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Synthesis and Characterization of Two Novel Lanthanide Coordination Polymers with an Open Framework Based on an Unprecedented $[Ln_7(\mu_3\text{-}OH)_8]^{13+}$ Cluster

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Two novel heptanuclear lanthanide clusters of the dicubane-like type $[Ln_7(\mu_3\text{-}OH)_8]^{13+}$ (Ln = Ho (**1**), Yb (**2**)) were obtained via hydrothermal reaction, and as building blocks, they were formally assembled into porous three-dimensional networks through the linkage of 1,4-naphthalenedicarboxylate (1,4-NDA), forming first examples of porous lanthanide polymers with 1,4-NDA, $[Ln_7(\mu_3\text{-}OH)_8(1{,}4\text{-}NDA)_6(OH)_{0.5}(Ac)_{0.5}(H_2O)_7]\cdot 4H_2O$ (Ln = Ho, Yb). The coordinating water molecules and lattice water molecules are enclathrated in the cavities.

High-nuclearity clusters are of great interest due to their novel structural characteristics and potential applications in magnetic, optical, electronic, and catalytic processes for their size-dependent physical properties.[1−5] The synthesis of the high-nuclearity clusters is still a great challenge. A common synthetic strategy is to control the hydrolysis of the salts of metal ions in the aid of supporting ligands.[6] Hydrophilic groups such as oxo, hydroxo, and carboxylate bridge the metal ion to make up a cluster core, while hydrophobic groups take up the positions in the periphery, preventing the core from further aggregation. In contrast to the well-established cluster chemistry of transition metals,[7] the analogous chemistry of lanthanides is less developed. Thus far, tetra-,[2,8] penta-,[9] hexa-,[8b,e,10] octa-,[11] nona-,[3] dodeca-,[8b,e] tetradeca-,[12] and pentadecanuclear[8b] lanthanide clusters have been obtained. But work about heptanuclear lanthanide clusters has not been reported yet. Gao[2] and Zheng[8e] et al. selected α-amino acid with dicarboxylate (L-aspartic acid and L-glutamic acid) as supporting ligand to bridge individual units containing the cubane-like $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cluster, and reported the first assembly of a discrete lanthanide cluster into a three-dimensional network via conventional solution reaction. In the present case, we obtained the first examples of heptanuclear lanthanide hydroxo clusters $[Ln_7(\mu_3\text{-}OH)_8]^{13+}$ via hydrothermal reaction, and we use it as a building block to form a 3-D framework through the linkage of a linear dicarboxylate 1,4-NDA.

A solution of $NaAc\cdot 3H_2O$ (0.04 g,0.3 mmol), $YbCl_3\cdot 6H_2O$ (0.039 g, 0.1 mmol), H_2O (10 mL), and aqueous NaOH (0.6 mL, 0.39 mmol) was stirred and precipitates were formed, then 1,4-naphthalenedicarboxylic acid (0.033 g, 0.15 mmol) was added. The mixture was sealed in a 25-mL stainless steel reactor with Teflon liner and heated at 120 °C for 72 h.

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Yellow crystals of **2**[13] were obtained in a yield of 0.018 g (44%). With the same method, crystals of **1**[14] were prepared in a yield of 0.02 g (50%). **1** and **2** are isomorphous. Therefore, only the structure of **2** was described in detail. The asymmetrical unit of **2** consists of a neutral heptanuclear $[Yb_7(\mu_3\text{-OH})_8(1,4\text{-NDA})_6(OH)_{0.5}(Ac)_{0.5}(H_2O)_7]$ (Figure 1) and four lattice water molecules. In the asymmetrical unit, seven Yb^{3+} ions are all eight-coordinate, but with markedly different coordination environments (Table 1), and the supporting ligand 1,4-NDA adopts three coordination modes: bis(bridging bidentate) (I), bis(chelating bidentate) (II), and bridging bidentate and chelating bidentate (III) in a ratio of 2:1:3. The terminal hydroxo and terminal acetate both coordinate to the Yb^{3+} ions in monodentate mode. The large neutral heptanuclear section has a heptanuclear $[Yb_7(\mu_3\text{-OH})_8]^{13+}$ core in which the metal skeleton can be regarded as two vertex-sharing tetrahedral tetranuclear units assembled via a metal ion Yb1. Yb1−Yb4 compose one tetrahedron with Yb···Yb distance in the range between 3.65 and 3.79 Å, and Yb1, Yb5−Yb7 make up the other with Yb···Yb distance in the range between 3.64 and 3.82 Å. Each triangular face of the tetrahedron is capped by one μ_3-OH group, so that the heptanuclear core is surrounded by eight μ_3-OH groups. The average distance of the μ_3-OH groups to the triangular metal faces is ca. 0.90 Å. In addition, besides the bridging of the μ_3-OH groups, seven 1,4-NDA ligands bridge Yb1 and Yb2, Yb2 and Yb3, Yb2 and Yb4, Yb1 and Yb5, Yb5 and Yb6, Yb5 and Yb7, Yb6 and Yb7, respectively with one of their carboxylate groups. Alternatively, the $[Yb_7(\mu_3\text{-OH})_8]^{13+}$ core displays a distorted vertex-sharing dicubane-like structure (Figure 2) in which the μ_3-OH groups are also considered as vertices of the polyhedron.

The cubane-like tetranuclear $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ unit is a common structural motif in lanthanide oxo−hydroxo clusters as demonstrated by the present work and others.[2,8c,e,f] The reported tetranuclear $[Dy_4(\mu_3\text{-OH})_4(asp)_3(H_2O)_8]^{2+}$,[2] dodecanuclear $[Er_{12}(\mu_3\text{-OH})_{16}(I)_2(\mu_3\text{-Tyr})_8(H_2O)_{20}]^{10+}$,[8b] and pentadecanuclear $[Gd_{15}(\mu_3\text{-OH})_{20}(\mu_5\text{-Cl})(\mu_3\text{-Tyr})_{10}(OH)(\mu_2\text{-H}_2O)_5(H_2O)_{19}]^{13+}$ [8b] can all be regarded as being composed of one or more $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ units. It can be deduced that, for a cyclic core composed of n vertex-sharing $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ cubanes, the nuclear number is $3n$ ($n \geq 3$), while for a chainlike core composed of n vertex-sharing $[Ln_4(\mu_3\text{-OH})_4]^{8+}$ cubanes, the nuclear number is $3n + 1$ ($n \geq 2$).

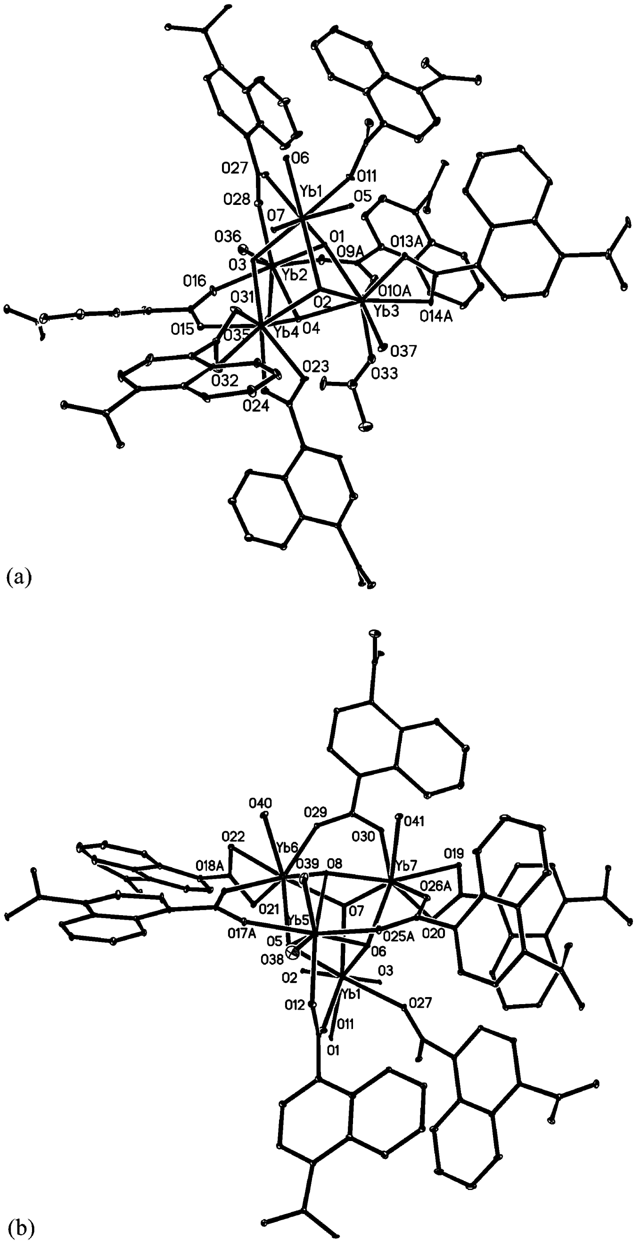

Figure 1. Coordination environment of the heptanuclear core in **2**: (a) Yb1−Yb4; (b) Yb1, Yb5−Yb7.

Table 1. The Coordination Environments of Yb^{3+} Ions in the Asymmetrical Unit of **2**

	no. of μ_3-OH	no. of carboxylate oxygen atoms			no. of H_2O	no. of OH or Ac
		I	II	III		
Yb1	6	2				
Yb2	3	2		1	2	
Yb3	3	1		2	1	1
Yb4	3		2	3		
Yb5	3	2		1	2	
Yb6	3		2	2	1	
Yb7	3	1		3	1	

Each 1,4-NDA ligand contributes one carboxylate group for the coordination of one $[Yb_7(\mu_3\text{-OH})_8]^{13+}$ cluster while

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[13] Crystal data for **2**: $[Yb_7(\mu_3\text{-OH})_8(1,4\text{-NDA})_6(OH)_{0.5}(Ac)_{0.5}(H_2O)_7]\cdot 4H_2O$, $C_{73}H_{68}O_{44.5}Yb_7$. $M_w = 2868.55$, monoclinic, space group $P2_1/n$, $a = 15.825(4)$ Å, $b = 23.261(6)$ Å, $c = 23.883(7)$ Å, $\beta = 91.142(5)°$, $V = 8789(4)$ Å^3, $Z = 4$, $D_c = 2.168$ g cm^{-3}, $F(000) = 5408$, μ(Mo Kα) = 7.465 mm^{-1}, $T = 293(2)$ K, final $R = 0.063$, $wR_2 = 0.1188$ for reflections ($I > 2\sigma(I)$), 44694 reflections collected, 15435 unique ($R_{int} = 0.1008$). Anal. Calcd for $C_{73}H_{68}O_{44.5}Yb_7$: C, 30.57; H, 2.39. Found: C, 30.79; H, 2.33%. IR data: ν/cm^{-1}: 3440s, 1599s, 1565s, 1515s, 1464s, 1420s, 1371s, 1264m, 841m, 787m, 585m.

[14] Crystal data for **1**: $[Ho_7(\mu_3\text{-OH})_8(1,4\text{-NDA})_6(OH)_{0.5}(Ac)_{0.5}(H_2O)_7]\cdot 4H_2O$, $C_{73}H_{68}Ho_7O_{44.5}$. $M_w = 2811.78$, monoclinic, space group $P2_1/n$, $a = 15.961(4)$ Å, $b = 23.415(6)$ Å, $c = 24.165(6)$ Å, $\beta = 91.832(5)°$, $V = 9027(4)$ Å^3, $Z = 4$, $D_c = 2.069$ g cm^{-3}, $F(000) = 5324$, μ(Mo Kα) = 6.152 mm^{-1}, $T = 293(2)$ K, final $R = 0.0619$, $wR_2 = 0.1303$ for reflections ($I > 2\sigma(I)$), 38149 reflections collected, 15845 unique ($R_{int} = 0.0899$). The structures of **1** and **2** were solved by direct methods due to Sheldrick and refined by full-matrix least squares on F^2 using SHELXL-97 (Sheldrick, G. M., University of Göttingen). Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. Anal. Calcd for $C_{73}H_{68}Ho_7O_{44.5}$: C, 31.18; H, 2.44. Found: C, 31.76; H, 2.14%. IR data: ν/cm^{-1}: 3443s, 1600s, 1561s, 1465s, 1421s, 1371s, 1267m, 849m, 787m.

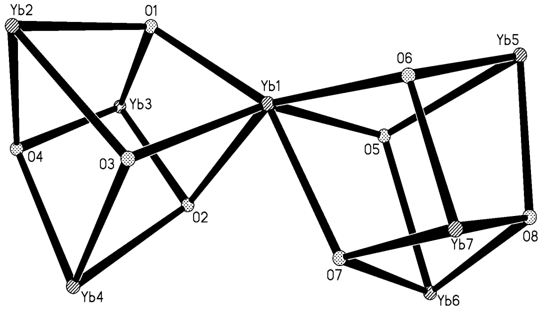

Figure 2. The vertex-sharing dicubane-like structure of $[Yb_7(\mu_3\text{-OH})_8]^{13+}$ in **2**.

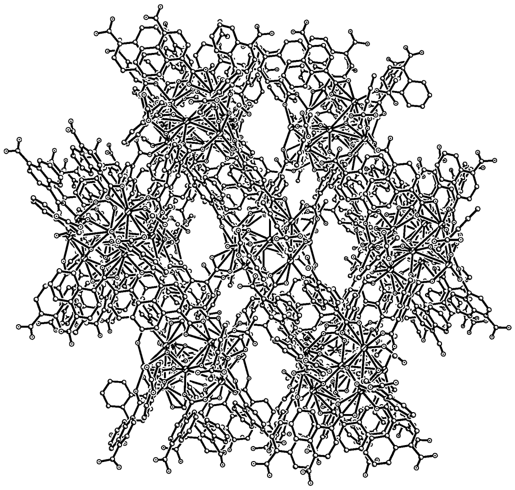

Figure 3. The 3-D open framework of **2** showing the cavities. All hydrogen atoms and water molecules were omitted.

using the remaining one to coordinate an adjacent lanthanide cluster cube. Around every heptanuclear cluster, there are twelve 1,4-NDA ligands which orientate in three directions: [110], [101], and $[1\bar{1}0]$. In every direction, there are four 1,4-NDA ligands linking three heptanuclear clusters. Thus every heptanuclear core is located in an octahedral center, surrounded by six other cores with the distance of the centers of the heptanuclear cores ranging from 12.7 to 15.6 Å. Every 2-connecting 1,4-NDA ligand links two heptanuclear cores. If every heptanuclear core is regarded as a point possessing a certain geometry, a 3-D open framework of α-Po-related topology[15] can be constructed. And the 3-D open framework exhibits many cavities (Figure 3).

Enclathrated in the cavities are coordinating water molecules and lattice water molecules which are hydrogen-bonded to the coordinating water molecules and coordinating carboxylate oxygen atoms.

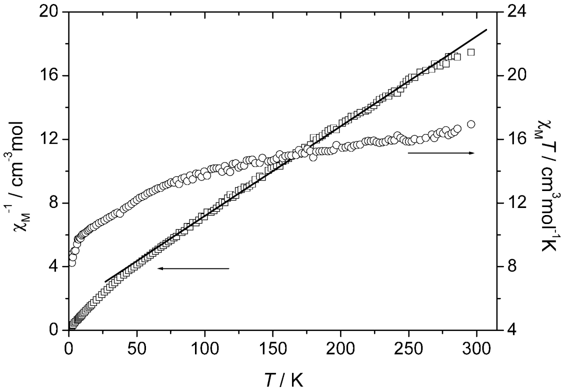

Figure 4. Plot of the temperature dependence of $\chi_M T$ (○) and χ_M^{-1} (□) for **2** (per $[Yb]_7$ unit).

The variable-temperature magnetic susceptibility of **2** was measured in the temperature range 2−300 K (Figure 4). The magnetic susceptibility above 50 K obeys the Curie−Weiss law $[\chi = C/(T - \theta)]$ with $C = 17.7(2)$ cm^3 K mol^{-1}, and $\theta = -27.3(4)$ K. The C value is very close to the expected value of 17.99 cm^3 K mol^{-1} for seven noninteracting Yb^{3+} free ions.[16] The continuous decrease in $\chi_M T$ upon cooling should be mainly attributed to the crystal field splitting of a single Yb^{3+} ion.

The thermal stability of **2** was investigated by thermogravimetric analysis. The first weight loss of 6.4% from 90 °C to 195 °C corresponds to the loss of seven coordinating water molecules and four lattice water molecules (calculated: 6.9%), leaving a framework of $[Yb_7(\mu_3\text{-OH})_8(1,4\text{-NDA})_6(OH)_{0.5}(Ac)_{0.5}]$. The framework begins to decompose at 433 °C and ends at 675 °C with the residue Yb_2O_3 obtained.

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Supporting Information Available: X-ray crystallographic files for complexes **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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