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Short communication

One three-dimensional Gd(III) coordination polymer with 1,2-phenylenediacetate exhibiting ferromagnetic interaction and large magnetocaloric effect

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ABSTRACT

One three-dimensional Gd(III) coordination polymer with 1,2-phenylenediacetate (PDA^{2-}), $[Gd_2(PDA)_3(H_2O)_2]\cdot 3H_2O$ (1), has been successfully synthesized and characterized. Single crystal X-ray diffraction analysis shows that 1 consists of 1D wave Gd-based chain unit and PDA^{2-} linker. Magnetic studies suggest the presence of ferromagnetic Gd⋯Gd coupling in the 1D chain unit of 1. Meanwhile, 1 has a significant cryogenic magnetocaloric effect with the maximum $-\Delta S_m$ of 33.44 at 2 K and 7 T.

In the last two decades, lanthanide-based coordination polymers (Ln-CPs) have attracted an increasing interest because of not only their various fascinating topologies, but also their potential applications in cryogenic magnetic refrigeration and high-density information storage [1–3]. For the different local magnetic anisotropy and the large-spin multiplicity of the spin ground-state, Ln^{3+} ions have been used to construct either single-molecule magnets (SMMs) and single-chain magnets (SCMs), especially for highly anisotropic Tb- and Dy-based systems [4,5], or as low-temperature molecular magnetic coolers for isotropic Gd-containing analogues [6–8]. Specifically, magnetic refrigerants, which were appraised by magnetocaloric effect (MCE), is of great interest to chemists in recent years due to the energy-efficient and environmentally friendly advantages as well as the potential to replace the rare and expensive He-3 in ultralow-temperature refrigeration [9–11]. The MCE stands for the change of isothermal magnetic entropy ($-\Delta S_m$) and adiabatic temperature (ΔT_{ad}) in change of applied magnetic field [12,13]. To obtain a large $-\Delta S_m$, it is usually requisite that a molecular contains the features of a large spin ground state S, negligible magnetic anisotropy, low-lying excited spin states, weak coupling and a high magnetic density (or a large metal/ligand mass ratio) [14–16]. Thus, Gd-containing CPs with light and multidentate organic ligands are promising candidates because the isotropic Gd(III) ion has a large spin value ($S = 7/2$) and usually shows weak superexchange interactions, and the light ligands could promote a large metal/ligand mass ratio [13,15]. So far, a lot of Gd-based molecular clusters and coordination polymers with significant MCE have been reported under this principle [12–18]. Compared with the discrete and one-dimensional (1D) analogues, the Gd-based two- (2D) and three-dimensional (3D) CPs may be better for obtaining a promising MCE, when considering the enhanced magnetic density due to the sharing of bridging ligands between magnetic centers and that the nonmagnetic guest or solvent molecules are more difficult to trap in such structures [19–21]. However, the high-dimensional, especially for 3D Gd-based CPs with remarkable MCEs are still limited, and further systematic study is still necessary and important to find their potential for cryogenic application.

To build such material, 1,2-phenylenediacetic acid (H_2PDA), which could display various bridging modes to metal ions [22], was selected as functional ligand to react hydrothermally with Gd(III) ion. As a result, one 3D Gd-based coordination polymer, $[Gd_2(PDA)_3(H_2O)_2]\cdot 3H_2O$ (1), was obtained, and its crystal structure and magnetic properties were discussed.

Single crystal X-ray diffraction analysis reveals that compound 1 crystallizes in the monoclinic C2/c space group and has a 3D framework structure. As shown in Fig. 1a, the asymmetric unit of 1 contains one Gd(III) ion, one and a half PDA^{2-} ligands, one coordinated water molecule as well as one and a half lattice water molecules. The Gd(III) ion is nine-coordinated and has a distorted monocapped square antiprismatic

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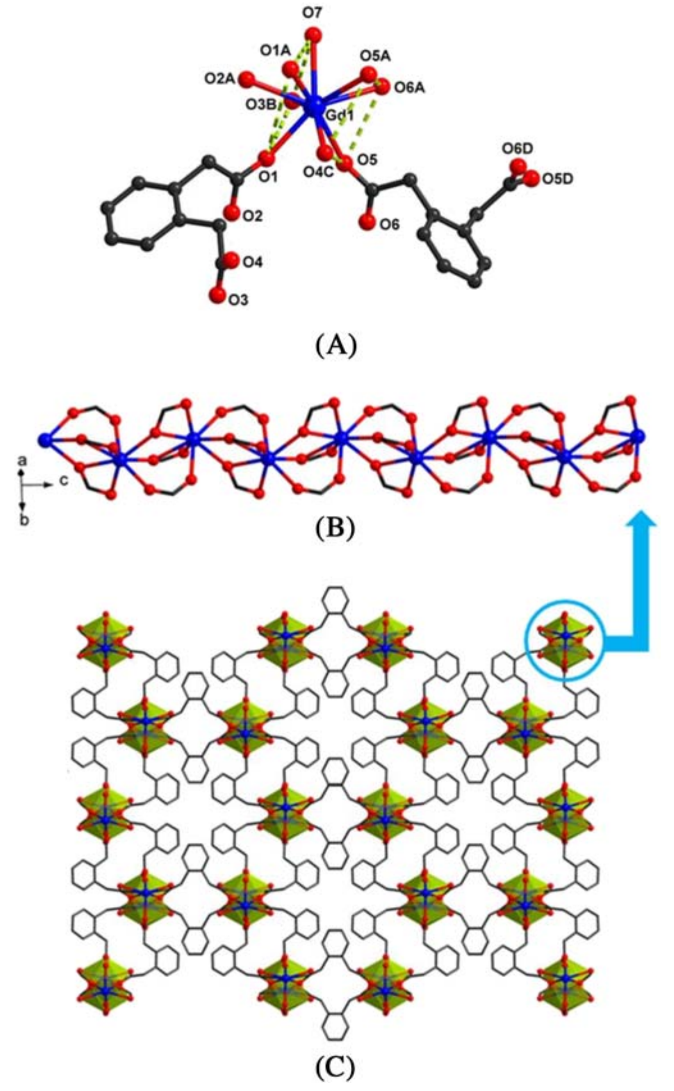
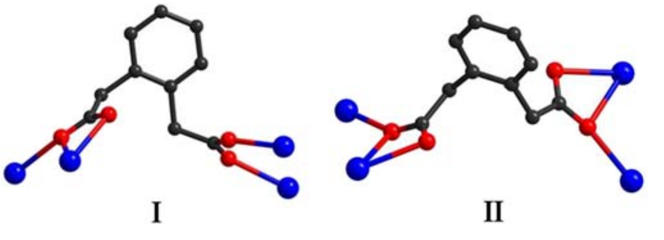


Fig. 1. (a) Coordination environment of the asymmetric Gd^{3+} ion in 1. Symmetry codes: A, x, 1-y, −0.5 + z; B, 0.5 − x, −0.5 + y, 1.5 − z; C, 0.5 − x, 1.5 − y, 1 − z; (b) The 1D chain-shaped $[Gd(COO)_3]$ building unit formed by the neighboring Gd(III) ions and carboxyl group of the PDA^{2-} ligand in 1; (c) View of the 3D framework structure of 1 along c axis.

geometry, completed by eight oxygen atoms (O1, O1A, O1A, O3B, O4C, O5, O5A and O6A) from six PDA^{2-} ligands and one oxygen atom (O7) from terminal water molecule. The bond lengths of Gd–O and the angles of O–Gd–O are in the range of 2.309(4)–2.512(5) Å and 52.24(15)–151.48(15)°, respectively, which are consistent with those in the reported Gd-containing compounds [5,11].

In the structure, the PDA^{2-} ligands adopt two coordination modes, μ_4-η^2: η^1: η^1: η^1 and μ_4-η^2: η^1: η^2: η^1 (Scheme 1). For mode I, the PDA^{2-} ligand has one tridentate bridging and one bidentate bridging carboxylate group to bridge four Gd(III) ions. The angle of Gd-O-Gd is 110.13(15)°. For mode II, the PDA^{2-} ligand uses two tridentate bridging carboxylate groups to link four Gd(III) ions with the Gd-O-Gd angle of 111.37(15)°. Around every Gd(III) ion, there are six PDA^{2-} ligands. The neighboring Gd(III) ions are connected together by one bidentate bridging carboxyl and two tridentate bridging carboxyls from three PDA^{2-} ligands (mode I and mode II) to result in a 1D wave $[Gd(COO)_3]$ chain unit (Fig. 1b). The Gd·Gd distance is 4.03(1) Å and the Gd–O–Gd–O dihedral angle is 12.78(1)° (Fig. S1). The neighboring chains are linked together by the other carboxyls of the PDA^{2-} ligands to form a 3D framework structure (Fig. 1c and S2). As shown in Fig. S3, when the lanthanide connectivity alone is considered in the structure, a 3D quasi-honeycomb arrangement is observed. For each hexagonal “honeycomb” unit, two paralleled sides are fastened by the PDA^{2-} ligands of mode II with the shortest interchain Gd·Gd distance of 9.40(1) Å. While the others are fixed by the PDA^{2-} ligands of mode I. The shortest interchain Gd···Gd distance is 7.84(1) Å.



Scheme 1. Coordinate modes of PDA^{2-} ligands in 1.

The thermal stability of 1 was studied by thermogravimetric (TG) analysis in a nitrogen atmosphere from 25 to 900 °C. As shown in Fig. S4, the TG curve of 1 displays three mass steps. In the first step, the weight loss of 1 in the range of 25–140 °C is 9.48%, which can be attributed to the loss of two coordinated and three free water molecules for each formula unit (calculated 9.18%). Then, the weight of 1 keeps constant between 140 and 334 °C, suggesting that it is thermal stable even up to 334 °C. After 334 °C, a striking weight loss was observed, indicating the complete decomposition of the framework. The experimental and computer simulated powder X-ray diffraction (PXRD) patterns of 1 are shown in Fig. S5. The PXRD pattern of the bulk sample is in good agreement with its simulated pattern from the single crystal structure, demonstrating the phase purity.

The magnetic susceptibility of 1 has been researched in the temperature range of 2–300 K under an applied direct current (dc) magnetic field of 1000 Oe (Fig. 2). At 300 K, the $\chi_M T$ value of 1 is 15.24 $cm^3\ mol^{-1}$ K, which is close to the expected value of 15.76 $cm^3\ mol^{-1}$ K calculated for two spin-only Gd(III) ($S = 7/2$, $g = 2$) ions. With lowering the temperature, the $\chi_M T$ values of 1 remain almost constant before 30 K, and then increase quickly to 20.12 $cm^3\ mol^{-1}$ K at 2 K. The data fit the Curie–Weiss law well in the temperature range of 2–300 K with Curie constant $C = 15.38\ cm^3\ K\ mol^{-1}$ and Weiss constant $\theta = 0.46$ K (Fig. S6). The positive θ value and the increase of $\chi_M T$ values suggest the presence of ferromagnetic interactions between adjacent Gd(III) ions in the 1D chain unit of 1.

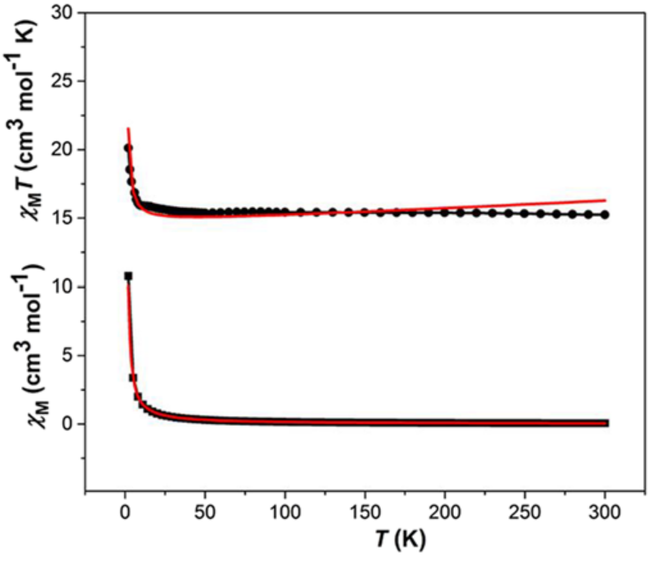


Fig. 2. Temperature dependence of the $\chi_M T$ (—■-) and χ_M (—●-) values for 1 at 1000 Oe dc magnetic field. The red solid lines represent the best fit to the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)