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Magnetic Properties of 3D Heptanuclear Lanthanide Frameworks Supported by Mixed Ligands

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Supporting Information

ABSTRACT: Two 3D lanthanide frameworks, $[Ln_7(DPA)_5(NA)_3(\mu_3\text{-}OH)_8(H_2O)_3]\cdot 2.5H_2O$ [H_2DPA = diphenic acid; HNA = nicotinic acid; Ln = Gd (**1**), Dy (**2**)], were synthesized and structurally characterized. They were rarely seen examples of 3D frameworks constructed from heptanuclear trigonal-antiprismatic lanthanide clusters with mixed H_2DPA and HNA ligands. Both **1** and **2** show typical antiferromagnetic interactions. Additionally, complex **1** possesses a large magnetocaloric effect of 34.15 J kg^{-1} K^{-1}.

Exploration of lanthanide clusters is one of the most important frontiers because of their charming and diverse structures as well as potential applications as molecular magnets[1] and imaging,[2] luminescence,[3] and catalysis.[4] As a result, a lot of pure lanthanide clusters, such as Ln_3−Ln_{10},[5] Ln_{12}−Ln_{15},[6] Ln_{20},[7] Ln_{22},[8] Ln_{24},[9] Ln_{36},[10] Ln_{38},[11] Ln_{48},[11,12] Ln_{60},[13] and Ln_{104},[14] have been documented. Recently, Yaghi et al. proposed that metal cluster units may self-assemble into coordination polymers,[15] which will bring about the particular characteristics of the clusters into the obtained frameworks. Up to now, many attempts have been made to introduce these polynuclear lanthanide clusters into the skeleton of polymer frameworks, but it is rarely realized.[16] The main reason may be that high-nuclearity lanthanide clusters either are prevented from further aggregation by big hydrophobic organic ligands or are surrounded by supporting ligands without further coordination sites. The mixed-ligand system may be an effective approach to constructing multidimensional lanthanide-based cluster frameworks because mixed organic ligands may extend the structure through their different coordination conformations or sites. At present, coordination polymers based on transition-metal clusters and mixed ligands have been well explored.[17] However, few lanthanide-based cluster frameworks have been obtained by mixed organic ligands.

On the basis of the above considerations, we selected two different ligands, diphenic acid (H_2DPA) and nicotinic acid (HNA), to build lanthanide-based cluster frameworks. Herein, we report two new 3D frameworks $[Ln_7(DPA)_5(NA)_3(\mu_3\text{-}OH)_8(H_2O)_3]\cdot 2.5H_2O$ [Ln = Gd (**1**), Dy (**2**)], which are rarely seen 3D heptanuclear lanthanide cluster frameworks linked by two kinds of organic ligands. Interestingly, complex **1** possesses a large MCE of 34.15 J kg^{-1} K^{-1}.

Pale-yellow crystals **1** and **2** can be obtained from the hydrothermal reaction of Ln_2O_3, HNA, and H_2DPA. Single-crystal X-ray diffraction analyses reveal **1** and **2** are isostructural and crystallize in the triclinic space group $P\bar{1}$. Thus, only the structure of **1** will be discussed in detail. The asymmetrical unit of **1** consists of a neutral heptanuclear $[Ln_7(DPA)_5(NA)_3(\mu_3\text{-}OH)_8(H_2O)_3]$ cluster and 2.5 lattice water molecules. The heptanuclear $[Gd_7(\mu_3\text{-}OH)_8]^{13+}$ core can be regarded as two vertex-sharing tetrahedra fused to each other through the Gd4 ion (Figure 1), which is similar to the reported Ln_7 cores.[16c] Gd1−Gd4 compose one tetrahedron with Gd···Gd separations in the range of 3.712−3.774 Å, and Gd4−Gd7 make up the other tetrahedron with Gd···Gd separations in the range of 3.663−3.848 Å. In **1**, it is possible to classify the Gd(III) ions into three types based on their coordination environments: (i) Gd5 in an O_7N coordination environment, (ii) Gd1, Gd3, Gd4, and Gd7 in an O_8 coordination environment, and (iii) Gd2 and Gd6 in an O_7 coordination environment. The Gd−N distance is 2.578(2) Å, and the Gd−O distances are in the range of 2.234(6)−2.575(9) Å, which are all in great agreement with the reported lengths.[18]

In the structure, the NA^- ligands present two types of coordination modes (IV and V), $\mu\text{-}\kappa^1OO'$ and $\mu_3\text{-}\kappa^1N,\kappa^1O,\kappa^1O'$, while the DPA^{2-} ligands present three types of coordination modes (I−III), $\mu_4\text{-}\kappa^1O,\kappa^1O',\kappa^1O'',\kappa^1O'''$, $\mu_3\text{-}\kappa^1O,\kappa^1O',\kappa^1O''O'''$, and $\mu_3\text{-}\kappa^1O,\kappa^1O'O'',\kappa^1O'''$ (Scheme S1 in the SI). It is noted that the DPA^{2-} ligands exhibit five different conformations and the dihedral angles between two benzene rings range from 51.239° to 79.382°.

Around every Gd_7 core, there are 10 extending ligands with three coordination modes, including eight DPA^{2-} (modes I and III) and two NA^- ligands (mode V). On the whole, the Gd_7 cores connect each other by these extending ligands with modes I, III, and V to produce a 3D framework, which is further stabilized by the DPA^{2-} ligands with modes II and III bonded to two tetrahedral units. Further analysis of the structure indicates the DPA^{2-} and NA^- ligands play different roles in the formation of the final structure. The DPA^{2-} ligands with modes I and III connect the Gd_7 clusters into a 2D layer (Figure 1). Then the extending NA^- ligands with mode V link these adjacent 2D layers to form the 3D framework. In contrast to previously reported Ln_7 cores,[16c,19] each Gd_7 core in **1** is surrounded by four other cores, and can be regarded as a four-

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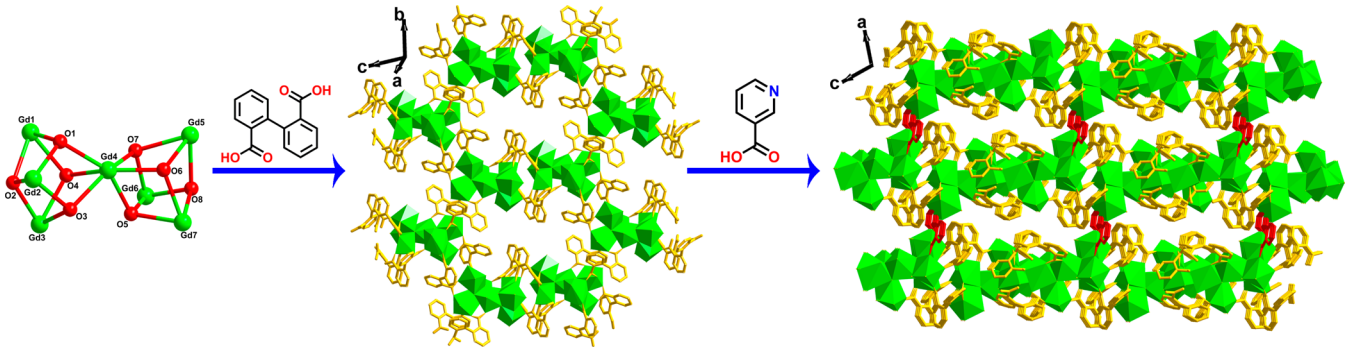

Figure 1. Views of the vertex-sharing dicubane cluster, the 2D layer, and the 3D structure of **1**.

connected node (Figure S2 in the SI). Thus, the framework can be described as a four-connected uninodal dia net (Figure S3 in the SI).

Variable-temperature magnetic susceptibilities for **1** and **2** were performed with polycrystal powders in the range of 2−300 K with an applied direct-current (dc) magnetic field of 1000 Oe (Figure 2). The $\chi_m T$ values of 54.99 cm^3 K mol^{-1} for

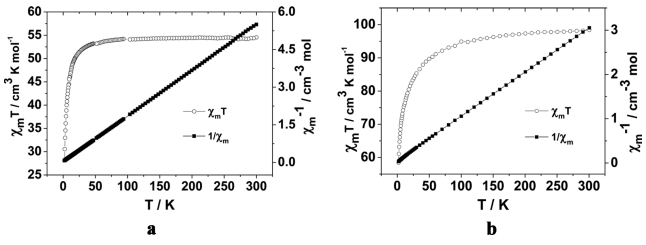

Figure 2. Plots of temperature-dependent $\chi_m T$ and $1/\chi_m$ under a 1000 Oe dc field between 2 and 300 K for **1** (a) and **2** (b).

1 and 98.39 cm^3 K mol^{-1} for **2** at 300 K are in close agreement with the expected values of 55.16 cm^3 K mol^{-1} for seven Gd(III) cations ($^8S_{7/2}$, $g = 2$) and 99.19 cm^3 K mol^{-1} for seven Dy(III) cations ($^6H_{15/2}$, $g = {}^4/_3$), respectively. For **1**, the $\chi_m T$ value slightly decreases with decreasing temperature to 50 K and then decreases quickly to 28.16 cm^3 K mol^{-1} at 2 K, thus suggesting the presence of dominant antiferromagnetic interactions between the Gd(III) cations. To estimate the intramolecular exchange constant, fitting the curve of $1/\chi_m$ versus T in the range of 50−300 K gives $C = 54.58$ cm^3 K mol^{-1} and $\theta = -0.89$K. For **2**, the $\chi_m T$ value decreases gradually from 300 to 50 K and then declines quickly upon further cooling to a minimum value of 58.42 cm^3 K mol^{-1} at 2 K. The decrease at low temperature may be due to a combination of intermolecular antiferromagnetic interactions and thermal population of the excited states of the Dy^{III} ions (Stark sublevels of the $^6H_{15/2}$ state).[10,20] Below 8 K, the field dependence of magnetization rises rapidly at low magnetic fields (Figure S5 in the SI). At higher fields, the magnetization increases without any sign of saturation to reach 44.41 μ_B around 8 T at 2 K. The nonsuperposition of the M versus H/T curves at different magnetic fields (Figure S6 in the SI) and the lack of saturation at high field suggest the presence of significant magnetic anisotropy and/or low-lying excited states.

Considering the low M_w/N_{Gd} ratio of 414.74, **1** is a good candidate for molecular refrigerants. To evaluate the MCE, we calculate the magnetic entropy change ΔS_m according to the Maxwell equation $\Delta S_m(T)_{\Delta H} = \int[\partial M(T, H)/\partial T]_H \, dH$. As shown in Figure 3a, the maximum of $-\Delta S_m$ for **1** is 34.15 J kg^{-1} K^{-1} at 2.5 K and $\Delta H = 7$ T. This value is smaller than that of 41.70 J kg^{-1} K^{-1} calculated for seven isolated Gd(III) spins using the equation $-\Delta S_m = nR \ln(2S + 1) = 7R \ln(8) = 14.6R$. However, this value is much higher than those observed in discrete Gd_7 cluster complexes, such as 23 J kg^{-1} K^{-1} at 3 K over 0−7 T for $[Gd_7(OH)_6(thmeH_2)_5(thmeH)(tpa)_6(MeCN)_2](NO_3)_2$ (M_w/N_{Gd} = 549.09)[5j] and 27.7 J kg^{-1} K^{-1} at 3 K over 0−7 T for $[Gd_7(L)_6(\mu_3\text{-}OH)_8(NO_3)_4(H_2O)]$ (M_w/N_{Gd} = 445.19),[21] but lower than 66.4 J kg^{-1} K^{-1} at $T = 1.8$ K and $\Delta H = 7$ T for the 3D framework $Gd(OH)CO_3$ (M_w/N_{Gd} ratio of 234.27).[22] Considering weak magnetic coupling between the Gd ions, the main reason may be ascribed to the M_w/N_{Gd} ratio.[1d] Usually, a lower M_w/N_{Gd} ratio, which means a higher Gd(III) density, leads to larger MCEs.

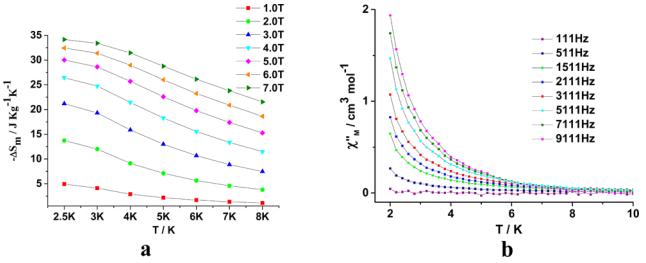

Figure 3. (a) $-\Delta S_m$ calculated from the magnetization data for **1** at various fields and temperatures. (b) Frequency dependence of the out-of-phase (χ'') ac susceptibility components for **2** at zero dc field.

For **2**, the dynamics of magnetization were also studied using alternating-current (ac) magnetic susceptibility measurements at a zero static field with an oscillation of 3.0 Oe from 111 to 9111 Hz, given in Figure 3b as a plot of χ''_M versus T. Interestingly, frequency-dependent out-of-phase signals are observed, indicating slow relaxation of magnetization.

In summary, two 3D heptanuclear lanthanide cluster-based frameworks have been successfully synthesized. The above results indicate that the mixed-ligand strategy may be an efficient approach to constructing multidimensional frameworks with high-nuclearity Ln(III) clusters. Additionally, the magnetic investigation shows **1** possesses a large MCE of 34.15 J kg^{-1} K^{-1} at 2.5 K and $\Delta H = 7$ T. Further investigations are now ongoing.

■ ASSOCIATED CONTENT

Supporting Information

Crystal data in CIF format, detailed experimental procedures, and additional figures and a table. The Supporting Information

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Notes

The authors declare no competing financial interest.

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