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Halide-Templated Assembly of Polynuclear Lanthanide-Hydroxo Complexes†

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A series of pentadecanuclear lanthanide-hydroxo complexes possessing a common core of the formula $[Ln_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}X)]^{24+}$(**1**, Ln = Eu, X = Cl^-; **2**, Ln = Nd, X = Cl^-; **3**, Ln = Gd, X = Cl^-; **4**, Ln = Pr, X = Br^-; **5**, Ln = Eu, X = Br^-) were prepared by *L*-tyrosine-controlled hydrolysis of corresponding lanthanide perchlorates in the presence of added Cl^- or Br^-. The cationic cluster core comprises five vertex-sharing cubane-like $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ units centered on the halide template. In the case of templating I^-, dodecanuclear complexes were isolated instead. The core component, $[Ln_{12}(\mu_3\text{-}OH)_{16}(I)_2]^{18+}$ (**6**, Ln = Dy; **7**, Ln = Er), consists of four vertex-sharing cubane-like $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ units and exists as a square-shaped cyclic structure with one I^- located on each side of the square plane. An analogous hydrolytic reaction involving $Er(NO_3)_3$, *L*-tyrosine, and NaOH affords the known hexanuclear complex $[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2$ whose core component is a face-capped octahedral $[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ cluster with an interstitial μ_6-oxo group (Wang, R.; Carducci, M. D.; Zheng, Z. *Inorg. Chem.* **2000**, *39*, 1836–1837.). The efficient self-assembly of halide-encapsulating multicubane complexes (**1**–**7**) and the inability to produce an analogous nitrate-containing complex demonstrate the superior templating roles played by the halide ion(s). Further credence for the halide template effects was provided by the isolation of the cationic pentadecanuclear complex **3** as the sole product when tyrosine-supported hydrolysis of $Gd(NO_3)_3$ was carried out in the presence of competitive Cl^-. Magnetic moments of complexes **1**–**7** measured at room temperature by using Evans' method are in excellent agreement with those calculated by the Van Vleck equation, assuming magnetically noninteractive lanthanide ions.

Introduction

Anion coordination chemistry has evolved into an established new realm of supramolecular chemistry over the last two decades.[2] A variety of synthetic receptors capable of anion complexation has been reported, and their coordination properties have been studied.[3] In the course of these efforts, an increasing number of anion-assisted syntheses have been realized,[4] and in some cases,[4i−n] the anion template effects have been unambiguously established.

We wish to report the halide template effects observed in the assembly of a novel class of polynuclear lanthanide-hydroxo complexes with tyrosinate ligands. As part of a more general study of lanthanide−amino acid interactions under near physiological pH conditions, we have recently reported

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† Dedicated to Professor Richard H. Holm.

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(2) *Supramolecular Chemistry of Anions*; Bianchi, A.; Bowman-James, K.; García-España, E., Eds.; Wiley-VCH: New York, 1997.

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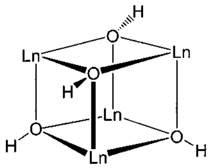

Figure 1. Structure of a generic cubane-like $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ core (Ln = trivalent lanthanide ions).

a series of high-nuclearity lanthanide-hydroxo complexes prepared via lanthanide hydrolysis controlled by α-amino acids as supporting ligands.[5,6] In the case of glycine, alanine, or valine, tetranuclear complexes containing a common cubane-like $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ (Figure 1, Ln = trivalent lanthanide ion) core were obtained;[6] the constituent lanthanide ions and the triply bridging μ_3-OH ligands occupy the alternate vertices of a distorted cube.[7] With glutamic acid, the ligand-controlled hydrolysis of $Er(ClO_4)_3$ produced a three-dimensional network that is composed of discrete $[Er_4(\mu_3\text{-OH})_4]^{8+}$ units interlinked by glutamate ligands.[6] However, when tyrosine was utilized, the analogous hydrolytic reactions of $Ln(ClO_4)_3$ (Ln = trivalent La, Pr, Nd, Sm, Eu, Gd, Dy) produced a series of pentadecanuclear lanthanide-hydroxo complexes.[5] Crystallographic analysis of the representative Eu(III) complex reveals an unprecedented structure whose core component, formulated as $[Eu_{15}(\mu_3\text{-OH})_{20}(\mu_5\text{-Cl})]^{24+}$, consists of five vertex-sharing $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ cubane units centered on a μ_5-Cl^- "axle" and is depicted in Figure 2.

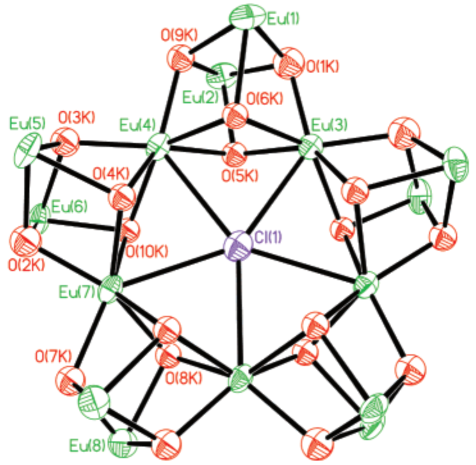

Figure 2. ORTEP representation of the core component of **1**, showing five vertex-sharing cuboid $[Eu_4(\mu_3\text{-OH})_4]^{8+}$ units centering around a μ_5-Cl^- ion. Color legend: chlorine (purple), europium (green), oxygen (red). Thermal ellipsoids are represented in 50% probability.

The formation of the pentadecanuclear complex was unexpected, as only complexes containing *discrete* cubane motifs were obtained with other α-amino acids,[6,7a,b] including phenylalanine.[8] The incorporation of a μ_5-Cl^- ion was even more surprising because no Cl^- was utilized in the original synthesis involving only $Ln(ClO_4)_3$, tyrosine, and NaOH. A possible source of the mystifying Cl^- was the impurity present in the perchloric acid used for the digestion of lanthanide oxides (see Experimental Section). Template effects exerted by Cl^-, presumably in minute amount in the original synthesis, were thus suspected and subsequently corroborated by the improved synthesis with the presence of added Cl^-.[5] Stimulated by these findings, the potential roles of other anionic species in promoting the assembly of analogous or distinct complexes were explored. It has been found that the composition of the resulting complex is profoundly affected by the anionic species present in the reaction mixture, but independent of the lanthanide ions. Results of these studies are summarized in the present work, including synthetic details, structural characterization, and discussions of the anion template effects involved in the efficient assembly of these aesthetically pleasing lanthanide complexes. Part of this work has been communicated previously.[5]

Experimental Section

Caution: Lanthanide perchlorates are potentially explosive! Only a small amount of materials should be prepared and handled with great care. However, careful tests on the materials in our studies showed no apparent hazards. Small amounts (5−10 mg) charred when heated in open air. All reagents were of commercial origin and were used as received. Aqueous solutions of lanthanide perchlorates and nitrates were prepared by digesting lanthanide

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(7) For other examples having a $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ motif, see: (a) Ma, B.; Zhang, D.; Gao, S.; Jin, T.; Yan, C.; Xu, G. X. *Angew. Chem., Int. Ed.* **2000**, *39*, 3644−3646. (b) Ma, B.; Zhang, D.; Gao, S.; Jin, T.; Yan, C. *New J. Chem.*, **2000**, *24*, 251−252. (c) Dubé, T.; Gambarotta, S.; Yap, G. *Organometallics* **1998**, *17*, 3967−3973. (d) Chen, X. M.; Wu, Y. L.; Tong, Y. X.; Sun, Z.; Hendrickson, D. N. *Polyhedron* **1997**, *16*, 4265−4272. (e) 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.

(8) $[Yb_4(\mu_3\text{-OH})_4(Phe)_6(H_2O)_7](ClO_4)_8\cdot 5H_2O$ (Phe, phenylalanine), triclinic, $P\bar{1}$, $a = 12.651(6)$ Å, $b = 15.653(7)$ Å, $c = 23.763(11)$ Å, $\alpha = 92.932(7)°$, $\beta = 93.059(7)°$, $\gamma = 91.278(7)°$, $V = 4691(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.956$ g cm^{-3}. The final $R = 0.0434$ ($R_w = 0.0976$), and GOF = 1.062 for 14 657 observed reflections (1264 parameters) with $I > 2.00\sigma(I)$ (Wang, R.; Liu, H.; Carducci, M. D.; Zheng, Z. Unpublished results).

oxides in concentrated perchloric and nitric acids, respectively. A suitable concentration was achieved by dilution of the concentrated solution with deionized water, and the exact concentration was determined by complexometric titration with EDTA, using xylenol orange as the indicator. The formulas used in this section are derived from the microanalysis data in combination with the crystallographic results and are corroborated with electrospray ionization mass spectroscopic (ESI-MS) results.

$[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)_2(\mu_2\text{-}H_2O)_5(H_2O)_{18}](ClO_4)_{12}\cdot 9H_2O$. *L*-Tyrosine (0.181 g, 1.0 mmol) was added as a solid to an aqueous solution of $Eu(ClO_4)_3$ (1.0 M, 4.0 mmol). An aqueous solution of HCl (0.25 mL, 1.0 M) was then added. The mixture (pH 1−2) was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (~5 mL, 0.5 M) was added drop by drop to cause an incipient but permanent precipitate. The mixture was then filtered, and the filtrate (pH 6−7) was reduced to about 4 mL. The hot solution was tightly covered with Parafilm and allowed to stand on the gradually cooling heating plate. Colorless parallelepipeds appeared in about one week. The solids were collected by filtration, washed with ice-cold water, and dried under dynamic vacuum in a desiccator charged with silica gel. Yield: 60% (based on tyrosine). Anal. Calcd for $C_{90}H_{186}Cl_{13}Eu_{15}N_{10}O_{132}$: C, 17.27; H, 2.97; N, 2.24; Eu, 36.41; Cl, 7.36. Found: C, 17.24; H, 2.74; N, 2.24; Eu, 36.25; Cl, 7.42. IR: ν 3418 s, 1585 s, 1516 m, 1426 m, 1349 w, 1231 w, 1105 s, 1075 s, 968 w, 931 w, 824 w, 626 m cm^{-1}. ESI-MS: *m*/*z*(%) 1936.1(30) $[M - 8H_2O - 3ClO_4^-]^{3+}$, 1474.7(100) $[M - 4ClO_4^-]^{4+}$, 1150.9(40) $[M - 5ClO_4^-]^{5+}$. $\mu_{eff}^{293K} = 12.9\ \mu_B$. Calcd: 13.2 μ_B.

$[Nd_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)_3(\mu_2\text{-}H_2O)(H_2O)_{23}]Cl_3(ClO_4)_8\cdot 2H_2O$. This compound was prepared following the preceding procedure using $Nd(ClO_4)_3$. Yield: 47%. Anal. Calcd for $C_{90}H_{175}Cl_{12}N_{10}Nd_{15}O_{111}$: C, 18.76; H, 3.06; N, 2.43; Nd, 37.55; Cl, 7.38. Found: C, 18.77; H, 3.02; N, 2.43; Nd, 37.38; Cl, 7.24. IR: ν 3384 s, 1580 s, 1515 s, 1422 s, 1350 m, 1227 m, 1139 s, 1108 s, 1088 s, 968 m, 940 w, 825 w, 635 m, 627 m, 537 m cm^{-1}. ESI-MS: *m*/*z*(%) 1870.8(25) $[M - 2H_2O - 3Cl^-]^{3+}$, 1789.0(20) $[M - 5H_2O - 3ClO_4\text{-}]^{3+}$, 1362.3(40) $[M - 2H_2O - 3Cl^- - ClO_4\text{-}]^{4+}$, 1094.4(25) $[M - 3Cl^- - 2ClO_4^-]^{5+}$. $\mu_{eff}^{293K} = 13.6\ \mu_B$. Calcd: 14.3 μ_B.

$[Gd_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)(\mu_2\text{-}H_2O)_5(H_2O)_{19}](ClO_4)_{13}\cdot 12H_2O$. This compound was prepared following the preceding procedure using $Gd(ClO_4)_3$. Yield: 52%. Anal. Calcd for $C_{90}H_{193}Cl_{14}Gd_{15}N_{10}O_{139}$: C, 16.64; H, 3.00; N, 2.16; Gd, 36.32; Cl, 7.64. Found: C, 16.52; H, 2.63; N, 2.17; Gd, 36.45; Cl, 7.39. IR: ν 3463 s, 1588 s, 1516 m, 1426 s, 1350 w, 1306 w, 1230 m, 1173 w, 1108 s, 1074 s, 974 m, 930 w, 825 m, 808 w, 626 m cm^{-1}. ESI-MS: *m*/*z*(%) 1911.9(35) $[M - 5H_2O - 2TyrH - 3ClO_4^-]^{3+}$, 1433.2(100) $[M - 2TyrH - 4ClO_4^-]^{4+}$, 1383.4(95) $[M - H_2O - 3TyrH - 4ClO_4^-]^{4+}$, 1136.6(20) $[M - 7H_2O - TyrH - 5ClO_4^-]^{5+}$. $\mu_{eff}^{293K} = 31.6\ \mu_B$. Calcd: 30.7 μ_B.

$[Pr_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Br)(\mu_3\text{-}Tyr)_{10}(\mu_2\text{-}TyrH)_2(\mu_2\text{-}H_2O)_3(H_2O)_{20}](ClO_4)_{14}\cdot 8H_2O$. This compound was prepared in a manner analogous to the chloride-containing complexes, using $Pr(ClO_4)_3$ with an added aqueous solution of HBr (0.25 mL, 1.0 M). Yield: 43%. Anal. Calcd for $C_{108}H_{204}BrCl_{14}N_{12}O_{143}Pr_{15}$: C, 19.51; H, 3.09; N, 2.53; Pr, 31.79; Cl, 7.47; Br, 1.20. Found: C, 19.50; H, 2.86; N, 2.53; Pr, 32.00; Cl, 7.16; Br, 1.56. IR: ν 3346 s, 1611 s, 1578 s, 1516 s, 1446 m, 1421 s, 1350 m, 1305 w, 1231 m, 1107 s, 1072 s, 966 m, 930 w, 885 w, 852 w, 826 m, 807 m, 625 s cm^{-1}. ESI-MS: *m*/*z*(%) 1989.9(20) $[M - H_2O - 2TyrH - 3ClO_4^-]^{3+}$, 1930.0(45) $[M - H_2O - 3TyrH - 3ClO_4^-]^{3+}$, 1869.8(45) $[M - H_2O - 4TyrH - 3ClO_4^-]^{3+}$, 1467.7(30) $[M - H_2O - 2TyrH - 4ClO_4^-]^{4+}$, 1423.3(60) $[M - H_2O - 3TyrH - 4ClO_4^-]^{4+}$, 1377.4(65) $[M - H_2O - 4TyrH - 4ClO_4^-]^{4+}$, 1118.8(25) $[M - H_2O - 3TyrH - 5ClO_4^-]^{5+}$. $\mu_{eff}^{\ 293K} = 13.2\ \mu_B$. Calcd: 14.0 μ_B.

Chart 1

$[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)_2(\mu_2\text{-}H_2O)_5(H_2O)_{18}]^{12+}$	**1**
$[Nd_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)_3(\mu_2\text{-}H_2O)(H_2O)_{23}]^{11+}$	**2**
$[Gd_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)(\mu_2\text{-}H_2O)_5(H_2O)_{19}]^{13+}$	**3**
$[Pr_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Br)(\mu_3\text{-}Tyr)_{10}(\mu_2\text{-}TyrH)_2(\mu_2\text{-}H_2O)_3(H_2O)_{20}]^{14+}$	**4**
$[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Br)(\mu_3\text{-}Tyr)_{10}(\mu_2\text{-}H_2O)_5(H_2O)_{20}]^{14+}$	**5**
$[Dy_{12}(\mu_3\text{-}OH)_{16}(I)_2(\mu_3\text{-}Tyr)_8(H_2O)_{20}]^{10+}$	**6**
$[Er_{12}(\mu_3\text{-}OH)_{16}(I)_2(\mu_3\text{-}Tyr)_8(H_2O)_{20}]^{10+}$	**7**

$[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Br)(\mu_3\text{-}Tyr)_{10}(\mu_2\text{-}H_2O)_5(H_2O)_{20}](ClO_4)_{14}\cdot 2H_2O$. This compound was prepared following the preceding procedure, using $Eu(ClO_4)_3$ with an added aqueous solution of HBr (0.25 mL, 1.0 M). Yield: 48%. Anal. Calcd for $C_{90}H_{274}BrCl_{14}Eu_{15}N_{10}O_{133}$: C, 16.94; H, 2.75; N, 2.20; Eu, 35.73; Cl, 7.78; Br, 1.25. Found: C, 16.96; H, 2.70; N, 2.19; Eu, 35.77; Cl, 7.85; Br, 1.46. IR: ν 3464 s, 1586 s, 1516 s, 1424 s, 1350 m, 1230 m, 1106 s, 1074 s, 971 m, 930 w, 824 m, 807 m, 730 m, 626 s, 535 m cm^{-1}. ESI-MS: *m*/*z*(%) 1925.2(50) $[M - 7H_2O - TyrH - 3ClO_4^-]^{3+}$, 1865.2(90) $[M - 7H_2O - 2TyrH - 3ClO_4^-]^{3+}$, 1393.7(100) $[M - 2H_2O - 2TyrH - 4ClO_4^-]^{4+}$, 1096.0(50) $[M - 2H_2O - 2TyrH - 5ClO_4^-]^{5+}$, 920.9(20) $[M - 4H_2O - TyrH - 6ClO_4^-]^{6+}$. $\mu_{eff}^{293K} = 13.2\ \mu_B$. Calcd: 13.2 μ_B.

$[Dy_{12}(\mu_3\text{-}OH)_{16}(I)_2(\mu_3\text{-}Tyr)_8(H_2O)_{20}](ClO_4)_{10}\cdot 8H_2O$. This compound was prepared in a manner analogous to the chloride-containing complexes, using $Dy(ClO_4)_3$ with an added aqueous solution of KI (0.25 mL, 1.0 M). Yield: 54%. Anal. Calcd for $C_{72}H_{152}Cl_{10}Dy_{12}I_2N_8O_{108}$: C, 15.96; H, 2.83; N, 2.07; Dy, 36.00. Found: C, 16.02; H, 2.69; N, 1.89; Dy, 36.28. IR: ν 3454 s, 1593 s, 1515 m, 1440 w, 1414 m, 1347 w, 1231 m, 1107 s, 1079 s, 976 w, 932 w, 824 w, 804 w, 688 w, 626 m, 550 w, 523 w cm^{-1}. ESI-MS: *m*/*z*(%) 1441.6(90) $[M - 3TyrH - 2HI - 3ClO_4^-]^{3+}$, 1141.5(80) $[M - TyrH - 2HI - 4ClO_4^-]^{4+}$, 969.9(35) $[M - 4H_2O - 5ClO_4^-]^{5+}$. $\mu_{eff}^{293K} = 38.6\ \mu_B$. Calcd: 36.7 μ_B.

$[Er_{12}(\mu_3\text{-}OH)_{16}(I)_2(\mu_3\text{-}Tyr)_8(H_2O)_{20}](ClO_4)_{10}\cdot 12H_2O$. This compound was prepared following the preceding procedure using $Er(ClO_4)_3$ with an added aqueous solution of KI (0.25 mL, 1.0 M). Yield: 46%. Anal. Calcd for $C_{72}H_{160}Cl_{10}Er_{12}I_2N_8O_{112}$: C, 15.59; H, 2.91; N, 2.02; Er, 36.19. Found: C, 15.60; H, 2.71; N, 2.03; Er, 35.89. IR: ν 3416 s, 1597 s, 1515 s, 1417 m, 1346 m, 1227 m, 1143 s, 1113 s, 1089 s, 982 m, 941 w, 870 w, 824 m, 805 m, 728 m, 630 s, 627 s, 540 m cm^{-1}. ESI-MS: *m*/*z*(%) 1595.6(90) $[M - H_2O - TyrH - 2HI - 3ClO_4^-]^{3+}$, 1203.2(100) $[M - H_2O - TyrH - HI - 4ClO_4^-]^{4+}$, 959.6(80) $[M - 4H_2O - TyrH - 5ClO_4^-]^{5+}$, 803.4(25) $[M - HI - 6ClO_4^-]^{6+}$. $\mu_{eff}^{293K} = 34.9\ \mu_B$. Calcd: 33.3 μ_B.

X-ray Structure Determinations. Structures were determined for the 7 compounds reported herein. Numerical designations of the cationic complexes are given in Chart 1. For simplicity, in this and following sections, the compounds are referred to by their cation numbers.

X-ray quality parallelepiped-shaped crystals of **1**−**7** were obtained from respective aqueous solutions at room temperature. The structures of **1**−**3** were determined at Harvard University, while those of **4**−**7** were solved at The University of Arizona. Data were collected with Mo Kα radiation (λ = 0.710 73 Å) using a Bruker SMART CCD-based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213(2) K (**1**−**3**) and 170(2) K

(**4**−**7**). Cell parameters were obtained using SMART software and refined using SAINT on all observed reflections. Empirical absorption and decay corrections were applied using the program SADABS (Sheldrick, 1998). The structures were solved using SHELXS in the Bruker SHELXTL (Version 5.0) software package. Refinements were performed using SHELXL, and illustrations were made using XP. Solution was achieved utilizing direct methods followed by Fourier synthesis.

Hydrogen atoms were added at idealized positions, constrained to ride on the atom to which they were bonded and given thermal parameters equal to 1.2 or 1.5 times *U*iso of that bonded atom. However, hydrogen atoms were not included for the terminal water/hydroxide ligands nor the solvent water because they could not be positively identified. In our original communication, charge balancing of **1** was satisfied by assigning a number of the oxygen-based terminal ligands as hydroxo groups. However, most of these terminal hydroxides should be aqua ligands, as they are more in line with the structural parameters. The complete elemental analysis (see text) indicated that additional chlorine-based counteranions, present in the solvent region and previously unidentified, were present in the structure and are responsible for the balance of charge. The structure of **1** was thus redetermined with the inclusion of extra chlorine in the model. Nevertheless, crystallographic changes resulting from such modifications were negligible.

Rotational disorder of perchlorate anions was observed for all structures. This disorder was modeled as partially occupied tetrahedral rigid bodies pivoting about the chloride ion, and/or the disordered groups were constrained to have the same geometry as a "well-behaved" perchlorate in the respective structures. Comments on 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 as Nujol mulls on a Nicolet 510P FT-IR spectrophotometer. ESI-MS experiments were performed on a JEOL HX110A spectrometer using MeCN as the solvent. Magnetic moments were determined by Evans' method[9] using ^1H NMR spectra recorded on a Bruker AM-250 spectrometer. Acetone-d_6 solutions were used with tetramethylsilane (TMS) as internal reference. Microanalytical services (carbon, hydrogen, nitrogen, and halides) were provided by Desert Analytics Laboratory, Tucson, Arizona. The metal content was determined by complexometric titration with EDTA using xylenol orange as the indicator.

Results and Discussion

Synthesis. In this investigation, we sought polynuclear lanthanide-hydroxo complexes via the hydrolysis of lanthanide perchlorates controlled by tyrosine ligands. In a representative synthesis, a dilute aqueous solution of NaOH was added to an aqueous mixture of a lanthanide perchlorate, tyrosine, and a halide (HCl, HBr, or KI). Heating of the reaction mixture was necessary to facilitate the hydrolytic process, and the endpoint (pH 6−7) was indicated by the incipient formation of a permanent precipitate, presumably of lanthanide hydroxides and/or oxohydroxides. The reaction produced pentadecanuclear complexes (**1**−**5**) when Cl^- or Br^- was involved, while dodecanuclear complexes (**6** and **7**) were obtained in the presence of I^-.

All complexes are extremely soluble in water, and an aqueous solution of the complex turns turbid after standing overnight at room temperature, presumably because of further hydrolysis of the complex. The compounds are also readily soluble in common organic solvents, such as tetrahydrofuran, dichloromethane, acetone, and acetonitrile, rendering product purification difficult. To ensure a sufficient amount of samples for analysis, large crops of crystals for each of the complexes were slowly grown, swiftly washed with ice-cold water, and then dried under vacuum. The compounds were characterized using a variety of techniques, including IR, ESI-MS, and microanalysis. In the infrared spectra,[10] a strong and broad absorption appears at $\nu = 3300-3500$ cm^{-1}, which is typical of molecules of high water content. A peak around 3580 cm^{-1}, previously reported and assigned to the stretching of a μ_3-OH,[7c] was not observed in any of the seven 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 frequency at about 825 cm^{-1}. Metal coordination results in appreciable shifts of the asymmetric stretching frequency of the carboxylate moiety of the tyrosinate ligand, from 1610 to about 1590 cm^{-1}, which happens to be coincident with that of the in-plane bending of the N−H moiety. The symmetric carboxylate stretching frequency shifts from 1416 to 1422 cm^{-1}. Strong and characteristic Cl−O stretching frequencies between 1050−1170 cm^{-1} (ν_3) and 620−630 cm^{-1} (ν_4) are observed for the ClO_4^- counterions in all complexes. The identity of the complexes and the robustness of the cluster core were established by ESI-MS studies because peaks corresponding to fragments containing their respective intact cluster core were clearly identified. For example, a peak envelope centered at 1150.9 amu was observed, corresponding to $[\mathbf{1} - 5ClO_4^-]^{5+}$. Mass peaks matching +3 and +4 charged species have also been observed under the ESI conditions employed. Similar results were obtained for each of the other members in the series reported herein. Mass envelopes corresponding to +6 charged species have also been observed for **5** and **7**. These results indicate that the integrity of the polynuclear complexes was maintained in solution.

Using Evans' method,[9] magnetic moments were determined for **1**−**7**. All the measured values of μ_{eff}/molecule are within 6% of those calculated by using the Van Vleck equation[11] for magnetically noninteractive lanthanide(III) ions. Insignificant exchange interactions between the metal ions at room temperature are thus implied, which is in agreement with the conclusion reached by Chen and coworkers for a $[Tb_4(\mu_3\text{-}OH)_4]^{8+}$ core-containing complex.[7d]

Several aspects of the synthesis merit further discussion. First, the actual lanthanide/tyrosine ratio (4/1) used in the present study was empirical and was based on solubility consideration instead of reaction stoichiometry.[6c] When a

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

[10] Interpretation of the infrared spectra is based on the following: *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; amino acid ligands, pp 62−67; perchlorate ion, pp 82−83.

[11] Van Vleck, J. H. *Prog. Sci. Technol. Rare Earths* **1966**, *2*, 1−22.

Table 1. Crystal Data[a] and Structure Refinement for Complexes **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$C_{90}H_{110}Cl_{13}Eu_{15}N_{10}O_{112}$	$C_{90}H_{110}Cl_{12}N_{10}Nd_{15}O_{107}$	$C_{90}H_{110}Cl_{14}Gd_{15}N_{10}O_{101}$	$C_{108}H_{142}BrCl_{14}N_{12}O_{100}Pr_{15}$	$C_{90}H_{130}BrCl_{14}Eu_{15}N_{10}O_{108}$
fw	5864.13	5632.88	5802.93	5898.20	5935.65
space group	*C*2	*C*2	*C*2	*C*2	*C*2
Z	2	2	2	2	2
a, Å	32.259(3)	33.8755(5)	31.9405(5)	34.154(2)	31.910(2)
b, Å	20.926(2)	19.8499(1)	21.0458(7)	20.497(1)	20.694(1)
c, Å	22.037(2)	20.8230(4)	21.9661(3)	20.837(1)	21.846(1)
α, deg	90	90	90	90	90
β, deg	130.956(4)	126.924(1)	131.175(1)	126.967(1)	131.099(1)
γ, deg	90	90	90	90	90
V, Å^3	11 234(2)	11 193.6(3)	11 114.3(4)	11 654.5(13)	10 871.4(9)
d_{calcd}, g/cm^3	1.734	1.671	1.734	1.681	1.813
μ, mm^{-1}	4.357	3.634	4.653	3.480	4.697
R1[b](wR2[c]), %	8.19(21.37)	7.55(18.95)	6.91(16.51)	7.16(19.43)	5.78(15.45)

[a] Obtained with graphite monochromated Mo Kα (λ = 0.710 73 Å) radiation. [b] $R1 = \sum||F_o| - |F_c||/\sum |F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$.

stoichiometric amount of tyrosine (Ln/Tyr = 3/2) was used, precipitation of the free ligand resulted; the putative lanthanide complex remained in solution and resisted crystallization. Second, the role of tyrosine ligands for controlling lanthanide hydrolysis is unique in that multicubane superstructures are obtained. In stark contrast, when glycine, alanine, valine, glutamic acid, or the closely related phenylalanine[8] were used, only single-cubane complexes were produced,[6] even in the presence of exogenous halide ions. It is not yet understood why tyrosine is so unique in this capacity, but work is in progress to elucidate the possible causes. It is clear that, however, tyrosine ligands are necessary but not sufficient for the formation of a multicubane complex;[12] the participation of a templating halide ion is essential. Third, the addition of Cl^- was prompted by the observation of the unexpected incorporation of a μ_5-Cl^- ion in complex **1**.[5] Much improved synthesis of **1** and its Nd (**2**) and Gd (**3**) cognates was subsequently achieved with the addition of extra Cl^-. When Br^- was involved, analogous pentadecanuclear complexes (**4** and **5**) featuring a μ_5-Br^- were obtained. When I^- was employed, however, dodecanuclear complexes **6** and **7** were isolated; the counterintuitive product features a cyclic core composed of four vertex-sharing $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ cubanes and two I^- guests.

Structural Studies. Structures were determined for the 7 compounds in Tables 1 and 2. These compounds can be divided into two classes based on the number of $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ cubanes present in their core structure: Complexes **1**−**5** are composed of five vertex-sharing cubanes, whereas **6** and **7** each contains four of such fundamental building units. Because of the close similarity in structural metric values over the set of complexes, only ranges and mean values of core parameters rather than data for the full set of the representatives, **1**, **4**, and **6**, are provided in Table 3. Tabulations of interatomic distances and angles for all compounds are available as Supporting Information.

Table 2. Crystal Data[a] and Structure Refinement for Complexes **6** and **7**

	6	**7**
formula	$C_{72}H_{96}Cl_{10}Dy_{12}I_2N_8O_{94}$	$C_{72}H_{96}Cl_{10}Er_{12}I_2N_8O_{100}$
fw	5135.87	5288.99
space group	*I*4	*I*4
Z	2	2
a, Å	16.577(2)	16.355(2)
b, Å	16.577(2)	16.355(2)
c, Å	31.602(7)	31.026(6)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	8684(2)	8300(2)
d_{cal}, g/cm^3	1.964	2.116
μ, mm^{-1}	5.692	6.625
R1[b](wR2[c]), %	5.26(12.66)	8.58(19.76)

[a] Obtained with graphite monochromated Mo Kα (λ = 0.710 73 Å) radiation. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$.

Table 3. Selected Interatomic Distances (Å) and Angles (deg.) for Complexes **1**, **4**, and **6**

	1	**4**	**6**
Ln−O(μ_3-OH)	2.39(1)−2.48(1)	2.41(1)−2.54(1)	2.31(1)−2.43(1)
mean	2.43(3)	2.47(3)	2.36(3)
Ln−O(carboxylato)	2.38(2)−2.60(1)	2.45(1)−2.67(1)	2.35(1)−2.58(1)
mean	2.51(8)	2.53(1)	2.46(1)
Ln−N	2.58(2)−2.65(16)	2.61(2)−2.68(1)	2.55(1)−2.56(1)
mean	2.63(3)	2.65(3)	2.56(1)
Ln−X	3.25(1)−3.34(1)	3.37(1)−3.44(1)	
mean	3.31(3)	3.39(3)	
Ln−O(μ_3-OH)-Ln	97.4(5)−110.7(5)	98.0(3)−110.9(3)	96.7(3)−110.8(3)
mean	105(5)	106(5)	105(6)
O(μ_3-OH)−Ln−O(μ_3-OH)	68.1(4)−76.0(5)	67.1(3)−74.1(3)	68.2(3)−76.1(3)
mean	72(3)	71(3)	72(3)

As shown in Figure 3, complex **1**, containing 15 Eu(III) ions and 10 tyrosinate ligands in addition to the hydroxo and aqua ligands, crystallizes as discrete barrel-shaped molecular units with space between these barrels filled with solvent water. The metal 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 average Eu−Eu separation within the two outer layers is 6.331 Å, while that in the middle layer is 3.896 Å. The five shared Eu atoms bond equally to a central μ_5-Cl^- atom. The tyrosinate-less core may alternatively be viewed as a "wheel" formed by five corner-sharing cubanes centered on the chloride ion in a perfectly planar fashion. The average Eu−Cl distance of 3.314 Å is significantly longer than the

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[12] For other multicubane structures, 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.

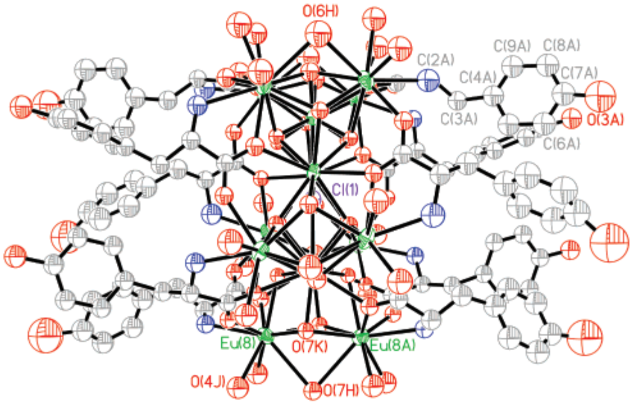

Figure 3. Perspective view of **1**, with lattice water molecules and perchlorate ions omitted for clarity. Color legend: carbon (gray), chlorine (purple), europium (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability.

sum of the van der Waals radii of Cl^- (1.81 Å)[13] and Eu(III) (0.95 Å),[13b] reflecting the primarily ionic interactions between the halide and the lanthanide ion. To the best of our knowledge, only one other example of μ_5-Cl^- was reported in the literature,[14] wherein significant covalency is involved in a Hg−Cl interaction.

The 10 tyrosinate ligands can be divided into two equivalent groups, each of which extend their 4-hydroxybenzyl side-chains in the direction perpendicular to the crystallographically imposed C_2 axis. The side-chains do not participate in, nor do they appreciably interfere with, the coordination. The coordination mode of the tyrosinate ligand with Eu(III) ions is significant: Each acts as a tridentate ligand by utilizing both its amino and carboxylate groups. The ligand can be described as a μ_3: η^1:η^2:η^1 anion (Figure 4), not only linking two neighboring Eu(III) centers within the same (outer) layer, but also coordinating a third Eu(III) ion in the middle layer through one of the carboxylate oxygen atoms. Such a mode has not been observed prior to our work; α-amino acids, in zwitterionic form, bind the lanthanide ions exclusively through the carboxylate oxygen atom(s) in previous studies. The coordination sphere of the Eu(III) ion is completed by hydroxo and aquo ligands. Thus, each of the 10 Eu(III) ions in the outer layers has a coordination number (CN) of 9, and the coordination polyhedra can be best described 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.

Except for the substitution of Br^- (van der Waals radius, 1.96 Å)[13] for Cl^-, the cationic complexes **4** and **5** are isostructural to **1**−**3**. The Br^- simultaneously coordinates the five inner-layer Ln(III) ions in a perfectly planar and previously unknown fashion (Figure 5). The average Ln−Br distances of 3.404 and 3.314 Å for **4** and **5**, respectively, are also significantly longer than the corresponding sum of the van der Waals radii (with van der Waals radii of Pr(III) and Eu(III) taken from ref 13b; **4**, 2.96 Å; **5**, 2.91 Å). In addition to the tyrosinate ligands, there are two zwitterionic tyrosine ligands that connect the outer two layers via only the carboxylate moieties in complex **4** (Figure 6). Although the coexistence of both neutral and negatively charged tyrosine-based ligands is interesting, this observation may not be a general one but may simply be due to the energetics of crystallization.

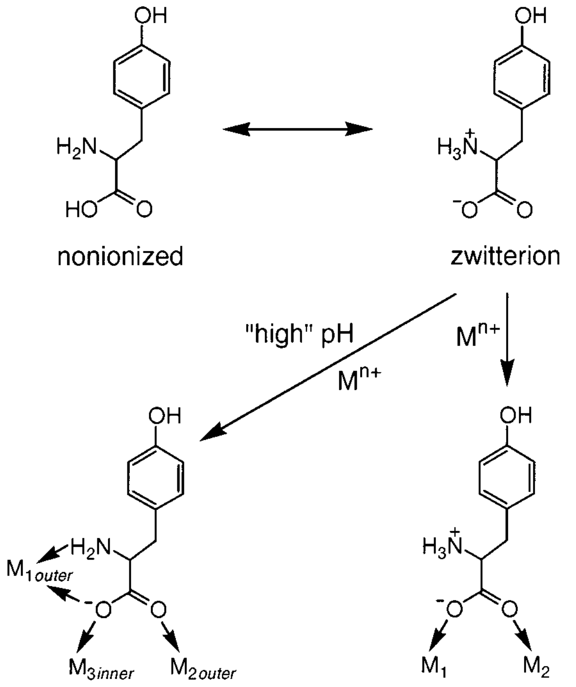

Figure 4. Two different coordination modes of a tyrosine-based ligand with lanthanide ions.

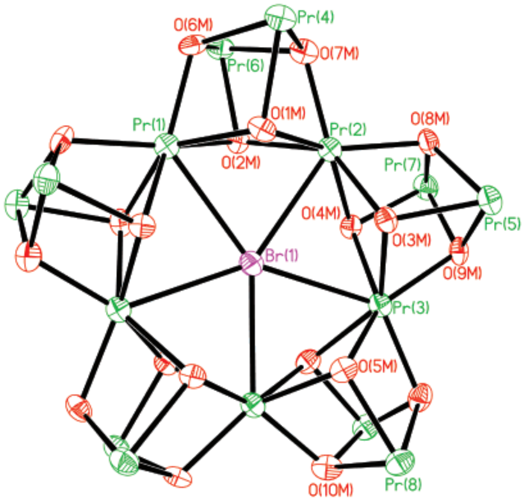

Figure 5. ORTEP representation of the core component of **4**, showing five vertex-sharing cuboid $[Pr_4(\mu_3\text{-}OH)_4]^{8+}$ units centering around a μ_5-Br^- ion. Color legend: bromine (purple), praseodymium (green), oxygen (red). Thermal ellipsoids are represented in 50% probability.

The dodecanuclear complexes **6** and **7**, isostructural to each other, are structurally analogous to their pentadecanuclear cognates (**1**−**5**). As shown in Figure 7, the cationic cluster core of **6** comprises four vertex-sharing $[Dy_4(\mu_3\text{-}OH)_4]^{8+}$

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[13] (a) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767. (b) Marcus, Y. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2995−2999.

[14] Shur, V. B.; Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Y. T.; Volkonsky, A. Yu.; Solodova, E. V.; Panov, S. Yu.; Petrovskii, P. V.; Vol'pin, M. E. *J. Organomet. Chem.* **1993**, *443*, C19−C21.

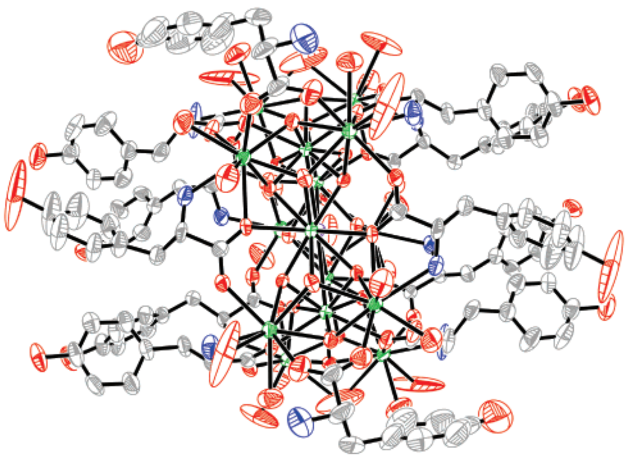

Figure 6. Perspective view of **4**, with lattice water molecules and perchlorate ions omitted for clarity. Color legend: carbon (gray), bromine (purple), praseodymium (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability. Please note that there are two additional tyrosine ligands along the "belt" of the barrel-shaped structure.

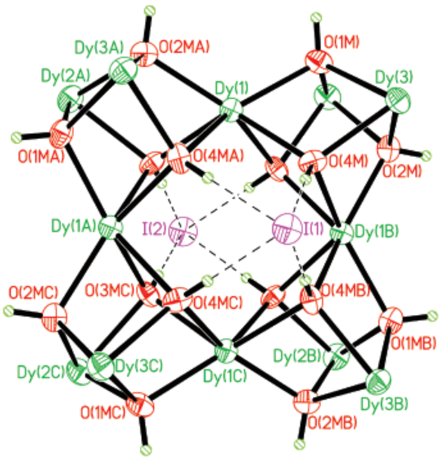

Figure 7. ORTEP representation of the core component of **6**, showing a square-shaped opening formed by four vertex-sharing cuboid $[Dy_4(\mu_3\text{-}OH)_4]^{8+}$ units. Two I^- ions are hydrogen-bonded to the μ_3-OH in a μ_4-I fashion, one on each side of the square. Color legend: iodine (purple), dysprosium (green), oxygen (red). Thermal ellipsoids are represented in 50% probability.

units in the form of a perfect square. Two iodide ions are incorporated in the structure. In contrast to Cl^- or Br^- that is situated in the center of the five-cubane wheel, the I^- ions are located on both sides of the wheel plane formed by the lanthanide ions. The average distance between the iodide ion and the hydrogen atoms of the μ_3-OH groups is 2.569 and 2.543 Å for **6** and **7**, respectively. These values are almost the same as the sum of the van der Waals radii of I^- (2.20 Å)[13] and H^+ (0.30 Å),[13b] indicating a very compact core structure in both cases and likely a hitherto unknown supramolecular motif. Eight tyrosinate ligands cap the wheel structure, four on each side (Figure 8). The coordination mode of the tyrosinate ligands is identical to that in compounds **1**−**5**.

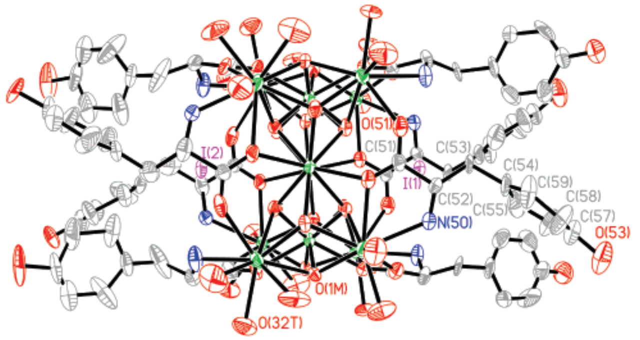

Figure 8. Perspective view of **6**, with lattice water molecules and perchlorate ions omitted for clarity. Color legend: carbon (gray), iodine (purple), dysprosium (green), nitrogen (cyan), oxygen (red). Thermal ellipsoids are represented in 50% probability. Please note that there are two additional tyrosine ligands along the "belt" of the barrel-shaped structure.

Anion Template Effects. It has long been recognized[15] in the synthesis of lanthanide alkoxides that the presence of a "central spherical negative charge density" such as a halide[16] and an oxo/hydroxo[17] group accounts for the driving force for product formation. However, the exact roles played by these anionic species have not yet been investigated. With the results summarized in Table 4, we wish to discuss the halide template effects involved in the assembly of polynuclear lanthanide-hydroxo complexes reported in this work. These efforts should aid in future work on assembling novel lanthanide complexes by utilizing templating anions of different *size* and *geometry*.

According to Busch, "a chemical template organizes an assembly of atoms, with respect to one or more geometric loci, to achieve a particular linking of atoms."[18] In other words, the outcome of a templated reaction depends on how the templating species interact with the substrate(s). Eventually the unambiguous demonstration of any template effects comes down to the demonstration of the dependence of product distribution upon the identity (size and geometry) of the template.

Several lines of evidence point convergently to the templating ability exercised by the halide ions in this work. The superb templating role of Cl^- was suspected at the outset when the unexpected Cl^--containing complex **1** (Table 4, entry 1) was isolated in the original "chloride-free" synthesis.[5] The encapsulated Cl^- presumably originated from the Cl^- impurity present in the perchloric acid used for the preparation of aqueous $Ln(ClO_4)_3$ solutions. Furthermore, a guest-free multicubane "barrel" is unlikely to be preformed for the later encapsulation of Cl^- because no such pentadecanuclear species were obtained when Cl^- was absent, as confirmed by the isolation of a drastically different complex

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(15) Anwander, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 599−602 and references therein.

(16) (a) Kretschmer, W.; Teuben, J. H.; Troyanov, S. I. *Angew. Chem., Int. Ed.* **1998**, *37*, 88−89. (b) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999−2009. (c) Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417−4423. (d) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 1962−1965.

(17) (a) Evans, W. J.; Greci, M. A.; Ziller, J. W. *Inorg. Chem.* **2000**, *39*, 3213−3220. (b) Xiong, R. G.; Zuo, J. L.; Yu, Z.; You, X. Z.; Chen, W. *Inorg. Chem. Commun.* **1999**, *2*, 490−494. (c) Pernin, C. G.; Ibers, J. A. *J. Cluster Sci.* **1999**, *10*, 71−90. (d) Poncelet, O.; Sartain, W. J.; Hubert-Pfalzgnof, L. G.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263−267. (e) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **1997**, *36*, 3802−3803. (f) Evans, W. J.; Sollberger, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 6095−6096.

(18) Busch, D. H. *J. Inclusion Phenom.* **1992**, *12*, 389−395.

Table 4. Evidence for Anion−Template Effects

entry	reaction mixture	product core structure[a]	guest(s)	counterion	yield (%)	ref
1	$Eu(ClO_4)_3$/tyr	*cyclo*-$[Eu_4(\mu_3\text{-}OH)_4]_5$	μ_5-Cl^-	ClO_4^-	<10	5
2	$Eu(ClO_4)_3$/tyr/HCl	*cyclo*-$[Eu_4(\mu_3\text{-}OH)_4]_5$	μ_5-Cl^-	ClO_4^-	60	5
3	$Nd(ClO_4)_3$/tyr/HCl	*cyclo*-$[Nd_4(\mu_3\text{-}OH)_4]_5$	μ_5-Cl^-	ClO_4^-	47	this work
4	$Gd(ClO_4)_3$/tyr/HCl	*cyclo*-$[Gd_4(\mu_3\text{-}OH)_4]_5$	μ_5-Cl^-	ClO_4^-	52	this work
5	$Pr(ClO_4)_3$/tyr/HBr	*cyclo*-$[Pr_4(\mu_3\text{-}OH)_4]_5$	μ_5-Br^-	ClO_4^-	43	this work
6	$Eu(ClO_4)_3$/tyr/HBr	*cyclo*-$[Eu_4(\mu_3\text{-}OH)_4]_5$	μ_5-Br^-	ClO_4^-	48	this work
7	$Dy(ClO_4)_3$/tyr/KI	*cyclo*-$[Dy_4(\mu_3\text{-}OH)_4]_4$	2 I^-	ClO_4^-	54	this work
8	$Er(ClO_4)_3$/tyr/KI	*cyclo*-$[Er_4(\mu_3\text{-}OH)_4]_4$	2 I^-	ClO_4^-	46	this work
9	$Er(NO_3)_3$/tyr	*oct*-$[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]$	μ_6-O^{2-}	NO_3^-	45	20
10	$Er(NO_3)_3$	*oct*-$[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]$	μ_6-O^{2-}	NO_3^-	40	19a, 20
11	$Nd(ClO_4)_3$	*oct*-$[Nd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]$	μ_6-O^{2-}	ClO_4^-	38	20
12	$Gd(ClO_4)_3$	*oct*-$[Gd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]$	μ_6-O^{2-}	ClO_4^-	45	20
13	$Gd(NO_3)_3$/tyr/NaCl	*cyclo*-$[Gd_4(\mu_3\text{-}OH)_4]_5$	μ_5-Cl^-	NO_3^-	48	this work

[a] The formulas do not reflect the exact compositions of the products; rather, they are meant to emphasize the cognizable building blocks in the supramolecular structures.

using $Ln(NO_3)_3$ in an analogous reaction (see later). Thus, *the formation of the pentadecanuclear complex may be best understood as chloride-induced self-assembly of the lanthanide ions with the assistance of tyrosinate ligands.* It follows that if the trace Cl^- impurity can efficiently direct the formation of the pentadecanuclear complexes, additional Cl^- in the reaction mixture should enhance the formation of the complex in terms of both product yield and purity. Indeed, the same complex (**1**) was obtained in 60% yield (Table 4, entry 2) with the addition of 1.0 M HCl solution, as compared to <10% in its absence.[5] More supporting evidence was provided with the good-yield syntheses of **2** and **3** in analogous reactions (Table 4, entries 3 and 4). In both cases, a Cl^- ion is located, as established by X-ray crystallography, in the wheel structure, simultaneously coordinating five lanthanide ions. The formation of such sophisticated structures may be viewed as the energetic compromise between the multiple stabilizing halide−lanthanide coordination and the destabilizing inter-cubane constraints.

As we were encouraged by these findings, the influences of anionic species of different size and geometry on tyrosine-controlled hydrolysis of representative lanthanide ions were investigated. It was found that the composition of the resulting complexes depends strongly on the nature of the anionic species present in the reaction mixture. Specifically, in the presence of added Br^-, the hydrolysis of $Pr(ClO_4)_3$ or $Eu(ClO_4)_3$ generated a pentadecanuclear complex with an encapsulated Br^- (Table 4, entries 5 and 6); the coordination mode of the Br^- ion is identical to that of the μ_5-Cl^- in complexes **1**−**3**.

An analogous hydrolytic reaction using $Dy(ClO_4)_3$ or $Er(ClO_4)_3$ in the presence of added KI afforded, to our surprise, a *dodecanuclear* complex whose core structure consists of four corner-sharing $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ (Ln = Dy, Er) cubanes (Table 4, entries 7 and 8). The formation of the smaller-sized four-cubane structure is counterintuitive, as the van der Waals radius of I^- (2.20 Å) is considerably larger than that of Cl^- (1.81 Å) or Br^- (1.96 Å) ion. However, this observation may be understood in terms of the possible energetically insurmountable constraint between adjacent cubane units if a larger wheel were formed. Comparable observations and similar arguments were made by Hawthorne and co-workers[4j] in halide-templated syntheses of tetrameric Hg(II) macrocycles supported by carborane cages.

The *geometric* implications of anion species for the formation of possibly different types of polynuclear complexes were also examined. The trigonal planar NO_3^- is of particular relevance because its size (1.79 Å)[13] is almost the same as that of Cl^-. In an analogous hydrolytic reaction, $Er(NO_3)_3$ rather than $Er(ClO_4)_3$ with added NO_3^- was utilized because it appeared that even a trace Cl^- would lead to the chloride-centered pentadecanuclear species.[5] The reaction produced the known and structurally characterized cationic complex $[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{12}]^{2+}$ (Table 4, entry 9).[19] Surprisingly, no tyrosinate ligands are incorporated in this compound, and the synthesis of the same complex was subsequently achieved by the direct hydrolysis of $Er(NO_3)_3$ (Table 4, entry 10).[20] The core component of this compound is a face-capped octahedral $[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ unit with an interstitial μ_6-oxo group (Figure 9). Its assembly is presumably assisted by the *templating* μ_6-oxo group[21] whose origin is unclear but is probably from hydroxide or water. Lending further support to the templating function of the μ_6-oxo group is the isolation of two complexes that contain the same octahedral core when direct hydrolysis of lanthanide perchlorates *in the absence of tyrosine* was performed (Table 4, entries 11 and 12).[20] These results clearly indicate the general importance of a spherical anionic species in governing the formation of polynuclear lanthanide complexes.

The most convincing evidence supporting the halide template effects is provided by the tyrosine-limited hydrolytic reaction of $Gd(NO_3)_3$ in the presence of competitive Cl^-: Structural determination by X-ray crystallography established

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[19] (a) Giester, G.; Unfried, P.; Žák, Z. *J. Alloys Compd.* **1997**, *257*, 175−181. (b) Žák, Z.; Unfried, P.; Giester, G. *J. Alloys Compd.* **1994**, *205*, 235−242.

[20] Wang, R.; Carducci, M. D.; Zheng, Z. *Inorg. Chem.* **2000**, *39*, 1836−1837.

[21] For additional examples containing a μ_6-O group, see: (a) Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 5410−5411. (b) Miele P.; Foulon, J. P.; Hovnanian, N.; Cot, L. *J. Chem. Soc., Chem. Commun.* **1993**, 29−31. (c) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1498−1499. (d) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 8593−8595.

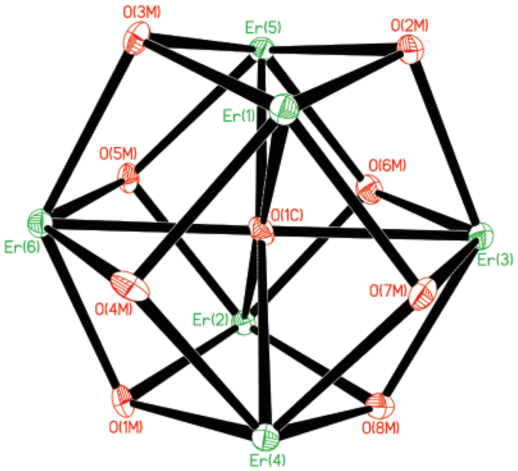

Figure 9. ORTEP representation of the cationic complex $[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{12}]^{2+}$, showing the core component of an octahedron of Er(III) ions centering on an interstitial μ_6-O group. Color legend: erbium (green), oxygen (red). The triangular metal faces are capped by triply bridging hydroxo ligands. Terminal aqua and nitrato ligands are omitted for clarity. Thermal ellipsoids are represented in 50% probability.

that the pentadecanuclear Cl^--containing complex **3** is the sole product with noncoordinating NO_3^- as counterions (Table 4, entry 13). This finding, coupled with the inability to produce a multicubane complex in the absence of a halide ion, suggests that the halide ion must be a stabilizing factor along the reaction coordinates to the "wheel"-structured complexes, and hence, a kinetic template.[22]

The possibility of de-complexing the halide guest(s) in the multicubane complexes was explored in order to assess the authenticity of the host−guest interaction. When an aqueous solution of complex **6** or **7** was treated with solid $AgSbF_6$, instant yellow precipitation, presumably of AgI, was observed. However, single crystals of the I^--free product suitable for X-ray diffraction studies have so far eluded us. Nevertheless, an anion-free square-shaped complex structure resembling the one in **6** and **7** was realized when the hydrolysis of Nd(III) was conducted at ∼pH 13 in the presence of EDTA,[23] suggesting the conceivable existence of a stable halide-free structure. Work is in progress to study the free host for the encapsulation of other guest species, including F^-.

Summary. A series of polynuclear lanthanide complexes with tyrosinate ligands have been isolated, with the assistance of templating halide ions, from the hydrolytic reaction of the lanthanide ions. When Cl^- or Br^- is utilized, pentadecanuclear complexes comprising five vertex-sharing cubane-like $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ units centering on the halide template are obtained. In the case of I^-, dodecanuclear complexes composed of four cubane units are instead formed, with the encapsulation of two I^- guests. Using lanthanide nitrates in analogous reactions generates a new class of hexanuclear complexes based on a common face-capped octahedral $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ core centering on a presumably templating interstitial μ_6-O group. Complexes containing the same core can also be produced via hydrolytic reaction of lanthanide perchlorates, but only in the absence of supporting tyrosine ligands. This finding, coupled with results from our previous work,[5,6] indicates the yet-to-be discerned critical role(s) played by the tyrosinate ligand in the formation of the multicubane complexes.

In summary, the superior ability of halide ions to template the efficient assembly of novel multicubane complexes has been demonstrated. The kinetic nature of the template effects is unambiguously established by (1) the strong dependence of the product composition on the nature of the halide ion; (2) the inability to generate analogous complexes utilizing lanthanide nitrates; a completely different class of hexanuclear complexes is afforded instead; and (3) the isolation of the halide-encapsulating complex in the presence of competing nitrate ions. This work provides a stimulating demonstration of the under-appreciated templating roles of anions in self-assembly processes.

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Supporting Information Available: Tables of crystal data, structural solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **1**−**7** (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] (a) Anderson, A.; Anderson, H. L.; Sanders, J. K. M. *Acc. Chem. Res.* **1993**, *26*, 469−475. (b) Busch, D. H.; Stephenson, N. A. *Coord. Chem. Rev.* **1990**, *100*, 119−140.

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