

Synthesis and Spectral Studies on Thorium (IV) Coordination Compounds of 4-[N-(2-Hydroxybenzalidene) amino] Antipyrine Semicarbazone and 4-[N-Cinnamalidene) amino]Antipyrine Semicarbazone

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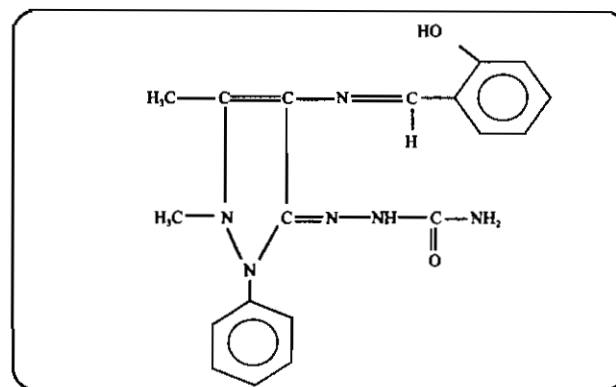
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ABSTRACT: The stereochemistry of the actinide elements has recently undergone considerable development and a wide variety of coordination numbers and geometries have been observed. This structural versatility arises from the lack of strong crystal field effects for the 5f-electronic configurations as well as from the large ionic radii of these metal ions, which change markedly with oxidation number, or atomic number for the actinides. To review the concept, in the present work, we wish to report the synthesis and spectral properties of some new thorium (IV) complexes of 4-[N-(2-Hydroxybenzalidene)amino] antipyrine semicarbazone (HBAAPS) and 4-[N-Cinnamalidene)-amino] antipyrine semicarbazone (CAAPS) with the general composition $ThX_4 \cdot 2L$ ($X=Cl^-, Br^-, I^-, NCS^-$ or ClO_4^-) and $Th(NO_3)_4 \cdot L$ ($L=HBAAPS$ or $CAAPS$). The infrared data suggest that the semicarbazones behave as tridentate N,N,O-donors. In conclusion thorium (IV) displays coordination numbers 6, 8, 10 or 11 depending on the nature of coordinating anions of these coordination compounds.

KEY WORDS: Thorium (IV), Coordination Compounds, Semicarbazone.

INTRODUCTION

Recently a number of workers have been interested in Schiff bases derived from 4-aminoantipyrine [1-3]. Agarwal *et al* [4-6] from this laboratory reported a number of Th^{4+} complexes of Schiff bases of 4-aminoantipyrine, Although two research papers [7-8] are available on the semicarbazones derived from 4-aminoantipyrine but no report is available on Th^{4+} complexes of semicarbazones of 4-aminoantipyrine. Thus in this paper, we report the synthesis, spectral and thermal studies of Th^{4+} complexes of 4-[N-(2-Hydroxybenzalidene)amino] antipyrine semicarbazone (HBAAPS) (I) and 4-[N-Cinnamalidene) amino] antipyrine semicarbazone (CAAPS) (II).



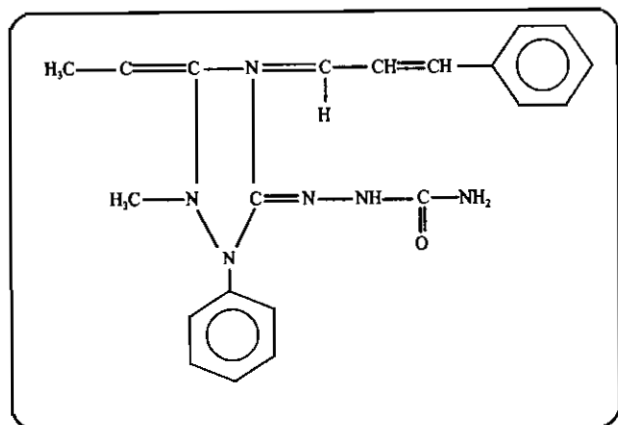
4-[N-(2-Hydroxybenzalidene)amino] antipyrine semicarbazone (HBAAPS) (I)

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4-[N-Cinnamalidene] amino] antipyrine semicarbazone (CAAPS) (II)

EXPERIMENTAL

$\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (B.D.H.) (AnalaR) was used as received. Thorium (IV) perchlorate was prepared as reported in the literature [9]. Thorium (IV) chloride and bromide were prepared by treating thorium (IV) hydroxide with the corresponding halo acid and concentrating the solution until crystallization occurred. ThI_4 and $\text{Th}(\text{NCS})_4$ were however prepared as follows:

10% Methanolic solution of $\text{Th}(\text{NO}_3)_4$ and KI or KSCN were mixed so as to give a Th: I or Th:SCN ratio of 1:4. The precipitated KNO_3 was filtered off. The filtrate containing ThI_4 was used for the preparation of complex. $\text{Th}(\text{NCS})_4$ was obtained from the filtrate after concentration by passing dry air through the solution. All the Th(IV) salts being hygroscopic were stored in a desiccator over concentrated sulfuric acid.

The ligands HBAAPS/CAAPS were prepared by refluxing an ethanolic solution of 1:1:1 molar ratio of 4-aminoantipyrine, 2-hydroxybenzaldehyde or cinnamaldehyde and neutralized semicarbazone hydrochloride for ~2h [10]. Upon cooling the respective ligand HBAAPS/CAAPS precipitated out. It was filtered, washed with ethanol, ether and finally dried in vacuum desiccator over P_4O_{10} .

PREPARATION OF THE COMPLEXES

The solid metal complexes were prepared by the following general methods:

1- The corresponding metal salt and the respective

ligand were taken in the required molar ratio in ethanol and the reaction mixture was refluxed for 1-2h. In each case a solid product was obtained on cooling which was washed with the solvent and finally with diethyl ether and dried in vacuum over P_4O_{10} .

2- To a solution of the metal salt in ethyl acetate was added the ligand in the same solvent and the reaction mixture refluxed for ~1h and left overnight at room temperature. The fine crystalline product obtained was filtered under suction, washed with ethyl acetate and finally dried in vacuum over P_4O_{10} .

All the physico-chemical studies were performed as reported earlier [11]. The halogens were estimated by Volhard's method [12]. The thiocyanate was estimated by titrating the slightly acidic solution of the complex with standard silver nitrate solution. The perchlorate determination was carried out by the procedures as described by Kurz *et al* [13].

RESULTS AND DISCUSSION

The interaction of thorium (IV) salts with HBAAPS and CAAPS results in the formation of $\text{ThX}_4 \cdot n\text{L}$ ($\text{X}=\text{Cl}^-$, Br^- , I^- , NCS^- or ClO_4^- ; $n=2$; $\text{X}=\text{NO}_3^-$; $n=1$) ($\text{L}=\text{HBAAPS}$ or CAAPS). The analytical data recorded in Table 1. The complexes are anhydrous in nature. All the complexes are quite stable and can be stored for long periods except the thorium (IV) iodide complexes, which decomposes slowly at room temperature with evolution of iodine vapours. All the complexes are generally soluble in common organic solvent. The molar conductance values in nitrobenzene suggest that the chloro-, bromo-, nitrate- and thiocyanato- complexes are non-electrolytes, whereas the iodo- and the perchlorato- complexes are 1:2 and 1:4 electrolytes respectively. Data on the molecular weight of the complexes in freezing nitrobenzene are presented in Table 1 along with the values calculated on the basis of established formula of the complexes. The ratio of the observed molecular weight for $\text{ThX}_4 \cdot 2\text{L}$ ($\text{X}=\text{Cl}^-$, Br^- or NCS^-) to that calculated is ~ 0.98 which indicates that the complexes are monomeric in solution. In the case of $\text{ThI}_4 \cdot 2\text{L}$ and $\text{Th}(\text{ClO}_4)_4 \cdot 2\text{L}$, the ratios are ~ 0.33 and ~ 0.20 respectively. These data further support that three species are formed in case of iodo-complexes and five species are formed in perchlorato-complexes.

Table 1: Analytical Data of Thorium (IV) Complexes

Complex (Colour)	Yield (%)	m.p. (°C)	Analysis: Found (Calculated)%					m.w. found (Theor.)	m (ohm ⁻¹ cm ² mole ⁻¹)
			C	H	Th	N	Anion		
ThCl ₄ .2(HBAAPS) (Yellow)	85	215	41.27 (41.37)	3.5 (3.62)	20.90 (21.05)	15.05 (15.24)	12.32 (12.88)	1099 (1102)	3.2
ThBr ₄ .2(HBAAPS) (Dark Yellow)	80	220	35.52 (35.62)	3.09 (3.12)	17.98 (18.12)	12.98 (13.12)	24.39 (25.00)	1273 (1280)	3.3
ThI ₄ .2(HBAAPS) (Brownish Yellow)	75	230d	30.98 (31.06)	2.67 (2.72)	15.57 (15.80)	11.27 (11.44)	34.20 (34.60)	487 (1468)	50.3
Th(NCS) ₄ .2(HBAAPS) (Yellow)	80	212	42.19 (42.28)	3.30 (3.35)	19.29 (19.46)	18.58 (18.79)	19.02 (19.46)	1187 (1192)	2.4
Th(NO ₃) ₄ .(HBAAPS) (Yellow)	82	220	26.76 (26.85)	2.31 (2.35)	27.28 (17.48)	26.32 (26.54)	-	840 (849)	2.3
Th(ClO ₄) ₄ .2(HBAAPS) (Yellow)	70	195d	33.48 (33.57)	2.89 (2.94)	16.82 (17.08)	12.18 (12.37)	28.87 (29.30)	268 (1358)	99.6
ThCl ₄ .2(CAAPS) (Yellow)	85	212	44.80 (44.91)	3.86 (3.92)	20.39 (10.67)	14.63 (14.97)	12.45 (12.65)	1118 (1122)	2.9
ThBr ₄ .2(CAAPS) (Dark Yellow)	82	215	38.63 (38.76)	3.34 (3.38)	17.59 (17.84)	12.73 (12.92)	24.32 (24.61)	1297 (1300)	3.3
ThI ₄ .2(CAAPS) (Yellow Brown)	70	225	33.74 (33.87)	2.91 (2.95)	15.32 (15.39)	11.05 (11.29)	33.82 (34.13)	489 (1488)	51.2
Th(NCS) ₄ .2(CAAPS) (Yellow)	78	210	45.43 (45.54)	3.58 (3.63)	18.93 (19.14)	18.29 (18.48)	18.89 (19.14)	1207 (1212)	2.3
Th(NO ₃) ₄ .(CAAPS) (Yellow)	80	230	29.41 (29.50)	2.53 (2.57)	26.89 (27.16)	26.03 (26.22)	-	850 (854)	2.7
Th(ClO ₄) ₄ .2(CAAPS) (Yellow)	70	200d	36.47 (36.57)	3.15 (3.19)	16.59 (16.83)	11.97 (12.19)	28.50 (28.88)	271 (1378)	98.7

Infrared Spectra

As expected the $\nu(\text{NH}_2)$ of the hydrazine nitrogen of semicarbazide ($\sim 1622 \text{ cm}^{-1}$) is absent in the infrared spectra of HBAAPS and CAAPS [14]. 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 [15]. The characteristic absorption of the carbonyl group in HBAAPS and CAAPS is observed in $1705\text{--}1702 \text{ cm}^{-1}$ region [14]. In the complexes, this band is shifted toward the lower energy i.e. the $1650\text{--}1645 \text{ cm}^{-1}$ region (Table 2). The amide-II band in the free ligands has been observed at $1565\text{--}1560 \text{ cm}^{-1}$ region. In all the complexes mentioned this band is also shifted towards the lower wave numbers by $30\text{--}25 \text{ cm}^{-1}$. This observation suggests coordination through the carbonyl-oxygen atom. The strong bands at $\sim 1605 \text{ cm}^{-1}$ in these semicarbazone apparently has a large contribution

from the $\nu(\text{C}=\text{N})$ mode of semicarbazone moiety [17]. This has been observed as a blue shift in the position of the $(\text{C}=\text{N})$ band in all the complexes as compared to the free ligands. Another strong band was observed at $1625\text{--}1620 \text{ cm}^{-1}$ region due to azomethine $(\text{C}=\text{N})$ absorption. Upon complexation this band is shifted towards the lower region, clearly indicating the coordination through the azomethine-N atom [18,19]. In far infrared region the bands due to $\nu(\text{Th-N})/\nu(\text{Th-O})$ are also observed [20,21]. The above discussion clearly indicates that these ligands serve as tridentates, coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms.

Anions

The occurrence of two strong bands at $\sim 1080 \text{ cm}^{-1}$ in the spectra of the perchlorato complexes, attributed to ν_3 and ν_4 vibrations of ionic perchlorato [22,23], suggests the presence of perchlorato group outside the coordina-

Table 2: Infrared absorption frequencies(cm^{-1}) of Thorium (IV) Complexes of HBAAPS and CAAPS

compounds	V(C=N) Azomethinic	$\nu(\text{C}=\text{N})$ Hydrazinic	$\nu(\text{C}=\text{O})$			$\nu(\text{Th}-\text{O})/\nu(\text{Th}-\text{N})$
			I	II	II	
HBAAPS	1620m	1605m	1702S	1565S	1345s	---
$\text{ThCl}_4 \cdot 2(\text{HBAAPS})$	1595s	1625s	1645s	1530M	1335s	480m, 382w
$\text{ThBr}_4 \cdot 2(\text{HBAAPS})$	1592s	1630s	1650s	1535m	1333m	485m, 380w
$\text{ThI}_4 \cdot 2(\text{HBAAPS})$	1590s	1628s	1648s	1540m	1330m	490m, 375w
$\text{Th}(\text{NCS})_4 \cdot 2(\text{HBAAPS})$	1593s	1630s	1645s	1542m	1328s	482m, 375w
$\text{Th}(\text{NO}_3)_4 \cdot (\text{HBAAPS})$	1595s	1628s	1650s	1542m	1330m	480m, 380w
$\text{Th}(\text{ClO}_4)_4 \cdot 2(\text{HBAAPS})$	1590s	1630s	1645s	1540m	1328m	485m, 382w
CAAPS	1625m	1608m	1705s	1560m	1340s	---
$\text{ThCl}_4 \cdot 2(\text{CAAPS})$	1582m	1630m	1650s	1530m	1325m	465m, 372m
$\text{ThBr}_4 \cdot 2(\text{CAAPS})$	1590m	1625m	1642s	1528m	1330m	468m, 370m
$\text{ThI}_4 \cdot 2(\text{CAAPS})$	1585m	1628m	1645s	1535m	1327m	460m, 375w
$\text{Th}(\text{NCS})_4 \cdot 2(\text{CAAPS})$	1588m	1620m	1642s	1537m	1325m	465m, 372w
$\text{Th}(\text{NO}_3)_4 \cdot (\text{CAAPS})$	1580m	1625m	1648s	1535m	1326m	470m, 378w
$\text{Th}(\text{ClO}_4)_4 \cdot 2(\text{CAAPS})$	1588m	1630m	1645s	1538m	1322m	472m, 270w

tion sphere. The C-N stretching frequency in the present thiocyanato complexes of thorium (IV) appears in 2070-2050 cm^{-1} region, which lies on the border line distinguishing between the sulfur and nitrogen bonding in thiocyanate [24,25] although the high relative intensity of the band in these cases suggests that the thiocyanate groups are N-bonded. The frequency of C-S stretching vibration has also been used to diagnose the bonding mode in thiocyanates [24,25]. The (C-S) band identified in 840-790 cm^{-1} region further confirm that the thiocyanate group is almost certainly N-bonded [24,25] the $\delta(\text{N}-\text{C}-\text{S})$ (ν_2) is also identified in these complexes. For thorium (IV) nitrate complexes the occurrence of two strong absorptions at 1520-1500 cm^{-1} region and 1310-1290 cm^{-1} region is attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate group respectively, suggesting that the nitrate groups lie inside the coordination sphere [26,27]. Another absorption band associated with the covalent nitrate groups is also observed in the spectra of nitrate complexes. If the ($\nu_4-\nu_1$) difference is taken as an approximate measure of the covalency of the nitrate group [27], a value of $\sim 200 \text{ cm}^{-1}$ for complexes studied suggests a strong covalency for the metal-nitrate bonding. The spectral band of $\text{Th}(\text{NO}_3)_4 \cdot \text{L}$ (L=HBAAPS or CAAPS) were compared with the known bands of

$\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ [28] i.e. 1520(ν_4), 1290 (ν_1), 1030 (ν_2), 808 (ν_6), 745(ν_3) and 715 cm^{-1} (ν_5) in which the bidentate character of the nitrate groups has been established by X-ray [29] and neutron diffraction studies [30]. It is inferred that the nitrate groups in these complexes also behave as bidentate [31,32].

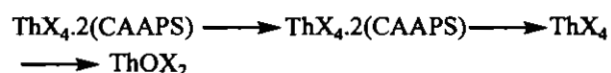
Thermal Studies

In the present investigation, we describe the thermal properties of thorium (IV) complexes of CAAPS (Table3) (Fig.1). The thermogravimetric curves of these complexes clearly indicate the absence of water molecules in the complexes. The pyrolysis curves of chloro-, bromo-and thiocyanato-complexes indicate that in the first step only one molecules of ligand is been lost, while at $\sim 435^\circ\text{C}$ the remaining ligand molecule is finally lost at $\sim 610^\circ\text{C}$, during which oxohalide and oxothiocyanate are formed $\text{Th}(\text{NO}_3)_4$. CAAPS decomposes in the 295-430 $^\circ\text{C}$ region losing the ligand molecule. Finally, ThO_2 is obtained as residual mass at $\sim 615^\circ\text{C}$. The TG-curve of $\text{Th}(\text{NO}_3)_4 \cdot (\text{CAAPS})$ shows that the complex starts to decompose at 220 $^\circ\text{C}$ and continues upto 610 $^\circ\text{C}$ after which ThO_2 is remained. From the pyrolysis curve, it is clear that no stable intermediate perchlorate complex is formed in this case. In the case of iodo complexes, a

Table 3: Thermal Data of Th(IV) Complexes of CAAPS

Complexes	Decomposition Temp. (°C)		Decomposition Product	Weight Loss (%)	
	Initial	Final		Found	Calculated
ThCl ₄ .2(CAAPS)	245	300	ThCl ₄ .CAAPS	33.82	33.33
	350	435	ThCl ₄	67.12	66.66
	515	605	ThOCl ₂	72.08	71.56
ThBr ₄ .2(CAAPS)	230	285	ThBr ₄ .CAAPS	29.11	28.76
	325	435	ThBr ₄	57.98	57.53
	520	610	ThOBr ₂	69.11	68.61
Th(NCS) ₄ .2 (CAAPS)	295	430	Th(NO ₃) ₄	44.11	43.79
	470	615	ThO ₂	69.98	69.08
Th(NO ₃) ₄ .(CAAPS)	240	305	Th(NCS) ₄ .CAAPS	31.25	30.85
	330	440	Th(NCS) ₄	62.23	61.71
	510	600	ThO(NCS) ₂	70.32	69.96
Th(ClO ₄) ₄ .2(CAAPS)	215	610	ThO ₂	81.39	80.84

sticky mass is formed. Therefore we did not study the thermal analyses of these complexes. The analyses of the thermograms indicate the following decomposition schemes:



(X=Cl⁻, Br⁻ or NCS⁻)

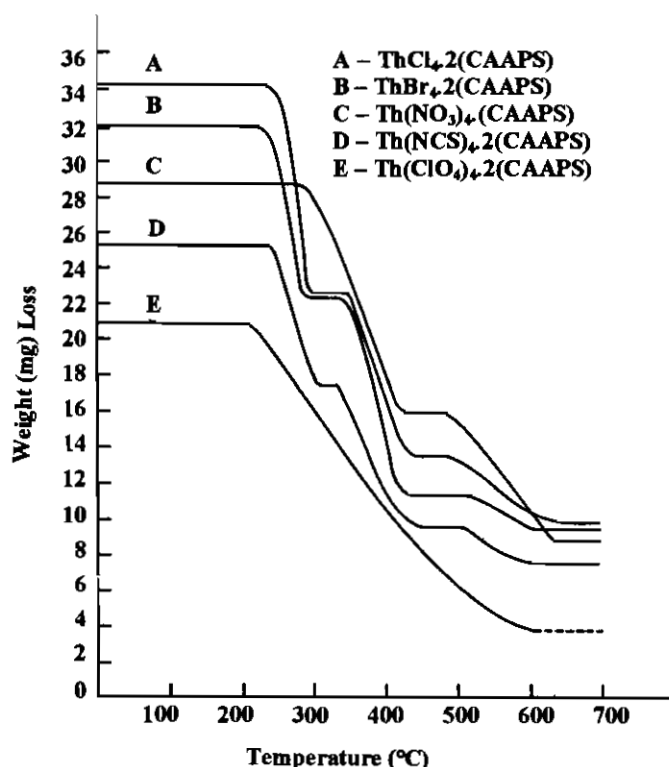


Fig1: Thermal curves of Th(IV) complexes.

STEREOCHEMISTRY

The preferred coordination number of Th (IV) is 6 or 8, but higher coordination numbers have also been observed [33]. In 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 these solvents. Thus in case of HBAAPS and CAAPS complexes of ThX₄ (X=Cl⁻, Br⁻ or NCS⁻) the coordination number of Th (IV) seems to be ten. In case of iodo complexes the 1:2 electrolytic nature suggest that two iodine atoms are present outside the coordination sphere and hence the coordination number of Th (IV) in [Th(L₂)I₂]₂ (L=HBAAPS or CAAPS) is suggested to be eight. 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 groups functioning a bidentate ligand [29,34]. In [Th(L)(NO₃)₄] (L=HBAAPS or CAAPS) complexes, the Th (IV) atom is surrounded by 9-oxygen (8-oxygen from four nitrate groups and 1-oxygen from amide group) and 2-nitrogen atoms of azomethine groups there by leading to a coordination number of

11 for the thorium atom. In $[\text{ThL}_2](\text{ClO}_4)_4$ (L=HBAAPS or CAAPS) the conductance, molecular weight and infrared studies reveal that all the four perchlorate groups are present outside the coordination sphere, suggesting the presence of six-coordinated thorium (IV) in these complexes.

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