

Ligand-controlled self-assembly of polynuclear lanthanide–oxo/hydroxo complexes: from synthetic serendipity to rational supramolecular design

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Lanthanide ions and complexes occupy a special position in developing synthetic nucleases capable of catalyzing the hydrolytic cleavage of RNA or DNA. Stimulated by a number of serendipitous lanthanide complexes that feature the common active-site structure of dinuclear metallo-phosphodiesterases, rational design and synthesis of polynuclear lanthanide–hydroxo species *via* ligand-controlled hydrolysis of the lanthanide ions were attempted. The efforts yielded a series of highly sophisticated yet structurally well-defined lanthanide–hydroxo complexes. These materials are potentially applicable to the study of biomimetic catalysis of phosphate diester cleavage. Research highlights are described in this Feature Article.

Introduction

Polynuclear metal complexes exhibit a fascinating variety of unusual symmetries and structural patterns.¹ The biological relevance of some of these compounds and their potentially important applications as advanced materials add to their interest and significance.^{2,3} Ligand-controlled hydrolysis is a time-honored approach to these unique chemical entities.⁴ In this method, auxiliary ligands occupy part of the metal coordination sphere, thereby reducing the number of sites available for water coordination and preventing extensive hydrolysis from occurring. As a result, finite-size polynuclear complexes rather than intractable metal hydroxides and/or oxides can be crystallized and structurally characterized. Several classes of ligands have been utilized in this capacity, among which carboxylates, polyketonates, polyamines, polyols, pyridonate and alkoxides are prominent.^{5–10} Spectacular examples in transition metal chemistry, such as molecular cages and wheels, have been reported.^{11,12} These novel complexes exhibit rather interesting magnetic properties owing to the presence of a large number of unpaired electrons.^{3–12}

Despite the impressive progress in the preparation of polynuclear complexes of the d-block elements, the number of large, polynuclear lanthanide complexes is still rather limited.^{13,14} Lanthanide elements, bearing special electronic and

spectroscopic properties mainly associated with their 4f electronic configurations, represent a unique series of metals in the Periodic Table. The position of mononuclear lanthanide complexes in a number of important areas has been firmly established,¹⁵ but polynuclear lanthanide complexes are expected to find such niche applications as precursors in sol–gel technology,¹⁶ new radiographic agents,¹⁷ and metalloenzyme mimics.¹⁸ Great prospects notwithstanding, the high expectations have been compromised by our current limited synthetic ability; the formation of polynuclear lanthanide complexes cannot yet be controlled and is frequently characterized by random self-organization.^{13,14,19}

The story begins

Our efforts to create structurally well-defined polynuclear lanthanide complexes were stimulated by the potential to develop synthetic nucleases that are capable of hydrolyzing RNA or DNA through the cleavage of the phosphate diester bonds.²⁰ X-Ray analysis of many phosphodiesterases indicates that these important metalloenzymes possess two or three divalent metal ions, such as Zn^{II}, in the active site.²⁰ It is generally agreed that the catalysis occurs *via* substrate activation by the electropositive metal ions, followed by nucleophilic attack by the activated hydroxo ligands (Fig. 1). Numerous

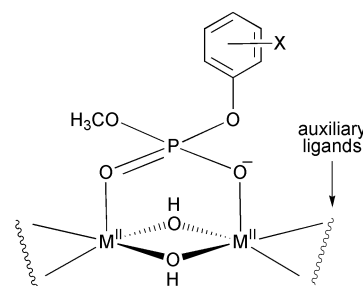


Fig. 1 A possible activation mechanism of a phosphate diester substrate by the dinuclear active site of a metallo-phosphodiesterase.

synthetic models have appeared in the literature in mimicking the dinuclear structural motif, most of which utilize transition metal ions, most notably Zn^{II}, Cu^{II} and Co^{III}, to activate the substrate.²¹ Trivalent lanthanide ions (Ln^{III}) are expected to be more effective in this capacity due to their strong Lewis acidity and the kinetic lability of their complexes. Elegant studies in this vein have been carried out by Chin, Schneider, Martell and others.¹⁸ However, the ease of lanthanide ion hydrolysis and the propensity for lanthanide–hydroxo species to form polynuclear aggregates in solution render unambiguous identification of the catalytically active species extremely difficult, if at all possible. There exist, nevertheless, a number of structurally characterized dinuclear²² and tetranuclear²³ lanthanide–hydroxo complexes

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whose core components (Fig. 2) feature the desired diamond-shaped dinuclear lanthanide–hydroxo motif. However, these species were either synthetic serendipity or accidents, and general synthetic guidelines are lacking, and not surprisingly, there were no studies of their catalytic potentials.

Toward the ultimate goal of achieving non-enzymatic hydrolysis of phosphate diesters using *structurally well-defined* lanthanide catalysts, we have recently embarked on a design and synthesis tour of lanthanide–hydroxo complexes whose core structure resembles that of the active site of phosphodiesterases. We were particularly interested in the tetranuclear species whose constituent lanthanide ions and triply bridging hydroxo groups occupy the alternate vertices of a distorted cube. Structurally, it may be viewed as the dimeric form of the dinuclear species. More importantly, a complex featuring this core may be catalytically more potent on per molecule basis due to the extra Lewis acidic metal ions. The three seemingly unrelated literature precedents²³ further stimulated our interest. That distinctly different routes yielded the common structural motif led to our suspicion that the cubane-like core may actually be a standard feature of this type of chemistry, analogous to its extensively studied d-block counterparts.²⁴

The presence of the hydroxo ligands suggests that these tetranuclear clusters may be synthesized *via* hydrolytic reactions of the lanthanide ions. However, hydrolysis of the lanthanide ions is commonly perceived as rather limited and unpredictable with intractable precipitates of lanthanide hydroxides and/or oxohydroxides as the end products.²⁵ Probably due to this very concern of extensive and uncontrollable hydrolysis, aqueous lanthanide coordination with organic ligands have been carried out almost exclusively under acidic conditions, typically below pH 5.²⁶ However, in light of the increasing number of unexpected and structurally characterized polynuclear lanthanide–oxo/hydroxo species,^{13,14a,19,22,23} we deemed a systematic investigation of the hydrolytic reactions of these unique metal ions to be not only worthwhile, but also important.

Providing further inspiration for this endeavor is the great success of creating polynuclear transition metal complexes using the hydrolytic approach.⁴ In such an approach, certain types of supporting ligands are necessary to control the hydrolysis in order to avoid the possible formation of intractable products. It is the subtle balance between the hydrolysis of a transition metal ion and its coordination with a chelating ligand that affords the novel high-nuclearity complexes. *We submit that an analogous ligand-controlled hydrolytic approach should be applicable to the lanthanide ions, provided that suitable supporting ligands are identified.* Our efforts have been concentrated on utilizing α -amino acids as auxiliary ligands to control the hydrolysis.²⁷ This exploratory synthesis has produced a number of spectacular and unprecedented polynuclear lanthanide–hydroxo complexes which may find important applications in biotechnology and chemotherapy. Research highlights are summarized in this Feature Article.

The story of α -amino acids – self-assembly of complexes featuring the $[Ln_4(\mu_3-OH)_4]$ core

The specific choice of α -amino acids as hydrolysis-limiting auxiliary ligands is mainly based on their biological relevance. It is reasonable to hypothesize that the metal coordination environment of the native enzyme can be better modeled by using such biological building blocks. In addition, lanthanide coordination with α -amino acids has been extensively investigated.²⁸ These studies have been conducted almost exclusively under low-pH (below 5) conditions. Typically, only the carboxylate group coordinates the lanthanide ion, as shown by more than 50 crystal structures of such complexes.^{28a} The great variety of α -amino acids due to the presence of different side-group(s), some of which being potentially lanthanide-coordinat-

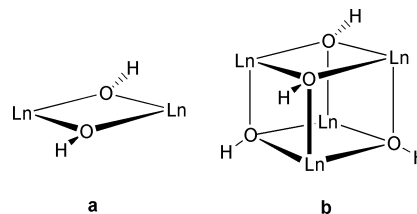


Fig. 2 Core components of crystallographically characterized dinuclear (a) and tetranuclear (b) lanthanide–hydroxo species.

ing, is especially beneficial for systematic studies of lanthanide complexation with this unique class of ligands.

The validity of this ligand-controlled hydrolytic approach was tested in a series of proof-of-concept syntheses, using a variety of α -amino acids, including glycine, alanine, valine, phenylalanine, tyrosine, proline, glutamic acid and aspartic acid as the supporting ligands.^{29–34} The zwitterionic structures of these amino acids are shown in Fig. 3.

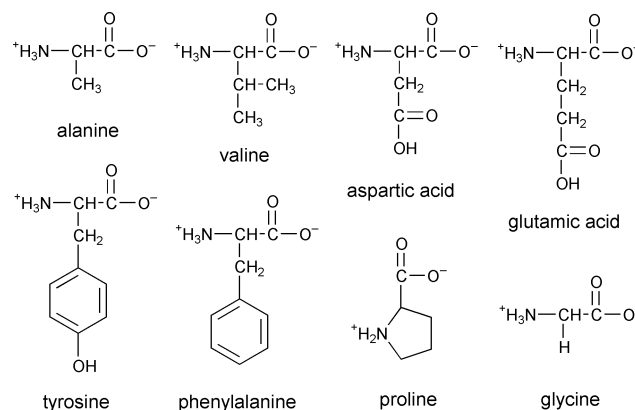


Fig. 3 Zwitterionic structures of the α -amino acids discussed in this article.

In a representative synthesis, a lanthanide chloride or perchlorate is mixed with an α -amino acid in aqueous solution. The mixture is subjected to hydrolysis with dilute NaOH. The end point of the reaction is indicated by the formation of an incipient but permanent precipitate, presumably of lanthanide hydroxide and/or oxohydroxide. Although the addition of base is seemingly arbitrary, lanthanide–amino acid (other than tyrosine) complexes composed of a cubane-like $[Ln_4(\mu_3-OH)_4]^{8+}$ core have invariably been obtained as crystalline solids upon slow concentration of the supernatant at room temperature. The ORTEP drawing of the cationic complex³⁵ formed by $Yb(ClO_4)_3$ and phenylalanine (Phe), representative of all the single-cubane complexes, is depicted in Fig. 4.†

The cluster core is ‘camouflaged’ by six phenylalanine ligands through bridging carboxylate groups, and the metal coordination sphere is completed by aqua ligands. The amino groups remain protonated, presumably affecting lanthanide complexation *via* electrostatic and steric effects. Because the amino groups do not participate in direct coordination with the lanthanide ion, the interaction of an α -amino acid with a lanthanide ion is structurally reminiscent of that of a carboxylic acid.³⁶ However, with carboxylic acids as supporting ligands, lanthanide acetates are typically obtained. These well-studied lanthanide materials exist in polymeric forms in the solid state, often featuring carboxylate-bridged dinuclear lanthanide units as the fundamental building blocks.³⁶ It is thus of interest to note that finite-size cluster-type polynuclear lanthanide–hydroxo complexes are generally isolated with the use of N-containing supporting ligands,³⁷ including α -amino acids. It is reasonable to assume that the higher water-solubility of lanthanide complexes with such ligands is due to possible hydrogen bonding interactions involving the N atom(s). In the case of α -amino acids, the zwitterionic character of these unique ligands

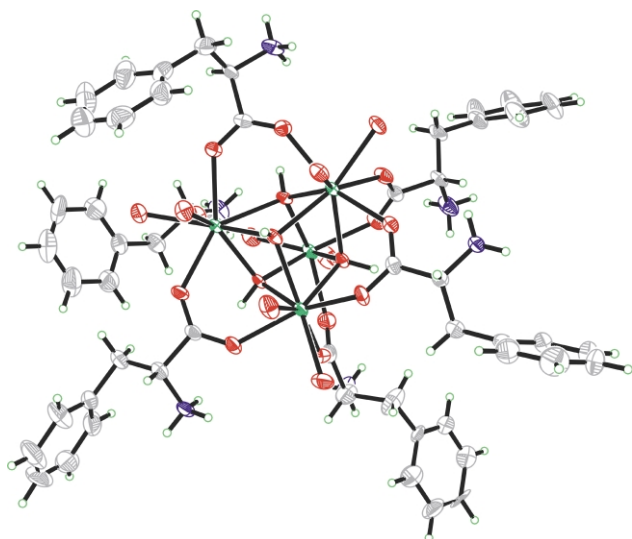


Fig. 4 An ORTEP representation of the cationic complex $[\text{Yb}_4(\mu_3\text{-OH})_4(\text{Phe})_6(\text{H}_2\text{O})_7]^{8+}$. The cubane-like tetranuclear Yb^{III} -hydroxo core is apparent.†

is expected to further contribute to the better water solubility of their complexes. As a result, a lanthanide complex with such ligands remains soluble in solution instead of precipitating out as less soluble coordination polymers. Addition of base to such a solution is expected to deprotonate the aqua ligands. Condensation of the lanthanide-hydroxo species thus generated eventually leads to the formation of the cluster-type lanthanide-hydroxo complexes.

The story of the networking glutamic acid

Having established that the cuboid $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ cluster is a common structural motif in lanthanide complexes, we entertained the idea of using this motif as a secondary building unit³⁸ for the creation of supramolecular assemblies with porosity. The practice of constructing such open framework structures is stimulated by the hope that these porous materials will display a range of molecular sieve, ion exchange and catalytic properties that are comparable to (or perhaps more extensive than) those observed in zeolites. As compared with the large amount of work concerning the construction of coordination networks of d-block metal ions with polydentate ligands, crystal engineering involving lanthanide ions remains relatively unexplored at the present time,³⁹ and the use of lanthanide clusters as building blocks is unknown. Nevertheless, by employing appropriate supporting ligands, it may be possible to assemble the $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ cluster units into zeolite-like polymeric forms, whereby the high coordination requirement and Lewis acidity of the lanthanide ions may be of important use for both laboratory research and industrial processes.

In this effort, an α -amino acid with more than one carboxylate group is necessary in order to support the hydrolytic formation of the $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ cluster and to bridge individual cluster units. A three-dimensional (3-D) network may be anticipated from such extended interactions between the carboxylate ligands and the lanthanide-hydroxo cluster core. As expected, by treating a mixture of $\text{Er}(\text{ClO}_4)_3$ and *L*-glutamic acid with aqueous NaOH to the point of incipient precipitation, a 3-D porous network comprised of discrete $[\text{Er}_4(\mu_3\text{-OH})_4]^{8+}$ units and cluster-linking glutamate ligands, $[\text{Er}_4(\mu_3\text{-OH})_4(\text{Glu})_3(\text{H}_2\text{O})_8][\text{ClO}_4]_5$ ($\text{Glu} = \text{glutamate}$), was obtained.³⁰ The structure of the complex was determined by single-crystal X-ray diffraction, and the elementary constituent of the open framework is depicted in Fig. 5. The cubane-like $[\text{Er}_4(\mu_3\text{-OH})_4]^{8+}$ building block is apparent, resembling its previously reported analogues. The six carboxylate groups ligating a particular cube are of two different types, one being α and the other (of the side

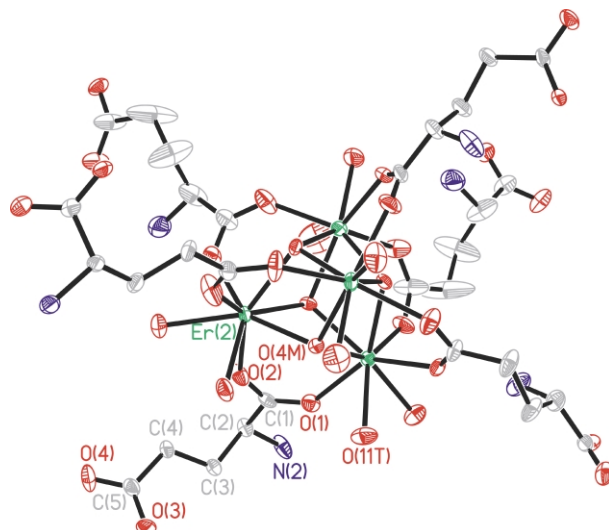


Fig. 5 An ORTEP drawing of the elementary building unit of $[\text{Er}_4(\mu_3\text{-OH})_4(\text{Glu})_3(\text{H}_2\text{O})_8]^{5+}$. Three symmetry-related glutamic acid "arms" are included to complete the coordination of the cuboid $[\text{Er}_4(\mu_3\text{-OH})_4]^{8+}$ core.

chain) being γ to the amino moiety; each glutamate ligand contributes one carboxylate group for the coordination of one $[\text{Er}_4(\mu_3\text{-OH})_4]^{8+}$ cluster while using the remaining one to coordinate an adjacent lanthanide cluster cube. The 3-D open framework exhibits nearly parallelogram-shaped pore apertures with approximate dimensions of $4.4 \times 9.1 \text{ \AA}$ for channels in the *c* direction (Fig. 6). Although the network structure is the result

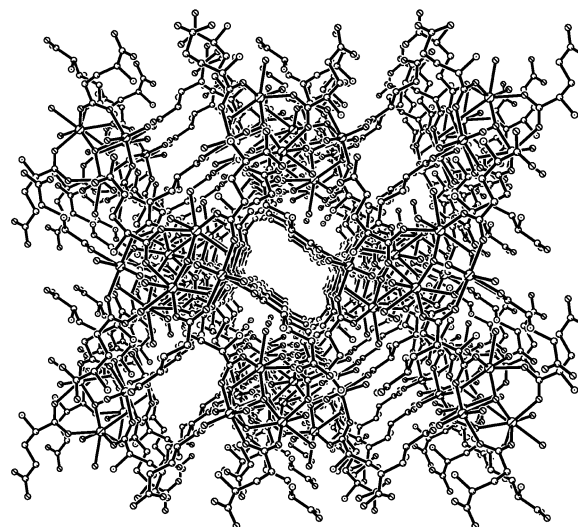


Fig. 6 3-D porous framework structure of $[\text{Er}_4(\mu_3\text{-OH})_4(\text{Glu})_3(\text{H}_2\text{O})_8]^{5+}$, shown along the *c* axis. The channel dimensions are approximately $4.4 \times 9.1 \text{ \AA}$.

of self-assembly, the $[\text{Er}_4(\mu_3\text{-OH})_4]^{8+}$ core may be *formally* considered as a *prefabricated* and *transferable* building block for the assembly of the extended structure. An analogous extended channel structure has also been obtained by the hydrolytic reaction of $\text{Dy}(\text{ClO}_4)_3$ using *L*-aspartic acid as supporting ligand,³⁴ which further supports our synthetic design in using the cubane-like units as building blocks for the extended solid state materials.

The unique story of tyrosine – anion-templated self-assembly of multi-cubane complexes

Using lanthanide perchlorates, analogous hydrolytic reactions with tyrosine as the supporting ligand were carried out in an effort to evaluate the possible effect(s) of the side-group of an α -amino acid has on the metal coordination.^{29,32} To our great surprise, complexes featuring a single lanthanide-hydroxo

cluster core were not obtained. Instead, the reactions produced a series of pentadecanuclear lanthanide–hydroxo complexes.

As a representative of these pentadecanuclear complexes, the sophisticated structure of an Eu^{III} complex is described in detail below. As shown in Fig. 7, the complex, containing 15 Eu^{III} ions

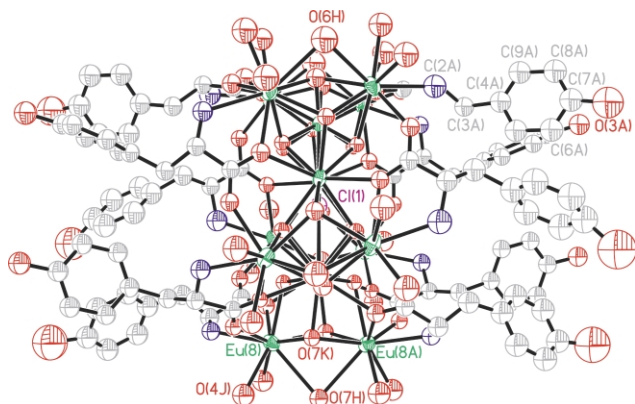


Fig. 7 A perspective view of the pentadecanuclear Eu^{III} -hydroxo complex with tyrosinato ligands. The cationic complex is formulated as $[\text{Eu}_{15}(\mu_3\text{-OH})_{20}(\mu_5\text{-Cl})(\mu_3\text{-Tyr})_{10}(\text{OH})_2(\mu\text{-H}_2\text{O})_5(\text{H}_2\text{O})_{18}]^{12+}$ (Tyr = tyrosinato ligand). Color legend: chlorine (purple).

and 10 tyrosinato ligands in addition to the hydroxo and aqua ligands associated with the hydrolysis, crystallizes as discrete barrel-shaped molecular units with space between these barrels filled with solvent water. The core component of the complex, formulated as $[\text{Eu}_{15}(\mu_3\text{-OH})_{20}(\mu_5\text{-Cl})]^{24+}$, consists of five vertex-sharing $[\text{Eu}_4(\mu_3\text{-OH})_4]^{8+}$ cubane units centered on a $\mu_5\text{-Cl}^-$ 'axle' (Fig. 8). The metal ions are assembled into a layered

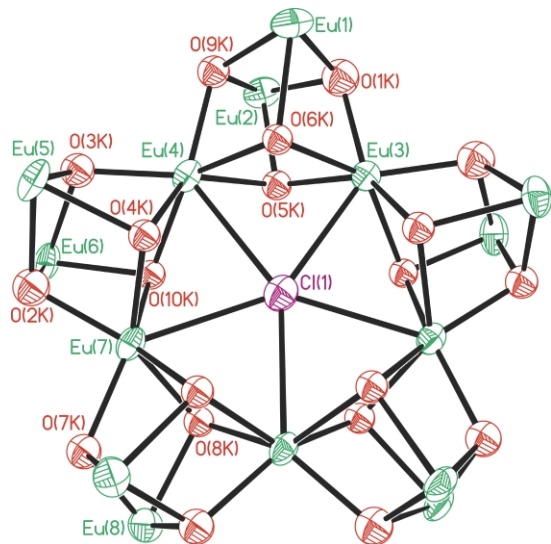


Fig. 8 An ORTEP drawing of the wheel-like core structure showing five vertex-sharing cuboid $[\text{Eu}_4(\mu_3\text{-OH})_4]^{8+}$ units centered on a $\mu_5\text{-Cl}^-$ ion.

arrangement; each of the three parallel layers contains five Eu^{III} ions that occupy the vertices of a nearly perfect pentagon. The average $\text{Eu}\text{-Eu}$ separation within the two outer layers is 6.331 Å, while that in the middle layer is 3.896 Å. The average $\text{Eu}\text{-Cl}$ distance of 3.314 Å is significantly longer than the sum of the van der Waals radii of Cl^- (1.81 Å)⁴⁰ and Eu^{III} (0.95 Å),^{40b} reflecting the primarily ionic interactions between the halide and the lanthanide ions. The coordination sphere of the Eu^{III} ion is completed by hydroxo and aqua ligands. Thus, each of the 10 Eu^{III} ions in the outer layers has a coordination number (CN) of nine, and the coordination polyhedra can be best described as monocapped square antiprismatic, while the inner-layer Eu^{III} centers also have a CN of nine, forming irregular square antiprisms monocapped by the central chloride ion.

The tyrosinato ligands can be divided into two equivalent groups, each of which extends their 4-hydroxybenzyl side-

chains in the direction perpendicular to the crystallographically imposed C_2 axis. The side-chains do not participate in the coordination. The coordination mode of the tyrosinato ligand with Eu^{III} is significant: each acts as a tridentate ligand by utilizing both its amino and carboxylate groups. The ligand can be described as a $\mu_3:\eta^1:\eta^2:\eta^1$ anion (Fig. 9), not only linking

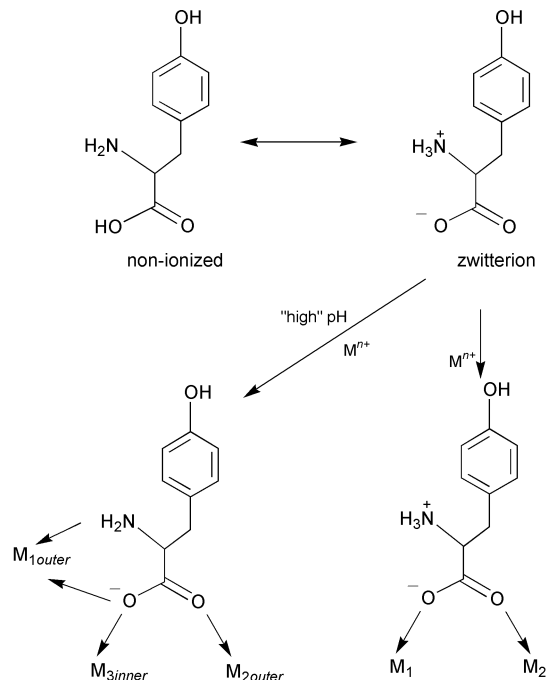


Fig. 9 Comparison of the lanthanide-coordination modes of tyrosine-based ligands under different pH conditions.

two neighboring Eu^{III} within the same (outer) layer, but also coordinating a third Eu^{III} ion in the middle layer through one of the carboxylate oxygen atoms. Such a mode has not been observed prior to our work.

The formation of the pentadecanuclear complex was unexpected, as only complexes containing discrete cubane unit(s) were obtained with other supporting α -amino acids,^{30,33–35} including the closely related phenylalanine.³⁵ It is not yet understood why tyrosine is so unique in this capacity, but work is in progress to elucidate the possible causes. The incorporation of a $\mu_5\text{-Cl}^-$ ion was even more surprising because no Cl^- was utilized in the original synthesis which involved only $\text{Ln}(\text{ClO}_4)_3$, tyrosine and NaOH . A possible source of the mystifying Cl^- was an impurity present in the perchloric acid used for the digestion of lanthanide oxides. Template effects exerted by Cl^- , presumably in minute amount in the original synthesis, were thus suspected, and subsequently corroborated by the improved synthesis, in both product yield and purity, with the presence of added Cl^- . Thus, *the formation of the pentadecanuclear complex may be best understood as chloride-templated self-assembly of the lanthanide ions with the assistance of tyrosinato ligands.*

Stimulated by these findings, the potential roles of other anionic species in promoting the assembly of similar or distinct complexes were explored.³² It has since been found that the composition of the resulting complex is profoundly affected by the anionic species present in the reaction mixture, but is independent of the lanthanide ions. For example, analogous pentadecanuclear complexes featuring a $\mu_5\text{-Br}^-$ were obtained when Br^- was involved. Except for the substitution of Br^- (van der Waals radius, 1.96 Å)⁴⁰ for Cl^- , the cationic complexes are isostructural to their Cl^- -containing cognates. The Br^- simultaneously coordinates the five inner-layer Ln^{III} ions in a perfectly planar and previously unknown fashion (Fig. 10). The $\text{Ln}\text{-Br}$ distances are also significantly longer than the corresponding sum of the van der Waals radii.

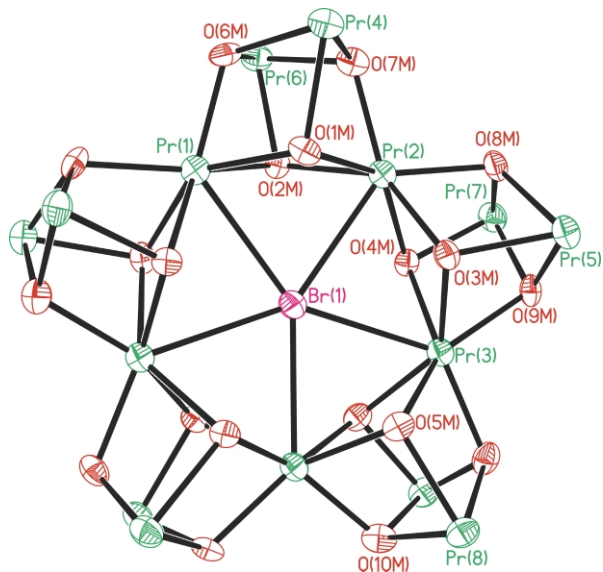


Fig. 10 An ORTEP drawing of the wheel-like core structure of the pentadecanuclear Pr^{III}-hydroxo complex showing five vertex-sharing [Pr₄(μ₃-OH)₄]⁸⁺ units centered on a μ₅-Br⁻ ion. Color legend: bromine (purple).

When I⁻ was employed, however, dodecanuclear complexes were isolated; the surprising product featured a cyclic core composed of four vertex-sharing [Ln₄(μ₃-OH)₄]⁸⁺ cubanes and two I⁻ guests (Fig. 11). In contrast to the single Cl⁻ or Br⁻ that

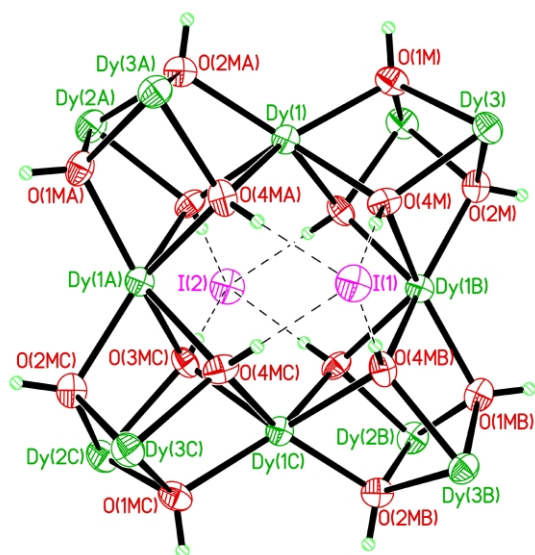


Fig. 11 An ORTEP representation of the core component of the dodecanuclear Dy^{III}-hydroxo complex showing four vertex-sharing [Dy₄(μ₃-OH)₄]⁸⁺ units in a square-shaped arrangement. Two I⁻ ions are found in the complex, one on each side of the square and interacting with the μ₃-OH groups in a μ₄-I⁻ fashion. Color legend: iodine (purple).

was situated in the center of the five-cubane wheel, the I⁻ ions were located on both sides of wheel plane formed by the lanthanide ions. The distances between the iodide ion and the hydrogen atoms of the μ₃-OH groups are almost the same as the corresponding sum of the van der Waals radii, indicating a very compact core structure and likely a hitherto unknown supramolecular motif. Eight tyrosinato ligands cap the wheel structure, four on each side (Fig. 12). The coordination mode of the tyrosinato ligands is identical to that in the Cl⁻ and Br⁻-containing complexes. Although the formation of a smaller cubane-wheel is counterintuitive, this observation may be understood in terms of the energetically insurmountable constraints between adjacent cubane units if a larger wheel were formed.

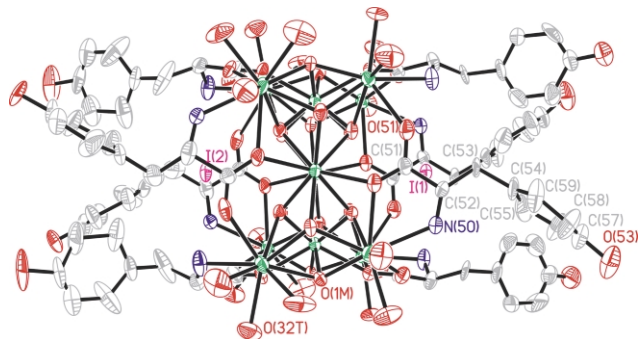


Fig. 12 A perspective view of the cationic dodecanuclear Dy^{III}-hydroxo complex, [Dy₁₂(μ₃-OH)₁₆(I)₂(μ₃-Tyr)₈(H₂O)₂₀]¹⁰⁺.

The identity of the multi-cubane complex is clearly dependent on the nature of the halide ion utilized. However, the templating roles of these spherical anions in establishing the wheel-like complexes remain to be confirmed because the key criterion of a legitimate template is the influence of both of its size and shape on the product distribution.⁴¹ Specifically, can one expect a different product with the presence of a non-spherical anion? Further, what outcome may one anticipate when two different types of anions coexist in the reaction mixture? To answer these questions, a reaction with the trigonal planar NO₃⁻ (1.79 Å),⁴⁰ which is of similar size to Cl⁻, was executed.^{32,42} The analogous hydrolytic reaction using Er(NO₃)₃ and tyrosine produced a known and structurally characterized, tyrosine-free cationic complex [Er₆(μ₆-O)(μ₃-OH)₈(NO₃)₆(H₂O)₁₂]²⁺ (Fig. 13) which was obtained pre-

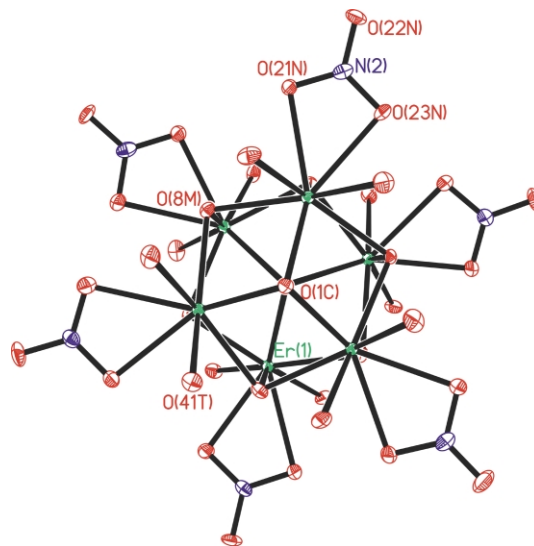


Fig. 13 An ORTEP representation of the cationic complex [Er₆(μ₆-O)(μ₃-OH)₈(NO₃)₆(H₂O)₁₂]²⁺.

viously by the thermal decomposition of hydrated Er(NO₃)₃ followed by hydrolysis of the decomposition products.⁴³ The core component of this compound is a face-capped octahedral [Er₆(μ₆-O)(μ₃-OH)₈]⁸⁺ unit with an interstitial μ₆-oxo group. Its assembly is presumably templated by the μ₆-oxo group whose origin is unclear, but is probably from hydroxide or water. These results clearly indicate the general importance of spherical anionic species in governing the formation of polynuclear lanthanide complexes.^{13,14a}

The most convincing evidence supporting the halide template effects was provided by the tyrosine-limited hydrolytic reaction of Gd(NO₃)₃ in the presence of competitive Cl⁻: Structural determination by X-ray crystallography established that the pentadecanuclear Cl⁻-containing complex was the sole product with non-coordinating NO₃⁻ as counter ions. This finding, coupled with the inability to produce a multi-cubane complex in the absence of a halide ion suggests that the halide ion must be

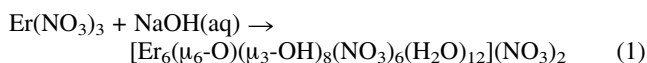
a stabilizing factor along the reaction coordinate to the ‘wheel’-structured complexes, and hence, a kinetic template.⁴¹

It has long been recognized in the chemistry of lanthanide alkoxides that the presence of a ‘central spherical negative charge density’ accounts for the driving force for product formation.¹³ However, the exact roles played by these anionic species have not yet been investigated. We have discovered several lines of evidence that point convergently to the superior ability of halide ions in templating the formation of unprecedented lanthanide–hydroxo complexes. Our work thus provides a stimulating demonstration of the under-appreciated templating roles of anions in self-assembly processes,⁴⁴ and should aid in future work in assembling novel lanthanide complexes by utilizing templating anions of different *size* and *geometry*.

Controlled or not? Direct hydrolysis of lanthanide nitrates and perchlorates

The isolation of polynuclear complexes containing the cubane-like $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ unit firmly establishes the critical importance of the organic ligands in controlling the hydrolysis of the lanthanide ions. However, the isolation of the tyrosine-free complex, $[\text{Er}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{NO}_3)_6(\text{H}_2\text{O})_{12}](\text{NO}_3)_2$, from a hydrolytic reaction involving $\text{Er}(\text{NO}_3)_3$, tyrosine and NaOH was unexpected and intriguing. Admittedly, this and related hexanuclear complexes^{43,45} are structurally drastically different from the cubane-like tetranuclear species. But are tyrosine or any organic ligands really necessary in controlling the hydrolysis of the lanthanide ions? Is the equivalent polyoxometalate chemistry⁴⁶ of the lanthanide ions a reasonable conceptual stretch? If so, how extensive is this chemistry?

The answers to these interesting questions were provided by the isolation of the same hexanuclear complex from the direct hydrolysis of $\text{Er}(\text{NO}_3)_3$ [eqn. (1)]:⁴²



Insolubility of this and analogous nitrate-containing complexes⁴³ in organic solvents and the strong coordination of nitrate ligands to the lanthanide ions preclude the potential use of these clusters in further research. Our efforts have therefore concentrated on the direct hydrolysis of lanthanide perchlorates. 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 ClO_4^- . The latter is essential for the preparation of novel oxo–hydroxo lanthanide precursors for future work.

Indeed, the direct hydrolysis of $\text{Nd}(\text{ClO}_4)_3$ and $\text{Gd}(\text{ClO}_4)_3$ afforded two new molecular oxo–hydroxo clusters.⁴² Shown in Fig. 14 is the structure of the cationic cluster complex obtained from the reaction of $\text{Nd}(\text{ClO}_4)_3$ with aqueous NaOH. Established by X-ray diffraction, the cationic cluster core, formulated as $[\text{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}]^{8+}$, is comprised of an octahedron of Nd^{III} centered on a μ_6 -oxo ligand. Each of the triangular metal faces is capped by a μ_3 -OH ligand. The metal coordination sphere is completed with four aqua ligands. Thus, each Nd^{III} is coordinated to nine oxygen atoms: one interstitial oxo unit, four face-capping hydroxo groups, and four terminal aqua ligands. Overall, the complex is structurally similar to the Lindqvist-type hexametallates of transition elements with the distinction of having eight face-capping hydroxo groups instead of 12 edge-bridging oxo ligands. To the best of our knowledge, this is the first molecular lanthanide cluster with *only co-existing* oxo, hydroxo and aqua ligands. Such hydrous species are the simplest and most fundamental forms of $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$ core-containing clusters and may be useful precursors for various substituted clusters in future work, including the construction of open framework structures using the octahedral clusters as building blocks. In fact, the octahedral core appears to be another common structural motif in lanthanide oxo–

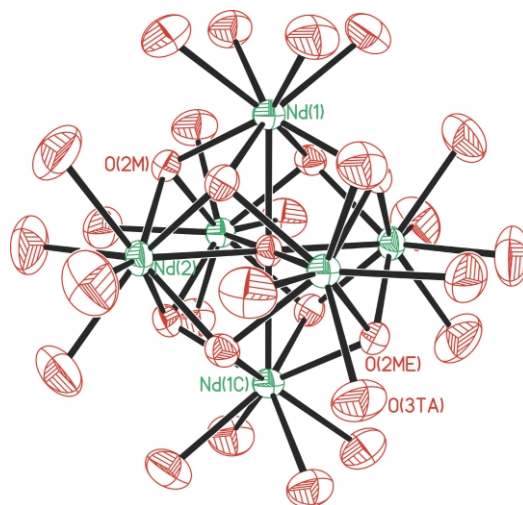


Fig. 14 An ORTEP drawing of $[\text{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}]^{8+}$, a cationic complex featuring a face-capped hexanuclear cluster core and containing only water-based ligands.

hydroxides, as demonstrated by our group⁴² and others.^{43,45} Its presence has also been recognized in a polymeric cyanide-bridged lanthanide–transition metal complex reported by Shore and coworkers.⁴⁷

In stark contrast to the extensive chemistry of the closely related lanthanide oxo–alkoxides,^{16a,48} the closely related chemistry of lanthanide oxo–hydroxides has essentially been unexplored. Thus, our demonstration of the direct hydrolysis of the lanthanide ions leading to hexanuclear lanthanide oxo–hydroxo complexes is significant. 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.

New tricks for an old dog – unusual lanthanide–EDTA coordination under high-pH conditions

Prompted by the close relationship between polyaminopolycarboxylic acids (PAPCs) and α -amino acids, we set out to re-evaluate, under much higher pH conditions however, the classical coordination chemistry of the lanthanide ions with PAPCs. If the solution pH condition can have such significant influence on the outcome of the well-established lanthanide–amino acid coordination chemistry, one should not be surprised if some new but admittedly hard-to-predict results are to be obtained with this venerable class of ligands⁴⁹ under similarly altered pH conditions.⁵⁰ In this section, we illustrate how the otherwise well-established chemistry can be profoundly affected by simply increasing the pH of the reaction mixture.

Our initial foray has been focused on ethylenediamine-*N,N,N',N'*-tetraacetic acid (H_4EDTA), one of the most studied PAPCs. Lanthanide–EDTA complexes, represented by the general chemical formula $\text{M}[\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_m] \cdot n\text{H}_2\text{O}$ (M = an alkali metal ion), have invariably 1 : 1 ($\text{EDTA}:\text{Ln}$) composition.⁵¹ Structural analyses always reveal a hexadentate EDTA ligand with two coordinating nitrogen atoms and four oxygens of the unidentate carboxylate groups (A, Fig. 15). The $\text{O}(\text{aqua})\text{-Ln-O}(\text{aqua})$ bond angles range from 70.0 to 83.3°, which are very close to the corresponding $\text{O}(\mu_3\text{-OH})\text{-Ln-O}(\mu_3\text{-OH})$ angles (ranging from 68.1 to 76.8°) in the $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ unit. An intriguing question then arises: *Can a cubane-like tetranuclear lanthanide–hydroxo cluster be assembled from a mononuclear tris aqua lanthanide complex with EDTA?*

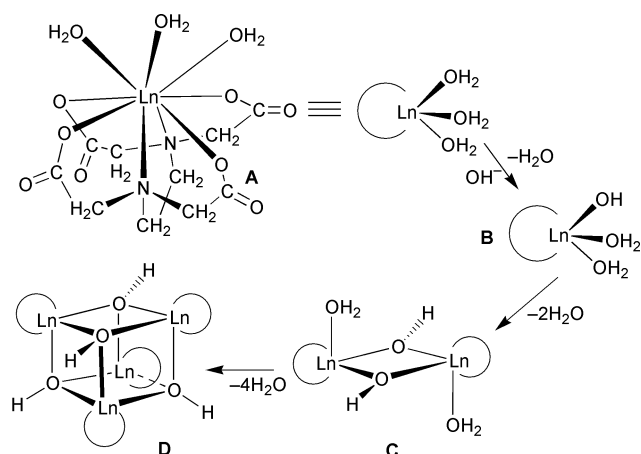


Fig. 15 A proposed mechanism for the self-assembly of a tetranuclear lanthanide-hydroxo complex with EDTA from its corresponding mononuclear aqua complex.

It seemed plausible that if the pH of a lanthanide-EDTA reaction mixture is raised, the aqua ligand(s) of the initially formed nine-coordinate complex would be deprotonated, giving rise to a hydroxo complex of lanthanide with EDTA (**B**, Fig. 15). Bimolecular reactions of species **B** leads to the formation of the μ_2 -OH bridged, diamond-shaped intermediate (**C**, Fig. 15), for which a number of literature precedents exist.²² Subsequent condensation of two of such dinuclear units would afford a tetranuclear lanthanide cluster, bearing the familiar cuboid $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ unit whose metal centers are capped by EDTA ligands (**D**, Fig. 15).

This hypothesis was validated: The La^{III} -EDTA complex, formulated as $\text{Na}_{10}[\text{La}_4(\mu_3\text{-OH})_4(\text{EDTA})_4](\text{ClO}_4)_2$, was obtained by mixing $\text{La}(\text{ClO}_4)_3$ and $\text{Na}_2\text{H}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ in an aqueous solution and subsequently adjusting the pH of the reaction mixture to about 13 with dilute aqueous NaOH .³¹ The molecular structure of the anionic cluster was established by X-ray diffraction and is shown in Fig. 16, wherein the presence of

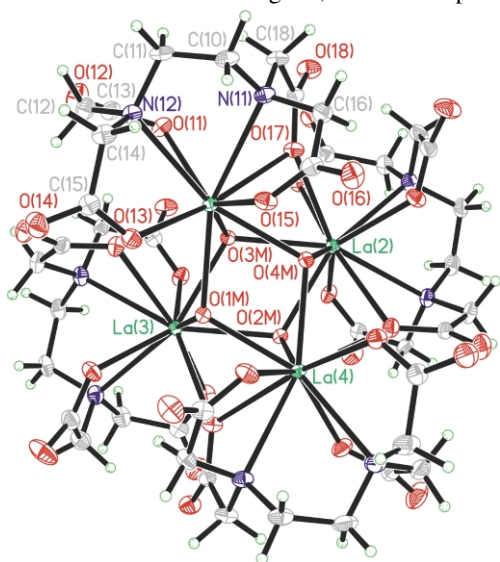


Fig. 16 An ORTEP representation of the anionic complex $[\text{La}_4(\mu_3\text{-OH})_4(\text{EDTA})_4]^{8-}$ featuring the familiar cubane-like $[\text{La}_4(\mu_3\text{-OH})_4]^{8+}$ core.

a cubane-like $[\text{La}_4(\mu_3\text{-OH})_4]^{8+}$ core is quite clear. Each metal vertex is capped by an EDTA ligand whose coordination mode is unusual: the EDTA ligand is hexadentate (a, Fig. 17), but with one of its four coordinating oxygen atoms bridging a second La^{III} ion. The two non-bridged La^{III} pairs (La1–La4 and La2–La3) correspond to a metal–metal separation of 4.278 Å, which is significantly longer than the other four (3.975 Å). Each La^{III} ion has a CN = 10, and its coordination polyhedron may be best described as a bicapped square antiprism. Although the

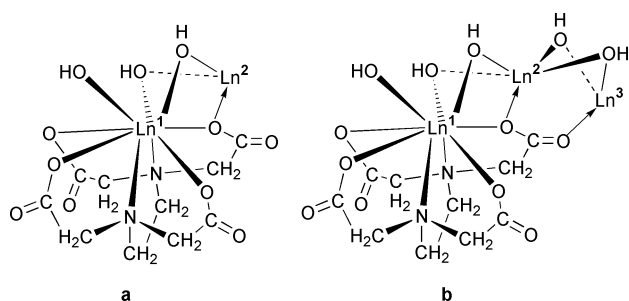


Fig. 17 The well-known hexadentate mode of an EDTA ligand to Ln^1 with the unprecedented bridging modes to additional lanthanide ions (Ln^2 and Ln^3).

complex is not exactly the one originally targeted, its formation can be readily rationalized based on the proposed condensation mechanism. An isostructural tetranuclear hydroxo complex of Pr^{III} with EDTA has been obtained;⁵² the Pr^{III} ion in this complex is also 10-coordinate.

Since one EDTA ligand contributes six coordinating atoms, only two aqua ligands would be possible for a lanthanide ion that prefers a coordination number of eight. A complex featuring the diamond-shaped lanthanide-hydroxo core would be the expected product, and the reaction would terminate at the stage of **C** upon increasing the pH of the reaction mixture. Indeed, a dinuclear Er^{III} -hydroxo complex was isolated from a reaction mixture of $\text{Na}[\text{Er}(\text{EDTA})(\text{H}_2\text{O})_2]$ (formed at pH 6) with KOH at pH 13–14.⁵² The structure of the complex, formulated as $\text{K}_4[(\text{EDTA})\text{Er}(\mu\text{-OH})_2\text{Er}(\text{EDTA})]$, has been determined by X-ray diffraction, and that of the anionic core component is depicted in Fig. 18.

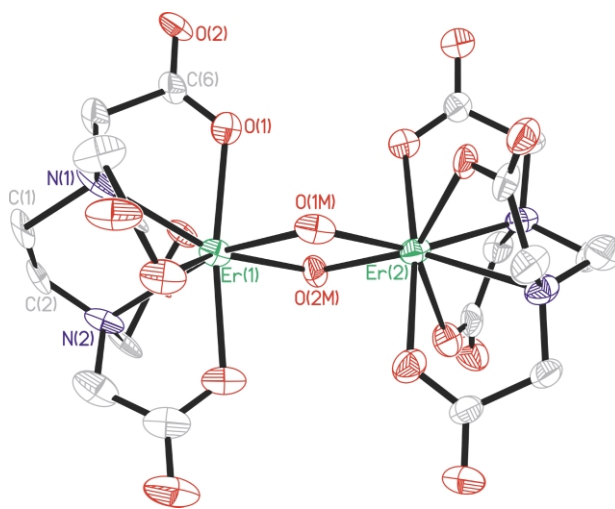


Fig. 18 An ORTEP representation of the diamond-shaped dinuclear Er^{III} -hydroxo complex with EDTA, $[(\text{EDTA})\text{Er}(\mu\text{-OH})_2\text{Er}(\text{EDTA})]^{4-}$.

The observation of ten-coordinate La^{III} and Pr^{III} in both of the tetranuclear complexes merits further discussion. While the high coordination number is not so unusual for La^{III} , ten-coordinate Pr^{III} is rather rare. It appears that the previously unknown bridging interaction by one of the EDTA carboxylate oxygens is a prerequisite for the formation of the cubane-like structure. What can one anticipate when a lanthanide ion preferring a CN = 9 is utilized in an analogous reaction? On the one hand, since a CN = 10 is very unlikely, it is a reasonable assessment that the tetranuclear complex will not form. On the other hand, since such a lanthanide ion may not be satisfied with a CN = 8, one may expect a coordination environment different from that of the dinuclear Er^{III} complex (Fig. 18). Once again, our efforts to seek answer to this question yielded pleasantly surprising results. A dodecanuclear complex composed of four vertex-sharing $[\text{Nd}_4(\mu_3\text{-OH})_4]^{8+}$ cubanes and eight EDTA

ligands was isolated from an aqueous mixture of EDTA and $\text{Nd}(\text{ClO}_4)_3$ at pH 14.^{27,31}

The crystal structure of the anionic cluster complex, formulated as $\{[\text{Na}(\text{H}_2\text{O})_2]_4[\text{Nd}_{12}(\mu_3\text{-OH})_{16}(\text{EDTA})_8]\}^{8-}$, is shown in Fig. 19. Its skeletal structure is identical to those of the

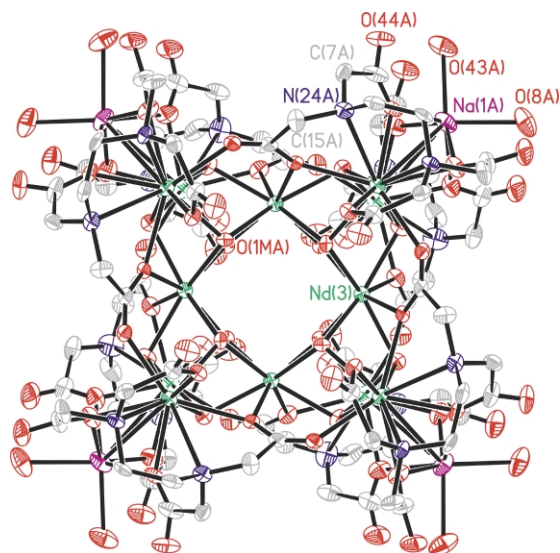


Fig. 19 An ORTEP representation of the dodecanuclear Nd^{III} -hydroxo complex featuring four vertex-sharing $[\text{Nd}_4(\mu_3\text{-OH})_4]^{8+}$ units in a square-shaped arrangement. The anionic complex is formulated as $\{[\text{Na}(\text{H}_2\text{O})_2]_4[\text{Nd}_{12}(\mu_3\text{-OH})_{16}(\text{EDTA})_8]\}^{8-}$. Color legend: sodium (purple).

diiodide complexes obtained from the tyrosine-supported hydrolytic reaction of $\text{Ln}(\text{ClO}_4)_3$ ($\text{Ln} = \text{Dy}^{\text{III}}, \text{Er}^{\text{III}}$) with templating I^- .³² The EDTA ligands occupy the vertices of a perfect tetragon, each capping one of the eight non-shared Nd^{III} . One may alternatively view the structure as a sandwich made with a four-cubane ‘patty’ and two slices of EDTA ‘bread’. The coordination mode of EDTA ligands in this complex is significant: each EDTA molecule acts as a *heptadentate* ligand (b, Fig. 17) as opposed to the well-known hexadentate one. One of the carboxylate groups together with the nitrogen atom to which it is bound can be described as $\mu_3:\eta^1:\eta^2:\eta^1$, a coordination mode first observed in the aforementioned lanthanide-tyrosine complexes,^{29,32} but unprecedented for EDTA. Hydroxo ligands complete the Nd^{III} coordination sphere. Thus, each inner-layer Nd^{III} ion has a CN of 8, forming an irregular square antiprism, while each outer layer Nd^{III} ion has a CN of 10, and its coordination polyhedron may be best described as a bicapped square antiprism. Both eight- and ten-coordinate Nd^{III} are uncommon; the metal ion is predominantly nine-coordinate with tricapped trigonal prism being the most frequently observed structure. Even more intriguing are the unprecedented co-existence of these rare coordination numbers and the accompanying absence of the commonly observed nine-coordination.

The square opening, clearly shown in Fig. 19, could potentially permit entry by a guest molecule or ion. The strong preference of Nd^{III} for nine-coordinate geometry coupled with the high affinity of a lanthanide ion for F^- suggests that a fluoride-containing complex with the anionic guest species sitting in the square-shaped opening is possible.⁵³

What the story tells us

The research described here was initially stimulated by the observation of several aesthetically pleasing polynuclear lanthanide-hydroxo complexes that were characterized as synthetic serendipity or accidents. The ultimate goal of making high-nuclearity lanthanide complexes aimed at potential applications in biomedical science and advanced technologies drove

us to study the lanthanide coordination with biologically relevant ligands under near physiological and even high pH conditions. A variety of novel lanthanide-hydroxo complexes have been isolated and structurally characterized. The results clearly illustrate that otherwise well-established chemistry can be profoundly affected by simply altering the reaction pH.

The following are the principal results and conclusions from the research described above.

1. Ligand-controlled hydrolysis of the lanthanide ions is a new avenue in lanthanide coordination chemistry. It is a valid and highly efficient approach to the assembly of finite-size polynuclear lanthanide-hydroxo complexes.
2. α -Amino acids are a novel class of supporting ligands for controlling the hydrolysis of the lanthanide ions. Under near physiological pH conditions, lanthanide complexation with amino acids may be achieved *via* only the carboxylate group or simultaneous coordination by both the carboxylate and amino moieties.
3. Lanthanide-amino acid complexes generated under near neutral conditions typically exist as discrete polynuclear lanthanide-hydroxo clusters, whereas their low-pH counterparts are in mononuclear, dinuclear or noncluster polynuclear forms. It is the high-pH conditions that promote the formation of the large molecular clusters. These complexes may be viewed as the precursors to stepwise, controllable sol-gel materials syntheses.
4. The cuboid $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ cluster, complementing its *d*-block counterparts, is a common structural motif in lanthanide coordination compounds. Extended supramolecular structures can be assembled by using the $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ cluster cores as building blocks.
5. Octahedral $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$ core-containing clusters with an interstitial $\mu_6\text{-O}$ ligand can be assembled *via* direct hydrolysis of lanthanide nitrates and perchlorates in the absence of any organic supporting ligands.
6. Spherical anionic species are important in templating the formation of wheel-like lanthanide cluster complexes.
7. pH conditions exert a strong and general influence on the outcome of lanthanide coordination chemistry, as demonstrated by the isolation of unprecedented EDTA-lanthanide complexes from otherwise well-established chemistry.

The story continues with an open end

The results detailed above suggest extensive and promising coordination chemistry of the lanthanide ions under physiological or higher pH conditions. Many important questions, both fundamental and practical, remain to be answered. For example, why is tyrosine so unique in that it uses both amino and carboxylate groups for simultaneous lanthanide coordination? Why are pentadecanuclear or dodecanuclear complexes composed of corner-sharing cuboid $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ cluster units formed with tyrosine ligands while monocluster complexes are generated with carboxylate-only coordination when other amino acids are utilized? Although the steric effect due to the side group of the amino acid may play an important role, answers to these questions are not yet available. Further, how extensively applicable to other metals and ligands is the hydrolytic approach to polynuclear complexes? What properties may be expected of these novel lanthanide-containing materials? From the work discussed herein, it is clear that ‘high’-pH lanthanide coordination chemistry represents a rich field of research that can be exploited to create novel lanthanide-containing materials with desirable properties. There are ample opportunities for investigation and high expectation for a broad range of applications of these novel polynuclear lanthanide complexes, including the well-characterized structural platform for potential development of lanthanide-based synthetic phosphodiesterases.

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† Note: unless indicated otherwise, color legends are as follows: carbon (gray), lanthanide (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability.

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