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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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First published on: 19 January 2010

To cite this Article Song, Wen-Dong , Yan, Jian-Bin , Wang, Hao , Ji, Li-Li , Ma, De-Yun and Weng Ng, Seik(2010) 'Hydro(solvo)thermal synthesis and structural characterization of three lanthanide-carboxylate coordination polymers based on BDC and/or EDTA', *Journal of Coordination Chemistry*, 63: 4, 625 – 633, First published on: 19 January 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970903560056

URL: <http://dx.doi.org/10.1080/00958970903560056>

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Hydro(solvo)thermal synthesis and structural characterization of three lanthanide–carboxylate coordination polymers based on BDC and/or EDTA

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(Received 29 September 2009; in final form 30 September 2009)

Three lanthanide coordination polymers, $[\text{Ln}_4(\text{BDC})_6(\text{H}_2\text{O})_2]_n$ ($\text{Ln} = \text{Er}$, **1**; $\text{Ln} = \text{Tm}$, **2**; BDC = 1,2-benzenedicarboxylate) and $\{[\text{Nd}_2(\text{BDC})(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$, **3**, were prepared by hydrothermal synthesis and characterized by elemental analysis, IR spectra, as well as single-crystal X-ray diffraction. The isostructural coordination polymers **1** and **2** exhibit four different coordination modes, which are rarely found in one lanthanide complex. Complex **3** displays a 2-D wave-like network assembled by two polycarboxylate ligands.

Keywords: Hydrothermal synthesis; Lanthanide–carboxylate; Coordination polymer; Magnetic behavior

1. Introduction

Coordination complexes such as 1-D chains and ladders, 2-D grids, 3-D networks, interpenetrated modes, and helical staircase networks are used as functional materials potentially applied in magnetism, molecular adsorption, optoelectronic devices, sensors, luminescent materials, and catalysis [1–4]. This work has focused on rational design of multidimensional infinite architectures by controlling the geometry of ligands and metals, with transition-metal carboxylates as a successful paradigm. However, in contrast to metal-organic frameworks (MOFs) with d-block transition metals, the design and control over high-dimensional lanthanide-based frameworks is a formidable task owing to the coordination diversity of lanthanide ions [5]. Hydrothermal synthesis is a powerful method for the preparation of metal complexes. Herein, polydentate ligands 1,2-benzenedicarboxylate (BDC) and EDTA were employed. BDC has a rigid 60° angle between the central phenyl ring and the two carboxylic acid groups and could potentially provide both discrete and consecutive metal complexes under appropriate conditions. Ethylenediaminetetraacetic acid (H_4EDTA), which possesses diverse

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functional groups, may serve as a probe of lanthanide construction and could form hydrogen bonds. In this contribution, using the above two ligands, we isolated three coordination polymers, $[\text{Ln}_4(\text{BDC})_6(\text{H}_2\text{O})_2]_n$ ($\text{Ln} = \text{Er}$, **1**; $\text{Ln} = \text{Tm}$, **2**) and $\{[\text{Nd}_2(\text{BDC})(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ **3**, by Ln_2O_3 with BDC or EDTA ligands under hydrothermal methods. The complexes exhibit a systematic variation in dimensionality from 1-D to 2-D and 3-D, demonstrating the influence of the lanthanide ions and organic ligands upon dimensionality.

2. Experimental

2.1. Materials and physical measurements

All chemicals purchased were of reagent grade and used without purification. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. IR spectra were acquired using a Nicolet Avatar 360 FT-IR spectrophotometer. Magnetism was studied with a QUANTUM MPMS XL-7.

2.2. Synthesis of compounds 1–3

2.2.1. $[\text{Er}_4(\text{BDC})_6(\text{H}_2\text{O})_2]_n$ (1**).** A mixture of Er_2O_3 (0.191 g; 0.5 mmol), H_2BDC (0.249 g; 1.5 mmol), HClO_4 (0.385 mmol), and water (10 mL) was heated at 160°C for 70 h; pink crystals were obtained by cooling to room temperature at 10°C h^{-1} (yield: 43% based on Er). Anal. Calcd for $\text{C}_{48}\text{H}_{28}\text{Er}_4\text{O}_{26}$: C, 34.12; H, 1.67. Found: C, 34.01; H, 1.54. (KBr pellet) (cm^{-1}): 3409, 1605, 1560, 1450, 1412, 849, 753, 690, 652, 569.

2.2.2. $[\text{Tm}_4(\text{BDC})_6(\text{H}_2\text{O})_2]_n$ (2**).** Identical procedure with **1** was followed to prepare **2** except Er_2O_3 was replaced by Tm_2O_3 (0.192 g; 0.5 mmol) (yield: 51% based on Tm). Anal. Calcd for $\text{C}_{48}\text{H}_{28}\text{Tm}_4\text{O}_{26}$: C, 33.98; H, 1.66. Found: C, 33.81; H, 1.59. (KBr pellet) (cm^{-1}): 3415, 1610, 1563, 1444, 1409, 850, 751, 684, 655, 568.

2.2.3. $\{[\text{Nd}_2(\text{BDC})(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (3**).** A mixture of Nd_2O_3 (0.168 g; 0.5 mmol), H_2BDC (0.83 g; 0.5 mmol), H_4EDTA (0.146 g; 0.5 mmol), HClO_4 (0.385 mmol), and water (10 mL) was heated at 170°C for 5 days; purple crystals were obtained by cooling to room temperature at 10°C h^{-1} (yield: 68% based on Nd). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{Nd}_2\text{O}_{15.5}$: C, 26.86; H, 3.01; N, 3.48. Found: C, 26.91; H, 2.96; N, 3.60. (KBr pellet) (cm^{-1}): 3421, 1617, 1574, 1488, 1402, 1366, 1337, 1032, 935, 841, 753.

2.3. X-ray crystallography

Diffraction intensities were collected on a computer-controlled Bruker Smart APEX II CCD diffractometer equipped with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -scan technique. Lorentz polarization and multi-scan

absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares using SHELXS-97 and SHELXL-97. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogens were generated geometrically. Water hydrogens were tentatively located in difference Fourier maps and refined with distance restraints of $\text{O-H} = 0.84 \text{ \AA}$ and $\text{H} \cdots \text{H} = 1.39 \text{ \AA}$, each within a standard deviation of 0.01 \AA , and with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$. Crystallographic data for **1–3** are listed in table 1 and selected bond lengths and angles for the compounds are given in table 2.

3. Results and discussion

3.1. Crystal structures

$[\text{Er}_4(\text{BDC})_6(\text{H}_2\text{O})_2]_n$ and $[\text{Tm}_4(\text{BDC})_6(\text{H}_2\text{O})_2]_n$, **1** and **2**, are isostructural; the structure of $[\text{Er}_4(\text{BDC})_6(\text{H}_2\text{O})_2]_n$ (**1**) is described in detail here. The asymmetric unit of **1** (figure 1) contains crystallographically independent four Er ions. The Er(III) ions are surrounded by six, seven, eight, and nine oxygens, respectively, in **1**. Er (1) coordinates eight oxygens from carboxylate of five BDC anions; Er (2) binds six oxygens of carboxylates of six BDC anions; Er (3) is surrounded by nine oxygens of six BDC anions, and Er (4) by seven oxygens, five from five BDC and the other two from two coordinated waters. It is rare that the same metal ion has four different coordination environments in the same complex. Corresponding to the four coordination environments, there are four coordination polyhedra, which can be described as octahedral (CN=6), capped trigonal prism (CN=7), bicapped trigonal prism (CN=8), and capped square antiprism (CN=9). The four coordination polyhedra connect into infinite chains by

Table 1. Crystal data and structure refinement information for **1–3**.

	1	2	3
Formula	$\text{C}_{48}\text{H}_{28}\text{Er}_4\text{O}_{26}$	$\text{C}_{48}\text{H}_{28}\text{Tm}_4\text{O}_{26}$	$\text{C}_{18}\text{H}_{24}\text{N}_2\text{Nd}_2\text{O}_{15.5}$
Formula weight	1689.74	1696.42	804.87
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P1</i>	<i>P1</i>	$P_2(1)/n$
Unit cell dimensions (\AA , $^\circ$)			
<i>a</i>	12.6217(6)	12.5598(4)	9.8738(6)
<i>b</i>	13.8053(6)	13.7827(4)	11.8691(7)
<i>c</i>	15.9232(7)	15.9026(5)	20.2247(1)
α	75.107(2)	75.286(2)	
β	68.829(2)	69.048(2)	95.130(3)
γ	65.551(2)	65.654(2)	
Volume (\AA^3), <i>Z</i>	2336.32(18), 2	2323.78(12), 2	2360.7(2), 4
<i>F</i> (000)	1592	1600	1560
Calculated density (mg cm^{-3})	2.402	2.424	2.265
Absorption coefficient (mm^{-1})	7.209	7.661	4.433
Goodness-of-fit	1.019	1.041	1.056
R_1 [$I > 2\sigma(I)$]	0.0231	0.0219	0.0207
wR_2 (all data)	0.0515	0.0555	0.0489

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}; wR_2 = \left\{ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum(F_o^2)^2} \right\}^{1/2}.$$

Table 2. Selected bond distances (Å) and angles (°).

Complex 1^a					
Er1–O15 ⁱⁱⁱ	2.209(3)	Er1–O13	2.226(3)	Er1–O12	2.251(2)
Er1–O8 ⁱⁱⁱ	2.290(2)	Er1–O23 ⁱⁱ	2.314(2)	Er1–O22	2.386(2)
Er1–O21	2.547(2)	Er1–O24 ⁱⁱ	2.788(3)	Er2–O19 ⁱⁱ	2.218(2)
Er2–O14	2.248(2)	Er2–O6	2.253(3)	Er2–O4 ^{iv}	2.256(3)
Er2–O11	2.257(3)	Er2–O24 ⁱⁱ	2.261(3)	Er3–O18 ^v	2.210(3)
Er3–O20 ⁱⁱ	2.214(3)	Er3–O5	2.321(2)	Er3–O1	2.330(2)
Er3–O9 ⁱ	2.396(2)	Er3–O3 ^{iv}	2.429(2)	Er3–O10 ⁱ	2.447(3)
Er3–O4 ^{iv}	2.823(3)	Er3–O2	2.852(3)	Er4–O17	2.225(2)
Er4–O16 ⁱⁱⁱ	2.234(3)	Er4–O2 ^{vi}	2.269(3)	Er4–O21	2.289(2)
Er4–O7 ⁱⁱⁱ	2.301(3)	Er4–O1W	2.321(3)	Er4–O2W	2.353(3)
O15 ⁱⁱⁱ –Er1–O13	83.6(1)	O13–Er1–O12	78.8(1)	O12–Er1–O8 ⁱⁱⁱ	108.5(9)
O13–Er1–O22	139.7(1)	O12–Er1–O22	73.8(9)	O13–Er1–O21	147.5(9)
O23 ⁱⁱ –Er1–O21	73.4(8)	O23 ⁱⁱ –Er1–O24 ⁱⁱ	49.86(8)	O22–Er1–O21	52.4(8)
O14–Er2–O6	87.9(1)	O6–Er2–O11	177.1(9)	O14–Er2–O11	92.1(9)
O4 ^{iv} –Er2–O24 ⁱⁱ	177.4(9)	O19 ⁱⁱ –Er2–O11	94.0(1)	O18 ^v –Er3–O5	148.0(9)
O20 ⁱⁱ –Er3–O1	147.1(1)	O3 ^{iv} –Er3–O10 ⁱ	153.5(8)	O9 ⁱ –Er3–O10 ⁱ	53.7(8)
O5–Er3–O9 ⁱ	132.5(9)	O5–Er3–O4 ^{iv}	72.1(8)	O17–Er4–O16 ⁱⁱⁱ	162.8(1)
O7 ⁱⁱⁱ –Er4–O1W	69.3(1)	O1W–Er4–O2W	142.5(2)	O7 ⁱⁱⁱ –Er4–O2W	148.3(1)
Complex 2^b					
Tm1–O23	2.277(3)	Tm1–O18	2.368(3)	Tm1–O17	2.539(3)
Tm1–O16 ^v	2.210(3)	Tm1–O8 ⁱ	2.244(3)	Tm1–O19 ⁱ	2.304(3)
Tm1–O20 ⁱ	2.800(3)	Tm2–O15 ⁱⁱⁱ	2.230(3)	Tm2–O22 ⁱⁱⁱ	2.241(3)
Tm2–O1	2.201(3)	Tm2–O20 ⁱⁱ	2.245(3)	Tm3–O2	2.200(3)
Tm2–O12 ⁱⁱⁱ	2.245(3)	Tm2–O7 ⁱⁱ	2.245(3)	Tm3–O3 ⁱⁱ	2.193(3)
Tm3–O5	2.437(3)	Tm3–O6	2.386(3)	Tm3–O9	2.871(3)
Tm3–O2 ⁱⁱⁱ	2.305(3)	Tm3–O1 ⁱⁱⁱ	2.415(3)	Tm3–O10	2.309(3)
Tm3–O12 ⁱⁱⁱ	2.833(3)	Tm4–O4 ⁱⁱ	2.205(3)	Tm4–O9	2.256(3)
Tm4–O13	2.210(3)	Tm1–O14	2.200(3)	Tm4–O17	2.283(2)
Tm4–O24	2.286(3)	Tm4–O1W	2.345(3)	Tm4–O2W	2.315(3)
O14–Tm1–O16 ^{iv}	83.3(1)	O14–Tm1–O8 ⁱ	149.7(1)	O14–Tm1–O23	91.5(1)
O23–Tm1–O19 ⁱ	151.8(1)	O18–Tm1–O17	52.8(9)	O23–Tm1–O18	82.7(1)
O1–Tm2–O15 ⁱⁱⁱ	171.6(1)	O20 ⁱⁱ –Tm2–O12 ⁱⁱⁱ	177.6(9)	O1Tm2–O7 ⁱⁱ	94.1(1)
O22 ⁱⁱⁱ –Tm2–O20 ⁱⁱ	94.5(1)	O12 ⁱⁱⁱ –Tm2–O7 ⁱⁱ	92.5(1)	O3 ⁱⁱ –Tm3–O2 ⁱⁱⁱ	148.2(1)
O10–Tm3–O5	74.7(1)	O3 ⁱⁱ –Tm3–O5	128.5(1)	O2Tm3–O10	147.8(1)
O2–Tm3–O11 ⁱⁱⁱ	122.5(1)	O11 ⁱⁱⁱ –Tm3–O12 ⁱⁱ	48.7(9)	O2W–Tm4–O1W	142.6(1)
O24–Tm4–O2W	69.1(1)	O13–Tm4–O2W	152.4(1)	O4 ⁱⁱ –Tm4–O24	112.7(1)
O4 ⁱⁱ –Tm4–O9	89.4(1)	O9–Tm4–O17	150.7(1)	O17–Tm4–O24	77.5(9)
Complex 3^c					
Nd1–O1	2.590(2)	Nd1–O5	2.434(2)	Nd1–O9	2.469(2)
Nd1–O2W	2.484(2)	Nd1–O7	2.501(2)	Nd1–O2	2.548(2)
Nd1–O10 ⁱⁱ	2.649(2)	Nd1–O11	2.674(2)	Nd2–O6 ⁱⁱ	2.355(2)
Nd2–O11	2.415(2)	Nd2–O1W	2.432(3)	Nd2–O3	2.450(2)
Nd2–O7	2.523(2)	Nd2–O3 ⁱ	2.526(2)	Nd2–O2	2.542(2)
Nd2–O8 ⁱ	2.553(2)	Nd2–O4 ⁱ	2.717(2)		
O5–Nd1–O9	70.7(7)	O9–Nd1–O2W	74.7(7)	O9–Nd1–O7	138.4(7)
O7–Nd1–O2	65.9(6)	O2W–Nd1–O1	121.2(8)	O7–Nd1–O10 ⁱⁱ	142.1(6)
O2–Nd1–O11	63.1(6)	O2W–Nd1–N2	140.6(7)	O2–Nd1–N2	125.7(7)
O7–Nd1–N1	88.5(7)	O2W–Nd1–N1	75.8(7)	N2–Nd1–N1	65.7(7)
O6 ⁱⁱⁱ –Nd2–O1W	83.9(1)	O6 ⁱⁱⁱ –Nd2–O3	141.2(7)	O6 ⁱⁱⁱ –Nd2–O7	133.1(7)
O6 ⁱⁱⁱ –Nd2–O2	141.7(8)	O11–Nd2–O8 ⁱ	155.3(7)	O6 ⁱⁱⁱ –Nd2–O3 ⁱ	80.5(8)
O1W–Nd2–O3 ⁱ	141.1(1)	O1WNd2–O4 ⁱ	149.7(1)	O11–Nd2–O1W	90.7(1)

^aSymmetry codes: ⁱ 1 – x, 1 – y, 1 – z; ⁱⁱ 2 – x, 1 – y, –z; ⁱⁱⁱ 1 – x, 1 – y, –z; ^{iv} –x, 1 – y, 1 – z; ^v –1 + x, y, 1 + z; ^(vi) 1 + x, y, –1 + z.

^bSymmetry codes: ⁱ –x, –y, 2 – z; ⁱⁱ 1 – x, –y, 1 – z; ⁱⁱⁱ –x, –y, 1 – z; ^{iv} –1 – x, –y, 2 – z.

^cSymmetry codes: ⁱ 2 – x, 1 – y, 2 – z; ⁱⁱ 1 – x, 2 – y, 2 – z; ⁱⁱⁱ 1 + x, y, z.

vertices connection (shared oxygen atoms of two adjacent Er ions) (figure 2). Similar coordination arrangements have been observed in Ln (1,2-BDC) (Ln = Y and Yb) coordination polymers [6].

The six 1,2-BDC anions show differences in their connection modes with Er ions (figure 3). One BDC adopts the (a) coordination mode connecting three Er(III) ions with one carboxylate bridging two Er ions in one chain and the other carboxylate group chelating one Er(III) in the neighboring chain; two adopt the (b) coordination mode with each carboxylate binding two Er(III) ions tridentate, while the other three BDC dianions adopt the (c) coordination mode with each carboxylate bidentate to two Er(III). Each phthalate bridges two adjacent chains with two carboxylate groups.

The 2-D layer network of **1** is composed of four repeated Er(III) ions in the asymmetric unit. Within the layer, π - π stacking interactions form a corrugated nature

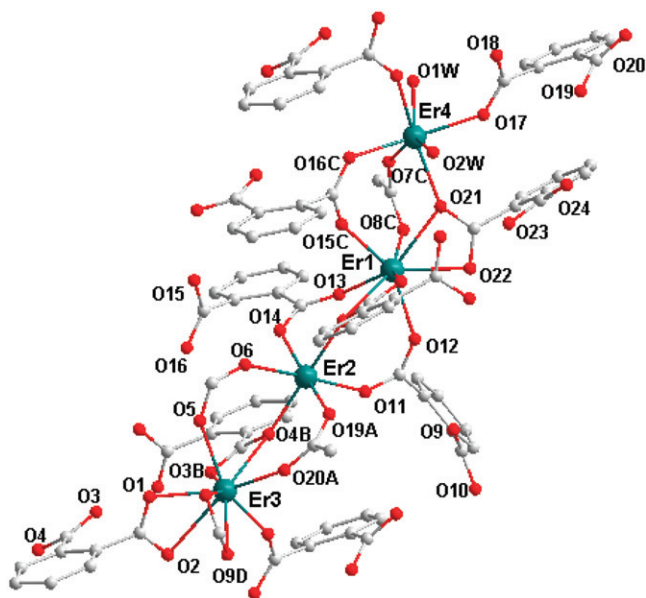


Figure 1. Asymmetric coordination unit of **1** (C, H, and O atoms were omitted for clarity).

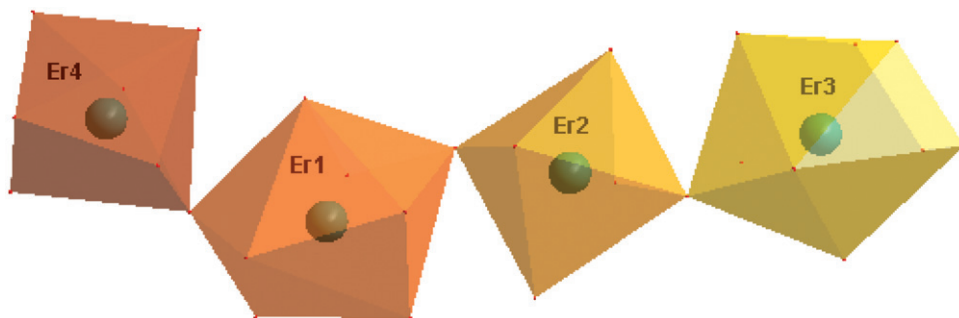


Figure 2. Diamond view of the connectivity between the differently coordinated Er atoms.

to the sheets. The Er(III) ions in the same layer arrange in *ABAB* sequence. The Er...Er distances in one chain are: Er1...Er2 = 4.299, Er1...Er4 = 4.218, Er2...Er3 = 4.408, Er3...Er4A = 4.613 Å. The Er...Er distances between the *A* and *B* chains are: Er1...Er3'' = 5.951, Er4...Er1' = 6.072 Å (figure 4a). Similarly, the Tm(III) chain distances are viewed in figure 4(b).

$\{[\text{Nd}_2(\text{BDC})(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 1.75\text{H}_2\text{O}\}_n$ (**3**). The reaction of Nd_2O_3 with 1,2-BDC and H_4EDTA under hydrothermal conditions gave **3**. Nd(III) ions have two types of coordination environments (figure 5). Nd1 is 10-coordinate from four oxygens and two nitrogens from one EDTA, two oxygens from one 1,2-BDC, one oxygen from another EDTA, and one water; Nd2 is nine-coordinate by nine oxygens from three EDTA and two 1,2-BDC ligands, and one water with tricapped trigonal prismatic coordination. The Nd–O and Nd–N bond lengths are within the range of those observed for other Nd(III) complexes with O or N donors [7], ranging from 2.355(2) to 2.717(2) Å and 2.722(2) and 2.772(2)°, respectively.

In **3**, two opposite 1,2-BDC ligands link Nd(III) ions to form a tetranuclear “Z” unit, with distances between adjacent Nd(III) ions of 3.957 and 5.716 Å. Carboxylate groups

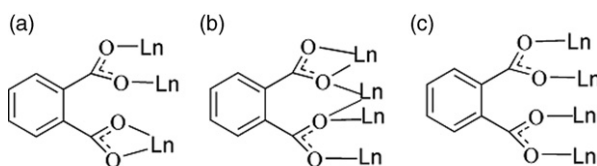


Figure 3. The coordination mode of BDC ligand in **1**.

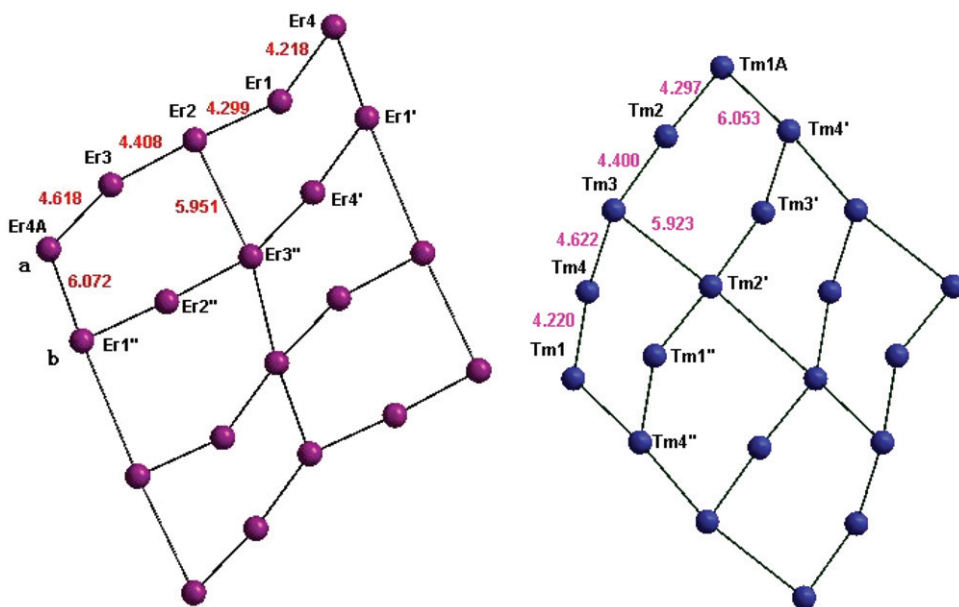


Figure 4. The corrugated sheet-like structures in **1** and **2** (C, H, and O atoms were omitted for clarity).

of EDTA link the “Z” units to form a 1-D neodymium-carboxylate helix and further connect into a 2-D neodymium-carboxylate layer in the *ab* plane (figure 6). The layer is not a smooth plane, but essentially a wave-like layer and is stabilized by $O \cdots H \cdots O$ hydrogen bonding interactions among the coordinating water, carboxyl oxygens, and interstitial water.

3.2. IR and magnetic properties

The IR spectra of 1–3 show broad bands in the region of $3300\text{--}3500\text{ cm}^{-1}$, assigned to $\nu(\text{O-H})$ of water. The features at 1605 and 1450 cm^{-1} for 1, 1610 and 1409 cm^{-1} for 2,

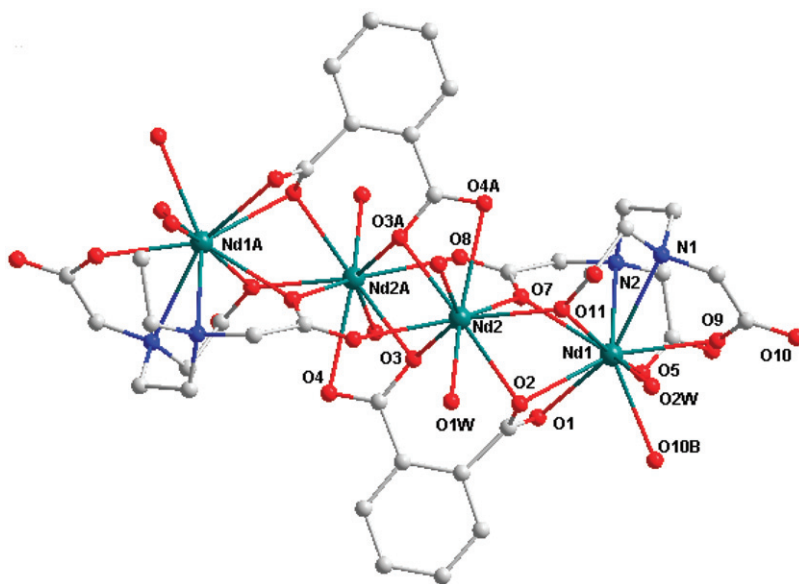


Figure 5. Asymmetric coordination unit of 3 [all H atoms were omitted for clarity. Symmetry code (A) $2-x, 1-y, 2-z$; (B) $1-x, 2-y, 2-z$].

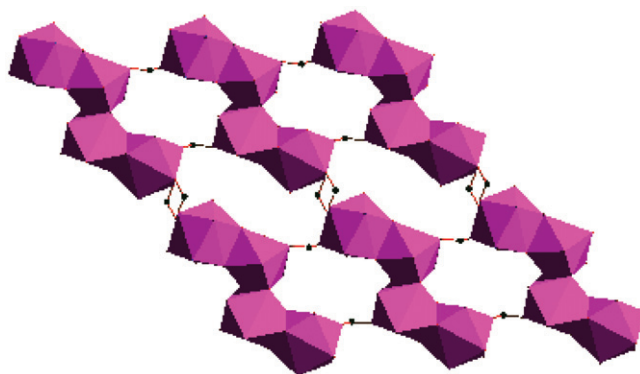


Figure 6. Diamond view of the 2-D-layer network.

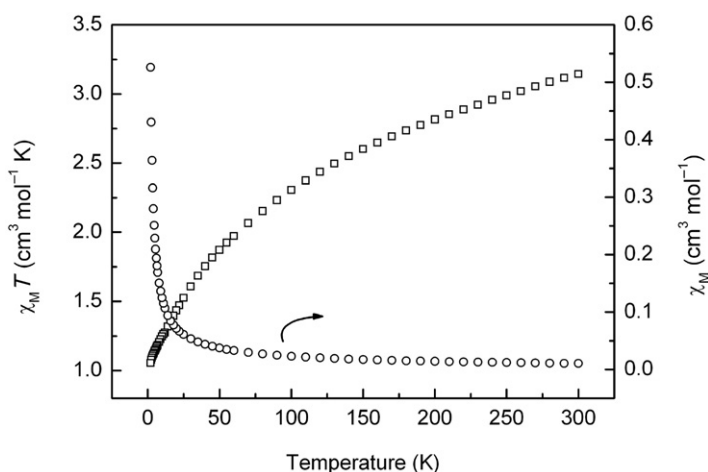


Figure 7. Plot of $\chi_M T$ vs. T in the range of 2–300 K for **3** measured under 1000 G black pane.

and 1617 and 1488 cm^{-1} for **3** are associated with asymmetric (COO) and symmetric (COO) stretching vibrations [8].

The variable temperature magnetic susceptibility of **3** was studied from 2 to 300 K under 1000 G. Figure 7 shows $\chi_M T$ versus T . For **3**, the $\chi_M T$ is 3.14 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at room temperature, then slightly decreases, when cooling and reaches its minimum 1.05 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 2 K, indicating antiferromagnetism. The $1/\chi_M$ versus T plot was fitted by the Curie–Weiss law in the range of 50–300 to give the $C = 3.67(1) \text{cm}^3 \text{mol}^{-1} \text{K}$ and $\theta = -57.25(1) \text{K}$. The negative Weiss constant confirms the antiferromagnetism of **3**; the Neel point is 50 K.

4. Conclusion

Based on a facile hydrothermal method, three lanthanide coordination polymers based on BDC and/or EDTA have been synthesized and structurally characterized; **1–3** are unusual among reported coordination polymers constructed from lanthanide, BDC and/or EDTA [9]. This synthetic approach provides new opportunities for preparing other high-dimensional lanthanide coordination polymers with particular properties.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC 614800, 614803, and 616234. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44 1223 336 033;

Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>) or also available from the author on request.

Acknowledgements

We kindly acknowledge Agriculture Key Projects Plan in Guangdong (20070409007 and 0087061110303030), Marine Fishery Science and Technology Extension Special Project in Guangdong for supporting this work.

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