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An Unprecedented Decanuclear Gd^{III} Cluster for Magnetic Refrigeration

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Supporting Information

ABSTRACT: An unprecedented decanuclear Gd^{III} cluster composed of the $[Gd_{10}(\mu_3\text{-}OH)_8]^{22+}$ core has been hydrothermally synthesized. Magnetic analyses indicate that this complex shows weak antiferromagnetic behavior with a relatively large magnetocaloric effect ($-\Delta S_m^{max}$ = 31.22 J kg^{-1} K^{-1}).

Because of the possibility of replacing the expensive and increasingly rare He-3 in ultralow-temperature refrigeration, considerable interest has been focused on the study of the magnetocaloric effect (MCE).[1] As a new type of material applied in energy-efficient and environmentally friendly cryogenic refrigerators, molecule-based magnetic coolers are compact and increase more focus.[2] Generally, a large-spin ground state (S), negligible magnetic anisotropy ($D_{cluster}$ = 0), low-lying excited spin states, weak exchange interaction, and a relatively large metal/nonmetal mass ratio could result in a large MCE of a molecule.[1a,3] In this regard, Gd^{III} cluster complexes without long-range order are promising candidates.[4] On the one hand, the magnetic interaction between Gd^{III} ions is expected to be very weak because of the shielding of the f orbitals and the consequent poor overlap with bridging ligand orbitals.[5] On the other hand, a large S of an isotropic Gd^{III} ion provides the largest entropy per single ion.[6] Therefore, investigating Gd^{III} clusters constructed by relatively small ligands has witnessed flourishing development for their potential application as molecule-based magnetic coolers.[3,4] Various structures of discrete Gd clusters have been reported;[7] nevertheless, the investigations about the MCE of pure high-nuclearity Gd clusters have rarely been reported so far, mostly because certain challenges still remain in the synthesis of such metal clusters.[4,7]

It is known that many methods such as in situ and template synthesis are being explored in the quest for high-nuclearity Gd^{III} clusters.[8] Especially, hydroxyl, carbonate, and other short bridging groups are usually introduced in situ by the addition of alkaline reactants or the decomposition of ligands and solvents.[9] Aromatic monocarboxylate ligands with steric effect could chelate and bridge Gd^{III} ions to form low-dimensional Gd-containing structures, even facilitating the high-nuclearity Gd^{III} cluster formation.[10] Thiophene-3-carboxylic acid (3-TCA) is typically an aromatic monocarboxylic acid that has been exploited in the formation of various low-dimensional complexes because of the carboxylate group with various coordination modes. However, 3-TCA has rarely been used in constructing multinuclear complexes, especially for the lanthanide type.[11] Moreover, Gd^{III} complexes were traditionally constructed with Gd^{III} salts or gadolinium hydroxide as the metal-ion source, while only a few using Gd_2O_3 under hydrothermal conditions were reported.[12] Additionally, the use of Gd_2O_3 in water provides the possibility of the introduction of a hydroxyl group.[13]

Herein we report the synthesis, structure, and magnetic properties of an unusual Gd$_{10}$ cluster, $[Gd_{10}(3\text{-TCA})_{22}(\mu_3\text{-}OH)_8(H_2O)_4]$ (**1**). Colorless crystals of **1** were obtained by the hydrothermal reaction of Gd_2O_3 and 3-TCA at 160 °C. Indeed, our results show that hydroxyl groups were generated in situ to take part in the formation of the Gd$_{10}$ cluster, which may be ascribed to the existence of Gd_2O_3 in the acidic system. Notably, Gd_2O_3 may serve as both a slow-release Gd^{III} ion source and a pH regulator of the reaction system.[14]

Crystallographic studies reveal that complex **1** crystallizes in a triclinic system with space group $P\bar{1}$. The asymmetric unit of **1** consists of 5 Gd^{III} ions, 11 3-TCA ligands, 4 μ_3-OH groups, and 2 coordinated water molecules (Figure 1a). The range of Gd−O bond lengths is 2.307(3)−2.861(3) Å, and O−Gd−O angles fall into the range of 48.68(8)−166.61(19)° (Table S3, Supporting Information, SI). Gd1, Gd3, and Gd5 are located in the eight-coordinated environments with different O atoms from 3-TCA, μ_3-OH, and water molecules (four μ_3-OH and four carboxylate O atoms for Gd1, one μ_3-OH, one water, and six carboxylate O atoms for Gd3 and Gd5). Gd2 shows a nine-coordinated environment and is surrounded by six carboxylate O atoms from five different 3-TCA ligands and three O atoms from μ_3-OH anions. The Gd4 center exhibits a seven-coordinated environment with three μ_3-OH anions and four carboxylate O atoms from four 3-TCA ligands (Figure S1, SI). In the asymmetric unit, three μ_3-OH anions bridge five Gd^{III} ions to form three different triangles. Then in the middle, the same two triangles bridged by two μ_3-OH connect two asymmetric units to form a $[Gd_{10}(\mu_3\text{-}OH)_8]^{22+}$ core (Figure 1c). Thus, eight μ_3-OH groups generated in situ take a key role in the construction of a $[Gd_{10}(\mu_3\text{-}OH)_8]^{22+}$ core. Further, the 3-TCA ligands chelate and bridge Gd^{III} ions of

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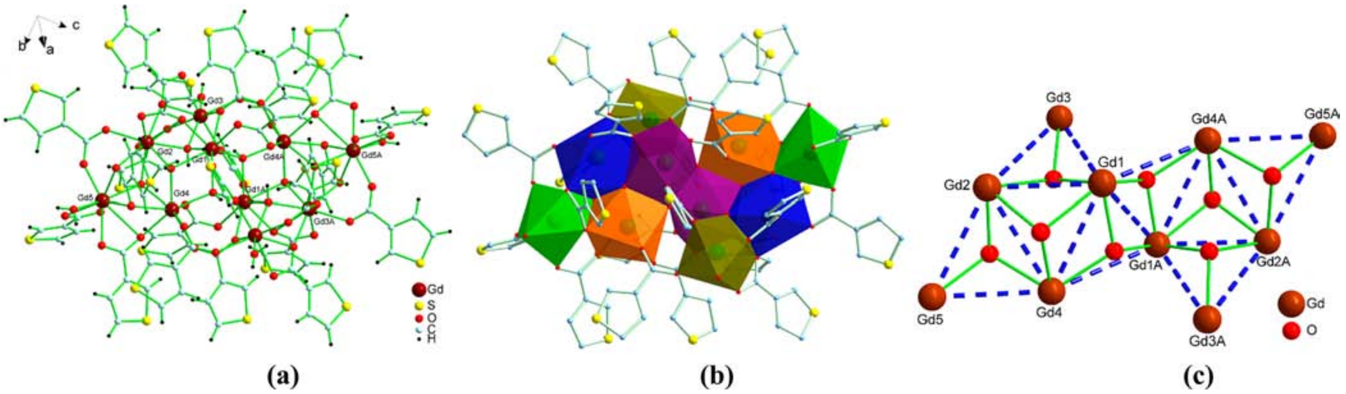

Figure 1. (a) Ball-and-stick view of the molecular structure of **1** (symmetry code: A, $-x + 2$, $-y + 1$, $-z + 1$). (b) Polyhedral view of the structure (H atoms omitted for clarity). (c) Different triangles constructed from the μ_3-OH groups in the $[Gd_{10}(\mu_3\text{-OH})_8]^{22+}$ core.

a Gd_{10} core to facilitate the formation of a Gd_{10} cluster (Figures 1a,b and S2a in the SI). The 3D packing structure (Figure S2b, SI) along the *b* direction indicates the existence of the weak intermolecular C−H···O hydrogen bonds because of short distances. Very interestingly, 3-TCA exhibits five different coordination modes in **1**, which is rare in the known complexes constructed by monocarboxylate ligands and feasible to construct much more complicated and fantastic frameworks with interesting properties (Scheme S1, SI).

All of the magnetic measurements were carried out on a crystalline sample, and its phase purity was confirmed by powder X-ray diffraction (see Figure S3, SI). Complex **1** contains $Gd^{III}(f^7)$ with a ground state $^8S_{7/2}$ and the first excited state $^6P_{7/2}$. The temperature-dependent magnetic susceptibility of **1** was investigated in the range of 2.0−300 K with a 1 kOe applied field (Figure 2). The $\chi_M T$ product of **1** at 300 K is 77.38 emu mol^{-1} K^{-1}, which is consistent with the expected value (7.88 emu mol^{-1} K^{-1} per Gd^{III} ion for $S = 7/2$ and $g = 2.0$). With decreasing temperature, the $\chi_M T$ value decreases slowly and reaches 75.23 emu mol^{-1} K^{-1} at 100 K, after which it drops abruptly to a minimum value of 52.01 emu mol^{-1} K^{-1} at 2.0 K. This plot is indicative of the occurrence of a weak antiferromagnetic (AF) interaction between the Gd^{III} ions. The temperature dependence of molar susceptibility in the temperature range 2.0−300 K is well fitted by the Curie−Weiss law with $C = 76.80$ emu mol^{-1} K^{-1} and $\theta = -1.78$ K, which further indicates weak AF coupling between Gd^{III} ions. The magnetization tends to a value of 66.72 $N\beta$ at 70 kOe and 2.0 K, and the experimental magnetization curve is below the red line that presents the Brillouin function for 10 magnetically uncoupled Gd^{III} ions with $S = {}^7/_2$ and $g = 2.0$, confirming again the weak AF coupling between the Gd^{III} ions in **1** (see Figure S4, SI).

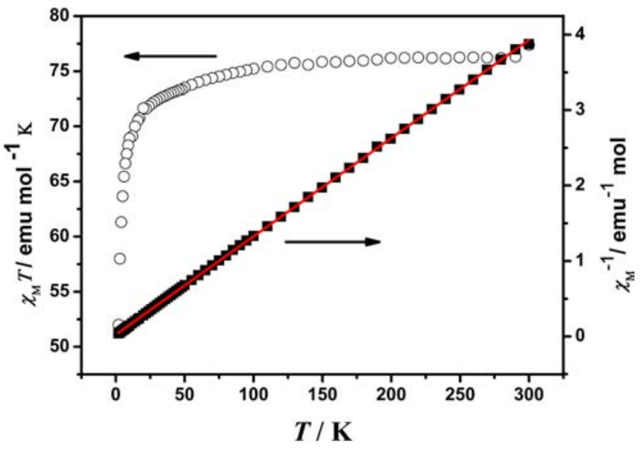

Figure 2. Plots of $\chi_M T$ vs T (○) and χ_M^{-1} vs T (■) (red part for the Curie−Weiss fitting) for **1**.

As shown in Figure S5 (SI), the field-cooled curve is consistent with the zero-field-cooled curve, and the magnetizations increase continuously with decreasing temperature; no maximum is observed. These observations indicate that **1** does not exhibit a magnetic ordering above 2.0 K. Then we explored the magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} as two key parameters in evaluating MCE on the Gd_{10} cluster, given the weak $Gd^{III}\cdots Gd^{III}$ magnetic coupling and relatively low M_W/N_{Gd} ratio. Therefore, isothermal magnetization in the range T = 2.0−10 K and H = 5−70 kG and temperature-dependent heat capacity measurements in the range T = 2.0−100 K and H = 0−70 kG were performed. According to the Maxwell relation $\int[\partial M(T,H)/\partial T]_H\, dH$,[15] we can obtain the $-\Delta S_m$ of **1** from the experimental magnetization data (Figure S6, SI), and the curves of $-\Delta S_m$ are depicted in Figure 3. It can be seen that the $-\Delta S_m$ value increases gradually with increasing ΔH and decreasing temperature, reaching a maximum of 31.22 J kg^{-1} K^{-1} for ΔH = 70 kG at 2.0 K, which is equivalent to 68.84 mJ cm^{-3} K^{-1} if it is given per unit of volume. The magnetic entropy change of the Gd_{10} cluster is relatively larger than those of most reported Gd^{III}-containing complexes but lower than the expected value [37.77 J

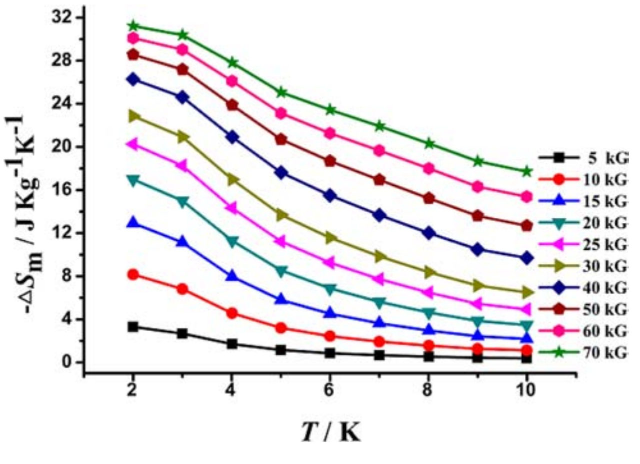

Figure 3. Experimental $-\Delta S_m$ obtained from magnetization data of **1** at different fields and temperatures.

$\mathrm{kg}^{-1}\,\mathrm{K}^{-1}$ calculated with $10R\ln(2S+1)$] because in this system a significant splitting of the low-lying spin levels is expected because of the AF exchange (see Table S1, SI).

The results normalized to R of temperature-dependent heat capacity (C) are presented in Figure S7a (SI). At high temperatures, the constant increase of experimental C indicates the domination of the lattice contribution resulting from thermal vibration, which can be modeled with the low-temperature Debye function (dotted lines) with the Debye temperature θ_D = 200(3) K, typical for this class of complexes.[16] At lower temperatures, C is dominated by an applied-field-sensitive magnetic contribution. Further, the corresponding magnetic entropy $S_m(T)$ (Figure S7b, SI) can be obtained using the following equation, where the contribution from an even lower temperature region is derived from the saturation of S_m at higher temperature:[2,3]

$$S_m(T) = \int_0^T C_m(T)/T \, dT$$

As shown in Figure 4, the $-\Delta S_m$ values obtained from the C data and those calculated from the magnetization data basically have an agreement. This remarkable field dependence of the MCE is also observed in ΔT_{ad}, and Figure S8 (SI) shows that ΔH = 7 T provides a maximum ΔT_{ad} = 8.68 K for 2.0 K, falling among the largest values known to date (Table S1, SI). In addition, the refrigerant capacity [$\mathrm{RC} = \Delta S_m(T_h - T_c)$][17] approach is adopted to give the RC value of about 136 J kg^{-1} for ΔH = 7 T.

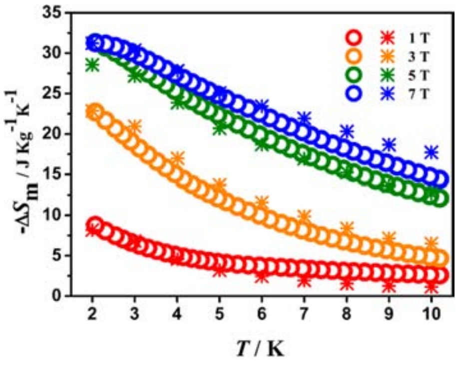

Figure 4. Temperature dependencies of $-\Delta S_m$ obtained from C (○) and magnetization (*) at various fields.

In conclusion, by employing Gd_2O_3 as the Gd^{III} ion source, an unprecedented decanuclear Gd^{III} cluster composed of a $[Gd_{10}(\mu_3\text{-}OH)_8]^{22+}$ core has been successfully obtained in which the 3-TCA ligand exhibits five different coordination modes. The in situ synthetic approach may be applicable to the assembly of other related high-nuclearity Gd^{III} clusters. Magnetic measurements indicate that **1** exhibits weak AF behavior and a large MCE ($-\Delta S_m^{max}$ = 31.22 J kg^{-1} K^{-1} and ΔT_{ad} = 8.68 K for ΔH = 7 T and T = 2.0 K). These results spur us to obtain Gd^{III} complexes with larger MCE because of their great potential for magnetic cooling.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic details (CIF), experimental section, supplementary tables, structural figures and scheme, and additional characterizations. 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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