

Oxo-centered regular octahedral lanthanide clusters

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Reaction of $\text{Ln}(\text{ClO}_4)_3$ ($\text{Ln} = \text{Nd}$ or Gd) with L-serine at pH 6.0 yielded the aqua hexanuclear clusters $[\text{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}](\text{ClO}_4)_8 \cdot 6 \text{H}_2\text{O}$ (**1**) and $[\text{Gd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}](\text{ClO}_4)_8 \cdot 6 \text{H}_2\text{O}$ (**2**). They are isomorphous and comprised of a regular octahedron of 6 lanthanide ions encapsulating a $\mu_6\text{-O}^{2-}$ anion and capped by a $\mu_3\text{-OH}$ group on each face. The structure can also be regarded as an oxo-centered octahedron embedded in a cube formed by 8 $\mu_3\text{-OH}$ groups.

Introduction

High-nuclearity clusters have attracted increasing interest due to their importance in biological and materials chemistry,¹ especially in the context of nano science. The preparation of such clusters is an efficient means for obtaining grain-homogenous, size-controllable nanoscopic dimensional particles, which can be expected to find application in magnetic, optical, electronic and catalytic processes.² In general, a proven synthetic strategy for the formation of a polynuclear complex is to control the hydrolysis or alcoholysis of metal ions in the presence of an auxiliary ligand. Some examples of commonly employed ligands are polyketonates,³ carboxylates,⁴ pyridionate⁵ and alkoxides.⁶ Very recently, we have succeeded in preparing a pentadecanuclear cluster and a series of tetranuclear lanthanide clusters using amino acid ligands at high pH values.⁷ While attempting to prepare lanthanide clusters supported by L-serine, we isolated two isomorphous aqua lanthanide clusters $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}](\text{ClO}_4)_8 \cdot 6 \text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}$, **1**; Gd , **2**) with an encapsulated oxo group in the center, whose structures and unique features are reported here.

The compounds were synthesized by mixing $\text{Ln}(\text{ClO}_4)_3$ ($\text{Ln} = \text{Nd}$, Gd) and L-serine in aqueous solution and subsequently adjusting its pH value to 6 with aqueous NaOH. Single crystal X-ray diffraction analysis revealed that they are isomorphous and consist of an octahedral framework constructed by six Ln^{III} ions as shown in Fig. 1 for **1**. In the asymmetric unit, there are two crystallography independent Nd ions; the Nd2 lie on a four-fold axis. The 6 Nd^{III} ions are connected through a $\mu_6\text{-oxo}$ group with the Nd1–O1 and Nd2–O1 bond lengths being almost the same [2.6239(5) and 2.6225(6) Å, respectively]. Each triangular face of the octahedron is capped by a $\mu_3\text{-OH}$ ligand with an average Nd–O bond length of 2.435 Å. The neighboring Nd1...Nd2 distance [3.7106(5) Å] is equal to the Nd1...Nd1A distance [3.7101(6) Å]. Thus, a regular octahedral cage is produced by 6 Nd ions within the limit of measurement error. Alternatively, the structure may be described as an octahedron of Nd^{III} ions, each

protruding out of the face of a cube formed by 8 $\mu_3\text{-OH}$ groups, as shown in Fig. 2(a). The metal ions and oxygen atoms are arranged following the closest density packing principle, very much like that of metal oxides [Fig. 2(b)]. Each Nd^{III} ion is nine-coordinated by 4 terminal water molecules, 4 hydroxo groups and the centered oxo ligand, forming a mono-capped square antiprism with the latter ligand occupying the cap position.

A similar $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$ core motif was observed in the cation of the nitrate salt $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{NO}_3)_6(\text{H}_2\text{O})_{12}](\text{NO}_3)_2 \cdot 5 \text{H}_2\text{O}$ ⁸ and in the cyanide-bridged one-dimensional chain $\{[\text{Yb}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{DMF})_{16}(\mu\text{-CN})\text{Pd}(\mu\text{-CN})(\text{CN})_2]^{6+}\}_n$.⁹ However, the coordination number and geometry of the lanthanide ions are different. A tricapped trigonal prism and distorted dodecahedral geometry are found in the last two compounds, respectively. Nevertheless, the $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$ cluster core appears to be a stable structural entity and can be expected to serve as a building block for more complex structures.

Generally speaking, hydrophilic groups such as oxo and hydroxo bridge the metal ions to give rise to a cluster core, whereas the hydrophobic groups take up positions in the periphery, preventing the core from further aggregation. A cluster

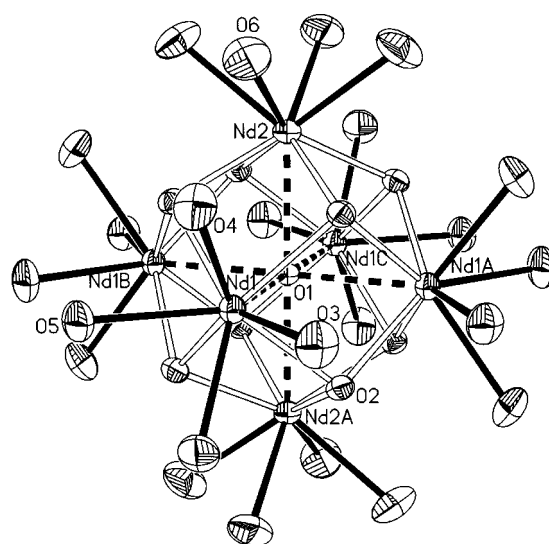


Fig. 1 ORTEP drawing of the $[\text{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$ cluster cation of **1** with 30% probability ellipsoids. Selected bond lengths (Å): Nd1–O2 = 2.436(4), Nd1–O4 = 2.571(6), Nd1–O3 = 2.578(8), Nd1–O5 = 2.617(8), Nd1–O1 = 2.6239(5), Nd2–O2^a = 2.441(5), Nd2–O6 = 2.588(7), Nd2–O1 = 2.6225(6). Symmetry code a: $-y + 1, x - 1, z$.

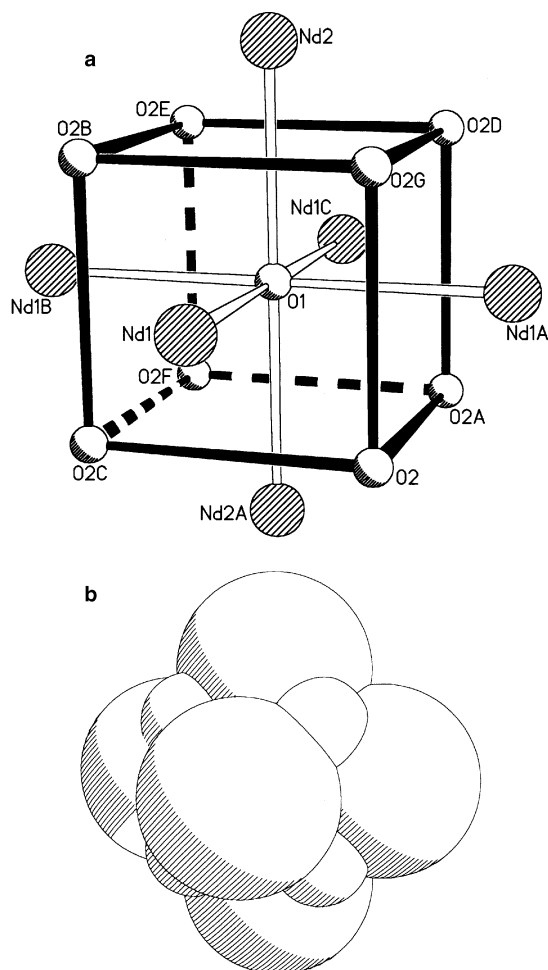


Fig. 2 (a) The oxo-centered Nd_6 octahedron embedded in a cube formed by 8 $\mu_3\text{-OH}$ groups. (b) The space filling model of the $[\text{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$ core, like the closest packing in a metal oxide.

of finite size can be assembled in this way. In our case, the whole cluster only contains oxo, hydroxo, and aqua ligands without any other supporting ligand or coordinated anion, making it the first such example in lanthanide cluster chemistry and also the simplest hexanuclear lanthanide cluster. For the production of the Ln_6 cluster, the L-serine ligand serves a useful function by suppressing the hydrolysis of lanthanide ions and by controlling the pH value of the solution, which will promote the formation of the cluster core.

The central oxo group undoubtedly plays a decisive role in the assembly of the octahedral Ln_6 cluster. Classically, cations have been incorporated in the cavity as a template or guest to promote the assembly of high-nuclearity clusters. Many examples can be enumerated, such as Na^+ in a Fe_6 cluster,³ and Ln^{3+} and Mn^{2+} in a Mn_6 cluster.¹⁰ Recently, increasing attention has been focused on anion templates. For example, the chloride ion serves as a template in the formation of Nd_{15} ,⁷ and Ni_6 ,¹¹ ClO_4^- for $\text{Cu}_{12}\text{Ln}_6$,¹² and C_2^{2-} for Ag_n ($n = 6-9$).¹³ In the present case, the oxo group functions as an anion template to induce the self-assembly of lanthanide ions. Since the Ln_6 octahedron adopts a closest packing structure, the very small interstice in its center cannot accommodate a larger anion such as perchlorate or nitrate. To test the validity of this viewpoint, a further study on the hydrolysis of other lanthanide salts, such as chloride, acetate, and trifluoromethanesulfate, is under way.

Experimental

Compound **1** was prepared by mixing $\text{Nd}(\text{ClO}_4)_3 \cdot 6 \text{H}_2\text{O}$ (1 mmol) and L-serine (4 mmol) in 20 ml water solution. The

slurry was stirred under heating and aqueous NaOH was added dropwise. The solution gradually became clear and NaOH was added continuously until pH 6 (monitored by pH meter) was reached. The pink precipitate produced was filtered off and the filtrate was condensed to 10 ml, which was allowed to stand at room temperature. Single crystals were obtained after 5 days. Compound **2** was obtained following the same procedure as **1**.

Crystal data for **1**: Formula $\text{H}_{72}\text{Cl}_8\text{Nd}_6\text{O}_{73}$, $M = 2389.62$, tetragonal, space group $P4/mnc$, $a = 14.5147(7)$, $b = 14.5079(7)$, $c = 15.2546(8)$ Å, $U = 3212.3(3)$ Å³, $Z = 2$, $D_c = 2.471$ Mg m⁻³, $\mu = 5.233$ mm⁻¹, $F(000) = 2304$, $\text{GoF} = 0.977$. The final R_1 and wR_2 are 0.0322 and 0.0827, respectively, for 147 parameters and 1641 independent reflections [$I > 2\sigma(I)$]. Crystal data for **2**: Formula $\text{H}_{72}\text{Cl}_8\text{Gd}_6\text{O}_{73}$, $M = 2467.68$, tetragonal, space group $P4/mnc$, $a = 14.2740(8)$, $b = 14.2140(6)$, $c = 15.1040(6)$ Å, $U = 3064.5(2)$ Å³, $Z = 2$, $D_c = 2.674$ Mg m⁻³, $\mu = 6.895$ mm⁻¹, $F(000) = 2352$, $\text{GoF} = 1.194$. The final R_1 and wR_2 are 0.0702 and 0.1726, respectively, for 128 parameters and 1370 independent reflections [$I > 2\sigma(I)$].

CCDC reference number 440/159. See <http://www.rsc.org/suppdata/nj/a9/a908471a/>, for crystallographic files in .cif format.

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References

- 1 R. B. Lauffer, *Chem. Rev.*, 1987, **87**, 901; D. Gatteschi, A. Caneschi, R. Sessoli and A. Cornia, *Chem. Soc. Rev.*, 1996, 101.
- 2 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature (London)*, 1993, **365**, 141; M. T. Pope and A. Muller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 215.
- 3 A. Caneschi, A. Cornia, A. C. Fabretti and D. Gatteschi, *Angew. Chem., Int. Ed.*, 1999, **38**, 1295; J. C. A. Boeyens and J. P. R. De Villiers, *J. Cryst. Mol. Struct.*, 1972, **2**, 197; G. L. Abbati, A. Caneschi, A. Cornia, A. C. Fabretti, D. Gatteschi, W. Malavasi and L. Schenetti, *Inorg. Chem.*, 1997, **36**, 6443.
- 4 S. P. Watton, P. Fuhrmann, L. Pence, A. Caneschi, A. Cornia, G. L. Abbati and S. J. Lippard, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2774; R. C. Squire, S. M. J. Aubin, K. Folting, W. E. Streib, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1995, **34**, 6463.
- 5 S. Parsons and R. E. P. Winpeny, *Acc. Chem. Res.*, 1997, **30**, 89.
- 6 R. C. Mehrotra, A. Singh and S. Sogani, *Chem. Soc. Rev.*, 1994, **23**, 215; K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.
- 7 R. Y. Wang, Z. P. Zheng, T. Z. Jin and R. J. Staples, *Angew. Chem., Int. Ed.*, 1999, **38**, 1813; T. Z. Jin, S. Gao, B. Q. Ma, D. S. Zhang and C. H. Yan, unpublished work.
- 8 Z. Zak, P. Unfried and G. Giester, *J. Alloys Compd.*, 1994, **205**, 235.
- 9 J. Liu, E. A. Meyers and S. G. Shore, *Inorg. Chem.*, 1998, **37**, 5410.
- 10 D. M. J. Doble, C. H. Benison, A. J. Blake, D. Fenske, M. S. Jackson, R. D. Kay, W. S. Li and M. Schroder, *Angew. Chem., Int. Ed.*, 1999, **38**, 1915.
- 11 R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1258.
- 12 X. M. Chen, S. M. J. Aubin, Y. L. Wu, Y. S. Yang, T. C. W. Mak and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **117**, 9600.
- 13 G.-C. Guo, G.-D. Zhou and T. C. W. Mak, *J. Am. Chem. Soc.*, 1999, **121**, 3136.

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