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Understanding the Scarcity of Thorium Peroxide Clusters

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Supporting Information

ABSTRACT: The reaction of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ with 3 equiv of 2,2',6',2''-terpyridine (terpy) in a mixture of acetonitrile and methanol results in formation of the trinuclear thorium peroxide cluster $[\text{Th}(\text{O}_2)(\text{terpy})(\text{NO}_3)_2]_3$. This cluster is assembled via bridging by $\mu\text{-}\eta^2\text{:}\eta^2$ peroxide anions between thorium centers. It decomposes upon removal from the mother liquor to yield $\text{Th}(\text{terpy})(\text{NO}_3)_4$ and $\text{Th}(\text{terpy})(\text{NO}_3)_4(\text{EtOH})$. The peroxide formation appears to be radiolytic in origin and is, most likely, generated from radiolysis of water by short-lived daughters generated from ^{232}Th decay. This cluster does not form when freshly recrystallized $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ is used as the starting material and requires an aged source of thorium. Analysis of the bonding in these clusters shows that, unlike uranium(VI) peroxide interactions, thorium(IV) complexation by peroxide is quite weak and largely ionic. This explains its much lower stability, which is more comparable to that observed in similar zirconium(IV) peroxide clusters.

Peroxide plays a key role in the extraction of uranium from ores possibly via the formation of uranyl peroxide clusters or uranyl carbonate peroxide complexes.^{1,2} The nature of the interaction between uranyl and peroxide is unusually covalent and may provide an explanation for why the only known peroxide minerals, studtite and metastudtite, persist over geological time scales.³ The peroxide present in these minerals is generated from α radiolysis of water.³ In fact, the formation of actinide peroxides has been used to separate thorium from uranium for nearly 5 decades via the precipitation of a thorium peroxide compound, while leaving the uranium in solution. Despite the utility of this method, this precipitate remains poorly characterized,^{4–6} and a well-defined thorium peroxide compound or complex remains elusive. Herein we show that radiolytic reactions from aged sources of thorium with water lead to the formation of a trinuclear thorium peroxide cluster that can be isolated through the use of capping ligands that inhibit agglomeration and precipitation.

The reaction of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ with 3 equiv of 2,2',6',2''-terpyridine (terpy) in a 1:4 ethanol (EtOH)/acetonitrile (CH_3CN) solvent mixture results in the formation of colorless tablets upon standing for 2 months. Single-crystal X-ray diffraction studies revealed that the initial compound that crystallizes is the trinuclear cluster $[\text{Th}(\text{O}_2)(\text{terpy})(\text{NO}_3)_2]_3 \cdot 3\text{CH}_3\text{CN}$. After removal from the mother liquor, this compound rapidly decomposes and only $\text{Th}(\text{terpy})(\text{NO}_3)_4$ and $\text{Th}(\text{terpy})(\text{NO}_3)_4(\text{EtOH})$ could be identified in the residue (vide infra).

A view of the structure of $[\text{Th}(\text{O}_2)(\text{terpy})(\text{NO}_3)_2]_3$ is shown in Figure 1. The cluster comprises three $[\text{Th}(\text{O}_2)(\text{terpy})$

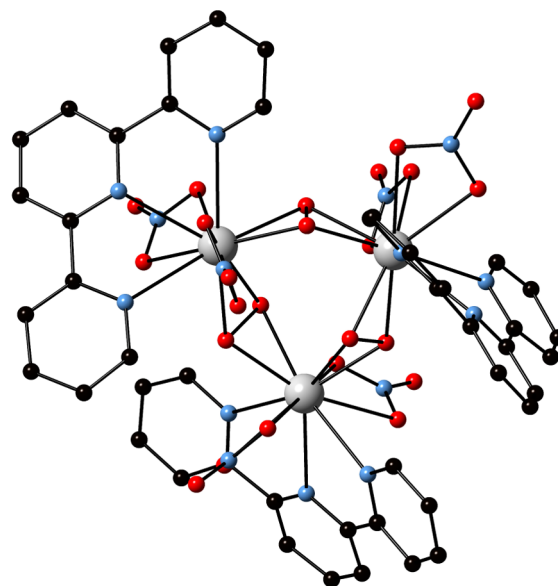


Figure 1. View of the structure of the trinuclear thorium peroxide cluster $[\text{Th}(\text{O}_2)(\text{terpy})(\text{NO}_3)_2]_3$. The thorium(IV) centers are 11-coordinate with augmented sphenocorona geometry that are bridged by $\mu\text{-}\eta^2\text{:}\eta^2$ peroxide anions. The periphery of the cluster is capped by tridentate terpy ligands. Hydrogen atoms on the terpy ligands have been omitted for clarity. Color code: Th, gray; O, red; N, blue; C, black.

$(\text{NO}_3)_2$ moieties that are bridged by $\mu\text{-}\eta^2\text{:}\eta^2$ peroxide anions. The presence of one tridentate and four bidentate ligands in the inner sphere creates a rare 11-coordinate environment around the thorium(IV) centers that are best described as augmented sphenocorona. A similar $[\text{M}_3(\text{O}_2)_3]$ core has been observed in several zirconium(IV) fluorides as well as in $\{\text{Zr}[\text{MeC}(\text{N}^i\text{Pr})_2]_2(\text{O}_2)\}_3$.^{7,8} In the latter compound, it was established that the reduction of O_2 to O_2^{2-} is ligand-based and appropriate ligand decomposition products are observed. However, this cluster is unstable in solution and ultimately decomposes to dimeric and polymeric oxo species via degradation of the peroxide anions.

In $\text{Zr}[\text{MeC}(\text{N}^i\text{Pr})_2]_2(\text{O}_2)_3$, the peroxide anions form by exposing a monomeric starting material to air at -30°C . However, in the case of the formation of $[\text{Th}(\text{O}_2)(\text{terpy})$

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$(\text{NO}_3)_2)_3$, reducing ligands or other peroxide-forming reagents are not present in the reaction, which suggests that peroxide formation is radiolytic in origin. The issue with this postulate is that the half-life of ^{232}Th is 1.4×10^{10} years, and from this basis alone, it is challenging to argue that appreciable amounts of peroxide could be generated from 10 mg of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ even after 2 months of standing in solution.

The key to solving this puzzle is the age of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ used in the reaction, which turned out to be 40 years old without any intervening purification. ^{232}Th is an α emitter and decays to ^{228}Ra ($t_{1/2} = 5.75$ years), followed by a series of very short-lived isotopes that ultimately decay to stable ^{208}Pb . It only takes ^{232}Th about 40 years to reestablish secular equilibrium after purification. Liquid scintillation counting of a dissolved sample of this old source of thorium revealed that it was undergoing more than 3 orders of magnitude more disintegration per second than freshly recrystallized $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$. Thus, while it is true that ^{232}Th itself does not generate enough radiolysis products to account for appreciable peroxide formation, its short-lived daughters provide ample activity for these radiolytic reactions to occur. This also provides a word of caution against the laissez-faire attitude that is often exhibited when working with thorium. To test this hypothesis, reactions with freshly recrystallized $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were performed, and these only yield $\text{Th}(\text{terpy})(\text{NO}_3)_4$ and $\text{Th}(\text{terpy})(\text{NO}_3)_4(\text{EtOH})$.

The structure of $[\text{Th}(\text{O}_2)(\text{terpy})(\text{NO}_3)_2)_3$ provides some important metrics for comparison with zirconium(IV) peroxides as well as with the large family of uranium(VI) peroxide clusters. The angles at the bridging oxygen atoms of the peroxide anions average $126.53(9)^\circ$. This angle has been examined in detail in uranyl peroxides, and the bending is sensitive to the counterions employed to balance charge with the anion clusters.⁹ In this case, the thorium peroxide clusters are neutral, and on the basis of the oxidation states, the zirconium(IV) peroxide clusters provide a better source of comparison. An averaging of the $\text{Zr}-\text{O}_2-\text{Zr}$ angles in both the fluoride and amido clusters yields a value comparable to that found in the thorium cluster of $125.14(4)^\circ$. The $\text{O}-\text{O}$ bond distance is also quite similar between the thorium(IV) and zirconium(IV) compounds, for which it averages $1.516(3)$ and $1.515(13)$ Å, respectively. It is interesting to note that while there is $<2^\circ$ angular deviation between the thorium(IV) and zirconium(IV) peroxide binding, the $\text{Th}-\text{O}$ and $\text{Zr}-\text{O}$ bond distances differ substantially with averages of $2.369(2)$ and $2.162(10)$ Å, respectively. This observation is not surprising given the large increase in the ionic radius between zirconium(IV) (0.86 Å) and thorium(IV) (1.08 Å). These structural data point to largely ionic interactions in both the thorium(IV) and zirconium(IV) clusters.

These observations are bolstered by density functional theory calculations, which have been successfully applied to other thorium(IV) complexes as well as much more complex open-shell actinide complexes such as those containing plutonium, berkelium, and californium.^{10–13} The optimized geometry of the $[\text{Th}_3(\text{O}_2)_3]$ cluster is in good agreement with that determined by X-ray diffraction (see the Supporting Information, SI),¹⁴ indicating the adequacy of the computational methods to deal with this system. The ground state of the complex is found to be a closed-shell singlet spin in line with three thorium(IV) centers. This was further confirmed by an f-in-core calculation (fixing the oxidation state of each thorium center to IV+). A deep analysis of the bonding was then carried out. First, the molecular orbitals were scrutinized. While the lowest unoccupied molecular orbital (LUMO) is located on the terpy ligand, the highest occupied

molecular orbitals (HOMOs) are three combinations of π orbitals on the peroxide (HOMO, HOMO–1, and HOMO–2; see the SI) without any interactions with the metal center. Bonding orbitals were found to be far lower in energy and involve a 6d orbital on thorium and the π^* orbital of the peroxide, as shown in Figure 2. Hence, unlike uranyl peroxide interactions, which make heavy use of the 5f orbitals, the only frontier orbital found to be involved in the $[\text{Th}_3(\text{O}_2)_3]$ cluster is 6d.^{15–24}

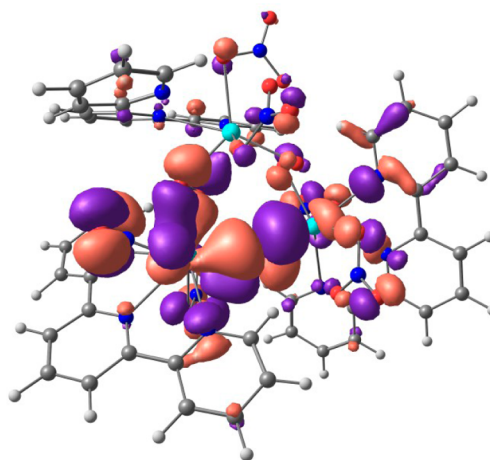


Figure 2. Depiction of the weak donor–acceptor interaction between thorium(IV) and a π^* orbital of the peroxide in $[\text{Th}(\text{O}_2)(\text{terpy})(\text{NO}_3)_2)_3$.

The nature of the bonding orbital is in line with a donor–acceptor-type interaction between O_2^{2-} and Th^{4+} . This is further highlighted by natural bond orbital analysis. In this analysis, interactions between the peroxide and the thorium centers were only found at the second-order donor–acceptor level. Therefore, the interaction is predicted to be quite weak, as substantiated by the Wiberg bond index of only 0.3 for thorium peroxide, which is only slightly larger than that of an agostic interaction.

Taken together, these experimental and computational results verify early findings from the thorium/uranium separations, where it was observed that, upon drying, thorium peroxide precipitates rapidly liberated oxygen.²⁵ Hence, the reason for the paucity of thorium peroxide in the literature can be ascribed to the instability imparted by largely ionic interactions between thorium(IV) and peroxide that sets them apart from their more covalent uranyl counterparts and places them in line with early-transition-metal analogues like zirconium(IV).

Caution! ^{232}Th element is an α -emitting radioisotope. Standard precautions should be followed during handling of these chemicals.

$\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (0.010 g, 0.0297 mmol) was allowed to age for 40 years, and terpy (0.0208 g, 0.0891 mmol) was dissolved in 5 mL of a 1:4 methanol/ CH_3CN mixture. The mixture was capped and allowed to stand for 2 months. Colorless tablets formed on the bottom of the vial during this time and were quickly isolated by removing most of the mother liquor, followed by washing with EtOH to remove residual terpy. The crystals rapidly decompose upon removal from the reaction mixture, and the reaction must be sealed because evaporation leads to decomposition of the desired peroxide-containing product.

X-ray structural analysis: $[\text{Th}(\text{O}_2)(\text{terpy})(\text{NO}_3)_2)_3 \cdot 3\text{CH}_3\text{CN}$; colorless tablet, space group $P\bar{1}$ (No. 2), $Z = 2$, $a = 13.2177(12)$ Å, $b = 13.9068(13)$ Å, $c = 18.4265(17)$ Å, $\alpha = 86.9880(15)^\circ$, $\beta = 88.0749(15)^\circ$, $\gamma = 83.8940(16)^\circ$, $V = 3361.9(5)$ Å³ ($T = 100$ K),

$\mu = 67.07 \text{ cm}^{-1}$, $R1 = 0.0313$, and $wR2 = 0.0987$. Bruker Quest diffractometer: $\theta_{\text{max}} = 55.222^\circ$, $\text{Mo K}\alpha$, $\lambda = 0.71073 \text{ \AA}$, $0.5^\circ \omega$ scans, 15563 reflections measured. All reflections were included in the refinement. The data were corrected for Lorentz-polarization effects, and for absorption, the structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least squares, 867 parameters.²⁶

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02216.

Selected crystallographic data and bond distance tables and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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