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Synthesis, structures and magnetocaloric properties of two dinuclear Gd^{III} clusters derived from monocarboxylate ligands

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ABSTRACT

Two dinuclear Gd^{III} clusters, namely $[Gd_2(piv)_6(phen)_2]$ (**1**) and $\{[Gd_2(2\text{-TCA})_6(phen)_2]\cdot 2H_2O\}$ (**2**) (Hpiv = pivalic acid, 2-TCA = Thiophene-2-carboxylic acid and phen = 1,10-phenanthroline), have been synthesized under hydrothermal conditions. Complex **1** features dinuclear structure with two *syn-syn*-μ_2-η^1:η^1 carboxylates bridging, while **2** exhibits dinuclear structure bridged by four carboxylates with *syn-syn*-μ_2-η^1:η^1 and *syn-syn*-μ_2-η^1:η^2 modes. Magnetic studies indicate that weak antiferromagnetic interactions between adjacent Gd^{III} ions exist in **1** and **2**. They exhibit relatively large magnetocaloric effects with $-\Delta S_m^{max}$ = 19.1 J kg^{-1} K^{-1} and 21.8 J kg^{-1} K^{-1} for ΔH = 70 kOe, respectively, influenced by relatively high magnetic density and weak magnetic interaction.

1. Introduction

Recently, magnetic refrigeration technology has attracted much attention from chemist, physicist and materials scientist due to the severe situation of energy shortage and environmental pollution [1–3]. The most important part of the magnetic refrigeration technology is the preparation of magnetorefrigerant with a large magnetocaloric effect (MCE) [4,5]. The MCE can be described by the isothermal magnetic entropy change (ΔS_m) [6,7], therefore, considerable interest has been focused on the study of molecular magnetorefrigerants because of the unique advantages of cropping structures and regulated functionalities, and the hope of replacing rare ^{3}He in ultralow-temperature refrigeration [8–10]. As an important part of high-performance and easy-accessible molecular magnetic coolers, Gd^{III} clusters have received much more attention considering the inherent properties of Gd^{III} ion, such as negligible magnetic anisotropy (D), large spin ground state (S) and low-lying excited spin states, and possible high magnetic density [11–13]. Additionally, weak interactions usually occur in the Gd^{III} clusters for the shielding of the f orbitals and the consequent poor overlap with bridging ligand orbitals, which is profitable to enhance the MCE [14,15].

On account of the synthetic challenge of high-nuclearity Gd^{III} clusters, the MCE exploration of low-nuclearity Gd^{III} clusters has become more active [16,17]. According to the reported literatures, the ΔS_m is influenced by magnetic density (M_W/N_{Gd} ratio) and magnetic interaction (θ) between Gd^{III} ions [18,19]. Therefore, the use of light organic molecules and suitable magnetic exchange channels should be necessary. Organic carboxylates with various coordination modes could participate in the coordination of molecule-based magnetic complexes [20–22]. Simple monocarboxylate ligands such as formate and acetate have been extensively used to construct Gd^{III}-based magnetorefrigerants, however, Gd^{III} clusters derived from sterically hindered monocarboxylates have less been studied [13,23–25].

Gadolinium salts are often employed as metal ion source for the construction of Gd-based complexes. Compared with gadolinium salts, $Gd(OH)_3$ and Gd_2O_3 could be used as slow-release metal ion sources and pH regulators under hydrothermal conditions to obtain some unique Gd^{III} cluster complexes [13,16]. Thus, Gd_2O_3 were selected as metal ion sources, while sterically hindered pivalic acid (Hpiv) and thiophene-2-carboxylic acid (2-TCA) were used as primary ligands (Scheme 1).

As an extension of our previous studies on molecule-based magnetorefrigerants [18,19,26,27], we report herein two

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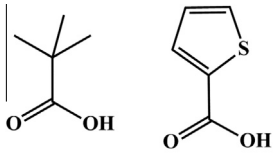

Hpiv 2-TCA

Scheme 1. The primary ligands used for the construction of **1** and **2**.

dinuclear Gd^{III} clusters derived from monocarboxylates, namely $[Gd_2(piv)_6(phen)_2]$ (**1**) and $\{[Gd_2(2\text{-TCA})_6(phen)_2]\cdot 2H_2O\}$ (**2**) (phen = 1,10-phenanthroline). Magnetic investigations indicate weak antiferromagnetic (AF) couplings between Gd^{III} ions exist in the cluster for **1** and **2**, and they display large MCEs with $-\Delta S_m^{max}$ = 19.09 and 21.80 J kg^{-1} K^{-1} for ΔH = 70 kOe, respectively.

2. Experimental

2.1. Materials and general methods

All chemicals were of reagent grade and used as purchased without further purification. Elemental analyses (C, H and N) were carried out with a Perkin–Elmer 240C analyzer. The X-ray powder diffraction (PXRD) spectra were recorded on an Empyrean (PANalytical B.V.) diffractometer 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 Bruker ALPHA FT-IR spectrometer using KBr pellets (Bruker, Germany). Magnetic data were measured by a Quantum Design MPMS-XL-7 SQUID magnetometer. 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*

Synthesis of $[Gd_2(piv)_6(phen)_2]$ (**1**): A mixture of Gd_2O_3 (181 mg, 0.5 mmol), Hpiv (204 mg, 2 mmol), 1,10-phenanthroline monohydrate (90 mg, 0.5 mmol) and H_2O (10 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 160 °C. After maintained for 72 h, the reaction vessel was cooled to room temperature in 12 h. Colorless crystals were collected with *ca.* 20% yield based on Hpiv. Elemental analysis (%) Calcd. for $C_{54}H_{70}Gd_2N_4O_{12}$: C, 50.60; H, 5.50; N, 4.37. Found: C, 50.48; H, 5.65; N, 4.48. FT-IR (KBr pellets, cm^{-1}): 3735*w*, 3447*w*, 3065*w*, 2959*s*, 2921*m*, 2866*m*, 2363*w*, 1621*m*, 1584*vs*, 1517*vs*, 1485*s*, 1424*vs*, 1364*m*, 1297*w*, 1226*m*, 1140*w*, 1099*w*, 1029*w*, 989*w*, 938*w*, 895*m*, 858*m*, 799*m*, 729*m*, 676*w*, 640*w*, 610*m*, 562*m*, 424*w*.

Synthesis of $\{[Gd_2(2\text{-TCA})_6(phen)_2]\cdot 2H_2O\}$ (**2**): The similar procedure has been used to synthesize this complex except that Hpiv (204 mg, 2 mmol) was replaced by 2-TCA (256 mg, 2 mmol). Colorless crystals were collected with *ca.* 22% yield based on Gd^{III}. Elemental analysis (%) Calcd. for $C_{54}H_{38}Gd_2N_4O_{14}S_6$: C, 44.01; H, 2.60; N, 3.80. Found: C, 44.08; H, 2.65; N, 3.67. FT-IR (KBr pellets, cm^{-1}): 3502*w*, 3437*w*, 3104*w*, 3070*w*, 1634*m*, 1575*s*, 1522*s*, 1430*vs*, 1394*s*, 1345*m*, 1225*w*, 1121*m*, 1034*w*, 850*m*, 814*w*, 780*m*, 718*w*, 660*w*, 422*w*.

2.3. X-ray crystallographic

The single-crystal X-ray diffraction data of **1** and **2** were collected on a Rigaku SCX-mini diffractometer with Mo Kα radiation

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

	1	2
Formula	$C_{54}H_{70}Gd_2N_4O_{12}$	$C_{54}H_{38}Gd_2N_4O_{14}S_6$
M_r	1281.64	1473.74
T (K)	293(2)	296(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.326(2)	10.9228(3)
b (Å)	12.028(2)	11.5556(3)
c (Å)	12.787(3)	12.0694(3)
α (°)	113.04(3)	94.214(10)
β (°)	99.89(3)	106.181(10)
γ (°)	96.86(3)	109.276(10)
V (Å^3)	1409.0(5)	1357.82(6)
ρ (g cm^{-3})	1.510	1.802
Z	1	1
$F(000)$	646	726
μ (mm^{-1})	2.394	2.723
Collected reflections	12295	37590
Unique reflections	4969	4781
R_{int}	0.0233	0.0194
R_1[a]/wR_2[b] [I > 2σ(I)]	0.0245/0.0614	0.0442/0.1302
Goodness-of-fit (GOF) on F^2	1.100	1.161

[a] $R = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$.
[b] $Rw = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

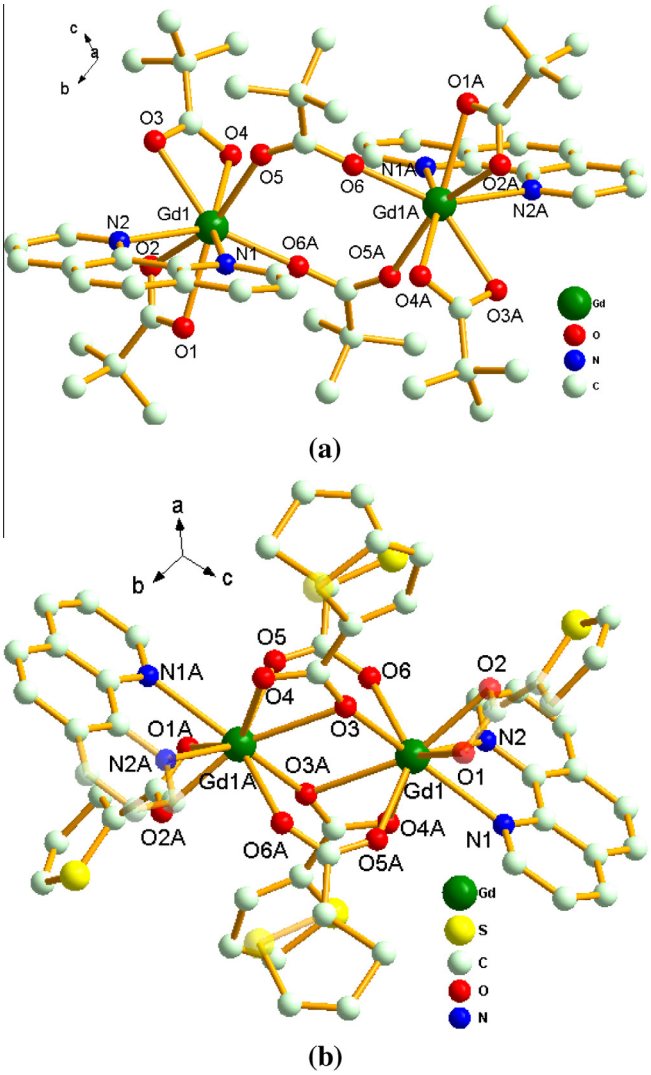

Fig. 1. View of the molecular structures of **1** (a) and **2** (b).