
Ram K. Agarwal*, Indranil Chakraborti and N.K. Sharma
Department of Chemistry, Lajpat Rai (PG) College, Sahibabad-201 005, (Ghaziabad), India

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 ThX₄.2L (X=CZ-, Br-, I, NCS⁻ or ClO₄⁻) and Th(NO₃)₄L (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 Th⁴⁺ 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 Th⁴⁺ complexes of semicarbazones of 4-aminoantipyrine. Thus in this paper, we report the synthesis, spectral and thermal studies of Th⁴⁺ complexes of 4-[N-(2-Hydroxybenzalidene)amino] antipyrine semicarbazone (HBAAPS) (I) and 4-[N-Cinnamalidene) amino] antipyrine semicarbazone (CAAPS) (II).

* To whom Correspondence should be addressed.
+ E-mail: ajchem@indiatimes.com
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EXPERIMENTAL

Th(NO₃)₄.5H₂O (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. ThI₄ and Th(NCS)₄ were however prepared as follows:

10% Methanolic solution of Th(NO₃)₄ and KI or KSCN were mixed so as to give a Th: I or Th:SCN ratio of 1:4. The precipitated KNO₃ was filtered off. The filtrate containing ThI₄ was used for the preparation of complex. Th(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 P₂O₁₀.

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 P₂O₁₀.

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 P₂O₁₀.

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 ThX₄.nL (X=Cl⁻, Br⁻, I⁻, NCS⁻ or ClO₄⁻; n=2; X=N0₃⁻; n=1) (L=HBAPS 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 perchlorato- complexes are 1:2 and 1:4 electrolytes respectively. Data on the molecular weight of the complexes in freezing nitrobenzene are presented in Table1 along with the values calculated on the basis of established formula of the complexes. The ratio of the observed molecular weight for ThX₄.2L (X=C1⁻, Br⁻ or NCS⁻) to that calculated is ~ 0.98 which indicates that the complexes are monomeric in solution. In the case of ThI₄.2L and Th(ClO₄)₄.2L, 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.
Infrared Spectra

As expected the \(\nu(\text{NH}_2)\) of the hydrazine nitrogen of semicarbazide (~1622 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 1705-1702 cm\(^{-1}\) region [14]. In the complexes, this band is shifted towards the lower energy i.e. the 1650-1645 cm\(^{-1}\) region (Table2). The amide-II band in the free ligands has been observed at 1565-1560 cm\(^{-1}\) region. In all the complexes mentioned this band is also shifted towards the lower wave numbers by 30-25 cm\(^{-1}\). This observation suggests coordination through the carbonyl-oxygen atom. The strong bands at ~1605 cm\(^{-1}\) in these semicarbazone apparently has a large contribution from the \(\nu(C=N)\) mode of semicarbazone moiety [17]. This has been observed as a blue shift in the position of the \(\nu(C=N)\) band in all the complexes as compared to the free ligands. Another strong band was observed at 1625-1620 cm\(^{-1}\) region due to azomethine (C=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].

Anions

The occurrence of two strong bands at ~1080 cm\(^{-1}\) in the spectra of the perchlorato complexes, attributed to \(\nu_3\) and \(\nu_4\) vibrations of ionic perchlorato [22,23], suggests the presence of perchlorato group outside the coordina-
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] and the bidentate character of the nitrato groups has been established by X-ray [29] and neutron diffraction studies [30]. It is inferred that the nitrato 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 (Table 3) (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 ~ 435°C the remaining ligand molecule is finally lost at ~ 610°C, during which oxohalide and oxothiocyanate are formed. Th(NO₃)₄·(CAAPS) decomposes in the 295-430°C region losing the ligand molecule. Finally, ThO₂ is obtained as residual mass at ~ 615°C. The TG-curve of Th(NO₃)₄·(CAAPS) shows that the complex starts to decompose at 220°C and continues up to 610°C after which ThO₂ 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>
<thead>
<tr>
<th>Compounds</th>
<th>V(C=N) Azomethinic</th>
<th>V(C=N) Hydrazinic</th>
<th>V(C=O) I</th>
<th>V(C=O) II</th>
<th>V(Th-O)/V(Th-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBAAPS</td>
<td>1620 m</td>
<td>1605 m</td>
<td>1702 S</td>
<td>1565 S</td>
<td>1345 S</td>
</tr>
<tr>
<td>ThCl₄·2(HBAAPS)</td>
<td>1595 s</td>
<td>1625 s</td>
<td>1645 s</td>
<td>1530 M</td>
<td>1335 S</td>
</tr>
<tr>
<td>ThBr₄·2(HBAAPS)</td>
<td>1592 s</td>
<td>1630 s</td>
<td>1650 s</td>
<td>1535 M</td>
<td>1333 M</td>
</tr>
<tr>
<td>ThI₄·2(HBAAPS)</td>
<td>1590 s</td>
<td>1628 s</td>
<td>1648 s</td>
<td>1540 M</td>
<td>1330 M</td>
</tr>
<tr>
<td>Th(NCS)₄·2(HBAAPS)</td>
<td>1593 s</td>
<td>1630 s</td>
<td>1645 s</td>
<td>1542 m</td>
<td>1328 s</td>
</tr>
<tr>
<td>Th(NO₃)₄·2(HBAAPS)</td>
<td>1595 s</td>
<td>1628 s</td>
<td>1650 s</td>
<td>1542 m</td>
<td>1330 m</td>
</tr>
<tr>
<td>Th(ClO₄)₄·2(HBAAPS)</td>
<td>1590 s</td>
<td>1630 s</td>
<td>1645 s</td>
<td>1540 m</td>
<td>1328 m</td>
</tr>
<tr>
<td>CAAPS</td>
<td>1625 m</td>
<td>1608 m</td>
<td>1705 s</td>
<td>1560 m</td>
<td>1340 s</td>
</tr>
<tr>
<td>ThCl₄·2(CAAPS)</td>
<td>1582 m</td>
<td>1630 m</td>
<td>1650 s</td>
<td>1530 m</td>
<td>1325 m</td>
</tr>
<tr>
<td>ThBr₄·2(CAAPS)</td>
<td>1590 m</td>
<td>1625 m</td>
<td>1642 s</td>
<td>1528 m</td>
<td>1330 m</td>
</tr>
<tr>
<td>ThI₄·2(CAAPS)</td>
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<td>1628 s</td>
<td>1645 s</td>
<td>1535 m</td>
<td>1327 m</td>
</tr>
<tr>
<td>Th(NCS)₄·2(CAAPS)</td>
<td>1588 m</td>
<td>1620 m</td>
<td>1642 s</td>
<td>1537 m</td>
<td>1325 m</td>
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<tr>
<td>Th(NO₃)₄·2(CAAPS)</td>
<td>1580 m</td>
<td>1625 m</td>
<td>1648 s</td>
<td>1535 m</td>
<td>1326 m</td>
</tr>
<tr>
<td>Th(ClO₄)₄·2(CAAPS)</td>
<td>1588 m</td>
<td>1630 m</td>
<td>1645 s</td>
<td>1538 m</td>
<td>1322 m</td>
</tr>
</tbody>
</table>
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:

\[
\text{ThX}_4.2(\text{CAAPS}) \rightarrow \text{ThX}_4.2(\text{CAAPS}) \rightarrow \text{ThX}_4 \rightarrow \text{ThOX}_2
\]

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Decomposition Temp. (°C)</th>
<th>Decomposition Product</th>
<th>Weight Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Found</td>
</tr>
<tr>
<td>ThCl(_4).2(\text{CAAPS})</td>
<td>245</td>
<td>300</td>
<td>33.82</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>435</td>
<td>67.12</td>
</tr>
<tr>
<td></td>
<td>515</td>
<td>605</td>
<td>72.08</td>
</tr>
<tr>
<td>ThBr(_4).2(\text{CAAPS})</td>
<td>230</td>
<td>285</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>435</td>
<td>57.98</td>
</tr>
<tr>
<td></td>
<td>520</td>
<td>610</td>
<td>69.11</td>
</tr>
<tr>
<td>Th(NCS)(_4).2(\text{CAAPS})</td>
<td>295</td>
<td>430</td>
<td>44.11</td>
</tr>
<tr>
<td></td>
<td>470</td>
<td>615</td>
<td>69.98</td>
</tr>
<tr>
<td>Th(NO(_3))(_4).(CAAPS)</td>
<td>240</td>
<td>305</td>
<td>31.25</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>440</td>
<td>62.23</td>
</tr>
<tr>
<td></td>
<td>510</td>
<td>600</td>
<td>70.32</td>
</tr>
<tr>
<td>Th(ClO(_4))(_4).2(\text{CAAPS})</td>
<td>215</td>
<td>610</td>
<td>81.39</td>
</tr>
</tbody>
</table>

\(X=\text{Cl}^-, \text{Br}^-, \text{or NCS}^-\)

\[
\text{Th(NO}_3\text{)}_4(\text{CAAPS}) \rightarrow \text{Th(NO}_3\text{)}_4 \rightarrow \text{ThO}_2
\]

\[
\text{Th(ClO}_4\text{)}_4.2(\text{CAAPS}) \rightarrow \text{ThO}_2
\]

**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 ThX\(_4\) \((X=\text{Cl}^-, \text{Br}^-\) 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(L\(_2\))I\(_2\)]\(_2\) (L=HBAAPS or CAAPS) is suggested to be eight. It has been found from single crystal X-ray structure determination of Th(NO\(_3\))\(_4\)·5H\(_2\)O that the nitrato groups are linked to thorium through two oxygen atoms. Each nitrato groups functioning a bidentate ligand [29,34]. In [Th(L)(NO\(_3\))\(_4\)] \((L=\text{HBAAPS or CAAPS})\) complexes, the Th (IV) atom is surrounded by 9-oxygen (8-oxygen from four nitrato 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 \([\text{ThL}_2]\) \((\text{ClO}_4)_4(\text{L}=	ext{HBAAPS or CAAPS})\) the conductance, molecular weight and infrared studies reveal that all the four perchlorato groups are present outside the coordination sphere, suggesting the presence of six-coordinated thorium (IV) in these complexes.

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