Coordination Chemistry of Lanthanides at "High" pH: Synthesis and Structure of the Pentadecanuclear Complex of Europium(III) with Tyrosine**

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Dedicated to Professor M. Frederick Hawthorne

The design and synthesis of high-nuclearity metal complexes is arguably one of the most stimulating research frontiers in contemporary chemistry.[1] The preparation of such complexes enables their nanoscopic dimensions to be combined with the rich redox and magnetic properties of the constituent metals, and leads to novel materials with promising electronic, magnetic, optical, and catalytic properties. A commonly employed strategy for the synthesis of polynuclear metal complexes is to utilize appropriate chelating ligands to control the hydrolysis of metal ions;[2] the auxiliary ligands prevent extensive hydrolysis from occurring—a process that would otherwise lead to the formation of intractable metal hydroxides and/or oxides—and as a result, finite-sized polymetal complexes can be crystallized and structurally characterized. Several classes of ligands have been utilized in this capacity, among which carboxylates,[3] polyketonates,[4] and alkoxides[5] are prominent. Spectacular clusters such as polyoxovanadates,[6] ferric weels,[3b] and manganese clusters[7] have been reported and proven to exhibit rather interesting magnetic properties.[5, 7, 8]

Despite all the progress that has been made in controlling excessive hydrolysis during the formation of metal clusters, a suitable and general class of supporting ligands is yet to be identified for the preparation of lanthanide-based clusters.[5] Lanthanide clusters are expected to exhibit more promising magnetic properties as a consequence of the unique spectroscopic and electronic properties mainly associated with their $4f^n$ electronic configurations.[9] With the intent of assembling novel lanthanide clusters and ultimately fabricating promising lanthanide-based magnetic materials,[9] we have recently initiated a program to study the coordination chemistry of lanthanides with amino acids, with the hope that amino acids may serve as a novel class of supporting ligands. Although the coordination chemistry of lanthanides with amino acids has been investigated to some extent,[10] these studies have been exclusively carried out at low pH values, typically under pH 4. This is understandable because lanthanide ions are so prone to hydrolysis that hydroxides and/or oxides would be the final products at higher pH values. In all the reported structures of such complexes, the ligands, not surprisingly, coordinate to the metal centers through only the oxygen atom(s) of the carboxylate moiety. The amino group remains protonated and serves merely as a "spectator" fragment, which affects the structure of the complex only by imposing electrostatic and/or steric effects.[10] At "high" pH values, however, multiple binding of a lanthanide ion by an amino acid (α-amino carboxylate, to be more exact) may be achieved with both the amino and the carboxylate groups participating in simultaneous coordination. We envision that such chelating effects may stabilize the metal complex by counteracting the undesirable hydrolysis and consequently, high-nuclearity lanthanide clusters would form.

To test the validity of this approach we have synthesized a series of lanthanide(III)–tyrosine complexes by mixing $Ln(ClO_4)_3$ ($Ln = La$, Pr, Nd, Sm, Eu, Gd, Dy) and tyrosine in an aqueous solution and subsequently adjusting its pH value to about 6. Single crystal X-ray analysis[11] establishes an appealing pentadecanuclear structure for all these complexes and to the best of our knowledge, they are the largest members of a fascinating family of homonuclear lanthanide clusters that have hitherto been reported.[12] Since these molecules are similar in composition, except for the different constituent lanthanide ions, and are isostructural in the solid state, we shall use the europium(III)–tyrosine complex **1** to discuss the novel features and significance of this research.

$$[Eu_{15}(Cl)(\mu_3\text{-Tyr})_{10}(\mu_3\text{-OH})_{20}(\mu_2\text{-}H_2O)_5(OH)_{12}(H_2O)_8][ClO_4]_2 \cdot 56\,H_2O \quad \mathbf{1}$$

As shown in Figure 1, the complex contains 15 Eu^{III} ions and 10 tyrosine ligands in addition to the hydroxo and aquo ligands associated with hydrolysis. The metal ions are assembled into a layered structure, and each of the three parallel layers contains five Eu^{III} ions, which occupy the vertices of a nearly perfect pentagon. The two outer layers are crystallographically equivalent with an average Eu–Eu distance of 6.331 Å, while the middle layer, with an average

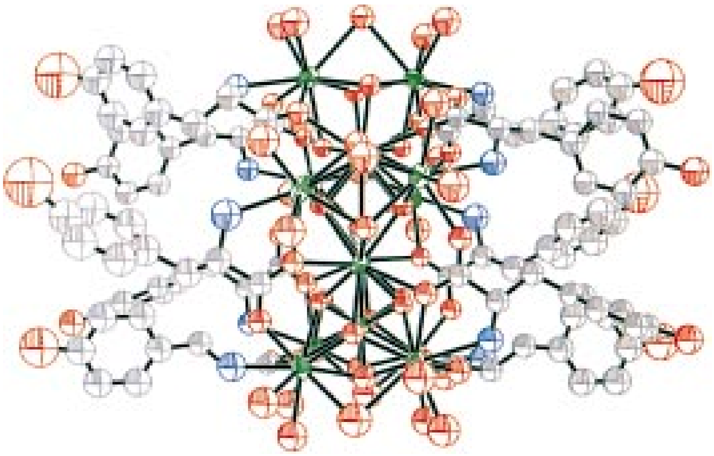

Figure 1. A perspective view of **1**: carbon: gray, chlorine: black, europium: green, nitrogen: cyan, oxygen: red. Lattice water molecules and perchlorate ions are omitted for clarity.

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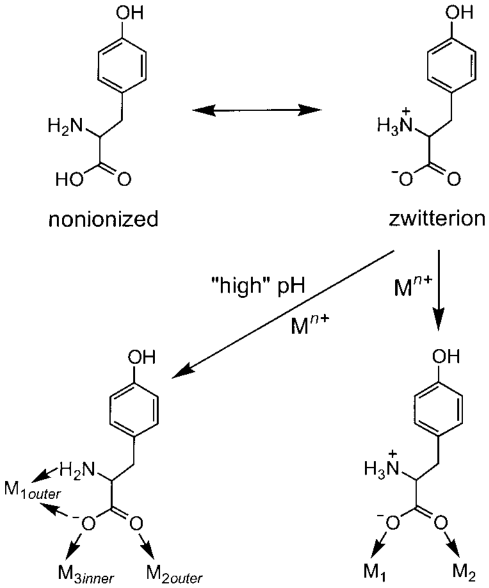
Eu–Eu distance of 3.896 Å, is unique and "tucked in". The ten tyrosinate ligands can be divided into two equivalent groups, each of which extend their 4-hydroxybenzyl side chains in the direction perpendicular to the crystallographically imposed C_2 axis. The side chains do not participate in, nor do they appreciably interfere with, the coordination. The coordination modes of the tyrosinate ligands with Eu^{III} ions in these molecules are significant: Each of the ten tyrosinate groups acts as a tetradentate ligand by utilizing both its amino and carboxylate groups (Scheme 1). The ligand can be described as a μ_3:η^1:η^2:η^1 anion, not only linking two neighboring Eu^{III} centers within the same (outer) layer, but also coordinating to a third Eu^{III} ion in the middle layer through one of the carboxylate oxygen atoms. It is apparent that such layer-crossing chelating interactions are critical to the formation of the cluster structure. In previous studies of the coordination of lanthanide ions with amino acids, the zwitterions bind the lanthanides exclusively through the oxygen atom of the carboxylate group. Such an interaction is included in Scheme 1 for comparison. The coordination sphere of the Eu^{III} centers is completed by hydroxo and aquo ligands (Figure 2). Thus, each of the ten Eu^{III} ions in the outer layers has a coordination number (CN) of 9, and the structure can be best described as monocapped square antiprismatic, while the inner-layer Eu^{III} centers too have a CN of 9, and form irregular square antiprisms monocapped by the central chloride ion (see below). From a different perspective, the core component of the cluster may be viewed as a "wheel" of five corner-sharing cubanes, each of which consists of four Eu^{III} ions and four μ_3-OH ligands (Figure 3).



Scheme 1. Two different coordination modes of a tyrosine ligand with lanthanide ions.

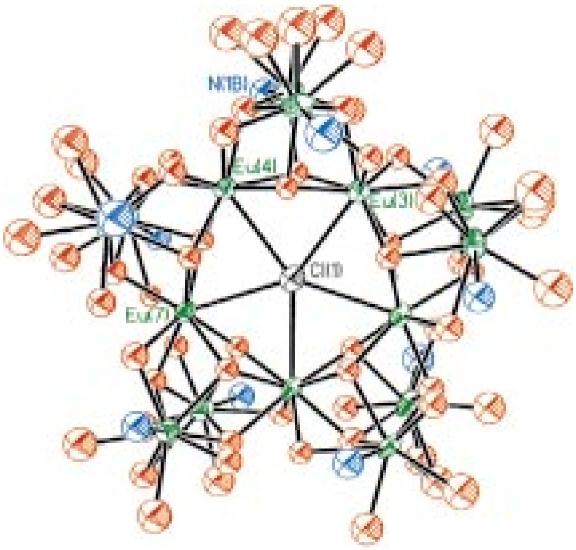


Figure 2. A perspective view of **1** showing only the Eu^{III}-coordination sphere.

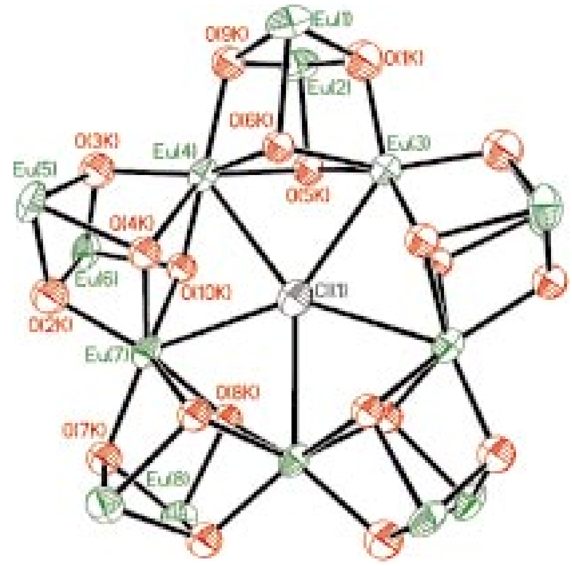


Figure 3. The "cubane-wheel" structure of **1**.

A particularly salient feature of the structure is a chloride ion being trapped within the "belly" of the barrel-shaped molecule, and serves as the bolt of the cubane wheel. The chloride ion simultaneously coordinates the five inner-layer Eu^{III} ions in a perfectly planar fashion with an average Eu–Cl distance of 3.314 Å. It is unlikely that an empty "barrel" is preformed for the encapsulation of the chloride ion, instead, the formation of the pentadecanuclear complex can be best described as a chloride-induced self-assembly of the lanthanide ions with the help of the tyrosine ligands. In other words, the chloride ion serves as a template in the formation of this novel cluster, and hence furnishes an exciting addition to the rare examples of anion-templated synthesis.[13]

In summary, we have demonstrated that amino acids are an effective class of ancillary ligands in the synthesis of lanthanide clusters. The reaction described herein stands in stark contrast to previous coordination chemistry of lanthanide ions with amino acids, wherein a low pH value is, at least is commonly perceived so, mandatory in order to avoid the formation of insoluble hydrolysis by-products. It is, however, the unconventionally "high" pH condition that promotes the formation of the large molecular clusters reported here, and hence a new paradigm in lanthanide coordination chemistry. The proof-of-concept demonstrations reported herein suggest that this synthesis concept is potentially expandable toward other metal systems. Mixed-metal clusters containing both lanthanides and d block transition elements such as copper, iron, and manganese, for example, may be prepared.[14] The synthetic opportunities abound when the rich varieties of amino acids and transition metals including lanthanide elements are considered. Furthermore, these pentadecanuclear clusters possess unprecedented layered structures that are complex yet architecturally pleasing. The highly ordered arrangement of the metal centers in these nano-sized clusters is expected to yield useful magnetic properties.[5, 7, 8] We believe that the novel structural patterns (and any accompanying physical/chemical properties), coupled with the ability to construct a huge variety of lanthanide clusters will undoubtedly enhance our understanding of lanthanide-based molecular magnetic materials.

Experimental Section

Tyrosine (0.181 g, 1.0 mmol) was added as a solid to an aqueous solution of $Eu(ClO_4)_3$ prepared by dissolution of Eu_2O_3 (1.408 g, 4.0 mmol) in 70% perchloric acid. To this clear solution was added one drop of 1.0 M aqueous HCl and the mixture was stirred at 80 °C for 5 min. The pH value of the above solution was then carefully adjusted by slow addition of 0.5 M aqueous NaOH until the precipitate thus formed remained. The mixture was then filtered and the filtrate was allowed to stand at room temperature. Parallelepipeds of the lanthanide complexes appeared in about one week. The complex was synthesized in a typical yield of 60% (based on tyrosine). Elemental analysis calcd: Eu 37.41; found: 37.36; ESI-MS: *m*/*z* (%): 1936.1 (30) $[(M^{+}{+}H) - 5H_2O - 2ClO_4^{-}]^{3+}$, 1474.7 (100) $[(M^{+}{+}2H) - 2ClO_4^{-}]^{4+}$, 1150.9 (40) $[(M^{+}{+}3H) - 8H_2O - 2ClO_4^{-}]^{5+}$.

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[11] Crystal structure determination of **1**: A colorless crystal (ca. 0.15 × 0.15 × 0.10 mm) was analyzed with a Bruker SMART CCD-based diffractometer at 213 K with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Monoclinic, space group C_2, $a = 32.259(3)$, $b = 20.926(2)$, $c = 22.037(2)$ Å, $\beta = 130.956(4)^{\circ}$, $V = 11234(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.801$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 4.254$ mm^{-1}, $F(000) = 5956$. ω–2θ scans, 29805 reflections measured ($2\theta_{max} = 50^{\circ}$), of which 13780 were independent and all are observed $[I = 2\sigma(I)]$, 528 refined parameters, $R = 0.0812$, $wR_2 = 0.2096$, residual electron density max./min. 2.229/ – 1.294 e Å^{-3}, max./min. transmission 0.9583/0.7456. Data reduction was performed with the SAINT software, which corrects for Lorentz and polarization factors as well as decay. Absorption corrections were applied with SADABS supplied by G. Sheldrick. The structure was solved by the direct method with the SHELXS-97 program and refined by least squares method on F^2, SHELXL-97, incorporated in SHELXTL-PC version 5.10. Only the metal atoms were refined anisotropically. Hydrogens were calculated by geometrical methods for the ligand and refined as a riding model. The solvated water molecules were found by using the program XWAT, supplied within SHELXTL. No hydrogen atoms were modeled for the hydroxides or water molecules in the cluster or solvated. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-410601.

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A Versatile Route to Porous Solids: Organic – Inorganic Hybrid Materials Assembled through Hydrogen Bonds**

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One of the many promising applications of supramolecular chemistry is in the design of crystalline host – guest materials, which have been pursued through two principal routes. First, coordination polymers[1] have been shown to form porous materials whose host frameworks can withstand the removal/addition of guest molecules[2] or exhibit high shape specificity in clathration.[3] Second, organic networks have been assembled through directional intermolecular forces[4] to form porous frameworks, which can be applied to homogeneous and heterogeneous[5, 6] separations. Remarkably, some three-dimensional (3D) organic frameworks assembled through hydrogen bonds are rugged enough for reversible guest

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