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A Series of Lanthanide-Based Cluster Organic Frameworks Made of Heptanuclear Trigonal-Prismatic Cluster Units

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Supporting Information

ABSTRACT: A series of lanthanide-based cluster organic frameworks, $[Ln_7(\mu_3\text{-}OH)_8L_9(H_2O)_6]\cdot 4ClO_4\cdot 3HL\cdot nH_2O$ [HL = 4-pyridin-4-ylbenzoic acid; Ln = Y (**1**), La (**2**), Gd (**3**), Yb (**6**), $n = 6$; Ln = Dy (**4**), Er (**5**), $n = 4$], were hydrothermally made and characterized. It is the first example of heptanuclear trigonal-prismatic lanthanide clusters via a hydrothermal reaction. The magnetic properties of **3** and **4** show typical antiferromagnetic interactions.

High-nuclearity lanthanide (Ln) clusters continue to attract considerable attention because of their fascinating structures and rich optical and magnetic properties associated with their size effects.[1] As a result, Ln clusters, such as Ln_3,[2] Ln_4,[3] Ln_5,[4] Ln_6,[5] Ln_7,[6] Ln_8,[7] Ln_9,[8] Ln_{10},[9] Ln_{12},[10] Ln_{13},[11] Ln_{14},[12] Ln_{15},[13] Ln_{22},[9d] Ln_{26},[14] and Er_{60},[15] have been reported. Generally, they were made by controlling the hydrolysis of Ln salts in the presence of supporting ligands, while the majority are discrete because they either prevented aggregation by hydrophobic groups or are encapsulated by supporting ligands without further coordination sites. Thus, the choice of organic ligands is critical to the construction and linking of Ln clusters.

The open frameworks based on Ln_{14}[16] and Er_{36}[17] cluster units have been successfully made by using isonicotinic acid (Hin) as a ligand and lanthanide oxide rather than Ln salts as the source of Ln's. To make more open Ln-based cluster organic frameworks for potential applications, that is lengthened Hin, 4-pyridin-4-ylbenzoic acid (HL) was introduced. So far, only several coordination polymers containing transition metal, Ln, and mixed 3d−4f heterometal have been made by the HL ligand.[18] Therefore, it is still a challenge to make polynuclear Ln clusters by this ligand. Here, we report the first examples of heptanuclear trigonal-prismatic Ln clusters derived from HL via hydrothermal reaction, $[Ln_7(\mu_3\text{-}OH)_8L_9(H_2O)_6]\cdot 4ClO_4\cdot 3\ HL\cdot nH_2O$ [Ln = Y (**1**), La (**2**), Gd (**3**), Yb (**6**), $n = 6$; Ln = Dy (**4**), Er (**5**), $n = 4$]. To the best of our knowledge, these are the highest-nuclearity Ln clusters linked by this ligand to date.

Yellow hexagonal crystals of **1**−**6** were made by the hydrothermal treatment of Ln_2O_3 and HL at 190 °C for 7 days in the presence of $HClO_4$ (pH 2).[19] X-ray structure analyses reveal that **1**−**6** are isostructural and crystallize in the high-symmetry trigonal space group *P*321.[20] Therefore, only the structure of **1** is described in detail. The asymmetric unit of **1** consists of two distinct motifs (Figure 1), two perchlorates, and three lattice water molecules. Motif I contains two unique Y^{3+} ions and two L ligands; motif II has only one free HL ligand. In the structure, the linkers present two types of coordination modes: μ_3-L-$\kappa^1N,\kappa^1O,\kappa^1O'$ and μ_2-L-κ^1O,κ^1O' (Scheme 1). The N1 atoms in mode I bond to $Y1^{3+}$ ions, while the N2 atoms in mode II are free. Thus, the N1 atoms play a key role in the formation of **1**. Y1 is eight-coordinated, and its geometry is close to that of a bicapped trigonal prism: three μ_3-OH groups, one N atom, three carboxylate O atoms (O_{COO^-}) from four ligands (N1/O1/O2 in mode I and O3 in mode II), and a terminal water molecule. The $Y2^{3+}$ ion located at the 6-fold axis links six hydroxyl bridges, and its geometry can be described as a trigonal prism (Figure S1 in the Supporting Information, SI).

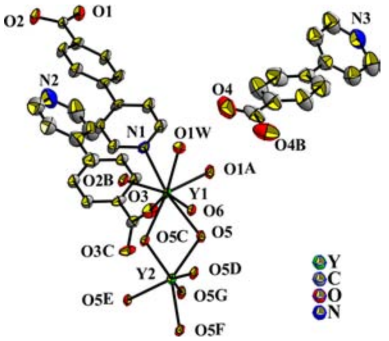
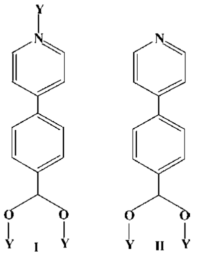


Figure 1. ORTEP of the asymmetric unit of **1** (30%), showing the coordination environments of Y1 and Y2 atoms, in which all H atoms and ClO_4^- ions are omitted for clarity. Atoms with A−G in their labels are symmetry-generated.

Scheme 1. Coordination Modes of the L Ligands in 1



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In motif I, three Y1^{3+} ions are linked by μ_3-OH to give a trinuclear unit $[Y_3(\mu_3\text{-OH})]^{8+}$ (Y_3). Two Y_3 units are joined by the central Y2^{3+} ion via six μ_3-OH groups to form a cationic heptanuclear cluster core, $[Y_7(\mu_3\text{-OH})_8]^{13+}$ (Y_7; Figure 2a). The Y_7 core can also be described as two $Y_4(OH)_4$ cubanes sharing a Y2 atom. In contrast to previously reported trigonal antiprismatic Ln_7 cores,[6a,b] the metal skeleton of the Y_7 core in **1** is a well regular trigonal prism, in which six Y1 and one Y2 atoms locate in the vertex and body center, respectively (Figure 2b). As shown in Figure 2c, 15 L ligands link the Y_7 core with two coordination modes. To each Y_3 unit, six ligands with mode I as the linkers alternately link the Y_3 unit by the N and O_{COO^-} atoms (Figure 2d) and then link to an adjacent Y_3 unit by the O_{COO^-} and N atoms (Figure 3a). To three ligands with mode II, each one only link two Y1 atoms of two Y_3 units by the O_{COO^-} atoms, while its N atom is free (Figures 2d and S2 in the SI). In the structure, the Y_7 cores connect each other by the ligands with mode I to produce a 2D Ln-based cluster organic layer (layer I) possessing a thickness about 10.92 Å along the *b* axis, which is further stabilized by the ligands with mode II bonded to two Y_3 units. Notice that the coordinated water molecules are pointing to the interbedded space (Figure S2 in the SI). In the layer I, each Y_7 core is surrounded by six of the same ones with a distance of 16.955 Å; three adjacent Y_7 cores form a trigonal-prismatic window on the *ab* plane. The ClO_4^- groups act as counterions and occupy the void of such a region to stabilize the lattice (Figure 3a).

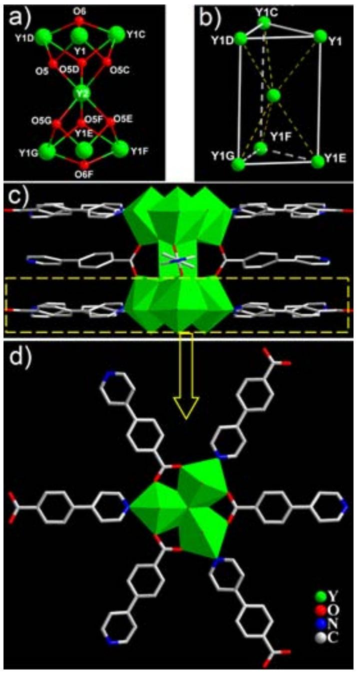

Figure 2. (a) Ball-and-stick view of the vertex-sharing dicubane cluster. (b) Metal skeleton for the trigonal-prismatic cluster. (c and d) Side and top views of the coordination environment of the Y_7 and Y_3 cores, respectively.

Motif II is only a free ligand. These free ligands are linked by three water molecules from the Y_7 cores via hydrogen bonds [O···O 2.708(8)−2.754(8) Å; Figure S3 in the SI] and then further stabilized by $\pi-\pi$ interaction between the free ligands with mode II and the linkers with mode I of adjacent Y_3 cores to form an organic layer (layer II; Figures 2c and S4 in the SI). In the structure, layer I is parallel to layer II (the interplanar distance between them is about 3.686 Å), forming an unusual face-to-face alignment of benzene and pyridine rings (Figure S4 in the SI).[21]

Furthermore, layer I constructed from motif I and layer II built from motif II are stacked in a −ABAB− sequence along the *c* axis (Figure 3b). From a topological point of view, layer I is a six-connected uninodal *hxl* net with Schläfli symbol $(3^6 \cdot 4^6 \cdot 5^3)$,[22] considering each Y_7 core as a six-connected node (Figure S5 in the SI). A *PLATON* program analysis based on the crystal structure suggests that approximately 18.1% of the crystal volume is accessible to the solvents.[23] The counterions and lattice water molecules as guests are enclathrated in the void.

Variable-temperature magnetic measurements were performed with polycrystalline samples of **3** and **4** at an applied magnetic field of 1 kOe in the range of 2−300 K. The resulting plot of χ_M and $\chi_M T$ versus T for **3** is depicted in Figure 4. The value of χ_M slowly increases from 0.19 to 2.14 cm^3 mol^{-1} and then exponentially to a maximum of 15.63 cm^3 mol^{-1} at 2 K. At 300 K, the $\chi_M T$ value of 55.86 cm^3 K mol^{-1} is close to the

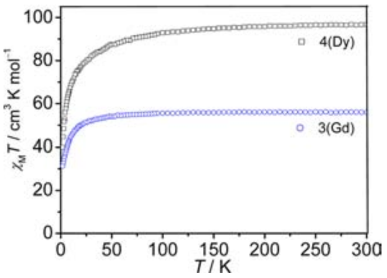

Figure 4. Plots of $\chi_M T$ versus T for **3** and **4** in a direct-current field of 1 kOe.

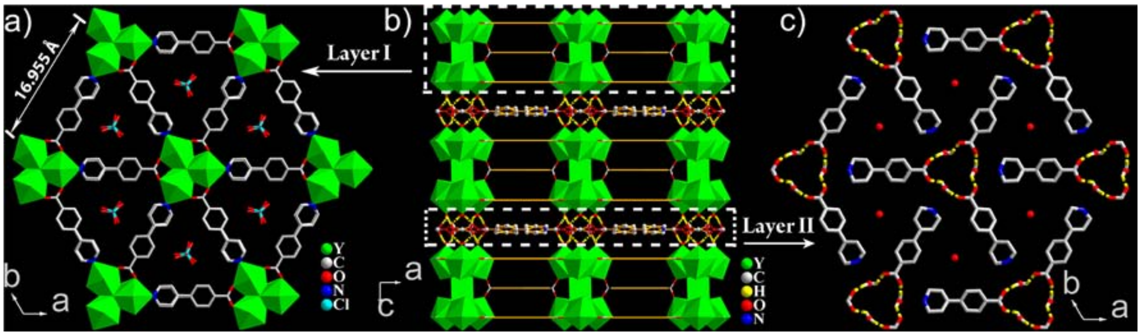

Figure 3. Top view of layers I (a) and II (c). (b) Structural cohesion of the crystalline stacking reinforced by the presence of highly directional hydrogen bonds between adjacent layers. ClO_4^- and lattice water molecules are omitted, and the orange lines stand for linear ligands for clarity.

theoretical value for seven noninteracting Gd^{3+} (55.16 cm^3 K mol^{-1}, $S = {}^7/_2$, $L = 0$, ${}^8S_{7/2}$, and $g = 2$).[24] Upon cooling, the $\chi_M T$ value continuously decreases to 31.28 cm^3 K mol^{-1} at 2 K, which is characteristic of the antiferromagnetic behavior. The magnetic data obey the Curie−Weiss law, affording $C = 57.01$ cm^3 K mol^{-1} and $\theta = -2.58$ K (Figures S6 and S7 in the SI), suggesting a weak antiferromagnetic interaction between the Gd^{3+} ions. For **4**, $\chi_M T$ of 96.79 cm^3 K mol^{-1} at 300 K gradually decreases with lowering temperature from 300 to 50 K and then drops quickly to 40.00 cm^3 K mol^{-1} at 2 K because of the progressive depopulation of the excited-state sublevel of Dy^{3+} and the very weak antiferromagnetic interaction between Dy^{3+} ions.[25]

In summary, the first examples of Ln-based cluster organic frameworks constructed from heptanuclear trigonal-prismatic cluster units have been made under mild hydrothermal conditions, in which the lengthened ligands successfully induce the Ln ions to form a Ln_7 cluster and further make them an extended framework rather than discrete. The magnetic properties of **3** and **4** reveal weak antiferromagnetic interacttions. These results present herein may provide a rational route for making multidimensional frameworks with high-nuclearity Ln clusters. Further work is continuing in this area.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystal data of **1−6** (CCDC 813910−813915), detailed experimental procedures, and additional figures of IR, TGA, and PXRD. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) Synthesis of **1**: A mixture of Y_2O_3 (0.5 mmol, 0.1130 g), HL (2 mmol, 0.3987 g), H_2O (10.0 mL, 0.22 mmol), and 3 drops of $HClO_4$ with a pH value of about 2.0 was sealed in a 30 mL Teflon-lined bomb at 190 °C for 7 days and then cooled to room temperature. Yellow hexagonal crystals of **1** were recovered by filtration, washed with distilled water, and dried at ambient temperature (yield 10% based on Y_2O_3). When $CuCl_2{\cdot}2H_2O$ or $ZnCl_2$ was introduced, the yield of crystals increased greatly (60% based on Y_2O_3). Anal. Calcd for $C_{144}H_{131}Cl_4Y_7N_{12}O_{60}$: C, 46.03; H, 3.49; N, 4.48. Found: C, 46.76; H, 3.37; N, 4.50. IR (KBr pellet, cm^{-1}): 3373(m), 1612(vs), 1554(vs), 1523(s), 1425(vs), 1225(w), 1092(vs), 1012(w), 825(m), 785(s), 621(m), 549(m), 492(m). **2−6** were obtained by procedures similar to that of **1**. For their IR, thermogravimetric analysis, and X-ray diffraction, see the SI (Figures S8−S10).

(20) Crystal data for **1**: $C_{144}H_{131}Cl_4Y_7N_{12}O_{60}$, $M_r = 3753.78$, trigonal, $P321$, $a = 16.955(2)$ Å, $c = 14.653(3)$ Å, $V = 3648.1(1)$ Å^3, $Z = 1$, $D_c = 1.709$ g cm^{-3}, $\mu = 2.926$ mm^{-1}, $F(000) = 1900$, and GOF = 1.038. Of a total of 27290 reflections collected, 5523 are unique ($R_{int} = 0.0458$). R1/wR2 = 0.0610/0.1712 for 4905 reflections and 307 parameters [$I > 2\sigma(I)$]. For the crystal data for **2−6**, see Table S1 in the SI.

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