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A New Series of Anhydrous Lanthanide-Based Octahedral Hexanuclear Complexes

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The synthesis of hexanuclear lanthanide oxido/hydroxido complexes by direct hydrolysis has been reinvestigated and optimized. Lanthanide oxido/hydroxido complexes of the general formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_x]2NO_3{\cdot}2H_2O$ (with $x = 12$ for Ln = Sm–Yb or Y, $x = 14$ for Ln = Pr or Nd, and $x = 16$ for Ln = Ce) have been obtained and characterized. The dehydration of all these complexes leads to isostructural anhydrous compounds with the general formula $[Ln_6O(OH)_8(NO_3)_8]_\infty$. The crystal structure has been solved on the basis of powder X-ray diffraction of the Y-containing compound. This compound crystallizes in the triclinic system, and the crystal structure can be described as the juxtaposition of infinite chains of hexanuclear complexes linked to each other by nitrate groups. These anhydrous compounds are readily soluble in most organic solvents and can be used as molecular precursors for further chemistry. When exposed to moisture, they rehydrate reversibly, which leads to their initial hydrated phase.

Introduction

For almost a decade there has been great activity devoted to coordination polymers because of their ability to provide potentially porous materials.[1] Numerous coordination polymers exhibiting great porosity have been reported.[2–12] One of the strategies to increase the porosity consists of designing coordination polymers in which polynuclear complexes act as metallic centers. This strategy has been successfully applied some years ago and very promising materials with zinc tetranuclear complexes have been obtained.[6,13] Up to now only a few coordination polymers with polynuclear lanthanide complexes have been reported.[14–17] In fact, while the cluster chemistry of d block transition metals is now firmly established,[18,19] analogous chemistry involving lanthanide ions is rather underdeveloped.

To date, only a few polynuclear lanthanide complexes have been reported, most of which have been obtained by use of ancillary ligands. These ligands pre-occupy part of the coordination sphere of the lanthanide ion. They prevent the formation of highly insoluble lanthanide hydroxide and allow the control of the hydrolysis of the lanthanide ion. Several polynuclear lanthanide complexes have been obtained in this manner, and contain dinuclear to penta-decanuclear lanthanide oxido/hydroxido entities.[16,20–28,53] Unfortunately, these entities are very often unstable in solution[28] and cannot be used as molecular precursors for further chemistry.

A second synthetic route, first described 15 years ago,[29–35] leads to hexanuclear lanthanide complexes with the general formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_x]^{2+}$ with $x = 12$ when Ln = Sm–Yb and $x = 14$ when Ln = Pr–Nd. This route, based on a subtle balance between the various experimental parameters (pH, concentration, temperature, etc.), consists of using lanthanide nitrate as a starting material and of hydrolyzing it by addition of sodium hydroxide. Through this synthetic method, numerous polymorphic phases of such hexanuclear lanthanide complexes have been obtained (Table 1).[14,33,34,36]

Table 1. Summary of the reported hexanuclear lanthanide complexes with general formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_x](NO_3)_2{\cdot}yH_2O$.

	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2{\cdot}2H_2O$					[14]	[14]	[14]	[14]	[14]	[14]		
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2{\cdot}4H_2O$									[33]	[34]		[33]
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2{\cdot}5H_2O$					[33]	[14]	[34]	[14]	[14]	[14]		
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2{\cdot}6H_2O$			[34]		[14]							
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{14}](NO_3)_2{\cdot}2H_2O$	[36]	[36]										

From Table 1 it can be seen that several polymorphic phases can exist for a given lanthanide ion. Moreover, no hexanuclear, cerium-based complex has been reported so

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far despite the great potential application in heterogeneous catalysis.[37,38] In other respects, these highly hydrated phases present limited stability in solution. Indeed, when dissolved in an organic solvent, they slowly hydrolyze. This constitutes a drawback for using them as molecular precursors for further chemistry.

Therefore, we had three objectives in mind for this study: (i) the rationalization of the synthesis of these hydrated phases, (ii) the expansion of the family by the synthesis of a cerium-based analogous complex, and (iii) the synthesis of anhydrous hexanuclear lanthanide complexes.

Results and Discussion

Hexanuclear lanthanide complexes present several polymorphic phases and until now no synthetic route has been suggested for selectively obtaining one of them. As already shown elsewhere,[36] the main difficulty encountered during the synthesis of these complexes is to avoid the formation of very stable polymeric species such as $Ln(OH)_2NO_3$,[19,30,31] $LnONO_3$,[39] and $Ln(OH)_3$.[40] Furthermore, the more these complexes are hydrated, the faster they hydrolyze. In order to reduce the hydration rate of the complexes, we have thus decided to conduct the reaction in a mixture ethanol/water instead of in water only. This new route led to two families of complexes with the formulae $[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2\cdot 2H_2O$ for Ln = Sm–Yb or Y (hereafter referred to as family **1**) and $[Ln_6O(OH)_8(NO_3)_6(H_2O)_{14}](NO_3)_2\cdot 2H_2O$ for Ln = Pr or Nd (hereafter referred to as family **2**). These complexes are isostructural to the previously described $[Er_6O(OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2\cdot 2H_2O$ [monoclinic system, space group $P2_1/n$ (no. 14), a = 12.5809(2) Å, b = 10.1800(2) Å, c = 15.6655(3) Å, β = 97.63(0)°][14] and $[Pr_6O(OH)_8(NO_3)_6(H_2O)_{14}](NO_3)_2\cdot 2H_2O$ [monoclinic system, space group $P2_1/n$ (no. 14), a = 12.4163(2) Å, b = 10.5121(1) Å, c = 16.0389(2) Å, β = 95.78(0)°] complexes, respectively.[36] This isostructurality has been assumed on the basis of elemental analysis and X-ray diffraction studies. A plot of the cell parameters vs. the ionic radius of the lanthanide ion involved is presented for both families in Figure 1.

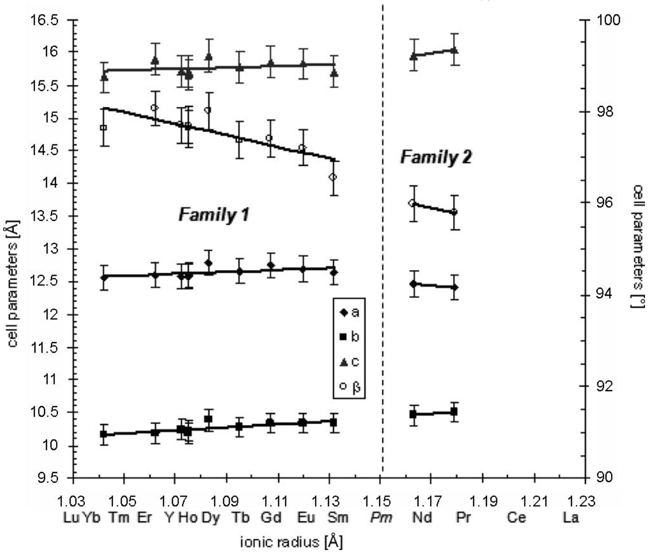

Figure 1. Cell parameters vs. ionic radius for compounds belonging to family **1** (left) and **2** (right). Ionic radii are for nine-coordinate ions.[41]

The synthetic approach developed offers us a series of hexanuclear lanthanide complexes with only two crystallization water molecules for all the lanthanides between praseodymium and ytterbium (except promethium) and also for yttrium. The synthesis of the analogous lutetium complex has not been attempted. The analogous lanthanum complex has not been obtained despite great synthetic efforts. The crystal structures of all the complexes are very similar; they can be described by the juxtaposition of perfect octahedrons with one lanthanide ion at each edge and a μ_6-O^{2-} anion at the center. Each face of the octahedrons is capped by a μ_3-OH^- anion, and each lanthanide ion is bonded in a bidentate manner to a nitrate anion. The main difference between the two families of compounds is the number of coordination water molecules. As shown in Figure 2, the complexes belonging to family 1 have 12 coordination water molecules (two per lanthanide ion), while those belonging to family 2 have 14. In these complexes, four out of the six lanthanide ions are bonded to two coordination water molecules, while the remaining two lanthanide ions are bonded to three coordination water molecules. All the lanthanide ions are thus nine-coordinate for compounds belonging to family1, and two out of the six lanthanide ions are ten-coordinate and the remaining four are nine-coordinate for compounds belonging to family 2.

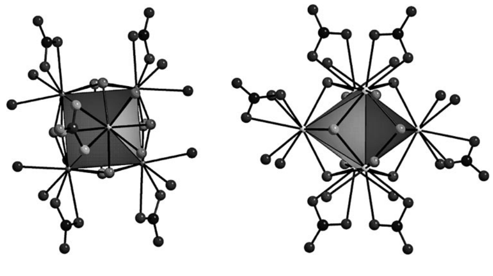

Figure 2. Views of the complexes $[Er_6O(OH)_8(NO_3)_6(H_2O)_{12}]^{2+}$ (left) and $[Pr_6O(OH)_8(NO_3)_6(H_2O)_{14}]^{2+}$ (right).

These complexes can be used as molecular precursors for further chemistry.[42,43] However, they still present some slight tendency to hydrolyze, even in dry organic solvents, because of the crystallization and coordination water molecules. In order to increase the chemical stability of the complexes, we thus decided to dehydrate them. The dehydration of these complexes is easy to realize thermally and leads to stable anhydrous phases. All the compounds were thermally studied by TGA/TD and TDXD and present similar behavior.[14,36] First, dehydration occurs between room temperature and about 150 °C. An anhydrous phase with general the formula $[Ln_6O(OH)_8(NO_3)_8]_\infty$ is then obtained, which is stable for at least 100 °C. Finally, this anhydrous phase decomposes, which leads first to $LnO(NO_3)$[39] and then to the lanthanide oxide. Figure 3 presents the temperatures at which the anhydrous phase appears and disappears as a function of the ionic radius of the lanthanide ion involved. An important decrease in the temperature domain of stability of the dehydrated phase occurs as the ionic radius of the lanthanide ion increases. This behavior has already been observed for other lanthanide-containing compounds.[44]

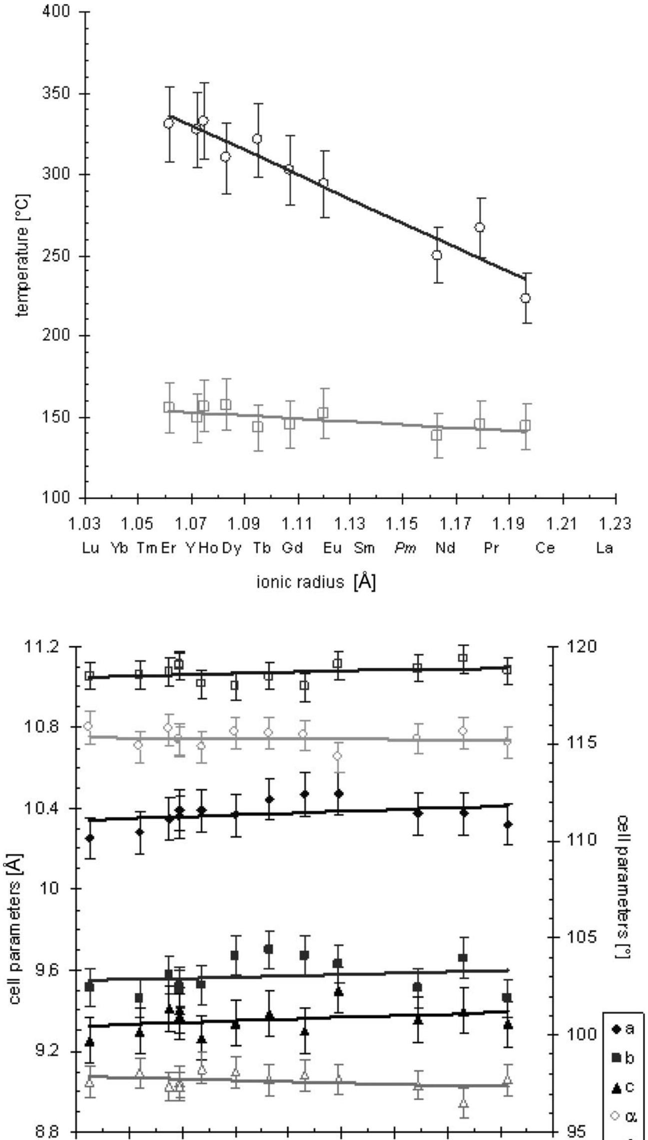

Figure 3. Temperature at which the anhydrous phase of $[Ln_6O(OH)_8(NO_3)_8]_\infty$ appear and disappear as a function of the ionic radius of the Ln^{3+} ion (top). Cell parameters for $[Ln_6O(OH)_8(NO_3)_8]_\infty$ vs. the ionic radius of the Ln^{3+} ion (bottom). Ionic Radii are for eight-coordinate ions.[41]

It is noticeable that all the dehydrated compounds present similar X-ray powder patterns, irrespective to which family the initial hydrated complex belongs. This isostructurality of the anhydrous compounds has been assumed on the basis of the powder X-ray diffractograms, and a plot of their refined cell parameters vs. the ionic radius of the lanthanide ion involved is presented in Figure 3.

As the anhydrous phase was synthesized by thermal treatment, no single crystal was obtained. The crystal structure of this phase has therefore been solved on the basis of the powder X-ray diffractogram of $[Y_6O(OH)_8(NO_3)_8]_\infty$; the experimental data are listed in Table 2.

Table 2. Experimental data for the X-ray diffraction study of $[Y_6O(OH)_8(NO_3)_8]_\infty$.

Molecular formula	$Y_3O_{17}N_4$
Formula weight	594.73
Temperature [K]	293
Crystal System	triclinic
Space group	$P\bar{1}$ (no. 2)
a [Å]	10.394(5)
b [Å]	9.507(5)
c [Å]	9.373(5)
α [°]	115.2(1)
β [°]	119.1(1)
γ [°]	97.35(9)
V [Å]	663.3
Z	2
λ [Å]	1.5418
$\rho_{calcd.}$ [g cm^{-3}]	2.977
Pattern range [°]	5–35
Step size, 2θ [°]	0.0084
Step scan time [s]	600
No. contributing reflections ($K_{\alpha1}$ + $K_{\alpha2}$)	100
No. refinement parameters	27 structural parameters (27 DOF) 9 profile parameters
Rwp	0.1438
Rp	0.1114

This compound crystallizes in the triclinic system, space group $P\bar{1}$ (no.°2) with the following cell parameters: a = 10.394(5) Å, b = 9.507(5) Å, c = 9.373(5) Å, α = 115.2(1)°, β = 119.1(1)°, γ = 97.35(9)°, and Z = 2. This structure can be described as neutral polymeric chains of anhydrous hexanuclear complexes with the formula $[Y_6O(OH)_8(NO_3)_8]_\infty$.

The core of the hexanuclear complexes (Figure 4) can be described as a quasi-perfect octahedron with a Y atom on each edge and a central μ_6-oxygen atom; this oxygen atom is located on an inversion center. The distances between the central oxygen atom and the Y atoms lie in the range 2.468–2.546 Å. Each face of the octahedron is capped by a μ_3-OH^- group. The distances between the capping oxygen atoms and the yttrium atoms are very similar; the average distance is 2.34(5) Å. Two out of the six yttrium atoms are coordinated by seven oxygen atoms: the central oxygen atom, four from the capping hydroxide groups, and two from a bidentate nitrate group. The remaining four yttrium atoms are bonded to an eighth of the oxygen atom belonging to an additional nitrate group. It should be noted that these two additional nitrate groups per octahedral unit constitute the main difference between this crystal structure and those of the hydrated phases. Actually, the crystal structure of the hydrated phases can all be described by the juxtaposition of isolated dicationic octahedral complexes; the electroneutrality of the framework is ensured by isolated nitrate groups. Upon heating and removal of the water molecules, these initially isolated nitrate groups link the hexanuclear complexes together, thus forming original neutral polymeric chains.

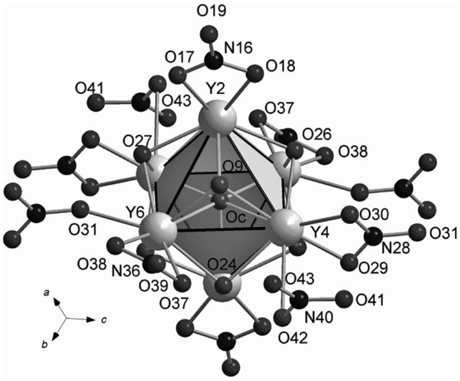

Figure 4. View of the hexanuclear unit $[Y_6O(OH)_8(NO_3)_8]$ along with the numbering scheme.

The polymeric chains spread along the *c* axis. The octahedral complexes are bonded to each other by nitrate groups. These nitrate groups are linked to one yttrium atom in a bidentate manner and to the second in a unidentate manner (Figure 5). The octahedral complexes are linked to each other by four yttrium atoms in a share-edge manner, thus a sort of ribbon-like molecular motif is formed that spreads along *c* in the (*b*,*c*) plane. The two yttrium atoms in the apical positions are the two seven-coordinate atoms.

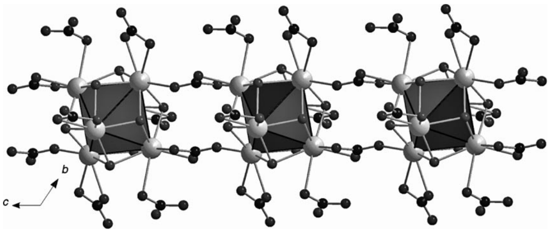

Figure 5. Projection view along *a* of a ribbon-like molecular motif.

Crystal packing (Figure 6) is ensured by a complex network of hydrogen bonds between the capping hydroxide and nitrate groups. These inter-chains interactions and the linkages between the hexanuclear units are labile, and this anhydrous phase dissolves readily in most organic solvents. It should also be noted that these dehydrated phases reversibly bind water when exposed to moisture, which leads to the initial hydrated phases (Figure 7). This rehydration is accompanied by a loss of crystallinity.

Because of the ability of cerium to provide both +III and +IV stable oxidation states, the analogous cerium(III) hexanuclear complex was synthesized under N_2 atmosphere, and despite great synthetic efforts, no single crystal suitable for structural characterization was obtained. The resulting micro-crystalline powder shows an unknown X-ray diffraction pattern (Figure 8). This diagram has been indexed by the Reflex module of the MS Modeling package.[45] All the observed peaks can been indexed in the triclinic system with the following cell parameters: a = 10.236 Å, b = 9.694 Å, c = 11.161 Å, α = 115.53°, β = 108.15°, and γ = 85.03°. The thermal behavior of this compound was studied by TGA/TD, which is very similar to those of the above-described hydrated compounds. However, the cerium(III)-containing compound is more hydrated than the praseodymium- and neodymium-containing complexes. On the basis of this study and on the results of the chemical analysis, the following formula can be proposed, $[Ce_6O(OH)_8(NO_3)_6(H_2O)_{16}](NO_3)_2{\cdot}2H_2O$.

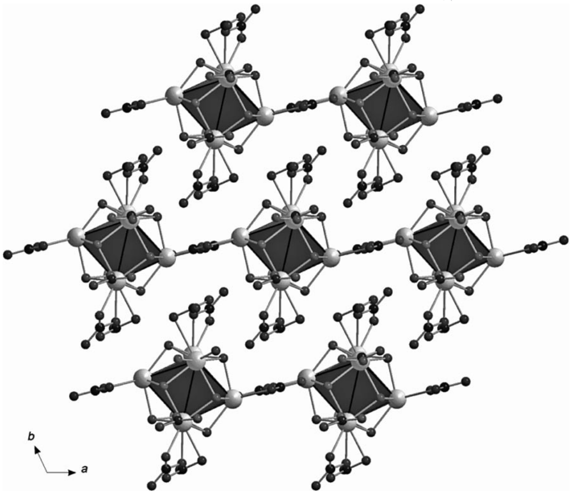

Figure 6. Projection view along the *c* axis for $[Y_6O(OH)_8(NO_3)_8]_\infty$.

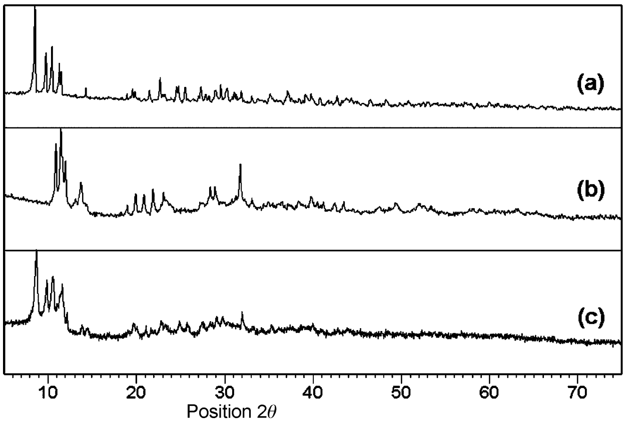

Figure 7. Powder X-ray diffractograms of the (a) initial hydrated phase $[Yb_6O(OH)_8(NO_3)_6(H_2O)_{12}]$ $(NO_3)_2{\cdot}2H_2O$, (b) the dehydrated phase $[Yb_6O(OH)_8(NO_3)_8]_\infty$, and (c) the rehydrated phase $[Yb_6O(OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2{\cdot}2H_2O$.

In order to verify this assumption, we dehydrated this compound using the same procedure as that for the other compounds. As expected (Figure 9), this leads to the anhydrous phase $[Ce_6O(OH)_8(NO_3)_8]_\infty$, which is isostructural to the above-described anhydrous phases. Rehydration of this anhydrous phase under moist conditions leads, once again, to the initial hydrated phase.

Like the other compounds belonging to this structural family, this compound is also readily soluble in most organic solvents (Table 3). This result is particularly interest-

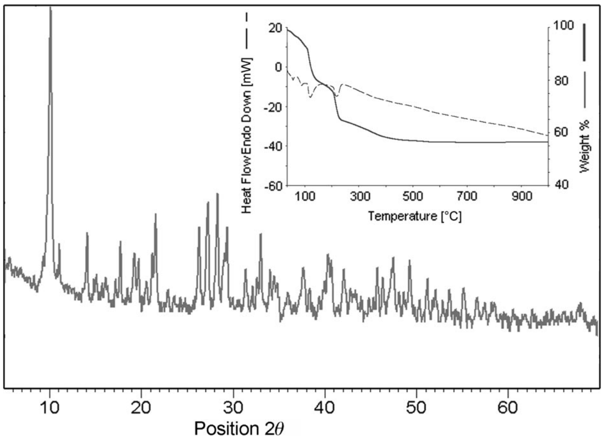

Figure 8. Normalized X-ray diffractogram of the Ce^{III}-containing hydrated phase. The main diffraction peaks are listed, 2θ (peak intensity): 10.87°(32), 11.36°(47), 11.47°(100), 11.66°(29), 11.99°(34), 13.75°(19), 18.89°(7), 19.86°(12), 20.85°(22), 21.82°(13), 23.02°(21), 23.45°(8), 24.08°(4), 28.32°(17), 28.79°(15), 29.09°(5), 29.49°(4), 31.18°(7), 31.66°(76), 32.25°(5), 34.82°(9), 38.28°(9), 39.55°(10), 40.33°(7), 40.98°(8), 42.38°(12), 43.28°(9), 47.32°(7), 53.11°(7). The inset shows the TGA/TD curves.

ing because of the great potential interest of the cerium-based complexes in catalysis. Furthermore, to the best of our knowledge, this anhydrous compound is the first hexanuclear oxido-hydroxido cerium(III) complex ever reported.

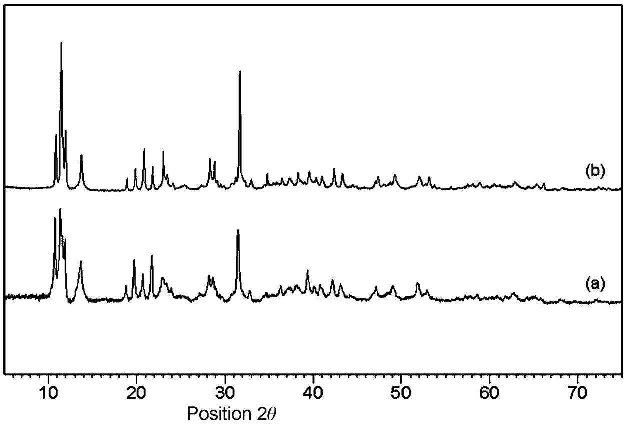

Figure 9. Powder X-ray diffractograms of (a) $[Er_6O(OH)_8(NO_3)_8]_\infty$ and (b) $[Ce_6O(OH)_8(NO_3)_8]_\infty$.

Table 3. Solubility of $[Ce_6O(OH)_8(NO_3)_8]_\infty$ in various dry organic solvents (evaluated by ICP).

Solvent	Solubility [ppm]
Hexane	1.9(1)
Methanol	8019(1)
Ethanol	5707(1)
Propan-1-ol	3939(1)
Butan-1-ol	4792(1)
Acetonitrile	2053(1)
DMF	12682(1)

Conclusions

The three goals that motivated this study have been reached. Firstly, we improved the synthesis of hexanuclear oxido-hydroxido lanthanide complexes. As a result of this improved procedure, it is now possible to control the hydration rate of these complexes (Table 4). Secondly, we succeeded, for the first time, in synthesizing a cerium(III)-containing hexanuclear oxido-hydroxido compound. Lastly, we synthesized and structurally characterized a new family of anhydrous hexanuclear oxido-hydroxido lanthanide compounds with the formula $[Ln_6O(OH)_8(NO_3)_8]_\infty$ with Ln = Ce–Yb and Y. Despite the polymeric character of these compounds in the solid phase, they all readily dissolve in most organic solvents. This indicates that in solution, the chains break down and lead to isolated hexanuclear complexes. This property is of great interest. Indeed, these compounds can be used as molecular precursors for further chemistry. This work is underway in our group and preliminary results are very promising.

Experimental Section

Synthesis of the Microcrystalline Powders of the Hydrated Compounds $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_x]2NO_3{\cdot}2H_2O$ (x = 12 for Ln = Sm–Yb and Y, x = 14 for Ln = Pr, and Nd and x = 16 for Ce): Hydrated lanthanide nitrates were purchased from STREM Chemicals and used without further purification. An aqueous solution of sodium hydroxide (3 mL of a 0.5 M solution) was carefully added dropwise to a solution of lanthanide nitrate (10 mL of a 1 M solution) in a mixture water/ethanol (1:9) whilst vigorously magnetically stirred. This slow addition was crucial in order to avoid any local over-concentration that would lead to the insoluble lanthanide hydroxide. The Ce^{III}-containing compound was synthesized under a nitrogen atmosphere in order to avoid oxidation of cerium. During the addition, a polycrystalline powder appears. Once the addition was complete, the mixture was continuously stirred for

Table 4. Hydration data for the hexanuclear lanthanide complexes.

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}](NO_3)_2{\cdot}2H_2O$				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{14}](NO_3)_2{\cdot}2H_2O$		▨	▨										
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{16}](NO_3)_2{\cdot}2H_2O$	▨												
Dehydration ↓ ↑ Rehydration													
$[Ln_6O(OH)_8(NO_3)_8]_\infty$	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨

10 min in order to ensure the completion of the reaction. The solid phase was then filtered and dried in air. Yield (relative to lanthanide ions): 18(1)%. The results of the chemical analysis are summarized in Tables 5, 6, and 7. All compounds present similar IR spectra: $\tilde{\nu}$ = 3550–3100 (s) ν(OH), 1488 (m) ν(OH), 1461 (m) $\nu(NO_3)$, 1387 (s) $\nu(NO_3)$, 1340 (s) $\nu(NO_3)$, 1040 (w) $\nu(NO_3)$, 800 (w) $\nu(NO_3)$, 615 (w) ν(Ln–OH), 421 (w) ν(Ln–OH) cm^{-1}.[46,47]

Table 5. Chemical analysis results for $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{12}]2NO_3\cdot 2H_2O$ with Ln = Sm–Yb and Y.

Ln	M_w [g mol^{-1}]	Calculated (found) Ln [%]	O [%]	N [%]	H [%]
Y	1433.9	37.2 (37.0)	52.5 (52.6)	7.8 (7.7)	2.5 (2.7)
Sm	1802.6	50.0 (50.1)	41.8 (41.5)	6.2 (6.3)	2.0 (2.8)
Eu	1812.2	50.3 (50.0)	41.5 (41.5)	6.2 (6.4)	2.0 (2.1)
Gd	1843.9	51.2 (51.1)	40.7 (40.8)	6.1 (6.2)	2.0 (1.9)
Tb	1854.0	51.4 (51.4)	40.6 (40.5)	6.0 (5.9)	2.0 (2.2)
Dy	1875.4	52.0 (52.1)	40.1 (40.1)	6.0 (6.1)	1.9 (2.1)
Ho	1890.0	52.4 (52.2)	39.8 (40.0)	5.9 (5.9)	1.9 (1.9)
Er	1904.0	52.7 (52.4)	39.5 (39.6)	5.9 (6.0)	1.9 (2.0)
Yb	1938.6	53.6 (53.6)	38.7 (39.0)	5.8 (5.6)	1.9 (1.8)

Table 6. Chemical analysis results for $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{14}]2NO_3\cdot 2H_2O$ with Ln = Pr and Nd.

Ln	M_w [g mol^{-1}]	Calculated (found) Ln [%]	O [%]	N [%]	H [%]
Pr	1781.9	47.4 (47.5)	44.0 (44.1)	6.3 (6.2)	2.3 (2.2)
Nd	1801.9	48.0 (48.2)	43.6 (43.5)	6.2 (6.1)	2.2 (2.2)

Table 7. Chemical analysis results for $[Ce_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_6(H_2O)_{16}]2NO_3\cdot 2H_2O$.

Ln	M_w [g mol^{-1}]	Calculated (found) Ln [%]	O [%]	N [%]	H [%]
Ce	1813.2	46.4 (46.6)	45.4 (45.4)	6.2 (6.2)	2.0 (1.8)

Synthesis of the Dehydrated Phases: The anhydrous phases were thermally obtained by heating the hydrated phases in a furnace at 180 °C for 2 h. All the anhydrous phases exhibit very similar X-ray powder diffractogram. The results of the chemical analysis are summarized in Table 8. All compounds present similar IR spectra: $\tilde{\nu}$ = 3550–3100 (s) ν(OH), 1488 (m) ν(OH), 1461 (m) $\nu(NO_3)$, 1387 (s) $\nu(NO_3)$, 1340 (s) $\nu(NO_3)$, 1040 (w) $\nu(NO_3)$, 800 (w) $\nu(NO_3)$, 615 (w) ν(Ln–OH), 421 (w) ν(Ln–OH) cm^{-1}.[46,47]

X-ray Powder Diffraction: The X-ray powder diffractograms were collected by using a Panalytical X′Pert Pro diffractometer with an X′celerator detector. The recording conditions were 40 kV, 40 mA for Cu-K_α (λ = 1.542 Å), the diagrams were recorded in θ/θ mode in 11 h between 5° and 75° (8378 measurements) with a step size of 0.0084° in 2θ and a scan time of 600 s. For pattern indexing, the extractions of the peak positions were carried out with the WINPLOTR[48] software. The pattern indexing was performed by the program McMaille,[49] and the refinement of the unit-cell parameters by means of the Chekcell program, which is a modified version of Cellref from the suite CRYSFIRE.[50] The identification of the phases on the basis of their X-ray diffractograms was done by using Highscore Software[51] with a JCPDS version PDF2/2000 (sets 1–50 and 70–88) database.

Table 8. Chemical analysis results for $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_8]_\infty$.

Ln	M_w [g mol^{-1}]	Calculated (found) Ln [%]	O [%]	N [%]	H [%]
Y	1181.6	45.1 (45.0)	44.7 (44.8)	9.5 (9.4)	0.7 (0.8)
Ce	1488.9	56.5 (56.6)	35.5 (35.4)	7.5 (7.6)	0.5 (0.4)
Pr	1493.6	56.6 (56.7)	35.4 (35.5)	7.5 (7.3)	0.5 (0.5)
Nd	1513.6	57.2 (57.0)	34.9 (34.8)	7.4 (7.5)	0.5 (0.7)
Sm	1550.3	58.2 (58.2)	34.1 (34.3)	7.2 (7.1)	0.5 (0.6)
Eu	1559.9	58.4 (58.7)	33.9 (33.8)	7.2 (7.1)	0.5 (0.4)
Gd	1591.6	59.3 (59.1)	33.2 (33.2)	7.0 (7.1)	0.5 (0.6)
Tb	1601.7	59.5 (59.5)	33.0 (33.2)	7.0 (6.9)	0.5(0.4)
Dy	1623.1	60.1 (60.2)	32.5 (32.5)	6.9 (7.0)	0.5 (0.5)
Ho	1637.7	60.4 (60.5)	32.3 (32.4)	6.8 (6.5)	0.5 (0.6)
Er	1651.7	60.8 (60.5)	31.9 (31.8)	6.8 (7.0)	0.5 (0.7)
Yb	1661.7	61.0 (61.0)	31.8 (31.9)	6.7 (6.6)	0.5 (0.5)

X-ray Structure Determination of $[Y_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_8]_\infty$: To solve the structure of the dehydrated compounds, we used the modeling and simulation software Materials Studio Modeling.[45] This software is convenient for molecular materials because it is able to compute a simulated annealing on fixed groups of atoms, here, for example, the octahedral hexanuclear complex, which we expected not be destroyed by the dehydration–rehydration cycle. After thousands of configurations checked, the software proposed a chemically suitable molecular structure, which we refined using the Rietveld calculation with a global isotropic temperature factor.[52] Hydrogen atoms were not localized. Crystal and final structure refinement data of the compound are listed in Table 1. The experimental and calculated diffractograms are shown in Figure 10. Further details of the crystal-structure investigation(s) (on the anhydrous yttrium-containing complex) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number(s) CSD-420441.

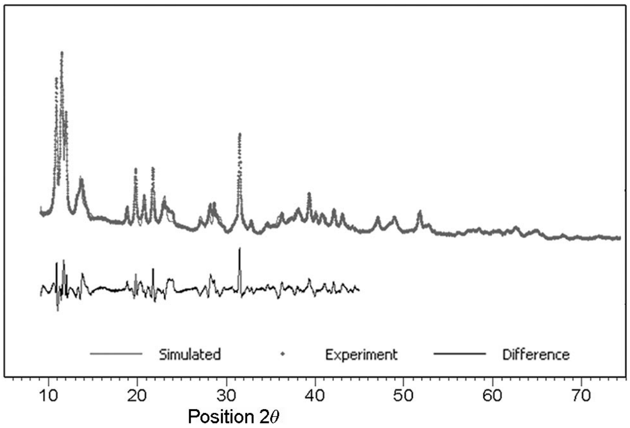

Figure 10. Calculated and experimental diffractograms of compound $[Y_6O(OH)_8(NO_3)_8]_\infty$.

Thermal Analysis: Thermogravimetric and thermal differential analyses were performed in a platinum crucible under a nitrogen atmosphere between room temperature and 1000 °C with a heating rate of 5 °C min^{-1} by using a Perkin–Elmer Pyris-Diamond thermal analyzer. The thermal-dependence X-ray diffraction experiments were performed with a Panalytical X′Pert Pro diffractometer with an X′celerator detector diffractometer by using Cu-K_α radiation in the range 5–70° in 2θ. The heating of the samples (from room temperature to 1000 °C) was performed with an Anton Paar HTK 1200 furnace under a nitrogen atmosphere.

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