Dynamic Article Links ▶

PAPER

Hydrolytic synthesis and structural characterization of lanthanide-acetylacetonato/hydroxo cluster complexes – A systematic study†

Yinglan Wu,[a] Scott Morton,[a] Xiangjian Kong,[b] Gary S. Nichol[a] and Zhiping Zheng*[a]

Lanthanide hydroxide cluster complexes with acetylacetonate were synthesized by the hydrolysis of the corresponding hydrated lanthanide acetylacetonates in methanol in the presence of triethylamine. Polymeric lanthanide hydroxide complexes based on diamond-shaped dinuclear repeating units of $[Ln_2(CH_3CO_2)_2]^{4+}$ (Ln = La, Pr) and discrete complexes featuring a tetranuclear distorted cubane core of $[Ln_4(\mu_3\text{-}OH)_2(\mu_3\text{-}OCH_3)_2]^{8+}$ (Ln = Nd, Sm) and a nonanuclear core of $[Ln_9(\mu_4\text{-}O)(\mu_4\text{-}OH)(\mu_3\text{-}OH)_8]^{16+}$ (Ln = Eu–Dy, Er, Yb) were obtained. The dependence of the cluster nuclearity on the identity of the lanthanide ion is rationalized in terms of the influences of a metal ion's Lewis acidity and the sterics about the Ln–OH unit on the kinetics of the assembly process that leads to a particular cluster.

Introduction

Polynuclear lanthanide hydroxide complexes are a class of interesting substances.[1,2] They generally possess a well-defined, cluster-type polyhedral core encapsulated in a coordination sphere formed by certain chelating ligands. These lanthanide-containing compounds have attracted increasing recent interest, not merely because of their appealing structures, but also because of the synthetic challenge and their potentially significant applications. Fundamentally, synthesis of polynuclear lanthanide complexes with a certain degree of confidence in predicting the product structure remains a great challenge; a meticulous design is frequently met with synthetic serendipities.[3,4] From the perspective of practical applications, some polynuclear lanthanide hydroxide complexes have been shown to be useful precursors for technologically important oxide materials[5] and can be used as nanoscopic building blocks, when incorporated into a polymer matrix, for the realization of hybrid materials with enhanced mechanical properties.[6] Complexes featuring lanthanide-hydroxo core motifs that mimic the active-site structure of naturally-occurring nucleases have been shown to effectively catalyze the hydrolytic cleavage of nucleic acids.[7] The use of lanthanide hydroxide complexes in facilitating certain organic transformations has also been demonstrated recently.[8] Unique magnetic properties of lanthanide hydroxide clusters have also been demonstrated in the form of a single-molecule magnet[9] and a contrast-enhancing

agent in magnetic resonance imaging.[10] More recently, fixation of atmospheric CO_2 by lanthanide hydroxide complexes has also been observed,[11] and such complexes are of environmental significance as they may lead to materials capable of fixing atmospheric CO_2 under ambient conditions or immobilizing radioactive wastes in the form of metal carbonate.[12] Research activities in pursuing the reproducible synthesis of cluster-type lanthanide hydroxide complexes and the exploration of their potential applications are thus of fundamental interest and practical significance.

Previous reports of lanthanide hydroxide cluster complexes focus on the structural description of such compounds whose unexpected formation has been conveniently ascribed to the adventitious hydrolysis of the metal ions.[1] The notion that such hydrolytic processes are hard to control is probably responsible for why the chemistry has not progressed more quickly. Nevertheless, the recurrence of certain lanthanide-hydroxo cluster core motifs such as the now well-known, distorted cubane[13] suggests that such cluster cores are more prevalent than originally thought and that more rational synthesis of these otherwise elusive species should be possible through deliberate hydrolysis of the lanthanide ions. We realized at the outset that the presence of certain kinds of ligands, multidentate ones in particular, would be necessary to preoccupy part of the coordination sphere of the bulky lanthanide ions, leaving only a limited number of sites available for aqua coordination. As such, deprotonation of the lanthanide-activated aqua ligands upon pH increase will be limited, and so will be olation – aggregation of the resulting lanthanide hydroxo (Ln-OH) species – leading eventually to the finite-size and well-defined polynuclear lanthanide hydroxide complexes rather than the intractable and undesirable precipitates of lanthanide oxides or hydroxides. This synthetic submission is schematically illustrated in Fig. 1.

The validity of this synthetic approach has been verified with the synthesis of a great variety of polynuclear lanthanide hydroxide clusters with the use of ancillary ligands such

[a]Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona, 85721, USA. E-mail: zhiping@u.arizona.edu; Fax: 520 621 8407; Tel: 520 626 6495

[b]College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian, 361005, China
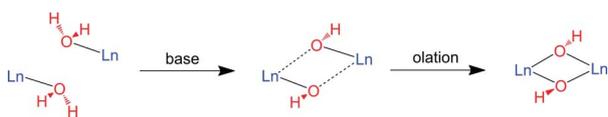
Fig. 1 Rationales of the ligand-controlled hydrolytic approach to the assembly of lanthanide hydroxide clusters.

as α-amino acids,[14] polyaminopolycarboxylates,[1] functionalized carboxylates,[13b,15] and other less commonly used multidentate ligands[16] for the control of the lanthanide hydrolysis. Hydroxide clusters can also be obtained from the direct hydrolysis of lanthanide salts,[17] but they are not nearly as stable as those with organic supporting ligands because the Ln–OH cores are not protected by a stabilizing organic coordination sphere.

Even with the use of organic supporting ligands, the instability of many of these complexes was noticed, most probably due to the further hydrolysis of the aqua ligands that often coexist with the hydroxo groups, leading to intractable precipitates upon standing over certain period of time in aqueous solutions. It is clearly desirable to avoid this complication. One possible solution is to deprotonate an organically soluble lanthanide complex featuring the coordination of some organic ligands but still with a small number of aqua ligands. The aqua ligands serve as the sole OH source upon deprotonation by an organic base in a non-aqueous solution, and the concern of further hydrolysis is largely eliminated. The end product is expected to remain organically soluble, making it a much less complicated task when further modifications of the complexes are necessary for any specific applications.

To this end, we have chosen lanthanide β-diketonates, arguably the most prolific and one of the most important classes of lanthanide complexes in terms of application,[18] as suitable starting complexes.[19] Adding confidence to our choice are the literature examples of a number of polynuclear lanthanide-diketonato/hydroxo complexes. These include Er$_8$(μ$_3$-OH)$_{12}$(μ$_4$-O)(thd)$_8$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate),[20a] La$_4$(μ$_4$-O)(acac)$_{10}$,[20b] Ln$_4$(μ$_3$-OH)$_2$(acac)$_{10}$ (Ln = Y, Nd; acac = acetylacetonate; Hacac = acetylacetone),[20c,d] [Gd$_4$(μ$_3$-OH)$_4$(hfpd)$_8$(H$_2$O)$_6$] (hfpd = hexafluoropentanedionate),[13a] Eu$_5$(μ$_4$-OH)(μ$_3$-OH)$_4$(dbm)$_{10}$ (dbm = dibenzoylmethanide)[20e] Ce$_6$(acac)$_{12}$(μ$_3$-O)$_4$(μ$_3$-OH)$_4$,[20f] [Ln$_9$(μ$_4$-OH)$_2$(μ$_3$-OH)$_8$(acac)$_{16}$]$^+$ (Ln = Sm–Gd, Dy, Yb),[20g–i] [Y$_9$(μ$_4$-O)$_2$(μ$_3$-OH)$_8${MeC(O)CHC-(O)OEt}$_8${MeC(O)CHC(O)OEt}$_8$]$^-$,[20j] and Ln$_{14}$(μ$_4$-OH)$_2$(μ$_3$-OH)$_{16}$(acac)$_{24}$ (Ln = Eu, Tb).[20k] These synthetic serendipities may all be viewed as the products of unintended hydrolysis, but most illustrative mechanistically is the formation of the aforementioned tetradecanuclear complexes from the reaction of Ln(acac)$_3$·2H$_2$O with 2,2-dipyridylsulfide apparently aiming at the displacement of the aqua ligands using the pyridyl-based ligand; the Lewis base instead promoted the deprotonation of the aqua ligands, leading to the first examples of tetradecanuclear hydroxide clusters.

Likely inspired by this work, a number of groups have independently developed the rational synthesis of polynuclear lanthanide-diketonato/hydroxo clusters. By reacting Ln(ba)$_3$·2H$_2$O (ba = benzoylacetonate; Ln = Sm–Gd, Dy, Er) with Et$_3$N in CH$_3$OH, Yan et al. obtained [Ln$_9$(μ$_4$-O)$_2$(μ$_3$-OH)$_8$(ba)$_{16}$]$^-$.[21] In an analogous study starting with Ln(dbm)$_3$·2H$_2$O, Roesky and coworkers obtained tetranuclear [Ln$_4$(μ$_3$-OH)$_2$(dbm)$_{10}$] (Ln = Pr, Nd, and Sm)[22] and pentanuclear [Ln$_5$(μ$_4$-O)(μ$_3$-O)$_4$(dbm)$_{10}$]$^{5-}$ (Ln = Dy,

Y) complexes.[8] Most recently, chiral clusters with dibenzoyl-methanide and enantiomerically pure amino acid ligands have also been reported.[9] The successful production of these well-structured clusters collectively validates the ligand-controlled hydrolysis in organic media, and reveals the sensitive dependence of cluster structure on the nature of the metal ions and the ligands. On the other hand, results from other studies clearly indicate the influence of experimental conditions, such as the metal:ligand ratio, the nature of the solvent and base used, and the reaction temperature and duration on the reaction outcome. Variation in even one of these conditions can significantly alter product identity.

In this contribution, we report the hydrolysis behavior of 10 lanthanide ions, representing the light, medium, and heavy members in the lanthanide series, in the presence of triethylamine and supporting acetylacetonate ligand in methanol. We note that similar studies have been reported by Roesky and coworkers, but this work is more extensive in its scope, and the previously reported hydroxide cluster complexes with acetylacetonate, of various nuclearities including 4 (tetrahedron[20b] and parallelogram[20c,d]), 6,[20f] 9,[20g–i] and 14,[20k] offer a rich database for comparative studies. It is with the hope of possibly establishing a relationship between the cluster nuclearity/structure and the reaction conditions that the present study was carried out.

Experimental

Syntheses

LnCl$_3$·nH$_2$O (n = 7, Ln = La, Pr; n = 6, Ln = Nd–Dy, Er, Yb), triethylamine, acetylacetone, and methanol were purchased from Aldrich and used as received. Elemental analyses (CHN) were performed by NuMega Resonances Labs. Inc, San Diego, USA.

[Pr(CH$_3$CO$_2$)(CH$_3$OH)(acac)$_2$]$_n$ (1). A mixture of PrCl$_3$·7H$_2$O (0.373 g, 1.00 mmol) and 0.26 mL of Hacac (2.5 mmol) in 10 mL of CH$_3$OH was stirred for 10 min, following which 1.4 mL of Et$_3$N (10 mmol) was added. The resulting mixture was stirred under reflux for 12 h. The resulting cloudy mixture was filtered while hot. The product was obtained as light-green crystals upon standing of the filtrate at room temperature (yield: 70% based on Pr). Anal. Calcd for PrC$_{13}$H$_{23}$O$_8$ (based on one water molecule of recrystallization) C, 34.84; H, 5.17. Found: C, 34.61; H, 4.72.

Sm$_4$(μ$_3$-OH)$_2$(μ$_3$-OCH$_3$)$_2$(CH$_3$OH)$_2$(acac)$_8$ (2). A mixture of SmCl$_3$·6H$_2$O (0.359 g, 1.00 mmol) and 0.26 mL of Hacac (2.5 mmol) in 10 mL of CH$_3$OH was stirred for 10 min, following which 0.70 mL of Et$_3$N (5.0 mmol) was added. The resulting mixture was stirred at room temperature for 12 h and then filtered. Upon standing of the filtrate light-yellow crystals of the product were obtained (yield: 64% based on Sm). Anal. Calcd for Sm$_4$C$_{46}$H$_{74}$O$_{24}$: C, 34.26; H, 4.63. Found: C, 34.02; H, 4.11.

Tb$_9$(μ$_4$-O)(μ$_4$-OH)(μ$_3$-OH)$_8$(acac)$_{16}$·4H$_2$O (3). This compound was prepared by the same procedure as the one used for the synthesis of 2, with TbCl$_3$·6H$_2$O as the starting lanthanide salt (yield: 67% based on Tb). Anal. Calcd for Tb$_9$C$_{80}$H$_{129}$O$_{46}$: C, 29.50; H, 3.99. Found: C, 29.51; H: 3.82.

Table 1 Crystal data and details of data collection and refinement (**1–3**)

Compound	1	2	3
Formula	$C_{13}H_{21}O_7Pr$	$C_{46}H_{74}O_{24}Sm_4$	$C_{80}H_{129}O_{46}Tb_9$
M_r	430.21	1612.45	3241.15
Cryt. syst.	Triclinic	Orthorhombic	Tetragonal
Space Group	$P\bar{1}$	$Pna2(1)$	$P4/n$
a/Å	6.9046(11)	14.517(2)	18.8879(9)
b/Å	10.4942(17)	19.882(3)	18.8879(9)
c/Å	12.242(2)	21.190(3)	15.3095(7)
α (°)	72.367(2)	90	90
β (°)	87.269(2)	90	90
γ (°)	76.238(3)	90	90
T/K	100(2)	100(2)	100(2)
V/Å^3	820.8(2)	6115.9(15)	5461.7(4)
Z	2	4	2
μ/mm^{-1}	2.995	3.858	5.823
$F(000)$	428	3168	3108
Refls	7987	7676	5403
Indep. refls (R_{int})	5241 (0.0169)	6533 (0.0816)	3937 (0.0692)
$R_1[I > 2\sigma(I)]$	0.0260	0.0600	0.0302
wR_2(all data)	0.0661	0.1485	0.0619

$R_1 = \sum \left| \left| F_o \right| - \left| F_c \right| \right| / \sum \left| F_o \right|. \ wR_2 = \left\{ \sum w \, (F_o{}^2 - F_c{}^2)^2 / \sum [w(F_o{}^2)^2] \right\}^{1/2}$

X-ray crystallography

Crystallographic data were collected on a Bruker SMART 1000 CCD diffractometer using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 100(2) K for **1** and **2**, and 123(2) K for **3**. Absorption corrections were applied using the multiscan program SADABS.[23] The structures were solved by direct methods (SHELXTL),[23] and the non-hydrogen atoms were refined anisotropically by a full-matrix least-squares method on F^2. The hydrogen atoms of the organic ligand were generated geometrically (C–H = 0.98 Å, aromatic 0.95 Å). Crystal data, as well as details of the data collection and refinement, for the complexes are summarized in Table 1.

For compound **2**, the μ$_3$-OH hydrogen atoms were added geometrically. However, since the position of such H atoms cannot be reliably calculated based on the surrounding geometry (as is the case with C-bound H atoms), and they also cannot be located from a difference map, then we have re-refined the structural model omitting these H atoms. The total formula is amended to reflect the true chemical composition, accounting for both hydroxo H atoms, and those on disordered methanol molecules. For compound **3**, the four disordered molecules of water were removed using SQUEEZE. The hydroxo H atoms could be located from a difference map, and refined using an O–H distance restraint of 0.84(1) Å. The H atoms are located in positions such that they form reasonable intramolecular O–H···O interactions with adjacent acac ligands. The total formula is amended to reflect the true chemical composition, accounting for disordered water.

Results and discussion

Preparation

We sought in this work the assembly of polynuclear lanthanide hydroxide complexes *via* the hydrolysis of the lanthanide ions limited by acetylacetonate. According to the generic synthetic scheme shown in Fig. 1, the initial formation of the mononuclear lanthanide-hydroxo species and its subsequent assembly into

a cluster are the two critical steps. The first is due to the deprotonation of the aqua ligand, activated by its coordination with the Lewis acidic lanthanide ion and facilitated by the added base. This step is understandably dependent on the acidity of the metal ion and the strength of the base with the former being dependent on the charge density, and more straightforwardly, the size of the metal ion. Considering the primarily ionic character of the lanthanide-ligand bonding and the kinetic lability of such bonds, the facility of the subsequent assembly of the hydroxo species – the olation reaction – depends on the sterics about the Ln–OH entity, and more directly, the size of the metal ion and the steric bulk of the ligands. Clearly, if any meaningful conclusions are to be drawn as to how reaction conditions may affect the identity of the final cluster species, experiments should be conducted systematically under conditions with only one variable.

The present study used a mixture of LnCl$_3$·nH$_2$O (n = 6, 7) and acetylacetone in a 2:5 ratio instead of starting with a preformed lanthanide acetylacetonate hydrate of the general formula Ln(acac)$_3$·nH$_2$O as in some previous studies. The 2:5 stoichiometry was adopted as our extensive screening showed that it was the stoichiometry with which crystalline products, necessary for systematic structural studies, can be more readily obtained. Interestingly, this particular metal:ligand ratio was also utilized in a number of closely related studies.[21,24]

The organic base Et$_3$N serves to deprotonate acetylacetone and to facilitate the production of hydroxo species upon deprotonation of an aqua ligand bound to the Lewis acidic lanthanide ion. Reaction conditions for various lanthanide salts were very similar, though not identical. Specifically, for the salts of the lighter and larger lanthanides (Ln = La, Pr, and Nd), mixtures with a molar ratio of Ln:Hacac:Et$_3$N = 1:2.5:10 were utilized, and it was necessary to carry out the reaction under reflux in order to obtain the hydrolysis products. In comparison, hydrolysing the heavier and smaller lanthanide ions under exactly the same conditions afforded only intractable precipitates, presumably an outcome of more extensive and uncontrollable hydrolysis. For these salts, the reaction conditions were subsequently tweaked in order to obtain finite-sized and structurally well-defined cluster complexes. Specifically, a molar ratio of Ln:Hacac:Et$_3$N = 1:2.5:5 (Ln = Sm–Dy, Er, Yb) with less Et$_3$N were used, and the reactions were carried out at room temperature. Three different types of polynuclear complexes, [Pr(CH$_3$CO$_2$)(CH$_3$OH)(acac)$_2$]$_n$ (Ln = La, Pr), Ln$_4$(μ$_3$-OH)$_2$(μ$_3$-OCH$_3$)$_2$(CH$_3$OH)$_2$(acac)$_8$ (Ln = Nd, Sm), and [Ln$_9$(μ$_4$-O)(μ$_4$-OH)(μ$_3$-OH)$_8$(acac)$_{16}$] (Ln = Eu–Dy, Er, Yb), formulated based on crystallographic studies and satisfactory elemental analyses, were obtained, two of which contain methanol and/or methoxido ligands in addition to the anticipated hydroxido and acetylacetonato ligands.

A number of points pertinent to the synthesis merit additional comments. First is the presence of the chelating/bridging acetate ligands in the polynuclear complexes of La(III) and Pr(III). Though unexpected, their formation can be rationalized as the *in situ* decomposition of the acetylacetonate in the presence of Lewis acidic lanthanide ions.[25]

Also of note is the distorted cubane core structure of the Nd(III) and Sm(III) complexes. Tetranuclear complexes are the most frequently observed lanthanide hydroxide clusters.[1] Three distinct core motifs have been identified: the distorted cubane,[13] the rhombus,[20c,d] and the square,[26] with the distorted cubane

being the most prevalent, not only present in discrete tetranuclear complexes, but also as formal building blocks in a great variety of multi-cubane assemblies.[14a,b,15a,b,27] Despite its prevalence, the present complexes represent interestingly, to the best of our knowledge, only the third example of hydroxide complexes with diketonate-based ligands.

As for the nonanuclear complexes, a number of lanthanide hydroxide clusters featuring a similar core motif have been reported,[20g–j,21] but they are either with different supporting ligands or obtained by distinctly different routes.

Structural description

Descriptions of crystal structures of the three different types of polynuclear lanthanide hydroxide complexes are detailed below using one representative for each of the isomorphous types.

[Pr(CH_3CO_2)(CH_3OH)(acac)_2]_n (Ln = La, Pr). The Pr(III) complex in the solid state forms an infinite chain with repeating $Pr_2(CH_3CO_3)_2(CH_3OH)_2(acac)_4$ units (Fig. 2). The salient feature is a diamond-shaped dinuclear core of Pr_2O_2 (Fig. 3). The O atoms are from two acetate ligands, each displaying an interesting μ_3-κ^2O,O:κ^2O,O mode with their O atoms participating in both chelating and bridging interactions. It is the bridging interaction that leads to the one-dimensional chain structure observed. Each metal atom is additionally coordinated by one CH_3OH molecule and two acac ligands that are in the usual chelating fashion. As such, the metal is nonacoordinate with a coordination geometry that may be best described as a monocapped distorted square antiprism. The metric values of the bond lengths and angles are normal, falling in the ranges reported for compounds featuring a similar core structure.[22]
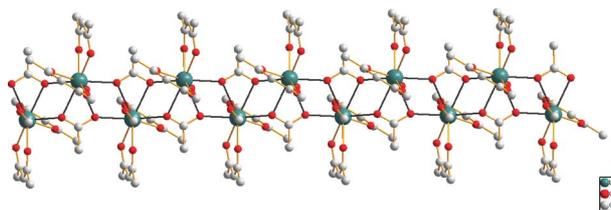

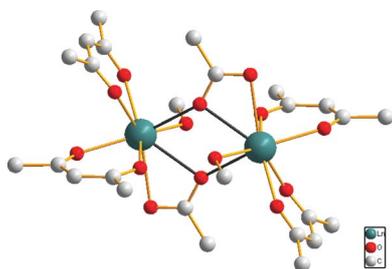**Fig. 2** Part of the polymeric structure of [Pr(CH_3CO_2)(CH_3OH)(acac)_2]_n.

Fig. 3 The structure of the repeating dinuclear unit present in the infinite chain of [Pr(CH_3CO_2)(CH_3OH)(acac)_2]_n.

Ln_4(μ_3-OH)_2(μ_3-OCH_3)_2(CH_3OH)_2(acac)_8 (Ln = Nd, Sm). The isostructural complexes feature a common core of $Ln_4(\mu_3$-$OH)_2(\mu_3$-$OCH_3)_2$. Considering just the four triply bridging O atoms, the core adopts a distorted cubane structure (Fig. 4),
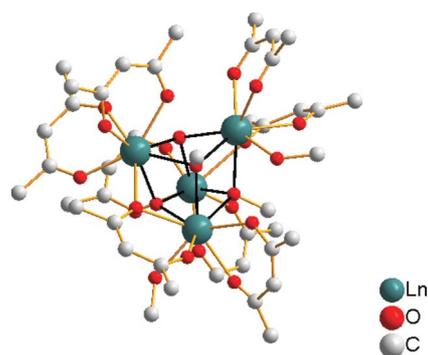

Fig. 4 The crystal structure of the tetranuclear cluster complex Sm_4(μ_3-OH)_2(μ_3-OCH_3)_2(CH_3OH)_2(acac)_8 featuring a distorted cubane–like core motif.

a motif commonly observed in lanthanide hydroxide cluster complexes.[13–16,27] Although the metal atoms are each octacoodinate with a bicapped trigonal prismatic coordination geometry, they are situated in two different kinds of coordination environments. Two of the four Sm atoms is each coordinated by 4 O atoms from two chelating acac ligands, two μ_3-OH groups, one μ_3-OCH_3 group, and one O atom from a bridging acac ligand that also chelates one of the remaining two Sm atoms. For this second-type of Sm atom, the coordination sphere of each has 4 O atoms from two different kinds of acac ligands, two from the one that is bridging and chelating, aforementioned, and the other two from the usual chelating one. The Sm atoms are each additionally coordinated with two μ_3-OCH_3 groups, one μ_3-OH group, and a terminally coordinated CH_3OH molecule.

Metric values of bond lengths and angles in the distorted cubane core are in agreement with those reported for compounds containing similar core structures.[20k] The Sm–O bond lengths involving the bridging/chelating acac O atoms range from 2.544(10) to 2.586(14) Å with an average of 2.568 Å, sizably longer than those associated with the chelating only acac O atoms (2.262(18)–2.457(14) Å, average 2.368 Å).

[Ln_9(μ_4-O)(μ_4-OH)(μ_3-OH)_8(acac)_16] (Ln = Eu–Dy, Er, Yb). The structure of the Tb(III) cluster complex (Fig. 5), representative of the series of nonanuclear hydroxide clusters, is briefly described below as a number of analogous complexes bearing a similar core have been reported in the literature.[20g–j,21] The monoanionic core can be viewed as two vertex-sharing square pyramids arranged
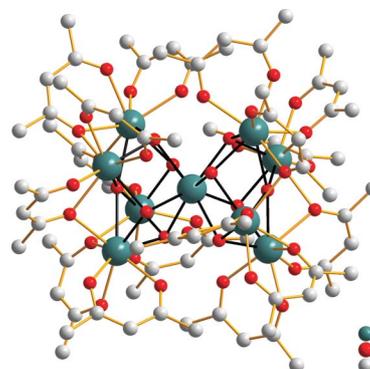

Fig. 5 The structure of the nonanuclear cluster anion [Tb_9(μ_4-O)_2-(μ_3-OH)_8(acac)_16]⁻.

in a "staggered" fashion with their basal planes rotated by 45° with respect to each other. Each of the triangular faces is capped by a μ_3-OH group (Tb–O bond lengths: 2.305(4) to 2.349(4) Å, average: 2.326 Å). Interestingly, one of the basal planes is capped by a μ_4-O (Tb–O 2.5622(7) Å) group, while the other by a μ_4-OH (Tb–O 2.5811(7) Å) group. This assignment is not only based on this noticeable bond length difference, but also consistent with the satisfactory elemental analysis. It is interesting to note that capping of the two square pyramid basal planes in the same cluster complex by either μ_4-OH[20g–i] or μ_4-O[20j,21] has been known in a number of lanthanide clusters, but the present situation is unique and quite intriguing as the same complex features the capping of co-existing μ_4-O and μ_4-OH groups, manifesting the subtlety of the synthesis of lanthanide hydroxide complexes, and in general, the coordination chemistry of the lanthanide ions.

This roughly cylindrical cluster core is sheathed by 16 peripheral acac ligands that show two kinds of coordination modes, 8 being chelating and the remaining 8 being both bridging and chelating. Each basal Tb atom is associated with three acac ligands that are different in their coordination modes, one chelating, the second chelating/bridging with an O atom connecting a neighboring Tb atom, and the third, offering only one O atom for the coordination but being chelating for a different neighboring Tb atom. The acac ligands not only render the cluster complex organically soluble, but also prevent further hydrolysis from occurring. In fact, the cluster remains intact even when the product mixture was extracted with water to remove the excess Et_3N. The acac ligands, together with the aforementioned face-capping (two μ_3-OH's) and basal plane-capping (one μ_4-O) groups, form a bicapped trigonal prismatic coordination geometry for each of the equivalent 8 basal Tb atoms. The unique Tb atom shared by the square pyramids at the vertex is also octacoordinate, but with only μ_3-OH (Tb–O distance: 2.440(4) Å) and the coordination geometry is a tetragonal antiprism.

Dependency of cluster nuclearity on the lanthanide ions

It is clear from the results presented herein and the findings by others, the identity (cluster nuclearity and overall structure) of a particular lanthanide hydroxide cluster complex is profoundly dependent on a number of factors. These include the nature of the metal ion and the supporting ligand, and the details of reaction conditions, such as the solvent used and reaction temperature and duration.

In the present work, we focus on the influence of the metal size on the nature of the resulting hydroxide clusters. Specifically, the size difference of the metal ions results in two immediate consequences, charge density or Lewis acidity and sterics, with a smaller metal ion being more acidic and more hindered for structural reorganization or access by a neighboring Ln–OH unit. Provided that there is an adequate amount of Ln–OH species, it may not be completely unreasonable to hypothesize that the aggregation of the hydroxo species is rate-determining and, the tardiness in adjusting the metal coordination sphere to accommodate approaching Ln–OH units would lead to the assembly of high-nuclearity clusters, whereas facility in reorganizing the metal coordination sphere would favor the formation of low-nuclearity clusters. This is analogous to the process of crystallization: slow kinetics favor the formation of lager crystals while a quick crystallization generally produces crystals of a small size. Indeed, when moving from the largest La(III) to Yb(III), clusters based on dinuclear, tetranuclear, and nonanuclear cores (Fig. 6) were obtained with distinct structural transitions between different-sized metal groups. There are no obvious structural connections between these hydroxo entities except that they all possess fundamental Ln–OH units. Different reaction pathways for the cluster formation are thus inferred, which should not be surprising considering the primarily ionic lanthanide-ligand interaction and the associated flexibility in achieving various coordination geometry.
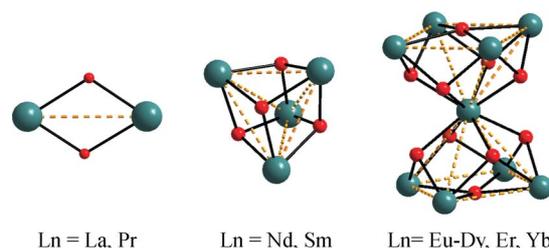

Ln = La, Pr   Ln = Nd, Sm   Ln= Eu-Dy, Er, Yb

Fig. 6 Structures of the dinuclear, tetranuclear, and nonanuclear cluster cores present in the title complexes.

Summary

A series of lanthanide β-diketonates (compounds **1–3** and their respective isostructural cognates) were synthesized and structurally characterized by single-crystal X-ray diffraction. Depending on the nature of the metal ion, polymeric hydroxide complexes based on diamond-shaped dinulcear repeating units of $[Ln_2(CH_3CO_3)_2]^{4+}$ (Ln = La, Pr) and discrete complexes featuring a tetranuclear distorted cubane core of $[Ln_4(\mu_3\text{-OH})_2(\mu_3\text{-OCH}_3)_2]^{8+}$ (Ln = Nd, Sm) or a nonanulcear core of $[Ln_9(\mu_4\text{-O})(\mu_4\text{-OH})(\mu_3\text{-OH})_8]^{16+}$ (Ln = Eu–Dy, Er, Yb) were obtained. The dependence of the cluster nuclearity on the size of the lanthanide ions has been established: The hydrolysis of the acetylacetonates of lighter and bigger lanthanide ions tend to produce hydroxide clusters of lower nuclearities while reactions using acetylacetonates of heavier and smaller lanthanide ions under otherwise identical conditions favor the formation of higher-nuclearity hydroxide clusters. The present study does not merely provide some new members of the fundamentally interesting cluster species, it offers important mechanistic insights into the elusive hydrolysis behavior of these well-studied lanthanide complexes, even though the specific structure of the resulting polynuclear species cannot be predicted *a priori*. The current work and those by others[8,9,19,21,22,25,28] extend the chemistry of the ligand-controlled lanthanide hydrolysis from aqueous solutions to organic media. With the use of appropriately functionalized supporting ligands,[28] organically soluble lanthanide hydroxide clusters that may be further modified for specific materials applications can be anticipated.

Acknowledgements

References

1 (a) Z. Zheng, in *Handbook on the Physics and Chemistry of Rare Earths Elements*, ed. K. A. Gschneidner Jr., J.-C. G. Bünzli and V. K. Pecharsky, Elsevier, Amsterdam, 2010, **40**, 109; (b) Z. Zheng, *Chem. Commun.*, 2001, 2521; (c) Z. Zheng, *Chemtracts*, 2003, **16**, 1; (d) Z. Zheng and R. Wang, *Comments Inorg. Chem.*, 2000, **22**, 1.

2 J.-C. G. Bunzli and C. Piguet, *Chem. Rev.*, 2002, **102**, 1897.

3 R. Anwander, *Angew. Chem., Int. Ed.*, 1998, **37**, 599.

4 M. K. Thompson, A. J. Lough, A. J. P. White, D. J. William and I. A. Kahwa, *Inorg. Chem.*, 2003, **42**, 4828.

5 L. G. Hubert-Pfalzgraf, N. M. Pajot, R. Papernik and J. Vaissermann, *J. Chem. Soc., Dalton Trans.*, 1999, 4127.

6 D. S. Thompson, D. W. Thompson and R. E. Southward, *Chem. Mater.*, 2002, **14**, 30.

7 (a) S. J. Franklin, *Curr. Opin. Chem. Biol.*, 2001, **5**, 201; (b) E. R. Farquhar, J. P. Richard and J. R. Morrow, *Inorg. Chem.*, 2007, **46**, 7169; (c) M. Komiyama, N. Takeda and H. Shigekawa, *Chem. Commun.*, 1999, 1443.

8 (a) P. W. Roesky, G. Canseco-Melchor and A. Zulys, *Chem. Commun.*, 2004, 738; (b) M. T. Gamer, Y. Lan, P. W. Roesky, A. K. Powell and R. Clerac, *Inorg. Chem.*, 2008, **47**, 6581.

9 D. T. Thielemann, I. Fernández and P. W. Roesky, *Dalton Trans.*, 2010, **39**, 6661, DOI: 10.1039/c001464h.

10 L. Messerle, D. Nolting, L. Bolinger, A. H. Stolpen, B. F. Mullan, D. Swenson and M. Madsen, *Acad. Radiol.*, 2005, **12**, S46.

11 (a) L. Natrajan, J. Pecaut and M. Mazzanti, *Dalton Trans.*, 2006, 1002; (b) P. C. Andrews, T. Beck, C. M. Forsyth, B. H. Fraser, P. C. Junk, M. Massi and P. W. Roesky, *Dalton Trans.*, 2007, 5651.

12 L. Clark, D. E. Hobart and M. P. Neu, *Chem. Rev.*, 1995, **95**, 25.

13 (a) J. C. Plakatouras, I. Baxter, M. B. Hursthouse, M. K. M. Abdul, J. McAleese and S. R. Drake, *Chem. Commun.*, 1994, 2455; (b) X. Chen, Y. Wu, Y. Tong, Z. Sun and D. N. Hendrickson, *Polyhedron*, 1997, **162**, 4265; (c) T. Dube, S. Gaboratta and G. Yap, *Organometallics*, 1998, **17**, 3967.

14 (a) R. Wang, Z. Zheng, T. Jin and R. J. Staples, *Angew. Chem., Int. Ed.*, 1999, **38**, 1813; (b) R. Wang, H. D. Selby, H. Liu, M. D. Carducci, T. Jin, Z. Zheng, J. W. Anthis and R. J. Staples, *Inorg. Chem.*, 2002, **41**, 278; (c) R. Wang, H. Liu, M. D. Carducci, T. Jin, C. Zheng and Z. Zheng, *Inorg. Chem.*, 2001, **40**, 2743.

15 (a) X. Kong, L. Long, L. Zheng, R. Wang and Z. Zheng, *Inorg. Chem.*, 2009, **48**, 3268; (b) X. Zheng, L. Jin and S. Gao, *Inorg. Chem.*, 2004, **43**, 1600; (c) O. Mamula, M. Lama, H. Stoeckli-Evans and S. Shova, *Angew. Chem., Int. Ed.*, 2006, **45**, 4940.

16 (a) S. Fleming, C. D. Gutsche, J. M. Harrowfield, M. I. Ogden, B. W. Skelton and D. F. Stewart, *Dalton Trans.*, 2003, 3319; (b) T. Kajiwara, K. Katagiri, M. Hasegawa, A. Ishii, M. Ferbinteanu and S. Takaishi, *Inorg. Chem.*, 2006, **45**, 4880; (c) O. A. Gerasko, E. A. Mainicheva, M. I. Naumova, M. Neumaier, M. M. Kappes and S. Lebedkin, *Inorg. Chem.*, 2008, **47**, 8869.

17 (a) R. Wang, M. D. Carducci and Z. Zheng, *Inorg. Chem.*, 2000, **39**, 1836; (b) G. Calvez, O. Guillou, C. Daiguebonne, P.-E. Car, V. Guillerm,

Y. Gérault, F. Le Dret and N. Mahé, *Inorg. Chim. Acta*, 2008, **361**, 2369; (c) A. Mudring, T. Timofte and A. Babai, *Inorg. Chem.*, 2006, **45**, 5162; (d) A. Babai and A. Mudring, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1956; (e) Z. Zák, P. Unfried and G. Giester, *J. Alloys Compd.*, 1994, **205**, 235; (f) G. Giester, P. Unfried and Z. Zák, *J. Alloys Compd.*, 1997, **257**, 175.

18 K. Binnemans, *Rare-Earth Beta-Diketonates, Handbook on the Physics and Chemistry of Rare Earths*, 2005.

19 Lanthanide clusters of the general formula $Ln_5(dbm)_{10}(OH)_5$ (dbm = dibenzoylmethanide; Ln = Nd, Gd, Er, Yb) were obtained by treating $Ln(dbm)_3(H_2O)_2$ with $Ln(OTf)_3$ (OTf, trifluoromethanesulfonate); the latter provides the metal source for cluster formation, and more importantly, serves to fine-tune the pH of the reaction mixture. Please see X. Chen, X. Yang and B. J. Holliday, *Inorg. Chem.*, 2010, **49**, 2583.

20 (a) J. C. A. Boeyens and J. P. R. D. Villiers, *J. Cryst. Mol. Struct.*, 1972, **2**, 197; (b) personal communication, Dr Steve McLain, DuPont, DE, USA; (c) E. H. Barash, P. S. Coan, E. B. Lobkovsky, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1993, **32**, 497; (d) O. Poncelet and L. G. Hubert-Pfalzgraf, *Polyhedron*, 1989, **8**, 2183; (e) R.-G. Xiong, J.-L. Zuo, Z. Yu, X.-Z. You and W. Chen, *Inorg. Chem. Commun.*, 1999, **2**, 490; (f) P. Toledano, F. Ribot and C. Sanchez, *Comptes Rendus de l'Academie des Sciences Serie II: Mecanique Physique Chimie Sciences de la Terre et de l'Univers*, 1990, **311**, 1315; (g) M. Addamo, G. Bombieri, E. Foresti, M. D. Grillone and M. Volpe, *Inorg. Chem.*, 2004, **43**, 1603; (h) M. Volpe, G. Bombieri and N. Marchini, *J. Alloy. Compd.*, 2006, **608–612**, 1066; (i) M. Volpe, G. Bombieri, D. A. Clemente, E. Foresti and M. D. Grillone, *J. Alloys Compd.*, 2004, **374**, 382; (j) L. G. Hubert-Pfalzgraf, N. Miele-Pajot, R. Papiernik and J. Vaissermann, *J. Chem. Soc. Dalton Trans*, 1999, 6127; (k) R. Wang, D. Song and S. Wang, *Chem. Commun.*, 2002, 368.

21 G. Xu, Z. Wang, Z. He, Z. Lu, C. Liao and C. Yan, *Inorg. Chem.*, 2002, **41**, 6802.

22 V. Baskar and P. W. Roesky, *Z. Anorg. Allg. Chem.*, 2005, **631**, 2782.

23 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112.

24 (a) P. C. Andrews, T. Beck, C. M. Forsyth, B. H. Fraser, P. C. Junk, M. Massi and P. W. Roesky, *Dalton Trans.*, 2007, 5651; (b) V. Baskar and P. W. Roesky, *Dalton Trans.*, 2006, 676.

25 J. J. Stephanos, *Bulletin of the Faculty of Science, University of Alexandria*, 1999, **39**, 133.

26 A. W. H. Lam, W. T. Wong, G. H. Wen, X. X. Zhang and S. Gao, *New J. Chem.*, 2001, **25**, 1325.

27 B. Ma, D. Zhang, S. Gao, T. Jin, C. Yan and G. Xu, *Angew. Chem. Intl. Ed.*, 2000, **39**, 3644.

28 (a) P. C. Andrews, T. Beck, B. H. Fraser, P. C. Junk, M. Massi, B. Moubaraki, K. S. Murray and M. Silberstein, *Polyhedron*, 2009, **28**, 2123; (b) L. Han, S. Zhang, Y. Wang, X. Yan and X. Lu, *Inorg. Chem.*, 2009, **48**, 786; (c) A. K. Jami, P. V. V. N. Kishore and V. Baskar, *Polyhedron*, 2009, **28**, 2284; (d) P. C. Andrews, G. B. Deacon, R. Frank, B. H. Fraser, P. C. Junk, J. G. MacLellan, M. Massi, B. Moubaraki, K. S. Murray and M. Silberstein, *Eur. J. Inorg. Chem.*, 2009, 744.