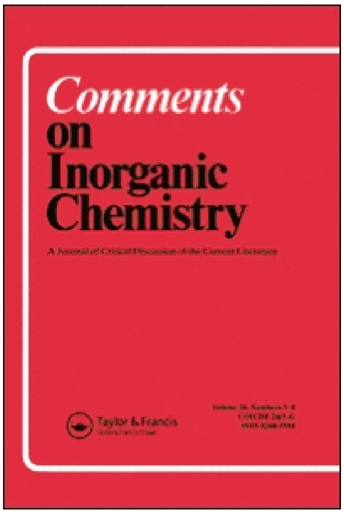


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Assembling Lanthanide Clusters Under Physiological or Higher pH-Conditions

Zhiping Zheng[a]; Ruiyao Wang[a]
[a] Department of Chemistry, The University of Arizona Tucson, Arizona, USA

To cite this Article Zheng, Zhiping and Wang, Ruiyao(2000) 'Assembling Lanthanide Clusters Under Physiological or Higher pH-Conditions', Comments on Inorganic Chemistry, 22: 1, 1 — 30
To link to this Article: DOI: 10.1080/02603590008050862
URL: http://dx.doi.org/10.1080/02603590008050862

Assembling Lanthanide Clusters Under Physiological or Higher pH-Conditions

ZHIPING ZHENG* and RUIYAO WANG

Department of Chemistry
The University of Arizona Tucson,
Arizona 85721 USA

(Received October 14, 1999)

High-nuclearity lanthanide complexes, having unique structures and potentially important applications, have been prepared via limited hydrolysis of lanthanide ions controlled by α-amino acids as supporting ligands. These novel complexes, synthesized under physiological or higher-pH conditions, exist as lanthanide-hydroxo clusters, reflecting the subtle balance between the hydrolysis of the metal ions and the multidentate supporting coordination of the ligands. A cuboid $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ unit with four lanthanide ions and four triply bridging hydroxo ligands occupying the alternate vertices of a distorted cube has been identified as a prevalent structural motif in these complexes, wherein lanthanide complexation may be achieved via only the carboxylate group or simultaneous coordination of both the carboxylate and the amino moieties of an amino acid ligand. Bridging ligands with more than one carboxylate group may support open framework structures utilizing the $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ unit as building blocks. In addition, "wheel-like" structures composed of four or five vertex-sharing $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ units can be realized by the halide-templated synthesis. It has been further demonstrated that octahedral $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ core-containing clusters with an interstitial μ_6-O ligand can be self-assembled via direct hydrolysis of lanthanide nitrates and perchlorates in the absence of any organic supporting ligands. Using a structurally unprecedented lanthanide-EDTA complex, the significant influence of pH conditions on the reaction outcome is illustrated.

Keywords: *lanthanides; clusters; cubanes; amino acids; hydrolysis; template synthesis*

---

* Correspondence Author.

Comments Inorg. Chem.
2000, Vol. 22, No. 1-2, pp. 1-30
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

INTRODUCTION

Lanthanide elements, bearing special electronic and spectroscopic properties mainly associated with their 4*f* electronic configurations, represent a unique series of metals in the periodic table.[1] Their paramagnetic and optical properties, hard Lewis acid character, and high coordination numbers make lanthanide complexes attractive for applications such as magnetic resonance imaging (MRI) contrast agents,[2] catalysts for organic transformations,[3] molecular magnetic materials,[4] and in photoluminescence studies.[5] Consequently, the coordination chemistry of trivalent lanthanoid cations has been thoroughly investigated over the last twenty years.[6]

One of the recent developments in lanthanide chemistry concerns the self-assembly of polynuclear lanthanide complexes.[7] These substances exhibit a fascinating variety of unusual symmetries and structural patterns.[7] More importantly, these complexes are potential precursors for metalloorganic chemical vapor deposition (MOCVD)[8]and sol-gel technology.[9] In addition, polynuclear lanthanide/transition metal complexes have more recently attracted considerable attention for their potential application as nanomagnetic materials.[10] However, the high expectations of using these substances as advanced materials have been compromised by historically limited synthetic ability. Lanthanide complexes typically exist in mononuclear, dinuclear, or polynuclear forms if they are prepared at low pH, whereas at high pH one usually obtains noncrystalline, nonstoichiometric materials of high nuclearity. The number of well-characterized finite-size lanthanide clusters is still limited. Their synthesis is characterized by random self-organization and cannot yet be planned.

With the intent of developing a general synthetic approach to high-nuclearity lanthanide complexes and ultimately creating lanthanide-containing materials, we have recently initiated a program to study the coordination chemistry of lanthanides with biologically relevant ligands under physiological or higher pH conditions.[11] Our efforts were stimulated by three isolated precedents[12–14] describing a novel cuboid structural motif, $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ (Ln = trivalent lanthanide), in which four lanthanide ions and four triply bridging hydroxo groups occupy alternating vertices of a distorted cube (Chart 1). It is noted that two Yb_4E_4 (E = S, Se) cubane clusters have also been reported recently.[15] The paucity of cuboid homonuclear lanthanide clusters in the literature is surprising because the family of M_4E_4 (M = *d*-block transition metal; E = S, Se, Te) cubane clusters has been well documented and extensively studied.[16] Nevertheless, the common key structural features of the three tetranuclear lanthanide-hydroxo complexes, synthesized via distinctly different routes, lead us to suspect that such a structural motif may well prove to be as general as its *d*-block counterparts. Further, the presence of the hydroxo ligands suggests that these clusters may be generated by the hydrolysis of lanthanide ions.

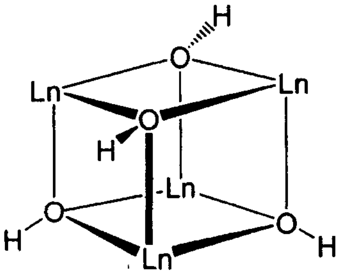
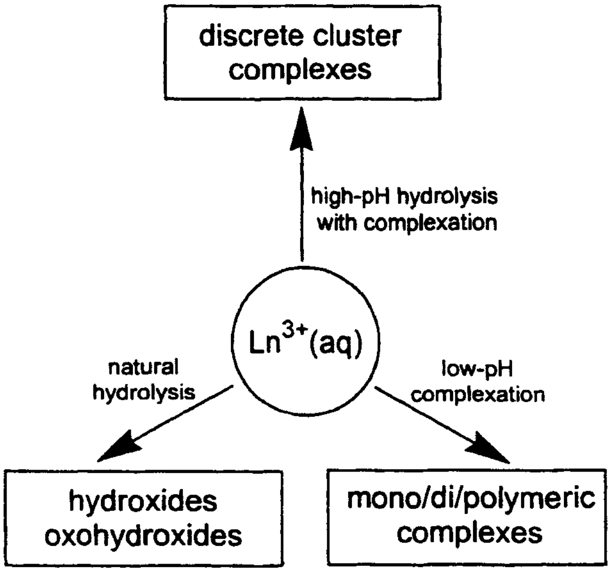


CHART I

It was realized at the outset that certain types of supporting ligands would be necessary in order to prevent the formation of intractable byproducts associated with natural hydrolysis. In fact, a commonly employed strategy for the synthesis of the *d*-block cluster complexes is utilizing appropriate chelating ligands to control the hydrolysis of the metal ions.[17] The auxiliary ligands prevent extensive hydrolysis from occurring by occupying part of the metal coordination sphere. As a result, finite-sized polymetal 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,[17,18] polyketonates,[19] polyamines,[20] polyols,[21] and alkoxides[22] are prominent. Spectacular clusters such as polyoxovanadates,[23] manganese clusters,[19] and ferric wheels[24] have been reported and proven to exhibit rather interesting magnetic properties due to the presence of an unusually large number of unpaired electrons in these molecules of aesthetically pleasing structures.[25]

Despite the impressive progress that has been made with the preparation of *d*-block metal clusters, the ligand-controlled hydrolytic synthetic approach has not yet been applied to the more elusive lanthanide clusters. In fact, the coordination of lanthanides with various ligands has been exclusively conducted under acidic conditions, typically under pH 6.[26] This is understandable considering the common perception that lanthanide ions are so prone to hydrolysis that intractable hydroxides and/or oxohydroxides would result under any higher pH conditions. In stark contrast, ***we submit that a subtle balance between the hydrolysis of a lanthanide ion and its multiple coordination with a chelating ligand should afford novel polynuclear lanthanide complexes, which is analogous to the ligand-controlled formation of d-block metal clusters*** (Scheme 1). As will be demonstrated by our studies[11,27,28] discussed in the following section, it is the unconventionally "high" pH conditions that promote the formation of unprecedented lanthanide clusters. We wish to illustrate with a comprehensive and systematic study detailed in this *Comment* article that ligand-controlled hydrolysis of lanthanides under physiological or even higher pH conditions indeed represents a new and rich research field and that it may well prove to be as general as its low-pH counterparts.



SCHEME I

Among the huge variety of suitable ancillary ligands, α-amino acids have been chosen to control the extensive hydrolysis of lanthanide ions based on the following criteria:

- *Extensive Low-pH Lanthanide Coordination Chemistry with Amino Acids*. The coordination chemistry of lanthanides with amino acids has been extensively investigated.[29,30] These studies have almost been conducted at low-pH values, typically below 5. About 50 solid state structures of such complexes have appeared.[29,30] These results serve as a useful database for comparison with lanthanide coordination under physiological or higher pH conditions.
- *Biological Relevance*. α-Amino acids are basic constructing units for proteins. Their interactions with metal ions have been studied extensively in an effort to elucidate metal functions in biomolecules.[31] Lanthanide complexes with amino acids may be used in immunofluorescence assays[5,6] or as contrast agents in MRI technology.[2] The carboxylate and amino groups as well as the side-chain of an amino acid would allow ready conjugation of the complexes to a suitable targeting vector, such as an engineered human antibody fragment (Fab).
- *Modular Structures*. α-Amino acids are optically active and are commercially available in both enantiomeric forms. This modular feature is especially beneficial for systematic studies of lanthanide coordination chemistry. Related to amino acids is the rich class of aminopolycarboxylic acids whose lanthanide complexes have been extensively studied.[32] However, lanthanide coordination with these polydentate ligands under basic conditions has essentially been untapped.[33,34] It is expected that the high-pH conditions would have a significant impact on the outcome of such reactions.

THE CUBOID $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ CLUSTER: A COMMON STRUCTURAL MOTIF IN LANTHANIDE COORDINATION CHEMISTRY AND ITS SELF-ASSEMBLY

To test the validity of the amino acid-supported hydrolytic approach to polynuclear lanthanide clusters, representative lanthanide chlorides or

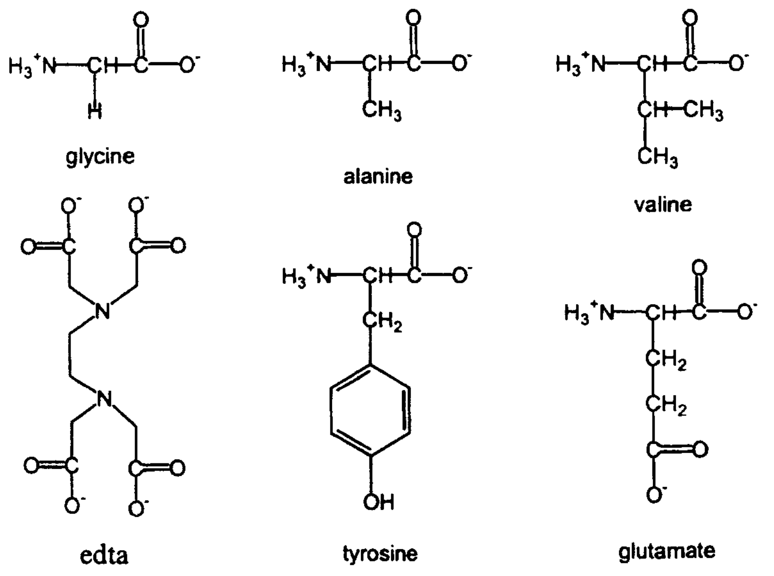


CHART II

perchlorates were subject to hydrolysis with aqueous NaOH in the presence of glycine, alanine, valine, tyrosine, and glutamic acid (Chart 2) *(Perchlorates are potentially explosive and should be handled in small amount with great care.)*.[11,28,35] A series of complexes composed of a single cuboid $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cluster core supported by 4–6 amino acid ligands have been obtained, in which the Ln_4 tetrahedron is "camouflaged" by the amino acid ligands through bridging carboxylate coordination (Fig. 1, 2). The cluster core has the following average metric values of interest: $Ln\text{-}O(\mu_3\text{-}OH)\text{-}Ln$ 106.2°, and $O(\mu_3\text{-}OH)\text{-}Ln\text{-}O(\mu_3\text{-}OH)$ 70.9°. Distortion of the core from a perfect cube is conspicuous from these geometric data, although the Ln_4 tetrahedron is fairly regular. The coordination sphere of the metal ions is completed by water molecules in addition to the hydroxo ligands associated with the limited hydrolysis. Thus, each of the 4 Ln(III) ions has a coordination number of 8 or 9.

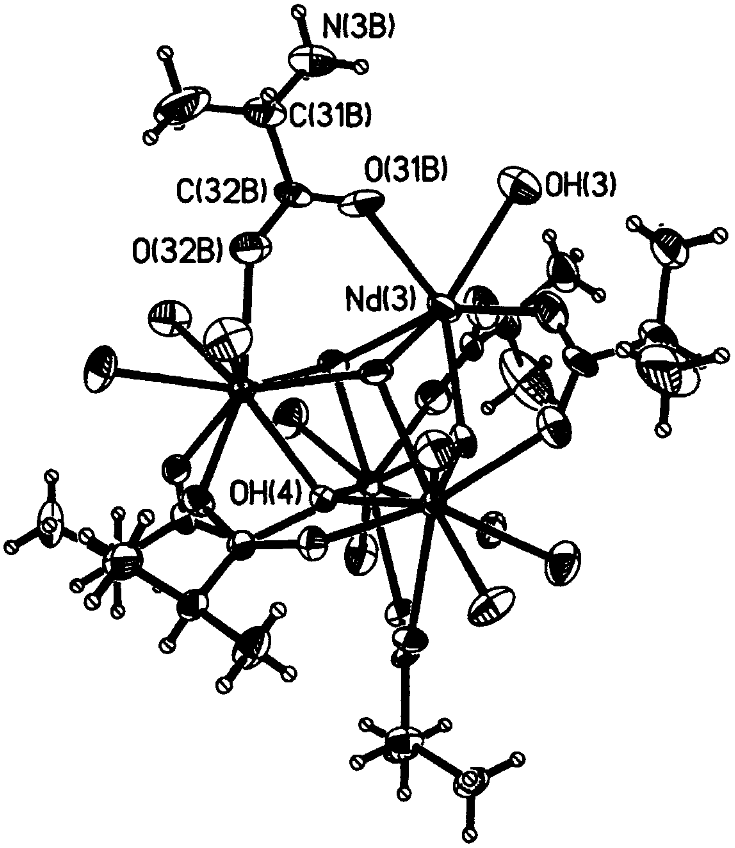


FIGURE 1 An ORTEP drawing of the cuboid $[Nd_4(\mu_3\text{-}OH)_4(Ala)_6]^{2+}$ core structure. Thermal ellipsoids are represented in 40% probability

Having shown that the cuboid $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cluster is a common structural motif in lanthanide complexes and that its formation can be aided and stabilized by chelating interactions with the carboxylate groups of amino acids, we considered the self-assembly of open lanthanide frameworks using the $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cluster unit and amino acids with more than one carboxylate group as the building blocks. In this consideration, an amino acid functions as both a supporting ligand

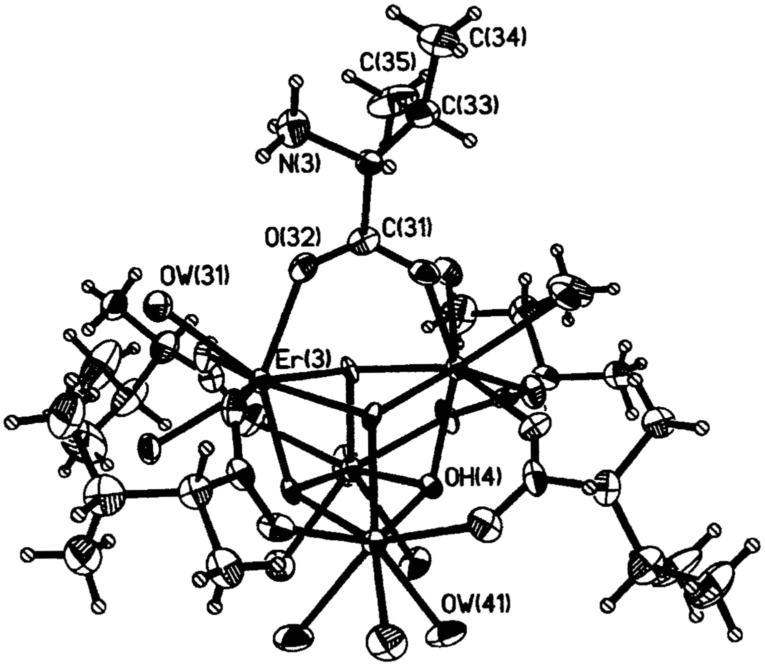


FIGURE 2 An ORTEP drawing of the cuboid $[Er_4(\mu_3\text{-}OH)_4(Val)_5]^{3+}$ core structure. Thermal ellipsoids are represented in 40% probability

for the hydrolytic formation of the $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cluster and as a bridging group between individual cluster units. By treating a mixture of $Er(ClO_4)_3$ and *L*-glutamic acid with aqueous NaOH to the point of incipient precipitation, a 3-D porous network, $[Er_4(\mu_3\text{-}OH)_4(Glu)_3(H_2O)_8][ClO_4]_5\cdot 6H_2O$ (**1**), comprised of discrete $[Er_4(\mu_3\text{-}OH)_4]^{8+}$ units and cluster-linking glutamate ligands has been obtained and its solid state structure been determined. The structure of the elementary constituent of the open framework is depicted in Figure 3, from which the complex 3D network (Fig. 4) is constructed. The cubane-like $[Er_4(\mu_3\text{-}OH)_4]^{8+}$ building blocks are apparent, resembling geometrically their previously reported analogues.[11,28,35] The six carboxylate groups ligating a particular cube are of two different types, one being α- and the other being γ- (from the side chain) to the amino moiety; each

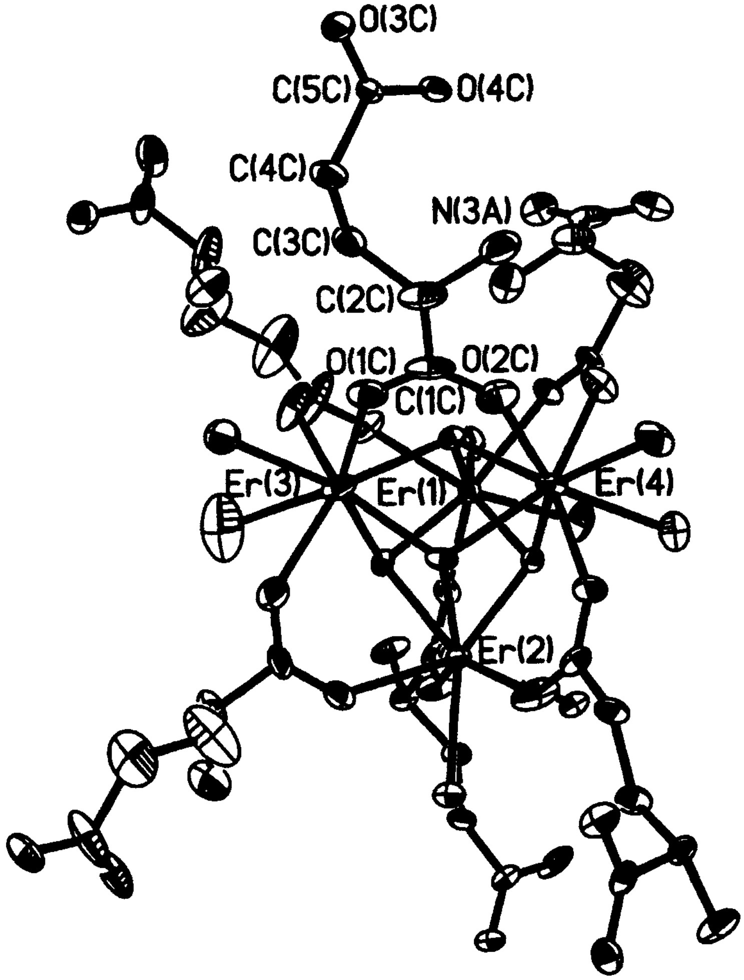


FIGURE 3 Thermal ellipsoid (40% probability) plot of the building block unit in the structure of **1**. Three symmetry-related glutamic acid "arms" are included to complete the coordination of the cuboid $Er_4(\mu_3\text{-}OH)_4$core

glutamate ligand contributes one carboxylate group for the coordination of an $[Er_4(\mu_3\text{-}OH)_4]^{8+}$ cluster while using the remaining one to coordinate an adjacent lanthanide cluster cube. The 3D open framework bears

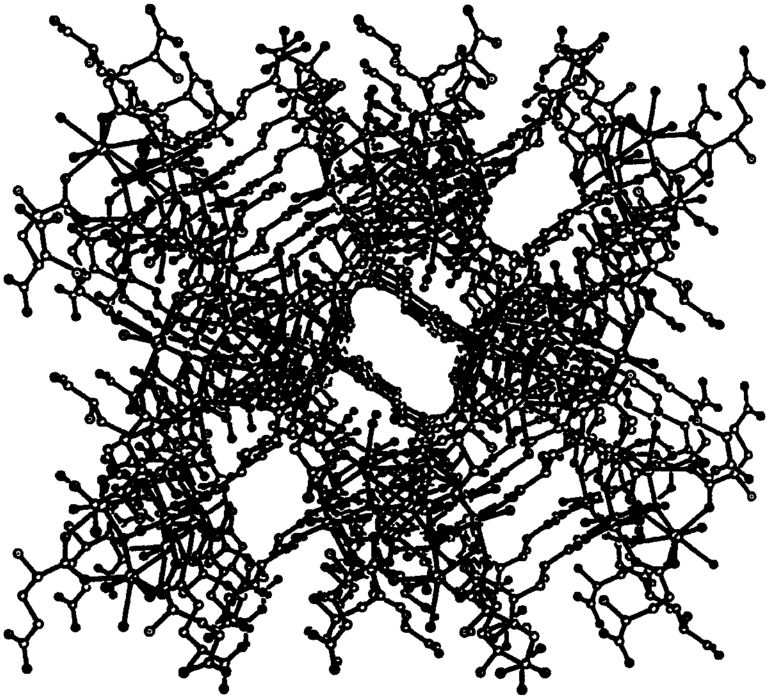


FIGURE 4 The crystal structure of the 3D porous framework of **1** shown along the *c*-axis. Hydrogens, the water, and perchlorate ions are omitted for clarity. The channel dimensions are approximately 4.4 Å × 9.1 Å

nearly parallelogram-shaped pore apertures with approximate dimensions of 4.4 Å × 9.1 Å for channels in the *c* direction. The channels extend parallel to the *b* and *c* axes along crystallographic 2_1 axes, housing six water molecules and five ClO_4^- ions, the latter, having their expected geometry, being hydrogen bonded to the amino group that does not participate in the coordination of the Er(III) ions.

Open-framework structures such as **1** may be used as hosts for small substrate encapsulation and catalysis.[36] The regular arrangement of paramagnetic lanthanide ions in these materials is especially significant in light of recent surging interest in molecular magnetism[4,10] displayed by polynuclear metal complexes. It is noteworthy that with adipic acid, a long-chain dicarboxylic acid structurally similar to glutamic acid, a 3-D network structure based on a dimeric lanthanide unit has been obtained,[37] reflecting the low solubility of these coordination polymers. In the present work, the zwitterionic characteristic of amino acids is believed to play a pivotal role in overcoming the charge-compensation (and therefore low-solubility) problem due to the attachment of carboxylate ligands to a metal center. In other words, only with the assistance of the ammonium group ($-NH_3^+$) can the hydrolysis of the lanthanide proceed to the point of lanthanide-hydroxo cluster formation without precipitating out insoluble coordination polymers.

ANION TEMPLATE EFFECTS IN THE SELF-ASSEMBLY OF POLYNUCLEAR LANTHANIDE COMPLEXES WITH TYROSINE

In evaluating the influence of the amino acid side groups on the structure of a lanthanide-hydroxo cluster, a rare example of anion-assisted synthesis was observed, and the template effects[38] involved were subsequently illustrated. Instead of a single tetranuclear lanthanide cluster containing a $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ unit and its accompanying supporting amino acid ligands, pentadecanuclear lanthanide complexes have been isolated when the reaction mixture of $Ln(ClO_4)_3$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Dy) and tyrosine was subject to hydrolysis with NaOH.[11] Single crystal X-ray analysis of the representative europium complex, formulated as $[Eu_{15}(\mu_3\text{-}Tyr)_{10}(\mu_3\text{-}OH)_{20}(\mu_2\text{-}H_2O)_5(OH)_{12}(H_2O)_8(Cl)](ClO_4)_2$ ($2{\bullet}Cl^-$) revealed an unprecedented layered structure comprised of 15 Eu(III) ions and 10 tyrosinate ligands in addition to the hydroxo and aquo ligands associated with the limited hydrolysis. To the best of our knowledge, these complexes are not only the largest members of a fascinating family of homonuclear lanthanide clusters that have hitherto been reported, but also the first examples of lanthanide-amino acid complexes that have been confirmed by X-ray crystallography with simultaneous Ln-O and Ln-N coordination.

As shown in Figure 5, the 15 Eu^{III} ions are assembled into a layered structure. Each of the three parallel layers contains 5 Eu^{III} ions that 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 Eu-Eu distance of 3.896 Å, is unique and "tucked in". The 10 tyrosinate ligands can be

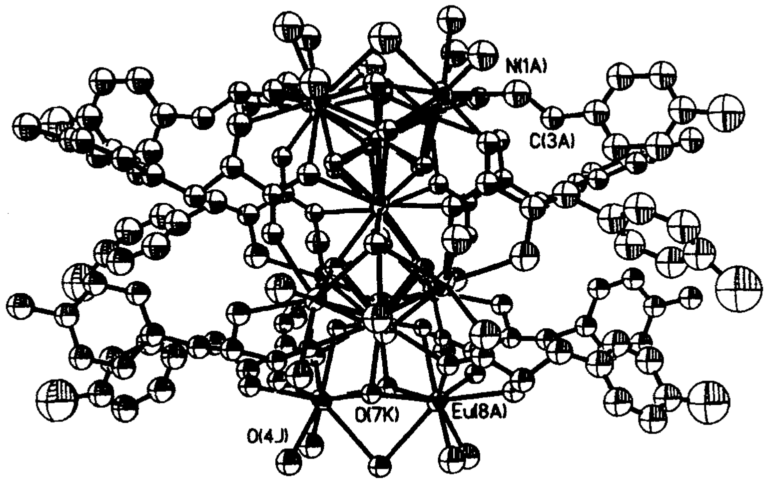


FIGURE 5 A perspective view of **2**, carbon (grey), chlorine (black), europium (green), nitrogen (cyan), oxygen (red). Lattice water molecules and perchlorate ions are omitted for clarity (See Color Plate I at the back of this issue)

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 $\mathrm{Eu^{III}}$ ions in these molecules are significant: Each of the 10 tyrosinates acts as a tetradentate ligand by utilizing both its amino and carboxylate groups Figure 6. The ligand can be described as a $\mu_3:\eta^1:\eta^2:\eta^1$ anion, not only linking two neighboring $\mathrm{Eu^{III}}$ centers within the same (outer) layer, but also coordinating a third $\mathrm{Eu^{III}}$ 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 lanthanides with amino acids, the zwitterions bind the lanthanides exclusively through the oxygen of the carboxylate.[29,30] Such interaction is included in Figure 6 for comparison. The coordination sphere of the $\mathrm{Eu^{III}}$ centers is completed by hydroxo and aquo ligands. Thus, each of the 10 $\mathrm{Eu^{III}}$ ions in the outer layers has a coordination number (CN) of 9, and the structure can be best described

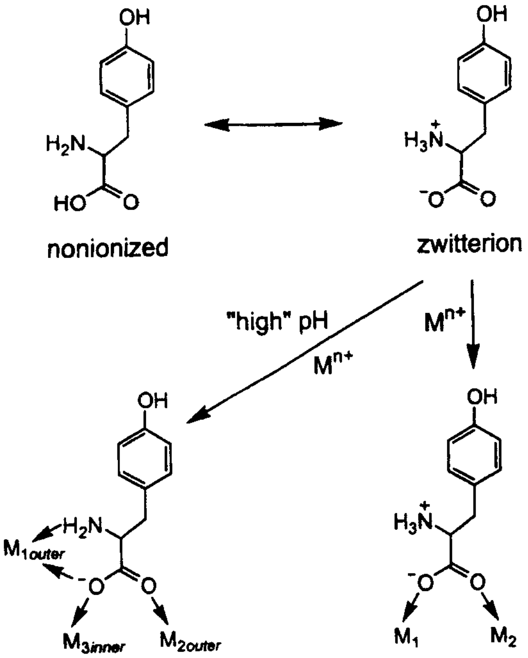


FIGURE 6 The distinct coordination modes of a tyrosine ligand with lanthanide ions under different pH conditions

as monocapped square antiprismatic, while the inner-layer Eu^{III} centers also have a CN of 9, forming irregular square antiprisms monocapped by the central chloride ion (vide infra). 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 4 Eu^{III} ions and 4 μ_3-OH ligands (Figure 7).

A particularly salient feature of the structure is a chloride ion being trapped within the "belly" of the barrel-shaped molecule, serving as the bolt of the cubane wheel. The chloride 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 chlo-

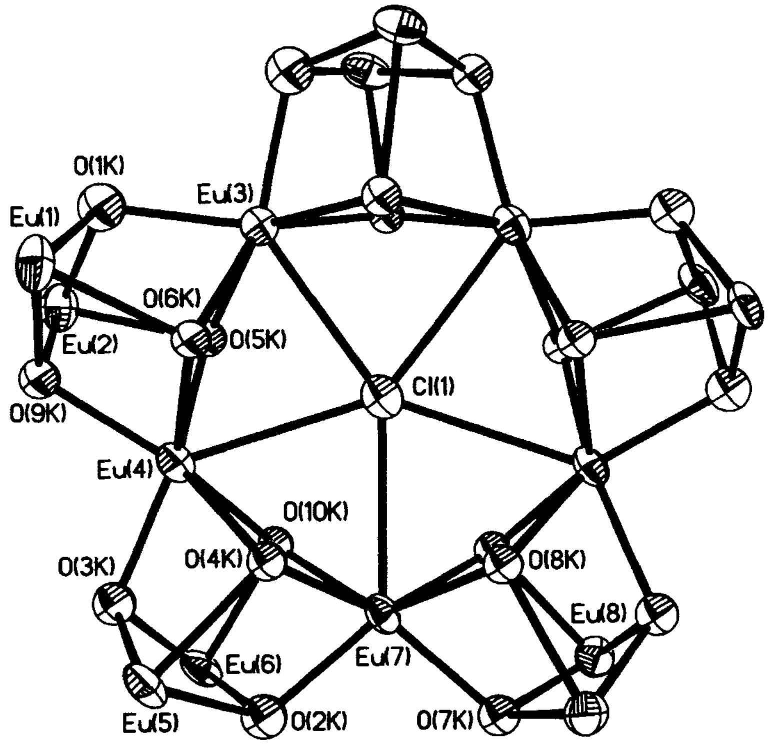


FIGURE 7 An ORTEP drawing of the pentadecanuclear "cubane wheel" structure of 2•Cl⁻. Thermal ellipsoids are represented in 40% probability

ride-induced self-assembly of the lanthanide ions with the help of the tyrosine ligands. The presence of the trapped Cl⁻ is, however, unexpected because no chloride was utilized during the formation of the complex; the only possible source would be the trace amount of Cl⁻ impurity present in the aqueous $HClO_4$ used to digest the lanthanide oxides. This surprising feature raises a natural but intriguing question: *Is the chloride a template*?

Although it has long been recognized in the synthesis of many homoleptic as well as heteroleptic alkoxide complexes of lanthanides that the presence of a "central spherical negative charge density" such as chloride and oxo groups accounts for the driving force for cluster formation,[7] the exact roles played by these anionic species have not yet been investigated, let alone understood. With the intent of unambiguously defining this anion-template effect and concomitantly assembling novel cluster structures by utilizing anions of different *size* and *geometry*, we have investigated the hydrolysis of $Ln(ClO_4)_3$ in the presence of added halides (Cl^-, 1.81 Å; Br^-, 1.96 Å; I^-, 2.20 Å)[39] using tyrosine as the ancillary ligand. To examine the potential templating role of trigonal planar NO_3^- ion (1.79 Å),[39] $Ln(NO_3)_3$ rather than the corresponding $Ln(ClO_4)_3$ with added NO_3^- were utilized because it appeared that even a trace amount of Cl^- impurity from the aqueous $HClO_4$ would lead to the formation of the chloride-centered pentadecarnuclear complex (*vide supra*). The results obtained from these studies are summarized in Table I.

TABLE I Evidence for Anion-Template Effects

Entry	*Reaction Mixture*[a]	*Product*				
		Core Structure[b]	*Guest(s)*	*Counte-rion*	*Yield (%)*[c]	*Ref*
1	$Eu(ClO_4)_3$/tyr	*cyclo*-$[Eu_4(\mu_3\text{-}OH)_4]_5$	$\mu_5\text{-}Cl^-$	ClO_4^-	< 10	11
2	$Eu(ClO_4)_3$/tyr/NaCl	*cyclo*-$[Eu_4(\mu_3\text{-}OH)_4]_5$	$\mu_5\text{-}Cl^-$	ClO_4^-	50–60	11
3	$Eu(ClO_4)_3$/tyr/HBr	*cyclo*-$[Eu_4(\mu_3\text{-}OH)_4]_5$	$\mu_5\text{-}Br^-$	ClO_4^-	50–60	28
4	$Dy(ClO_4)_3$/tyr/HI	*cyclo*-$[Dy_4(\mu_3\text{-}OH)_4]_4$	2 I^-	ClO_4^-	30–40	28
5	$Gd(ClO_4)_3$/tyr	*cyclo*-$[Gd_4(\mu_3\text{-}OH)_4]_5$	$\mu_5\text{-}Cl^-$	ClO_4^-	< 10	11
6	$Er(NO_3)_3$/tyr	*oct*-$[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]$	$\mu_6\text{-}O^{2-}$	NO_3^-	> 70	27
7	$Gd(NO_3)_3$/tyr/NaCl	*cyclo*-$[Gd_4(\mu_3\text{-}OH)_4]_5$	$\mu_5\text{-}Cl^-$	NO_3^-	50–60	28

a. Reactions were carried out following the previously reported procedure.[11]

b. The formulae do not reflect the exact compositions of the products; instead they are meant to emphasize the cognizable building blocks in the supramolecular structures.

c. These are estimated yields due to the high water-solubility of the complexes. A significant amount of the product was lost during work-up.

The superb templating role of the chloride ion was suspected at the outset based on the unexpected formation of the chloride-containing complexes.[11] Extra chloride in the reaction mixture would presumably ameliorate the formation of the complex in terms of product yield and purity. Indeed, the same complex (**2**•Cl^-) was obtained in 50–60% yield

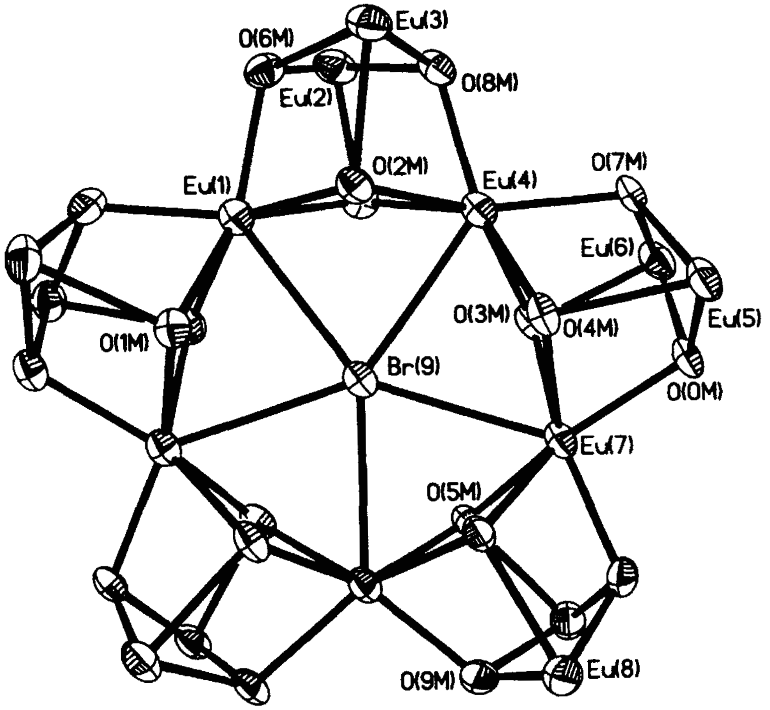


FIGURE 8 An ORTEP drawing of the pentadecanuclear "cubane wheel" structure of 2•Br$^-$. Thermal ellipsoids are represented in 40% probability

with the addition of an aqueous NaCl solution, as compared to < 10% in its absence (Table I, entries 1, 2, and 5). In an analogous experiment, Eu(ClO$_4$)$_3$/tyrosine mixture was subjected to hydrolysis by aqueous NaOH in the presence of added bromide (aqueous HBr), 2•Br$^-$, a pentadecanuclear complex isostructural to 2•Cl$^-$, was obtained with an encapsulated Br$^-$ replacing the corresponding Cl$^-$ (Fig. 8, entry 3). A similar reaction employing Dy(ClO$_4$)$_3$/tyrosine and I$^-$ produced, to our surprise, a ***dodecanuclear*** complex (**3**) whose core structure consists of four corner-sharing [Dy$_4$(μ_3-OH)$_4$]$^{8+}$ cubanes and eight tyrosinate ligands. Two I$^-$ ions are found to be located in the "barrel"-shaped molecule, one above and the other below the middle plane formed by four Dy(III) ions (Fig. 9, entry 4).

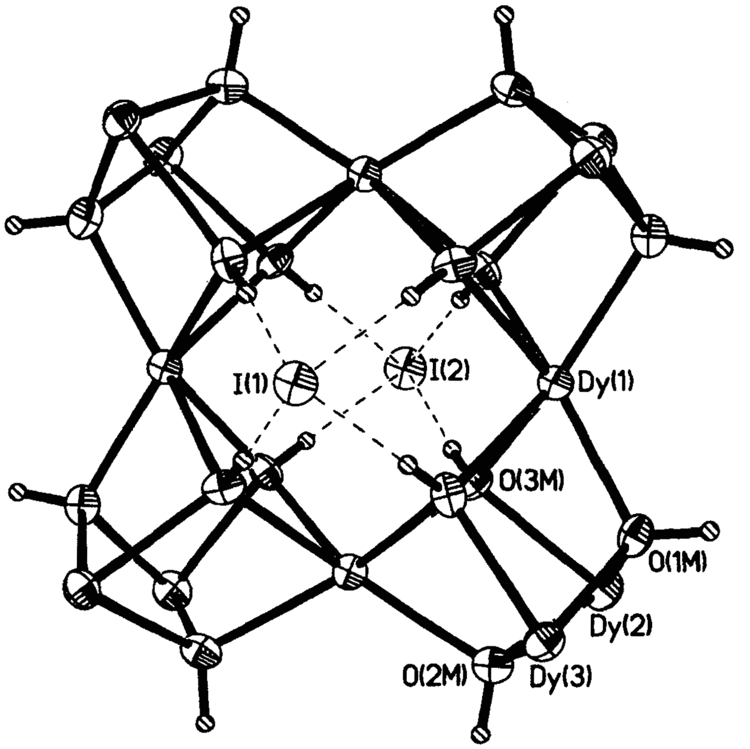


FIGURE 9 An ORTEP drawing of the dodecanuclear "cubane wheel" structure of $3 \cdot (I^-)_2$. Thermal ellipsoids are represented in 50% probability

When $Ln(NO_3)_3$/tyrosine was subject to hydrolysis with no added halide ions, drastically different products of a general formula of $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2$ (**4**) were obtained with no tyrosine ligands incorporated (entry 6)! Further studies demonstrated that direct hydrolysis of $Ln(NO_3)_3$ afforded the same products (see below). The structures of several μ_6-oxo-centered hexanuclear lanthanide clusters have been determined by X-ray diffraction, wherein the nitrate ions act as auxiliary ligands, controlling the spatial extension of the $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]$ core (Figure 10, Ln = Er). However, these structural reports[40,41] hardly compromise the significance of our findings in the context of supporting the anion-template effects. Furthermore, the present study presents the first examples of direct hydrolysis of inorganic salts to afford polynuclear complexes in the absence of any organic supporting ligands. We believe that it is the operation of the μ_6-oxo templating effect that leads to the formation of such complexes. However, when the experiments were conducted in the presence of competitive Cl^-, pentadecanuclear complexes having a core structure identical to that of $2{\bullet}Cl^-$ were obtained as the sole products with NO_3^- counterions (entry 7).

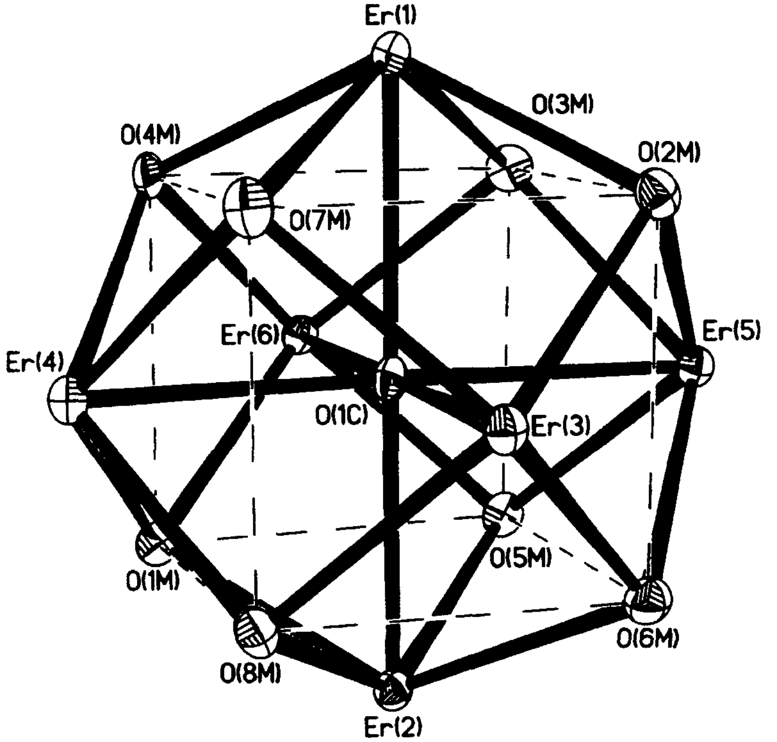


FIGURE 10 An ORTEP drawing of the $[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]$ coordination polyhedron. Thermal ellipsoids are represented in 40% probability

In summary, both *positive* and *negative* evidence has been presented of halide ions serving as templates for the formation of novel polynuclear lanthanide complexes. The generality of the halide-assisted self-assembly of these aesthetically pleasing complexes is supported by the ability to synthesize both the pentadecanuclear complexes incorporating Cl^- and Br^- ions and the analogous dodecanuclear complexes containing two loosely bound iodide ions. The superior templating role played by halide ions is manifested by the competitive formation of the pentadecanuclear chloride-containing complex in a reaction involving both Cl^- and NO_3^- ions. The inability to produce an analogous nitrate-containing complex in the sole presence of NO_3^- ions lends further credence to the templating role played only by a spherical anion. In this case, octahedral complexes were produced with six lanthanide ions centered around a spherical and presumably templating μ_6-O group.[42]

DIRECT HYDROLYTIC ROUTES TO MOLECULAR POLYOXO LANTHANIDE CLUSTERS

The nitrate-containing complexes, $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2$, isolated from the hydrolytic reaction of a mixture of $Ln(NO_3)_3$ and tyrosine and later prepared via direct hydrolysis of $Ln(NO_3)_3$ (eq. 1), represent rare examples of molecular hydrous lanthanide oxides and hydroxides. These compounds were first synthesized by the thermal decomposition of hydrated $Ln(NO_3)_3$ followed by hydrolysis of the decomposition products.[40,41] In the present case, the cluster was obtained regardless of the presence of tyrosine ligands in the reaction mixture, thus excluding the possible suggestion that tyrosine acts as a buffer in such a synthesis. We have subsequently examined the hydrolysis of other lanthanide nitrates and perchlorates in the absence of any conceivable supporting ligands in order to define the scope and limitation of such a direct hydrolytic route to polyoxo lanthanide complexes. Octahedral hexanuclear lanthanide clusters with the common $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ core structure have invariably been isolated.

$$\begin{aligned}&Er(NO_3)_3 + NaOH(aq) \longrightarrow\\&\qquad [Er_6(\mu_6 - O)(\mu_3 - OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2 \qquad \text{(eq.1)}.\end{aligned}$$

Shown in Figure 11 is the core structure of the cationic cluster obtained from the reaction of $Nd(ClO_4)_3$ with aqueous NaOH and established by

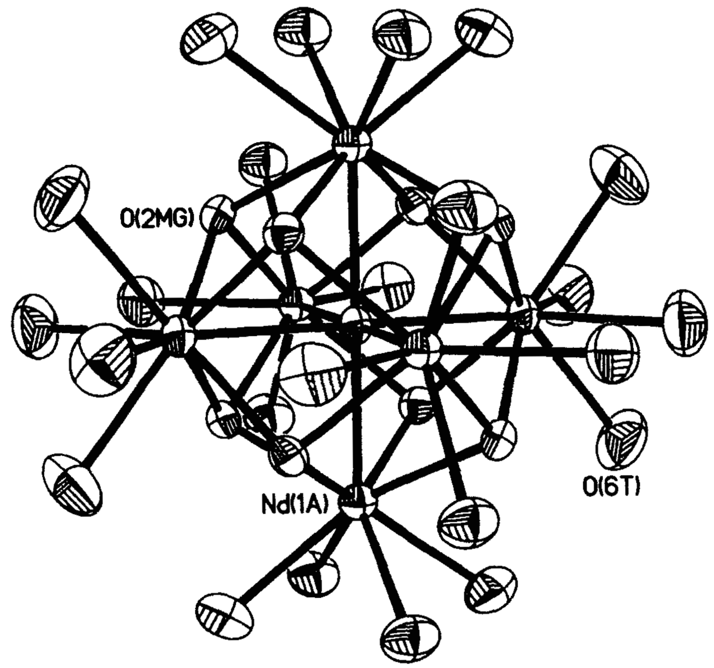


FIGURE 11 Molecular structure of the cation in $[Nd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}](ClO_4)_8\cdot 8H_2O$ with the H atoms removed for clarity. Thermal ellipsoids are shown at the 50% probability level

X-ray diffraction analysis as $[Nd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}](ClO_4)_8\cdot 8H_2O$ (**5**) . It is comprised of an octahedron of neodymium(III) ions centered on a μ_6-oxo ligand. Each of the triangular metal faces is capped by a μ_3-OH ligand. Alternatively, the structure may be described as an octahedron of neodymium protruding out of a cube formed by eight μ_3-OH ligands. Each face of the cube forms the basal plane of a square pyramid with a neodymium occupying the apical position. The average distance from the neodymium to the center of the basal plane is 1.070 Å. The metal coordination sphere is completed with four aqua ligands. Thus, each neodymium ion 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. Complex **5** is, to the best of our knowledge, the first molecular lanthanide cluster with *only co-existing* oxo, hydroxo, and aqua ligands. The 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 various substituted clusters in future work including the construction of open framework structures using the octahedral clusters as building blocks.

Using $Gd(ClO_4)_3$ in an analogous reaction produced complex **6**, formulated as $[Gd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\eta^2\text{-}ClO_4)_2(H_2O)_{20}](ClO_4)_6{\cdot}4H_2O$. The complex bears virtually the same core structure as **5** except that two perchlorate ions are found in the coordination sphere, each of which bridges two adjacent gadolinium ions within the same plane (Fig. 12). Accordingly, only three water molecules are terminally coordinated to each of these four perchlorate-ligated gadolinium centers, whereas four aqua ligands are found with the two remaining metal ions. It is noteworthy that these are highly regular structures 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, either from the aqua ligands or the coordinated perchlorate ions).

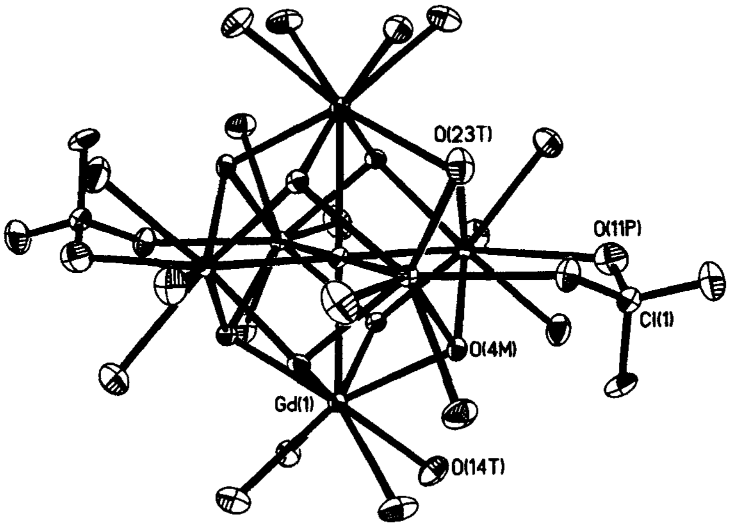


FIGURE 12 Molecular structure of the cation in $[Gd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\eta^2\text{-}ClO_4)_2(H_2O)_{20}](ClO_4)_6{\cdot}4H_2O$ with the H atoms removed for clarity. Thermal ellipsoids are shown at the 40% probability level

The octahedral $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ cluster core appears to be a common structural motif in lanthanide oxides and hydroxides, as demonstrated by this work and others.[40,41] Its presence has also been recognized in the polymeric cyanide bridged lanthanide-transition metal complex $\{[Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(DMF)_{16}(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2]^{6+}\}_\infty$,[43] suggesting its unusual stability. Due to its close resemblance to the lanthanide-oxygen lattice of rock salt-type metal oxides, these molecular lanthanide clusters may serve as models for chemistry in the extended lanthanide oxide frameworks. Moreover, lanthanides are involved in a variety of oxide-based advanced materials.[8,9] A current trend is to use lanthanide alkoxides and oxo-alkoxides as precursors for chemical routes (sol-gel process, for example) to such materials.[8,9,44] Molecular oxides and hydroxides are more desirable precursors as compared to the extremely moisture-sensitive alkoxides.[44] As exemplified by the formation of complexes **4–6**, these molecular lanthanide clusters can be achieved via direct hydrolysis of lanthanide perchlorates and nitrates, thus providing a new procedure for the synthesis of otherwise hard-to-achieve molecular lanthanide clusters.

UNUSUAL EDTA-LANTHANIDE COORDINATION CHEMISTRY UNDER HIGH-PH CONDITIONS

Prompted by the close relationship between polyaminopolycarboxylic acids and amino acids and in an attempt to evaluate the scope of the high-pH hydrolytic approach to polynuclear lanthanide clusters, we set out to re-evaluate, under much higher pH conditions however, the classical coordination chemistry of lanthanide with polyaminopolycarboxylic acids.[32] A major underlying goal of this effort is to synthesize new MRI contrast agents.[2] On the one hand, extra stability of such agents is likely to be derived from the compact cluster structure in addition to that gained from ligand chelating interactions. On the other hand, the performance of the agents would be enhanced due to the high content of paramagnetic centers and the increased number of exchangeable aqua ligands.[2]

Our initial foray has been focused on ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA), the venerable and one of the most studied polyaminopolycarboxylic acids.[45] Since its introduction more than five decades ago for the complexometric determination of metal ions,[46] the EDTA ligand has literally revolutionized analytical chemistry. Its successful uses as a volumetric reagent or a masking agent in such techniques as colorimetry, chromatography, polarography, and electrophoresis lie in its ability to form elaborate metal complexes with stable five-membered rings involving the metal ion and both the oxygen and nitrogen atoms of the ligand. For lanthanide ions, their exclusively mononuclear complexes with EDTA are normally prepared at pH 5–6 in aqueous solutions.[45] These complexes, represented by the general chemical formula $M[Ln(EDTA)(H_2O)_m]{\bullet}nH_2O$ (M = an alkali metal ion), have invariable 1:1 (EDTA:Ln) composition, wherein an EDTA molecule acts as a hexadentate ligand with contribution from its two coordinating nitrogen atoms and four unidentate carboxylate groups (Fig. 13, **A**). It is our intent, using a structurally unprecedented EDTA-neodymium complex, to illustrate how the otherwise well-established chemistry can be profoundly affected by simply increasing the pH of the reaction mixture.

Our efforts started with a detailed structural analysis of the crystallographically characterized Ln-EDTA complexes. Although the coordination numbers (CN) of these complexes range from 8 to 10 depending on both M and Ln sizes, the 9-coordinate geometry is the predominant one with the coordination of one hexadentate EDTA and three accompanying aqua ligands (Fig. 13, **B**).[47] Further analysis of these structures provides the O(water)-Ln-O(water) bond angle values that rang from 70.0° to 83.3°.[47] These values are very close to those (from 68.1° to 76.8°) found for the $O(\mu_3\text{-}OH)\text{-}Ln\text{-}O(\mu_3\text{-}OH)$ angles in the $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ unit.[11] It seemed plausible that if the pH of a lanthanide-EDTA reaction mixture is raised, the aqua ligand(s) of the initially formed 9-coordinate complex would be deprotonated, giving rise to a hydroxo complex of lanthanide with EDTA (Fig. 13, **C**). Subsequent condensation of this hydroxo complex would afford a tetranuclear lanthanide cluster, bearing the cuboid $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ unit whose metal centers are capped by EDTA ligands (Fig. 13, **D**). Although the product (**7**, *see below*) isolated from a mixture of $Nd(ClO_4)_3$ and $Na_2H_2EDTA{\bullet}2H_2O$ subject to a high-pH condition is not exactly the one originally targeted, its formation can be readily rationalized based on the initial design.

The structure of this compound $Na_8\{[Na(H_2O)_2]_4[Nd_{12}(\mu_3\text{-}OH)_{16}(EDTA)_8]\}21H_2O$ was established by single crystal X-ray diffraction. The IR spectrum of **7** exhibits a strong and broad absorption at 3443 cm^{-1}, consistent with its high water con-

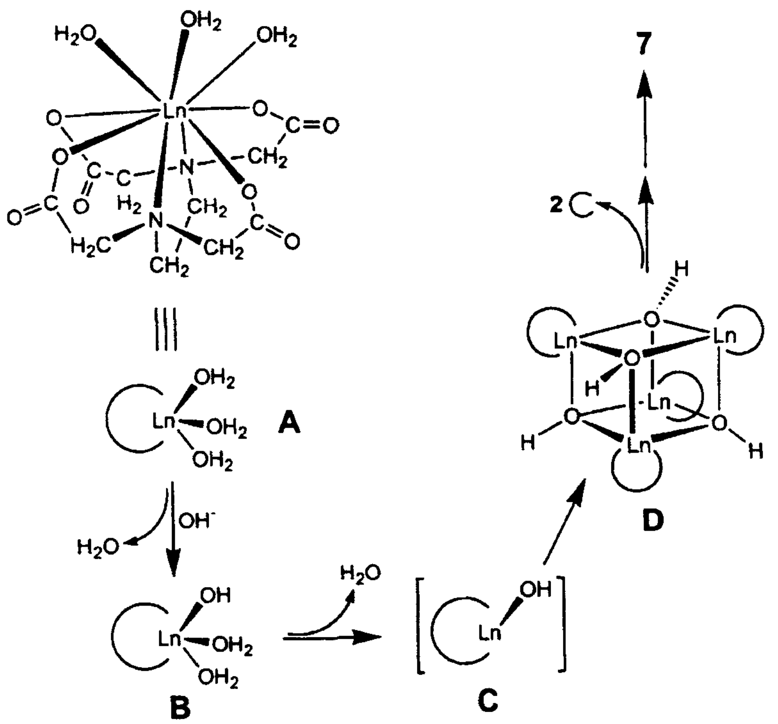


FIGURE 13 Postulated synthesis of a dodecanuclear lanthanide complex with EDTA ligands

tent.[48] This band possibly obscures a peak around 3600 cm^{-1} that is attributable to the stretching of the hydroxo ligands.[14] Furthermore, a strong and broad band appears at 1600 cm^{-1}, comprising both the stretching of the lanthanide-coordinating carboxylate groups and the bending of water molecules.[34]

The anionic cluster whose structure is shown in Figure 14 contains 12 Nd(III) ions and 8 EDTA ligands in addition to 16 hydroxo groups associated with hydrolysis. Its skeletal structure is identical to that of the diiodide complex obtained from the hydrolytic reaction of $Dy(ClO_4)_3$, KI, and tyrosine at pH ~ 7.[28] The metal ions are assembled into a layered structure. Each of the three parallel layers contains 4 Nd(III) ions, occupying the vertices of a perfect square. The two outer layers are crystallo-

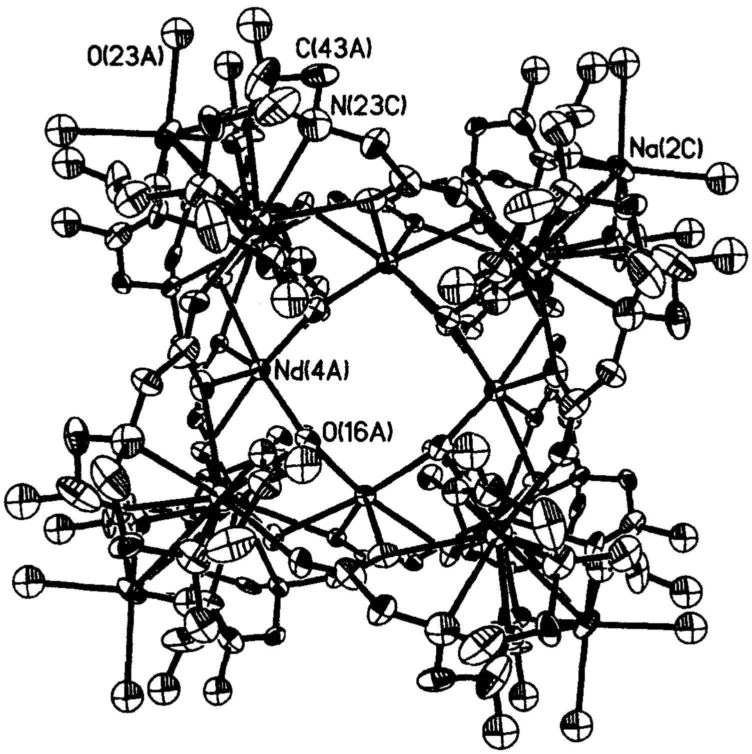


FIGURE 14 Molecular structure of the anion in $\{[Na(H_2O)_2]_4[Nd_{12}(\mu_3\text{-}OH)_{16}(EDTA)_8]\}^{8-}$ with the H atoms removed for clarity. Thermal ellipsoids are shown at the 25% probability level (See Color Plate II at the back of this issue)

graphically equivalent with an Nd-Nd distance of 6.465 Å, while the middle layer, with an Nd-Nd distance of 3.996 Å, is unique and "tucked in". The 8 EDTA ligands occupy the vertices of a perfect tetragon, each capping one of the eight metal ion in the two outer layers. The coordination mode of EDTA in **7** is significant: Each EDTA ligand acts as an *octadentate* (Fig. 15) as opposed to the well-known hexadentate one. One of the carboxylate groups together with the nitrogen atom onto which it attaches can be described as a $\mu_3{:}\eta^1{:}\eta^2{:}\eta^1$ anion, not only linking two neighboring Nd(III) centers within the same (outer) layer, but also coordinating a third Nd(III) ion in the middle layer through one of

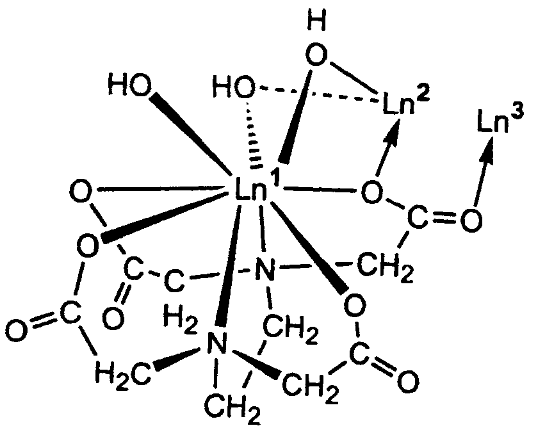


FIGURE 15 The well-known hexadentate mode of an EDTA ligand to Ln[1] with the unprecedented octadentate coordination mode to three lanthanide ions indicated by inclusion of the bridging sites to Ln[2] and Ln[3]

the carboxylate oxygen atoms. Such a coordination mode, first observed in the aforementioned lanthanide-tyrosine complexes,[11] is unprecedented for EDTA. It is apparent that such layer-crossing chelating interactions are critical to the cluster formation. 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 out layer Nd(III) ion has a CN of 10, and its coordination polyhedron may be best described as a bicapped square antiprism. Examples of 8- and 10-coordinate Nd(III) are rare; Nd-containing complexes are predominantly 9-coordinate with the tricapped trigonal prism being the favored structure.[49] The core component of the cluster may alternatively be viewed as a "wheel" of four corner-sharing $[Nd_4(\mu_3\text{-}OH)_4]^{8+}$ cubanes and the overall structure may be described as a "cubane wheel" caged by a tetragon formed by the eight EDTA ligands. In the solid state, such individual cages are connected via Na-O (EDTA carboxylate) interactions to form a 1-D polymeric array.

The square openings in **7** could potentially permit entry by a guest molecule or ion. The strong preference of light lanthanide ions such as Nd(III) for 9-coordinate geometry[50] coupled with the high affinity of

Ln(III) for a fluoride ion[51] suggest that the fluoride complex of **7** with the anionic guest species sitting in the square-shaped opening is possible.

PRINCIPAL RESULTS AND CONCLUSIONS

- Ligand-controlled hydrolysis is a valid approach to the synthesis of polynuclear lanthanide complexes.
- Amino acids are a novel class of supporting ligands for controlling the hydrolysis of lanthanide ions. Under physiological or even higher pH conditions, lanthanide complexation with amino acids may be achieved via only the carboxylate group or simultaneous coordination of both the carboxylate and the amino moieties.
- pH conditions have strong influence on the outcome of lanthanide coordination chemistry, as demonstrated by the unprecedented EDTA-lanthanide complexes from otherwise well-established chemistry.
- Lanthanide complexes generated by "high"-pH coordination typically exist as discrete lanthanide-hydroxo clusters, whereas their low-pH counterparts are in mono-, di-, or polynuclear forms.[52] It is the unconventionally "high" pH condition that promotes the formation of the large molecular clusters.
- Cuboid $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$clusters are a common structural motif in lanthanide coordination compounds, which complement their *d*-block metal counterparts. Bridging ligands with more than one carboxylate group may support open framework structures using the $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cluster unit as building blocks.
- Octahedral $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ core-containing clusters with an interstitial μ_6-O ligand can be assembled via direct hydrolysis of lanthanide nitrates and perchlorates in the absence of any organic supporting ligands.
- Spherical anionic species are important in templating the formation of ring-like lanthanide cluster complexes.

OUTLOOKS

The results detailed above suggest extensive and promising coordination chemistry of lanthanides 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 $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cluster units formed with tyrosine ligands while monocluster complexes are generated with carboxylate-only coordination when alanine, valine, glycine, or glutamic acid 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 readily 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 research 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 desired properties.

Acknowledgements

The financial support of this work from the State of Arizona (Materials Characterization Program) and The University of Arizona (start-up fund) is gratefully acknowledged. The authors thank Dr. Michael D. Carducci for his splendid crystallography that has continually oriented our research and Professor F.A. Walker for her valuable suggestions.

References

1. G.R. Choppin and J.-C.G. Bünzli, eds. *Lanthanide Probes in Life, Chemical and Earth Science*, (Elsevier, Amsterdam, 1989).
2. S. Aime, M. Botta, M. Fasano and E. Terreno, Chem. Soc. Rev. **27**, 19–29 (1998).
3. T. Imamoto, *Lanthanides in Organic Synthesis*, (Academic Press, New York, 1994).
4. C. Benelli, A. Caneschi, D. Gatteschi and L. Pardi, in *Magnetic Molecular Materials*, D. Gatteschi, O. Kahn, J.S. Miller and F. Palacio, eds. (NATO ASI Series 198, Kluwer Academic, Dordrecht, 1991), pp. 233–244.
5. N. Sabbatini, M. Guardigli and J.-M. Lehn, Coord. Chem. Rev. **123**, 201–228 (1993).
6. D. Parker and J.A.G. Williams, J. Chem. Soc. Dalton Trans. 3613–3628 (1996).
7. R. Anwander, Angew. Chem. Int. Ed. **37**, 599–602 (1998).
8. L.G. Hubert-Pfalzgraf, New J. Chem. **19**, 727–750 (1995).

9. P. Chanaud, A. Julbe, P. Vaija, M. Persin and L. Cot, J. Mater. Sci. **29**, 4244–4251 (1994).
10. X. Chen, S.M.J. Aubin, Y. Wu, Y. Yang, T.C.W. Mak and D.N. Hendrickson, J. Am. Chem. Soc. **117**, 9600–9601 (1995).
11. R. Wang, T. Jin, Z. Zheng and R.J. Staples, Angew. Chem. Int. Ed. **38**, 1813–1815 (1999).
12. J.C. Plakatouras, I. Baxter, M.B. Hursthouse, K.M. Abdul Malik, J. McAleese and S.R. Drake, J. Chem. Soc. Chem. Commun. 2455–2456 (1994).
13. X.M. Chen, Y.L. Wu, Y.X. Tong, Z. Sun and D.N. Hendrickson, Polyhedron **16**, 4265–4272 (1997).
14. T. Dubé, S. Gambarotta and G. Yap, Organometallics **17**, 3967–3973 (1998).
15. D. Freedman, J.H. Melman, T.J. Emge and J.G. Brennan, Inorg. Chem. **37**, 4162–4163 (1998).
16. J.E. McGrady, J. Chem. Soc. Dalton Trans. 1393–1399 (1999).
17. G.L. Abbati, A. Cornia, A.C. Fabretti, A. Caneschi and D. Gatteschi, Inorg. Chem. **37**, 3759–3766 (1998).
18. G. Christou, in ***Magnetism: A Supramolecular Function***, O. Kahn, ed. (NATO ASI Series 484, Kluwer Academic, Dordrecht, 1996), pp. 383–409.
19. Caneschi, A. Cornia, A.C. Fabretti and D. Gatteschi, Angew. Chem. Int. Ed. **38**, 1295–1297 (1999).
20. R. Bhula and D.C. Weatherburn, Angew. Chem. Int. Ed. Engl. **30**, 688–689 (1991).
21. M. Cavalluzzo, Q. Chen and J. Zubieta, J. Chem. Soc. Chem. Commun. 131–133 (1993).
22. Goldberg, D.P.; Caneschi, A.; Delfs, C.D.; Sessoli, R.; Lippard, S.J.J. Am. Chem. Soc. **117**, 5789–5800 (1995).
23. Müller and J. Döring, Angew. Chem. Int. Ed. Engl. **27**, 1721–1721 (1988).
24. K.L. Taft, C.D. Delfs, G.C. Papaefthymiou, S. Foner, D. Gatteschi and S.J. Lippard, J. Am. Chem. Soc. **116**, 823–832 (1994).
25. D. Gatteschi, A. Caneschi, L. Pardi and R. Sessoli, Science **265**, 1054–1058 (1994).
26. Complexes of the Rare Earths; Sinha, S.P. Pergamon: New York, 1966; pp 36–81.
27. R. Wang, M.D. Carducci, T. Jin and Z. Zheng, Inorg. Chem. Submitted (1999).
28. R. Wang, M.D. Carducci, T. Jin and Z. Zheng, J. Am. Chem. Soc. In preparation (1999).
29. K. Apana, S.S. Krishnamurthy and M. Nethaji, Polyhedron **13**, 2993–2997 (1994).
30. R. Wang, F. Gao and T. Jin, Huaxue Tongbao, **10**, 14–20 (1996).
31. K. Severin, R. Bergs and W. Beck, Angew. Chem. Int. Ed. **37**, 1634–1654 (1998).
32. G.R. Choppin and P.J. Wong, in *Coordination* Chemistry: ***A Century of Progress***, G.B. Kauffman, ed. (ACS Symposium Series 565, Washington, DC, 1994), pp 346–360.
33. O.E. Zvyagintsev and E.V. Goncharov, Russ. J. Inorg. Chem. **7**, 970–977 (1962).
34. Djordjevic and N. Vuletic, Inorg. Chem. **19**, 3049–3053 (1980).
35. R. Wang, M.D. Carducci, T. Jin and Z. Zheng, Chem. Commun. Submitted (1999).
36. T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O.M. Yaghi, J. Am. Chem. Soc. **121**, 1651–1657 (1999).
37. V. Kiritis, A. Michaelides, S. Skoulika, S. Golhen and L. Ouahab, Inorg. Chem. **37**, 3407–3410 (1998).
38. J.L. Sessler, P.I. Sansom, A. Andrievsky and V. Kral, in ***Supramolecular Chemistry of Anions***, A. Bianchi, K. Bowman-James and E. García-España, eds.; (Wiley-VCH, New York, 1997), pp. 355–403.
39. Y. Marcus, Chem. Soc. Faraday Trans. **87**, 2995–2999 (1991).
40. Zák, P. Unfried and G. Giester, J. Alloys and Compd. **205**, 235–242 (1994).
41. G. Giester, P. Unfried and Z. Zák, J. Alloys and Compd. **257**, 175–181 (1997).

42. E.H. Barash, P.S. Coan, E.B. Lobkovsky, W.E. Streib and K.G. Caulton, Inorg. Chem. **32**, 497–501 (1993).
43. J. Liu, E.A. Meyers and S.G. Shore, Inorg. Chem. **37**, 5410–5411 (1998).
44. R.C. Mehrotra and A. Singh, Chem. Soc. Rev. 1–13 (1996).
45. R. Přibil, *Analytical Applications of EDTA and Related Compounds*, (Pergamon Press, New York, 1972).
46. G. Schwarzenbach and H. Flaschka, *Complexometric Titrations*, (2nd ed. Methuen, London, 1969).
47. N. Sakagami, Y. Yamada, T. Konno and K. Okamoto, Inorg. Chim. Acta **288**, 7–16 (1999).
48. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, (5th ed., Wiley, New York, 1997).
49. L. Niinistö, in *Systematics and the Properties of the Lanthanides*, S.P. Sinha ed. (NATO ASI Series C No. 109, Reidel Publishing Company, Dordrecht, 1982), pp. 125–152.
50. Leclaire, J. Solid State Chem. **28**, 235–244 (1979).
51. T. Kurisaki, T. Yamaguchi and H. Wakita, J. Alloys and Compd. **192**, 293–295 (1993).
52. Ouchi, Y. Suzuki, Y. Ohki and Y. Koizumi, Coord. Chem. Rev. **92**, 29–43 (1988).