

## New Heteroligand Peroxothorates(IV) of the Type $A_2[Th(O_2)F_2(OH)_2] \cdot nH_2O$ ( $A = NH_4, n = 3; A = Na \text{ or } K, n = 1$ ) and Molecular Peroxothorium(IV) Complexes of the Type $[Th_2(O_2)_3L(H_2O)_4] \cdot 5H_2O$ ( $L = C_2O_4 \text{ or } SO_4$ )

CHIRA R. BHATTACHARJEE, MIHIR K. CHAUDHURI\* and R. N. DUTTA PURKAYASTHA

Department of Chemistry, North-Eastern Hill University, Shillong 793003 (India)

(Received October 19, 1988)

### Abstract

Synthesis of complex difluorodihydroxomono-peroxothorates(IV),  $A_2[Th(O_2)F_2(OH)_2] \cdot nH_2O$  ( $A = NH_4, n = 3; A = Na \text{ or } K, n = 1$ ) have been achieved from the reaction of hydrated thorium oxide,  $ThO_2 \cdot nH_2O$ , with 30%  $H_2O_2$  and 48% hydrofluoric acid in the concentration ratio of  $Th:H_2O_2:HF$  as 1:77.6:56.5 at a pH range 10–11 maintained by the addition of aqueous ammonia or alkali metal hydroxides. Novel dimeric molecular complexes diperoxotetra-aquo- $\mu$ -peroxo- $\mu$ -oxalatodithorium(IV) pentahydrate,  $[Th_2(O_2)_3(C_2O_4)(H_2O)_4] \cdot 5H_2O$  and diperoxotetra-aquo- $\mu$ -peroxo- $\mu$ -sulphatodithorium(IV) pentahydrate,  $[Th_2(O_2)_3SO_4(H_2O)_4] \cdot 5H_2O$  have been synthesised directly from the reaction of an aqueous solution of thorium nitrate, with ammonium oxalate or ammonium sulphate and 30% hydrogen peroxide in the respective cases, at pH 7–8 and at pH 2, respectively. Characterisation and structural assessment of the compounds have been made from the results of chemical analysis, pyrolysis studies, magnetic susceptibility measurements and ESR, IR and laser Raman spectroscopic studies. An internal comparison of the results so obtained with those of titanium and zirconium analogues has been made.

### Introduction

The chemistry of heteroligand peroxo-metallates embraces a fascinating and worthwhile area of investigation in its own right [1–3]. The synthesis of well defined heteroligand peroxo–metal complexes therefore is an important prerequisite for a heuristic approach in this field of chemistry. It is imperative to note that in recent years a commendable progress [4–7] has been made in this aspect of lighter metals and a good amount of newer informations as well as materials has emerged thereof. However, similar

studies involving heavy metal especially the actinides have not received due attention. This could, in part, be due to the very complicated nature of peroxo-actinide chemistry [8, 9]. The syntheses and characterisations of heteroligand peroxo complexes of titanium and zirconium have been dealt with in our earlier reports [10–12]. However, as one moves down in the group from titanium to thorium, a significant difference in their familiar chemistry becomes evident particularly because of a much higher tendency of hydrolysis of the latter [8]. Reports on peroxothorium complex are rather scanty [8, 13]. Recent reports [2] still describe that molecular complexes of actinide are only a few although actinides have long been known to form peroxo compounds. As a sequel to our endeavour [4, 10, 12, 14–16] in the field of peroxo–metal chemistry, it was of interest to us to evaluate appropriate reaction conditions in order to have an access to the hitherto unreported heteroligand peroxothorium(IV) complexes. It was expected that the new results would enable an internal comparison to be made with those of titanium [10, 11] and zirconium [12]. The present paper describes synthesis, characterisation and structural assessment of alkali-metal and ammonium difluorodihydroxomono-peroxothorate(IV) hydrates,  $A_2[Th(O_2)F_2(OH)_2] \cdot nH_2O$  ( $A = NH_4, n = 3; A = Na \text{ or } K, n = 1$ ) and molecular complexes diperoxotetra-aquo- $\mu$ -peroxo- $\mu$ -oxalatodithorium(IV) pentahydrate,  $[Th_2(O_2)_3C_2O_4(H_2O)_4] \cdot 5H_2O$  and diperoxotetra-aquo- $\mu$ -peroxo- $\mu$ -sulphatodithorium(IV) pentahydrate,  $[Th_2(O_2)_3SO_4(H_2O)_4] \cdot 5H_2O$  along with a set of internally consistent information as emerged out of the comparative studies on some facets of heteroligand peroxo chemistry of Ti, Zr and Th (present work).

### Experimental

Reagent grade chemicals were used. Infrared (IR) and laser Raman (l-R) spectra were recorded on the instruments and by the methods described in our

\*Author to whom correspondence should be addressed.

previous papers [11, 14–18]. Laser Raman spectra were recorded on solids due to the insolubility of the compounds. Measurements of magnetic susceptibility were accomplished by the Gouy method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the standard. A systronics type 335 digital pH meter and pH indicator paper (BDH) were used to measure the pH of the reaction solutions. All reactions pertaining to the synthesis of  $\text{A}_2[\text{Th}(\text{O}_2)\text{F}_2(\text{OH})_2] \cdot n\text{H}_2\text{O}$  were carried out in polyethylene apparatus.

(i) *Synthesis of Alkali-metal and Ammonium Difluorodihydroxomonoperoxothorate(IV) Hydrates,  $\text{A}_2[\text{Th}(\text{O}_2)\text{F}_2(\text{OH})_2] \cdot n\text{H}_2\text{O}$  ( $\text{A} = \text{NH}_4$ ,  $n = 3$ ;  $\text{A} = \text{Na}$  or  $\text{K}$ ,  $n = 1$ )*

Following a typical procedure, representative of the general method, to a solution of 1 g (1.70 mmol)  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  in 15  $\text{cm}^3$  of water was added 25% aqueous solution of ammonia (sp. gr. 0.9) or a 15% aqueous solution of AOH ( $\text{A} = \text{Na}$  or  $\text{K}$ ) until the white gelatinous precipitate of hydrated thorium oxide ceased to appear. The hydrated oxide was then washed free from ammonia or alkali or nitrate. To a water suspension of hydrated oxide was added 15  $\text{cm}^3$  (132.25 mmol) of 30%  $\text{H}_2\text{O}_2$  solution and the mixture was stirred for c. 15 min followed by the addition of 4 ml (96.0 mmol) of 48% HF drop by drop with continuous stirring to obtain a clear solution. The pH of the reaction solution at this stage was found to be c. 2 which was slowly raised to 10–11 by the addition of corresponding alkali-metal hydroxide or aqueous ammonia. Stirring was continued for a further period of 10 min. A small volume of ethanol was added to facilitate precipitation of alkali-metal or ammonium difluorodihydroxomonoperoxothorate(IV) hydrates. The compound was isolated by filtration and dried *in vacuo* over conc.  $\text{H}_2\text{SO}_4$ . Starting from 1 g of  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ , in each case the yields were recorded as:  $(\text{NH}_4)_2[\text{Th}(\text{O}_2)\text{F}_2(\text{OH})_2] \cdot 3\text{H}_2\text{O}$ , 0.58 g (74%);  $\text{Na}_2[\text{Th}(\text{O}_2)\text{F}_2(\text{OH})_2] \cdot \text{H}_2\text{O}$ , 0.51 g (75%);  $\text{K}_2[\text{Th}(\text{O}_2)\text{F}_2(\text{OH})_2] \cdot \text{H}_2\text{O}$ , 0.6 g (80%).

(ii) *Synthesis of Diperoxotetra-aquo- $\mu$ -peroxo- $\mu$ -oxalatodithorium(IV) Pentahydrates,  $[\text{Th}_2(\text{O}_2)_3\text{C}_2\text{O}_4(\text{H}_2\text{O})_4] \cdot 5\text{H}_2\text{O}$*

To a solution of 1 g (1.70 mmol)  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ , in 20  $\text{cm}^3$  of water was added a solution of 0.20 g (1.70 mmol) oxalic acid in 15  $\text{cm}^3$  (132.35 mmol) of 30%  $\text{H}_2\text{O}_2$ . The white gelatinous mass that appeared was stirred for c. 10 min followed by a rise in pH to 7–8 by the addition of aqueous ammonia (sp.gr. 0.9) or 15% AOH ( $\text{A} = \text{Na}$  or  $\text{K}$ ) solution. The whole was again stirred for c. 5 min and then the product was isolated by filtration, washed with water and portions of ethyl alcohol and finally dried *in vacuo* over conc.  $\text{H}_2\text{SO}_4$ . The yield of the compound was ~1 g (73%).

(iii) *Synthesis of Diperoxotetra-aquo- $\mu$ -peroxo- $\mu$ -sulphatodithorium(IV) Pentahydrates,  $[\text{Th}_2(\text{O}_2)_3\text{SO}_4(\text{H}_2\text{O})_4] \cdot 5\text{H}_2\text{O}$*

To a solution of 1 g (1.70 mmol)  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  in 20  $\text{cm}^3$  of water was added 1.70 mmol of  $\text{A}_2\text{SO}_4$  ( $\text{A} = \text{NH}_4$  or  $\text{Na}$  or  $\text{K}$ ) and the whole was stirred for c. 10 min until a clear solution was obtained. To this was added 15  $\text{cm}^3$  (132.35 mmol) of 30%  $\text{H}_2\text{O}_2$  whereupon a white product appeared. Stirring was continued for a further period of 10 min. Isolation, purification, and drying of the compound were accomplished in a manner similar to those mentioned under (ii). The yield was recorded as 0.9 g (65%).

*Elemental Analyses*

The results of the elemental analyses are given in Table 1. Thorium was estimated gravimetrically as thoria,  $\text{ThO}_2$  [19a]. The peroxide content was determined by redox titrations with standard solution of  $\text{KMnO}_4$  [19b] or  $\text{Ce}^{4+}$  solution [19c]. Fluoride was precipitated as  $\text{PbClF}$ , and chloride was estimated by Volhard's method, from which the fluoride content was calculated [19d]. Carbon, nitrogen, potassium and sodium were estimated by the methods described in our earlier papers [17b]. Oxalate content was determined by microanalysis on carbon as well as by the volumetric method [19c]. In order to determine oxalate volumetrically, it was necessary to remove  $\text{O}_2^{2-}$ . The removal of  $\text{O}_2^{2-}$  was achieved by decomposing the compound in an ammoniacal medium by heating for c. 30 min. The hydrated thorium oxide was separated by filtration and the filtrate was collected quantitatively, acidified with dilute  $\text{H}_2\text{SO}_4$  and then titrated with standard  $\text{KMnO}_4$  solution. The peroxide content in the peroxo-oxalato complex of thorium was, however, determined indirectly by first titrating the total peroxide and oxalate content and then subtracting the contribution due to oxalate from the whole. Sulphate content was estimated as  $\text{BaSO}_4$  by gravimetric method [19f].

**Results and Discussion**

*Synthesis*

That the peroxo-metal compounds can be stabilised under a suitably chosen heteroligand environment has been earlier [4, 20] emphasised by us. In order to have an access to the synthesis of heteroligand peroxothorates(IV) simple heteroligands viz.  $\text{F}^-$ ,  $\text{C}_2\text{O}_4^{2-}$  and  $\text{SO}_4^{2-}$  were chosen in the first instance for the present work as these ligands are not only known to stabilise the Th(IV) state individually but also make their detection and determination rather easy. Since each of the aforementioned heteroligands and peroxide ( $\text{O}_2^{2-}$ ), independent of each other, forms stable compounds with the chosen metal, it was anticipated that under appropriate

TABLE 1. Analytical data and structurally significant IR and IR bands of  $A_2[Th(O_2)F_2(OH)_2] \cdot nH_2O$  ( $A = NH_4, n = 3; Na$  or  $K, n = 1$ ) and  $[Th_2(O_2)_3L(H_2O)_4] \cdot 5H_2O$  ( $L = C_2O_4$  or  $SO_4$ )

Compound	Found (calc.) (%)				IR ( $cm^{-1}$ )	IR ( $cm^{-1}$ )	Assignment
	A or N	Th	O <sup>a</sup>	C <sub>2</sub> O <sub>4</sub> <sup>b</sup> or SO <sub>4</sub> or F			
(NH <sub>4</sub> ) <sub>2</sub> [Th(O <sub>2</sub> )F <sub>2</sub> (OH) <sub>2</sub> ]·3H <sub>2</sub> O	6.58 (6.62)	54.9 (54.83)	7.3 (7.56)	8.65 (8.98)	850(w) 355(m) 3560(s) 3420(s) 1640(s)	850	$\nu(O-O)$ $\nu(Th-F)$ $\nu(O-H)(OH^-)$ $\nu(O-H)(H_2O)$ $\delta(H-O-H)$
Na <sub>2</sub> [Th(O <sub>2</sub> )F <sub>2</sub> (OH) <sub>2</sub> ]·H <sub>2</sub> O	11.7 (11.52)	58.32 (58.14)	7.8 (8.02)	9.48 (9.52)	845(w) 355(m) 3555(s) 3415(s) 1638(s)	845	$\nu(O-O)$ $\nu(Th-F)$ $\nu(O-H)(OH^-)$ $\nu(O-H)(H_2O)$ $\delta(H-O-H)$
K <sub>2</sub> [Th(O <sub>2</sub> )F <sub>2</sub> (OH) <sub>2</sub> ]·H <sub>2</sub> O	17.83 (18.13)	53.3 (53.80)	7.1 (7.42)	8.67 (8.81)	850(w) 360(m) 3565(s) 3425(s) 1635(s)	845	$\nu(O-O)$ $\nu(Th-F)$ $\nu(O-H)(OH^-)$ $\nu(O-H)(H_2O)$ $\delta(H-O-H)$
[Th <sub>2</sub> (O <sub>2</sub> ) <sub>3</sub> C <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]·5H <sub>2</sub> O		58.22 (57.92)	11.68 (11.98)	10.62 <sup>c</sup> (10.98) <sup>c</sup>	835(w) 725(m) 1640(s) 3455(s) 1670(s) 1360(w) 1320(m) 780(m) 750(w)	835 845	$\nu(O-O)$ $\rho_2(H_2O)$ $\delta(H-O-H)$ $\nu(O-H)$ $\nu_{as}(O-C-O)$ $\nu_s(O-C-O)$ $\delta(O-C-O)$
[Th <sub>2</sub> (O <sub>2</sub> ) <sub>3</sub> SO <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]·5H <sub>2</sub> O		57.81 (57.34)	11.65 (11.86)	12.07 <sup>d</sup> (11.87) <sup>d</sup>	830(w) 728(m) 1635(s) 3460(s) 1155(s) 1115(s) 1060(s) 990(m) 677(s) 618(s) 520(s) 460(s,br)	835 845	$\nu(O-O)$ $\rho_2(H_2O)$ $\delta(H-O-H)$ $\nu(O-H)$ $\nu_3$ $\nu_1$ $\nu_4$ $\nu_2$ } $\nu(S-O)$

<sup>a</sup>Peroxy oxygen.<sup>b</sup>Microanalysis on C: found 3.15% (calc. 3%).<sup>c</sup>C<sub>2</sub>O<sub>4</sub>.<sup>d</sup>SO<sub>4</sub>.

experimental conditions both the selected heteroligands and peroxide could be made to simultaneously coordinate with the metal centre. While freshly prepared hydrated thorium oxide, ThO<sub>2</sub>·*n*H<sub>2</sub>O, was used in the synthesis of fluoroperoxothorates(IV), aqueous solutions of thorium nitrate hexahydrate, Th(NO<sub>3</sub>)<sub>4</sub>·6H<sub>2</sub>O, were used for the preparation of the molecular complexes described herein. An important criterion for the successful

synthesis of peroxometallate is the evaluation of appropriate pH of the reaction medium [1, 4]. Accordingly it was found that the reaction of hydrated thorium oxide, hydrogen peroxide and hydrofluoric acid leading to the synthesis of the fluoroperoxo complex of thorium, was successful at pH 10–11. The conducive pH for the synthesis of peroxo-oxalato complex of thorium was found to be 7–8 while for the peroxo-sulphato complex it

was found to be 2. The strategy for the reaction leading to fluoroperoxothorates(IV) was that hydrated thorium oxide would first react with  $\text{H}_2\text{O}_2$  to form a thorium peroxo compound which in turn would interact with  $\text{F}^-$  to afford the desired compound. The order of addition of the two reagents  $\text{H}_2\text{O}_2$  and hydrofluoric acid is important since a reverse order of addition of the reagents is detrimental to the successful synthesis of fluoroperoxothorates(IV) owing to the formation of a sparingly soluble binary fluoro complex of thorium(IV).

The white gelatinous mass, resulting from the addition of hydrogen peroxide to hydrated thorium oxide, was dissolved by careful addition of aqueous HF. The pH of the reaction solution was then raised to *c.* 10–11 by slow dropwise addition of aqueous ammonia or alkali-metal hydroxides until the  $\text{Th}:\text{O}_2^{2-}$  ratio reached 1:1. Products isolated at a pH relatively lower than 10–11, on being analysed, were found to contain both  $\text{O}_2^{2-}$  and  $\text{F}^-$  but in a nonstoichiometric manner. It is therefore evident that although the  $\text{O}_2^{2-}$  uptake process might have been in progress at a lower pH, a compound of definite stoichiometry could only be synthesised at pH 10–11. However, apart from  $\text{O}_2^{2-}$  and  $\text{F}^-$  getting coordinated to the Th(IV) centre, two hydroxyl ( $\text{OH}^-$ ) groups were also found to enter into the coordination sphere of thorium at this pH. This therefore suggests that although a high concentration of alkaline media is essential for the synthesis of peroxofluorothorates(IV), at a higher pH  $\text{OH}^-$  groups compete with  $\text{O}_2^{2-}$  and  $\text{F}^-$  for getting coordinated to the metal centre resulting in the formation of hydroxofluoroperoxothorates(IV), as obtained. Incorporation of  $\text{OH}^-$  groups is explained in terms of extensive hydrolysis of the  $\text{Th}^{4+}$  ion in aqueous solution at a higher pH [8, 21].

The diperoxotetra-aquo- $\mu$ -peroxo- $\mu$ -oxalatodithorium(IV) pentahydrate,  $[\text{Th}_2(\text{O}_2)_3\text{C}_2\text{O}_4(\text{H}_2\text{O})_4]\cdot 5\text{H}_2\text{O}$  and diperoxotetra-aquo- $\mu$ -peroxo- $\mu$ -sulphatodithorium(IV) pentahydrate,  $[\text{Th}_2(\text{O}_2)_3\text{SO}_4(\text{H}_2\text{O})_4]\cdot 5\text{H}_2\text{O}$  were synthesised directly from the reaction of an aqueous solution of  $\text{Th}(\text{NO}_3)_4\cdot 6\text{H}_2\text{O}$  with  $\text{A}_2\text{C}_2\text{O}_4$  or  $\text{A}_2\text{SO}_4$  ( $\text{A} = \text{Na}, \text{K}$  or  $\text{NH}_4$ ), respectively, and  $\text{H}_2\text{O}_2$ . The appropriate pH required for the synthesis of  $[\text{Th}_2(\text{O}_2)_3\text{C}_2\text{O}_4(\text{H}_2\text{O})_4]\cdot 5\text{H}_2\text{O}$  was ascertained to be 7–8, maintained by the addition of aqueous ammonia or 15% solution of AOH ( $\text{A} = \text{Na}$  or  $\text{K}$ ). The reaction leading to the corresponding sulphato complex was, however, found to be complete at pH 2 maintained automatically. In order to ascertain the effect of pH similar reactions were conducted between pH 2 and 9, however, the products isolated were found to be similar to the one obtained at pH 2. This causes us to state that the dimeric  $[\text{Th}_2(\text{O}_2)_3\text{SO}_4(\text{H}_2\text{O})_4]\cdot 5\text{H}_2\text{O}$  compound formed at pH 2 does not undergo any change in its composition within the aforesaid pH range.

A point worth commenting on at this stage is that while the fluoroperoxothorates(IV) contain hydroxo ligands, the molecular heteroperoxo complexes containing either 'oxalato' or 'sulphato' involve aquo ligands. Evidently this difference must be owing to the fact that the latter compounds were synthesised at a considerably lower pH than the fluoroperoxothorates(IV). It is believed that at pH lower than that mentioned for the synthesis of fluoroperoxothorates(IV), Th(IV) exists as aquated species and partial substitution of  $\text{H}_2\text{O}$  molecules by  $\text{O}_2^{2-}$  and  $\text{SO}_4^{2-}$  or  $\text{C}_2\text{O}_4^{2-}$  leads to the kind of compounds obtained herein. In this way, the synthesis of heteroligand peroxothorium(IV) complexes of the types  $\text{A}_2[\text{Th}(\text{O}_2)\text{F}_2(\text{OH})_2]\cdot n\text{H}_2\text{O}$  ( $\text{A} = \text{NH}_4$ ,  $n = 3$ ;  $\text{A} = \text{Na}$  or  $\text{K}$ ,  $n = 1$ ) and  $[\text{Th}_2(\text{O}_2)_3\text{L}(\text{H}_2\text{O})_4]\cdot 5\text{H}_2\text{O}$  ( $\text{L} = \text{C}_2\text{O}_4$  or  $\text{SO}_4$ ) has been achieved.

#### Characterisation and Structural Assessment

All the compounds were obtained as white microcrystalline products and were found to be stable for a prolonged period. The stability of the compounds was checked by the analysis of  $\text{O}_2^{2-}$  content from time to time. Recording of ESR spectra on solids at room temperature and results of magnetic susceptibility measurements provide evidence for the diamagnetic nature of the products concurrent with the occurrence of Th(IV) in each of the compounds. The compounds are practically insoluble in water thus precluding their molar conductance measurements. Unlike the fluoroperoxothorates(IV) the peroxoxalato and peroxosulphato compounds were obtained as molecular complexes. All the peroxothorium compounds mentioned herein slowly decompose in dilute sulphuric acid, liberating hydrogen peroxide quantitatively, and thus facilitate determination of active oxygen content. The importance of the chemical determination of active oxygen content has been emphasised earlier [18, 22]. In the present work, this was accomplished by redox titration separately involving standard  $\text{Ce}^{4+}$  solution as well as standard  $\text{KMnO}_4$  solution. The redox titrations were performed in the presence of boric acid in order to prevent any loss of active oxygen. The results of chemical analyses of fluoroperoxothorates gave  $\text{Th}:\text{F}:\text{O}_2^{2-}$  as 1:2:1 while those for molecular complexes  $\text{Th}:\text{L}(\text{C}_2\text{O}_4^{2-}$  or  $\text{SO}_4^{2-}):\text{O}_2^{2-}$  were found to be 2:1:3 in accord with their formulae.

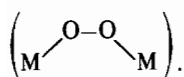
Infrared and laser Raman spectroscopic studies were carried out on all the compounds and the results (Table 1) were found to be in order with the assigned formulae. The significant features of the IR spectra of  $\text{A}_2[\text{Th}(\text{O}_2)\text{F}_2(\text{OH})_2]\cdot n\text{H}_2\text{O}$  ( $\text{A} = \text{NH}_4$ ,  $n = 3$ ;  $\text{A} = \text{Na}$  or  $\text{K}$ ,  $n = 1$ ) involve absorption of coordinated fluoride, coordinated peroxide, coordinated  $\text{OH}^-$  and those of uncoordinated water. The band at *c.*  $850\text{ cm}^{-1}$ , though weak in intensity, is typical of the  $\nu(\text{O}-\text{O})$  mode of  $\text{O}_2^{2-}$  and is indicative of triangu-

larly bonded bidentate chelating  $O_2^{2-}(C_{2v})$  group, commonly encountered in peroxo-metallates [17, 18, 20, 22]. This is complemented by a band at *c.* 850  $cm^{-1}$  in the IR spectra. The IR absorption at *c.* 360  $cm^{-1}$  is attributed to the  $\nu_3(Th-F)$  mode arising from the terminally coordinated  $F^-$  ligand [23]. The consistent appearance of a broad band at *c.* 3560  $cm^{-1}$  led us to assign it to the O-H stretching mode of coordinated  $OH^-$  groups [24a]. The Th-O stretching modes assignments associated with  $Th(O_2)$ , however, were not attempted. The presence of several modes owing to Th-OH, Th- $O_2$  and Th-F in the low energy region makes this task a difficult one. Over and above the band due to coordinated  $OH^-$  groups two other bands at *c.* 3420 ( $\nu(O-H)$ ) and *c.* 1640 ( $\delta(H-O-H)$ )  $cm^{-1}$  were observed in the IR spectra of fluoroperoxothorium complexes which are typical of the ones expected for uncoordinated water molecules [24b]. In the ammonium salt, however, one additional sharp band appears at 1400  $cm^{-1}$  which is clearly due to the N-H deformation mode of  $NH_4^+$  ion. The  $\nu(N-H)$  modes arising from  $NH_4^+$  could not be identified clearly owing to their overlap with the  $\nu(O-H)$  modes originating from the lattice water. Thus leaving aside the modes due to the  $NH_4^+$  ion in  $(NH_4)_2[Th(O_2)_2F_2(OH)_2] \cdot 3H_2O$ , the IR spectrum of all the compounds display a common feature.

The common features of the IR spectra of  $[Th_2(O_2)_3C_2O_4(H_2O)_4] \cdot 5H_2O$  and  $[Th_2(O_2)_3SO_4(H_2O)_4] \cdot 5H_2O$  are the bands at *c.* 835w, *c.* 725m, *c.* 1640s and *c.* 3455  $cm^{-1}$  which owe their origins to  $\nu(O-O)$  ( $O_2^{2-}$ ),  $\rho_r$  (coordinated water),  $\delta(H-O-H)$  and  $\nu(O-H)$ , respectively. Although from the appearance and observed positions for the  $\delta(H-O-H)$  and  $\nu(O-H)$  modes of water no clear inference can be made regarding the nature of the water molecules, the consistent appearance of a distinct band at *c.* 725  $cm^{-1}$  provides evidence for the notion that at least some water molecules are coordinated [25] to the metal centres, in line with the formula assigned. Appearance of signals at *c.* 830 and 845  $cm^{-1}$  in the laser Raman (IR) spectra of both the compounds are indicative of presence of two types of peroxo groups [26] viz. triangularly bidentate type



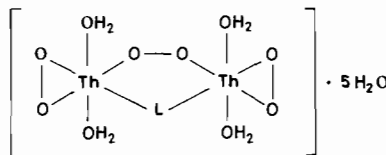
and bridging type



The IR spectrum of  $[Th_2(O_2)_3C_2O_4(H_2O)_4] \cdot 5H_2O$ , in addition to the common features enumerated above, also exhibits patterns at  $\sim 1670s$  ( $\nu_{as}(O-$

$C-O)$ ,  $\sim 1630w$  and  $\sim 1320m$  ( $\nu_s(O-C-O)$ ), 780m and  $\sim 750w$  ( $\delta(O-C-O)$ )  $cm^{-1}$  which are in conformity with the occurrence of a bridging oxalato group. These assignments are in good agreement with those described in the literature [27, 28]. That the oxalato group occurs as a bridging ligand is further augmented by the absence of any band at 1680–1750  $cm^{-1}$  which is expected of a chelated oxalato group. Like for  $[Th_2(O_2)_3C_2O_4(H_2O)_4] \cdot 5H_2O$ , the IR spectrum of the  $[Th_2(O_2)_3SO_4(H_2O)_4] \cdot 5H_2O$  complex also shows characteristic patterns for the occurrence of a bridging sulphato ligand. The bands arising from  $SO_4^{2-}$  are observed at 1155s, 1115s, 1060s  $cm^{-1}$  due to  $\nu_3$ , at 990m  $cm^{-1}$  due to  $\nu_1$ , at 677s, 618s and 520s  $cm^{-1}$  due to  $\nu_4$ , and at 460s br due to  $\nu_2$  of the coordinated sulphate [26, 29–31]. The IR spectrum recorded on solids exhibited signals at 1150,  $\sim 1120$ ,  $\sim 1050$   $cm^{-1}$  due to  $\nu_3$ , at  $\sim 975$   $cm^{-1}$  due to  $\nu_1$ , at 660,  $\sim 610$  and  $\sim 550$   $cm^{-1}$  due to  $\nu_4$  and 460 due to  $\nu_2$  of the sulphato ligand. The IR and IR spectral patterns particularly the appearance of  $\nu_1$  and  $\nu_2$  vibrations, the splitting of  $\nu_3$  and  $\nu_4$  into three bands each and the observation of  $\nu_3$  bands at a lower energy than generally observed for a chelated  $SO_4^{2-}$  ligand, supports the contention that  $SO_4^{2-}$  occurs as a bridging ligand in the compound under study.

Pyrolysis studies yielded similar results for both the molecular complexes. The results show that near 100 °C the compound starts losing weight and between 125–130 °C almost all the peroxy oxygen is lost along with 4.5–5 water molecules. The remaining water molecules were lost above 150 °C. The thermal studies therefore clearly suggest the presence of four coordinated water molecules and five uncoordinated water molecules in each of the compounds. Thus on the basis of chemical analyses in conjunction with IR, IR, ESR and pyrolysis studies the following molecular structure can be put forth for the complexes.



A similar structural representation was proposed [26] for  $[Zr_2(O_2)_3SO_4(H_2O)_4] \cdot 6H_2O$ , an analogue of the thorium peroxosulphato complex reported herein. The number of water molecules associated with such complexes needs to be characterised carefully as vibrational spectroscopy alone makes it very difficult to distinguish between lattice and coordinated water [32].

The successful synthesis of peroxothorates(IV) calls for an internal comparison to be made with

those of our earlier work on peroxotitanates(IV) [10, 11] and peroxozirconates(IV) [12], particularly in view of the fact that Ti, Zr and Th all belong to group IVB of the periodic table. The points that emerge out of the comparative studies are listed below.

(i) While both mono- and di-peroxofluoro complexes can be obtained with Ti [10, 11] and Zr [12] no diperoxofluorothorates could be obtained within the present experimental conditions.

(ii) All three elements Ti, Zr and Th permit synthesis of fluoroperoxo compounds of the corresponding metal, the fluoroperoxotitanates(IV) [10, 11] contain a Ti(IV) centre and fluoroperoxo-zirconates(IV) [12] contain a zirconyl (Zr=O) centre, whereas the fluoroperoxo thorates(IV) (present work) have been shown to contain hydroxo (OH<sup>-</sup>) groups bonded to the metal centre.

### Concluding Remarks

Thus from the results of the present investigation, it is evident that under the appropriate reaction conditions, it is not only possible to accomplish the synthesis of both heteroligand peroxothorates as well as molecular peroxothorium complexes but such reaction strategies may also serve as a paradigm for the synthesis of new heteroligand peroxothorium(IV) compounds which in turn is expected to throw more light on the complicated peroxothorium chemistry.

### Acknowledgements

The authors are thankful to the CSIR, New Delhi for awarding a Research Fellowship to C.R.B. Partial support from the Department of Atomic Energy is also gratefully acknowledged.

### References

- 1 M. K. Chaudhuri, *Proc. Indian Natl. Sci. Acad., Part A*, 52 (1986) 996.
- 2 (a) H. Mimoun, in S. Patai (ed.), *The Chemistry of Functional Groups, Peroxides*, Wiley, New York, 1983; (b) H. Mimoun, L. Saussine, E. Daire, M. Postal, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, 105 (1983) 3101; (c) H. Mimoun, M. Mignard, P. Brechot and L. Saussine, *J. Am. Chem. Soc.*, 108 (1986) 3711.
- 3 C. Djordjevic and G. L. Wampler, *J. Inorg. Biochem.*, 25 (1985) 51.
- 4 M. K. Chaudhuri, *J. Mol. Catal.*, 44 (1988) 129, and refs. therein.

- 5 J. T. Groves and Y. Watanabe, *J. Am. Chem. Soc.*, 108 (1986) 7834.
- 6 H. J. Lowson and J. D. Atwood, *J. Am. Chem. Soc.*, 110 (1986) 3680.
- 7 J. N. Burstyn, J. A. Roe, A. R. Miksztal, B. A. Shaevitz, G. Lang and J. S. Valentine, *J. Am. Chem. Soc.*, 110 (1988) 1382.
- 8 S. Ahrland, K. W. Bagnall, D. Brown, R. M. Dell, S. H. Eberle, C. Keller, J. A. Lee, J. O. Liljenzin, P. G. Mardon, J. A. C. Marples, G. W. C. Milner, G. Phillips, P. E. Potter and J. Rydberg, *The Chemistry of Actinides*, Pergamon, New York, 1975.
- 9 J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 6 (1964) 344.
- 10 M. K. Chaudhuri and B. Das, *Inorg. Chem.*, 25 (1986) 168.
- 11 M. K. Chaudhuri and B. Das, *Polyhedron*, 4 (1985) 1449.
- 12 M. Bhattacharjee, M. K. Chaudhuri and S. Choudhury, submitted for publication.
- 13 A. D. Westland and M. T. H. Tarafdar, *Inorg. Chem.*, 28 (1982) 3228.
- 14 M. K. Chaudhuri and S. K. Ghosh, *Inorg. Chem.*, 23 (1984) 534.
- 15 J. K. Basumatary, M. K. Chaudhuri, R. N. Dutta Purkayastha and Z. Hiese, *J. Chem. Soc., Dalton Trans.*, (1986) 709.
- 16 M. N. Bhattacharjee, M. K. Chaudhuri and R. N. Dutta Purkayastha, *J. Chem. Soc., Dalton Trans.*, (1985) 409.
- 17 (a) M. K. Chaudhuri and S. K. Ghosh, *Polyhedron*, 1 (1982) 553; (b) *Inorg. Chem.*, 21 (1982) 4020; (c) *J. Chem. Soc., Dalton Trans.*, (1984) 507.
- 18 M. K. Chaudhuri, S. K. Ghosh and N. S. Islam, *Inorg. Chem.*, 24 (1985) 2706.
- 19 A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, Longmans, New York, 1962, (a) p. 540, (b) p. 295, (c) p. 325, (d) p. 269, (e) p. 284, (f) p. 462.
- 20 C. Djordjevic, *Chem. Br.*, 18 (1982) 554; C. Djordjevic, S. A. Craig and E. Sinn, *Inorg. Chem.*, 24 (1985) 1281.
- 21 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry, A Comprehensive Text*, Wiley Interscience, New York, 4th edn., 1980, p. 1025.
- 22 M. Bhattacharjee, M. K. Chaudhuri and R. N. Dutta Purkayastha, *Inorg. Chem.*, 25 (1986) 2354.
- 23 J. R. Ferraro, *Low-Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum, New York, 1971, p. 119.
- 24 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 4th edn., 1986, (a) p. 107, (b) p. 228.
- 25 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 20 (1964) 429.
- 26 G. V. Jere and G. D. Gupta, *J. Inorg. Nucl. Chem.*, 32 (1970) 537.
- 27 N. F. Kurtis, *J. Chem. Soc.*, (1963) 4109; (1964) 2644; *J. Chem. Soc. A*, (1968) 1584.
- 28 M. N. Bhattacharjee, M. K. Chaudhuri and R. N. Dutta Purkayastha, *Inorg. Chem.*, 24 (1985) 447.
- 29 M. N. Bhattacharjee, M. K. Chaudhuri, M. Devi and K. Yhome, *J. Chem. Soc., Dalton Trans.*, (1987) 1055.
- 30 K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Am. Chem. Soc.*, 79 (1957) 4904.
- 31 A. R. Miksztal and J. S. Valentine, *Inorg. Chem.*, 23 (1984) 3548.
- 32 D. M. Adams, *Metal-Ligand and Related Vibrations*, Arnold, London, 1967, p. 235.