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Syntheses, crystal structures and properties of two novel lanthanide-carboxylate polymeric complexes

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Two novel lanthanide–carboxylate polymeric complexes containing nine-coordinate lanthanide metal centers, $[Nd(H_2btec)_{1/2}(btec)_{1/2}(H_2O)]_n$ (**1**), $[Gd(Hbtec)]_n$ (**2**), have been prepared by hydrothermal reaction of $NdCl_3\cdot6H_2O$ or $Gd(NO_3)_3\cdot6H_2O$ with 1,2,4,5-benzenetetracarboxylic dianhydride. Complex **1** crystallizes in triclinic space group $P\bar{1}$, with $a = 6.3822(5)$, $b = 9.3323(7)$, $c = 9.5201(7)$ Å, $\alpha = 88.422(2)$, $\beta = 74.446(2)$, $\gamma = 76.647(10)°$, $V = 531.13(7)$ Å^3 and $Z = 2$. Complex **2** crystallizes in triclinic space group $P\bar{1}$, with $a = 7.2325(7)$, $b = 7.9946(8)$, $c = 8.7833(9)$ Å, $\alpha = 65.4120(10)$, $\beta = 86.272(2)$, $\gamma = 84.377(2)°$; $V = 459.42(8)$ Å^3 and $Z = 2$. The two complexes have high thermal stability and are stable up to 400 °C. Magnetic susceptibility measurements for **1** and **2** are consistent with the occurrence of antiferromagnetic interactions through carboxylate bridges.

Introduction

The solid state assembly of metal–organic polymers has attracted increasing attention due to the potential applications in non-linear optics, magnetism and molecular recognition.[1] With the aim of investigating the nature of the magnetic exchange interactions between 3d and 4f metal ions in magnetic materials, many polymeric complexes comprising of lanthanide and transition metal ions have been studied in the past two decades.[2–4] Recently, polymeric complexes only constructed by lanthanide centers have been reported in multicarboxylates[5–8] or hybrid nitrogen–oxygen ligand systems,[9–11] however, most of such work focused on studying the framework structures of the complexes rather than on magnetic properties.[12] As known, benzoic multicarboxylate ligands are versatile building blocks for the architectures of polymeric structures due to their variety of bridging abilities,[13–15] and a series of interesting lanthanide polymers have been obtained by employing benzoic multicarboxylate ligands.[5] Our previous work has proved that 1,2,4,5-benzenetetracarboxylic acid (H_4btec) is a good building block for the construction of lanthanide polymers through full or partial deprotonation of its carboxylic groups. Through hydrothermal reactions of 1,2,4,5-benzenetetracarboxylic dianhydride with Ln(III), we have obtained several open framework structures containing channels with guest water molecules.[16] The successful isolation of these complexes prompted us to assembly lanthanide complexes containing magnetic centers using H_4btec. We selected Nd(III) and Gd(III) as the lanthanide ions and hoped to obtain novel polymers with interesting structures and magnetic properties. This paper reports the synthesis and characterization of two magnetic complexes, $[Nd(H_2btec)_{1/2}(btec)_{1/2}(H_2O)]_n$ (**1**) and $[Gd(Hbtec)]_n$ (**2**).

Experimental

Preparation of complexes

$[Nd(H_2btec)_{1/2}(btec)_{1/2}(H_2O)]_n$ (1). A mixture of $NdCl_3\cdot6H_2O$ (0.09 g, 0.25 mmol), 1,2,4,5-benzenetetracarboxylic dianhydride (0.1 g, 0.5 mmol) and H_2O (16.0 ml) in a mol ratio of *ca.* 1 : 2 : 3560 was sealed in a 25 ml stainless-steel reactor with Teflon liner and directly heated to 170 °C and kept at 170 °C for 3 days, then cooled to room temperature during 5 hours. Light gray block-like crystals of **1** were obtained in 52% yield. Anal. Calc. for $C_{10}H_5NdO_9$: C, 27.90; H, 1.21%; found: C, 27.87; H, 1.26%. IR (KBr, cm^{-1}): 3491(s), 2804(m), 2644(m), 1668(vs), 1556(vs), 1394(vs), 1296(s), 1124(s), 879(s), 845(s), 791(s), 588(m).

$[Gd(Hbtec)]_n$ (2). A mixture of $Gd(NO_3)_3\cdot6H_2O$ (0.11 g, 0.25 mmol), 1,2,4,5-benzenetetracarboxylic dianhydride (0.1 g, 0.5 mmol) and H_2O (16 ml) in a mole ratio of *ca.* 1 : 2 : 3560 was sealed in a 25 ml stainless-steel reactor with Teflon liner and directly heated to 170 °C and kept at 170 °C for 3 days, then cooled to room temperature during 5 hours. Colorless prism-like crystals of **2** were obtained in 35% yield. Anal. Calc. for $C_{10}H_3GdO_8$: C, 29.39; H, 0.73%; found: C, 29.34; H, 0.81%. IR (KBr, cm^{-1}): 2783(s), 2505(s), 1811(w), 1676(vs), 1575(vs), 1493(vs), 1392(vs), 1342(vs), 1255(vs), 1184(s), 1005(m), 879(m), 854(s), 806(s), 548(s).

Crystallography

The intensity data of **1** and **2** were collected on a SIEMENS SMART CCD diffractometer with graphite-monochromated MoKα (λ = 0.71073 Å) radiation at room temperature. All absorption corrections were performed using the SADABS program.[17] The structures were solved by direct methods[18] and refined on F^2 by full-matrix least squares using the SHELXTL-97 program package[19] on a legend 586 computer. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å). The crystallographic data of complexes **1** and **2** are listed in Table 1 with selected bond lengths and angles in Tables 2 and 3.

CCDC reference numbers 173159 for **1** and 173158 for **2**.

See http://www.rsc.org/suppdata/dt/b1/b109985j/ for crystallographic data in CIF or other electronic format.

Physical measurements

The elementary analyses were performed in this institute. Thermal gravimetric analysis was performed on a Delta Series TGA7 instrument. Variable-temperature magnetic susceptibility data for polycrystalline samples of complexes **1** and **2** were obtained in an external field of 10.0 kG on a Quantum Design PPMS Model 6000 magnetometer from 300 to 4 K.

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Table 1 The crystallographic data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{10}H_5O_9Nd$	$C_{10}H_3O_8Gd$
M_w	413.38	408.37
Space group	$P\bar{1}$	$P\bar{1}$
T/°C	293	293
a/Å	6.3822(5)	7.2325(7)
b/Å	9.3323(7)	7.9946(8)
c/Å	9.5201(7)	8.7833(9)
α/°	88.422(2)	65.4120(10)
β/°	74.446(2)	86.272(2)
γ/°	76.647(10)	84.377(2)
V/Å^3	531.13(7)	459.42(8)
Z	2	2
D_c/g cm^{-3}	2.585	2.952
λ/Å	0.71073	0.71073
μ/mm^{-1}	4.937	7.260
$R1$	0.0281	0.0432
$wR2$	0.0727	0.1057

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Nd–O(4)#1	2.376(3)	C(7)–O(1)	1.216(6)
Nd–O(3)#2	2.430(3)	C(7)–O(2)	1.314(6)
Nd–O(9)	2.458(4)	C(8)–O(3)	1.267(6)
Nd–O(6)	2.493(3)	C(8)–O(4)	1.252(6)
Nd–O(5)#3	2.505(3)	C(9)–O(5)	1.272(6)
Nd–O(8)#4	2.528(3)	C(9)–O(6)	1.257(6)
Nd–O(1)	2.528(3)	C(10)–O(7)	1.242(6)
Nd–O(7)#4	2.558(3)	C(10)–O(8)	1.248(6)
Nd–O(5)	2.599(3)		
O(4)#1–Nd–O(3)#2	76.96(12)	O(6)–Nd–O(1)	158.54(12)
O(4)#1–Nd–O(9)	139.98(14)	O(5)#3–Nd–O(1)	85.70(12)
O(3)#2–Nd–O(9)	66.75(13)	O(8)#4–Nd–O(1)	70.72(11)
O(4)#1–Nd–O(6)	81.07(12)	O(4)#1–Nd–O(7)#4	73.40(13)
O(3)#2–Nd–O(6)	72.28(12)	O(3)#2–Nd–O(7)#4	137.29(11)
O(9)–Nd–O(6)	102.48(14)	O(9)–Nd–O(7)#4	146.27(13)
O(4)#1–Nd–O(5)#3	145.42(12)	O(6)–Nd–O(7)#4	73.32(11)
O(3)#2–Nd–O(5)#3	136.54(11)	O(5)#3–Nd–O(7)#4	80.83(11)
O(9)–Nd–O(5)#3	70.08(13)	O(8)#4–Nd–O(7)#4	50.93(11)
O(6)–Nd–O(5)#3	113.35(10)	O(1)–Nd–O(7)#4	121.59(11)
O(4)#1–Nd–O(8)#4	72.42(12)	O(4)#1–Nd–O(5)	128.18(12)
O(3)#2–Nd–O(8)#4	142.26(12)	O(3)#2–Nd–O(5)	101.92(11)
O(9)–Nd–O(8)#4	130.26(14)	O(9)–Nd–O(5)	77.29(14)
O(6)–Nd–O(8)#4	122.73(11)	O(6)–Nd–O(5)	51.13(10)
O(5)#3–Nd–O(8)#4	73.49(12)	O(5)#3–Nd–O(5)	63.13(13)
O(4)#1–Nd–O(1)	88.51(13)	O(8)#4–Nd–O(5)	114.19(11)
O(3)#2–Nd–O(1)	87.16(12)	O(1)–Nd–O(5)	143.24(12)
O(9)–Nd–O(1)	73.85(14)	O(7)#4–Nd–O(5)	74.48(11)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 2$, $-z$. #2 $x + 1$, $y - 1$, z. #3 $-x$, $-y + 1$, $-z + 1$. #4 x, $y + 1$, z.

Table 3 Selected bond lengths (Å) and angles (°) for **2**

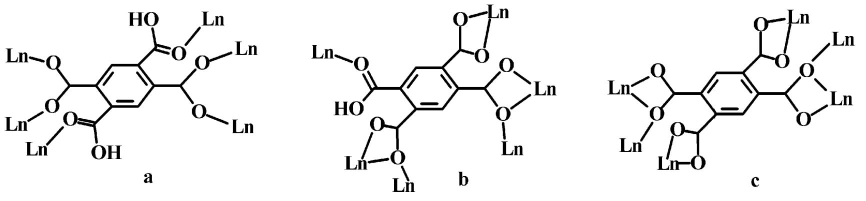
Gd–O(8)#1	2.363(6)	C(1)–O(1)	1.252(11)
Gd–O(1)#2	2.374(6)	C(1)–O(2)	1.267(12)
Gd–O(5)#3	2.432(6)	C(4)–O(3)	1.278(12)
Gd–O(7)#4	2.445(7)	C(4)–O(4)	1.240(11)
Gd–O(4)#5	2.451(7)	C(7)–O(5)	1.208(12)
Gd–O(3)#5	2.483(7)	C(7)–O(6)	1.283(14)
Gd–O(2)	2.485(7)	C(9)–O(7)	1.240(12)
Gd–O(8)#4	2.547(6)	C(9)–O(8)	1.285(12)
Gd–O(1)	2.588(6)		
O(8)#1–Gd–O(1)#2	156.4(2)	O(7)#4–Gd–O(4)#5	153.7(3)
O(8)#1–Gd–O(5)#3	84.9(2)	O(8)#1–Gd–O(3)#5	81.0(2)
O(1)#2–Gd–O(5)#3	86.3(2)	O(1)#2–Gd–O(3)#5	75.5(2)
O(8)#1–Gd–O(7)#4	119.0(2)	O(5)#3–Gd–O(3)#5	72.4(2)
O(1)#2–Gd–O(7)#4	78.9(2)	O(7)#4–Gd–O(3)#5	138.0(2)
O(5)#3–Gd–O(7)#4	73.2(2)	O(4)#5–Gd–O(3)#5	52.6(2)
O(8)#1–Gd–O(4)#5	84.0(2)	O(8)#1–Gd–O(2)	78.1(2)
O(1)#2–Gd–O(4)#5	83.2(2)	O(1)#2–Gd–O(2)	117.1(2)
O(5)#3–Gd–O(4)#5	124.9(2)	O(5)#3–Gd–O(2)	152.8(2)
O(7)#4–Gd–O(2)	96.6(2)	O(2)–Gd–O(8)#4	80.9(2)
O(4)#5–Gd–O(2)	74.6(2)	O(8)#1–Gd–O(1)	127.5(2)
O(3)#5–Gd–O(2)	124.7(2)	O(1)#2–Gd–O(1)	66.6(2)
O(8)#1–Gd–O(8)#4	67.2(3)	O(5)#3–Gd–O(1)	146.8(2)
O(1)#2–Gd–O(8)#4	130.2(2)	O(7)#4–Gd–O(1)	82.7(2)
O(5)#3–Gd–O(8)#4	72.9(2)	O(4)#5–Gd–O(1)	472.5(2)
O(7)#4–Gd–O(8)#4	52.1(2)	O(3)#5–Gd–O(1)	115.7(2)
O(4)#5–Gd–O(8)#4	145.5(2)	O(2)–Gd–O(1)	50.8(2)
O(3)#5–Gd–O(8)#4	134.3(2)	O(8)#4–Gd–O(1)	109.7(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z + 2$. #2 $-x$, $-y$, $-z + 1$. #3 $x + 1$, $y + 1$, $z - 1$. #4 x, $y + 1$, $z - 1$. #5 $x + 1$, y, z.

Results and discussions

Crystal structures

[Nd(H_2btec)$_{1/2}$(btec)$_{1/2}$(H_2O)]$_n$ (1). Single crystal X-ray analysis reveals complex **1** is a three-dimensional framework containing nine-coordinate neodymium centers; the local environment around Nd(III) ion is depicted in Fig. 1(a). The observation of an absorption peak at 1668 cm^{-1} for –COOH in the IR spectrum indicates the presence of protonated carboxylic groups in the complex, and structural data (see below) show there are two kinds of carboxylate ligands, H_2btec^{2-} and btec^{4-}, in the structure. H_2btec^{2-} acts as μ_6-bridge to link six neodymium atoms, in which each protonated carboxylic group coordinates to one neodymium atom through carbonyl oxygen atoms, while each deprotonated carboxylic group bridges two neodymium atoms (Scheme 1(a)); btec^{4-} also acts as μ_6-bridge linking six neodymium atoms, in which two *para*-carboxylate groups adopt a bidentate chelating mode coordinating to one neodymium atom while the other two *para*-carboxylate groups adopt a bidentate chelating-bridging mode connecting two neodymium atoms (Scheme 1(c)). Thus, the neodymium atom is coordinated by nine oxygen atoms, three from H_2btc^{2-}, five from btec^{4-} and one from a coordinated water molecule, the Nd–O distances range from 2.376(3) to 2.599(3) Å and the nearest Nd ··· Nd distance is 4.350(3) Å, indicating the absence of a direct metal–metal interaction. The C–O distances of the deprotonated carboxylic groups are typical, ranging from 1.242(6) to 1.272(6) Å while a clear difference of C–O bond distances within the protonated carboxylic group is observed: C(7)–O(1) (1.216(6) Å) is much shorter than C(7)–O(2) (1.314(6) Å), in accord with IR data. If we neglect the bridging functions of the carboxylate groups in H_2btc^{2-} and btec^{4-}, each btec^{4-} ligand links two Nd(III)-couples and *vice versa* to form a one-dimensional chain structure. Every two adjacent chains is linked by the carbonyl oxygen in H_2btc^{2-} to generate a two-dimensional layer structure (Fig. 2(a)), and all ligands in the layer are almost coplanar. The bridging carboxylate groups in H_2btc^{2-} and btec^{4-} further connect the layers, producing the final three-dimensional structure (Fig. 3(a)).



Scheme 1

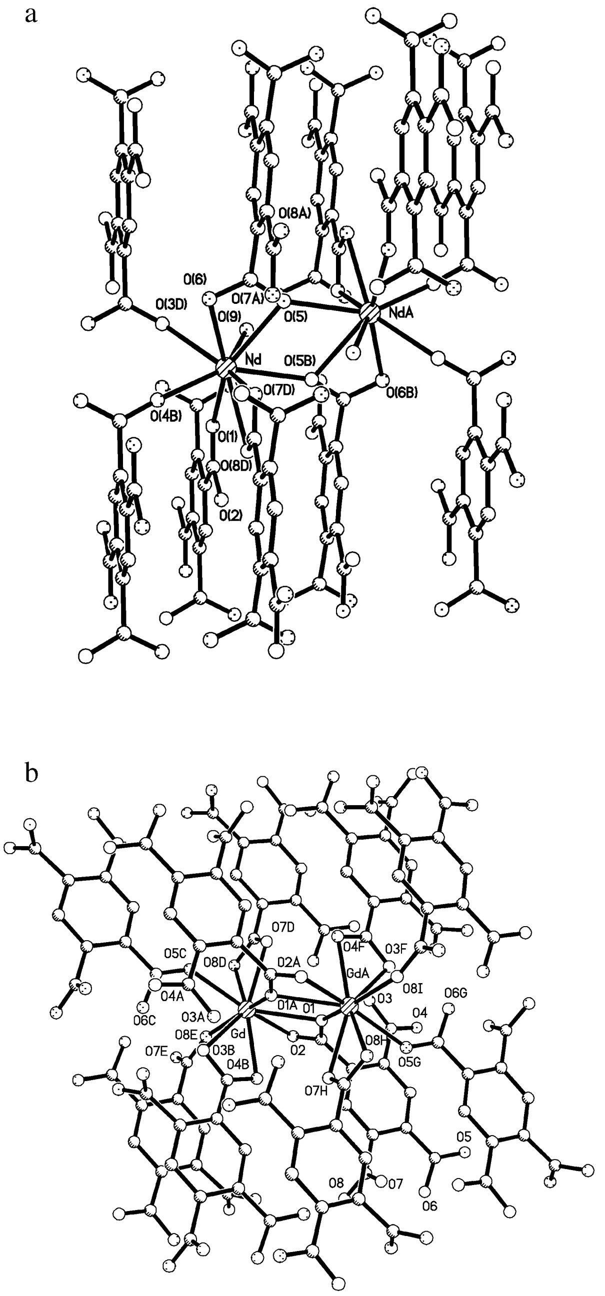


Fig. 1 The local coordination environment of lanthanide ion: (a) for **1**, (b) for **2**.

[Gd(Hbtec)]$_n$ (2). Complex **2** is also a three-dimensional polymer, Fig. 1(b) shows the local environment around the Gd(III) ion. The central gadolinium ion is coordinated by nine oxygen atoms from six Hbtec^{3-} ligands with Gd–O distances ranging from 2.363(6) to 2.588(6) Å with the nearest Gd ··· Gd distance being 4.150(6) Å. Similarly to **1**, a difference of C–O bond distances is observed in the protonated carboxylic group: C(7)–O(5) (1.208(12) Å) is shorter than C(7)–O(6) (1.283(14) Å), in agreement with the presence of the absorption peak at 1676 cm^{-1} for –COOH in IR spectrum. As depicted in Scheme 1(b), Hbtec^{3-} acts as a μ_6-bridge linking six Gd atoms; the protonated carboxylic group coordinates to one Gd atom *via* a carbonyl oxygen atom, the carboxylate group at the *meta* position of the protonated carboxylic group chelates one Gd atom, while each of the other two carboxylate groups adopt a chelating-bridging mode linking two Gd atoms. If the bridging function of the ligands is neglected each gadolinium atom is linked by four ligands and *vice versa* to form a two-dimensional layer structure (Fig. 2(b)). Every two adjacent layers is further connected by bridging carboxylate groups, generating the final three-dimensional network structure (Fig. 3b).

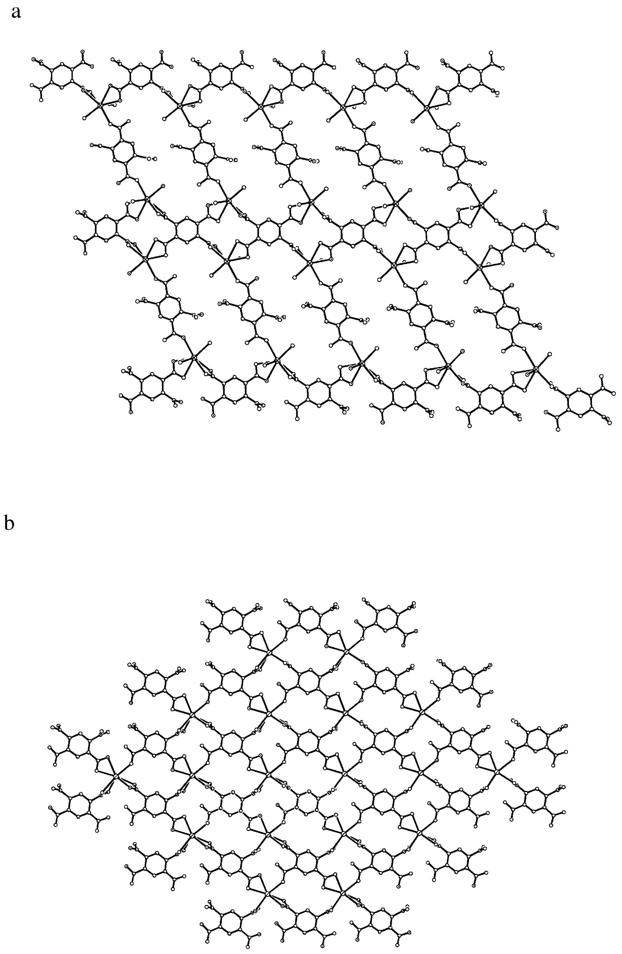


Fig. 2 The 2-D layer structure: (a) for **1**, (b) for **2**.

Thermal properties

The results of thermalgravimetric analyses (TGA) show that the two complexes have high thermal stability. For **1**, the weight loss from 264 to 360 °C (4.26%) corresponds well to the loss of the coordination water (calc. 4.35%). The final weight (95.74%) leaves the framework [Nd(H$_2$btec)$_{1/2}$(btec)$_{1/2}$] (calc. 95.64%). Decomposition of **1** begins at 400 °C and is complete at about 480 °C. For **2**, no weight loss is observed before 410 °C, above which, **2** starts to decompose and the decomposition is complete above 520 °C.

Magnetic properties

Temperature-dependent magnetic susceptibility measurements for **1** and **2** were performed for polycrystalline samples from 300 to 4 K on a Quantum Design PPMS Model 6000 magnetometer. For both complexes, as the temperature is lowered, the χ_M values increase gradually down to around 25 K, and then increase dramatically (Fig. 4 and 5). According to the structural characteristics, complexes **1** and **2** may exhibit Ln(III)–Ln(III) magnetic exchange interactions mediated by carboxylate group between layers. Scheme 2 shows the possible Ln(III)–Ln(III) magnetic exchange chain.

The magnetic behavior of **1** is well interpreted based on a modified analytical expression (eqn. (1)),[20] which is derived from Fisher model.

$$\chi = \frac{N\beta^2 g^2}{3kT} S(S+1)(1+u)/(1-u) \qquad (1)$$

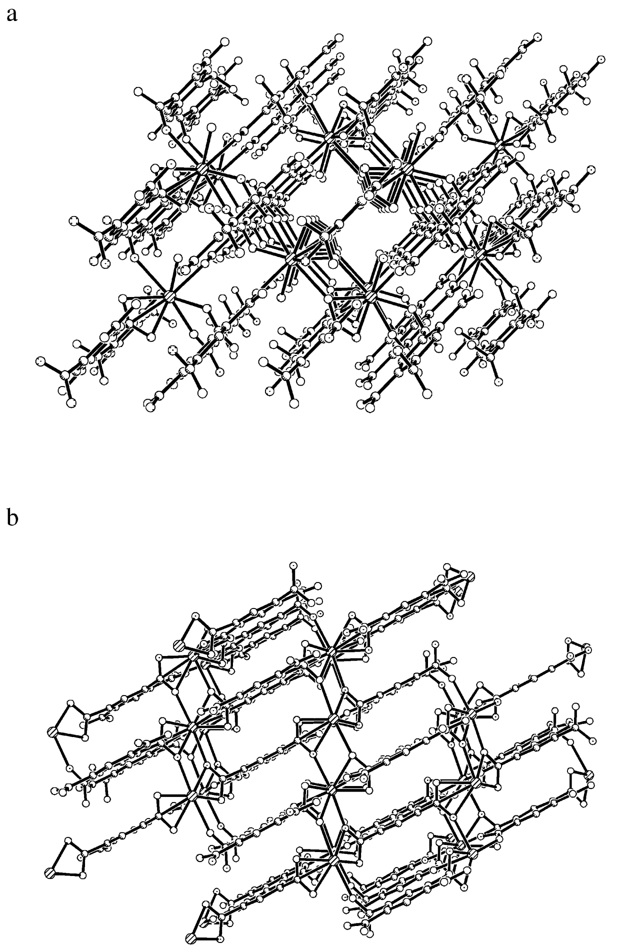


Fig. 3 The packing structure: (a) for **1** along the *b* axis, (b) for **2** along the *a* axis.

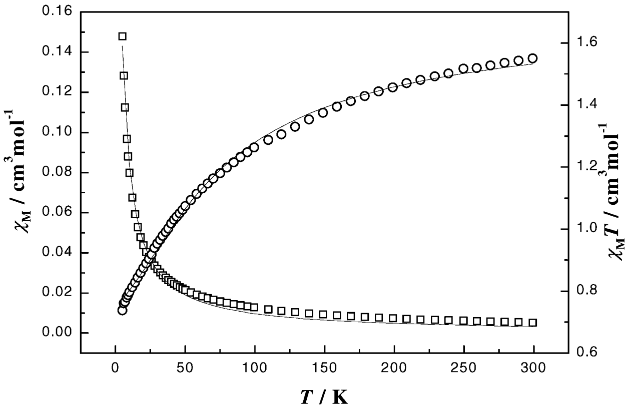
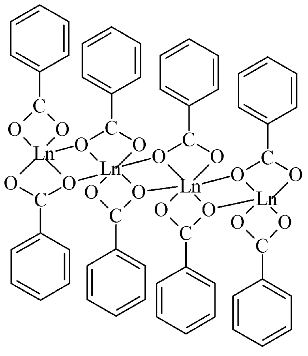


Fig. 4 Experimental χ_M and $\chi_M T$ *vs.* T curves for complex **1**.



Scheme 2 Possible Ln(III)–Ln(III) magnetic exchange interactions.

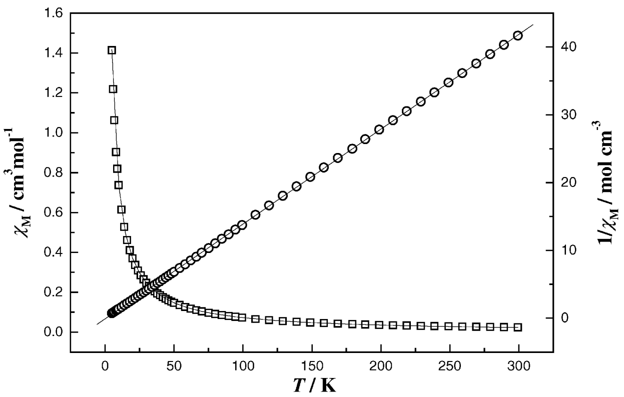


Fig. 5 Experimental χ_M and $\chi_M T$ *vs.* T curves for complex **2**.

Where $u = \coth(J/kT) - kT/J$. By using least-squares method, a satisfied fit of the data at 4–300 K was obtained with the set of parameters of $J = -18.7$ K and $g = 2$. The goodness of fit R, defined as $R = \Sigma\,[(\chi_M)_i^{obs} - (\chi_M)_i^{calc}]^2/\Sigma(\chi_M)_i^{obs}$ is 5.5×10^{-4}. The result illustrates the presence of antiferromagnetic Nd(III)–Nd(III) interactions in **1** through bridging carboxylate groups as shown in Scheme 2. However, the case in **2** is much more complicated and all our attempts to model the experimental data of **2** were unsuccessful, thus the χ_M data of **2** were fitted to a modified Curie–Weiss law $\chi = \chi_0 + C/(T + \theta)$. The calculated value of C_m is 7.137 and the Weiss temperature $\theta = -0.834$ K. The negative Weiss temperature indicates the presence of antiferromagnetic Gd(III)–Gd(III) though a detailed elucidation of the magnetic interaction in **2** is still awaited.

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