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Caging Peroxide: Anion-Templated Synthesis and Characterization of a Rare-Earth Cluster

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S *Supporting Information*

ABSTRACT: Sequestration of peroxide derived from molecular oxygen has resulted in the templated synthesis of a terbium picolinate cluster, isolated as a 2D sodiated network in the solid state. This first example of an air-stable rare-earth peroxide cluster represents key evidence for a peroxide-containing intermediate in rare-earth-cluster-catalyzed oxidation reactions. Luminescent and magnetic properties have also been investigated.

Anion-templated synthesis as a strategy to access previously unknown motifs with potentially unique properties has become a topical area of research within rare-earth-cluster chemistry.[1] Some recent, noteworthy examples include halide-templated pentadecanuclear complexes,[2] carbonate-templated dodecanuclear clusters,[3] hexanuclear clusters,[4] a 60-metal sodalite cage,[5] and related sodium carbonate templated tetranuclear clusters.[6] Of these examples, a select few carbonate-templated examples merit further attention, owing to atmospheric carbon dioxide sourcing the templating agent.[3,4]

Atmospheric oxygen also has the potential to be a source of templating agent by reduction to peroxide, a transformation known to occur in the presence of bioinorganic complexes containing copper or iron.[7] However, despite countless inorganic syntheses performed under air, no templated cluster synthesis utilizing peroxides has thus far been reported. Focusing on the oxophilic rare earths, the addition of pure oxygen to rare-earth chlorides with strict exclusion of moisture is known to yield chloride-bridged tetranuclear rare-earth clusters containing two μ_3-η^2:η^2:η^2-coordinated peroxide dianions.[8] Additionally, dimeric complexes exhibiting μ-η^2:η^2 peroxo bridges have also been isolated from moisture-sensitive rare-earth precursors[9] and rare-earth macrocycles dissolved in dioxane solvent mixtures.[10] The clusters can be likened to an oxidized form of the trinuclear $[\mathrm{Ln_3(\mu_3\text{-}OH)_2}]$ cluster motif, known for interesting single-molecule-magnet and catalytic behavior.[11]

Moisture-stable rare-earth clusters are known to catalyze oxidations of aldehydes to carboxylates, an unusual transformation exemplified by a single yttrium cluster.[12] These reactions were postulated to proceed by the insertion of oxygen originating from air into an acyl functionality, yielding a peroxy acid. A subsequent rearrangement was then proposed to yield the carboxylic acids.[12] A later example of ketone oxidation during the assembly of a lanthanum cluster is also likely to occur by similar means.[3] The identity of the oxidizing species generated from air in the presence of rare-earth clusters has yet to be determined.

Herein we report the first example of peroxide-templated cluster formation in the form of a terbium triangular motif. The sequestration of peroxide into the cluster is thought to occur with the breakdown of a hydroperoxide species generated by air autoxidation of 2-acetylpyridine. The peroxide cluster represents the first direct evidence that peroxide interacts with polynuclear rare-earth species under mild conditions and, by extension, the oxidation reactions they catalyze.

The reaction of sodium picolinate (Napic) with hydrated terbium chloride in the presence of 2-acetylpyridine has yielded an anionic terbium triangular motif with the composition $[\mathrm{Tb_3(O_2)(pic)_9}]^{2-}$ (**1**). Single crystals were obtained from the solution after an extended period of time open to air. X-ray crystallographic analysis allowed visualization of the solid-state structure, identifying a 2D network of anionic clusters bridged by sodium cations. The structure of **1** consists of a triangular array of terbium atoms coordinating a central peroxide anion in a μ_3-η^2:η^2:η^2 fashion (Figure 1). The molecule contains 3-fold rotational symmetry, with the asymmetric unit consisting of a single terbium atom coordinated by three picolinate ligands and a peroxide molecule, the latter possessing one-third occupancy. The peroxide "hub" is shielded from solvent interaction by three hydrophobic aromatic ring layers, demonstrating **1** to be an efficient container molecule for peroxide anions (Figure 2). Each terbium atom is nine-coordinate. The extended 2D network incorporates sodium atoms that bridge from the

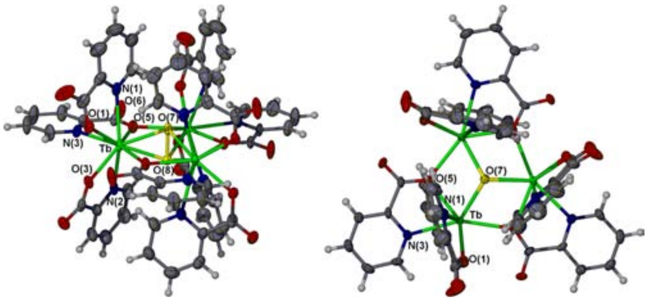

Figure 1. Two perspectives of terbium triangle **1** generated by the templating of peroxide (the peroxide core is highlighted in yellow). Sodium cations and the lattice solvent have been omitted for clarity.

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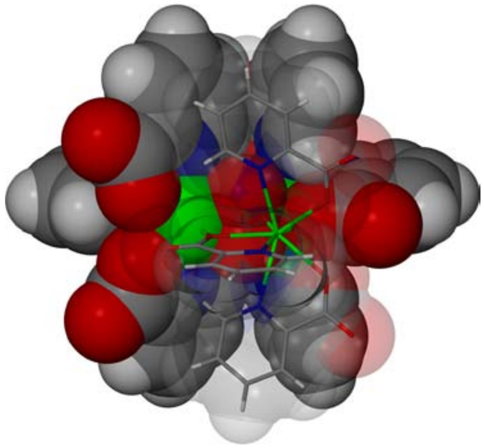


Figure 2. Space-filling model showing the peroxide anion (red, center) coordinated by terbium atoms (green) and highlighting the caging effect of the hydrophobic aromatic rings of picolinate. One corner of the triangle has been made transparent with the inclusion of a wire frame guide for clarity.

picolinic carboxylate groups. Picolinate was observed to coordinate in η^2-(N:μ-O) and η^2-(N:μ-O):η^1(O) fashion, bridging between terbium atoms or a terbium atom and a sodium atom (Figure 3). The exposed carboxylate groups link clusters of **1** together by coordinating sodium cations that are linked by a bridging methoxide ion. The 2D sheet can be described as a 6^3 net comprised of six three-coordinate $Tb_3(O_2)$ nodes linked by sodiated methoxide spacers. A simplified schematic of the net can been seen in Figure 4.

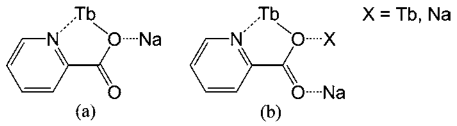


Figure 3. Coordination modes observed for picolinate in cluster **1**: (a) η^2-(N:μ-O) and (b) η^2-(N:μ-O):η^1(O).

Assignment of the peroxide core of **1** was evidenced by crystallography and vibrational spectroscopy. The observed O–O distance of 1.545(12) Å is consistent with reported peroxide-containing complexes.[13] A full list of the bond lengths and angles can be found in the Supporting Information. The IR spectrum contains a weak band at 883 cm^{-1} that was attributed to the ν(O–O) vibration in line with previous reports.[10] Additionally, a band observed in the Raman spectrum at 863 cm^{-1} has been assigned to the ν(O–O) stretching frequency, further strengthening this assignment.[13]

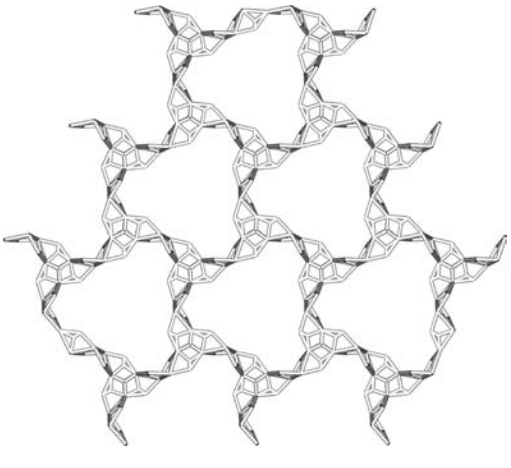
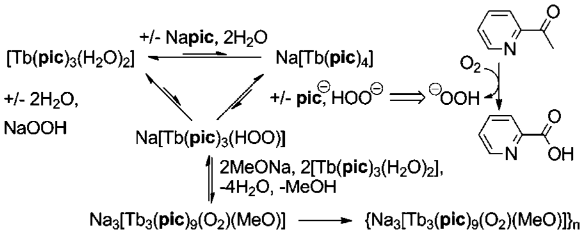


Figure 4. Wire-frame representation of the extended 6^3 network, with each node corresponding to anionic **1**, which is linked in three directions by sodium bridges.

The means for the formation of **1** was next considered. An initial autoxidation process coupled with the reduction of molecular oxygen to peroxide is required to obtain template formation of the cluster. Autoxidation is known to occur in two stages: the initial formation of hydroperoxide followed by the breakdown of this species.[14] In the case of ketones, the adjacent methylene group is activated, allowing the formation of ketone hydroperoxide (Scheme 1).[15] To investigate this behavior, a ketone source, 2-acetylpyridine, was included in the reaction mixture. The lanthanoid species undertakes the role of peroxidation promoter and sequester of liberated peroxide as ketone hydroperoxide breaks down. Repeating the synthesis in the absence of 2-acetylpyridine failed to yield a peroxide-containing product, with periodic testing with starch iodide paper giving no indication of peroxide formation. The peroxide anion possesses the optimal size to disrupt the equilibrium of monomeric species and promote aggregation (Figure 2), lowering the solubility in the process and prompting crystallization. The templating process of **1** traps the reactive peroxide, yielding the first tangible evidence for a mechanism of oxidation induced by peroxide intermediates that are promoted by rare-earth clusters. The lack of metal species containing peroxide in the literature suggests that radical reactions are usually favored over peroxide incorporation.

Scheme 1. Postulated Route of Formation for the $\{Na_3[Tb_3(O_2)(pic)_9]\}_n$ Network



The luminescent properties of the network were next investigated by fluorescence spectroscopy. Excitation of **1** in the solid state, in water, or in an aqueous sodium chloride solution (2:1) with ultraviolet radiation (λ = 300 nm) resulted in characteristic green emission.[16] The most intense transitions from the $^5D_4$ excited state to the $^7F_5$ (J = 6–3) ground state are shown in Figure 5. The luminescent intensity in aqueous solution is attributed to fragmentation of the cluster motif to the component monomeric units according to Scheme 1. Mass spectrometry has identified the dominant emitting species in aqueous solution to be the $[Tb(pic)_4]^-$ anion.[17] While direct comparisons between the relative luminescent intensities between crystalline **1** and the aqueous species cannot be inferred from the present work, it is likely that efficient quenching of the $^5D_4$ excited state by coordinated water will influence the emission intensity of the aqueous species in equilibrium.

The magnetic properties of lanthanide clusters are of great interest because of the possibility of displaying single-molecule

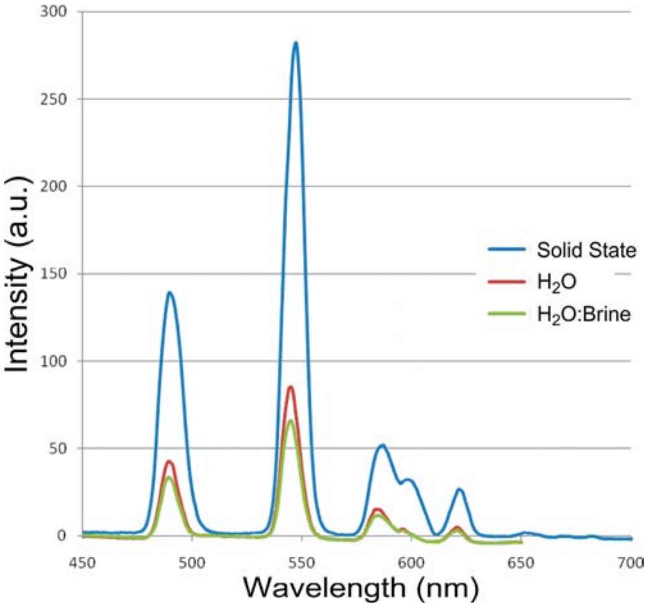


Figure 5. Emission spectra of terbium species **1** in the solid state and aqueous solvents with an excitation wavelength of 300 nm.

magnetism (SMM) with slow relaxation of magnetization. Anisotropic ions such as dysprosium, for example, in triangles of the type $[Dy_3(\mu_3\text{-}OH)_2L_3Cl(OH_2)_5]$-$Cl_3 \cdot 4H_2O \cdot 2MeOH \cdot 0.7MeCN$ (L =*o*-vanillato) showed intriguing SMM features.[17] The direct-current susceptibility data for **1**, in a field of 1 T, is shown in Figure S1 in the Supporting Information. $\chi_M T$ values of 25.5 cm^3 mol^{-1} K remain constant between 300 and 100 K and then decrease more rapidly to reach 10 cm^3 mol^{-1} K at 2 K, with the field dependence noted below ~20 K due to Zeeman depopulation effects. Free-ion Tb^{III} ions, with $^7F_6$ ground states and $g = {}^3/_2$, yield $\chi_M T = 11.82$ cm^3 mol^{-1} K, viz., 35.46 cm^3 mol^{-1} K per Tb_3, much higher than that observed. The present data are indicative of very weak or zero antiferromagnetc coupling, via the peroxo bridge, which contrasts with the ferromagnetic coupling noted in a linear, phenoxo-bridged Tb_3 trimer.[18] Neither of these Tb_3 complexes displays SMM features in their alternating-current χ'' data.

This preliminary study has identified the first example of a peroxide-templated cluster aggregate. The caged peroxide represents the first structural evidence for a mechanism containing intermediate peroxide for rare-earth-cluster-mediated oxidation reactions. Solid-state luminescence measurements have determined characteristic green luminescence for the terbium triangular motif, and magnetic studies have revealed very weak coupling and a lack of SMM properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental preparation, analytical and spectroscopic characterization of **1**, crystallographic tables of the bond lengths and angles, crystallographic data in CIF format, and magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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