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Ferromagnetic interactions and slow magnetic relaxation behaviors of two lanthanide coordination polymers bridged by 2,6-naphthalenedicarboxylate ligand

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ABSTRACT

Two lanthanide-based frameworks: $\{Ln(phen)(NDA)_{1.5}(H_2O)\}_n$ (Ln=Gd(**1**), NDA=2,6-naphthalenedicarboxylate anion, phen=1,10-phenanthroline), and $\{[Dy(phen)(NDA)_{1.5}]\cdot 0.5H_2NDA\}_n$ (**2**) were structurally and magnetically characterized. Compound **1** exhibits 2D layer structure, belonging to the triclinic system with space group $P-1$, while compound **2** features a 3D framework with space group $P-1$. The magnetic studies revealed that ferromagnetic coupling existed between adjacent lanthanide ions in **1** and **2**, and frequency-dependence out-of-phase signals in the measurement of alternate-current susceptibilities were observed for **2**, albeit without reaching the characteristic maxima above 2 K, implying slow magnetic relaxation behavior in **2**. After the application of a *dc* field, good peak shapes of *ac* signal were obtained and got the energy barrier $\Delta E/k_B=29$ K and the pre-exponential factor $\tau_0=4.47\times10^{-7}$ s at 2000 Oe field; and when the dc field was in 5000 Oe, giving $\Delta E/k_B=40$ K and $\tau_0=2.82\times10^{-6}$.

1. Introduction

In recent years, scientists pay great attentions to designing and synthesizing of low-dimensional magnets including single-molecule magnet (SMM) and single-chain magnet (SCM), because of their unique properties and potential applications in high-density data storage technologies and molecular spintronics [1]. It is well-known in SMM the energy barrier (U) for the reversal of the magnetization derives from a combination of two features, namely a high-spin ground state (S) and an easy axis type of magneto-anisotropy (negative zero-field splitting parameter, D). Therefore, Co^{2+} and Mn^{3+} with significant magneto-anisotropy were frequently employed to design and construct SMMs. More recently, significant attention has been directed towards the incorporation of 4*f* ions into SMMs, in both heterometallic 3*d*/4*f* and homometallic 4*f* compounds, since many lanthanide (Ln) ions possess large unquenched orbital angular momenta which impart significant anisotropy [2]. Up to now, some impressive lanthanide-based SMMs have been reported, including 3*d*–4*f* SMMs [3–5] and lanthanide-only SMMs, [6–8] and most of them show good magnetic properties. Nevertheless, most complexes with SMM behaviors focused on the discrete clusters, and the investigations of two- or three-dimensional frameworks featuring slow magnetic relaxation were less developed [9]. Furthermore, it was also hardly observed that ferromagnetic coupling and slow magnetic relaxation coexisted in lanthanide-only compounds [10].

In this contribution, two lanthanide-only frameworks: $\{(Ln(phen)(NDA)_{1.5}(H_2O))\}_n$ (Ln=Gd (**1**), NDA=2,6-naphthalenedicarboxylate ions, phen=1,10-phenanthroline) and $\{(Dy(phen)(NDA)_{1.5})\cdot 0.5H_2NDA\}_n$ (**2**) were fabricated and structurally characterized. Magnetic measurements were performed on compounds **1–2**, and the results revealed that ferromagnetic coupling existed between adjacent lanthanide ions in **1** and **2**. Interestingly, further magnetic analysis reveals that **2** displays slow magnetic relaxation behavior.

2. Experiment section

2.1. Materials and physical measurements

All chemicals purchased were of reagent grade and used without further purification. Water used in the reactions is distilled water. The elemental analyses (C, H and N) were carried out a Perkin-Elmer elemental analyzer. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu*K*α radiation. Variable-temperature magnetic susceptibilities under 1000 Oe were performed on a Quantum Design MPMS-XL7 magnetometer, the

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alternating current (*ac*) magnetic measurements were performed on a PPMS-9 ACMS magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

2.2. Crystallographic studies

Single-crystal X-ray diffraction measurements of **1** and **2** were carried out at room temperature on a Rigaku SCXmini X-ray diffractometer equipped with graphitemonochromated MoKα radiation ($\lambda = 0.71073$ Å). Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs. All the nonhydrogen atoms were refined with anisotropic parameters while H atoms were placed in calculated positions and refined using a riding model. Crystallographic data for **1** and **2** were summarized in Table 1. Selected bond lengths and angles were summarized in Table S1.

Table 1
Crystal data and structure refinement for **1** and **2**.

Complex	1	2
Formula	$C_{30}H_{19}GdN_2O_7$	$C_{36}H_{21}DyN_2O_8$
Fw	676.72	772.05
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a (Å)	8.2095(16)	10.8237(11)
b (Å)	12.047(2)	12.1862(13)
c (Å)	12.653(2)	12.2493(12)
α (deg)	78.026(4)	94.301(3)
β (deg)	82.467(4)	106.530(4)
γ (deg)	89.128(5)	101.281(3)
V (Å^3)	1213.5(4)	1504.2(3)
Z	2	2
Dc (g cm^{-3})	1.852	1.705
μ (mm^{-1})	2.789	2.543
obs reflns	5433	5269
θ range, deg	3.02/27.48	3.05 to 25.01
F (0 0 0)	666	762
GOF on F^2	1.117	1.107
R_1/wR_2 ($I > 2\sigma(I)$)	$R_1 = 0.0691$, $wR_2 = 1348$	$R_1 = 0.0448$, $wR_2 = 0.0980$
R_1/wR_2 (all data)	$R_1 = 0.0967$, $wR_2 = 0.01501$	$R_1 = 0.0540$, $R_2 = 0.1114$

2.3. Synthesis of $\{(Ln(phen)(NDA)_{1.5}(H_2O))\}_n$ ($Ln = Gd$(1) and $\{(Dy(phen)(NDA)_{1.5}) \cdot 0.5H_2NDA\}_n$ (**2**)

A mixture of H_2NDA (0.0216 g, 0.1 mmol), 1,10-phen (0.0180 g, 0.1 mmol), $LiOH \cdot H_2O$ (0.0126 g, 0.3 mmol), 0.1 mmol $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Gd (**1**, 0.0451 g) and Dy (**2**, 0.0456 g) and water (10 mL) was sealed in a 25 mL stainless steel reactor with a Teflon-liner and heated at 180 °C for 72 h, then cooled to 100 °C in 24 h and kept at 100 °C for 24 h, then cooled to room temperature slowly. The crystals of **1** and **2** were obtained in 38% and 53% yields (based on H_2NDA), respectively. Anal. Calcd for $C_{30}H_{19}N_2O_7Gd$ (**1**): C, 53.24; H, 2.83; N, 4.14. Found: C, 53.11; H, 2.76; N, 4.08; $C_{36}H_{21}N_2O_8Dy$ (**2**): C, 56.00; H, 2.74; N, 3.63. Found: C, 56.06; H, 2.73; N, 3.58.

3. Results and discussion

3.1. Crystal structure of $\{Gd(phen)(NDA)_{1.5}(H_2O)\}_n$ (**1**)

Single crystal X-ray diffraction analysis reveals that compounds **1** crystallized in space group $P-1$, which is similar with the structure containing Eu^{3+} reported by us [11]. Two nitrogen atoms from a bidentate chelating phen ligand, five oxygen atoms from five NDA anions and one water molecule complete the coordinated sphere of Gd^{3+}, as shown in Fig. 1a. The coordination geometry for the eight-coordinated Gd^{3+} can be described as a slightly distorted square-antiprism (Fig. 1a). The Gd–N bond distance is 2.572(8) and 2.625(8) Å, respectively, and the Gd–O distances are in the range of 2.306(6)–2.415(6) Å. Four of the five ligands coordinated to the metal center act as bridges to connect with another Gd^{3+}, thus two Gd^{3+} are bridged by four carboxyl groups to form a paddle–wheel binuclear unit (Fig. 1b). The binuclear units are further connected by NDA ligands, forming a regular rhombus with the dimension of about 17 × 12 Å^2 (defined by the distances of the binuclear unit). The rhombus as a unit is further assembled into a 2D lattice structure (Fig. 2).

3.2. Crystal structure of $\{[Dy(phen)(NDA)_{1.5}] \cdot 0.5H_2NDA\}_n$ (**2**)

The self-assembly of H_2NDA with Dy(III) salt and phen gave a 3D coordination polymer **2**. The X-ray structural analysis reveals that **2** belong to triclinic crystal system with space group $P-1$. The

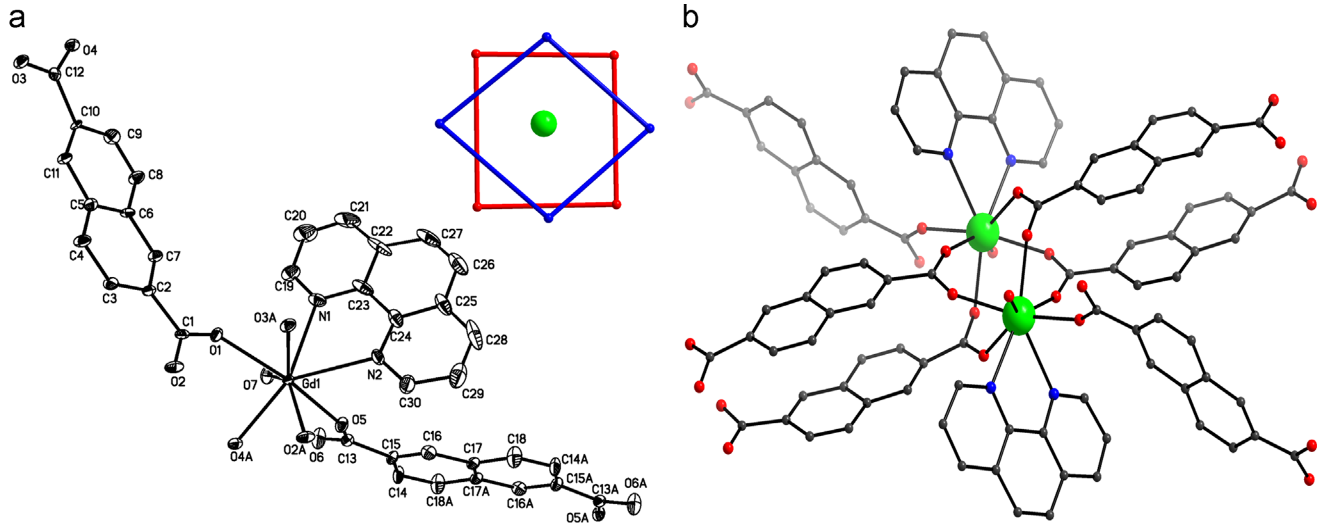

Fig. 1. (a) Molecular structure of **1**, showing the coordination environment of Gd^{3+}; (Inset) The coordination geometry of Gd^{3+} of **1**; (b) the paddle–wheel binuclear structure of compound **1** bridged by carboxylic oxygen atoms. Color codes: red, O; gray, C; green, Gd. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)