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Direct Hydrolytic Route to Molecular Oxo−Hydroxo Lanthanide Clusters

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Polynuclear lanthanide complexes feature a fascinating variety of unusual symmetries and structural patterns.[1,2] More importantly, some of these compounds are potential precursors for applications in metalloorganic chemical vapor deposition[3] and sol−gel technology.[3−5] The examples of well-characterized finite-size lanthanide clusters are limited, however, and their syntheses are still characterized by random self-organization.[1] A foremost objective is therefore to develop synthetic approaches to these substances with the ultimate goal of creating novel lanthanide-containing materials.

To this end, we have recently reported a series of pentadecanuclear lanthanide complexes synthesized via ligand-controlled hydrolysis of lanthanide perchlorates with tyrosine as the supporting ligand.[6] In an analogous reaction where erbium nitrate was utilized, the unexpected formation of the previously reported hexanuclear oxo−hydroxo lanthanide cluster, $[Er_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(NO_3)_6(H_2O)_{12}](NO_3)_2\cdot 4H_2O$ (**1**),[7] was observed. The absence of tyrosine ligands in the isolated product is surprising, and the suggestion that tyrosine possibly acts as a buffer in such a synthesis was subsequently excluded on the basis that direct hydrolysis of $Er(NO_3)_3$ with dilute aqueous NaOH yielded the same complex **1**. These observations prompted us to investigate the hydrolysis of lanthanides in the absence of any supporting ligands as a general approach to molecular oxo−hydroxo lanthanide clusters.[7−9] The chemistry of these materials remains virtually undeveloped despite the fact that the closely related polynuclear oxo−alkoxides have been extensively studied.[3,10−13] These two classes of compounds can be viewed as the intermediates of polymetallic oxides in sol−gel processes[3−5] with the oxo−hydroxo clusters being more desirable due to their lack of high moisture sensitivity, and hence ease of handling.

Our interest in the direct hydrolysis of lanthanide nitrates was attenuated by the fact that six lanthanide oxo−hydro clusters with a general formula of $[Ln_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(NO_3)_6(H_2O)_{12}](NO_3)_2$ had been prepared,[7,8] though via the thermal decomposition of hydrated $Ln(NO_3)_3$ followed by hydrolysis of the decomposition products. Furthermore, the insolubility of these compounds in organic solvents,[7,8] their further undefined hydrolysis,[7,8] and the strong coordination of a nitrato ligand to a lanthanide ion[14] preclude the use of these clusters in further research. Our efforts have therefore concentrated on the study of the direct hydrolysis of lanthanide perchlorates.[15] Although these starting materials are potentially explosive, they have been utilized extensively in lanthanide research because of their *water solubility* and the *weakly coordinating* nature of a perchlorate ion. The latter is essential for the preparation of novel oxo−hydroxo lanthanide precursors for future work. We report here the findings of the direct hydrolysis of $Nd(ClO_4)_3$ and $Gd(ClO_4)_3$ leading to the assembly of two new molecular oxo−hydroxo clusters. Preliminary results indicated that analogous clusters resulted starting from $Eu(ClO_4)_3$ and $Er(ClO_4)_3$. The generality of such a hydrolytic approach to hexanuclear oxo−hydroxo lanthanide clusters is thus suspected.

An aqueous solution of NaOH (0.4 M, 10 mL) in 5 aliquots was added dropwise to a solution of $Nd(ClO_4)_3$ or $Gd(ClO_4)_3$ (1.0 M, 16 mL) with vigorous stirring and at boiling temperature to the point of incipient precipitation. The volume of the reaction mixture was reduced to ca. 5 mL. The mixture was then filtered, and the filtrate was allowed to stand at room temperature. Block-shaped crystalline solids appeared after about 1 week and were collected by filtration. More products were obtained by treating the mother liquor with dilute aqueous NaOH solution following the same procedure, but the yields were not optimized. Using $Nd(ClO_4)_3$ as the starting material, complex **2**, formulated as $[Nd_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(H_2O)_{24}](ClO_4)_8\cdot 8H_2O$,[16] was isolated in 38% yield, while complex **3**, formulated as $[Gd_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\eta^2\text{-}ClO_4)_2(H_2O)_{20}](ClO_4)_6\cdot 4H_2O$,[17] was obtained in 45% yield starting from $Gd(ClO_4)_3$. Both compounds are readily soluble in polar organic solvents, such as tetrahydrofuran, acetone, and acetonitrile, but further hydrolyze to generate gelatinous precipitates. The complexes were characterized by IR and electrospray ionization mass spectroscopy. The integrity of the $[Ln_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$ unit[7,8,18] was manifested by the presence of the intact multiply charged cluster core. Using the ^1H NMR method pioneered by Evans[19] and modified by Sur,[20] magnetic susceptibilities and magnetic moments were determined for **2** and **3** in acetone-d_6

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(15) **CAUTION:** *Metal perchlorates are potentially explosive! Only a small amount of materials should be prepared and handled with great care.* However, careful tests on the materials in our studies showed no apparent hazards. Small amounts (5−10 mg) charred when heated in open air.

(16) Anal. Calcd for $Nd_6H_{72}O_{73}Cl_8$: Nd, 36.22. Found (complexometric titration): Nd, 36.20. IR (KBr): ν 3419, 1621, 1384, 1144, 1111, 1089, 941, 637, 627, 451 cm^{-1}. ESI-MS: *m/z* (%) 663.6 (100) $[M - 6H_2O - 3ClO_4^-]^{3+}$, 906.1 (60) $[M - 21H_2O - 2ClO_4^-]^{2+}$, 993.0 (40) $[M - 11H_2O - 2ClO_4^-]^{2+}$.

(17) Anal. Calcd for $Gd_6H_{56}O_{65}Cl_8$: Gd, 40.61. Found (complexometric titration): Gd, 39.87. IR (KBr): ν 3439, 1622, 1384, 1144, 1108, 1090, 941, 636, 627, 477 cm^{-1}. ESI-MS: *m/z* (%) 677.7 (90) $[M - 3ClO_4^-]^{3+}$, 918.2 (60) $[M - 16H_2O - 2ClO_4^-]^{2+}$, 1007.1 (90) $[M - 6H_2O - 2ClO_4^-]^{2+}$.

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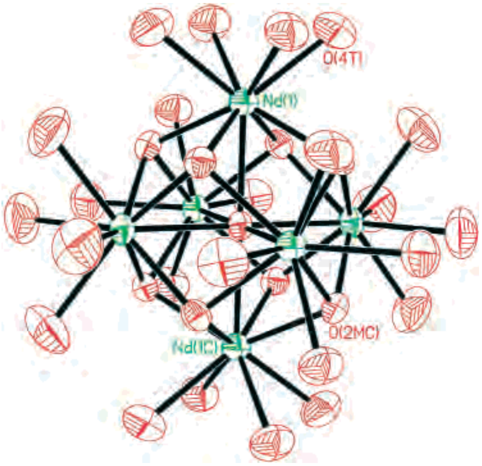

Figure 1. Molecular structure of $[Nd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]^{8+}$ with the H atoms removed for clarity. The average Nd−O(aqua) bond length is 2.562 Å (2.556(2)−2.590(3) Å). The average Nd−O(μ_3-OH) bond length is 2.433 Å (2.428(2)−2.438(3) Å). The average Nd−O(μ_6-O) bond length is 2.618 Å. Thermal ellipsoids are shown at the 50% probability level.

solutions with tetramethylsilane as the reference. The values of μ_{eff}/molecule of 8.45 and 19.8 μ_B measured respectively for complexes **2** and **3** are close to the corresponding values calculated by the Van Vleck equation (for **2**, $(6)^{1/2} \times 3.68 = 9.01\ \mu_B$; for **3**, $(6)^{1/2} \times 7.94 = 19.5\ \mu_B$) for six non-interactive Nd(III) and Gd(III) ions, indicating that the room-temperature magnetic exchange interactions, if any, between the six lanthanide ions are very weak in both complexes.[21]

The structure of the cationic cluster of **2** (Figure 1) is composed of an octahedron of Nd(III) ions centered on a μ_6-oxo ligand[1,2,22,24] (average Nd−O 2.618 Å). Each of the triangular metal faces is capped by a μ_3-OH ligand (average Nd−O 2.433 Å), and the metal coordination sphere is completed with four aqua ligands (average Nd−O 2.562 Å). Thus, each Nd(III) is coordinated to nine oxygen atoms: one interstitial oxo unit, four face-capping hydroxo groups, and four terminal aqua ligands. The coordination polyhedron can be best described as a square antiprism monocapped by the interstitial oxo ligand. The cationic cluster of **3** bears virtually the same core structure as **2** except that two perchlorate ions are found in the metal coordination sphere, each of which bridges two adjacent Gd(III) ions within the same plane (Figure 2). However, such a solid-state structure may not be representative of the cluster structure in bulk because a perchlorate ion is generally lanthanide noncoordinating. In fact, the IR spectra of **2** and **3** are almost identical with stretching frequencies supporting the presence of only ionic perchlorate ions.[25] Both structures are highly regular with each of the three equatorial planes containing four metal ions, one μ_6-oxo, and eight terminal oxygen atoms (two on each metal center, from either the aqua ligands or the coordinated perchlorate ions). The metric values of both clusters are comparable to those reported for respectively relevant complexes in the literature.[8,9,12,26−28]

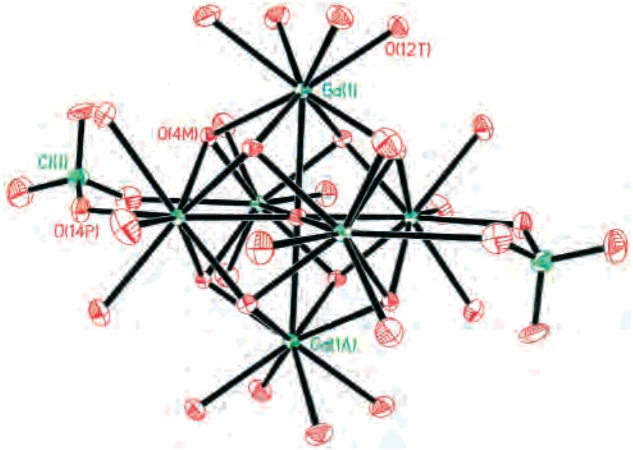

Figure 2. Molecular structure of $[Gd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\eta^2\text{-}ClO_4)_2(H_2O)_{20}]^{6+}$ with the H atoms removed for clarity. The average Gd−O(ClO_4^-) distance is 2.746 Å. The average Gd−O(aqua) bond length is 2.489 Å (2.430(2)−2.588(3) Å). The average Gd−O(μ_3-OH) bond length is 2.374 Å (2.347(2)−2.405(3) Å). The average Gd−O(μ_6-O) bond length is 2.545 Å (2.513(2)−2.591(3) Å). Thermal ellipsoids are shown at the 50% probability level.

Several aspects of this work merit further discussion. First, the use of organic supporting ligands to prevent the formation of intractable hydrolysis products has been an integral part of lanthanide cluster chemistry.[1,2] However, as exemplified by the formation of complexes **1**−**3**, molecular oxo−hydroxo lanthanide clusters can be achieved via direct hydrolysis of lanthanide perchlorates and nitrates in the absence of any organic supporting ligands, hence a new synthetic paradigm for these otherwise hard-to-obtain lanthanide clusters. Second, the octahedral $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ core appears to be a common structural motif in polyoxo lanthanide clusters, as demonstrated by this work and others.[7,8,18] Third, complex **2** is the first lanthanide cluster with *only coexisting* oxo, hydroxo, and aqua ligands. Such hydrous species are the simplest and most fundamental forms of $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ core-containing clusters and are expected to be useful precursors for other cluster derivatives including the construction of supramolecular structures using the octahedral clusters as building blocks.[29−32]

In summary, the present work has furnished two new members of molecular oxo−hydroxo lanthanide clusters. More importantly, it demonstrates a new and general synthetic route to these otherwise hard-to-achieve substances. The structural integrity, the highly ordered arrangement of paramagnetic centers, and the anticipated substitutional lability of the cluster terminal aqua ligands portend their applications as structural and functional building blocks for a variety of lanthanide-containing materials.

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Supporting Information Available: Listings of crystallographic data and structural refinement, atomic coordinates, bond lengths and angles, and final thermal parameters of compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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