

Hydrolytic Synthesis and Structural Characterization of Lanthanide Hydroxide Clusters Supported by Nicotinic Acid

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Polynuclear lanthanide hydroxide complexes featuring the cubane-like $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ [Ln = Eu(III), Gd(III)] cluster core have been synthesized by controlled hydrolysis of the lanthanide ions using nicotinic acid as the ancillary ligand. The synthetic procedure has been found to significantly influence the nature of the resulting cluster species. In a one-pot synthesis, adjusting the pH of the reaction mixture containing $\text{Ln}(\text{ClO}_4)_3$ and nicotinic acid afforded tetranuclear complexes of the general formula $[\text{Ln}_4(\mu_3\text{-OH})_4(\text{Hnic})_5(\text{H}_2\text{O})_{12}](\text{ClO}_4)_8$ with the $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ (Ln = Eu, Gd) cluster core encapsulated by zwitterionic nicotinate ligands. In stark contrast, mixing aqueous solutions of $\text{Ln}(\text{ClO}_4)_3$ and nicotinic acid whose pH had been preadjusted produced assemblies composed of two of the cubane-like cluster cores that are related by a crystallographic inversion center and are doubly bridged by nicotinate ligands using both the carboxylate group and pyridyl N atom for coordination. The influences of pH conditions and synthetic procedures on the identity of the resulting cluster species are discussed, so is the structural relevance of the low-pH complexes to their cluster analogues obtained under higher-pH conditions.

Introduction

Polynuclear lanthanide hydroxide clusters are an interesting class of lanthanide-containing substances. They have attracted increasing interest because of the synthetic challenges, their appealing structures, and their interesting properties and potentially useful applications.¹ Similar to the development of many other research areas, the development of the chemistry of lanthanide hydroxide clusters is originally stimulated by some serendipitous discoveries.^{2–6} A number

of polynuclear lanthanide hydroxide complexes featuring structurally well-defined core structures were obtained unexpectedly, and their formation was invariably ascribed to adventitious hydrolysis of the lanthanide ions. Despite the distinctly different synthetic procedures for their formation, certain cluster motifs have appeared repetitively in the literature, which provided the fundamental impetus for the efforts to develop rational methodologies for the reproducible synthesis of these otherwise elusive lanthanide-containing species.¹ Such efforts are further enhanced by their interesting properties and envisioned applications. For example, certain lanthanide hydroxide clusters have been used as precursors for the preparation of oxide materials in advanced technologies (electrical, optical, magnetic, and luminescent materials),⁷ while others have been incorporated into polymeric matrixes to prepare hybrid materials with enhanced mechanical properties.⁸ Interesting molecule-based magnetic phenomena have been observed in a number of lanthanide

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hydroxide clusters.^{9,10} In addition, some of these complexes have been found to catalyze useful chemical transformations¹¹ and the hydrolytic cleavage of nucleic acids.^{12–14} Lanthanide hydroxide clusters have also been proposed as new paradigms of contrast-enhancing agents in biomedical imaging.^{15,16} More recently, fixation of atmospheric CO₂ by lanthanide hydroxides has been observed,^{17–19} which carries significant ramifications from the environmental viewpoint. It is thus reasonable to predict that the research activities of lanthanide hydroxide clusters will continue to grow with high possibility of finding interesting materials with useful applications that have not yet been realized or even contemplated.

The most successful synthetic route to lanthanide hydroxide clusters is the ligand-controlled hydrolytic approach.¹ Although the synthesis of structurally well-defined transition metal clusters by hydrolysis or solvolysis starting from their corresponding mononuclear precursors has been well established,^{20–24} an analogous synthetic approach to lanthanide cluster based upon deliberate hydrolysis of the lanthanide ions was not available until about a decade ago.²⁵ In such an approach (Figure 1), an ancillary ligand pre-occupies part of the coordination sphere of a lanthanide ion, leaving only a limited number of sites for aqua coordination. Raising the pH of the reaction mixture causes deprotonation of the aqua ligand(s), generating the corresponding hydroxo complex. The hydroxo group, being unsaturated both coordinatively and electrically, has a propensity to bridge one or more lanthanide ions, leading eventually to the assembly of finite and structurally well-defined lanthanide hydroxide cluster complexes.

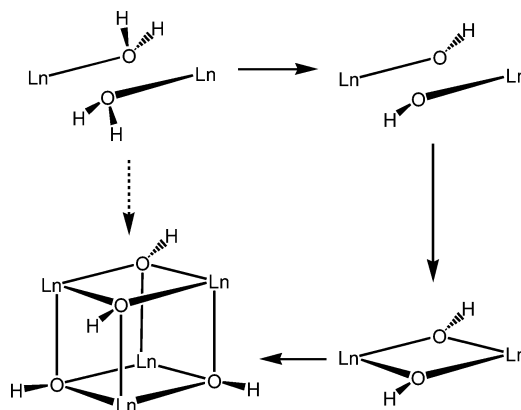


Figure 1. Three formal stages in the ligand-controlled lanthanide hydrolysis leading to polynuclear lanthanide hydroxide clusters.

A number of ancillary ligands,^{25–38} including coordinating inorganic anions,^{39–41} have since been utilized in this capacity, among which α -amino acids have been studied most extensively.^{25–27} In this contribution, 3-pyridine carboxylic acid (nicotinic acid) is used as the ancillary ligand to control the degree of lanthanide hydrolysis. This choice is based on a number of considerations. First, it is formally a β -amino acid. Previously the uses of α -amino acids^{25–27}

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and polyaminopolycarboxylic acids^{28–30} have led to the discovery of a great variety of novel cluster motifs. It is of interest to evaluate whether a β -amino acid would support and control lanthanide hydrolysis in a similar manner. Second, as compared with the ligands previously studied, nicotinic acid is structurally more rigid because of the presence of the aromatic ring and its conjugation with the carboxylate group. In addition, because of its much weaker basicity than a regular amino group, the pyridyl group may maintain its basic form as opposed to the protonated amino group of a typical zwitterionic amino acid under similar conditions in the pH range suitable for lanthanide hydrolysis. The availability of this free pyridyl group offers practical opportunities for additional metal coordination and the formation of new clusters.¹² Third, a number of lanthanide complexes with nicotinic acid and its cognates, namely 2-pyridine carboxylic acid (picolinic acid)^{42–46} and 4-pyridine carboxylic acid (isonicotinic acid),^{43b,47,48} have already been synthesized under low-pH conditions and characterized crystallographically. Structural comparisons of these low-pH complexes with the hydroxide clusters anticipated at higher pH may reveal correlations between these species, thus offering much desired insights into the mechanism responsible for the cluster assembly. In this contribution, the synthesis and structural characterization of four lanthanide hydroxide clusters are reported. Possible mechanisms for the assembly of these cluster species from their corresponding low-pH complexes are discussed.

Experimental Section

Caution! Metal perchlorates are potentially explosive. Only a small amount of materials should be prepared and handled with great care. All chemicals were purchased from Aldrich and used as received. Aqueous solutions of lanthanide perchlorates were prepared by digesting lanthanide oxides in concentrated perchloric acids and diluted to appropriate concentrations. Elemental analyses were performed by Numega Resonance Laboratories, Inc. (San Diego, CA).

Synthesis of [Eu₄(μ_3 -OH)₄(Hnic)₅(H₂O)₁₂](ClO₄)₈·6H₂O (1) (Hnic = Pyridyl-Protonated Nicotinate or the Zwitterionic Form of Nicotinic Acid, C₆H₅O₂N). A mixture containing 10 mL of Eu(ClO₄)₃ (1.0 M) and nicotinic acid (0.62 g, 4 mmol) in 15 mL of deionized water was stirred at 90 °C while a freshly prepared aqueous solution of NaOH (1.0 M) was added dropwisely to the

point of incipient but permanent precipitation. The mixture was then brought to and maintained under reflux for one additional hour. The mixture thus obtained was filtered while hot, and the filtrate was cooled naturally to room temperature. Block-shaped colorless crystals were obtained after 1 week (Yield 45%). Anal. Calcd for C₃₀Cl₈H₆₅Eu₄N₅O₆₄ (FW = 2411.31): C, 14.94%; H, 2.72%; N, 2.90%. Found: C, 14.82%; H, 2.41%; N, 2.89%.

Synthesis of [Gd₄(μ_3 -OH)₄(Hnic)₅(H₂O)₁₂](ClO₄)₈·7H₂O (2). This compound was prepared using the same procedure as described above for the synthesis of its Eu(III) cognate but using Gd(ClO₄)₃ in place of Eu(ClO₄)₃. The product was obtained as block-shaped colorless crystals in about 48% yield. Anal. Calcd for C₃₀Cl₈H₆₇Gd₄N₅O₆₅ (FW = 2450.47): C, 14.70%; H, 2.76%; N, 2.86%. Found: C, 14.47%; H, 2.22%; N, 2.91%.

Synthesis of [Eu₄(μ_3 -OH)₄(nic)₆(H₂O)₈]₂(ClO₄)₄·3H₂O (3) (nic = Nicotinate, C₆H₄O₂N). With stirring a freshly prepared aqueous solution of NaOH (1.0 M) was added dropwise to a 10 mL solution of Eu(ClO₄)₃ (1.0 M) at 90 °C to the point of incipient but permanent precipitation. Another solution was prepared by adding aqueous solution of NaOH (1.0 M) to nicotinic acid (0.62 g, 4 mmol) in 5 mL of deionized water to reach a pH of 8. This solution was then added dropwise to the above pH-adjusted solution of “lanthanide perchlorate”. The resulting mixture was stirred at 90 °C for one additional hour and then filtered while hot. The product was obtained as block-shaped colorless crystals upon standing of the filtrate at room temperature for 2 days (Yield 30%). Anal. Calcd for C₇₂H₉₄Eu₈Cl₄N₁₂O₆₇ (FW = 3557.08): C, 24.31%; H, 2.66%; N, 4.73%. Found: C, 24.31%; H, 2.48%; N, 4.80%.

Synthesis of [Gd₄(μ_3 -OH)₄(nic)₆(H₂O)₈]₂(ClO₄)₄ (4). Using Gd(ClO₄)₃ in place of Eu(ClO₄)₃, this compound was prepared by adopting the same procedure as the one describe above for the synthesis of compound 3. The product was obtained as block-shaped colorless crystals (Yield 32%). Anal. Calcd for C₇₂H₈₈Gd₈Cl₄N₁₂O₆₄ (FW = 3545.32): C, 24.39%; H, 2.50%; N, 4.74%. Found: C, 24.96%; H, 2.49%; N, 4.79%.

X-ray Structure Determinations. Data were collected on a Bruker SMART Apex CCD diffractometer using graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 119 K (**1**) or 223 K (**2**, **3**, and **4**). Absorption corrections were applied using the multiscan program SADABS.^{49a} The structures were solved by direct methods (SHELXTL Version 5.10).^{49b} Non-hydrogen atoms were refined anisotropically by full-matrix least-squares method on F^2 . The hydrogen atoms of organic ligand were generated geometrically (C–H = 0.96 Å, N–H = 0.90 Å). The crystallization water molecules in compounds **1–4** were removed by SQUEEZE.^{49c} Crystal data, as well as details of the data collection and refinement, for the complexes are summarized in Table 1.

Results and Discussion

Synthesis of Compounds 1–4. The synthesis of compounds **1–4** followed the ligand-controlled hydrolytic approach previously established,^{25–27} but the procedures for **1** and **2** are slightly different from those for **3** and **4**. The synthesis of the former two complexes adopted a one-pot synthesis whereby the pH of the aqueous mixture containing both the ancillary ligand and the lanthanide salts was adjusted by the addition of an aqueous solution of NaOH. In comparison, the synthesis of **3** and **4** took a two-step procedure; the pH of the aqueous solutions of the ligand and the lanthanide perchlorate was adjusted individually to appropriate values prior to their mixing. The outcome of

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Table 1. Crystal Data As Well As Details of Data Collection and Refinement for the Complexes 1–4

complex	1	2	3	4
formula	C ₃₀ H ₅₈ Cl ₈ Eu ₄ N ₅ O _{60.50}	C ₃₀ H ₅₉ Cl ₈ Gd ₄ N ₅ O ₆₁	C ₇₂ Cl ₄ Eu ₈ H ₈₈ N ₁₂ O ₆₄	C ₇₂ Cl ₄ Gd ₈ H ₈₈ N ₁₂ O ₆₄
<i>M_r</i>	2348.25	2378.42	3503.02	3545.34
<i>T</i> (K)	119(2)	223(2)	223(2)	223(2)
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> , Å	13.3198(10)	13.398(2)	16.835(4)	16.859(4)
<i>b</i> , Å	14.0587(10)	14.045(2)	21.687(5)	21.749(6)
<i>c</i> , Å	18.9634(14)	19.151(3)	18.583(4)	18.641(5)
α , deg	89.9210(10)	90.136(2)	90	90
β , deg	87.6400(10)	92.534(2)	105.435(4)	105.453(4)
γ , deg	78.2150(10)	102.018(2)	90	90
<i>V</i> , Å ³	3473.2(4)	3521.0(10)	6540(3)	6588(3)
<i>Z</i>	2	2	2	2
<i>D_c</i> , (g cm ⁻³)	2.245	2.243	1.779	1.787
μ , (mm ⁻¹)	4.000	4.151	3.948	4.138
data/params	14885/958	13495/970	12801/721	12918/721
θ (deg)	1.07–27.00	1.81–26.00	1.57–26.00	1.45–26.00
obsd reflns	12609	10091	10282	10006
<i>R</i> ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0350	0.0409	0.0401	0.0483
<i>wR</i> ₂ ^b (all data)	0.0854	0.1071	0.1151	0.1352

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum w(F_o^2)^2 \}^{1/2}.$$

these two reactions differs markedly with the one-pot synthesis producing tetranuclear clusters of the general formula [Ln₄(μ_3 -OH)₄(Hnic)₅(H₂O)₁₂](ClO₄)₈ [Ln = Eu(**1**), Gd(**2**)] while the two-step synthesis affording [Ln₄(μ_3 -OH)₄(nic)₆(H₂O)₈](ClO₄)₄ [Ln = Eu(**3**), Gd(**4**)]. The latter complexes are ligand-bridged dimers of the tetranuclear cluster (see below for structural description of the complexes) wherein the ligands are monoanionic while in the former, the ligands are zwitterionic with protonated pyridyl groups. The compositions of these different cluster complexes are supported by satisfactory elemental analyses of individual compounds in addition to crystallographic studies.

The distinctly different results can be rationalized in terms of the specific ligand forms under the different reaction conditions applied. In the one-pot synthesis, a highly acidic solution mixture containing the ligand and Ln(ClO₄)₃ was first obtained wherein the pyridyl group of the ligand is protonated. Addition of NaOH first caused the deprotonation of the acid group (p*K*_a of nicotinic acid ~ 3.0 at 25 °C), but the pyridyl group should remain protonated because of its much weaker acidity (p*K*_a of pyridinium ~ 4.9 at 25 °C).⁵⁰ Addition of the base also caused the hydrolysis of the lanthanide ion, and aggregation of the resulting hydroxo species led to the formation of the cluster core, which is readily coordinated by the carboxylate group of the zwitterionic ligand to give the product. The situation is similar to those when zwitterionic α -amino acids were utilized in the synthesis of lanthanide hydroxide complexes.^{25–27} It is also of interest to note that there exists an analogous tetranuclear cluster of Tb(III) formed by using pyridinioacetate as ancillary ligand.⁵ The function of the ligand is probably similar to that of nicotinic acid in the present case.

The two-step synthesis was different in that the ligand was first converted, with the added base, to its monoanionic form whose pyridyl and carboxylate groups are both capable of metal coordination. Since the pH of the lanthanide salt

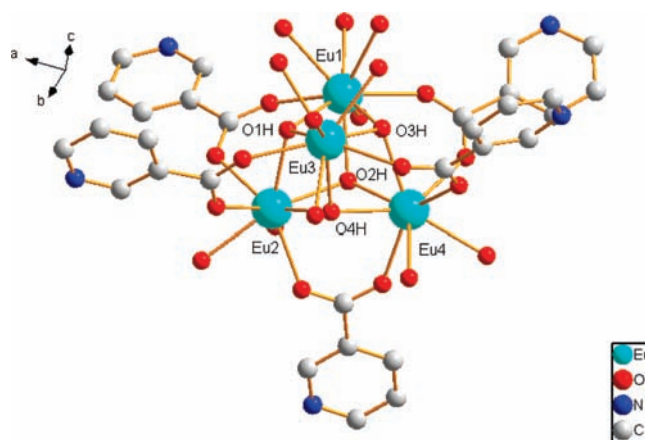


Figure 2. Structure of the cationic cluster complex [Eu₄(μ_3 -OH)₄(Hnic)₅(H₂O)₁₂]⁸⁺ of **1**. Hydrogen atoms are removed for clarity.

solution was preadjusted by base addition, mixing this solution with the one of the monoanionic ligand was not likely to cause the protonation of the pyridyl group. As such, while the carboxylate group coordinates and encapsulates the cluster core as in the case of **1** or **2**, the pyridyl group is positioned for possible coordination of additional metal ions, and hence the bridged di-cluster assemblies **3** and **4**.

Crystal Structures of Compounds 1–4. Crystallographic studies revealed the tetranuclear structures of **1** and its isostructural Gd(III) analogue **2**. As shown in Figure 2, the cationic cluster of **1** has a distorted cubane-shaped core of [Eu₄(μ_3 -OH)₄]⁸⁺. The four component metal atoms form a nearly perfect tetrahedron with 5 of its 6 edges each bridged by a carboxylate group of the organic ligand. All nicotinate ligands display the same coordination mode (a, Figure 3). The Eu1–Eu3 edge is not bridged, and each of these two metal atoms is nona-coordinate with contributions from three μ_3 -OH, two O atoms each from a different nicotinate ligand, and four terminal aqua ligands. The coordination geometry may be described as a tricapped trigonal prism. In comparison, Eu2 and Eu4 are each octa-coordinate with contributions from three μ_3 -OH groups, three O atoms each from a different nicotinate ligand, and two terminal aqua ligands

(50) Appleby, C. A.; Wittenberg, B. A.; Wittenberg, J. B. *Proc. Nat. Acad. Sci. U.S.A.* **1973**, *70*, 564.

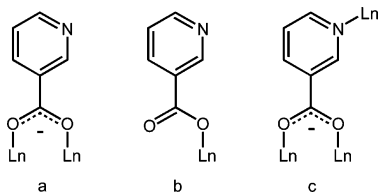


Figure 3. Three different coordination modes of a monoanionic nicotinate ligand.

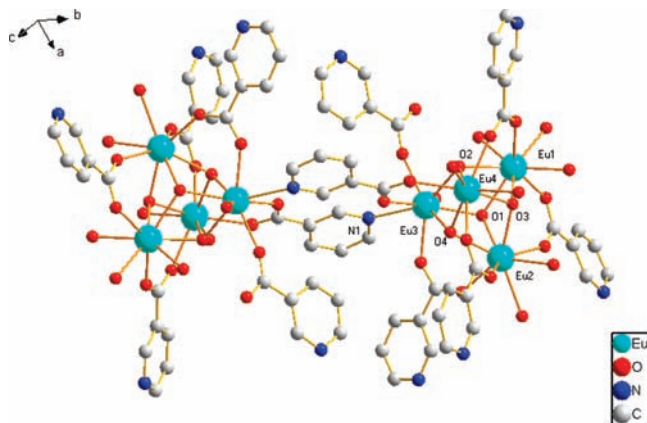


Figure 4. Structure of the cationic cluster complex $\{[Eu_4(\mu_3\text{-OH})_4(\text{nic})_6(\text{H}_2\text{O})_8]_2\}^{4+}$ of **3**. Hydrogen atoms are removed for clarity.

organized into a square-antiprismatic arrangement. The metric ranges of Eu–O bonds and Eu···Eu separations are 2.356(4)–2.583(4) Å and 3.7855(4)–3.9650(4) Å, respectively, both similar to the corresponding values reported for cluster complexes containing the same $[Eu_4(\mu_3\text{-OH})_4]^{8+}$ core.²⁵ The metric values of other bond lengths and angles involving the ligand are similar to those reported for its low-pH counterpart.^{45–47}

Compound **2** is isostructural to **1** (Supporting Information, Figure S1), with the main differences being the metric values of bond lengths and angles, anticipated because of the different metal size. The ranges for Gd–O bonds and Gd···Gd separations are 2.337(4)–2.547(4) Å and 3.7747(6)–3.9388(6) Å, respectively, both within the ranges reported for similar $[Gd_4(\mu_3\text{-OH})_4]^{8+}$ core-containing cluster complexes²⁵ and a low-pH Gd(III) complex with nicotinic acid ligand.⁴⁶

Compound **3** is a dimer of $[Eu_4(\mu_3\text{-OH})_4(\text{nic})_6(\text{H}_2\text{O})_8]^{2+}$ (Figure 4). Each of the component tetranuclear cluster units is encapsulated by six nicotinate ligands. These ligands display three different coordination modes, four of which using only their carboxylate groups to bridge two lanthanide ions in the same fashion as the zwitterionic ligands in **1** and **2** (a, Figure 3), one being monodentate using its carboxylate O atom (b, Figure 3), and the sixth one bridging the two cluster units, using its carboxylate group for two lanthanide ions of one of the cubanes while using its pyridyl N atom to coordinate a lanthanide ion within the other tetranuclear cluster core (c, Figure 3). The most salient feature of this di-cluster assembly is thus the coexistence of three different coordination modes of the organic ligands, and to our best knowledge, this third coordination mode has not previously been reported. All Eu(III) ions are octa-coordinate with a square antiprismatic coordination geometry. Eu1, Eu2, and

Eu4 each has in its coordination sphere three $\mu_3\text{-OH}$, two O atoms from different nicotinate ligands, and three terminal aqua ligands, while Eu3 is coordinated by three $\mu_3\text{-OH}$ groups, three O atoms each from a different nicotinate ligand, one terminal aqua ligand, and the pyridyl N atom of the unique cluster-bridging ligand. The Eu–N distance is 2.749(7) Å, slightly longer than the corresponding value [2.58(2)–2.65(2) Å, average 2.63 Å] reported for the Eu-tyrosinate cluster complex.^{25a,27} The ranges of Eu–O bonds and Eu···Eu separations are 2.332(6)–2.549(6) Å and 3.7719(10)–3.9112(8) Å, respectively, both within the ranges reported for similar complexes.⁴⁶

Compound **4** is isostructural to **3** (Supporting Information, Figure S2). The Gd–N distance is 2.753(8) Å. The ranges for Gd–O bonds and Gd···Gd separations are 2.326(7)–2.565(7) Å and 3.7644(12)–3.9134(10) Å, respectively. These metric values are also within the ranges reported for similar complexes.^{45–47}

Structural Comparison of the Cluster Complexes with Their Low-pH Counterparts. The coordination chemistry of a number of lanthanide ions with nicotinic acid and its isomeric pyridine carboxylic acids under non-hydrolytic conditions has been studied, and the crystal structures of several such complexes have been established.^{42–48} Three structural types have been identified, all possessing either a discrete or a recognizable dinuclear unit present in a polymeric structure. Complexes of the first structural type have a general formula of $[\text{Ln}(\text{nic})_3(\text{H}_2\text{O})_2]_2$ and are electrically neutral, containing two centrosymmetrically related lanthanide ions bridged by four monoanionic ligand with each using its carboxylate group for coordination (a, Figure 5).^{42,43a,46} Each metal atom is also chelated by the carboxylate group of an additional ligand. The coordination sphere is completed by two aqua ligands. The second and third type of low-pH lanthanide complexes are formed with zwitterionic nicotinate ligands, and their dinuclear core units are cationic. Such a species can either be a discrete molecular entity (b, Figure 5)⁴⁴ or as a dinuclear repeating unit within a polymeric chain (c, Figure 5),^{43b,44} both being structurally similar to the foregoing electrically neutral complexes. Subtle structural differences exist. A discrete cationic complex contains only four organic ligands, two of them being bridging and the other two being both bridging and chelating. The lanthanide coordination sphere is completed by terminal aqua ligands. Such cationic complexes have been found as counterions in a family of anionic coordination polymers composed of lanthanide ions and polyoxometalate ligands.⁴⁴ In comparison, a dinuclear unit present in a polymeric structure is associated with six zwitterionic nicotinate ligands, four being bridging and the remaining two being monodentate (c, Figure 5).^{43b,44} The other carboxylate O atom of this monodentate ligand coordinates a neighboring dimeric unit. In other words, this particular ligand serves to bridge two dimeric repeating units by acting as a monodentate ligand for each.

In the present synthesis, the low-pH complexes are formed first, followed by hydrolysis induced by the added base. As previously proposed,^{25b} the base is probably responsible for not only the deprotonation of the aqua ligands but also the

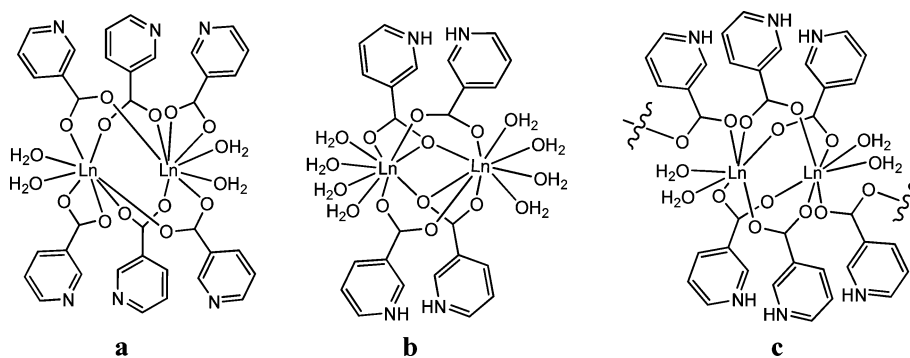


Figure 5. Three different structure types reported for lanthanide complex with nicotinic acid under low-pH or non-hydrolytic conditions. The + charge signs of the pyridinium groups and the complex ions (**b** and **c** each carrying a charge of +6) are omitted for clarity.

displacement of some of the nicotinate ligands. The resulting lanthanide hydroxo species, due largely to the electrical and coordinative unsaturation of the hydroxo group, are expected to aggregate via Ln–OH–Ln bridging interactions (olation reaction, Figure 1). The degree of aggregation is controlled and limited by the ancillary ligands, leading eventually to the assembly of the clusters. Although the exact steps leading to the assembly of the clusters are unclear, the diamond-shaped dinuclear complex doubly bridged by hydroxo groups is a reasonable intermediate as it resembles structurally the low-pH dinuclear complex described above. This hypothesis is also supported by a large number of complexes containing the same core motif of $[\text{Ln}(\mu_2\text{-OH})_2\text{Ln}]$, including one directly derived from the deprotonation of the mononuclear aqua complex of EDTA.^{1b,c} As long as allowed stereochemically, the dinuclear bis-hydroxo unit will dimerize to form the cubane-like tetranuclear cluster core. This is probably the case with compounds **1** and **2**. Although the pyridyl groups in these two clusters remain protonated, deprotonation is possible if more base is added. In our experiments, however, base addition was halted as soon as the reaction mixture turned and remained turbid. The small amount of precipitate is putatively that of intractable lanthanide hydroxides or oxides as excess lanthanide perchlorate was present in the reaction mixture. The excess lanthanide ion was essentially an indicator for the base addition. As such, the reaction was stopped at the stage when the cluster was already assembled using just the coordination of the carboxylate group while the pyridyl group remained protonated.

The situation was different in the syntheses of compounds **3** and **4**. Since the pyridyl group is already in its basic form, its N atom is capable of coordinating a lanthanide ion of a

neighboring cluster unit. Clearly the formation of the doubly bridged cubane assemblies was made possible by the appropriately positioned N atom with respect to the carboxylate group of the same ligand. Providing support to this conclusion are the failed attempts to obtain similar cluster compounds using the isomeric 2-pyridine carboxylic acid or 4-pyridine carboxylic acids under otherwise identical reaction conditions.

Conclusions

Four lanthanide hydroxide cluster complexes with nicotinic acid as ancillary ligand have been prepared by hydrolytic synthetic routes using nicotinic acid as the ancillary ligand. Depending on the reaction procedures, either single, tetranuclear clusters characterized by a distorted cubane core structure or di-cluster assemblies featuring two of the tetranuclear cluster cores doubly bridged by nicotinate ligands were obtained. These results provide new examples of lanthanide hydroxide clusters prepared by using the ligand-controlled hydrolysis. They also indicate the delicacy associated with the synthesis of these generally elusive lanthanide-containing substances.

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Supporting Information Available: CIF files of compounds **1–4**. ORTEP drawings of complexes **2** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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