Three Gd-based magnetic refrigerant materials with high magnetic entropy: From di-nuclearity to hexa-nuclearity to octa-nuclearity

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Magnetocaloric effect (MCE) is one of the most promising features of molecular-based magnetic materials. We reported three Gd-based magnetic refrigerant materials, namely, Gd₂[L](NO₃)(H₂O)·CH₃CN·H₂O (1), H₂L = (Z)-N-(1E)-(2-hydroxy-3-methphenyl)methylidene]pyrazine-2-carbohydrazonic acid), {Gd₆(L)₆(CO₃)₂(CH₃OH)₂(H₂O)₃Cl}Cl·4CH₃CN (2), and Gd₈(L)₈(CO₃)₄(H₂O)₈·2H₂O (3). Complex 1 contains two Gd₃ ions linked by two η²-η¹-η¹-μ₂-L₂- ligands, which are seven-coordinated in a capped trigonal prism, and complex 2 possesses six Gd₃ ions, contributing to a triangular prism configuration. For complex 3, eight Gd₈ ions form a distorted cube arrangement. Moreover, the large values of magnetic entropy in the three complexes prove to be excellent candidates as cryogenic magnetic coolants.

KEYWORDS magnetocaloric effect, polynuclear, lanthanide, Schiff-based ligand, magnetic entropy

Introduction

Ln-based complexes play a critical role in molecular-based materials not only due to the charming geometrical structures but also because of the extensive applications such as luminescence, catalysis, especially for magnetic materials including magnetocaloric effect (MCE) (Wu D et al., 2020; Shang et al., 2021; Wei et al., 2021), and single-molecule magnets (SMMs) (Liu et al., 2014; Liu et al., 2016; Zhang and Cheng, 2016; Reis, 2020). As a member of the Ln elements, the Gd ion is a perfect candidate in the synthesis of molecular-based magnetic refrigeration materials because of the large magnetothermal effects (Evangelisti et al., 2011; Chen et al., 2013; Chen et al., 2014; Wang et al., 2020a; Li et al., 2021; Lin et al., 2021; Wu T et al., 2021; Zhou et al., 2021). Some of the reported magnetic materials even possess a large cryogenic MCE, which is comparable to that of the commercial coolant [Gd₃Ga₅O₁₂] (Pecharsky and Gschneidner, 1997; Zhang S. et al., 2015; Zhang S.-W. et al., 2015).
It is worth mentioning that in the pure 4f system, improving magnetic density is the ideal method to gain MCE performance (Zhang et al., 2016; Reis, 2020). Therefore, organic ligands play an important role in the building units of the complexes. In previous studies, various organic ligands (e.g., Schiff-based ligands (Aronica et al., 2006; Boulon et al., 2013; Mannini et al., 2014; Burgess et al., 2015; Nava et al., 2015; Wang et al., 2015; Lakma et al., 2019; Li et al., 2019; Wang et al., 2020b; Wang J. et al., 2021; Wang M. et al., 2021), carboxylates (Milos et al., 2007; Dermitzaki et al., 2015; Yin et al., 2015; Botezat et al., 2017; Feltham et al., 2015; Li et al., 2019; Zheng et al., 2020; Han et al., 2021; Zhou et al., 2021), diketones (Zhu et al., 2014; Yao et al., 2018; Wang et al., 2019a; Wang et al., 2019b; Shi et al., 2021), and diamines (Neves et al., 1992; Zhang et al., 2013; Cornia et al., 2014; Oyarzabal et al., 2014; Feltham et al., 2015; Luan et al., 2015; Lu et al., 2019) etc.) have been successfully utilized in the synthesis of MCE materials. Among them, Schiff-based ligands comprise rich O and N sites, which are widely used in the synthesis of many Ln complexes because of the simple synthesis and structural diversity.

In this work, three Gd-based magnetic refrigerant materials based on Schiff-based ligands \((Z)-N\{1(\text{E})-(2\text{-hydroxy-3-methphenyl})\text{methylidene}\}\text{pyrazine-2-carboxydranonic acid} (H_2L)\) were synthesized, namely, \(\text{Gd}_2(L)(\text{NO}_3)(\text{H}_2\text{O})\cdot\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}\) (1), \(\text{Gd}_6(L)_6(\text{CO}_3)_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_3\cdot\text{Cl}\cdot4\text{CH}_3\text{CN}\) (2), and \(\text{Gd}_6(L)_6(\text{CO}_3)_2(\text{H}_2\text{O})_3\cdot2\text{H}_2\text{O}\) (3). Magnetic studies indicate that all complexes exhibit antiferromagnetic interactions between the spin centers and display large magnetic entropies.

**Materials and methods**

**Materials**

All reactions and manipulations were performed in the ambient atmosphere. The Schiff-based \(H_2L\) ligand was prepared by condensation with o-vanillin and hydrazine-2-carboxydranonic acid in methanol according to the literature (Chandrasekhar et al., 2013; Chen et al., 2016). Metal salts and other reagents were commercially available and used without further purification.

**Synthesis**

Synthesis of \(\text{Gd}_2(L)_2(\text{NO}_3)_2(\text{H}_2\text{O})_2\cdot\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}\) (1): a mixture of \(H_2L\) (0.1 mmol, 27.2 mg) and \(\text{Gd}(\text{NO}_3)_3\cdot6\text{H}_2\text{O}\) (0.1 mmol, 45.7 mg) was dissolved in \(\text{CH}_3\text{CN}\) (5 ml) and \(\text{CH}_3\text{OH}\) (2.5 ml). After stirring for 5 min, pyridine (0.04 ml) was added and stirred for another 10 min. The solution was filtered and left to slowly evaporate. Well-shaped orange crystals were obtained after 1 week. Yield: 20 mg, 36% based on Gd. Elemental analysis (EA) calc. (%) for \(\text{Gd}_2\text{C}_{30}\text{H}_{30}\text{N}_{12}\text{O}_{16}\), C: 31.91, H: 2.68, N: 14.89; found (%), C: 32.03, H: 2.61, N: 14.93.

\[\text{Gd}_2(L)_6(\text{CO}_3)_2(\text{H}_2\text{O})_2\cdot\text{Cl}\cdot4\text{CH}_3\text{CN} \] (2): a mixture of \(H_2L\) (0.2 mmol, 54.4 mg) and \(\text{GdCl}_3\cdot6\text{H}_2\text{O}\) (0.2 mmol, 74.3 mg) was dissolved in \(\text{CH}_3\text{CN}\) (10 ml) and \(\text{CH}_3\text{OH}\) (5 ml). After stirring for 5 min, \(\text{NaHCO}_3\) (0.2 mmol, 33.6 mg) was added and stirred for another 3 h. Well-shaped orange crystals were obtained after 1 week. Yield: 32 mg, 32% based on Gd. Elemental analysis (EA) calc. (%) for \(\text{Gd}_8\text{C}_{10}\text{H}_{10}\text{N}_{32}\text{O}_{46}\), C: 33.78, H: 2.62, N: 11.67; found (%), C: 33.83, H: 2.51, N: 11.84.

\[\text{Gd}_6(L)_6(\text{CO}_3)_2(\text{H}_2\text{O})_3\cdot2\text{H}_2\text{O} \] (3): a mixture of \(H_2L\) (0.2 mmol, 13.6 mg) and \(\text{GdCl}_3\cdot6\text{H}_2\text{O}\) (0.2 mmol, 18.6 mg) was dissolved in \(\text{CH}_2\text{CN}\) (5 ml) and \(\text{CH}_3\text{OH}\) (2.5 ml). After stirring for 5 min, \(\text{NaCO}_3\) (0.2 mmol, 10.6 mg) was added and stirred for another 2 h. Well-shaped orange crystals were obtained after 1 week. Yield: 28 mg, 29% based on Gd. Elemental analysis (EA) calc. (%) for \(\text{Gd}_8\text{C}_{10}\text{H}_{10}\text{N}_{32}\text{O}_{46}\), C: 33.78, H: 2.62, N: 11.67; found (%), C: 33.83, H: 2.51, N: 11.84.

**Physical measurements**

The C, H, and N elemental analyses were performed using an Elementar Vario-EL CHNS elemental analyzer. The Fourier transform-infrared (FT-IR) spectra were carried out from KBr pellets in the range 4,000–400 cm\(^{-1}\) using an EQUINOX 55 spectrometer. Powder X-ray diffraction (PXRD) patterns were performed using the Bruker D8 Advance diffractometer (Cu–K\(\alpha\), \(\lambda = 1.54056 \text{ Å}\)). Magnetic susceptibility measurements were measured with a Quantum Design MPMS-XL7 SQUID. Polycrystalline samples were embedded in vaseline to prevent torquing. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

**Crystallographic study**

Suitable single crystals for 1–3 were selected for single-crystal X-ray diffraction analysis. Data were collected using a Rigaku Oxford diffractometer with a Mo–K\(\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)) at 120 K. The structures were solved by direct methods and refined by least-squares on \(F^2\) utilizing the SHELXTL program suite and Olex2 (Dolomanov et al., 2009; Sheldrick, 2015a,b). The hydrogen atoms were set in calculated positions and refined as riding atoms with common fixed isotropic thermal parameters. EA was used to detect the content of C, H, and N atoms. Detailed information about the crystal data and structure refinements is summarized in Table 1. Selected bond lengths and angles of complexes 1–3 are listed in Supplementary Table S1–S3.
Results and discussion

Description of the structures of 1–3

Complexes 1–3 are synthesized by the evolution method with H2L and gadolinium salt in the solution of CH3CN/CH3OH (V1: V2 = 2:1) under the existence of alkali. The alkali is added to be conducive to protonate the ligand H2L, which is beneficial to incorporate GdIII ions. The H2L ligand in all complexes is completely dehydrogenated adopting the μ2:η1:η1:η1:η1-mode (Scheme 1A), which is similar to the reported literature (Chandrasekhar et al., 2013; Chen et al., 2016; Zhang et al., 2017; Jiang et al., 2016).

Complex 1 is crystallized in the triclinic P-1 space group. As shown in Figure 1, the crystallography independent unit of 1 contains half of the molecule, including one GdIII ion, one L2 ligand, one NO3− anion, and half of CH3CN and H2O molecules. The metallic GdIII ions (Gd1 and Gd1A) are surrounded by two L2 ligands using the aforementioned

TABLE 1 Crystallographic data and structural refinement parameters for complexes 1–3.

| Complex | 1 | 2 | 3 |
|---------|---|---|---|
| Formula | Gd3(L)2(NO3)2(H2O)2·CH3CN·H2O | [Gd3(L)2(CO3)2(CH3OH)2(H2O)2]Cl4·CH3CN | Gd6(L)6(CO3)2(CH3OH)2·2H2O |
| Mr [g mol−1] | 1127.17 | 3044.31 | 3840.19 |
| T [K] | 120 (2) | 120 (2) | 120 (2) |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | P-1 | P-1 | P-1 |
| a [Å] | 8.8137 (8) | 13.5408 (9) | 17.8476 (16) |
| b [Å] | 9.4123 (9) | 18.8679 (15) | 18.2321 (2) |
| c [Å] | 13.3026 (12) | 23.2844 (16) | 28.0616 (3) |
| α [°] | 95.912 (3) | 90.424 (3) | 73.0978 (10) |
| β [°] | 109.101 (3) | 92.888 (2) | 77.7530 (8) |
| γ [°] | 107.900 (3) | 106.296 (2) | 61.2890 (11) |
| V [Å3] | 966.55 (16) | 5701.2 (7) | 7634.03 (16) |
| Z | 1 | 2 | 2 |
| ρcalcd [g cm−3] | 1.936 | 1.773 | 1.671 |
| μ [mm−1] | 3.487 | 3.569 | 3.506 |
| F (000) | 550.7 | 2956.0 | 3704.0 |
| Reflected/unique | 8376/3895 | 70871/25093 | 124216/39110 |
| GOF on F2 | 1.0385 | 1.030 | 1.033 |
| R1/wR2 (I > 2σ(I), squeeze) | 0.0379/0.0963 | 0.0393/0.0943 | 0.0378/0.0887 |
| R1/wR2 (all data, squeeze) | 0.0424/0.1001 | 0.0454/0.0995 | 0.0512/0.0946 |
| CCDC No. | 2174539 | 2174540 | 2174541 |

* R1 = Σ||Fo|−|Fc||/Σ|Fo|. wR2 = [Σw(Fo2−Fc2)^2/Σw(Fo2)]^1/2.
mode, two NO$_3^−$ anions and two H$_2$O molecules located above and below the plane, respectively. The average bond lengths of Gd-O and Gd-N are 2.379 (5) Å and 2.460 (5) Å (Supplementary Table S1), respectively, which are in accordance with those of the reported Gd-based complexes (Chen et al., 1995; Zhao et al., 2017; Mayans and Escuer, 2021; Ren et al., 2021). In complex 1, the Gd ion is seven-coordinated to form a capped trigonal prism, which is confirmed by CShM calculations (Alvarez et al., 2005; Casanova et al., 2005) (Supplementary Figure S1, Supplementary Table S4).

Complex 2 crystalizes in the same space group as complex 1, and the asymmetric unit comprises the whole molecule with six crystallographically independent Gd$^{III}$ ions (Figure 2A). The six Gd ions are held together to form a [Gd$_6$] triangular prism metallic skeleton (Figure 2B). Therein, three Gd ions in the plane (Gd1, Gd2, and Gd3 or Gd4, Gd5, and Gd6) contribute a triangular configuration, which are bridged by one CO$_3^{2−}$ anion in $μ_3$-$η_1$-$η_2$-$η_2$-mode (Scheme 1B). The two triangular metallic skeletons are then linked together by six $μ_2$-O bridges from ligands.

All Gd ions are eight coordinated, showing two kinds of coordination geometry confirmed by CShM calculations (Alvarez et al., 2005; Casanova et al., 2005) (Supplementary Table S5). The Gd1, Gd2, Gd3, Gd5, and Gd6 ions are in [O$_6$N$_2$] environment with six O atoms and two N atoms from two chelated L$_2^−$ ligands, one CO$_3^{2−}$ anion and one CH$_3$OH/H$_2$O molecule, which display a biaugmented trigonal prism configuration (Supplementary Figure S2). The average Gd-O and Gd-N distances are 2.352 (4) Å and 2.475 (4) Å, respectively (Supplementary Table S2), which are consistent with those reported Gd-based complexes (Chen et al., 1995; Zhao et al., 2017; Mayans and Escuer, 2021; Ren et al., 2021).

However, Gd4 has triangular dodecahedron coordination geometry and is located in an [O$_2$N$_2$Cl] environment with five O and two N atoms from two chelated L$^2$ ligands and one Cl$^−$ ion. The bond length of Gd4-Cl1 is 2.746 (1) Å, which is longer than that of Gd-O and Gd-N.

For complex 3, the synthetic method is the same as complex 2; except NaHCO$_3$ was used in place of Na$_2$CO$_3$. Surprisingly, complex 3 possesses an octa-nuclearity structure, which crystalizes in the triclinic $P$-1 space group. The asymmetric unit consists of a completed molecule, and there are eight crystallographically independent Gd atoms in the molecular structure (Figure 3A). As shown in Figure 3B, the eight Gd$^{III}$ ions contribute to a cubic trapezoid metallic core, Gd1, Gd4, Gd5, and Gd8 ions lie in the four vertices of the plane below the cubic trapezoid, while Gd2, Gd3, Gd6, and Gd7 ions situate in the upper plane. The metallic core is held together by four CO$_3^{2−}$ anions in $μ_3$-$η_1$-$η_2$-$η_2$-mode (Scheme 1C). The periphery of the metal core is ligated by eight L$_2^−$ ligands, eight H$_2$O molecules, and two lattice H$_2$O molecules.

There are two coordination numbers of Gd$^{III}$ ions in complex 3 (Supplementary Figure S3). Gd1, Gd3, Gd5, and Gd7 are eight-coordinated ions in [O$_6$N$_2$] donor set from two L$_2^−$ ligands, two CO$_3^{2−}$ anions, and one H$_2$O molecule, while Gd2, Gd4, Gd6, and Gd8 ions are nine-coordinated in the [O$_7$N$_2$] donor set. The difference between the two kinds of Gd ions is the diverse coordination modes of the CO$_3^{2−}$ anion. There is only one coordination bond of O atom in CO$_3^{2−}$ anion, which is adopted in Gd1, Gd3, Gd5, and Gd7 ions. For Gd2, Gd4, Gd6, and Gd8 ions, the bonding mode of the CO$_3^{2−}$ anion is adopted in the bidentate mode. The eight metal ions exhibit three coordination geometries: biaugmented trigonal prism (Gd1), triangular dodecahedron (Gd3, Gd5, and Gd7), and muffin

![FIGURE 2](image-url)

Crystal structure (A) and metallic core (B) of complex 2. The hydrogen atoms are omitted for clarity. Color codes: Gd, purple; O, pink; N, blue; and C, gray.
(Gd2, Gd4, Gd6, and Gd8) (Supplementary Tables S5,6). The average Gd-O distance is 2.361 (4) Å, which is shorter than that of Gd-N (2.564 (4) Å) lengths. The O/N-Gd-O/N angles are in the range of 60.99°–154.86°, which are in the normal range (Chen et al., 1995; Zhao et al., 2017; Mayans and Escuer, 2021; Ren et al., 2021).

It is worth mentioning that the use of different alkalis can affect the number of formed metal nuclearity. For the organic weak alkali triethylamine, which is used in complex 1, it only facilitates protonation of the ligand H2L but is not involved in the final formation of complex 1. However, for complexes 2 and 3, the inorganic alkalis not only deprotonate the ligand but also participate in the construction of the molecules. Compared to NaHCO3 in complex 2, the alkalinity of Na2CO3 is relatively strong. Moreover, mainly due to the degree of hydrolysis of carbonates being higher, there are more carbonate triangle skeletons in complex 3, making it easier to coordinate with Gd ions, thus forming an octanuclearity complex.

IR spectra and PXRD studies

The FT-IR spectra of complexes 1–3 were acquired (ν = 4,000–500 cm⁻¹), which are shown in Supplementary Figure S4. Powder X-ray diffraction (PXRD) measurements for complexes 1–3 were performed for the crystalline crystals (Supplementary Figure S5), and the experimental patterns are in good agreement with the simulated ones from the crystallographic data. The minor inconsistencies in the intensity and shape of the peaks indicate the phase purity of complexes 1–3.

Magnetic studies

The direct current magnetic susceptibilities of complexes 1–3 were studied for polycrystalline samples in the temperature range of 2–300 K at an external magnetic field of 1000 Oe (Figure 4A). At room temperature, the χM/T values of complexes 1–3 are 15.77, 47.16, and 62.81 cm³ K mol⁻¹, respectively, which is in good agreement with the expected spin-only values (GdIII ion: 7.875 cm³ K mol⁻¹, g = 2). Upon cooling, the χM/T values in all cases stay essentially unchanged until approximately 25 K and then followed by an obvious decrease to the minimum values of 13.29, 38.46, and 58.30 cm³ K mol⁻¹, indicating antiferromagnetic interactions (Kahn et al., 2000). Fitting the curve of χM⁻¹ vs. T with the Curie–Weiss Law (Figure 4B) gives the resulting C and θ values, which are listed in Supplementary Table S7. The negative θ values imply the presence of weak antiferromagnetic interaction within complexes 1–3.

The field dependence of the magnetization plots for complexes 1–3 was performed in the field range of 1–7T at 2–8 K (Supplementary Figure S6). Magnetizations in all complexes are increased gradually at the entire field region, reaching saturation values of 13.81, 41.75, and 55.83 NμB at 7 T and 2 K, respectively, close to the theoretical value (1: 14 NμB; 2: 42 NμB; 3: 56 NμB). The reduced magnetization plots (M vs. HT⁻¹) in all complexes are superposable due to the isotropic system (Supplementary Figure S7).

Due to the complicated systems in complexes 2 and 3, only complex 1 is attempted to analyze the magnetic interactions by using a simplified spin Hamiltonian with the PHI program (Eq. 1):
\[ H_{\text{Gd-Gd}} = -2J_{\text{Gd-Gd}} S_{\text{Gd}} S_{\text{Gd}}. \]  

(1)

The best-fit parameters are \( J = -0.022 \) (2) cm\(^{-1}\) and \( g = 1.98 \) (Figure 4A; Supplementary Figure S8). The negative \( J \) value confirms the antiferromagnetic interactions between the Gd\textsuperscript{III} ions, which is in accordance with the trend of the \( \chi M T \) product with cooling and the result of the Curie–Weiss Law.

The isothermal magnetization for complexes 1–3 was measured from 2 to 8 K in an applied DC field up to 7 T to calculate the magnetic entropy (-\( \Delta S_m \)) according to the Maxwell equation (Pecharsky and Gschneidner, 1999)
TABLE 2 Summary of $\Delta S_m$ in different $\Delta H$ at a given temperature for reported di-nuclearity, hexa-nuclearity, octa-nuclearity, and other multinuclear Gd-based complexes.

| Complex | $\Delta S_m$ [J kg$^{-1}$ K$^{-1}$] | $\Delta H$ [T], T [K] | Ref |
|--------|-------------------------------|------------------|-----|
| $\text{Gd}_2(\text{OA})_2(\text{H}_2\text{O})_4$·2H$_2$O | 40.6 | 7, 1.8 | Evangelisti et al. (2011) |
| $\text{Gd}_2(\text{OA})_2(\text{Ph}_2\text{O})_2$ (MeOH)$_2$ | 23.7 | 7, 2.4 | Guo et al. (2012) |
| $\text{Gd}_2$ (hfac)$_2$ (fpmoco)$_2$ | 17.1 | 8, 3.0 | Wang et al. (2015) |
| $\text{Gd}_2$ (hfac)$_3$ (hbo)$_2$ | 16.9 | 8, 2.0 | Shen et al. (2015) |
| $\text{Gd}_2$ (Ln) (dbm)$_2$ | 17.69 | 8, 2.0 | Wang et al. (2021a) |
| $\text{Gd}_2$ (hfac)$_2$ (bipy)$_2$ | 9.3 | 7, 2.0 | Zhou et al. (2021) |
| $\text{Gd}_2$ (niac)$_6$(H$_2$O)$_4$ | 27.4 | 7, 2.0 | Zhou et al. (2021) |
| $\text{Gd}_2$ (iba)$_6$ (bipy)$_2$ | 29.3 | 7, 2.0 | Zhou et al. (2021) |
| $\text{Gd}_2$ (L)$_2$(dbm)$_2$(H$_2$O)$_2$ | 24.75 | 7, 2.0 | Shi et al. (2020) |
| $\text{Gd}_2$ (L)$_2$ (HCO$_2$)$_4$ | 35.3 | 7, 2.0 | Wang et al. (2020b) |
| $\text{Gd}_2$ (hfac)$_4$ (btoq)$_2$ | 16.9 | 8, 2.0 | Shen et al. (2015) |
| $\text{Gd}_2$ (hfac)$_4$ (fpmoq)$_2$ | 17.1 | 8, 3.0 | Wang et al. (2015) |
| $\text{Gd}_2$ (L)$_2$ (dbm)$_2$(H$_2$O)$_2$ | 27.21 | 7, 2.0 | This work |
| $\text{Gd}_2$ (L)$_2$ (DBM)$_2$(H$_2$O)$_4$ | 23.2 | 7, 2.0 | Shi et al. (2021) |
| $\text{Gd}_2$ (Hnsa)$_2$(nsa)$_2$(phen)$_2$(H$_2$O)$_2$ | 22.2 | 7, 2.0 | Zheng et al. (2020) |
| $\text{Gd}_2$(dnba)$_2$(phen)$_2$(H$_2$O)$_2$ | 16.8 | 7, 2.0 | Zheng et al. (2020) |

(Eq. 2). It can be seen that the curves of $\Delta S_m$ of complexes 1–3 gradually increase with decreasing temperature and increasing of magnetic field without saturation, the maximum $\Delta S_m$ values are 25.05 J kg$^{-1}$ K$^{-1}$, 27.21 J kg$^{-1}$ K$^{-1}$, and 30.79 J kg$^{-1}$ K$^{-1}$ at 2 K, $\Delta H = 7$ T, respectively (Figure 5). These values are smaller than the theoretical values, which is mainly caused by antiferromagnetic interactions between the metal core, which is also confirmed by PHI fitting. Complexes 2 and 3 are hexa-nuclearity with a biaugmented trigonal prism configuration and octa-nuclearity with a cubic trapezoid structure. Magnetic investigations indicate the antiferromagnetic interactions between Gd$^{3+}$ ions are smaller than the theoretical values, which is mainly caused by antiferromagnetic coupling. Furthermore, complex 1 exhibits a large magnetic

$$\Delta S_m(T) = nR\ln(2S + 1).$$  

3

Conclusion

In conclusion, three clusters 1–[Gd$_2$], 2–[Gd$_3$], and 3–[Gd$_6$] based on Schiff ligand H$_2$L were synthesized. Complex 1 contains two Gd$^{3+}$ ions, and magnetic measurement indicates antiferromagnetic interactions between the metal core, which is also confirmed by PHI fitting. Complexes 2 and 3 are hexa-nuclearity with a biaugmented trigonal prism configuration and octa-nuclearity with a cubic trapezoid structure. Magnetic investigations indicate the antiferromagnetic interactions between Gd$^{3+}$ ions are observed in complexes 2 and 3. Magnetocaloric studies for complexes 1–3 show that the magnetic entropies of complexes 1–3 are smaller than the theoretical values, which is mainly caused by antiferromagnetic coupling. Furthermore, complex 1 exhibits a large magnetic...
entropy of 25.05 J kg⁻¹ K⁻¹ at 2.0 K in di-nuclearity magnetic refrigerant materials, while complexes 2 and 3 belong to the normal range in hexa-nuclearity and octa-nuclearity complexes, respectively, demonstrating that they are promising molecular magnetic coolants for low-temperature cooling applications.

Data availability statement

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found in the article/Supplementary Material.

Author contributions

MW and CS: writing—original draft; YG, HX, LH, and YZ: investigation and formal analysis; JW: project administration and funding acquisition; YP: measurement; YT: validation, editing, and funding acquisition.

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References

Adhikary, A., Sheikh, J. A., Biswas, S., and Konar, S. (2014). Synthesis, crystal structure and study of magnetocaloric effect and single molecular magnetic behaviour in discrete lanthanide complexes. Dalton Trans. 43, 9334–9343. doi:10.1039/C4DT00540F

Alvarez, S., Alemany, P., Casanova, D., Cirera, J., Llunell, M., and Avnir, D. (2005). Shape maps and polyhedral interconversion paths in transition metal chemistry. Coord. Chem. Rev. 249, 1693–1708. doi:10.1016/j.ccr.2005.03.031

Aronica, C., Pilet, G., Chastanet, G., Wernsdorfer, W., Jacquot, J.-F., and Luneau, D. (2006). A nonanuclear dysprosium(III)–copper(II) complex exhibiting single-molecule magnet behavior with very slow zero-field relaxation. Angew. Chem. Int. Ed. 45, 4659–4662. doi:10.1002/anie.200600513

Botezat, O., van Leusen, J., Krawtsov, V. C., Kogerler, P., and Baca, S. G. (2017). Ultralarge 3d/4f coordination wheels: From carboxylate/amino alcohol-supported [Fe3L4n] to [Fe3L4n] rings. Inorg. Chem. 56, 1814–1822. doi:10.1021/acs.inorgchem.6b02100

Boulon, M. E., Cucinotta, G., Luzon, J., Deg’Innocenti, C., Perfetti, M., Bernot, K., et al. (2013). Magnetic anisotropy and spin-parity effect along the series of lanthanide complexes with DOTA. Angew. Chem. Int. Ed. 52, 350–354. doi:10.1002/anie.201205938

Burgess, J. A., Malavolti, L., Lanzilotto, V., Mannini, M., Yan, S., Ninova, S., et al. (2015). Magnetic fingerprint of individual Fe₃M₇O₁₉ magnets under compression by a scanning tunnelling microscope. Nat. Commun. 6, 8216–8222. doi:10.1038/ncomms9216

Casanova, D., Llunell, M., Alemany, P., and Alvarez, S. (2005). The rich stereochemistry of eight-vertex polyhedra: A continuous shape measures study. Chem. Eur. J. 11, 1479–1494. doi:10.1002/chem.200400799

Chandrasekhar, V., Das, S., Dey, A., Hossain, S., and Sutter, J.-P. (2013). Tetranuclear lanthanide (III) complexes containing dimeric subunits: Single-molecule magnet behavior for the Dy₄ analogues. Inorg. Chem. 52, 11956–11965. doi:10.1021/ic401652f

Chen, Q., Ma, F., Meng, Y.-S., Sun, H.-L., Zhang, Y.-Q., and Gao, S. (2016). Assembling dysprosium dimer units into a novel chain featuring slow magnetic relaxation via formate linker. Inorg. Chem. 55, 12904–12911. doi:10.1021/acs.inorgchem.6b02276

Chen, X.-M., Aubin, S. M. J., Wu, Y.-L., Yang, Y.-S., Mak, T. C. W., and Hendrickson, D. N. (1995). Polynuclear Cu[II]₆M₆[OH]₁₂(H₂O)₁₈(pyb)₁₂(ClO₄)₁₇(ClO₄)₁₇·9H₂O (pyb = pyridine betaine). J. Am. Chem. Soc. 117, 9680–9691. doi:10.1021/ja0142a043

Chen, Y.-C., Guo, F.-S., Zheng, Y.-Z., Liu, J.-L., Leng, J.-D., Tarasenko, R., et al. (2013). Gadolinium(III)-hydroxy ladders trapped in succinate frameworks with optimized magnetocaloric effect. Chem. Eur. J. 19, 13504–13510. doi:10.1002/chem.201302221

Chen, Y.-C., Qin, L., Meng, Z.-S., Yang, D.-F., Wu, C., Fu, Z., et al. (2014). Study of a magnetic-cooling material Gd(OH)CO₃. J. Mat. Chem. A 2, 9851–9858. doi:10.1039/C4TA06146G

Cornia, A., Rigamonti, L., Boccioli, S., Clerac, R., Rouzieres, M., and Sorace, L. (2014). Magnetic blocking in extended metal atom chains: A pentachromium(II) complex behaving as a single-molecule magnet. Chem. Commun. 50, 15191–15194. doi:10.1039/C4CC06693F

Dermittaz, D., Raptopoulou, C. P., Psycharis, V., Escuer, A., Perlepes, S. P., and Stamatatos, T. C. (2015). Nonemployed simple carboxylate ions in well-investigated areas of heterometallic carboxylate cluster chemistry: A new family of [CuII(CO₃)]−

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Conflict of interest

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Supplementary material

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complexes bearing tert-butylacetate bridging ligands. Inorg. Chem. 54, 7555–7561. doi:10.1021/acs.inorgchem.5b01179

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., and Puschmann, H. (2009). OLEX2: A complete structure solution, refinement and analysis program. J. Appl. Crystallogr. 42, 331–341. doi:10.1107/S002188980942276

Evangelisti, M., Roubert, O., Palacios, E., Camón, A., Hooper, T. N., Brehin, E. K., et al. (2011). Cryogenic magnetocaloric effect in a ferromagnetic molecular dimer. Angew. Chem. Int. Ed. 50, 6606–6649. doi:10.1002/anie.201102640

Feltham, H. L. C., Dbers, S., Rouzières, M., Clerc, R., Powell, A. K., and Brooker, S. (2015). A family of fourteen soluble stable macrocyclic [NiIIILnIII] heterometallic 4f complexes. Inorg. Chem. Front. 2, 982–990. doi:10.3389/fchem.2012.00130g

Feltham, H. L. C., Dumas, C., Mamin, M., Otero, E., Sanzavt, P., Sessoli, R., et al. (2017). Proof of principle: Imobilisation of robust Cu3 IIIIM-acrocycles on small, suitably pre-functionalised gold nanoparticles. Chem. Eur. J. 23, 2517–2521. doi:10.1002/chem.201604821

Guo, F.-S., Leng, J.-D., Liu, J.-L., Meng, Z.-S., and Tong, M.-L. (2012). Polynuclear and polymeric gadolinium acetate derivatives with large magnetocaloric effect. Inorg. Chem. 51, 11156–11163. doi:10.1021/ic301635b

Han, L.-J., Wang, W.-M., Wang, X.-W., Huai, L., Qiao, N., and Fang, M. (2021). A rhombohedrally shaped [GdIII2CoIII2] heterometallic cluster exhibiting larger cryogenic magnetocaloric effect. Inorg. Chem. 50, 120020. doi:10.1021/acs.inorgchem.0c03184

Hou, T.-L., Han, X., Xu, X.-Y., Shen, J.-X., Wang, J., Shi, Y., et al. (2020). Two LnIIILnIII (Db = Dy and Gd) clusters constructed by 8-hydroxyquinoline Schiff base and β-diketone coigand: Magnetic refrigeration property and single-molecule magnet behavior. Inorg. Chem. Acta 502, 119250–119303. doi:10.1016/j.ica.2019.119250

Jiang, Y., Brunet, G., Holmberg, R. J., Hahib, F., Korobkov, I., and Singh, A. K. (2019). Tetranauclear MnIII, CoII, CuII and ZnII grid complexes of an unsymmetrical ditopic β2,diketonate coligand: Magnetic refrigeration property and single-molecule magnet behavior. Inorg. Chem. 58, 4749–4755. doi:10.1021/acs.inorganichem.9c00490

Oyarzabal, I., Ruiz, I., Seco, J. M., Evangelisti, M., Camón, A., Ruiz, E., et al. (2014). Rational electrostatic design of easy-axis axial anisotropy in a ZnIII(DyIII)-ZnII single-molecule magnet with a high energy barrier. Chem. Eur. J. 20, 14226–14269. doi:10.1002/chem.201403670

Pecharsky, V. K., and Gschneidner, K. J. A. (1997). Giant magnetocaloric effect in Gd3S4Ge4. Phys. Rev. Lett. 78, 4494–4497. doi:10.1103/PhysRevLett.78.4494

Pecharsky, V. K., and Gschneidner, K. A. Jr (1999). Magnetocaloric effect and magnetic refrigeration. J. Magn. Magn. Mat. 200, 44–56. doi:10.1016/S0304-8853(98)00397-9

Rens, M. S. (2020). Magnetocaloric and barocaloric effects of metal complexes for solid state cooling: Review, trends and perspectives. Coord. Chem. Rev. 417, 213357. doi:10.1016/j.ccr.2020.213357

Ren, J., Wei, X. Q., Xu, R. S., Chen, Z. Y., Wang, J., Wang, M., et al. (2021). A potential ferromagnetic lanthanide–transition hybrid magnetic–based bacteriostatic agent. J. Mol. Struct. 1229, 129783. doi:10.1016/j.molstruc.2020.129783

Shang, Y., Cao, Y., Xie, Y., Zhang, S., and Cheng, P. (2021). A 1D Mn-based coordination polymer with significant magnetic refrigeration effect. Polyhedron 202, 115173–115179. doi:10.1016/j.poly.2021.115173

Sheldrick, G. M. (2015a). Crystal structure refinement with SHELXL. Acta Crystallogr. C. Cryst. Struct. Chem. 71, 3–8. doi:10.1107/S2053229614042218

Sheldrick, G. M. (2015b). SHELXT – integrated space-group and crystal-structure determination with SHELXL. Acta Crystallogr. A Found. Adv. 71, 3–8. doi:10.1107/S2053237314024218

Shen, H.-Y., Wang, W.-M., Bi, Y.-X., Gao, H.-L., Liu, S., and Cui, J.-Z. (2015). Luminescence, magnetocaloric effect and single-molecule magnet behaviour in lanthamide complexes based on a tridentate ligand derived from 8-hydroxyquinoline. Dalton Trans. 44, 18893–18891. doi:10.1039/c5dt02894a

Shi, Q.-X., Yue, C.-L., Fan, C.-J., Yan, L.-Q., Qiao, N., Fang, M., et al. (2020). Magnetic refrigeration property and slow magnetic relaxation behavior of five dinuclear LnIII-based compounds. Polyhedron 194, 114938. doi:10.1016/j.poly.2020.114938

Shi, X.-H., Hao, S.-S., Wang, M.-J., Zhang, L., Liang, W.-H., Gao, H.-M., et al. (2020). Magnetic refrigeration property and slow magnetic relaxation behavior of five dinuclear LnIII-based compounds. Polyhedron 194, 114938. doi:10.1016/j.poly.2020.114938

Wang, J., Wu, Z.-L., Yang, L.-R., Xue, F.-M., Fang, X.-Z., Luo, S.-C., et al. (2021a). Two lanthamide-based dinuclear complexes (GdIII and DyIII) with Schiff base derivatives: Synthesis, structures and magnetic properties. Inorganica Chim. Acta 514, 120015. doi:10.1016/j.ica.2020.120015

Wang, M., Lu, L., Song, W., Wang, X., Sun, T., Zhu, J., et al. (2021b). AIE-active Schiff base compounds as fluorescent probe for the highly sensitive and selective detection of Al III ions. J. Lumin. 233, 117911. doi:10.1016/j.jlumin.2021.117911

Wang, W.-M., Gao, Y., Yue, R.-X., Qiao, N., Wang, D.-T., Shi, Y., et al. (2020). Construction of a family of LnIII clusters using multifunctional Schiff base and β-diketone ligands: Fluorescence properties, magnetic effect and slow magnetic relaxation. New J. Chem. 44, 9230–9237. doi:10.1039/d0nj01172j

Wang, W.-M., He, L.-Y., Wang, X.-X., Shi, Y., Wu, Z.-L., and Cui, J.-Z. (2019b). Linear-shaped LnIII and LnIIIIII clusters constructed by a polydentate Schiff base ligand and a β-diketone co-ligand: Structures, fluorescence properties, magnetic refrigeration and single-molecule magnet behavior. Dalton Trans. 48, 16744–16755. doi:10.1039/c8dt04347a
Wang, W.-M., Huai, L., Wang, X.-W., Jiang, K.-J., Shen, H.-Y., Gao, H.-L., et al. (2020d). Structures, magnetic refrigeration and single molecule magnet behavior of five rhombus-shaped lanthanide(III) based compounds. *New J. Chem.* 44, 10266–10274. doi:10.1039/d0nj00156k

Wang, W.-M., Wang, M.-J., Hao, S.-S., Shen, Q.-Y., Wang, M.-L., Liu, Q.-L., et al. (2020a). "Windmill"-shaped LnIII 4 (LnIII = Gd and Dy) clusters: Magneticcaloric effect and single-molecule-magnet behavior. *New J. Chem.* 44, 4631–4638. doi:10.1039/d0nj0317d

Wang, W.-M., Yue, C.-L., Jing, B.-Y., Ma, X., Yang, L.-N., Luo, S.-C., et al. (2020b). Two hexanuclear lanthanide LnII clusters featuring remarkable magnetocaloric effect and slow magnetic relaxation behavior. *New J. Chem.* 44, 18025–18306. doi:10.1039/D0NJ03442H

Wang, W.-M., Yue, R.-X., Gao, Y., Wang, M.-J., Hao, S.-S., Shi, Y., et al. (2019a). Large magnetocaloric effect and remarkable single-molecule-magnet behavior in triangle-assembled LnIII 6 clusters. *New J. Chem.* 43, 16639–16646. doi:10.1039/C9CN03921I

Wang, W.-M., Zhang, H.-X., Wang, S.-Y., Shen, H.-Y., Gao, H.-L., Cui, J.-Z., et al. (2015). Ligand field affected single molecule magnet behavior of lanthanide(III) dinuclear complexes with an 8-hydroxyquinoline Schiff base derivative as bridging ligand. *Inorg. Chem.* 54, 10610–10622. doi:10.1021/acs.inorgchem.5b01404

Wang, Y.-X., Xu, Q.-R., Ren, P., Shi, W., and Cheng, P. (2019c). Solvent-induced formation of two gadolinium clusters demonstrating strong magnetocaloric effects and ferroelectric properties. *Dalton Trans.* 48, 2228–2233. doi:10.1039/c9dt01427e

Wei, W., Wang, X., Zhang, K., Tian, C.-B., and Du, S.-W. (2019). Tuning the topology from fcu to pccu: Synthesis and magnetocaloric effect of metal-organic frameworks based on a hexanuclear GdIII-hydroxy cluster. *Cryst. Growth Des.* 19, 55–59. doi:10.1021/acs.cgd.8b01566

Wei, W., Xie, R.-K., Du, S.-W., Tian, C.-B., and Chai, G.-L. (2021). Synthesis, structure, magnetocaloric effect and DFT calculations of a MnII cluster-based inorganic coordination polymer. *J. Alloys Compd.* 878, 160353–160361. doi:10.1016/j.jallcom.2021.160353

Wu, D. Q., Zhang, M. L., Li, Z. Y., Zhang, P. P., Zhang, M. Y., Wu, C. F., et al. (2021). A two dimensional GdII coordination polymer based on isonicotinic acid N-oxide with large magnetocaloric effect. *J. Organomet. Chem.* 878, 1542–1546. doi:10.1002/zaac.202000193

Wu, T. X., Yao, Y., He, Q. J., Li, H. Y., Bian, H. D., and Huang, F. P. (2021). Constructing an unprecedented [MnII 38] matryoshka doll with a [Mn18(CO3)9]3− inorganic core and a magneticcaloric effect. *Chem. Commun.* 57, 2732–2735. doi:10.1039/d1cc07884k

Xu, C., Wu, Z., Fan, C., Yan, L., Wang, W., and Ji, B. (2021). Synthesis of two lanthanide clusters LnIII 4 (Gd 4 and Dy 4) with [2×2] square grid shape. *J. Rare Earths* 39, 1082–1088. doi:10.1016/j.jre.2020.08.015

Yao, X., Yan, P., An, G., Li, Y., Li, W., and Li, G. (2018). Magnetocaloric effect and slow magnetic relaxation behaviors. *New J. Chem.* 42, 3976–3984. doi:10.1039/c8nj00476a

Yin, D.-D., Chen, Q., Meng, Y.-S., Sun, H.-L., Zhang, Y.-Q., and Gao, S. (2015). Slow magnetic relaxation in a novel carboxylate/oxalate/hydroxyl bridged dysprosium layer. *Chem. Sci.* 6, 3095–3101. doi:10.1039/c5sc04911b

Zhang, L., Jung, I., Zhang, P., Guo, M., Zhao, L., Tang, J., et al. (2016). Site-resolved two-step relaxation process in an asymmetric Dy single-molecule magnet. *Chem. Eur. J.* 22, 1392–1398. doi:10.1002/chem.201503422

Zhang, L., Zhang, Y.-Q., Zhang, P., Zhao, L., Guo, M., and Tang, J. (2017). Single-molecule magnet behavior enhanced by synergic effect of single-ion anisotropy and magnetic interactions. *Inorg. Chem.* 56, 7882–7889. doi:10.1021/acs.inorgchem.7b00625

Zhang, P., Zhang, L., Lin, S.-Y., and Tang, J. (2013). Tetranuclear [MDy]2 compounds and their dinuclear [MDy] (M = Zn/Cu) building units: Their assembly, structures, and magnetic properties. *Inorg. Chem.* 52, 6595–6602. doi:10.1021/ic400620d

Zhao, W.-M., Duan, E., and Cheng, P. (2015b). An exceptionally stable 3D GdIII-organic framework for use as a magnetocaloric refrigerant. *J. Mat. Chem. A* 3, 7157–7162. doi:10.1039/c5ta0269d

Zhang, S., and Cheng, P. (2018). Coordination-cluster-based molecular magnetic refrigerants. *Chem. Rec.* 18, 2077–2126. doi:10.1002/chem.201503422

Zhang, S., Duan, E., Han, Z., Li, L., and Cheng, P. (2015a). Lanthanide coordination polymers with 4-, 4′-azobenzoic acid: Enhanced stability and magnetocaloric effect by removing guest solvents. *Inorg. Chem.* 54, 6498–6503. doi:10.1021/acs.inorgchem.5b00797

Zhao, X., Yang, J., Yao, Z., Su, Y., and Li, Y. (2019). The ferromagnetic [Li2Co2] heterometallic complexes. *Dalton Trans.* 46, 2196–2203. doi:10.1039/c7dt07891a

Zheng, T.-F., Tian, X.-M., Ji, J., Luo, H., Yao, S.-L., Liu, S.-F., et al. (2020). Two Gd2 cluster complexes with monocarboxylate ligands displaying significant magnetic entropy changes. *J. Mol. Struct.* 1200, 127094. doi:10.1016/j.molstruc.2019.127094

Zhou, M., Wu, L.-H., Wu, X.-Y., Yao, S.-L., Zheng, T.-F., Xie, X., et al. (2021). Two dinuclear GdII clusters based on isobutyric acid and nicotinic acid with large magnetocaloric effects. *J. Mol. Struct.* 1227, 129689. doi:10.1016/j.molstruc.2020.129689

Zhu, J., Wang, C., Luan, F., Liu, T., Yan, P., and Li, G. (2014). Local coordination geometry perturbed beta-diketone dysprosium single-ion magnets. *Inorg. Chem.* 53, 8895–8901. doi:10.1021/ic50501r