

## Synthesis and Characterization of Mixed Ligand Complexes of Thorium(IV) with N,N'-Triethylenediamine-bis-(3-carboxypropenamide) and Various Anions

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The present research paper is concerned with the synthesis and characterization of some mixed ligand complexes of thorium(IV) with N,N'-triethylenediamine-bis-(3-carboxypropenamide) [TEBCPH<sub>2</sub>] and various anions such as nitrate, perchlorate and thiocyanate. The analytical data include determination of molecular mass, metal percentage, anion percentage, molar conductance, spectral and thermal studies. The complexes confirm the composition: [Th(TEBCP)X<sub>2</sub>] where X = NO<sub>3</sub><sup>-</sup> or NCS<sup>-</sup> and [Th(TEBCP)ClO<sub>4</sub>]ClO<sub>4</sub>.

**Key Words:** Synthesis, Mixed ligand complexes, Thorium(IV).

### INTRODUCTION

In continuation of our early studies<sup>1,2</sup> on the complexing characteristics of TEBCPH<sub>2</sub>, we report here the synthesis and characterization of solid mixed ligand complexes of nitrate, perchlorate and thiocyanate of thorium(IV) ion. The primary ligand TEBCPH<sub>2</sub> acts as a hexadentate ligand coordinating through the carboxylate groups, carbonyl groups of the secondary amide and NH of the secondary amino groups.

### EXPERIMENTAL

The reagents and solvents were of analytical grade. The ligand TEBCPH<sub>2</sub> was prepared by literature method<sup>1,2</sup>.

**Preparation of N,N'-Triethylenediamine-bis-(3-carboxypropenamide), [TEBCPH<sub>2</sub>]:** Maleic anhydride (0.1 mol) was dissolved in glacial acetic acid (50 mL) and to this triethylenetetramine (0.05 mol) was added dropwise with constant stirring under ice-cold conditions. The white solid formed was filtered, washed several times with acetone and then recrystallized from aqueous ethanol. The pure ligand has the m.p. 176°C.

**Preparation of the complexes of thorium(IV) with TEBCPH<sub>2</sub>:** The nitrate and perchlorate complexes were prepared by refluxing a methanolic solution of the ligand with the metal salt in stoichiometric amounts for 2–3 h. The resulting solution was concentrated to half of its volume and cooled. The solid complexes were filtered, washed and dried. The thiocyanato complex was prepared by

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refluxing the nitrate complex with stoichiometric amounts of thiocyanate or acetate for 2–3 h.

The thorium content of the complex was determined by oxalate-oxide method<sup>3</sup>. The nitrate content of the complex was determined gravimetrically by using nitron reagent<sup>4</sup>. The thiocyanate content of the complex was determined gravimetrically as AgSCN<sup>4</sup>. The amount of perchlorate was determined by Kurz's method<sup>5</sup>. The molar conductances of the complexes in acetonitrile, methanol, nitrobenzene and DMF (*ca.*  $10^{-3}$  M) solutions were measured at room temperature ( $28 \pm 2^\circ\text{C}$ ). Magnetic susceptibilities of the complexes were measured at room temperature. The IR spectra of the ligand and the complexes were recorded in the range of  $4000\text{--}400\text{ cm}^{-1}$  by KBr disc technique. Molar masses of the complexes were determined by the Rast method using biphenyl as the solvent<sup>6</sup>.

The TG and DTG curves of the complexes were recorded on a thermal analyzer from ambient to  $800^\circ\text{C}$ . Independent pyrolysis experiment was also carried out for each of the complexes studied and loss of mass determined in each case was compared with the obtained from TG.

## RESULTS AND DISCUSSION

The analytical data and molar masses of the complexes are presented in Table-1. The molar conductance values (Table-2) were compared with the data available for standard substances to see whether the anions are coordinated or not<sup>7,8</sup>. It was observed that the nitrate and thiocyanate complexes behave like

TABLE -1  
ANALYTICAL AND MOLAR MASS DATA OF THE COMPLEXES OF TEBCPH<sub>2</sub>  
WITH THE NITRATES, THIOCYANATES AND PERCHLORATES OF Th(IV)

Complex	Thorium (%)	Anion (%)	Molar mass
[Th(TEBCP)(NO <sub>3</sub> ) <sub>2</sub> ]	32.50 (33.33)	17.94 (18.39)	721 (696)
[Th(TEBCP)(NCS) <sub>2</sub> ]	32.62 (33.72)	16.43 (16.86)	712 (688)
[Th(TEBCP)ClO <sub>4</sub> ] <sub>2</sub> ClO <sub>4</sub>	30.01 (30.09)	25.19 (25.80)	789 (771)

Calculated values are given in parentheses.

TABLE- 2  
MOLAR CONDUCTANCE DATA OF Th(IV) COMPLEXES WITH TEBCPH<sub>2</sub>

Complex	Molar conductance ( $\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ )			
	Methanol	Acetonitrile	Nitrobenzene	DMF
[Th(TEBCP)(NO <sub>3</sub> ) <sub>2</sub> ]	31	11	5	3
[Th(TEBCP)(NCS) <sub>2</sub> ]	27	9	4	2
[Th(TEBCP)ClO <sub>4</sub> ] <sub>2</sub> ClO <sub>4</sub>	104	149	29	84

Concentration *ca.*  $10^{-3}$  M.

non-electrolytes in all the solvents used indicating that the anions present in all the complexes are coordinated to the metal ions. The perchlorato complex behaves like 1 : 1 electrolyte. These values suggest that one  $\text{ClO}_4^-$  is coordinated to the metal ion. All the Th(IV) complexes are found to be diamagnetic as expected in view of the noble gas electronic configuration of Th(IV).

The infrared spectra of ligand TEBCPH<sub>2</sub> and its complexes of Th(IV) in presence of various anions give the bonding nature of the ligand and the anions towards the metal ion. The spectra of the thorium(IV) complexes with TEBCPH<sub>2</sub> show the hexadentate nature of the ligand with two carbonyl oxygen, two secondary amino groups and two carbonyl groups of secondary amides acting as donor sites. The infrared spectra of the ligand showed a medium band at  $3100\text{ cm}^{-1}$  and it is assigned to  $\nu(\text{O—H})$  of carboxylic acid group<sup>9</sup>. This group is hydrogen bonded (intramolecular) with the carbonyl group of the amide. The disappearance of this band in the complexes shows the deprotonation of the acid group and its coordination through the hydroxyl oxygen. This is further supported by the disappearance of the characteristic carboxylic absorption (at  $1700\text{ cm}^{-1}$ ) and the appearance of two new bands at  $1560\text{--}1540$  and  $1360\text{--}1340\text{ cm}^{-1}$  which may be assigned to asymmetric and symmetric stretching frequencies respectively of coordinated carboxylate group. Shifting of the medium band at  $1400\text{ cm}^{-1}$  due to  $\nu(\text{C—O})$  of  $\text{—COOH}$  group to a lower frequency of  $1380\text{ cm}^{-1}$  also supports the argument of deprotonation of  $\text{—COOH}$  group and coordination through the hydroxyl oxygen. Here  $\Delta\nu(\text{COO}^-)$  is about  $200\text{ cm}^{-1}$  which indicates the monodentate nature of the carboxyl group. The medium band around  $3320\text{ cm}^{-1}$  in the spectrum of the ligand which is due to the  $\nu(\text{N—H})$  of the secondary amino group is shifted to a lower frequency,  $3290\text{--}3280\text{ cm}^{-1}$ , on complex formation. This indicates the participation of the secondary amino group in complex formation. The amide carbonyl stretching frequency at  $1620\text{ cm}^{-1}$  is shifted to lower frequency,  $1590\text{--}1580\text{ cm}^{-1}$ , on complex formation. This shows the participation of the amide carbonyl group in complex formation. Medium intensity bands observed around  $490\text{--}430\text{ cm}^{-1}$  and  $600\text{--}515\text{ cm}^{-1}$  are assigned to  $\nu(\text{M—O})$  and  $\nu(\text{M—N})$  respectively.

The neutral nature of the nitrate complex indicates the presence of two nitrate ions inside the coordination sphere. The IR spectrum of the nitrate complex of Th(IV) with TEBCPH<sub>2</sub> as primary ligand shows three additional bands at  $1430$ ,  $1300$  and  $1020\text{ cm}^{-1}$ , which are not present in the spectrum of TEBCPH<sub>2</sub>. These three bands are attributed respectively to  $\nu_4$ ,  $\nu_1$  and  $\nu_2$  modes of the coordinated nitrate ions<sup>10–12</sup>. Since the difference between  $\nu_4$  and  $\nu_1$  ( $\Delta\nu = \nu_4 - \nu_1$ ) is *ca.*  $130\text{ cm}^{-1}$ , it is inferred that the nitrate ions are coordinated unidentately to Th(IV). The IR spectrum of the thiocyanato complex of Th(IV) with TEBCPH<sub>2</sub> as primary ligand exhibits some additional bands at  $2050\text{--}2040$ ,  $860$  and  $460\text{ cm}^{-1}$  which are assigned to  $\nu(\text{CN})$ ,  $\nu(\text{CS})$  and  $\delta(\text{NCS})$  modes of the coordinated thiocyanate ion. It has been well established that  $\nu(\text{CN})$  occurs at a lower wavenumber around  $2050\text{ cm}^{-1}$  in N-bonded complexes as compared to the position in the case of S-bonded complexes<sup>13</sup> appearing around  $2100\text{ cm}^{-1}$ . Moreover,  $\nu(\text{CS})$  mode appears in the range  $860\text{--}780\text{ cm}^{-1}$  for N-bonded complex while it appears in the range  $720\text{--}690\text{ cm}^{-1}$  for S-bonded complexes. N-bonded

complexes also exhibit a single sharp band corresponding to  $\delta(\text{NCS})$  mode<sup>14, 15</sup> around  $480 \text{ cm}^{-1}$  and S-bonded complexes show several bands with lower intensities around  $420 \text{ cm}^{-1}$ . In view of these, it may be concluded that thiocyanate is coordinated unidentately to Th(IV) through the N-atom. Coordination of thiocyanate ions is supported by the non-electrolytic nature of the complex. In the infrared spectra of the perchlorate complexes, there are five additional bands which have no corresponding bands in the spectrum of the ligand at  $1100, 1080, 1020, 970$  and  $620 \text{ cm}^{-1}$ . The three bands at  $1100, 1080$  and  $620 \text{ cm}^{-1}$  may be assigned to  $\nu_4, \nu_1$  and  $\nu_3$  modes of coordinated perchlorate ion. This shows the unidentate coordination of  $\text{ClO}_4^-$  ion to Th(IV) ion<sup>16</sup>. Two bands observed at  $1020$  and  $970 \text{ cm}^{-1}$  are attributed to  $\nu(\text{ClO}_4)$  (ionic) present in the complexes. Thus, the IR spectral data of the ligand and perchlorato complexes suggest the presence of both ionic as well as unidentately coordinated perchlorate ions in these complexes. This has been supported by the conductance data which show 1 : 1 electrolytic behaviour.

Thermal studies were conducted on  $[\text{Th}(\text{TEBCP})(\text{NO}_3)_2]$  and  $[\text{Th}(\text{TEBCP})(\text{NCS})_2]$ . Independent pyrolysis experiment in air was also carried out for each of the complexes studied. For this a known amount of the complex was heated in a porcelain crucible up to  $800^\circ\text{C}$  for about 1 h. From the mass of the residue obtained, the loss of mass was calculated in each case, which was compared with the percentage loss of mass obtained from the experiment. For the complex,  $[\text{Th}(\text{TEBCP})(\text{NO}_3)_2]$  the TG plateau up to  $210^\circ\text{C}$  shows its stability and the complex starts decomposition after this temperature. There are two stages of decomposition as shown by the DTG peaks at  $228$  and  $485^\circ\text{C}$ . The TG curve shows a second plateau after  $520^\circ\text{C}$ . This indicates the completion of the decomposition. The decomposition at  $228^\circ\text{C}$  is due to the dissociation of the organic moiety, making a mass loss of 48%. The decomposition continues with a gradual decrease in weight and a constant weight is obtained at about  $520^\circ\text{C}$ . The residual mass obtained is about 37% which confirms that the decomposition product is  $\text{ThO}_2$ .

For the complex  $[\text{Th}(\text{TEBCP})(\text{NCS})_2]$ , the TG plateau is up to  $198^\circ\text{C}$  indicating that this complex is stable up to  $198^\circ\text{C}$ . The DTG curve has two peaks at  $212$  and  $451^\circ\text{C}$  showing that this complex undergoes decomposition in two stages. The TG curve exhibits a second plateau after  $490^\circ\text{C}$  indicating the completion of decomposition. The complex shows a weight loss of about 49% at  $212^\circ\text{C}$ . The complex decomposes rapidly at  $212^\circ\text{C}$  due to the breaking up of the organic moiety of the complex. The decomposition continues with a gradual decrease in weight and a constant weight due to the formation of  $\text{ThO}_2$  is obtained at about  $490^\circ\text{C}$ . The residual weight is about 38% which corresponds to the decomposition product,  $\text{ThO}_2$ . The independent pyrolysis also confirms that  $\text{ThO}_2$  is the decomposition product.

All these studies confirm the structure of the complexes as  $[\text{Th}(\text{TEBCP})\text{X}_2]$  where  $\text{X} = \text{NO}_3^-$  or  $\text{SCN}^-$ . For perchlorato complex the structure was found to be  $[\text{Th}(\text{TEBCP})\text{ClO}_4]\text{ClO}_4$ . Thus, a coordination number of 8 is assigned to thorium in  $[\text{Th}(\text{TEBCP})\text{X}_2]$  and 7 in  $[\text{Th}(\text{TEBCP})\text{ClO}_4]\text{ClO}_4$ .

## REFERENCES

1. M. Viswanathan and G. Krishnan, *Asian J. Chem.*, **16**, 169 (2004).
2. ———, *Asian J. Chem.*, **16**, 439 (2004).
3. I.M. Kolthoff and P.S. Elving, *Treatise on Analytical Chemistry, Part II, Vol. 8*, Interscience, New York (1963).
4. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, John Wiley & Sons, New York (1963).
5. E. Kurz, G. Kober and M. Berl, *Anal. Chem.*, **30**, 1983 (1958).
6. W.G. Palmer, *Experimental Physical Chemistry*, The University Press, Cambridge (1954).
7. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
8. G.B. Deacon, J.H.S. Green and R.S. Nyholm, *J. Chem. Soc.*, 3411 (1965).
9. W. Kemp, *Organic Spectroscopy, ELBS (English Language Book Society)-MacMillan, Hong Kong* (1985).
10. J.R. Ferraro, *J. Mol. Spectra*, **4**, 99 (1960).
11. H. Mohanta and K.C. Dash, *J. Indian Chem. Soc.*, **54**, 166 (1977).
12. B.S. Manhas, A.K. Trikha and M. Singh, *J. Inorg. Nucl. Chem.*, **43**, 305 (1981).
13. P.C.H. Mitchell and R.J.P. Williams, *J. Chem. Soc.*, 1912 (1960).
14. J. Lewis, R.S. Nyholm and P.W. Smith, *J. Chem. Soc.*, 4590 (1961).
15. A. Sabatini and Bertini, *Inorg. Chem.*, **4**, 959 (1965).
16. B.J. Hathaway and V.E. Underhill, *J. Chem. Soc.*, 3191 (1961).

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