

Synthesis and Characterization of Thorium(IV) Complexes with *N,N'*-Diethyleneamine-bis(3-carboxypropenamide)

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A new series of complexes of Th(IV) with a polydentate ligand, *N,N'*-diethyleneamine-bis(3-carboxypropenamide), [DBCPH₂] derived from maleic anhydride and diethylene triamine and various anions such as nitrate, perchlorate and thiocyanate have been synthesized. These complexes were characterized by various physico-chemical data such as CHN, metal ion contents, spectral, magnetic and molar conductivities. The complexes confirm the composition [Th(DBCP)X₂] where X = NO₃⁻, NCS⁻ or ClO₄⁻.

Key Words: Synthesis, Thorium(IV), Complexes, *N,N'*-diethyleneamine-bis(3-carboxypropenamide).

INTRODUCTION

In continuation of our early studies¹ on the complexing characteristics of *N,N'*-diethyleneami-bis-(3-carboxypropenamide) derived from maleic anhydride and diethylene triamine, DBCPH₂, we report here the synthesis and characterization of solid mixed ligand complexes of thorium(IV) with polydentate ligand, in the presence of various anions like nitrate, perchlorate and thiocyanate.

EXPERIMENTAL

The reagents and solvents were of analytical grade. The ligand DBCPH₂ was prepared by literature method¹.

Preparation of *N,N'*-diethyleneamine-bis(3-carboxypropenamide)(DBCPH₂)

Maleic anhydride (9.8 g, 0.1 mmol) was dissolved in glacial acetic acid and to this diethylenetriamine (5.4 mL, 0.05 mmol) was added dropwise with constant stirring while cooling in ice. The white solid formed was filtered, washed thoroughly with acetone and dried. It was purified by dissolving in sodium carbonate solution (5%) and reprecipitated by the addition of dilute hydrochloric acid in cold (m.p. 193°C).

Preparation of the complexes of thorium(IV) with DBCPH₂

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 its volume and cooled. The solid complexes were filtered, washed and dried. The thiocyanato complex was prepared by refluxing the nitrate complex with stoichiometric amounts of thiocyanate² for 2–3 h.

The thorium content of the complex was determined by oxalate-oxide method³. The nitrate content of the complex was determined gravimetrically by using nitron reagent⁴. The thiocyanate content of the complex was determined gravimetrically as AgSCN⁴. The amount of perchlorate was determined by Kurz's method⁵. The molar conductance of the complexes in acetonitrile, methanol, nitrobenzene and DMF (10⁻³ M) solutions were measured at room temperature (28 ± 2°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 4000–400 cm⁻¹ by KBr disc technique. Molar masses of the complexes were determined by the Rast method using biphenyl as the solvent⁶.

The TG and DTG curves of the complexes were recorded on a thermal analyzer from ambient to 800°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 that obtained from TG.

RESULTS AND DISCUSSION

All the complexes are non-hygroscopic crystalline solids. They are insoluble in benzene, petroleum ether and chloroform, but are sparingly soluble in acetonitrile, methanol and nitrobenzene. 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^{7,8}. It was observed that all the complexes behave like non-electrolytes in all the solvents used indicating that the anions present in all the complexes are coordinated to the metal ions.

TABLE-1
ANALYTICAL AND MOLAR MASS DATA OF THE COMPLEXES OF DBCPH₂ WITH THE NITRATES, THIOCYANATES AND PERCHLORATES OF Th(IV)

| Complex | Thorium (%) | Anion (%) | Molar mass |
|---|-------------|--------------|------------|
| [Th(DBCP)(NO ₃) ₂] | 31.8 (33.6) | 16.3 (17.81) | 632 (653) |
| [Th(DBCP)(NCS) ₂] | 33.7 (35.9) | 16.3 (17.90) | 621 (645) |
| [Th(DBCP)(ClO ₄) ₂] | 29.7 (31.8) | 26.9 (27.30) | 702 (728) |

Calculated values are given in parentheses.

TABLE-2
MOLAR CONDUCTANCE DATA OF Th(IV) COMPLEXES WITH DBCPH₂

| Complex | Molar conductance (ohm ⁻¹ cm ² mol ⁻¹) | | | |
|---|--|--------------|--------------|-----|
| | Methanol | Acetonitrate | Nitrobenzene | DMF |
| [Th(DBCP)(NO ₃) ₂] | 21 | 11 | 15 | 13 |
| [Th(DBCP)(NCS) ₂] | 17 | 9 | 14 | 12 |
| [Th(DBCP)(ClO ₄) ₂] | 30 | 28 | 17 | 14 |

Concentration in 10⁻³ M.

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 DBCPH₂ 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 DBCPH₂ show the pentadentate nature of the ligand with two carbonyl oxygen, one secondary amino group and two carbonyl groups of secondary amides acting as donor sites. The infrared spectra of the ligand showed a medium band at 3100 cm⁻¹ and it is assigned to $\nu(\text{O—H})$ of carboxylic acid group⁹. This group is hydrogen bonded (intramolecular) with carbonyl group of the amide. The disappearance of the band in the complexes shows the deprotonation of the acid group and its coordination through the hydroxyl hydrogen. This is further supported by the disappearance of characteristic carboxylic absorption at 1700 cm⁻¹ and the appearance of two new bands at 1560–1540 and 1360–1340 cm⁻¹ which may be assigned to asymmetric and symmetric stretching frequencies respectively of coordinated carboxyl group. Shifting the medium band at 1400 cm⁻¹ due to $\nu(\text{C—O})$ of —COOH group to a lower frequency of 1380 cm⁻¹ also supports the argument of deprotonation of —COOH group and coordination through the hydroxyl group. Here the large separation (*ca.* 200 cm⁻¹) between the two bands confirms the unidentate nature of carboxylate ion¹⁰. The medium band around 3320 cm⁻¹ in the spectrum of the ligand which is due to the $\nu(\text{N—H})$ of the secondary amino group which is shifted to a lower frequency *ca.* 3280 cm⁻¹ on complex formation. This indicates the participation of the secondary amino group in complex formation. The amide carbonyl stretching frequency at 1620 cm⁻¹ is shifted to lower frequency, 1590–1580 cm⁻¹, on complexation. This shows the participation of the amide carbonyl group in complex formation. Medium intensity bands observed around 450 and 540 cm⁻¹ are assigned to $\nu(\text{Th—O})$ and $\nu(\text{Th—N})$ respectively.

The nature of the nitrate complex indicates the presence of two nitrate ions inside the coordination sphere. The IR spectrum of Th(IV) with DBCPH₂ as primary ligand shows three additional bands at 1430, 1300 and 1020 cm⁻¹, which are not in the spectrum of DBCPH₂. These three bands are attributed respectively

to ν_4 , ν_1 and ν_2 modes of the coordinated nitrate ions¹¹⁻¹³. Since the difference between ν_4 and ν_1 is around 130 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 DBCPH₂ as primary ligand exhibits some additional bands at 2050–2040, 860 and 460 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 cm^{-1} in N-bonded complexes as compared to the position in the case of S-bonded complexes¹⁴ appearing around 2100 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 $720\text{--}690$ for S-bonded complexes. N-bonded complexes also exhibit a single sharp band corresponding to $\delta(\text{NCS})$ mode^{15, 16} around 480 cm^{-1} and S-bonded complexes show several bands with lower intensities at 420 cm^{-1} . In view of these, it may be concluded that thiocyanate is coordinated unidentately to Th(IV) through the N-atom. Coordination of the thiocyanate is supported by the non-electrolyte nature of the complex. In the infrared spectrum of the perchlorate complexes, there are three additional bands, which have no corresponding bands in the spectrum of the ligand at 1100, 1080 and 620 cm^{-1} . The three bands may be assigned to ν_4 , ν_1 and ν_3 modes of perchlorate ion. This shows the unidentate coordination of ClO_4^- ion to Th(IV) ion¹⁷. Thus, the IR spectra of the ligand and perchlorato complexes suggest the presence of unidentately coordinated perchlorate ion in these complexes. This has been supported by the conductance data, which show non-electrolytic behaviour.

Thermal studies were conducted on $[\text{Th}(\text{DBCP})(\text{NO}_3)_2]$ and $[\text{Th}(\text{DBCP})(\text{NCS})_2]$. Independent pyrolysis experiment in air was also carried out for each in a porcelain crucible up to 800°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 $[\text{Th}(\text{DBCP})(\text{NO}_3)_2]$ the TG plateau up to 220°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 238 and 495°C . The TG curve shows a second plateau after 530°C . This shows the completion of the decomposition. The decomposition at 238°C is due to the decomposition of the organic moiety, making a loss of 43%. The decomposition continues with the gradual decrease in weight and a constant weight is obtained at about 530°C . The residual mass obtained is about 37% which confirms that the decomposition product is ThO_2 .

In the case of $[\text{Th}(\text{DBCP})(\text{NCS})_2]$ the TG plateau is up to 200°C indicating that this complex is stable up to this temperature. The DTG curve has two peaks at 225 and 465°C showing that this complex undergoes decomposition in two stages. The TG curve exhibits a second plateau after 500°C indicating the completion of the decomposition. The complex shows a weight loss about 40%, which corresponds to the decomposition product, ThO_2 . The independent pyrolysis also confirms that ThO_2 is the final decomposition product.

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