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An Unprecedented Decanuclear Gd^{III} Cluster for Magnetic RefrigerationSui-Jun Liu,[†] Jiong-Peng Zhao,[†] Jun Tao,[‡] Ji-Min Jia,[†] Song-De Han,[†] Yue Li,[†] Yan-Cong Chen,[§] and Xian-He Bu^{*,†}[†]Department of Chemistry, TKL of Metal- and Molecule-Based Material Chemistry and Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China[‡]College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China[§]School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

S Supporting Information

ABSTRACT: An unprecedented decanuclear Gd^{III} cluster composed of the [Gd₁₀(μ₃-OH)₈]²²⁺ core has been hydrothermally synthesized. Magnetic analyses indicate that this complex shows weak antiferromagnetic behavior with a relatively large magnetocaloric effect ($-\Delta S_m^{\max} = 31.22 \text{ J kg}^{-1} \text{ K}^{-1}$).

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 ($D_{\text{cluster}} = 0$), 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 Gd₂O₃ under hydrothermal conditions were reported.¹² Additionally, the use of Gd₂O₃ 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 Gd₁₀ cluster, [Gd₁₀(3-TCA)₂₂(μ₃-OH)₈(H₂O)₄] (1). Colorless crystals of 1 were obtained by the hydrothermal reaction of Gd₂O₃ 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 Gd₁₀ cluster, which may be ascribed to the existence of Gd₂O₃ in the acidic system. Notably, Gd₂O₃ 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 μ₃-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, μ₃-OH, and water molecules (four μ₃-OH and four carboxylate O atoms for Gd1, one μ₃-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 μ₃-OH anions. The Gd4 center exhibits a seven-coordinated environment with three μ₃-OH anions and four carboxylate O atoms from four 3-TCA ligands (Figure S1, SI). In the asymmetric unit, three μ₃-OH anions bridge five Gd^{III} ions to form three different triangles. Then in the middle, the same two triangles bridged by two μ₃-OH connect two asymmetric units to form a [Gd₁₀(μ₃-OH)₈]²²⁺ core (Figure 1c). Thus, eight μ₃-OH groups generated in situ take a key role in the construction of a [Gd₁₀(μ₃-OH)₈]²²⁺ core. Further, the 3-TCA ligands chelate and bridge Gd^{III} ions of

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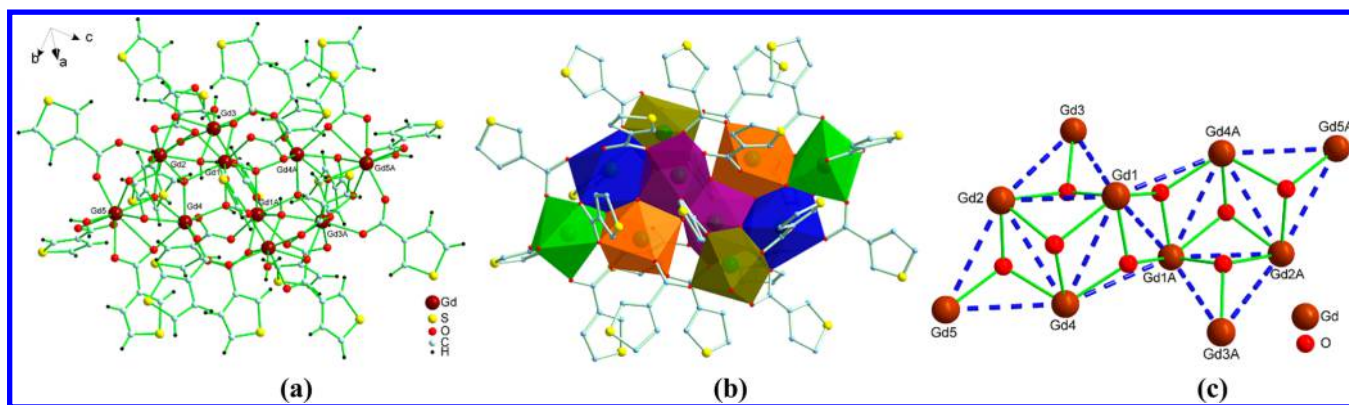


Figure 1. (a) Ball-and-stick view of the molecular structure of **1** (symmetry code: A, $-x + 2, -y + 1, -z + 1$). (b) Polyhedral view of the structure (H atoms omitted for clarity). (c) Different triangles constructed from the μ_3 -OH groups in the $[\text{Gd}_{10}(\mu_3\text{-OH})_8]^{22+}$ core.

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 \cdots 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 $\text{Gd}^{\text{III}}(f^7)$ 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 $\chi_{\text{M}}T$ product of **1** at 300 K is $77.38 \text{ emu mol}^{-1}$

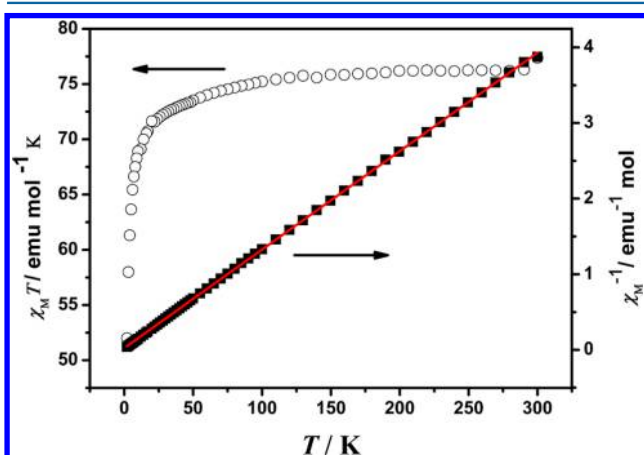


Figure 2. Plots of $\chi_{\text{M}}T$ vs T (○) and χ_{M}^{-1} vs T (■) (red part for the Curie–Weiss fitting) for **1**.

K^{-1} , which is consistent with the expected value ($7.88 \text{ emu mol}^{-1} \text{K}^{-1}$ per Gd^{III} ion for $S = 7/2$ and $g = 2.0$). With decreasing temperature, the $\chi_{\text{M}}T$ value decreases slowly and reaches $75.23 \text{ emu mol}^{-1} \text{K}^{-1}$ at 100 K, after which it drops abruptly to a minimum value of $52.01 \text{ emu mol}^{-1} \text{K}^{-1}$ 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 $C = 76.80 \text{ emu mol}^{-1} \text{K}^{-1}$ and $\theta = -1.78 \text{ K}$, which further indicates weak AF coupling

between Gd^{III} ions. The magnetization tends to a value of $66.72 \text{ N}\beta$ 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).

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 $\text{Gd}^{\text{III}}\cdots\text{Gd}^{\text{III}}$ magnetic coupling and relatively low $M_{\text{W}}/N_{\text{Gd}}$ ratio. Therefore, isothermal magnetization in the range $T = 2.0\text{--}10 \text{ K}$ and $H = 5\text{--}70 \text{ kG}$ and temperature-dependent heat capacity measurements in the range $T = 2.0\text{--}100 \text{ K}$ and $H = 0\text{--}70 \text{ kG}$ were performed. According to the Maxwell relation $\int [\partial M(T, H) / \partial T]_{\text{H}} dH$,¹⁵ we can obtain the $-\Delta S_{\text{m}}$ of **1** from the experimental magnetization data (Figure S6, SI), and the curves of $-\Delta S_{\text{m}}$ are depicted in Figure 3. It can be seen that the $-\Delta S_{\text{m}}$ value increases gradually with increasing ΔH and decreasing temperature, reaching a maximum of $31.22 \text{ J kg}^{-1} \text{K}^{-1}$ for $\Delta H = 70 \text{ kG}$ at 2.0 K, which is equivalent to $68.84 \text{ mJ cm}^{-3} \text{K}^{-1}$ 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

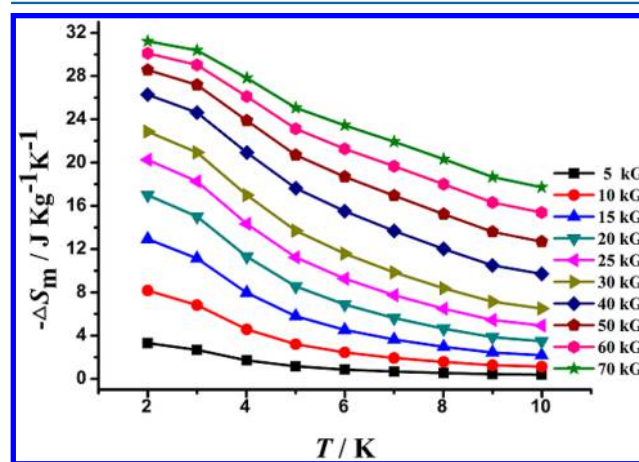


Figure 3. Experimental $-\Delta S_{\text{m}}$ obtained from magnetization data of **1** at different fields and temperatures.

$\text{kg}^{-1} \text{K}^{-1}$ 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 $\theta_D = 200(3)$ 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

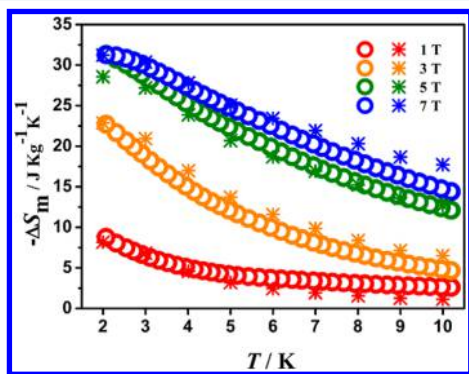


Figure 4. Temperature dependencies of $-\Delta S_m$ obtained from C (○) and magnetization (*) at various fields.

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

In conclusion, by employing Gd_2O_3 as the Gd^{III} ion source, an unprecedented decanuclear Gd^{III} cluster composed of a $[\text{Gd}_{10}(\mu_3\text{-OH})_8]^{22+}$ 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 ($-\Delta S_m^{\text{max}} = 31.22 \text{ J kg}^{-1} \text{K}^{-1}$ and $\Delta T_{ad} = 8.68$ K for $\Delta H = 7$ 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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