

Short communication

A new family of interdimer $[\text{Mn}^{\text{II}}_2\text{Ln}^{\text{III}}_2]_2$ clusters: Syntheses, structures, and magnetic properties

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ABSTRACT

A new family of isostructural Mn/Ln clusters: $[\text{Mn}^{\text{II}}_2\text{Ln}^{\text{III}}_2(\text{hmp})_6(\text{NO}_3)_4(\text{CH}_3\text{OH})_2][\text{Mn}^{\text{II}}_2\text{Ln}^{\text{III}}_2(\text{hmp})_6(\text{NO}_3)_4(\text{H}_2\text{O})_2]$ (Ln = Gd (**1**), Tb (**2**), Dy (**3**), hmpH = 2-(hydroxymethyl)pyridine) have been synthesized by the reaction of $\text{Mn}(\text{NO}_3)_2$ and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with hmpH as ligand under solvothermal conditions. Compounds **1–3** are isostructural and possess butterfly core. That the antiferromagnetic interactions within compounds **1–3** were suggested by solid-state dc magnetic susceptibility analyses. Compound **1** displays a magnetic-caloric effect (MCE) with $21.91 \text{ J Kg}^{-1} \text{ K}^{-1}$ of the entropy change at 5 K for $\Delta H = 8 \text{ T}$. Compounds **2** and **3** exhibit frequency-dependent ac susceptibility signals suggestive of slow magnetic relaxation.

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In last decade, polynuclear 3d–4f clusters as molecule based magnets have drawn intense attention for their versatile magnetic properties which can be utilized for information storage and cryogenic technology [1], especially the 3d–4f single-molecule-magnets (SMMs) have been investigated as a focus research. The SMMs are individual molecules whose magnetic properties arise from a high energy barrier to reversal of the magnetisation leading to slow magnetization relaxation below a certain blocking temperature [2]. The materials with high ground spin state and large magnetic anisotropy are considered to be potential SMMs. Compared with traditional 3d clusters which we have mainly explored, mixing the transition metal and lanthanide ion in different proportions may modulate magnetic properties as lanthanide ion often has large ground-state spin and significant single-ion anisotropy. On the other hand, magnetic cooler materials based on the magnetic-caloric effect (MCE) have emerged as attractive candidates to replace the rare and expensive [3]. He in some ultralow temperature region [3]. The MCE is associated with the change of magnetic entropy upon variation of the magnetic field, which could be applied to cooling technique via adiabatic demagnetization [4]. It is critical to possess a large spin ground state and negligible anisotropy for an ideal molecule refrigerator. Thus, heterometallic clusters with high spin Mn^{II} (d5), Gd^{III} (f7) ions and small ligands could be a good candidate for magnetic cooler materials.

For molecule-based heterometallic magnets behaving as SMMs or magnetic refrigerants, an appropriate ligand to coordinate the 3d and 4f metal ions is important. The 2-(hydroxymethyl)pyridine (hmpH) is bridging ligand, possessing a N/O bidentate chelate which could facilitate the coordination affinities of Mn and Ln metal ions, and it has

been employed for the synthesis of high-nuclearity Mn clusters, such as Mn_{10} , Mn_{12} , Mn_{18} , Mn_{21} [5]. However, only few examples of Mn/Ln clusters used hmpH as ligand have been reported to date with the four family clusters $\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_2$, $\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_4$, $\text{Mn}^{\text{III}}_8\text{Ln}^{\text{III}}_4$ and $\text{Mn}^{\text{III}}_4\text{Ce}^{\text{III}}_2$ [6]. Besides, few Mn/Ln clusters reported were yielded by the means of solvothermal reaction [7], though the metal-organic frameworks always were synthesized by this method.

In the present work, solvothermal reactions of $\text{Mn}(\text{NO}_3)_2$ with hmpH, NEt_3 and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Ln = Gd; Tb; Dy) in MeOH afforded a family of $[\text{Mn}^{\text{II}}_2\text{Ln}^{\text{III}}_2]_2$ clusters, the NEt_3 is assumed to be the proton acceptor. Different reaction conditions have been explored, such as diverse solvents and reaction temperatures. The temperatures of reactions like 90 °C, 100 °C, 110 °C, 120 °C have been explored, and in the temperature of 120 °C products with the highest yield and best quality were obtained. Using benzoic acid, propionic acid and sodium formate as the ancillary ligands yielded the same crystallized products in poor quality. It is considered that the reaction system with $[\text{Mn}_2\text{Ln}_2]_2$ is quite stable. Reactions with lighter Lanthanide ions (like La, Ce, Pr and Nd) and heavier lanthanide ions (like Er, Yb and Lu) afforded no crystallized products. We assumed that the radius of lanthanide ions affect the formation of compounds. Otherwise, it should be noted that the other solvents instead of MeOH were used, such as MeCN, while no crystallized products were yielded.

Compounds **1–3** are isostructural, therefore the structure of compound **1** will be described in detail as representative of this series. The partially labeled structure and core of compound **1** are shown in Fig. 1. Compound **1** crystallizes in the triclinic space group P-1, and the asymmetric unit contains two similar structure units of $[\text{Mn}_2\text{Gd}_2]$ with a little difference in the peripheral ligands. Each unit of Mn_2Gd_2 can be described as two face-sharing defected cubane units of two $\text{Mn}_2\text{Gd}(\mu_3-$

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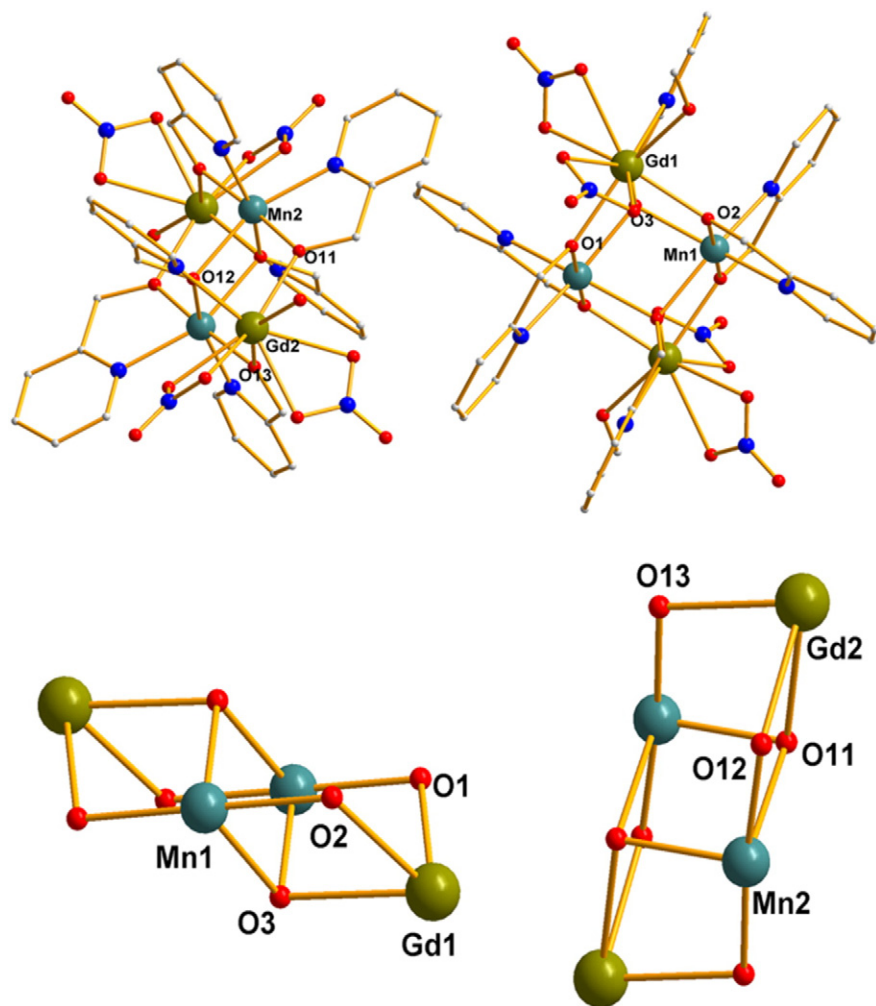


Fig. 1. (Top) Partially labeled structure of compound **1**. (Bottom) The core of compound **1**. Color scheme: Gd, green; Mn, teal; O, red; N, blue. Hydrogen atoms and crystallization solvents have been omitted for clarity.

OR)₂(μ₂-OR)₂, the two Mn₂Gd units are bridged by two μ₃-O atoms which are of two η³:η¹:μ₃ hmp⁻ groups. It should be noted that this is the first μ₃-O of hmp⁻ group bridged Mn^{II} and Ln^{III} atoms. In the core the metal atoms also held together by four μ₂-O atoms of four η²:η¹:μ₂ hmp⁻ groups. The structure of core can also be described as butterfly subunit with the Mn atoms at the body positions and the Gd atoms at the ring positions, which is common in M₄ clusters [8]. The peripheral ligation is completed by two chelating η¹:η¹:μ₁ NO₃⁻ ligands and two η¹:μ₁ H₂O or MeOH terminal groups. The oxidation states of Mn atoms and the protonation level of O atoms were established by the metric parameters and charge balance consideration, which confirmed by bond valence sum (BVS) [9] calculations (Table S3). All four Mn^{II} atoms are six coordinate, and the Mn–O distances range from 1.999 to 2.271 Å. The Gd atom is nine-coordinate and can be described as a capped square antiprism geometry using SHAPE-analysis [10] which is formed by four oxygen atoms from two NO₃⁻ counterions, two bridging μ₂-O from two η²:η¹:μ₂ hmp⁻ ligands, one nitrogen atom and one oxygen atom from a η³:η¹:μ₃ hmp⁻ group, one oxygen atom of η¹:μ₁ H₂O or MeOH group. The Gd–O bond distances range from 2.323 to 2.576 Å and the distances of Gd–N bonds are 2.552 and 2.579 Å.

The solid-state, variable-temperature dc magnetic susceptibility data of compounds **1–3** were measured in the 2–300 K temperature range with an applied field of 0.1 T. Plots of χ_MT versus T for compounds **1–3** are depicted in Fig. 2. The χ_MT versus T plots of compounds **1** and **2** show similar trends. For both compounds, the χ_MT product is nearly independent of the temperature within the span of 300 K to 48 K,

indicating very weak magnetic interactions. Upon lowering the temperature, it undergoes a slightly decrease, which display paramagnetic states. For compound **3**, the χ_MT value decreases slowly upon lowering the temperature until approximately 10 K, and then rapidly decreases.

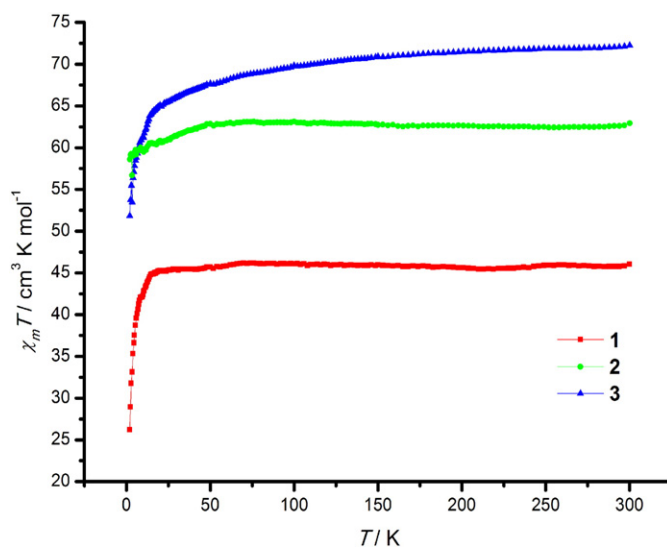


Fig. 2. The χ_MT vs. T plots for compounds **1–3** in a 0.1 T dc field.

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