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Substitution reactions of thorium(IV) acetate to synthesize nano-sized carboxylate complexes

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ABSTRACT

Some mixed-ligand thorium(IV) complexes with the general formula $[\mathrm{Th(OOCCH_3)}_{4-n}\mathrm{L}_n]$ (L = anions of myristic, palmitic or stearic acid and $n = 1$–4) have been synthesized by the stepwise substitution of acetate ions of thorium(IV) acetate with straight chain carboxylic acids in toluene under reflux. The complexes were characterized by elemental analyses, spectral (electronic, infrared, NMR and powder XRD) studies, electrical conductance and magnetic susceptibility measurements. Doubly and triply bridged coordination modes of the ligands were established by their infrared spectra and nano-size of the complexes by powder XRD. Room temperature magnetic susceptibility measurements revealed diamagnetic nature of the complexes. Electronic absorption spectra of the complexes showed $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$ and charge transfer transitions. Molar conductance values indicated the complex to be non-electrolytes. These are a new type of mixed-ligand thorium(IV) complexes for which a nano-sized, oxygen bridged polymeric structure has been established on the basis of physico-chemical studies.

1. Introduction

Thorium, an important and first member of 5f-series elements, is known to form complexes in +4 oxidation state having different coordination numbers. However, the complexes with coordination numbers 10–14 are only few [1]. This may be mainly due to steric hinderance. The interaction of thorium(IV) with organic materials has become a potential and challenging subject [2–4]. Thorium(IV) with an ionic radius 1.08 Å and a high charge (+4) fulfils the optimum conditions required for a high coordination [5] and are an extraordinarily reactive, readily employed promotor of the hydrolysis of a variety of model phosphodiester substrates including plasmid DNA and RNA [6]. Several complexes of thorium(IV) are found useful in catalysis [7,8], sensors [9], single molecule magnets [3,6], three-dimensional connectivity [10], pathological applications (antifungal and antibacterial), pharmacological activity (antitumour and cytotoxic) [11,12] as well as in analytical chemistry [13].

Literature survey revealed that an extensive work was done on carboxylate complexes with d-block metals [14–16] but a very little attention was paid on the similar derivatives of f-block metals. The organometallic actinide chemistry has received a little attention recently [17–19]. It has also been noticed from the literature that no work has been done on the substitution reaction of thorium(IV) acetate which may be due to its polymeric nature. With these objectives, in this paper we report the stepwise substitutions of thorium(IV) acetate to synthesize a number of mixed-ligand carboxylates of thorium(IV). A convenient route of synthesis has been suggested and the complexes are characterized to establish their structure. The order of their solubility in non-polar solvents after stepwise substitution of acetate ion is correlated with length of the carboxylate chain.

2. Experimental

2.1. Materials and analytical methods

Organic solvents (Qualigens) were dried and distilled before use by standard methods. The carboxylic acids were used after distillation under reduced pressure (m.p. of myristic acid: 53 °C; palmitic acid: 63 °C and stearic acid: 70 °C). Thorium(IV) acetate (BDH, LR) was used as received. Thorium was determined gravimetrically as thorium oxide [21]. The liberated acetic acid in the collected azeotrope was determined by titration with standard sodium hydroxide solution using phenolphthalein as indicator.

2.2. Physico-chemical measurements

Electronic spectra were recorded on Hitachi U-2000 spectrophotometer in chloroform, infrared spectra were recorded on Perkin Elmer 1600 series FTIR spectrophotometer in KBr discs, magnetic moment was measured on a Gouy balance using $\mathrm{Hg[Co(SCN)_4]}$ as

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Table 1
Analytical results for thorium(IV) carboxylato complexes.

Reactants[a] (g; mmol)	Product colour, % yield	Found (calculated)				
		CH_3COOH[b] (g)	Th	C	H	O
$[Th(OOCCH_3)_4]$ (2.14; 4.57) + $C_{13}H_{27}COOH$ (4.18; 18.31)	$[Th(OOCC_{13}H_{27})_4]$ brown, 99	1.03 (1.09)	20.30 (20.33)	58.79 (58.92)	9.48 (9.53)	11.24 (11.21)
$[Th(OOCCH_3)_4]$ (1.10; 2.36) + $C_{15}H_{31}COOH$ (1.35; 5.28)	$[Th(OOCCH_3)_2(OOCC_{15}H_{31})_2]$ light yellow, 94	0.24 (0.28)	26.91 (26.95)	50.26 (50.22)	7.98 (7.96)	14.80 (14.86)
$[Th(OOCCH_3)_4]$ (4.04; 8.64) + $C_{15}H_{31}COOH$ (8.92; 34.79)	$[Th(OOCC_{15}H_{31})_4]$ light yellow, 93	2.00 (2.07)	18.44 (18.51)	61.38 (61.31)	9.81 (9.96)	10.15
$[Th(OOCCH_3)_4]$ (2.33; 4.97) + $C_{17}H_{35}COOH$ (1.42; 4.98)	$[Th(OOCCH_3)_3(OOCC_{17}H_{35})]$ light yellow, 97	0.27 (0.29)	33.14 (33.49)	41.55 (41.62)	6.47 (6.40)	18.50 (18.47)
$[Th(OOCCH_3)_4]$ (2.11; 4.50) + $C_{17}H_{35}COOH$ (3.02; 10.63)	$[Th(OOCCH_3)_2(OOCC_{17}H_{35})_2]$ light yellow, 91	0.24 (0.27)	25.12 (25.30)	52.46 (52.38)	8.12 (8.35)	13.78 (13.95)
$[Th(OOCCH_3)_4]$ (1.80; 3.85) + $C_{17}H_{35}COOH$ (4.40; 15.47)	$[Th(OOCC_{17}H_{35})_4]$ light yellow, 93	0.22 (0.23)	16.90 (16.98)	63.22 (63.31)	10.35 (10.33)	9.32 (9.37)

[a] Refluxing time 14–40 h.

[b] In azeotrope.

a calibrant. Electrical conductances were measured on a century CC-601 digital conductivity meter with a dip type cell using 10^{-2} to 10^{-3} molar solutions in nitrobenzene. ^1H NMR spectra were recorded at 250.17 MHz on a Bruker DPX 250 NMR spectrometer in $CDCl_3$. All chemical shifts were reported in ppm and relative to TMS. The C, H and O were analyzed on Carlo Erba 1108 elemental analyzer. Powder X-ray diffraction data were collected on a Mini Flex 2 goniometer with Cu/30 kV/15 mA.

2.3. *Synthesis of $[Th(OOCCH_3)_3(OOCC_{17}H_{35})]$*

A toluene solution of stearic acid (1.42 g; 4.98 mmol) was slowly added with constant stirring to the toluene suspension of thorium tetraacetate (2.33 g; 4.97 mmol). The reaction mixture was refluxed for 40 h with slow and continuous azeotropic fractionation of liberated acetic acid and toluene (b.p. 106–110 °C). The product was found soluble in toluene. After removing the excess solvent *in vacuo*, a light yellow solid was obtained. This was purified by reprecipitation by adding methanol (in excess) to their toluene solution. The resulting precipitate was finally dried *in vacuo* to yield the product having the formula $[Th(OOCCH_3)_3(OOCC_{17}H_{35})]$. A similar procedure was adopted to synthesize other carboxylato derivatives of thorium(IV) and the analytical results are given in Table 1.

3. Results and discussion

A number of carboxylato complexes of thorium(IV) were synthesized by the stepwise substitutions of thorium acetate $[Th(OOCCH_3)_4]$ with straight chain carboxylic acids in 1:1 to 1:4 molar ratios under reflux using toluene as a solvent

$$[Th(OOCCH_3)_4] + nRCOOH \overset{\text{toluene}}{\underset{\text{reflux}}{\longrightarrow}} [Th(OOCCH_3)_{4-n}(OOCR)_n] + nCH_3COOH\uparrow \quad (1)$$

where R = $C_{13}H_{27}$, $C_{15}H_{31}$ or $C_{17}H_{35}$ and n = 1–4.

Toluene was a suitable choice of solvent in these substitutions because it helps in pushing the reactions in the forward direction by fractionating the liberated acetic acid below 110 °C (b.p. of toluene). It has been observed that the solubility of the carboxylate complexes in non-polar organic solvents like benzene or toluene is directly proportional to the length of the fatty acid used. The 1:1 substituted products with myristic and palmitic acids were insoluble whereas 1:1 product of stearic acid was soluble. Similarly, 1:2 product of myristic acid was insoluble and that of palmitic acid was soluble. Therefore, the following order of solubility of substituted carboxylates of thorium(IV) may be sought:

myristicacid < palmiticacid < stearicacid

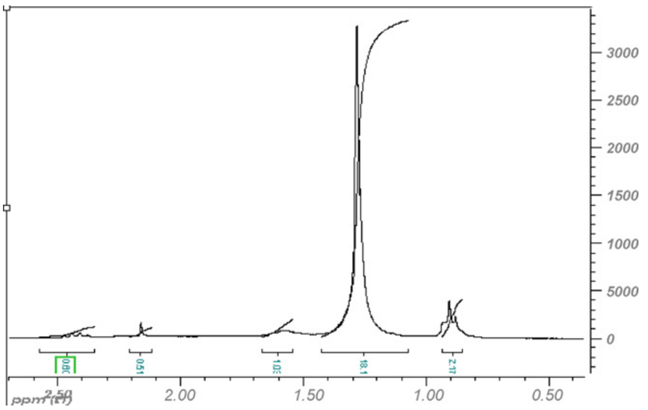

Fig. 1. ^1H NMR spectrum of $[Th(OOCCH_3)_2(OOCC_{15}H_{31})_2]$.