Lanthanide Coordination with α-Amino Acids under Near Physiological pH Conditions: Polymetallic Complexes Containing the Cubane-Like [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ Cluster Core

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Tetranuclear lanthanide−hydroxo complexes of the general formula [Ln$_4$(μ_3-OH)$_4$(AA)$_x$(H$_2$O)$_y$]$^{8+}$ (**1**, Ln = Sm, AA = Gly, x = 5, y = 11; **2**, Ln = Nd, AA = Ala, x = 6, y = 10; **3**, Ln = Er, AA = Val, x = 5, y = 10) have been prepared by α-amino acid controlled hydrolysis of lanthanide ions under near physiological pH conditions (pH 6−7). The core component of these compounds is a cationic cluster [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ whose constituent lanthanide ions and triply bridging hydroxo groups occupy the alternate vertexes of a distorted cube. The amino acid ligands coordinate the lanthanide ions via bridging carboxylate groups. Utilizing L-glutamic acid as the supporting ligand, a cationic cluster complex (**4**) formulated as [Er$_4$(μ_3-OH)$_4$(Glu)$_3$(H$_2$O)$_8$]$^{5+}$ has been obtained. Its extended solid-state structure is composed of the cubane-like [Er$_4$(μ_3-OH)$_4$]$^{8+}$ cluster building units interlinked by the carboxylate groups of the glutamate ligands. All compounds are characterized by using a combination of spectroscopic techniques and microanalysis (CHN and metal). Infrared spectra of the complexes suggest the coordinated amino acids to be zwitterionic. The presence of mass (MALDI-TOF) envelopes corresponding to the [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ (Ln = trivalent Sm, Nd, or Er) core containing fragments manifests the integrity of the cubane-like cluster unit. Magnetic studies using Evans' method suggest that exchange interactions between the lanthanide ions are insignificant at ambient temperature. The structural identities of all four compounds have been established crystallographically. The tetranuclear cluster core has been demonstrated to be a common structural motif in these complexes. A mechanism responsible for its self-assembly is postulated.

Introduction

Recently, the catalytic roles of lanthanide ions and their complexes in hydrolytic cleavage of phosphate diesters have received considerable attention.[2] It is generally agreed that the catalysis occurs via substrate activation by the electropositive lanthanide ions, followed by nucleophilic attack by the activated hydroxo ligands (Figure 1).[2b,d,e,g,l] However, the ease of lanthanide ion hydrolysis and the tendency of lanthanide−hydroxo species to form polynuclear aggregates in solution render unambiguous identification of the catalytically active species extremely difficult, if at all possible.[2b−i] On the other hand, although there are a few reports of structurally characterized dinuclear[3] and tetranuclear[4] lanthanide−hydroxo complexes
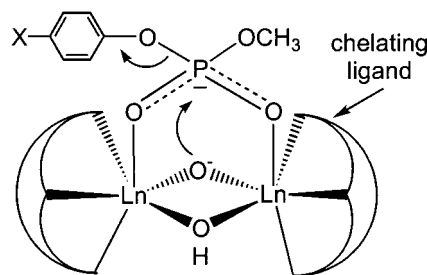
Figure 1. A possible mechanism of the activation and cleavage of a phosphate diester substrate by a dinuclear lanthanide−hydroxo species.

(Figure 2), the catalytic potential of these species has not yet been assessed. Furthermore, these compounds are either synthetic serendipities or accidents, and general synthetic guidelines are lacking. With the ultimate goal of achieving nonenzymatic hydrolysis of phosphate diesters using lanthanide catalysts, our *initial* efforts[5] focus on the *design* and *synthesis* of structurally well-defined lanthanide−hydroxo complexes with biologically relevant ligands.

(1) (a) University of Arizona. (b) Peking University. (c) Northern Illinois University.

(2) For leading references on lanthanide-catalyzed hydrolysis of phosphate diester substrates, see: (a) Williams, N. H.; Takasaki, B.; Wall, M.; Chin, J. *Acc. Chem. Res.* **1999**, *32*, 485−493. (b) Schneider, H.-J.; Rammo, J.; Hettich, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1716−1719. (c) Rammo, J.; Hettich, R.; Roigk, A.; Schneider, H.-J. *Chem. Commun.* **1996**, 105−107. (d) Oh, S. J.; Song, K. H.; Whang, D.; Kim, K.; Yoon, T. H.; Moon, H.; Park, J. W. *Inorg. Chem.* **1996**, *35*, 3780−3785. (e) Oh, S. J.; Choi, Y.-S.; Hwangbo, S.; Bae, S. C.; Ku, J. K.; Park, J. W. *Chem. Commun.* **1998**, 2189−2190. (f) Roigk, A.; Hettich, R.; Schneider, H.-J. *Inorg. Chem.* **1998**, *37*, 751−756. (g) Jurek, P. E.; Jurek, A. M.; Martell, A. E. *Inorg. Chem.* **2000**, *39*, 1016−1020. (h) Ragunathan, K. G.; Schneider, H.-J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1219−1221. (i) Takasaki, B. K.; Chin, J. *J. Am. Chem. Soc.* **1993**, *115*, 9337−9338. (j) Komiyama, M. *J. Biochem.* **1995**, *118*, 665−670. (k) Takasaki, B. K.; Chin, J. *J. Am. Chem. Soc.* **1995**, *117*, 8582−8585. (l) Hurst, P.; Takasaki, B. K.; Chin, J. *J. Am. Chem. Soc.* **1996**, *118*, 9982−9983. (m) Bracken, K.; Moss, R. A.; Ragunathan, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 9323−9324.

(3) (a) Baraniak, E.; Bruce, R. St. L.; Freeman, H. C.; Hair, N. J.; James, J. *Inorg. Chem.* **1976**, *15*, 2226−2230. (b) Grillone, M. D.; Benetollo, F.; Bombieri, G. *Polyhedron* **1991**, *10*, 2171−2177. (c) Wang, R.; Zhao, J.; Jin, T.; Xu, G.; Zhou, Z.; Zhou, X. *Polyhedron* **1998**, *17*, 43−47.

(4) (a) Dubé, T.; Gambarotta, S.; Yap, G. *Organometallics* **1998**, *17*, 3967−3973. (b) Chen, X. M.; Wu, Y. L.; Tong, Y. X.; Sun, Z.; Hendrickson, D. N. *Polyhedron* **1997**, *16*, 4265−4272. (c) Plakatouras, J. C.; Baxter, I.; Hursthouse, M. B.; Abdul Malik, K. M.; McAleese, J.; Drake, S. R. *J. Chem. Soc. Chem. Commun.* **1994**, 2455−2456.
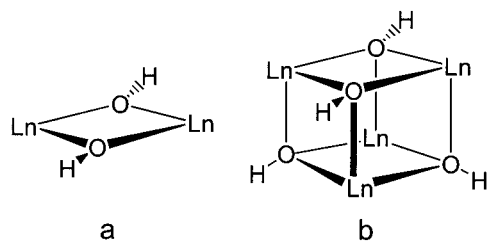
Figure 2. Core components of crystallographically characterized dinuclear (a) and tetranuclear (b) lanthanide–hydroxo species.

As synthetic targets, the tetranuclear hydroxo complexes are of particular interest because they may be considered structurally as the dimeric form of the dinuclear species. More importantly, they may be more potent than the previously postulated dinuclear species for catalysis because of the extra Lewis acidic metal ions. Our striving to systematically and reliably produce such tetranuclear complexes was stimulated by the three seemingly unrelated literature precedents,[4] each of which possesses a tetranuclear cluster core whose constituent lanthanide ions and triply bridging hydroxo groups occupy the alternate vertexes of a distorted cube. This common motif led to our suspicion that such a cubane-like structure may actually be a general one, analogous to its extensively studied d-block counterparts.[6] Furthermore, the presence of the hydroxo ligands suggests that these clusters may be synthesized by the carefully controlled hydrolysis of the lanthanide ions.

It was realized at the outset that certain types of supporting ligands would be necessary to limit the hydrolysis to avoid the formation of intractable lanthanide hydroxides and/or oxohydroxides. Using α-amino acids, including glycine, alanine, valine, tyrosine,[7] and glutamic acid (Figure 3) in this capacity, the validity of this ligand-controlled hydrolytic approach was tested in a series of proof-of-concept syntheses. Polymetallic complexes containing the cuboid [Ln₄(μ₃-OH)₄]⁸⁺ cluster unit(s) were indeed obtained under near physiological pH conditions (6−7). We report here the synthetic details and structural characterization of these compounds. The synthetic significance of preparing lanthanide cluster complexes using a general ligand-controlled hydrolytic approach and the implications of assembling lanthanide–hydroxo complexes with biologically relevant ligands for nonenzymatic catalysis will be discussed.
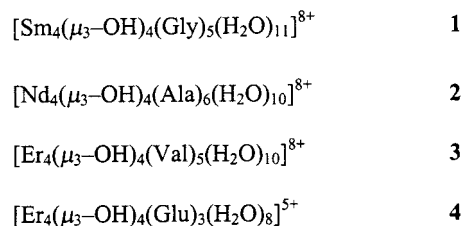
Experimental Section

Preparation of Compounds. *Caution: Metal perchlorates are potentially explosive! Only a small amount of materials should be prepared and handled with great care.* However, careful tests on the
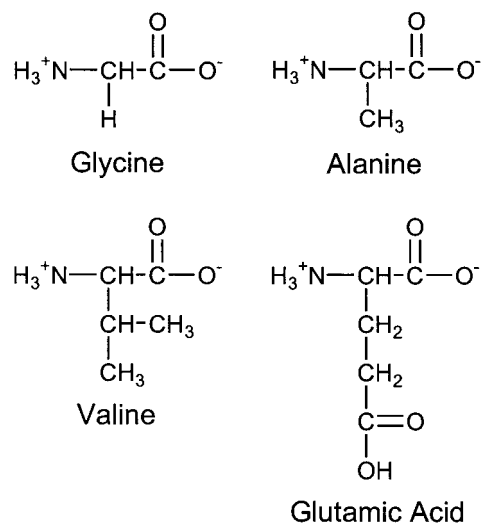
Figure 3. Zwitterionic structures of the α-amino acids discussed in this work.

Chart 1

$$[Sm_4(\mu_3{-}OH)_4(Gly)_5(H_2O)_{11}]^{8+} \qquad \textbf{1}$$

$$[Nd_4(\mu_3{-}OH)_4(Ala)_6(H_2O)_{10}]^{8+} \qquad \textbf{2}$$

$$[Er_4(\mu_3{-}OH)_4(Val)_5(H_2O)_{10}]^{8+} \qquad \textbf{3}$$

$$[Er_4(\mu_3{-}OH)_4(Glu)_3(H_2O)_8]^{5+} \qquad \textbf{4}$$

materials in our studies showed no apparent hazards. Small amounts (5−10 mg) charred when heated in open air. All reagents[8] were of commercial origin, and were used as received. Aqueous solutions of lanthanide perchlorates and chlorides were prepared by digestion of lanthanide oxides in concentrated perchloric acid and hydrochloric acid, respectively. A suitable concentration was achieved by dilution with deionized water, and the exact concentration was determined by complexometric titration with EDTA using xylenol orange as the indicator. Compounds were characterized by IR, elemental analysis, and MALDI-TOF mass spectrometry. The structural identities of the compounds were established by X-ray diffraction studies. The formulas used in this section are the analytical ones. For complexes **1** and **4** (see Chart 1 for designation), they are the same as the crystallographic ones, whereas the analytical formulas of complexes **2** and **3** contain 10 and 3 more water molecules, respectively, than the corresponding crystallographic formulas (Table 1).

[Sm₄(μ₃-OH)₄(Gly)₅(H₂O)₁₁(ClO₄)](ClO₄)₇·NaClO₄. Glycine (0.600 g, 8.00 mmol) was added as a solid to an aqueous solution of Sm(ClO₄)₃ (1.0 M, 16 mL). With stirring and at 80 °C, an aqueous NaOH solution (0.5 M, ca. 5 mL) was added dropwise to the above solution (pH ≈ 2) to the point of incipient precipitation. The mixture was then filtered, and the filtrate was allowed to stand at room temperature. Parallelepiped crystals of the lanthanide complexes appeared in about one week. The crystalline product was collected by filtration, washed with a mixture of THF/ether (1:1 v/v), and dried in a desiccator charged with silica gel. Yield: 45%. Anal. Calcd for C₁₀H₅₁-Cl₉N₅NaO₆₁Sm₄: C, 5.55; H, 2.38; N, 3.24; Sm, 27.83. Found: C, 5.49; H, 2.29; N, 3.20; Sm, 27.52. IR: ν 3444 s, 3253 m, 1620 s, 1487 m, 1456 m, 1417 m, 1341 m, 1120 s, 1108 s, 1085 s, 903 w, 627 s, 535 m cm⁻¹. μ_{eff}^{293K} = 2.74 μ_B, calcd 3.10 μ_B. MALDI-MS (rel intens, %): 1840.00 (21) [M − 2H₂O − 2ClO₄⁻ − NaClO₄]²⁺, 1671.82 (35) [M − 3H₂O − 2Gly − 2ClO₄⁻ − NaClO₄]²⁺, 1066.45 (100) [M − 9H₂O − 2Gly − 7ClO₄⁻ − NaClO₄]⁷⁺, 934.31 (92) [M − 8H₂O − 4Gly − 7ClO₄⁻ − NaClO₄]⁷⁺, 916.29 (62) [M − 9H₂O − 4Gly − 7ClO₄⁻ − NaClO₄]⁷⁺.

(5) (a) Zheng, Z.; Wang, R. *Comments Inorg. Chem.* **2000**, *22*, 1−30. (b) Wang, R.; Jin, T.; Zheng, Z.; Zheng, Z.; Staples, R. J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1813−1815. (c) Ma, B.; Zhang, D.; Gao, S.; Jin, T.; Yan, C. *New J. Chem.* **2000**, *24*, 251−252. (d) Ma, B.; Zhang, D.; Gao, S.; Jin, T.; Yan, C.; Xu, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3644−3646.

(6) For leading references on cubane-like transition-metal clusters, see: (a) Seino, H.; Mizobe, Y.; Hidai, M. *Organometallics* **2000**, *19*, 3631−3639. (b) McGrady, J. E. *J. Chem. Soc., Dalton Trans.* **1999**, 1393−1399. (c) Herskovitz, T.; Averill, B. A.; Holm, R. H.; Ibers, James A.; Phillips, W. D.; Weiher, J. F. *Proc. Nat. Acad. Sci. U.S.A* **1972**, *69*, 2437−41. (d) Holm, R. H. *Adv. Inorg. Chem.* **1992**, *38*, 1−71. (e) Taft, K. L.; Caneschi, A.; Pence, L. E.; Delfs, C. D.; Papaefthymiou, G. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 11753−11766. (f) Dimitrou, K.; Brown, A. D.; Folting, K.; Christou, G. *Inorg. Chem.* **1999**, *38*, 1834−1841. (g) Real, J. A.; Munno, G. D.; Chiappetta, R.; Julve, M.; Lloret, F.; Journaux, Y.; Colin, J.-C.; Blondin, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1184−1186.

(7) When tyrosine was utilized as the supporting ligand, halide-templated cyclic lanthanide complexes composed of four or five vertex-sharing [Ln₄(μ₃-OH)₄]⁸⁺ building blocks were obtained. See ref 5b.

(8) Abbreviations: Ala, alanine; Gly, glycine; Val, valine; Glu, glutamic acid.

Table 1. Crystal Data[a] and Structure Refinement of Complexes **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{10}H_{51}Cl_{19}N_5NaO_{61}Sm_4$	$C_{18}H_{72}Cl_{12}N_6Na_4Nd_4O_{87}$	$C_{25}H_{103}Cl_8Er_4N_5O_{36}$	$C_{15}H_{54}Cl_5Er_4N_3O_{50}$
fw	2161.02	2859.14	2002.76	1922.9
space group	$P\bar{1}$	$R32$	$P1$	$P2_12_12_1$
Z	2	6	1	4
a, Å	12.155(3)	19.549(3)	11.6306(10)	14.619(4)
b, Å	20.474(6)	19.549(3)	12.6918(11)	17.211(4)
c, Å	25.394(7)	41.816(8)	13.1148(12)	21.215(5)
α, deg	106.473(5)	90	82.466(2)	90
β, deg	98.575(5)	90	65.7640(10)	90
γ, deg	93.820(5)	120	87.649(2)	90
V, Å^3	5953(3)	13840(4)	1749.9(3)	5338(2)
d_{calcd}, g/cm^3	2.411	2.058	1.901	2.393
μ, mm^{-1}	4.438	2.714	5.134	6.600
R1[b] (wR2[c]), %	4.37 (12.67)	4.31 (8.47)	3.31 (8.53)	3.85 (9.72)

[a] Obtained with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. [c] wR2 $= \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$.

[Nd$_4$(μ_3-OH)$_4$(H$_2$O)$_{10}$(Ala)$_6$](ClO$_4$)$_8$·4NaClO$_4$·23H$_2$O. This compound was prepared following the preceding procedure using D,L-alanine (0.713 g, 8.00 mmol) and an aqueous solution of Nd(ClO$_4$)$_3$ (1.0 M, 16 mL). Yield: 60%. Anal. Calcd for C$_{18}$H$_{112}$Cl$_{12}$N$_6$Na$_4$Nd$_4$O$_{97}$: C, 7.06; H, 3.70; N, 2.75; Er, 18.86. Found: C, 7.04; H, 3.22; N, 2.69; Er, 18.94. IR: ν 3419 w, 1620 s, 1480 m, 1428 m, 1380 w, 1347 w, 1305 w, 1142 s, 1108 s, 1188 s, 636 s, 627 s, 548 m cm^{-1}. $\mu_{eff}^{293K} = 6.78$ μ_B, calcd 7.36 μ_B. MALDI-MS (rel intens, %): 2019.97 (34) [M − 25H$_2$O − ClO$_4^-$ − 4NaClO$_4$]$^+$, 1279.11 (48) [M − 33H$_2$O − 7ClO$_4^-$ − 4NaClO$_4$]$^{7+}$, 1227.03 (61) [M − 26H$_2$O − 2Ala − 7ClO$_4^-$ − 4NaClO$_4$]$^{7+}$, 1190.00 (45) [M − 33H$_2$O − Ala − 7ClO$_4^-$ − 4NaClO$_4$]$^{8+}$.

[Er$_4$(μ_3-OH)$_4$(H$_2$O)$_{10}$(Val)$_5$]Cl$_8$·15H$_2$O. This compound was prepared following the preceding procedure using D,L-valine (0.469 g, 4.00 mmol) and an aqueous solution of ErCl$_3$ (1.0 M, 8 mL). Yield: 70%. Anal. Calcd for C$_{25}$H$_{109}$Cl$_8$Er$_4$N$_5$O$_{39}$: C, 14.59; H, 5.34; N, 3.40; Er, 32.53. Found: C, 14.69; H, 5.09; N, 3.08; Er, 32.39. IR: ν 3405 s, 3038 s, 2967 s, 2925 s, 1643 s, 1495 s, 1471 s, 1440 s, 1394 w, 1349 s, 558 s, 485 m cm^{-1}. $\mu_{eff}^{293K} = 18.2$ μ_B, calcd 19.2 μ_B. MALDI-MS (rel intens, %): 1274.22 (54) [M − 21H$_2$O − Val − 8Cl$^-$]$^{8+}$, 1203.32 (56) [M − 20H$_2$O − 3Val − 4Cl$^-$]$^{4+}$, 1043.50 (20) [M − 21H$_2$O − 3Val − 8Cl$^-$]$^{8+}$, 926.33 (12) [M − 21H$_2$O − 4Val − 8Cl$^-$]$^{8+}$, 809.16 (12) [M − 25H$_2$O − 5Val − 8Cl$^-$]$^{8+}$.

[Er$_4$(μ_3-OH)$_4$(Glu)$_3$(H$_2$O)$_8$](ClO$_4$)$_5$·6H$_2$O. This compound was prepared following the preceding procedure using L-glutamic acid (0.588 g, 4.00 mmol) and an aqueous solution of Er(ClO$_4$)$_3$ (1.0 M, 8 mL). Yield: 85%. Anal. Calcd for C$_{15}$H$_{54}$Cl$_5$Er$_4$N$_3$O$_{50}$: C, 9.37; H, 2.84; N, 2.18; Er, 34.79. Found: C, 9.42; H, 2.66; N, 2.10; Er, 34.57. IR: ν 3450 s, 2920 w, 2849 w, 1633 s, 1435 s, 1351 w, 1290 w, 1266 w, 1120 s, 1110 s, 1090 s, 758 m, 627 s, 563 m cm^{-1}.

X-ray Structure Determinations. Structures were determined for all four compounds reported in Table 1. Numerical designations of the clusters are given in Chart 1. For simplicity, in this and the following sections, compounds are referred to by their cation numbers.

X-ray-quality parallelepiped-shaped crystals of **1**−**4** were obtained from the corresponding aqueous solutions at room temperature. Crystals in a glass capillary (**1**, **3**) or coated with paratone oil (**2**, **4**) were attached to glass fibers and transferred to a Bruker SMART 1000 CCD-based diffractometer at 170(2) K (except for **2**, which was at 296(2) K) with Mo Kα radiation ($\lambda = 0.71073$ Å). Preliminary cell constants and an orientation matrix for integration were determined from reflections obtained in three orthogonal 5° wedges of reciprocal space. None of the crystals showed significant decay. The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure amplitudes and their esd's using the program SAINT PLUS and SHELXTL, which corrects for Lp and decay. Absorption corrections were applied using SADABS, supplied by G. Sheldrick. Space group assignments were based on systematic absences, E statistics, and successful refinement of the structural models. The structures were solved with direct methods using the SHELXS-97 program and refined by the least-squares method on F^2 with SHELXL-97, incorporated in SHELXTL-PC v. 5.10. All non-

hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). The solvated water molecules were found by using the program XWAT, supplied within SHELXTL.

In structure **1**, the tangled network of Na$^+$, ClO$_4^-$, and water surrounding the samarium clusters is highly disordered. Eleven of the eighteen ClO$_4^-$ sites required splitting into two or three rotational fragments. High correlations between parameters of the overlapping atoms were combated by restraining individual fragments to have approximately the same geometry as one of the ordered ClO$_4^-$ ions, and where atoms closely overlapped, they were constrained to have the same positional and thermal parameters.

In the refinement of **2**, the well-refined ClO$_4^-$ was used as a similarity model for other independent ClO$_4^-$ units. This compound crystallizes in a noncentrosymmetric space group. The absolute configuration was determined by refinement of the Flack x parameter. Because (R)- and (S)-alanine have very similar shapes, sizes, and X-ray scattering, they may substitute for each other, in which case the methyl and protonated N change positions. In the final model one alanine was given the R configuration while the other alanine was given the S configuration. Other combinations were tried, but were found to be equally well fitting. In addition to the alanine configuration, the orientation and occupancies of Na$^+$ and ClO$_4^-$ can be changed, and most of these sites are partially occupied and/or disordered.

Complex **4** requires five ClO$_4^-$ ions for charge balancing. These were found in four ordered and two half-occupied partially disordered sites. In the refinement, the ClO$_4^-$ ions named in residues 7−11 were constrained to have a geometry similar to that in residue 6, which was the least disordered. The ClO$_4^-$ ions in residues 10 and 11 showed signs of partial occupancy, and as such their refined occupancies (sum constrained to one, but very similar when unconstrained) were 0.57965-(494) and 0.42035(494). This compound crystallizes in a noncentrosymmetric space group. The absolute configuration was determined by refinement of the Flack x parameter. Inspection of the glutamate reveals that all have the L configuration.

Comments on the specific refinement models used, together with other details of the structural determinations, are deposited as Supporting Information.

Other Physical Measurements. The IR spectra were recorded with KBr disks on a Nicolet 510P FTIR spectrophotometer. MALDI-TOF mass spectra were obtained with a Finnigan LCQ spectrometer using MeOH/H$_2$O (1:1) as the solvent. Magnetic moments were measured by Evans' method[9] using ^{1}H NMR spectra recorded on a Bruker AM-250 spectrometer. Acetone-d_6 solutions of the compounds were used, with tetramethylsilane as external reference. Microanalytical services (carbon, hydrogen, and nitrogen) were provided by Desert Analytics Laboratory, Tucson, AZ. The metal content was determined by complexometric titration with EDTA, using xylenol orange as indicator.

(9) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005. (b) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169−173.

Results and Discussion

Ligand-Controlled Hydrolytic Approach to Lanthanide Clusters. In this investigation, we sought polymetallic lanthanide−hydroxo complexes with α-amino acids via ligand-controlled hydrolysis of the lanthanide ions. A similar approach to the assembly of polynuclear complexes of d-block metal ions has yielded great success,[10−14] in that an impressive collection of metal cluster complexes of a variety of unusual symmetries and structural patterns have been obtained. Comparable achievements have not yet been realized with the lanthanide ions. Although a few examples of lanthanide−hydroxo complexes with chelating ligands do exist in the literature,[3,4] most of these species seem to form via partial but uncontrolled hydrolysis of the reaction mixture, and the syntheses are hard to reproduce. However, our recent reports[5] and those by others[15] suggest that the hydrolysis of the lanthanide ions supported by suitable ligands may be used as a general approach to this class of otherwise elusive substances. Closely related to this strategy is the controlled hydrolysis of chemically modified alkoxide precursors in sol−gel processes.[16]

Several classes of ligands have been successfully employed to control the hydrolysis of d-block metal ions, among which carboxylates,[10] polyketonates,[11] polyamines,[12] polyols,[13] and alkoxides[14] are prominent. α-Amino acids are unique in this capacity because they may be viewed as a combination of the carboxylate and amine functional groups. Their modular structures are especially beneficial for systematic studies. Most importantly, α-amino acids are building blocks of proteins; this biological relevance is of special significance in mimicking the enzymatic environment. Interactions of various α-amino acids with the lanthanide ions under acidic conditions (pH 1−4) have been extensively investigated,[17] whereby the resultant complexes
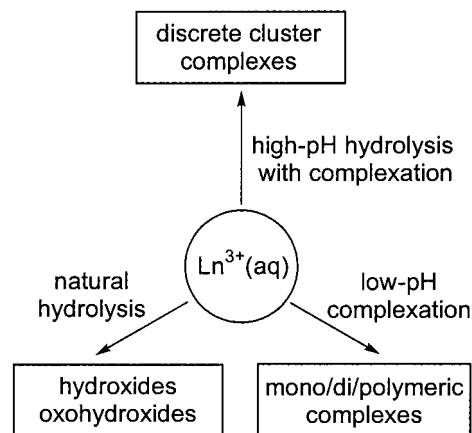
Figure 4. Synthesis of discrete lanthanide cluster complexes via ligand-controlled hydrolytic reactions. Both the low-pH coordination chemistry and the natural hydrolysis of the lanthanide ions are included for comparison.

exist in mononuclear, dinuclear, or noncluster polynuclear forms.[17a] In stark contrast, *we submit that a subtle balance between the hydrolysis of a lanthanide ion and its multiple coordination with a chelating ligand would afford novel polynuclear lanthanide−hydroxo complexes, ideally under physiological pH conditions* (Figure 4). The results from previous low-pH studies serve as a useful database for comparison purposes.

Synthesis. Both lanthanide perchlorates and chlorides are applicable in these reactions. When a stoichiometric amount of an α-amino acid (Ln:AA = 4:6) was used, precipitation of the free ligand resulted; the putative lanthanide complex remained in solution and resisted crystallization. The particular Ln:AA ratio (2:1) used in the present study is based empirically on this solubility consideration. The incorporation of only five amino acid ligands in **1** and **3** may be a reflection of the subtle interplay of kinetics and thermodynamics. The pH of the reaction mixture was adjusted by addition of a dilute aqueous solution of NaOH. The seemingly arbitrary addition of base notwithstanding, the reaction is virtually "fool-proof", and invariably generates the desired products. Heating of the reaction mixture was necessary to facilitate the hydrolytic process, and the end point (pH 6−7) was indicated by the incipient formation of permanent precipitates, presumably of lanthanide hydroxides and/or oxohydroxides. With glycine, D,L-alanine, and D,L-valine, tetranuclear lanthanide complexes of the general formula $[Ln_4(\mu_3\text{-OH})_4(AA)_x(H_2O)_y]^{8+}$ (**1**, Ln = Sm, AA = Gly, $x = 5$, $y = 11$; **2**, Ln = Nd, AA = Ala, $x = 6$, $y = 10$; **3**, Ln = Er, AA = Val, $x = 5$, $y = 10$) were isolated as crystalline solids in good yields from the filtrate. The compounds have excellent water solubility, which rendered product purification difficult. However, analytically pure samples were obtained by washing the raw materials with a THF/ether mixture (1:1 v/v), and by drying the products under vacuum in the presence of silica gel.

By treating a mixture of $Er(ClO_4)_3$ and L-glutamic acid with aqueous NaOH in an analogous experiment, complex **4**, formulated as $[Er_4(\mu_3\text{-OH})_4(Glu)_3(H_2O)_8](ClO_4)_5 \cdot 6H_2O$, was obtained. This compound, once crystallized, is sparingly soluble in acetone, MeCN, DMF, or DMSO. Resolubilization in water also proved to be difficult. The poor solubility of the complex is presumably a reflection of its extended network structure, as established by X-ray diffraction (see below).

All compounds were characterized using a variety of techniques, including IR, MALDI-TOF MS, and microanalysis (CHN and metal). The metal content was determined by

(10) (a) Squire, R. C.; Aubin, S.; Folting, K.; Streib, W.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1995**, *34*, 6463−6471. (b) Lis, T. *Acta Crystallogr.* **1980**, *B36*, 2042−2046. (c) Low, D. W.; Eichhorn, D. E.; Dragonescu, A.; Armstrong, W. H. *Inorg. Chem.* **1991**, *30*, 877−878. (d) Blackman, A.; Huffman, J. C.; Lobkovsky, E.; Christou, C. *Polyhedron* **1992**, *11*, 251−255. (e) Baike, A.; Howes, A.; Hursthouse, M.; Quick, A.; Thornton, P. *J. Chem. Soc., Chem. Commun.* **1986**, 1587. (f) Lis, T.; Jezowska-Trzebiatowska, B. *Acta Crystallogr.* **1977**, *B33*, 2112−2116.

(11) Le Gall, F.; Fabrizi de Biani, F.; Caneschi, A.; Cinelli, P.; Cornia, A.; Fabretti, A. C.; Gatteschi, D. *Inorg. Chim. Acta* **1997**, *262*, 123−132. (b) Caneschi, A.; Cornia, A.; Fabretti, A. C.; Gatteschi, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 1295−1297. (c) Caneschi, A.; Cornia, A.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 467−469.

(12) (a) Bhula, R.; Weatherburn, D. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 688−689. (b) Grillo, V.; Knapp, M.; Bollinger, J.; Hendrickson, D. N.; Christou, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1818−1820. (c) Hagen, K. S.; Armstrong, W. H.; Olmstead, M. *J. Am. Chem. Soc.* **1989**, *111*, 774−774. (d) Wieghardt, K.; Bossek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328−329.

(13) (a) Cavalluzzo, M.; Chen, Q.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1993**, 191−192. (b) Xia, X.; Verelst, M.; Daran, J.-C.; Tuchagues, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 2155−2157.

(14) (a) Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Caneschi, A.; Gatteschi, D. *Inorg. Chem.* **1998**, *37*, 3759−3766. (b) Goldberg, D. P.; Caneschi, A.; Delfs, C. D.; Sessoli, R.; Lippard, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 5789−5800. (c) Caneschi, A.; Cornia, A.; Fabretti, A. C.; Gatteschi, D.; Malavasi, W. *Inorg. Chem.* **1995**, *34*, 4660−4668.

(15) (a) Bürgstein, M. R.; Roesky, P. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 549−551. (b) Anwander, R.; Munck, F. C.; Piermeier, T.; Scherer, W.; Runte, O.; Herrmann, W. A. *Inorg. Chem.* **1997**, *36*, 3545−3552. (c) Anwander, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 599−602.

(16) (a) Livage, J.; Sanchez, C.; Babonneau, F. In *Chemistry of Advanced Materials: An Overview*; Interrante, L. V., Hampden-Smith, M. J., Eds.; Wiley-VCH: New York, 1998; Chapter 9, pp 389−448. (b) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1995**, *19*, 727−750.

(17) (a) Wang, R.; Gao, F.; Jin, T. *Huaxue Tongbao* **1996**, *10*, 14−20 and references therein. (b) Reuben, J. In *Handbook on Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, 1979; Vol. 4, pp 515−552.

complexometric titration with EDTA. Infrared spectra[18] of all compounds were recorded with KBr disks. A strong and broad absorption appears at $\nu = 3500-3600$ cm^{-1}, which is typical of molecules of high water content. A sharp peak around 3580 cm^{-1}, previously reported[4a] and assigned to the stretching of a μ_3-OH, was not observed in any of the four compounds. The peak is probably obscured by the broad water absorption. The presence of coordinated water molecules in all complexes is indicated by their characteristic rocking and wagging frequencies between 700 and 800 cm^{-1} and between 500 and 650 cm^{-1}, respectively. Coordination of amino acid ligands as zwitterions does not result in any significant shifts of the carboxylate stretching frequency. For example, upon coordination the frequencies of the asymmetric and symmetric stretching modes of the carboxylate moiety shift from 1622 to 1615 cm^{-1} and from 1410 to 1428 cm^{-1}, respectively. For complexes **1**, **2**, and **4**, where ionic ClO$_4^-$ serves as the counteranion, characteristic strong Cl–O stretching frequencies between 1090 and 1145 cm^{-1} (ν_3) are observed. In addition, a relatively strong peak at 903 cm^{-1} (ν_4) indicates the presence of a unidentate ClO$_4^-$ in **1** in the solid state. Corresponding frequencies are absent from the IR spectrum of **3**, where the counteranions are chlorides. The identity of the complexes and the robustness of the cluster core were established by MALDI-TOF mass spectrometric studies because peaks corresponding to fragments containing their respective intact cluster core were clearly identified. For example, a peak envelope at 1840 amu was observed, corresponding to $\{[Sm_4(\mu_3\text{-}OH)_4(Gly)_5(H_2O)_{11}(ClO_4)](ClO_4)_5\}^{2+}$. Similarly, mass envelopes centered at 2020 and 1274 amu, corresponding to $\{[Nd_4(\mu_3\text{-}OH)_4(H_2O)_8(Ala)_6](ClO_4)_7\}^+$ and $[Er_4(\mu_3\text{-}OH)_4(H_2O)_4(Val)_4]^{8+}$, respectively, were observed in the mass spectra of **2** and **3**. These results (see the Supporting Information for full reports of the mass spectroscopic measurements) clearly indicate that the tetrameric structure is retained in solution.

Using Evans' method,[9] magnetic moments were determined for **1**–**3** in acetone-d_6 solutions with tetramethylsilane as external reference. All the measured values of μ_{eff}/molecule are within 10% of those calculated by using the Van Vleck equation[19] for four magnetically noninteractive lanthanide(III) ions. Insignificant room-temperature magnetic exchange interaction between the metal ions is implied, which is in agreement with the conclusion reached by Chen and co-workers for a [Tb$_4$-$(\mu_3\text{-}OH)_4$]$^{8+}$ core-containing complex.[4b]

Attempts to conduct analogous cluster-forming chemistry employing supporting carboxylato ligands were unsuccessful. For example, adjusting the pH of an aqueous mixture of Nd-(ClO$_4$)$_3$ and phenylacetic acid with dilute NaOH only yielded the known aqua complex of neodymium(III) phenylacetate. Its polymeric solid-state structure, consisting of repeating dinuclear Nd(III) units, has previously been determined.[20] Using adipic acid, a long-chain dicarboxylic acid structurally similar to glutamic acid, a noncluster polymeric network structure was obtained.[21] These observations, coupled with those of others,[4b,22,23]
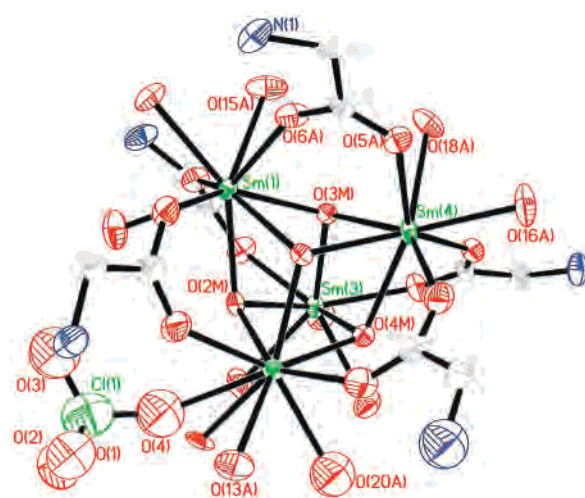
Figure 5. An ORTEP drawing of **1**, with H atoms omitted for clarity. Color legend: carbon (gray), samarium (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability.

clearly indicate the critical importance of the zwitterionic character of an amino acid in assisting the formation and isolation of the finite-size molecular clusters while preventing the "premature" precipitation of product as less soluble coordination polymers.

X-ray Structure Determinations. Structures were determined for the compounds listed in Table 1. A cubane-like [Ln$_4$-$(\mu_3\text{-}OH)_4$]$^{8+}$ core, resembling previously reported structural analogues,[4,5,7] is present in all cases. α-Amino acid and terminal aqua ligands complete the metal coordination sphere. The structural features of the cuboid [Ln$_4(\mu_3\text{-}OH)_4$]$^{8+}$ cluster cores are not significantly dependent on the nature of the amino acids used. Therefore, only the structural description of **1**, representative of single-cubane-containing complexes (**1**–**3**), is presented.

As shown in Figure 5, the cationic cluster exists as a tetranuclear species with four Sm(III) ions at the four apexes of a fairly regular tetrahedron (Sm–Sm = 3.8261(9)–3.9568-(9) Å, average 3.8920 Å; Sm–Sm–Sm = 58.43(1)–61.78(2)°). Each of the four triangular faces of the metal tetrahedron is capped by a μ_3-OH group, forming a cubane-like [Sm$_4(\mu_3$-OH)$_4$]$^{8+}$ cluster structure (Sm–O(μ_3-OH) = 2.356(5)–2.483-(5) Å, average 2.415 Å). Distortion of the core from a perfect cube is conspicuous, as reflected by the average values of Sm–O(μ_3-OH)–Sm (104.2(2)–111.5(2)°, average 107.1°) and O(μ_3--OH)–Sm–O(μ_3-OH) (67.3(2)–72.2(2)°, average 69.6°). All these structural parameters compare well with those of [(3,5-Bu$^t_4$-salophen)Sm(μ_3-OH)$_4$] (3,5-Bu$^t_4$-salophen-H$_2$ = phenylenebis(3,5-Bu$^t_4$-salicyclideneimine)).[4a] The cubane-like core is "camouflaged" by five glycine ligands through bridging carboxylato coordination. The Sm–O(carboxylato) distance ranges from 2.342(6) to 2.595(5) Å (average 2.45 Å), which is comparable to that (2.348(3)–2.445(9) Å, average 2.404 Å) of $\{[Sm_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot(H_2O)_5\}_n$,[24] a polymeric Sm(III)–glycine complex formed at pH ≈ 4. Terminal aqua ligands complete the metal coordination sphere. Thus, the coordination number of Sm(III) is 8, and the coordination geometry can be best described as tetragonal antiprismatic. The cationic cluster structures **2** and **3**, depicted in Figures 6 and 7, respectively,

(18) Interpretation of the infrared spectra is based on *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 5th ed.; Nakamoto, K., Ed.; Wiley-Interscience: New York, 1997; lattice water, aqua ligands, and hydroxo ligands, pp 53–57; zwitterionic amino acid ligands, pp 62–67; ionic and coordinated perchlorate ion, pp 82–83.

(19) Van Vleck, J. H. *Prog. Sci. Technol. Rare Earths* **1966**, *2*, 1–22.

(20) Wang, Z. L.; Jin, Z. S.; Niu, C. J.; Ni, J. Z. *Chin. J. Rare Earth* **1992**, *10*, 102–105.

(21) Kiritis, V.; Michaelides, A.; Skoulika, S.; Golhen, S.; Ouahab, L. *Inorg. Chem.* **1998**, *37*, 3407–3410.

(22) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651–1657.

(23) (a) Chen, X.; Aubin, S. M. J.; Wu, Y.; Yang, Y.; Mak, T. C. W.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9600–9601. (b) Chen, X. M.; Wu, Y. L.; Tong, Y. X.; Huang, X. Y. *J. Chem. Soc., Dalton Trans.* **1996**, 2443–2448.

(24) Ma, A.; Li, L.; Lin, Y.; Xi, S. *J. Inorg. Chem.* **1993**, *9*, 401–406.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Complexes **1**−**4**

	1	**2**	**3**	**4**
Ln−O(μ_3-OH)	2.36(1)−2.48(1)	2.43(1)−2.48(1)	2.28(1)−2.41(1)	2.30(1)−2.39(1)
mean	2.42(4)	2.45(2)	2.32 (9)	2.34(3)
O(μ_3-OH)−Ln−O(μ_3-OH)	67.2(2)−72.2(2)	67.7(1)−70.8(1)	68.9(3)−72.6(3)	69.5 (2)−72.2(2)
mean	70(1)	70(2)	70(1)	71(1)
Ln−O(μ_3-OH)−Ln	104.0(2)−111.5(2)	106(2)−109(1)	101.4(3)−109.1(3)	102.9(2)−108.2(2)
mean	107(2)	108(1)	106(2)	106(2)
Ln−O(carboxylato)	2.34(1)−2.60(1)	2.37(1)−2.51(1)	2.29(1)−2.36(1)	2.29(1)−2.35(1)
mean	2.45(6)	2.43(6)	2.33(2)	2.31(2)
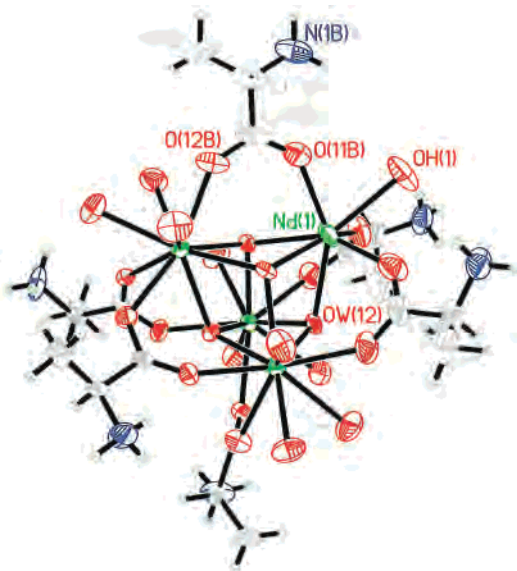
Figure 6. An ORTEP drawing of **2**. Color legend: carbon (gray), neodymium (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability.
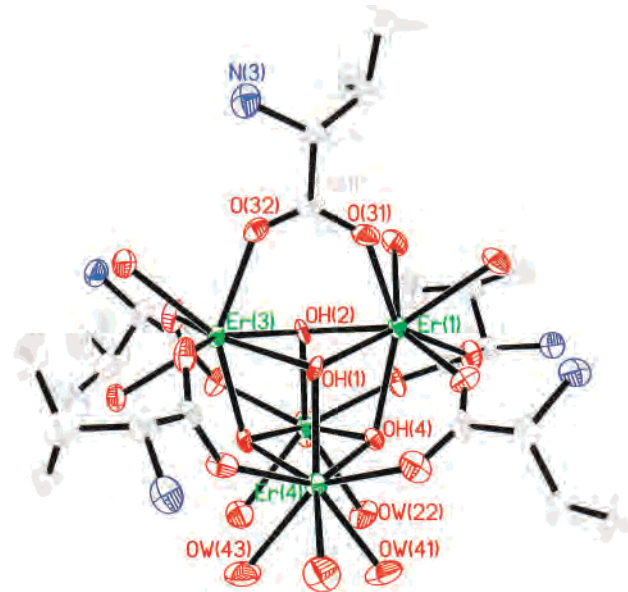
Figure 7. An ORTEP drawing of **3**, with H atoms omitted for clarity. Color legend: carbon (gray), erbium (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability.

are very similar to that of **1**; they differ only in the corresponding amino acid ligands. The metric values of interatomic distances and angles of these cluster complexes are quite normal,[3−5] and are reported in Table 2, mainly as ranges and mean values. The full data set is provided as Supporting Information.

The structure of **4** is a three-dimensional (3-D) network (Figure 8) based on the cuboid building block. The structure of its elementary component is depicted in Figure 9, from which the complex network is constructed. The [Er$_4$(μ_3-OH)$_4$]$^{8+}$ cluster core has the following average metric values of interest: Er−O(μ_3-OH) = 2.339 Å, Er−O(μ_3-OH)−Er = 106.2°, and O(μ_3-OH)−Er−O(μ_3-OH) = 70.9°. Each of the six edges of the Er$_4$ tetrahedron core (Er−Er = 3.6961(7)−3.7693(7) Å, average 3.739 Å; Er−Er−Er = 58.80(1)−60.72(1)°) is chelated by a carboxylate group from a glutamate ligand. These core parameters compare well with those of [Er$_{12}$(μ_3-Tyr)$_8$(μ_3-OH)$_{16}$-(H$_2$O)$_{20}$(I)$_2$](ClO$_4$)$_{10}$·12H$_2$O (Tyr = tyrosinate)[25] whose core component consists of four vertex-sharing [Er$_4$(μ_3-OH)$_4$]$^{8+}$ units. Two terminal aqua ligands complete the coordination sphere of the Er(III) centers (average Er−O = 2.444 Å). Thus, each of the 4 Er(III) ions has a coordination number of 8, and the coordination geometry can also be described as tetragonal antiprismatic. The six carboxylate groups ligating a particular cube are of two different types, one being α (average Er−O = 2.313 Å) and the other being γ (from the side chain, average Er−O = 2.314 Å) to the amino moiety, and the average Er−O(carboxylato) distance is shorter than that (2.375 Å) of the Er(III)−glutamic acid complex formed at pH ≈ 4.[26] Each glutamate ligand contributes one carboxylate group for the coordination of a particular [Er$_4$(μ_3-OH)$_4$]$^{8+}$ unit while using the remaining carboxylate to coordinate an adjacent cluster cube. As such, a 3-D open framework results, having nearly parallelogram-shaped pore apertures with dimensions of 4.4 Å × 9.1 Å in the *c* direction (Figure 10). 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, are hydrogen bonded to the amino groups that are not part of the Er(III) coordination sphere.

Cuboid [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ Cluster: A Common Structural Motif of Lanthanide Complexes. The family of cubane-like [M$_4$(μ_3-E)$_4$] (M = d-block transition metal; E = O, S, Se, Te) clusters has been well documented and extensively studied.[6] In contrast, only three serendipitous cuboid lanthanide−hydroxo clusters[4] and two [Yb$_4$(μ_3-E)$_4$]$^{8+}$ (E = S, Se) cubane clusters[27] have been reported prior to our work. However, our studies[5,7] illustrate that the cubane-like cluster unit is actually a prevalent structural motif in lanthanide coordination compounds. Its assembly can be regarded as a reflection of the subtle balance between the hydrolysis of the lanthanide ion and its chelation with the supporting ligands. It should be noted that a tetrameric cluster containing a [Yb$_4$(μ_3-O)$_4$] cuboidal core has recently appeared in the literature.[28]

The postulated mechanism of the tetranuclear complex assembly is illustrated in Figure 11. It seems plausible to start

(25) Wang, R.; Selby, H. D.; Jin, T.; Carducci, M. D.; Staples, R. J.; Anthis, J. W.; Zheng, Z. To be submitted for publication.

(26) Jin, Q.; Wang, X.; Jin, T.; Xu, G.; Zhang, S. *Polyhedron* **1994**, *13*, 2957−2961.

(27) Freedman, D.; Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 4162−4163.

(28) (a) Clegg, W.; Izod, K.; Liddle, S. T.; O'Shaughnessy, P.; Sheffield, J. M. *Organometallics* **2000**, *19*, 2090−2096. (b) Izod, K.; Clegg, W.; Liddle, S. T. *Organometallics* **2000**, *19*, 3640−3643.
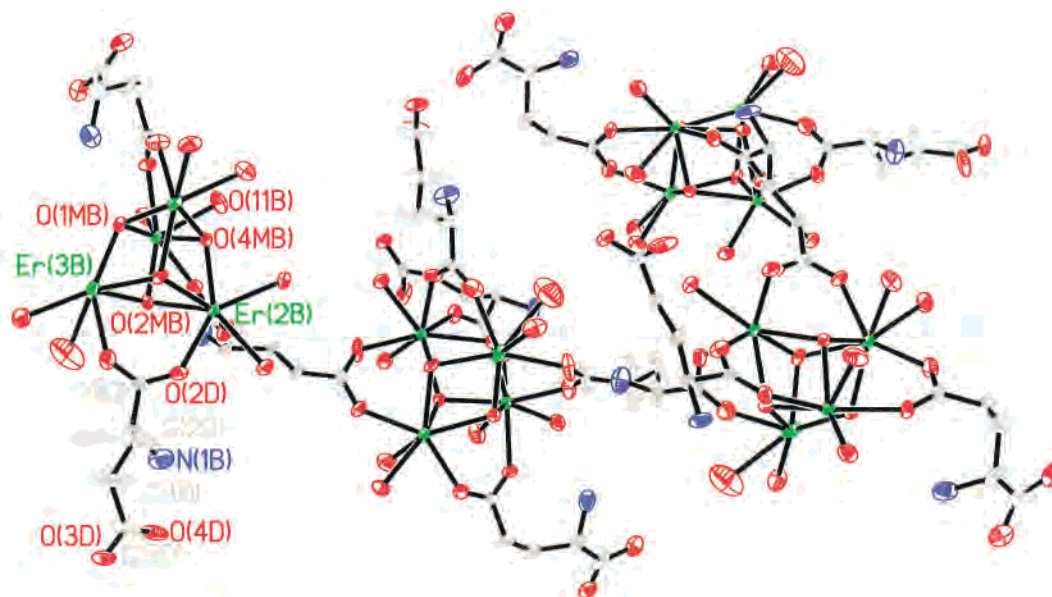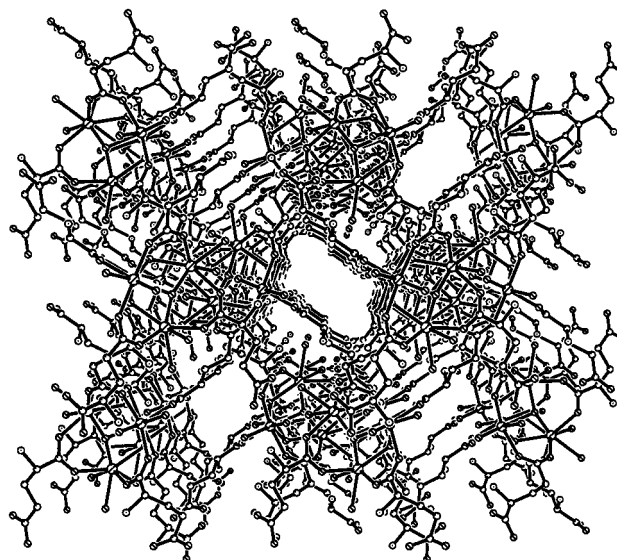
Figure 8. Extended network structure of **4**. H atoms are omitted for clarity. Color legend: carbon (gray), erbium (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability.
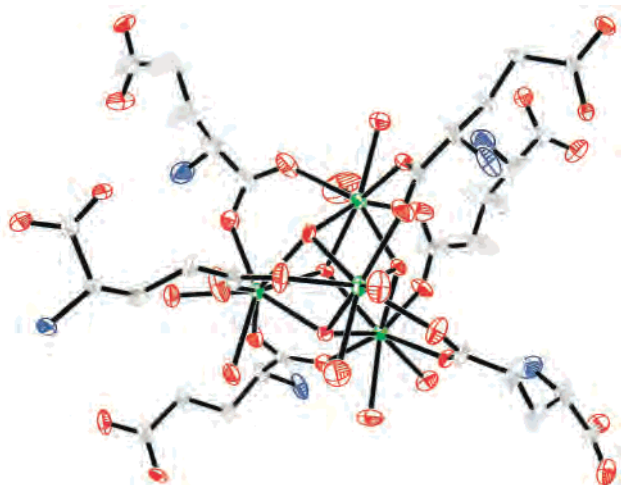
Figure 9. An ORTEP drawing of the elementary building unit of **4**. H atoms are omitted for clarity. Three symmetry-related glutamic acid "arms" are included to complete the coordination of the cuboid [Er$_4$(μ_3-OH)$_4$]$^{8+}$ core. Color legend: carbon (gray), erbium (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability.


Figure 10. 3-D porous framework structure of **4**, shown along the *c* axis. Hydrogens, water, and perchlorate ions are omitted for clarity. The channel dimensions are approximately 4.4 Å × 9.1 Å.

with a quadruply bridged dinuclear lanthanide complex (**A**), as it is known that many lanthanide complexes with α-amino acid ligands prepared at low pH (<4) exist in dinuclear forms.[17a] Amino acid−lanthanide complexation, expected to take place at the ionized carboxylate group, is weaker than that with simple carboxylates due to the proximity of the positively charged amino group. When the pH of the reaction mixture is raised, the formation of an intermediate (**B**) is assumed, wherein one Ln(III) is coordinated by an incoming hydroxo ligand, while the other is coordinated by a unidentate amino acid carboxylato ligand resulting from the hydroxo attack of **A**. Subsequent replacement of the unidentate amino acid ligand by a second hydroxo group affords a triply bridged hydroxo complex (**C**). Concurrently, the remaining amino acid ligands, by occupying part of the metal coordination sphere, prevent extensive hydrolysis from occurring. Intramolecular ligand substitution reactions involving two terminally bound hydroxo ligands and two bridging carboxylate groups lead to the formation of the

μ_2-OH-bridged intermediate (**D**). Precedents exist for such hydroxo-bridged dinuclear lanthanide complexes.[3] Subsequent condensation of two of such dimeric units would yield the targeted tetranuclear cluster (**E**). The formation of a five-membered ring (Ln−O(carboxylato)−C−O(carboxylato)−Ln) and four synergestic Ln−OH operations presumably provide the necessary driving force for the coupling of two dinuclear units and, ultimately, the assembly of the tetranuclear complex. This final step is reasonable considering the chelation by the hydroxo groups and the close proximity (and thus high local concentration) of the uncoordinated oxygen of the carboxylato ligand to the metal centers.

Lending credence to the above hypothesis are the mechanistic studies of hydrolytic reactions involving mononuclear lanthanide−EDTA complexes.[29] Since one EDTA ligand contrib-

(29) Wang, R.; Roland, B. K.; Carducci, M. D.; Jin, T.; Zheng, Z. Work in progress.
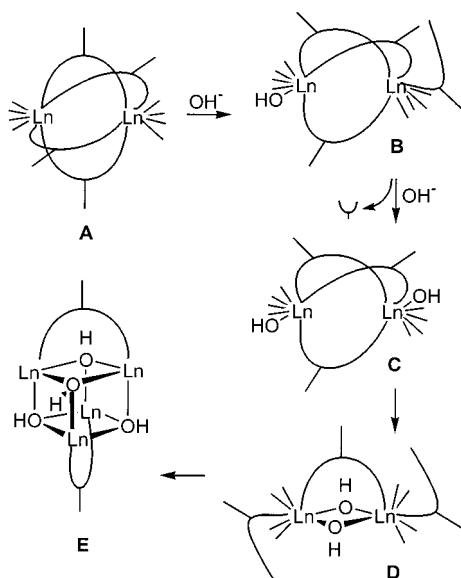
Figure 11. Postulated synthesis of a cubane-like tetranuclear lanthanide−hydroxo complex with amino acid ligands: amino acid (coordination with Ln(III) via only carboxylato oxygens), curved line with dash; aqua ligand, unlabeled dash. For clarity, only two of the six possible amino acid ligands are shown in **E**.

utes six coordinating atoms, only two aqua ligands would be possible for a mononuclear complex of a lanthanide ion (Er-(III), for example) preferring a coordination number of 8. Upon increasing the pH of the reaction mixture, a dinuclear hydroxo complex would be the expected product and the reaction would terminate at the stage of **D** if the above postulation were reasonable. Indeed, a dinuclear Er(III)−hydroxo complex was isolated from a reaction mixture of Na[Er(EDTA)(H$_2$O)$_2$] (formed at pH ≈ 6) with KOH at pH 13−14. The complex anion, formulated as [(EDTA)Er(μ_2-OH)$_2$Er(EDTA)]$^{4-}$, bears the same diamond-shaped lanthanide−hydroxo core, as shown in Figure 11, **D**. Further supporting evidence is provided by the formation of the tetranuclear La(III)− and Pr(III)−hydroxo complexes, as expected for lanthanide ions requiring a coordination number of 9 or 10. The solid-state structures of these compounds have been established by X-ray crystallography, wherein a cubane-like [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ core is supported by four EDTA ligands. Details of these mechanistic studies will be published as a separate report.

Using L-glutamic acid as supporting ligand, the prevalence of the [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ motif is further demonstrated with the formation of a 3-D infinite network, wherein the [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ units are interlinked by the amino acid carboxylate group and the one on the side chain. Although the synthesis is probably self-assembly by nature, the [Er$_4$(μ_3-OH)$_4$]$^{8+}$ core may be *formally* considered as a prefabricated and transferable building block for the assembly of the extended structure. The approach can potentially be taken for the construction of other

functional materials based on the same lanthanide cluster construction unit.[30]

Summary. The following are the principal results and conclusions of this investigation, including certain findings from previous studies.[5,7]

(1) Ligand-controlled hydrolysis of lanthanide ions is a new avenue in lanthanide coordination chemistry. It is a valid approach to the synthesis of polynuclear lanthanide−hydroxo complexes.

(2) α-Amino acids are a novel class of supporting ligands for controlling the hydrolysis of lanthanide ions. Under near physiological pH conditions, lanthanide complexation with amino acids may be achieved via only the carboxylate group or simultaneous coordination[5a,7] by the carboxylate and amino moieties.

(3) Polynuclear lanthanide complexes generated under near neutral conditions typically exist as discrete lanthanide−hydroxo clusters, whereas their low-pH counterparts are in mononuclear, dinuclear, or noncluster polynuclear forms. It is the pH conditions that promote the formation of the large molecular clusters.

(4) The cuboid [Ln$_4$(μ_3-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 [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ cluster cores as building blocks.[5a,d]

From the results reported herein, it is clear that ligand-controlled hydrolysis of lanthanide ions represents a rich field of research and can be exploited to create novel lanthanide-containing materials, including the well-characterized structural platform for potential development of lanthanide-based synthetic phosphate esterases.[31] Preliminary results have shown encouraging catalytic activities of these lanthanide−hydroxo species for the hydrolysis of bis(4-nitrophenyl) phosphate, an informal "standard" phosphodiester substrate.[2] Kinetic and mechanistic studies of such reactions are underway.

(30) For structures composed of multiple cubane units, see: (a) Osterloh, F.; Segal, B. M.; Achim, C.; Holm, R. H. *Inorg. Chem.* **2000**, *39*, 980−989. (b) Goh, C.; Segal, B. M.; Huang, J.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 11844−11853.

(31) Straeter, N.; Lipscomb, W. N.; Klabunde, T.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2025−2055.