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Lanthanide-based hexanuclear complexes usable as molecular precursors for new hybrid materials

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ABSTRACT

Lanthanide containing octahedral hexanuclear complexes with general chemical formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_x].2NO_3.yH_2O$ where Ln = Ce–Lu (except Pm) or Y, x = 0, 6, 12, 14 or 16 and y = 0, 2, 4 or 5 constitute a great family of polymorphic compounds. The synthesis and the crystal structures of all these compounds are overviewed. The hydration/dehydration processes that allow the structural transitions from one compound to another are described. The crystal structure of compounds with general chemical formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_6].2NO_3$ where Ln = Ce–Lu (except Pm) or Y is described. It has been solved on the basis of a powder XRD diagram. The use of such hexanuclear complexes as molecular precursors for new materials is also discussed.

RÉSUMÉ

Les complexes octaédriques hexanucléaires à base d'ions lanthanides de formule chimique générale $[Ln_6O(OH)_8(NO_3)_6(H_2O)_x].2NO_3.yH_2O$ où Ln = Ce–Lu (sauf Pm) ou Y, x = 0, 6, 12, 14 ou 16 et y = 0, 2, 4 or 5 constituent une vaste famille de composés polymorphiques ; les synthèses et les structures cristallines de ces composés sont passées en revue. Les procédés d'hydratation/déshydratation qui permettent de passer d'un composé à l'autre sont décrits. La structure cristalline des composés de formule chimique générale $[Ln_6O(OH)_8(NO_3)_6(H_2O)_6].2NO_3$ où Ln = Ce–Lu (sauf Pm) ou Y est décrite. Elle a été résolue à partir d'un diagramme de diffraction des rayons X sur poudre. L'utilisation de ces complexes hexanucléaires comme précurseurs moléculaires à de nouveaux matériaux est également discutée.

1. Introduction

For almost a decade, there has been a great activity devoted to lanthanide-containing coordination polymers [1]. This activity is motivated by their interesting luminescent properties [2] and by their ability to provide potentially porous materials. Several lanthanide-based coordination polymers exhibiting porosity have been reported [3–14]. One of the possible strategies to increase the porosity consists in designing coordination polymers where poly-nuclear complexes would act as metallic centers. This strategy has been successfully applied some years ago and very promising materials involving zinc tetra-nuclear complexes have been obtained [15]. However, up to now, only a few potentially porous coordination polymers involving poly-nuclear lanthanide complexes

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have been reported [16–23]. In fact, while the cluster chemistry of d-block transition metals is now firmly established [24,25], the analogous chemistry involving the lanthanide ions is rather underdeveloped.

To date, only a few poly-nuclear lanthanide complexes have been reported. Most of them have been obtained by use of ancillary ligands. These ligands pre-occupy part of the coordination sphere of the lanthanide ion. By the way, they prevent the formation of the highly insoluble lanthanide hydroxide and allow the control of the lanthanide ion hydrolysis. Several poly-nuclear lanthanide complexes have so been obtained ranging from di-nuclear to pentadeca-nuclear lanthanide oxo/hydroxo entities [17,26–34]. Unfortunately, these entities are most often very unstable in solution [34] and cannot be used as molecular precursors for further chemistry.

A second synthetic route, first described 15 years ago [35–41], leads to hexa-nuclear lanthanide complexes with general chemical formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_x]^{2+}$ with $x = 12$ when Ln = Sm–Yb, $x = 14$ when Ln = Pr–Nd and $x = 16$ for Ln = Ce. This route consists in using lanthanide nitrate as a starting material and in hydrolyzing it by addition of sodium hydroxide. As illustrated by Fig. 1, this synthetic pathway is based on a subtle balance between the various experimental parameters (pH, concentrations, temperature…). The main difficulty encountered during the synthesis of these complexes is to avoid the formation of very stable polymeric species such as $Ln(OH)_2NO_3$ [25,36,37], $LnONO_3$ [42] and $Ln(OH)_3$ [43].

Owing to this synthetic method, numerous polymorphic phases of such hexa-nuclear lanthanide complexes have been reported so far [39,40,44–47]. They are listed in Table 1 where it can be noticed that several polymorphic phases can exist for a given lanthanide ion.

All these compounds, except $[Ce_6O(OH)_8(NO_3)_6(H_2O)_{16}].(NO_3)_2.2H_2O$, have been structurally described. All the crystal structures are very similar. They can be described as the juxtaposition of perfect octahedrons with one lanthanide ion in each edge and one μ_6–O^{2-} anion at the center. Each face of the octahedrons is shaped by a μ_3–OH^- anion and each lanthanide ion is bounded in a bidentate manner to a nitrate anion. The main difference between the two families of compounds concerns the coordination water molecules. As shown in Fig. 2, the complexes involving a lanthanide ion comprised between Yb and Sm or Y contain 12 coordination water molecules (two per lanthanide ion) while those involving Nd or Pr include 14 of them. In these two latter complexes, four out of the six lanthanide ion are bounded to two coordination water molecules while the remaining two lanthanide ions are bounded to three coordination water molecules. So, all the lanthanide ions are nine-coordinated in compounds belonging to the former family while for compounds belonging to the latter family two out of the six are 10-coordinated and the remaining four are nine-coordinated.

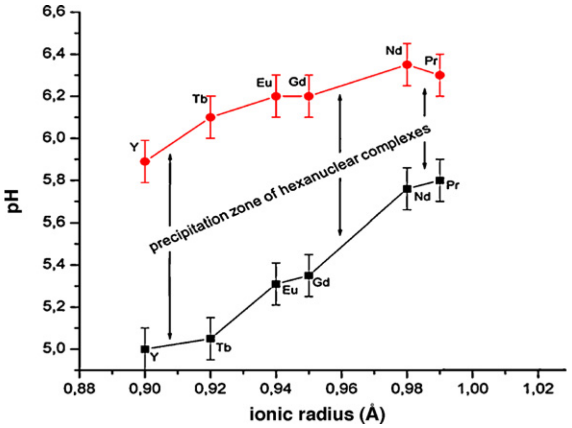

Fig. 1. Obtaining domain of compounds with general chemical formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_n].(NO_3)_2.2H_2O$ with Ln = Pr–Tb plus Y at room temperature [44].

These complexes can be used as molecular precursors for further chemistry [48,49]. However, they still present a slight tendency to hydrolyze even in dry organic solvents because of their crystallization and coordination water molecules. In order to increase the chemical stability of the complexes it is possible to dehydrate them. The dehydration of these complexes is easy to realize thermally and leads to stable anhydrous compounds with general chemical formula $[Ln_6O(OH)_8(NO_3)_8]_\infty$ with Ln = Ce–Yb (except Pm) or Y. It is noticeable that all the dehydrated compounds present similar X-ray powder patterns whatever the initial hydrated complex belongs to one or the other family.

The crystal structure of these compounds has been solved on the basis of the powder X-ray diffraction diagram of $[Y_6O(OH)_8(NO_3)_8]_\infty$. It can be described as neutral polymeric chains of anhydrous hexa-nuclear complexes. The octahedral complexes are bounded 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 (Fig. 3). The octahedral complexes are linked to each other by four yttrium atoms in a share-edges manner thereby forming a ribbon-like molecular motif.

Table 1
Summary of the reported hexa-nuclear lanthanide complexes with general chemical formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_x].(NO_3)_2.yH_2O$.

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}].(NO_3)_2.2H_2O$				[46]		[45]						[46]	
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{14}].(NO_3)_2.2H_2O$		[44]											
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{16}].(NO_3)_2.2H_2O$	[46]												
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}].(NO_3)_2.3H_2O$								[47]			[47]		
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}].(NO_3)_2.4H_2O$										[39]	[40]		[39]
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}].(NO_3)_2.5H_2O$						[39]	[45]	[40]	[45]				
$[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}].(NO_3)_2.6H_2O$				[40]		[45]							