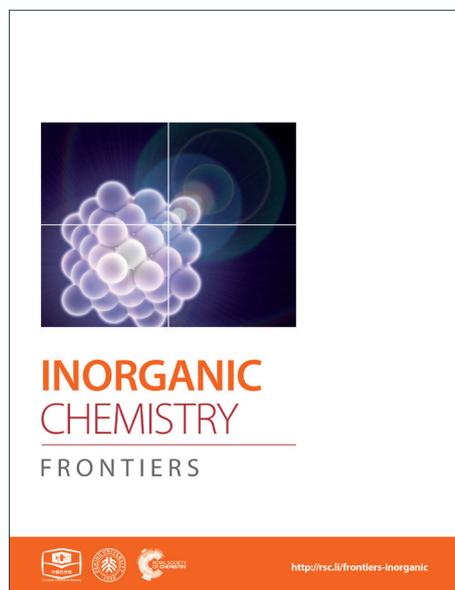
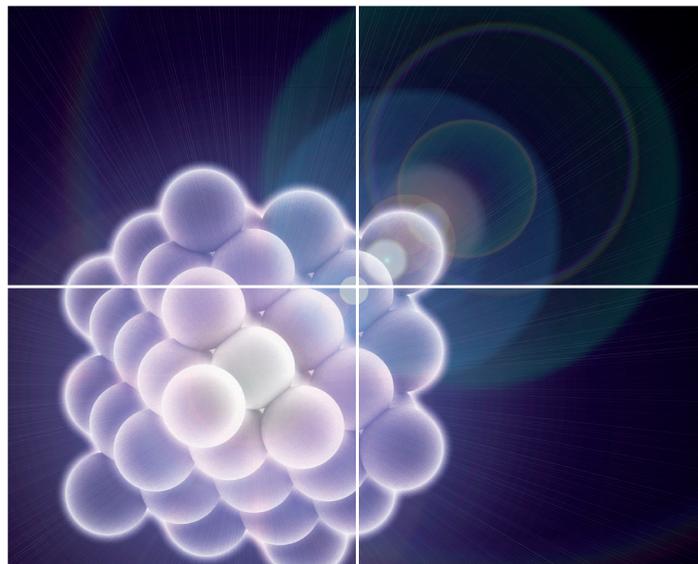


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COMMUNICATION

Magnetocaloric Effect and Slow Magnetic Relaxation in Two Dense (3,12)-connected Lanthanide Complexes

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Two (3,12)-connected complexes with distorted cubic [Ln₄O₄] (Ln = Gd (1), Dy (2)) as building units were synthesized. The magnetic studies reveal that 1 features a large magnetocaloric effect with $-\Delta S_m^{\max} = 51.29 \text{ J kg}^{-1} \text{ K}^{-1}$, and 2 displays slow magnetic relaxation behavior.

Magnetocaloric effect (MCE) defined as the changes of the isothermal magnetic entropy (ΔS_m) and adiabatic temperature (ΔT_{ad}) of a magnetic material induced by a change in the applied magnetic field (ΔH), was first discovered in 1881 by Warburg.¹ Magnetic refrigeration based on MCE, has received much recent interest due to the possibility of replacing the expensive and increasingly rare He-3 in ultralow-temperature refrigeration.² Since observations of the MCE in Mn₁₂ and Fe₈ molecular clusters opened the door to molecular magnetic cryogenic materials, this fascinating field has attracted huge attention of chemists and been rapidly expanding, stemming from not only their high-efficient, environmentally friendly, and energy-saving superiority, but also their synthetic tunability and functional tailorability.^{3–8}

To design molecular magnetic coolers with remarkable MCE, Gd^{III} with seven unpaired 4*f* electrons is a promising candidate for the intrinsic nature of Gd^{III} fulfils the requirements of improving MCEs well, such as a large spin ground state *S*, negligible magnetic anisotropy ($D_{ion} = 0$) and low-lying excited spin states.⁴ Furthermore, due to the efficient shielding of the 4*f* orbitals of the Gd^{III} ion, the magnetic interactions of Gd^{III}-Gd^{III}/3*d*-Gd^{III} are usually anticipated to be weak, which is also helpful to prompt the MCE. Hence, the assembly of Gd^{III}/3*d*-Gd^{III} with light or polydentate ligands is a feasible strategy to the aforementioned target, which has been well corroborated in recent publications.^{5,6} To our knowledge, most of the reported Gd-based complexes with significant MCE are discrete [Gd_n]^{4a,5} and [3*d*-Gd]⁶ (3*d* = Cr, Mn, Fe, Co, Ni, Cu) clusters and few cases are low dimensional Gd-based coordination polymers.^{4a,7} Research of MCE on 3D coordinations polymers is still rare.⁸ The potential advantages of 3D framework not only lie in that the adjacent metal ions/metal clusters share the bridging ligands among them, which can enhance the magnetic density and result in large MCE, but also their relatively higher thermal and/or solvent stabilities than discrete molecule clusters, which provides a solid

foundation for future applications.^{3e,f,8b,c} However, to date, most of the reported Gd-based complexes with significant MCE from 0D discrete cluster to 3D framework are constructed via organic ligands,^{5,6} and cases fabricated by inorganic ligands are very rare.^{8c,i} In fact, some inorganic ligands like sulfate, phosphate, carbonate are also polydentate. For example, the tetradentate sulfate with rich coordination modes is preferable to bond to lanthanide ions, which has been widely utilized to synthesize metal–organic frameworks (MOFs).⁹ Moreover, weak exchange interactions and relatively high density may be expected in Gd-containing complexes bridged by sulfate.^{9b,10} Both of these characteristics are helpful to enhance the performance in MCE, which could be well demonstrated by the early studied molecular magnetic cooler [Gd₂(SO₄)₃·8H₂O].¹¹

On the other hand, Dy clusters are being well explored in single-molecule magnets (SMMs) due to the large single-ion magnetic anisotropy of Dy^{III}. Hitherto, various [Dy_n] clusters with slow magnetic relaxation behavior have been reported, including Dy₂,^{12a} Dy₃,^{12b} Dy₄,^{12c} Dy₅,^{12d} Dy₆,^{12e} Dy₇,^{12f} Dy₈,^{12g} Dy₉,^{12h} Dy₁₀,¹²ⁱ Dy₁₁,^{12j} Dy₁₂,^{12k} Dy₁₄,^{12l} Dy₂₄.^{5b} However, the observations of such behavior in 2D or 3D complexes utilizing Dy clusters as nodes are remain scarce.^{8c,13} Therefore, it is interesting and worth to investigate the magnetic properties of high dimensional complexes based on Dy

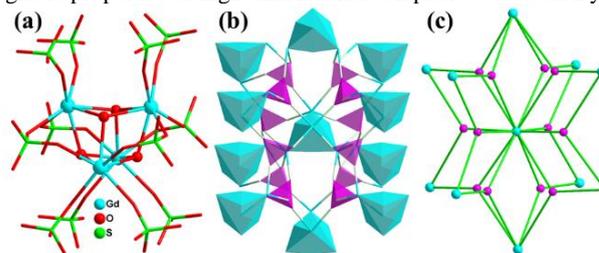


Fig. 1 (a) The structure of [Gd₄(OH)₄]⁸⁺ units coordinated by twelve SO₄²⁻, all H atoms were omitted for clarity. (b) 3-connected SO₄²⁻ (purple polyhedrons) and 12-connected [Gd₄] clusters (blue polyhedrons). (c) The binodal (3,12)-connected topology of **1**.

clusters as nodes.

Herein, we report the synthesis, structures, and magnetic properties of two (3,12)-connected sulfate-based lanthanide complexes $[\text{Ln}_4(\text{SO}_4)_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_n]$ ($\text{Ln} = \text{Gd}$, $n = 4$ for **1**, and $\text{Ln} = \text{Dy}$, $n = 3$ for **2**). Magnetic measurements exhibit that complex **1** displays a magnetic entropy change $-\Delta S_m^{\text{max}} = 51.29 \text{ J kg}^{-1} \text{ K}^{-1}$, being the third largest value to date, and simultaneously presents high solvent stabilities. Complex **2** exhibits slow magnetic relaxation behavior at low temperature, which is rare in 2D or 3D complexes based on Dy clusters as nodes. Colorless crystals of **1** and **2** were obtained by the solvothermal reaction of Hbms HCl (Hbms = (1*H*-benzimidazol-2-yl)methanethiol), and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in a $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixed solvent at 140°C . It is notable that the sulfate are generated *in situ* due to the oxidation of thiol under acid conditions in the presence of NO_3^- . The *in situ* transformation of thiol to sulfate have been documented in a recent publication.¹⁴ The SO_4^{2-} in **1** and **2** can also be undisputedly demonstrated by the IR characteristic peaks at about 1100 cm^{-1} (Fig. S12†).

Two similar complexes ($\text{Ln} = \text{Y}$, Er) with differences only in terminal ligands of Gd^{III} ions for **1** have been previously reported.¹⁵ Therefore, the structure of **1** is discussed briefly here. Complex **1** crystallizes in the orthorhombic space group $P2_12_12_1$ and contains hydroxyl bridged tetranuclear units $[\text{Gd}_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_4]^{8+}$ ($[\text{Gd}_4]$, for short), which are further connected via SO_4^{2-} ligands to generate a 3D framework. Each Gd^{III} connects three neighboring Gd^{III} ions with four $\mu_3\text{-OH}$ bridging ligands, forming a distorted cubic $[\text{Gd}_4]$ unit, in which four Gd^{III} ions are located at the corners of the tetrahedron. Each SO_4^{2-} bridges three $[\text{Gd}_4]$ units, and each $[\text{Gd}_4]$ unit links twelve SO_4^{2-} groups (Fig. 1a and 1b†). Thus the SO_4^{2-} and $[\text{Gd}_4]$ cluster can be considered as 3-connected and 12-connected nodes, respectively, giving rise to a unique (3,12)-connected topological network with the point (Schläfli) symbol of $(4^{20} 6^{28} 8^{18})(4^3)_4$ calculated by TOPOS (Fig. 1c†).¹⁶ To our knowledge, several (3,12)-connected frameworks have been reported, while only four examples are based on multi-nuclear lanthanide clusters.^{8c,14,17}

Both **1** and **2** are stable in air, confirmed by their stimulated and experimental PXRD (powder X-ray diffraction) patterns (Fig. S1†). Importantly, the simulated PXRD pattern of **1** from single crystal data reaches good agreement with the corresponding experimental ones after being soaked in common solvents, such as H_2O , CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CN , CH_2Cl_2 , acetone, DMF, tetrahydrofuran, and cyclohexane solution for 48 hours (Fig. S1†), which notably manifests that **1** possesses excellent and extensive solvent stability.

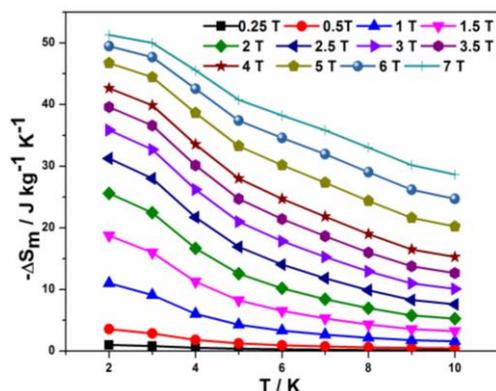


Fig. 2 $-\Delta S_m$ calculated by using the magnetization data of **1** at different fields and temperatures.

The phase purity of complexes **1** and **2** was confirmed by PXRD patterns (Fig. S1 and S2†). Variable-temperature magnetic susceptibility measurements were investigated on polycrystalline samples of complexes **1** and **2** with an applied dc field of 1000 Oe (Fig. S3†). The observed $\chi_M T$ products of 31.61 and $55.73 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K for **1** and **2** are in good agreement with the theoretical values for the unit of four non-interacted Gd^{III} ($31.50 \text{ cm}^3 \text{ K mol}^{-1}$, $^8S_{7/2}$, $g = 2$) in **1** and four isolated Dy^{III} ($56.67 \text{ cm}^3 \text{ K mol}^{-1}$, $^6H_{15/2}$, $g = 4/3$) in **2**. Upon cooling, the $\chi_M T$ value of **1** stays essentially constant until approximately 25 K, while the $\chi_M T$ value of **2** gradually decreases from 300 K to 50 K, followed by an obvious decrease to the minimum value of $19.74 \text{ cm}^3 \text{ K mol}^{-1}$ for **1** and $38.88 \text{ cm}^3 \text{ K mol}^{-1}$ for **2** at 2 K. The decline of the curve for **1** indicates that antiferromagnetic coupling exists between adjacent Gd^{III} ions, which is further corroborated by the negative Weiss constant $\theta = -1.57 \text{ K}$ from Curie–Weiss fitting (Fig. S4†).

Magnetization measurements were investigated in the range of 0–7 T at 2–10 K for **1** and 0–7 T at 2 K for **2** (Fig. S5 and S6†). The plots of M versus H display a steady increase with the increasing field. For **1**, the M reaches a value of $28.30 \text{ N}\beta$ at 2 K and 7 T, which agrees with the theoretical value of $28 \text{ N}\beta$ for four Gd^{III} ($g = 2$, $S = 7/2$). For **2**, the M value is $25.20 \text{ N}\beta$ at 2 K and 7 T, far from the theoretical saturated value of $40 \text{ N}\beta$ for four Dy^{III} ($g = 4/3$, $J = 15/2$). The magnetic unsaturation even at 7 T may be attributed to the magnetic anisotropy and/or low-lying excited states of Dy^{III} , which was supported by the non-superposition of magnetization curves at different temperatures (Fig. S7†). The beautiful superposition of the field-cooled (FC) curve and the zero-field-cooled (ZFC) curve preclude the existence of long-range magnetic ordering above 2 K in **1** (Fig. S8†).

The weak magnetic interactions and large metal/ligand mass ratio make complex **1** as promising candidate for low-temperature magnetic cooling, as magnetic entropy change ΔS_m , a key parameter in evaluating the MCE, can be derived by applying the Maxwell equation $\Delta S_m(T)_{\Delta H} = \int [\partial M(T, H) / \partial T]_H dH$ to the experimentally obtained magnetization data.^{5–8} The entropy changes at various magnetic fields and temperatures are summarized in Fig. 2, with an impressive $-\Delta S_m^{\text{max}} = 51.29 \text{ J kg}^{-1} \text{ K}^{-1}$ for $T = 2 \text{ K}$ and $\Delta H = 7 \text{ T}$. The value of $-\Delta S_m^{\text{max}}$ is smaller than the value of $59.96 \text{ J kg}^{-1} \text{ K}^{-1}$ for four uncoupled Gd^{III} (judged by $4R \ln(2S+1)$, where R is the gas constant and S is the spin state). The gap between experimental data and theoretical value mainly originated from the intracluster antiferromagnetic interactions in **1**. Among reported molecule-based magnetic cryogen, magnetic entropy change $-\Delta S_m^{\text{max}}$ above $40.0 \text{ J kg}^{-1} \text{ K}^{-1}$ is limited, as listed in Table S1. It is notable that only three cases with magnetic entropy change $-\Delta S_m^{\text{max}}$ above $50.0 \text{ J kg}^{-1} \text{ K}^{-1}$ have been reported. It is still very competitive when considered from the volumetric aspect with $-\Delta S_m^{\text{max}} = 198.85 \text{ mJ cm}^{-3} \text{ K}^{-1}$, being among the highest throughout the Gd^{III} -containing complexes (Tab. S1†). Indeed, evaluating the molecule-based magnetocaloric materials from the volumetric aspect is more meaningful for practical application.¹⁸ The large MCE per unit mass and/or per unit volume of **1** is primarily ascribed to the high magnetic density and the small linker among the clusters. Furthermore, the $-\Delta S_m$ per unit mass reaches the value of $42.63 \text{ J kg}^{-1} \text{ K}^{-1}$ for $T = 2 \text{ K}$ and $\Delta H = 40 \text{ kG}$, which is larger than most reported Gd^{III} -based complexes.^{4–7,8a–g}

To further explore the magnetic dynamics of **2**, the frequency and temperature dependencies of the alternating current (AC) susceptibilities were collected under a zero direct current (DC) field and a 3 Oe AC magnetic field (Fig. 3 and Fig. S9†). The out-of-phase

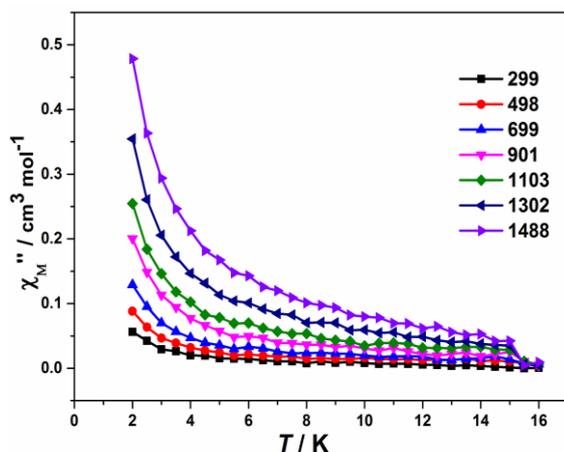


Fig. 3 Frequency dependence of the out-of-phase (χ'') ac susceptibility components for **2** at zero dc field.

constituent of AC susceptibilities exhibits frequency dependent signals below 15 K, suggesting the slow magnetic relaxation behaviour of **2**, which might be an indication of SMM behaviour. However, similar with some reported Dy-based complexes,¹⁹ the peaks of the out-of-phase signals were not observed in the technically available temperature range due to the fast quantum tunneling. To reduce the quantum tunneling effect, a proper DC field needs to be exerted. The optimal field was found from field-dependent AC susceptibility measurements (0–5 kOe). As shown in Fig. S10, the peak of χ''_M appeared at ca. 800 Oe. Thus, a 800 Oe DC field was exerted. However, the peak of χ''_M still could not be observed because the strong quantum tunneling effect was not effectively suppressed (Fig. S11†).

Conclusions

In conclusion, two (3,12)-connected complexes based on cubic [Ln₄O₄] clusters bridged by sulfate were structurally and magnetically characterized. The significant MCE of **1** and the slow magnetic relaxation behaviour of **2** were observed. More importantly, **1** shows a large $-\Delta S_m$ value of 51.29 J kg⁻¹ K⁻¹, being among the highest values in reported molecular magnetic cooling Gd-based compounds known to date. The high MCE make **1** a good candidate in the application of cryogenic refrigeration. The successful synthesis of **1** not only enriches the existing field of molecular magnetic coolers, but also confirms the potential of developing other outstanding complexes with remarkable MCE via the assembly of suitable inorganic ligands and metal ions.

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Notes and references

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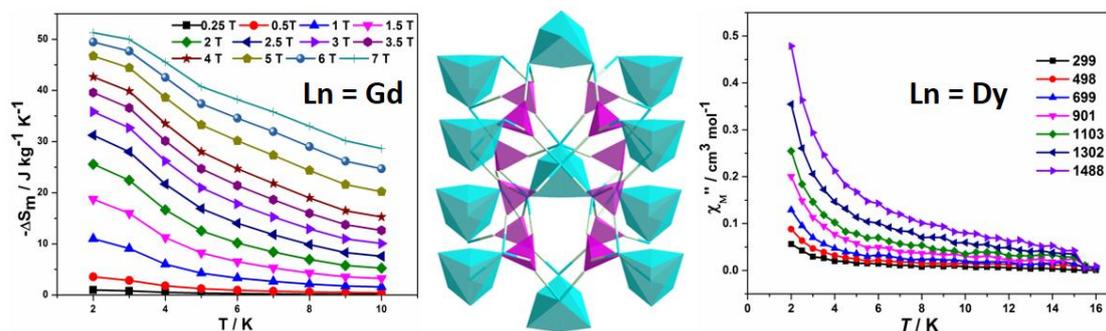
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Graphic Abstract

Magnetocaloric Effect and Slow Magnetic Relaxation in Two Dense (3,12)-connected Lanthanide Complexes

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We report two (3,12)-connected complexes with distorted cubic $[\text{Ln}_4\text{O}_4]$ ($\text{Ln} = \text{Gd}$ (**1**), Dy (**2**)) units as nodes bridged by *in situ* generated sulfate. **1** features a large magnetocaloric effect with $-\Delta S_m^{\text{max}} = 51.29 \text{ J kg}^{-1} \text{ K}^{-1}$, and **2** displays slow magnetic relaxation behavior.