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A Chiral 60-Metal Sodalite Cage Featuring 24 Vertex-Sharing [$Er_4(\mu_3\text{-}OH)_4$] Cubanes

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The study of high-nuclearity metal complexes has been a field of rapid growth in coordination and materials chemistry.[1−3] A large number of these large yet molecular species have been reported, many of which display aesthetically pleasing structures and interesting properties.[4−8] A subgroup of materials in this context are clusterlike polynuclear lanthanide hydroxide complexes.[9−15] Originally the elusive products of adventitious hydrolysis, they can now be rationally synthesized via a ligand-controlled hydrolytic approach with the use of judiciously chosen ancillary ligands to limit the degree of lanthanide hydrolysis and the aggregation of the hydroxo intermediates; finite and structurally well-defined cluster species can thus be obtained.[13a] Important applications of such high-nuclearity complexes, envisioned or realized, include their uses as molecule-based magnetic materials,[12] artificial nucleases for the hydrolytic cleavage of DNA and RNA,[16] contrast agents for magnetic resonance imaging,[17] and fixation media for atmospheric CO_2.[15]

The synthetic challenges and potential applications of polynuclear lanthanide hydroxide complexes have provided an unabated impetus for continuous research. Exactly a decade ago, a pentadecanuclear Eu(III) complex with tyrosinate ligands was reported by one of us and co-workers.[13b] Crystallographic analysis revealed an appealing "cubane-wheel" structure featuring five vertex-sharing cubane-like units of $Eu_4(\mu_3\text{-}OH)_4$ centered around a Cl^- ion (Figure 1, left). Subsequent studies established the indispensable templating effects of this and other halide ions.[13c] Interestingly, using the significantly bulkier I^- ion afforded a smaller dodecanuclear cubane wheel (Figure 1, right).

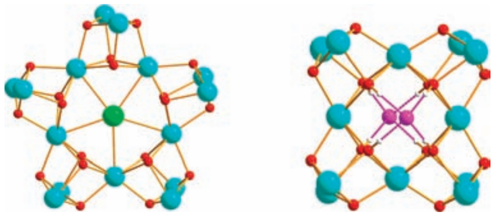

Figure 1. (left) Pentadecanuclear cluster templated by a μ_5-X^- ion (X = Cl, Br) ion. (right) Dodecanuclear cluster templated by two μ_4-I^- ions.

We report herein a giant cagelike lanthanide hydroxide cluster, **1**, formulated as $[Er_{60}(\text{L-thre})_{34}(\mu_6\text{-}CO_3)_8(\mu_3\text{-}OH)_{96}(\mu_2\text{-}O)_2(H_2O)_{18}]\text{-}Br_{12}(ClO_4)_{18}(H_2O)_{40}$ (L-thre = L-threonine), wherein the long-sought-after hexagonal cubane wheel can be identified (Figure 2). Complex **1** was isolated from the controlled hydrolysis of $Er(ClO_4)_3$ in the presence of L-threonine. The syntheses of its cognate with D-thre and its Ho(III) and Y(III) analogues were equally successful [see the Supporting Information (SI)].

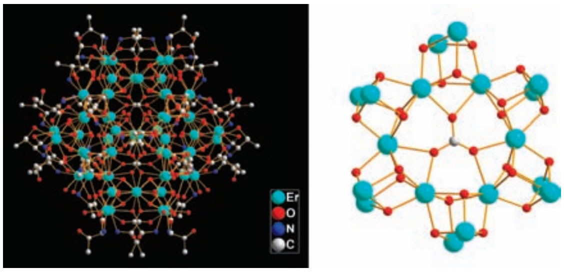

Figure 2. (left) Crystal structure of cationic cluster $[Er_{60}(\text{L-thre})_{34}(CO_3)_8(\mu_3\text{-}OH)_{96}(\mu_2\text{-}O)_2(H_2O)_{18}]^{30+}$. (right) Structure of the hexagonal cubane wheel templated by a μ_6-CO_3^{2-} ion.

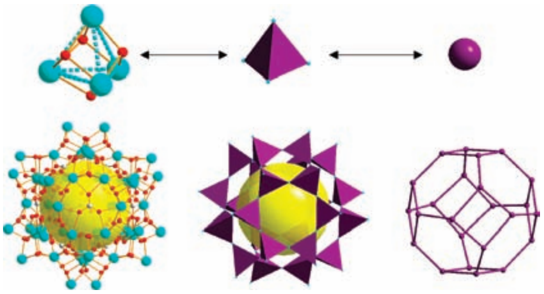

Figure 3. Illustration of the assembly of 24 cubane-like $[Er_4(\mu_3\text{-}OH)_4]^{8+}$ units into a sodalite cage structure by vertex sharing.

Cluster **1** is likely the largest known member of the fascinating family of homonuclear lanthanide complexes (Figure 2, left). It also represents a rare example of a chiral cluster complex (crystallized in the chiral space group $C222_1$). Its 60 Er atoms are organized into 24 $Er_4(\mu_3\text{-}OH)_4$ units, each represented as a tetrahedron or a sphere in Figure 3. These cubane units are joined together by sharing corners with three identical neighbors, forming six squares and eight hexagons of the cubane units, as shown in Figure 3. The assembly of the salient cubane hexagon is templated by the μ_6-CO_3^{2-} ion, which is situated at the center of the wheel-like structure and bridges six Er atoms in a μ_6:η^1:η^1:η^1:η^1:η^1:η^1 fashion (Figure 2, right). Although more than 10 different kinds of coordination modes have been reported for carbonate ion, this particular mode has only been observed in a limited number of complexes.[18] The unexpected carbonate ion is probably the byproduct of ligand decomposition, as previously observed by us and others.[8,19]

The vertex configuration (4,6,6) means that one square and two hexagons meet at a vertex, generating the truncated octahedron as in the well-known sodalite network structure (Figure 3). Carbonate-based networks with the sodalite topology obtained using templating guanidinium cations have been reported.[20] The structural complexity and aesthetics of the present cluster are comparable to those of the nanocapsule of polyoxometalates,[21] the fullerene-like clusters,[4,22] and the Pd_{145} cluster.[23]

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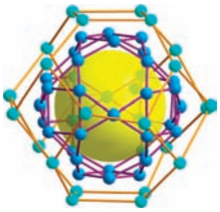

Figure 4. An alternative view of the 60-metal-atom cluster core structure. The metal atoms can be grouped into two distinct polyhedral shells, with an outer, truncated octahedral shell of 24 metal atoms encapsulating an inner, doubly truncated octahedral shell of 36 metal atoms.

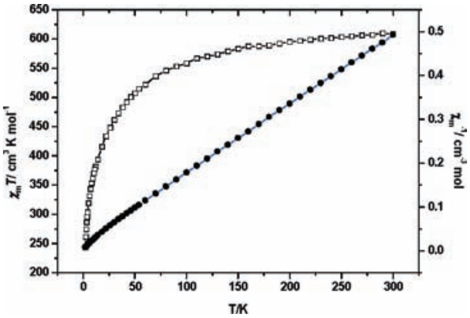

Figure 5. Temperature dependence of $\chi_M T$ (□) and χ_M^{-1} (●) for **1**.

Alternatively, this 60-metal-atom core can be viewed as a fascinating double-shell structure with an outer shell of 24 unshared Er atoms encapsulating an inner shell of 36 metal atoms (Figure 4). This core is encapsulated in a coordination sphere formed by 34 threonine ligands,[24] for which three different coordination modes can be identified (Figure S1 in the SI). Each of the inner-shell Er atoms is octacoordinate, with contributions by six μ_3-OH groups and either two CO_3^{2-} or one CO_3^{2-} and one threonine carboxylate O atom. The coordination geometry can be described as a bicapped trigonal prism. The cage possesses a nanoscopic interior with an $Er_{inner}\cdots Er_{inner}$ separation of 1.2 nm, which is large enough to accommodate six Br^- ions. The 24 outer-shell Er atoms form a cage with an $Er_{outer}\cdots Er_{outer}$ separation of 1.8 nm. These metal atoms are bridged by the threonine carboxylate and amine groups, and their coordination spheres are completed by terminal aqua ligands. A more detailed description of the crystal structure can be found in the SI.

The temperature dependence of the magnetic susceptibility of **1** was measured from 2 to 300 K in an applied magnetic field of 1000 Oe; the data are shown in Figure 5 as plots of $\chi_M T$ and χ_M^{-1} versus T. The $\chi_M T$ value is 608.87 cm^3 K mol^{-1} at 300 K, which is smaller than the value of 688.80 cm^3 K mol^{-1} calculated for 60 noninteracting Er(III) ions ($^4I_{15/2}$, $g = 6/5$). This discrepancy is similar to that reported for $Er_2O_2CO_3$,[25] the closest species in terms of the molecular composition of the cluster core. The $\chi_M T$ value decreases gradually upon cooling, and a value of 243.70 cm^3 K mol^{-1} is reached at 2 K. The data in the 20−300 K range can be fitted nicely to the Curie−Weiss law, yielding $C = 632.9$ cm^3 K mol^{-1} and $\Theta = -11.91$ K.

In summary, a chiral, cagelike, high-nuclearity lanthanide hydroxide cluster containing 60 Er(III) ions has been obtained from the hydrolysis of Er(III) ions controlled by threonine. The cluster core possesses a fascinating sodalite-like structure with 24 vertex-sharing cubane-like $[Er_4(\mu_3\text{-}OH)_4]^{8+}$ units. The hexagonal face of the sodalite cage features a templating μ_6-CO_3^{2-} ion. Magnetic studies revealed that the cluster is magnetically isolated, and the decrease in $\chi_M T$ with decreasing temperature is probably due to thermal depopulation of the Stark components derived from the splitting of the free Er(III) ground state by the crystal field, as the ligand-mediated antiferromagnetic couplings between Er(III) ions are expected to be weak.[26]

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Supporting Information Available: Synthesis and characterization details and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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