318 w	1565 s	1365 s 1240 m	1172 m 1130 m	1072 w	770 s 745 s	340 m 315 w
$UO_2(ClO_4)_2$.2(HNAAPTS)	3420 m 3312 w	1570 s	1365 s 1242 m	1170 m 1125 m	1070 m	760 s 760 m	338 m 302 w
$UO_2(CH_3COO)_2$.(HNAAPTS)	3420 m 3310 m	1568 s	1370 s 1245 s	1172 m 1125 m	1070 m	782 s 755 m	340 m 305 w

In substituted thioureas, the (C=S) stretching vibrations are contributed much with some other vibrations as (CN) stretching and bending as well as (N-C-S) bending modes [25]. In the spectra of present ligand the bands observed in 1320-1195 cm^{-1}, 1120-1095 cm^{-1} and 840-820 cm^{-1} regions are assigned to [ν(C=S) + ν(C=N) + ν(C-N)], [δ(NCS) + δ(CS)] and ν(C=S), respectively, following the observations of previous workers [26, 27]. Coordination of sulfur with the metal ion would result in the displacement of electrons towards the latter, thus resulting in the weakening of (C=S) bond. Hence on complexation (C=S) stretching vibrations should decrease and that of (CN) should increase [27, 28]. In all the present complexes of Th(IV) and UO_2(VI) with HNAAPTS, the frequencies in the range of 1320-1195 cm^{-1} get an increase by nearly 50-60 cm^{-1}. Similarly bending modes of (N-C-S) and (C=S) also get an increase, but in lesser amount. On the other hand, on complexation the frequencies in 840-820 cm^{-1} are shifted to lower wave number and intensity of the bands are also reduced. All these peculiar changes on complexation confidently preclude any unambiguous ascertain of metal-sulfur bonding.

The possibility of thione-thiol tautomerism (H–N–C=S) $\leftrightarrows$ (C=N–SH) in HNAAPTS has been ruled out for no bands around 2700-2500 cm^{-1} characteristics of the thiol group are displayed in the infrared absorption [29, 30]. In free ligand the stretching frequency in 3500-3480 cm^{-1} is attributed to ν(OH). In all the complexes the –OH frequency appears at the same region as in free ligand clearly indicating the non-involvement of –OH group in metal-coordination. In far infrared spectra, some medium to weak absorption bands in 387-302 cm^{-1} region appeared due to ν(M-N)/ν(M-S) modes. In conclusion, the infrared spectral studies suggest the tridentate (N,N,S) nature of HNAAPTS in these coordination compounds.

Anions

A comparison of five infrared bands in $Th(NO_3)_4$.(HNAAPTS) which occur at 1530 (ν_4), 1280 (ν_1), 1025 (ν_2), 805 (ν_6), 735 (ν_3) and 710 (ν_5) with the known bands of $Th(NO_3)_4.5H_2O$ [31], i.e. 1520 (ν_4), 1290 (ν_1), 1030 (ν_2), 808 (ν_6), 745 (ν_3) and 715 (ν_5) in which bidentate character of the nitrato groups has been established by X-ray diffraction [32] and neutron diffraction studies [33]. Thus by analogy it is inferred that the nitrato groups in these complexes also behave as bidentate [34]. The infrared studies of dioxouranium(VI) nitrato complexes have been carried out since 1941 [35], but detailed proposal for the assignment of bands were first reported by Gatehouse and Comyn [36]. Although McGlynn *et al.* [37] and then Topping [38] reported the infrared of a series of complexes of dioxouranium(VI) nitrate, but no satisfactory explanation have been made for deciding between monodentate and bidentate nitrate complexes. But Curtis *et al.* [39] show that the overtone and the combination bands of the nitrate group may sometimes be used to distinguish the monodentate and bidentate complexes. Many infrared data on dioxouranium(VI) complexes can be found in a work of Bullock [40], in which all the complexes are in consistent with the presence of bidentate nitrato groups. The infrared spectra of $UO_2(NO_3)_2$.(HNAAPTS) show weak band at 705 cm^{-1} (ν_5), while ν_3 occurs at 756 cm^{-1}. The separation of these two frequencies is of the order of 50 cm^{-1} and similar values are reported in previous work [39]. Other frequencies, i.e. ν_1, ν_2, ν_4 and ν_6 are reported at 1287, 1028, 1510 and 805 cm^{-1}, respectively, which are comparable to those of reported bidentate complexes. Thus we inferred that in the present complex, the nitrato groups behave as bidentate ligand.

The occurrence of two strong bands at ~1085 and 620 cm^{-1} in both Th(IV) and UO_2(VI) perchlorato complexes attributed to ν_3 and ν_4 vibrations of the ionic perchlorate suggest that the perchlorate group are present outside the coordination sphere [41, 42].

In case of thiocyanate complexes, it is difficult to establish unambiguously from the infrared spectra whether the thiocyanate group is N- or S-bonded to Th(IV) or UO_2(VI) ions. The (C-N) stretching frequency in the present thiocyanato complexes of Th(IV) and UO_2(VI) appear at ~2050 cm^{-1} which is on the border line for distinguishing between sulfur and nitrogen bonding in the thiocyanate complexes [43, 44], although the high relative intensity of the band in these cases suggests that the thiocyanate groups are N-bonded [40, 41]. The frequency of the (C-S) stretching vibration has also been used to diagnose the bonding mode in thiocyanate [41, 42]. The (C-S) bond identified at ~840 cm^{-1} further confirms that the thiocyanate group is almost N-bonded [43, 44].The (N-C-S) bending (ν_2) is also identified in both the complexes at ~ 470 cm^{-1}.

Oxocation (O=U=O) vibrations

Uranyl ion UO_2^{2+} is quite peculiar both in its own structure and its coordination compounds [37, 45, 46]. The ion retains its identity over a wide range of vibrations in the experimental conditions as can be considered from the geometric point of view, as a single particle. It has three fundamental vibrations [46, 47], (i) non-degenerate symmetric stretching vibration ν_1, normally infrared forbidden occurs in the range 900-800 cm^{-1}, (ii) non-degenerate asymetric stretching vibrations ν_3, which is infrared active occurs at ~1000-900 cm^{-1}, and (iii) doubly degenerate OUO bending vibration ν_2 is infrared active and appears at ~250 cm^{-1}. In the present work, the ν(U=O) in all the dioxouranium(VI) complexes has been assigned in 950-920 cm^{-1} and 840-825 cm^{-1} region as ν_3 and ν_1 frequency respectively (Table 3).

Table 3. Various force constants (m dynes/Å), U—O bond distances (Å) and frequencies (cm^{-1}) ν_3 and ν_4 of UO_2(VI) complexes of HNAAPTS.

Complex	U—O force constant	Force constant due to interaction between bonds	U—O bond distance	ν_1	ν_3
UO_2Br_2.2(HNAAPTS)	6.7242	-0.3085	1.7423	825	920
UO_2I_2.2(HNAAPTS)	6.8025	-0.2302	1.7402	835	920
$UO_2(NCS)_2$.2(HNAAPTS)	6.7242	-0.3085	1.7423	825	920
$UO_2(NO_3)_2$.(HNAAPTS)	6.8166	-0.3698	1.7399	827	930
$UO_2(OAc)_2$.(HNAAPTS)	6.8793	-0.2302	1.7402	835	930
$UO_2(ClO_4)_2$.2(HNAAPTS)	6.8557	-0.3307	1.7384	832	930

The infrared absorption spectra of dioxouranium(VI) complexes give valuable information regarding the various vibrations due to uranyl ion, anions and crystal lattice. The available structural data indicate that the uranyl bond length is not contrast in the various uranyl compounds. In general single X-ray studies have been required to have accurate bond lengths. Due to the poor X-ray diffracting power of oxygen as compared to the uranium, only a few compounds have been studied by these techniques. Hence alternate methods have become essential to have an idea of the bond lengths from the force-constants, which can be calculated from the vibrational data. In the present studies, it has been observed that the ν_1 mode of the uranyl ion appears as weak intensity and ν_3 as strong intensity in the infrared spectra (Table 3). A group theoretical treatment [48] shows that a linear and symmetrical triatomic UO_2^{2+} ion possessing $D_{\infty}h$ symmetry which gives rise to three fundamental modes of vibrations. Wilson's G-F matrix method [49] has been used to determine the stretching and interaction force constants. The results are in turn used to determine the U-O bond distances, following Badgers' formula [50]. The force-constants, bond distances and spectral data used here in are summarized in Table 3. It is apparent from the Table 3 that the bond-length increases with decrease in the value of symmetric stretching frequency (ν_1) [48, 51]. Another observation is that a plot of (ν_1 + ν_3) versus force constant gives a straight line with the increase in the symmetric stretching vibration on complexation. U-O force constant and force constant due to 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 upon the equatorial ligand. The calculated values of the U-O bond distances of the present complexes are well within the range.

Thermal studies

The thermal results of Th(IV) complexes of HNAAPTS are presented in Table 4. The TG-curves of all the Th(IV) complexes do not show the presence of water molecule either in or out of the coordination sphere. The TG-curves of chloro and thiocyanato complexes indicate that in first step only one molecule of HNAAPTS has been lost, while at ~ 430 °C, the remaining ligand molecule has also been lost. Finally in 605-610 °C temperature range, oxohalide formation takes place [52, 53]. The decomposition of thorium(IV) nitrate complex in the 285-425 °C temperature region indicate the loss of only ligand molecule at this stage. Finally ThO_2 is obtained as residual mass at ~ 610 °C [52, 53].

The analysis of the thermograms indicates the following decomposition scheme:

ThX_4.2(HNAAPTS) $\rightarrow$ ThX_4.(HNAAPTS) $\rightarrow$ ThX_4 $\rightarrow$ $ThOX_2$
(X = Cl or NCS)

$Th(NO_3)_4$.(HNAAPTS) $\rightarrow$ $Th(NO_3)_4$ $\rightarrow$ ThO_2.

Table 4. Thermal analysis data thorium (IV) complexes of HNAAPTS.

Complex	Decomposition temp. (°C)		Decomposition product	Weight loss (%)	
	Initial	Final		Theor.	Exp.
$ThCl_4$.2(HNAAPTS)	240	300	$ThCl_4$.(HNAAPTS)	35.10	34.84
	350	430	$ThCl_4$	69.82	69.69
	510	610	$ThOCl_2$	74.45	74.14
$Th(NCS)_4$.2(HNAAPTS)	235	290	$Th(NCS)_4$.(HNAAPTS)	32.78	32.47
	340	435	$Th(NCS)_4$	65.38	64.95
	510	605	$ThO(NCS)_2$	72.82	72.50
$Th(NO_3)_4$.(HNAAPTS)	285	425	$Th(NO_3)_4$	47.92	47.25
	460	610	ThO_2	67.85	67.47

The thermal results of UO_2(VI) complexes of HNAAPTS are presented in Table 5. The TG-curves of the complexes clearly indicate the absence of water molecule in these complexes. All the pyrolysis curves behave similarly and show that the decompositions of these complexes have started at ~190 °C and are completed at 300 °C. The break in the curves in 190-225 °C region indicates that at this stage only one molecule of HNAAPTS has been lost. In this temperature range of 250-300 °C, there is an additional decrease in weight due to loss of both organic ligand molecule. The oxide U_3O_8 is formed around 835 °C, via the formation of UO_3, following which there is no measurable change in weight [54, 55]. The analysis of thermograms indicates the following decomposition scheme:

UO_2X_2.2(HNAAPTS) $\rightarrow UO_2X_2$.(HNAAPTS) $\rightarrow UO_2X_2 \rightarrow [UO_3] \rightarrow U_3O_8$.
(X = Br, NCS or ClO_4)

$UO_2(NO_3)_2$.(HNAAPTS) $\rightarrow UO_2(NO_3)_2 \rightarrow [UO_3] \rightarrow U_3O_8$.

Table 5. Thermal analysis data on UO_2(VI) complexes of HNAAPTS.

Complex	Sample wt (mg)	Residual mass (mg)	Ligand mass loss (%)				Residual (%) ~ 835 °C	
			140 – 225 °C		250-300 °C			
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.
UO_2Br_2.2(HNAAPTS)	30.20	6.72	33.75	33.98	67.50	67.82	22.03	22.26
$UO_2(NCS)_2$.2HNAAPTS)	26.20	6.00	34.95	35.26	69.91	70.24	22.81	22.98
$UO_2(NO_3)_2$.(HNAAPTS)	28.40	9.91	53.21	53.44	----	---	34.73	34.90
$UO_2(ClO_4)_2$.2(HNAAPTS)	31.60	6.79	32.74	32.98	65.49	65.69	21.37	21.51

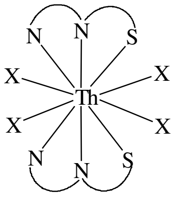
a – Calculated for loss of one molecule of HNAAPTS. b – Calculated for total loss of HNAAPTS.
c – Calculated as U_3O_8.

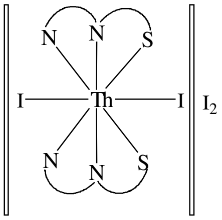
Stereochemistry

Thorium(IV) complexes

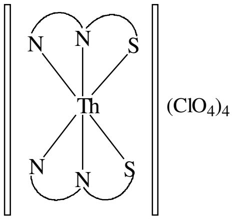
The preferred coordination number of thorium(IV) is either 6 or 8, but higher coordination numbers have also been observed [34, 56]. In chloro, bromo and isothiocyanato complexes, the conductance and molecular weight determinations suggest that the complexes are non-ionic in nature and do not dissociate in this solvent. Thus in present studies, ThX_4.2(HNAAPTS) (X = Cl, Br or NCS) complexes the coordination number of Th(IV) is found to be ten. In case of iodo complex, the 1:2 electrolytic nature suggests that the two iodine atoms are present outside the coordination sphere and hence the coordination number of Th(IV) is found to be eight. It has been found from single crystal X-ray structural determination of $Th(NO_3)_4.5H_2O$ that the nitrato groups are linked to thorium(IV) through two oxygen atoms, each nitrato group thus functioning as bidentate ligand [31]. In $Th(NO_3)_4$.HNAAPTS complex, the thorium(IV) atom is surrounded by 8-oxygen atoms of four nitrato groups, 2-nitrogen atoms of azomethine groups and 1-sulfur of thio-keto group. This produce a coordination number eleven for the thorium(IV) atom in this complex. In $Th(ClO_4)_4$.2HNAAPTS, the conductance, molecular weight and infrared studies reveal that all the four perchlorato groups are present outside the coordination sphere and hence suggesting the presence of six-coordinate thorium(IV) in present coordination compound.

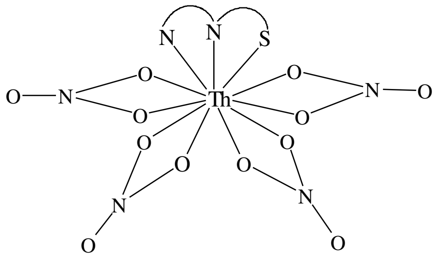
For dioxouranium(VI) coordination compounds of HNAAPTS, the conductance and molecular weight data suggest that in bromo, iodo and thiocyanato complexes, both the anions are covalently bonded. Thus in UO_2X_2.2(HNAAPTS) (X = Br, I or NCS), it may be considered to have a ten-coordinated uranium(VI) atom. Glueckauf and McKay [57] suggested that dioxouranium(VI) nitrate forms covalent complexes possibly involving 5*f*-orbitals. The infrared data of $UO_2(NO_3)_2$.(HNAAPTS) also suggests a bidentate nature of the nitrato groups in this complex. Hence the coordination number of U(VI) is nine in this complex. Similar to nitrato complex, dioxouranium(VI) acetato complex, the tridentate nature of HNAAPTS and bidentate chelating groups, nine-coordinated structureis suggested. In $[UO_2(HNAAPTS)_2](ClO_4)_2$, both perchlorato groups are ionic in nature suggest a coordination number of eight for the uranium(VI) atom. In conclusion, the following general structures of these complexes may be shown as follows:



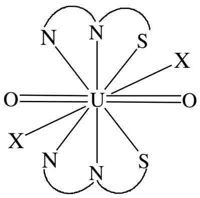


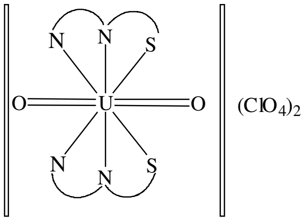
(a) $[Th(HNAAPTS)_2X_4]$ (X = Cl, Br or NCS) (C.N. = 10) (b) $[Th(HNAAPTS)_2I_2]I_2$ (C.N. = 8)



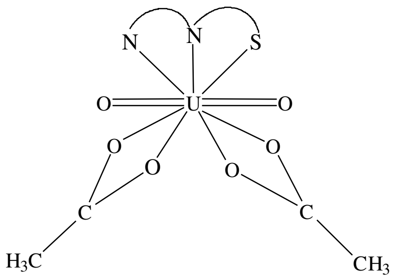


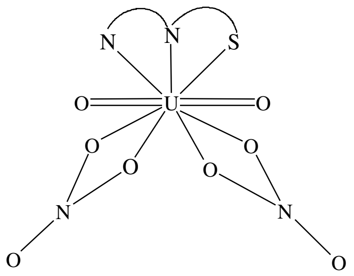
(c) $[Th(HNAAPTS)_2](ClO_4)_4$ (C.N. = 6) (d) $[Th(HNAAPTS)(NO_3)_4]$ (C.N. = 11)





(e) $[UO_2(HNAAPTS)_2X_2]$ (X = Br, I or NCS) (C.N. = 10) (f) $[UO_2(HNAAPTS)_2](ClO_4)_2$ (C.N. = 8)





(g) $[UO_2(HNAAPTS)(OOCCH_3)_2]$ (C.N. = 9) (h) $[UO_2(HNAAPTS)(NO_3)_2]$ (C.N. = 9)

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