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PEROXOTHORIUM(IV) COMPLEXES CONTAINING HYDROXO AND PHOSPHATO COLIGANDS. SPECTROSCOPIC EVIDENCE FOR η^2 AND $\sigma:\sigma$ PEROXIDE

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An aqueous solution of $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ reacts with H_2O_2 at pH 9 to afford $[\text{Th}_2(\text{O}_2)_3(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$, **1**. The complexes $\text{NH}_4[\text{Th}(\text{O}_2)(\text{PO}_4)(\text{H}_2\text{O})_2]$, **2**, and $\text{Na}[\text{Th}(\text{O}_2)\text{PO}_4(\text{H}_2\text{O})_2]$, **3**, were synthesised by reaction of $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ with A_2HPO_4 ($\text{A} = \text{NH}_4$ or Na) and H_2O_2 at pH 7.5–8. The Cs salt was prepared metathetically from the NH_4^+ salt. The complexes are diamagnetic, air-stable and insoluble in water and common organic solvents. Characterization of the complexes was by analysis, magnetic susceptibility, EPR measurements, vibrational spectroscopy and pyrolysis studies. IR and laser Raman evidence suggests the presence of both η^2 and $\sigma:\sigma$ bonded peroxide in **1**. Complexes **1** and **2** in aqueous medium converts SO_2 and PPh_3 into SO_4^{2-} and PPh_3O , respectively.

KEYWORDS: thorium(IV), peroxides hydroxide, phosphate, complexes

INTRODUCTION

Owing to the rather complicated nature of peroxyactinide chemistry,^{1,2} research on this aspect has been rather tardy. Peroxothorium compounds, for instance, are few, except for those with nitrate, sulphate and chloride as coligand.¹ A few peroxothorium complexes with carboxylato- and phenoxo-ligands are reported³ in the literature and some with Schiff bases were reported recently.^{3b} The present work stems from our interest in peroxyactinide chemistry. In an earlier report, we dealt with peroxosulphato- and peroxooxalato- dinuclear thorium(IV) complexes providing the first examples containing both η^2 and $\sigma^1:\sigma^1$ peroxy (O_2^{2-}) ligand, and mononuclear peroxothorates with fluoride as the co-ligand.⁵ Very recently, we described the synthesis of a dinuclear peroxouranium(VI) complex containing structurally different, metal-bound peroxides.⁶ Herein is provided a new example of a molecular peroxothorium(IV) complex that incorporates both η^2 and $\sigma^1:\sigma^1$ bonded peroxide. Also included in this report are the syntheses, characterization and reactivity of hitherto unknown peroxophosphatothorates(IV).

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EXPERIMENTAL

The chemicals used were reagent grade products. Infrared (IR) spectra of the compounds were recorded on a Perkin Elmer 983 spectrophotometer in KBr pellets. Laser Raman spectra were recorded for solids, due to the insolubility of the products, using the 4880Å laser line from a Spectra-Physics 165-09 argon laser. Magnetic susceptibility measurements were made using the Gouy method; Hg[Co(NCS)₄] was the calibrant. The pH values were measured with a Systronics 335 digital pH meter. EPR spectra were recorded for solids using a Varian E109 X-band EPR spectrometer. The water used for the reactivity studies was deoxygenated by first boiling the water sample for ca 30 min. under N₂ and cooling to room temperature, followed by bubbling of N₂ gas through it for a period of ca 15 min.

Diperoxotetraaquodihydroxo-μ-peroxodithorium(IV) Tetrahydrate,
 $[Th_2(O_2)_3(OH)_2(H_2O)_4] \cdot 4H_2O$

To a solution of 1 g (1.70 mmol) Th(NO₃)₄·6H₂O, in 20 cm³ of water was added 15 cm³ (132.35 mmol) of 30% H₂O₂. The white gelatinous mass that appeared was stirred for ca 10 min. The pH was then raised to 9 by addition of aqueous ammonia (sp. gr. 0.9) or 15% AOH (A = Na or K) solution. The mixture was stirred for a further 10 min. The product was isolated by filtration, washed with water, ethyl alcohol, and finally dried *in vacuo* over conc. H₂SO₄. The yield of the product was 0.46 g (73%).

Ammonium and Alkali Diaquomonoperoxomonophosphatothorates(IV),
 $A[Th(O_2)(PO_4)(H_2O)_2]$ (A = NH₄ or Na)

Following a typical procedure, representative of the general method, to a solution of 1 g (1.70 mmol) of Th(NO₃)₄·6H₂O in 15 cm³ of water was added a solution of 0.23 g or 0.25 g (1.70 mmol) of A₂HPO₄ (A = NH₄ or Na) dissolved in 15 cm³ (132.35 mmol) of 30% H₂O₂. The white gelatinous mass that formed was stirred for ca 10 min. The pH was then raised to 7.5–8 by addition of aqueous ammonia (sp. gr. 0.9) or a 15% solution of NaOH. The mixture was stirred for ca 10 min. and the product isolated by filtration. It was washed with ethanol and dried *in vacuo* over conc H₂SO₄. The yields of NH₄[Th(O₂)PO₄(H₂O)₂] and Na[Th(O₂)(PO₄)(H₂O)₂] were 0.51 g (73%) and 0.6 g (85%), respectively.

Caesium Diaquomonoperoxomonophosphatothorate(IV)

NH₄[Th(O₂)(PO₄)(H₂O)₂] was thoroughly mixed with Cs₂CO₃ in a mortar until all ammonia was expelled, to afford Cs₂[Th(O₂)(PO₄)(H₂O)₂].

Elemental Analyses

Analytical results are collected in Table 1. Thorium was determined gravimetrically as ThO₂.⁷ The peroxide content was determined by redox titrations either with a standardised solution of KMnO₄ or a standard Ce⁴⁺ solution. The results were verified by iodometry. Boric acid was used to prevent any loss of active oxygen

content. Potassium and caesium were analysed using a Perkin Elmer 2380 absorption spectrometer. Sodium was determined by flame photometry. The phosphate content was estimated gravimetrically as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

RESULTS AND DISCUSSION

The dinuclear, molecular peroxothorium(IV) compound $[\text{Th}_2(\text{O}_2)_3(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ has been synthesized from direct reaction of an aqueous solution of $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ with 30% H_2O_2 at pH 9. The strategy was to react Th^{4+} ion in aqueous solution with O_2^{2-} at a relatively high pH in the absence of any additional heteroligand, unlike the cases involving $[\text{Th}(\text{O}_2)_3\text{L}(\text{H}_2\text{O})_4] \cdot 5\text{H}_2\text{O}$ ($\text{L} = \text{C}_2\text{O}_4$ or SO_4)⁵; it was anticipated that a complex with a higher $\text{O}_2^{2-}:\text{Th}$ ratio would result. However, no compounds with $\text{O}_2^{2-}:\text{Th} > 1.5$ could be obtained in the present case. Products isolated below pH 9 were found to be non-stoichiometric and occasionally contained nitrate. Thus, while a pH value of 9 is found to be the most conducive for the synthesis of **1**, hydroxyl groups were found to enter into the coordination sphere of Th(IV) at this pH, as has earlier been noted.⁵ Extensive hydrolysis of Th^{4+} at higher pH,^{1,8} also favours hydroxo ligation.

Peroxo(phosphato)thorates(IV) of the type $\text{A}[\text{Th}(\text{O}_2)\text{PO}_4(\text{H}_2\text{O})_2]$ ($\text{A} = \text{NH}_4$ or Na) were synthesised directly from the reaction of $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ with A_2HPO_4 dissolved in H_2O_2 at pH 7.5-8. The simultaneous addition of A_2HPO_4 and H_2O_2 is crucial since prior addition of either of the reagents lead to the formation of highly insoluble thorium phosphates or hydrated thorium peroxide, as the case may be. The products obtained at pH lower than 7.5 did not analyse to a definite composition. Furthermore, these products almost invariably were found to be contaminated with nitrate, an observation similar to that encountered in the synthesis of **1**. It may therefore be inferred that not all coordinated NO_3^- groups are removed from the starting material before a relatively high pH (>7) is reached. A point worth noting at this stage is that while complex **1** contains hydroxo ligands, the peroxo(phosphato)thorates(IV) incorporate aqua groups. This evidently is due to different pH conditions of synthesis.

All complexes were isolated as white microcrystalline products. Stored in sealed polyethylene bags, the compounds were found to be stable indefinitely. EPR spectra and results of magnetic susceptibility measurements indicate the diamagnetic nature of the products, concordant with the presence of Th(IV). Insolubility of the complexes precluded any measurements of solution electrical conductances. The complexes slowly decompose in dilute sulphuric acid with quantitative liberation of hydrogen peroxide, thus facilitating determination of active oxygen content. Analytical results (Table 1) for **1** gave $\text{Th}:\text{O}_2^{2-}$ as 1:1.5 thus pointing to the dinuclear nature of the complex while those for the peroxophosphatothorates gave $\text{Th}:\text{O}_2^{2-}:\text{PO}_4^{3-}$ ratios of 1:1:1, in agreement with the suggested formulae.

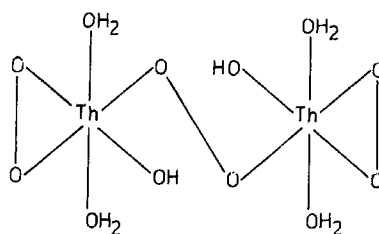
Vibrational spectroscopic studies of the complexes gave useful structural information. The significant features of the IR spectrum of $[\text{Th}(\text{O}_2)_3(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ involve absorptions due to coordinated peroxide, coordinated OH^- and both lattice and bonded water. A band at ca 840 cm^{-1} owes its origin to the ν_1 mode of a triangularly bonded, bidentate, chelating O_2^{2-} (C_{2v}) group.⁹ The symmetric (ν_s) and antisymmetric (ν_{as}) modes associated with $\text{M}-\text{O}_2$ stretches were located at 635 cm^{-1} and 540 cm^{-1} , respectively. Laser Raman (LR) spectra

Table 1 Analytical and structurally significant spectroscopic data for the complexes.

Compound	Analysis ^a (%)			Vibrational data (cm ⁻¹)		Assignments
	N or Na or Cs	Th	O ₂ ²⁻	IR	LR	
[Th ₂ (O ₂) ₃ (OH) ₂ (H ₂ O) ₄]·4H ₂ O		62.35 (62.86)	12.8 (13)	840	835	v(O-O) (triangular bidentate O ₂ ²⁻)
				635 540 730 850	825	v(O-O) (bridging O ₂ ²⁻) v _s (Th-O ₂) v _{as} (Th=O ₂) p _r (H-O-H) v (O-O) (triangular bidentate O ₂ ²⁻)
NH ₄ [Th(O ₂)PO ₄ (H ₂ O) ₂]	3.6 (3.41)	56.01 (56.58)	8.01 (7.8)	1090 1050 1025 970 620 580 550 840		v ₃ v ₁ } v (P-O) v ₄ v(O-O) (triangularly bidentate O ₂ ²⁻)
				1085 1050 1020 965 615 585 545 845		v ₃ v ₁ } v (P-O) v ₄ v (O-O) (triangularly bidentate O ₂ ²⁻)
Na[Th(O ₂)PO ₄ (H ₂ O) ₂]	6.0 (5.53)	56.3 (55.91)	7.2 (7.71)	23.0 (22.88)		
				1085 1050 1020 965 615 585 545 845		v ₃ v ₁ } v (P-O) v ₄ v (O-O) (triangularly bidentate O ₂ ²⁻)
Cs[Th(O ₂)PO ₄ (H ₂ O) ₂]	(25.8) (25.31)	43.8 (44.2)	5.7 (6.09)	18.4 (18.09)		
				1085 1055 1015 960 620 580 540		v ₃ v ₁ } v (P-O) v ₄ v (O-O) (triangularly bidentate O ₂ ²⁻)

^a Calculated values in parenthesis.

exhibited two, closely spaced, medium intensity bands at 825 and 835 cm^{-1} , attributable to the $\nu(\text{O-O})$ mode of bridging ($\sigma:\sigma$) and chelated (η^2) peroxide, respectively. Use of IR coupled with LR spectroscopy has been successfully employed by us^{5,6} and others¹⁰ in distinguishing structurally different, metal-bound peroxide. The region 3000-4000 cm^{-1} in the IR is rather complicated due to the occurrence of hydroxo groups and both coordinated and uncoordinated water molecules in the complex. However, a strong band at 3550 cm^{-1} coupled with a broad feature in the 3400-3500 region was assigned to O-H stretching of coordinated hydroxo groups.¹¹ Absence of any band near ca 1300 cm^{-1} ruled out the possibility of OH groups being bridged.¹² Although from the shape and position for $\delta(\text{H-O-H})$ [$<3000 \text{ cm}^{-1}$] no inference can be drawn as to the nature of water molecules, a distinct band at ca 730 cm^{-1} , assigned to ρ_r mode of bonded water, suggests unambiguously that at least some water molecules are coordinated.¹³ Pyrolysis studies show that **1** begins to lose weight under 100°C and between 120–130°C almost all the peroxide and ca 3.5–4 molecules of water are lost. The remaining water molecules are lost beyond 160°C, lending credence to the suggested number of coordinated water molecules. Thus, complex **1** can be envisioned to have the following gross molecular structure.



Scheme 1

Peroxo(phosphato)thorates(IV) displayed typical IR patterns (Table 1). Attempts to record LR spectra were not successful owing to fluorescence. The diagnostic band for the chelated peroxide (C_{2v}) was located at ca 850 cm^{-1} . IR features owing to the coordinated 'phosphato' ligand were observed at ca 970s (ν_1), 1085, 1050, 1020 (ν_3); and 550, 580, 615 cm^{-1} (ν_4). From this alone it is not possible to distinguish mono- and bidentate coordination or a bidentate chelate from a bidentate bridging coordination. However, considering that one split band for each of ν_3 and ν_4 was observed beyond 1050 cm^{-1} and 600 cm^{-1} , respectively, a bidentate chelate coordination mode for the phosphato ligand seems quite probable.¹⁴ This in any case does not rule out the possibility of PO_4^{3-} groups serving as bridges between contiguous Th^{4+} centres. Absorption at ca 720 cm^{-1} is attributed¹² to rocking modes of bonded water. The results of pyrolysis studies of $\text{Na}[\text{Th}(\text{O}_2)\text{PO}_4(\text{H}_2\text{O})_2]$ show that while the peroxide group is lost at ca 90°C, no loss of water molecules was registered below 150°C, thus suggesting that the aquo groups are coordinated to the Th(IV) centre.

Although the potential of actinide peroxo complexes as oxo-transfer agents has been briefly noted earlier,^{15,16} this aspect of their chemistry remained virtually unexplored. The insolubility of the complexes in aqueous and non-aqueous solvents

did not prove to be ideal for such studies. Nonetheless the coordinatively unsaturated Th(IV) compounds were anticipated to exhibit oxygen-transfer reactions. Accordingly, two very typical reaction involving $\text{SO}_2 \cdot n\text{H}_2\text{O}$ and an other involving PPh_3 with an aqueous suspension of **1** and **2** were carried out separately. The former reaction produced sulphate which did not remain coordinated to the Th(IV) centre, an observation not ubiquitous in the reactions of SO_2 with metal-peroxides.⁶ The latter reaction led to the formation of OPPh_3 as evidenced by TLC, its m.p. and a band at 1190 cm^{-1} for $\nu(\text{P}=\text{O})$ in its IR spectrum.

The new Th(IV) complexes reported here might serve as useful synthons as the labile aquo groups may be replaced by a variety of chosen ligands. Further work to this regard is now in progress.

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