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Original article

Two lanthanide(III)–copper(II) chains based on $[Cu_2Ln_2]$ clusters exhibiting high stability, magnetocaloric effect and slow magnetic relaxation

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ABSTRACT

Two 3*d*–4*f* heterometallic one-dimensional chains with neutral 4,4′-bipyridine ligands as linkers and $[Cu_2Ln_2]$ clusters (Ln = Gd for **1**, Dy for **2**) as nodes have been hydrothermally synthesized and structurally characterized. Magnetic studies indicate that complex **1** exhibits a relatively large magnetocaloric effect, with an entropy change $-\Delta S_m^{max} = 24.8\ J\ kg^{-1}\ K^{-1}$, whilst, complex **2** features slow magnetic relaxation at low temperature.

1. Introduction

Over the last decades, investigating magnetic properties of 3*d*–4*f* heterometallic complexes has witnessed flourishing development [1]. Because of their differences in electron clouds (*d* and *f* orbitals), coordination geometries/numbers, and coordination preferences to donor atoms (N or O-atom), huge effort has been paid to integrating such different spin centers to fabricate optimized materials that could combine the superiority of both of them for practical applications [2].

Recently, molecular magnetic cryogenic materials based on magnetocaloric effect (MCE), as an alternative to the expensive and rare He-3 in some ultra-low temperature cooling applications, have received great attention because of not only their high-efficient, energy-saving and environmentally friendly nature, but also their synthetic tunability and tailorability [3]. Owing to its large spin ground state *S*, negligible magnetic anisotropy ($D_{ion} = 0$) and low-lying excited spin states, Gd^{III} ion is a competitive candidate to construct desirable molecular magnetic coolers [4]. Additionally, due to the efficient shielding of the 4*f* orbitals of the Gd^{III} ion, the magnetic exchange interactions of Gd^{III}–Gd^{III}/3d–Gd^{III} are usually expected to be weak, which is also favorable to enhance MCE [4]. Therefore, Gd-containing complexes attract intensive interest and have been extensively exploited [4,5].

On the other hand, since slow relaxation of magnetization and hysteresis loops were first discovered in $\{Mn_{12}\}$ cluster, considerable attention has been focused on the study of single-molecule magnets (SMMs) in molecular materials [6]. It is known that energy barriers for the slow magnetic relaxation are mainly dependent on the spin ground state and uniaxial magnetic anisotropy. Previous publications have shown that large spin ground state and significant uniaxial anisotropy are hard to be achieved simultaneously in pure 3*d* complexes [7]. In contrast, the incorporation of lanthanide ions into 3*d*–4*f* systems provides the possibilities to give rise to high spin and/or large anisotropy, to some extent, which may overcome the drawback of 3*d* homometallic ones. Recently, assembling SMMs into extended structures with the goal of investigating the effects of inter-SMMs magnetic interactions has been reported, which shed new light on the study of SMMs [8]. To the best of our knowledge, most of the corresponding cases are based on the homometallic SMMs, like trinuclear $\{Mn_3\}$, tetranuclear $\{Mn_4\}$, and hexanuclear $\{Mn_6\}$ [8]. Cases based on 3*d*–4*f* heterometallic SMMs are still limited [9].

Although notable progress has been made in the synthetic and theoretic approaches [10], the design and synthesis of 3*d*–4*f* magnetic materials are still a challenging task for synthetic chemists due to the fact that the assembly process at a molecular level does not fully follow the will of chemists. When building

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3*d*–4*f* magnetic materials, one of the basic principles needed to be considered is the distinct affinity and/or preference of the 3*d* and 4*f* metal ions to N/O-donors [11]. In terms of the hard-soft acid base theory, 3*d* transition metal ions have a strong tendency to bind to N-donor and 4*f* lanthanide ions with high coordination numbers and variable coordination geometries preferentially bond to O-donor [12]. In this work, we utilized a dicarboxylic acid phthalic acid (H_2pta) as main ligand and 4,4′-bipyridine (4,4′-bipy) as co-ligand, to synthesize 3*d*–4*f* complexes based on the following considerations: (1) The two carboxyl groups of H_2pta may be completely or partially deprotonated, yielding a variety of coordination modes, which is helpful to form interesting structures; (2) The phenyl group may exhibit additional steric hindrance, which is profitable to produce low dimensional complexes; (3) Neutral co-ligand 4,4′-bipy as a linker can reduce the competition between phthalic anions and 4,4′-bipy when binding metal ions, which is also beneficial to the process of assembly. Herein, we report the synthesis, structures, and magnetic properties of two cluster-based 1D chains, $[\mathrm{CuLn(pta)_2(Hpta)(4,4'\text{-}bipy)_{0.5}(H_2O)}]_n$ (Ln = Gd for **1**; Ln = Dy for **2**). Blue block crystals of **1** and **2** were obtained by the hydrothermal reaction of $Cu(NO_3)_2{\cdot}3H_2O$, $Ln(NO_3)_3{\cdot}6H_2O$, H_2pta and 4,4′-bipy at 140 °C. Magnetic measurements revealed that these two isostructural heterometallic chains exhibited different magnetic properties, depending on the different anisotropies of the lanthanide spin carriers: complex **1** displayed a relatively large MCE, with an entropy change $-\Delta S_{\mathrm{m}}^{\mathrm{max}} = 24.8$ J kg^{-1} K^{-1} (T = 3 K, ΔH = 7 T), while complex **2** exhibited slow magnetic relaxation at low temperature.

2. Experimental

2.1. Materials and measurements

All chemicals were commercially purchased and used without further purification. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). The PXRD spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the PXRD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org. IR spectra were measured in the range of 400–4000 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German). Magnetic data were measured by a Quantum Design MPMS superconducting quantum interference device (SQUID). Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

2.2. Synthesis of complexes 1 and 2

$[\mathrm{CuGd(pta)_2(Hpta)(4,4'\text{-}bipy)_{0.5}(H_2O)}]_n$ (**1**). A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.0483 g, 0.20 mmol), $Gd(NO_3)_3{\cdot}6H_2O$ (0.181 g, 0.40 mmol), H_2pta (0.199 g, 1.2 mmol), 4,4′-bipy (0.125 g, 0.8 mmol) and H_2O (10 mL) were placed in a Teflon-lined stainless container, then heated to 140 °C and kept at that temperature for 48 h, finally cooled to 30 °C. Yield: *ca.* 60% with respect to Cu. Elemental analysis (%): Calcd. for $C_{29}H_{19}CuGdNO_{13}$ (810.25): C, 42.95; H, 2.34; N, 1.73. Found: C, 42.65; H, 2.83; N, 1.56. IR (KBr pellets, cm^{-1}): 3521(w), 3406(w), 1624(s), 1573(s), 1539(s), 1488(m), 1425(s), 1390(s), 1305(m), 1289(m), 1220(w), 1143(w), 1083(w), 973(w), 879(w), 841(w), 803(w), 773(w), 752(m), 727(w), 701(w), 684(w), 645(w), 531(w).

$[\mathrm{CuDy(pta)_2(Hpta)(4,4'\text{-}bipy)_{0.5}(H_2O)}]_n$ (**2**). Complex **2** was prepared by a similar procedure as described for **1**, but $Dy(NO_3)_3{\cdot}6H_2O$ (0.183 g, 0.40 mmol) was used instead of $Gd(NO_3)_3{\cdot}6H_2O$. Yield: *ca.* 65% with respect to Cu. Elemental analysis (%): Calcd. for $C_{29}H_{19}CuDyNO_{13}$ (815.50): C, 42.67; H, 2.33; N, 1.72. Found: C, 42.32; H, 2.70; N, 1.52. IR (KBr pellets, cm^{-1}): 3518(m), 3416(m), 1629(s), 1573(s), 1539(s), 1493(m), 1420(s), 1395(s), 1305(m), 1289(m), 1220(w), 1143(w), 1083(w), 973(w), 879(w), 841(w), 803(w), 773(w), 752(m), 727(w), 701(w), 684(w), 645(w), 531(w).

Table 1
Crystallographic data and refinement details for **1** and **2**.

	1	**2**
Formula	$C_{29}H_{19}CuGdNO_{13}$	$C_{29}H_{19}CuDyNO_{13}$
F_w	810.25	815.50
T/K	293(2)	293(2)
λ/Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a/Å	10.893(2)	10.779(2)
b/Å	11.639(2)	11.507(2)
c/Å	12.166(2)	11.991(2)
α/°	65.35(3)	65.16(3)
β/°	78.14(3)	78.17(3)
γ/°	79.71(3)	79.58(3)
V/Å^3	1364.5(5)	1313.5(5)
Z	2	2
D_c/g cm^{-3}	1.972	2.062
μ/mm^{-1}	3.264	3.710
F (0 0 0)	794	798
Total reflns	14,580	13,975
Unique reflns	6247	6012
R_1 [$I > 2\sigma(I)$][a]	0.0371	0.0419
wR_2 (all data)[b]	0.0741	0.0963
GOF on F^2	1.004	1.151

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR_2 = \left\{ \frac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma w(F_o^2)^2} \right\}^{1/2}$.

2.3. X-ray diffraction studies

The single-crystal X-ray diffraction data of **1** and **2** were collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The program *CrystClear* [13] was used for the integration of the diffraction profiles. Both the structures were solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied by using the SADABS program) [14]. Metal atoms in each complex were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. All hydrogen atoms of organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of water molecules in **1** and **2** were added by the difference Fourier maps and refined with suitable constrains. Detailed crystallographic data are summarized in Table 1 and the selected bond lengths and angles are given in Tables S2 and S3 in Supporting information.

3. Results and discussion

3.1. Powder X-ray diffraction (PXRD) and the thermogravimetric analyses (TGA)

The phase purity of crystalline powders of complexes **1** and **2** was confirmed by comparing experimental PXRD peaks with the simulated PXRD peaks from the single-crystal X-ray data (Fig. 1).