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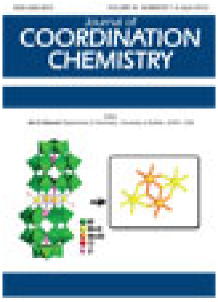

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Assembly of three 3-D MOFs from 2-phenyl-4,5-imidazole dicarboxylate and oxalate

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Assembly of three 3-D MOFs from 2-phenyl-4,5-imidazole dicarboxylate and oxalate

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Three lanthanide–organic polymers, $\{[\mathrm{Ln}(\mu_3\text{-HPhIDC})(\mu_2\text{-C}_2\mathrm{O}_4)_{0.5}(\mathrm{H_2O})]\cdot 2\mathrm{H_2O}\}_n$ (Ln = Nd (**1**), Sm (**2**), and Tb (**3**)), have been isolated from the reaction of 2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3PhIDC) with equal amount of Ln(III) salts under solvothermal condition with the rigid coligand oxalate. The three polymers, which are isomorphous and isostructural, have been structurally characterized by elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction. Each exhibits a 3-D framework constructed from infinite 2-D layers joined by μ_2-C_2O_4, which are composed of μ_3-HPhIDC^{2-} and trivalent lanthanide. Thermal properties have also been investigated.

Keywords: Phenyl imidazole dicarboxylate; Lanthanide–organic polymer; Crystal structure; Properties

1. Introduction

Preparation of metal–organic frameworks (MOFs) and investigations on applications as functional materials have attracted attention [1–8]. The geometry of donors within a polynucleating ligand, the flexibility of the ligand backbone, and additional functional groups of ligands play important roles in directing extended structures of MOFs [9–15]. Thus, design of organic bridging ligands is very important in construction of MOFs.

Imidazole-4,5-dicarboxylic (H_3IDC) and 2-substituted derivatives have attracted attention in preparation of MOFs under hydro(solvo)thermal conditions owing to versatile coordination modes [8, 16–35]. Our group has strong interests in adopting an analog of H_3IDC, 2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3PhIDC) bearing a bulky aromatic group to prepare MOFs. The coordination ability and various coordination modes of H_3PhIDC have been confirmed by our research [19–21]. However, MOFs bearing H_3PhIDC ligands are limited; we have synthesized only six transition metal and two main group metal MOFs. There are no reports concerning

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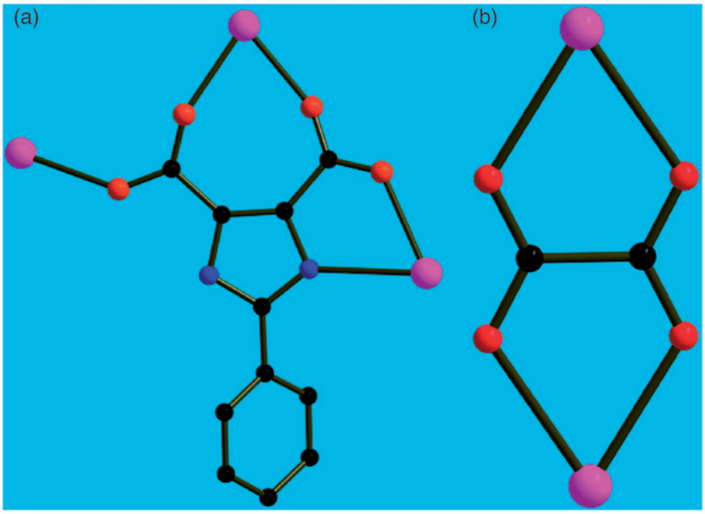

Scheme 1. $HPhIDC^{2-}$ and oxalate coordination modes.

lanthanide polymers with H_3PhIDC. Thus, we hope to continue to employ H_3PhIDC to establish lanthanide-based frameworks.

Herein, we present three lanthanide–organic frameworks, $\{[Ln(\mu_3\text{-}HPhIDC)(\mu_2\text{-}C_2O_4)_{0.5}(H_2O)] \cdot 2H_2O\}_n$ (Ln = Nd (**1**), Sm (**2**), and Tb (**3**)). Single-crystal X-ray diffractions reveal that the doubly deprotonated $HPhIDC^{2-}$ adopts a $(\kappa^1\text{–}\kappa^1\text{–}\mu^2)\text{–}(\kappa^1\text{–}\kappa^1\text{–}\mu^2)\text{–}(\kappa^1)\text{–}\mu^3$ (scheme 1a) coordination mode [19] to assemble with lanthanide ions. The thermal properties of **1**–**3** have also been determined.

2. Experimental

2.1. *Materials and physical techniques*

All chemicals were of reagent grade, obtained from commercial sources, and used without purification. H_3PhIDC was prepared according to the literature [36].

Infrared (IR) spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses (C, H, and N) were carried out on a FLASH EA1112 Elemental Analyzer. Thermogravimetric analysis (TGA) measurement was performed by heating crystalline sample from 20°C to 850°C at 10°C min^{-1} in air on a Netzsch STA 409PC differential thermal analyzer.

2.2. *Synthesis of crystalline* $\{[Nd(\mu_3\text{-}HPhIDC)(\mu_2\text{-}C_2O_4)_{0.5}(H_2O)] \cdot 2H_2O\}_n$ *(1)*

A mixture of H_3PhIDC (23.2 mg, 0.1 mmol), $Nd(NO_3)_3 \cdot 6H_2O$ (43.8 mg, 0.1 mmol), $(NH_4)_2C_2O_4 \cdot H_2O$ (14.2 mg, 0.1 mmol), NaOH (8.0 mg), ethanol (3 mL), and water (4 mL) was sealed in 25 mL Teflon-lined autoclave and heated for 96 h at 150°C under autogenous pressure. The pH of the mixture was 8. The reaction mixture was then allowed to cool to room temperature at a rate of 10°C h^{-1}. Lavender needle-shaped crystals of **1** were collected in 50% yield (based on Nd), washed with deionized water, and dried in air. Crystals of **1** were stable in air. Anal. Calcd for $C_{12}H_{12}N_2O_9Nd$ (%): C, 30.50; H, 2.56; N, 5.93. Found (%): C, 30.21; H, 2.82; N, 5.80. IR (cm^{-1}, KBr): 3443(s), 2955(w), 2922(m), 2851(w), 1635(s), 1555(w), 1458(w), 1361(m), 1311(w), 1117(m), 860(w), 794(w), 731(m), 621(w), 531(w).

2.3. *Synthesis of crystalline* $\{[Sm(\mu_3\text{-HPhIDC})(\mu_2\text{-}C_2O_4)_{0.5}(H_2O)]\cdot 2H_2O\}_n$ *(2)*

Complex **2** was synthesized by a method similar to that of **1**, except that neodymium nitrate was replaced by samarium nitrate. Yellowish needle-shaped crystals of **2** were collected in 62% yield (based on Sm), washed with deionized water, and dried in air. Crystals of **2** were stable in air. Anal. Calcd for $C_{12}H_{12}N_2O_9Sm$ (%): C, 30.12; H, 2.53; N, 5.85. Found (%): C, 29.76; H, 2.38; N, 5.68. IR (cm^{-1}, KBr): 3442(s), 2963(w), 2921(m), 2856(w), 1684(m), 1599(s), 1540(w), 1460(w), 1359(m), 1316(w), 1120(m), 866(w), 794(w), 731(m), 616(w), 540(w).

2.4. *Synthesis of crystalline* $\{[Tb(\mu_3\text{-HPhIDC})(\mu_2\text{-}C_2O_4)_{0.5}(H_2O)]\cdot 2H_2O\}_n$ *(3)*

Complex **3** was synthesized by a method similar to **1**, except that neodymium nitrate was replaced by samarium nitrate. Colorless needle-shaped crystals of **3** were collected in 71% yield (based on Tb), washed with deionized water, and dried in air. Crystals of **3** were also stable in air. Anal. Calcd for $C_{12}H_{12}N_2O_9Tb$ (%): C, 29.58; H, 2.48; N, 5.75. Found (%): C, 29.36; H, 2.79; N, 5.34. IR (cm^{-1}, KBr): 3441(s), 2955(w), 2924(m), 2841(w), 1635(s), 1556(w), 1459(w), 1359(m), 1316(w), 1199(w), 1120(m), 868(s), 793(w), 731(m), 621(w), 525(w).

2.5. *X-ray crystallography*

Crystal data and experimental details for **1**–**3** are presented in table 1. All measurements were made on a Bruker Smart APEXII CCD diffractometer with a graphite-monochromated imaging plate area detector with Mo-Kα radiation ($\lambda = 0.71073$ Å). Suitable single crystals were selected and mounted on a glass fiber. All data were collected at room temperature using the ω–2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The three structures were solved by direct methods and expanded using the Fourier technique. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 6339 observed reflections and 2657 variable parameters for **1**; 6502 observed reflections and 3065 variable parameters for **2**; and 10,670 observed reflections and 2987 variable parameters for **3**. All calculations were performed using the SHELX-97 crystallographic software package [37]. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data for polymers **1**–**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{12}H_{12}O_9N_2Nd$	$C_{12}H_{12}O_9N_2Sm$	$C_{12}H_{12}N_2O_9Tb$
Formula weight	472.48	478.59	487.16
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)			
a	9.2521(5)	9.1948(3)	9.1449(13)
b	13.8933(8)	13.9029(6)	13.8080(19)
c	11.8460(9)	11.7227(4)	11.6090(16)
α	90.00	90.00	90.00
β	90.80	91.00	91.42
γ	90.00	90.00	90.00
Volume (Å^3), Z	1522.57(17), 4	1498.32(10), 4	1465.4(4), 4
Calculated density (Mg m^{-3})	2.061	2.122	2.208
Absorption coefficient (mm^{-1})	26.526	3.972	4.880
Crystal size (mm^3)	0.24 × 0.06 × 0.04	0.20 × 0.15 × 0.15	0.20 × 0.18 × 0.18
Reflections collected	6339	6502	10,670
Independent reflection	2657 [R(int) = 0.0305]	3065 [R(int) = 0.0301]	2987 [R(int) = 0.0563]
Data/restraints/parameters	2657/5/225	3065/7/229	2987/10/217
Goodness-of-fit on F^2	1.031	1.054	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0288$, $wR_2 = 0.0748$	$R_1 = 0.0289$, $wR_2 = 0.0568$	$R_1 = 0.0340$, $wR_2 = 0.0678$
R indices (all data)	$R_1 = 0.0318$, $wR_2 = 0.0769$	$R_1 = 0.0358$, $wR_2 = 0.0605$	$R_1 = 0.0494$, $wR_2 = 0.0729$
$\Delta\rho_{min}$ and $\Delta\rho_{max}$(e Å^{-3})	−0.603 and 1.040	−0.740 and 0.915	−0.799 and 1.002

3. Results and discussion

3.1. *Synthesis*

Polymers **1**–**3** were synthesized under solvothermal conditions with ethanol and water solvent. At the beginning, we tried to seal lanthanide salts and H_3PhIDC in appropriate proportions under hydrothermal condition and only crystallites were obtained. To adjust the crystal size and shape, mixed solvents HCN/H_2O, CH_3OH/H_2O, CH_3CH_2OH/H_2O were selected for the reactions. The other conditions were maintained and the crystals were prepared successfully with ethanol as the organic solvent. It can be concluded that the alcohol may be favorable in directing the synthesis of lanthanide complexes from our experiments and in related reports [16, 25, 34]. Allowing for the high affinity for oxygen donors of lanthanides, we introduce the "template" ligand, rigid dianionic oxalate, which is widely utilized in preparation of lanthanide-containing MOFs [28, 33–35, 38–40]. The pH plays a crucial role in crystal growth. Organic amines such as trimethylamine and ethylenediamine are used to adjust the pH value and several lanthanide-containing complexes have been prepared with trimethylamine [25, 34]. However, nitrogen bases were not suitable for the lanthanide–H_3PhIDC systems and sodium hydroxide was used for our experiments. Three 3-D complexes were isolated in suitable size for X-ray determination.

The reasons for choosing imidazole dicarboxylate that bears the 2-position phenyl in H_3PhIDC are as follows: (1) from our previous theoretical calculations concerning natural bond orbital (NBO) charge distributions of H_3PhIDC, we determined that the negative NBO charges mainly distribute on the oxygen and nitrogen, which show that the oxygen and nitrogen of H_3PhIDC have ability to coordinate to metal ions.

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
Nd(1)–O(1)#1	2.418(3)	Nd(1)–O(2)#2	2.366(3)
Nd(1)–O(3)#2	2.344(3)	Nd(1)–O(4)	2.427(3)
Nd(1)–O(5)	2.535(4)	Nd(1)–O(6)	2.432(3)
Nd(1)–O(7)#3	2.507(4)	Nd(1)–N(1)	2.661(4)
Nd(1)#4–O(1)	2.418(3)	Nd(1)#5–O(2)	2.366(3)
Nd(1)#5–O(3)	2.344(3)	Nd(1)#3–O(7)	2.507(4)
O(1)#1–Nd(1)–O(4)	73.39(12)	O(1)#1–Nd(1)–O(5)	141.59(13)
O(1)#1–Nd(1)–O(6)	76.01(13)	O(1)#1–Nd(1)–O(7)#2	123.75(12)
O(1)#1–Nd(1)–N(1)	83.58(14)	O(2)#3–Nd(1)–O(1)#1	79.43(12)
O(2)#3–Nd(1)–O(4)	151.85(13)	O(2)#3–Nd(1)–O(5)	136.56(13)
O(2)#3–Nd(1)–O(6)	104.62(13)	O(2)#3–Nd(1)–O(7)#2	72.57(13)
O(2)#3–Nd(1)–N(1)	106.00(13)	O(3)#3–Nd(1)–O(1)#1	139.02(13)
O(3)#3–Nd(1)–O(2)#3	75.04(12)	O(3)#3–Nd(1)–O(4)	123.37(12)
O(3)#3–Nd(1)–O(5)	75.20(13)	O(3)#3–Nd(1)–O(6)	141.36(13)
O(3)#3–Nd(1)–O(7)#2	77.89(12)	O(3)#3–Nd(1)–N(1)	73.52(13)
O(4)–Nd(1)–O(7)#2	129.52(12)	O(4)–Nd(1)–O(5)	71.59(13)
O(4)–Nd(1)–O(6)	76.00(12)	O(5)–Nd(1)–N(1)	94.97(14)
O(6)–Nd(1)–O(5)	80.66(14)	O(6)–Nd(1)–O(7)#2	65.78(12)
O(6)–Nd(1)–N(1)	139.05(13)	O(7)#2–Nd(1)–O(5)	70.78(13)
O(7)#2–Nd(1)–N(1)	150.57(13)		
2			
Sm(1)–O(1)	2.398(2)	Sm(1)–O(2)#1	2.320(3)
Sm(1)–O(3)#1	2.330(3)	Sm(1)–O(4)#2	2.397(3)
Sm(1)–O(5)	2.405(3)	Sm(1)–O(6)#3	2.480(3)
Sm(1)–O(7)	2.507(3)	Sm(1)–N(1)	2.625(3)
Sm(1)#4–O(2)	2.320(3)	Sm(1)#4–O(3)	2.330(3)
Sm(1)#5–O(4)	2.397(3)	Sm(1)#3–O(6)	2.480(3)
O(1)–Sm(1)–O(5)	75.72(9)	O(1)–Sm(1)–O(6)#1	130.32(9)
O(1)–Sm(1)–O(7)	71.95(10)	O(1)–Sm(1)–N1	64.62(9)
O(2)#2–Sm(1)–O(1)	122.10(10)	O(2)#2–Sm(1)–O(3)#2	75.72(9)
O(2)#2–Sm(1)–O(4)#3	139.97(10)	O(2)#2–Sm(1)–O(5)	140.91(10)
O(2)#2–Sm(1)–O(6)#1	77.26(10)	O(2)#2–Sm(1)–O(7)	73.84(10)
O(2)#2–Sm(1)–N1	73.08(10)	O(3)#2–Sm(1)–O(1)	151.36(10)
O(3)#2–Sm(1)–O(4)#3	78.99(10)	O(3)#2–Sm(1)–O(5)	105.10(10)
O(3)#2–Sm(1)–O(6)#1	72.30(10)	O(3)#2–Sm(1)–O(7)	136.68(10)
O(3)#2–Sm(1)–N1	105.51(11)	O(4)#3–Sm(1)–O(1)	73.46(10)
O(4)#3–Sm(1)–O(5)	75.71(10)	O(4)#3–Sm(1)–O(6)#1	123.21(11)
O(4)#3–Sm(1)–O(7)	142.08(9)	O(4)#3–Sm(1)–N(1)	84.60(11)
O(5)–Sm(1)–O(6)#1	66.43(9)	O(5)–Sm(1)–O(7)	81.13(11)
O(5)–Sm(1)–N1	139.36(9)	O(6)#1–Sm(1)–O(7)	71.47(10)
O(6)#1–Sm(1)–N(1)	149.72(10)	O(7)–Sm(1)–N(1)	94.26(11)
3			
Tb(1)–O(1)	2.292(5)	Tb(1)–O(2)#1	2.364(5)
Tb(1)–O(3)	2.288(5)	Tb(1)–O(4)#2	2.362(5)
Tb(1)–O(5)	2.364(5)	Tb(1)–O(6)#3	2.458(3)
Tb(1)–O(7)	2.461(5)	Tb(1)–N(11)#1	2.583(6)
Tb(1)#4–O(2)	2.364(5)	Tb(1)#2–O(4)	2.362(5)
Tb(1)#3–O(6)	2.458(5)	Tb(1)#4–N(11)	2.583(6)
O(1)–Tb(1)–O(2)#1	122.50(18)	O(1)–Tb(1)–O(4)#2	140.1(2)
O(1)–Tb(1)–O(5)	140.6(2)	O(1)–Tb(1)–O(6)#3	76.41(19)
O(1)–Tb(1)–O(7)	73.73(19)	O(1)–Tb(1)–N(11)#1	73.3(2)
O(2)#1–Tb(1)–O(5)	74.89(18)	O(2)#1–Tb(1)–O(6)#3	130.51(18)
O(2)#1–Tb(1)–O(7)	71.85(19)	O(2)#1–Tb(1)–N(11)#1	65.25(19)
O(3)–Tb(1)–O(1)	76.42(19)	O(3)–Tb(1)–O(2)#1	150.64(19)
O(3)–Tb(1)–O(4)#2	78.02(19)	O(3)–Tb(1)–O(5)	105.4(2)
O(3)–Tb(1)–O(6)#3	72.50(19)	O(3)–Tb(1)–O(7)	137.5(2)

(*Continued*)

Table 2. Continued.

O(3)–Tb(1)–N(11)#1	105.0(2)	O(4)#2–Tb(1)–O(2)#1	73.58(18)
O(4)#2–Tb(1)–O(5)	75.93(19)	O(4)#2–Tb(1)–O(6)#3	123.42(19)
O(4)#2–Tb(1)–O(7)	142.17(19)	O(4)#2–Tb(1)–N(11)#1	84.5(2)
O(5)–Tb(1)–O(6)#3	67.25(18)	O(5)–Tb(1)–O(7)	80.7(2)
O(5)–Tb(1)–N(11)#1	139.17(19)	O(6)#3–Tb(1)–O(7)	71.59(19)
O(6)#3–Tb(1)–N(11)#1	149.27(19)	O(7)–Tb(1)–N(11)#1	94.6(2)

Symmetry transformations used to generate equivalent atoms for **1**: #1: 1 − *x*, −1/2 + *y*, 1/2 − *z*; #2: −*x*, −*y*, −*z*; #3: *x*, 1/2 − *y*, −1/2 + *z*; #4: 1 − *x*, 1/2 + *y*, 1/2 − *z*; #5: *x*, 1/2 − *y*, 1/2 + *z*. For **2**: #1: 1 − *x*, 2 − *y*, 1 − *z*; #2: *x*, 3/2 − *y*, 1/2 + *z*; #3: −*x*, 1/2 + *y*, 1/2 − *z*; #4: *x*, 3/2 − *y*, −1/2 + *z*; #5: −*x*, −1/2 + *y*, 1/2 − *z*. For **3**: #1: *x*, 1/2 − *y*, −1/2 + *z*; #2: −*x*, 1 − *y*, −*z*; #3: 1 − *x*, 1 − *y*, −*z*; #4: *x*, 1/2 − *y*, 1/2 + *z*.

(2) Our previous results [19–21] have confirmed that H$_3$PhIDC has various coordination modes and is a promising candidate for construction of MOFs. We, thus, selected H$_3$PhIDC to construct lanthanide-based coordination polymers.

3.2. *Crystal structures of crystalline polymers 1–3*

Single-crystal X-ray analyses reveal that **1**–**3** all possess a 3-D network and crystallize in the monoclinic space group $P2_1/c$. On account of highly isomorphous and isostructural architectures, we select **1** to describe details.

Polymer **1** exhibits unusual 3-D framework assembled by [Nd(HPhIDC)(C$_2$O$_4$)$_{0.5}$(H$_2$O)] and two free water molecules. As depicted in figure 1(a), the asymmetric unit of **1** consists of one eight-coordinate Nd(III). Around Nd^{3+}, there are three crystallographically independent HPhIDC^{2-}, one oxalate, one coordinated water molecule, and two non-coordinated water molecules. Although HPhIDC^{2-} adopts one kind of coordination, $(\kappa^1\text{–}\kappa^1\text{–}\mu^2)\text{–}(\kappa^1\text{–}\kappa^1\text{–}\mu^2)\text{–}(\kappa^1)\text{–}\mu^3$ (scheme 1a), the atoms bonded to Nd^{3+} are unique: O2B and O3B from one carboxylato-chelating HPhIDC^{2-}, N1 and O4 from another *N*, *O*-bidentate chelating ligand, and O1A from the third ligand. The coligand oxalate is *bis*-bidentate, μ_2-*k*O, O′: *k*O″, O‴ (scheme 1b). The angle of O6–Nd1–O7C is 65.78(12)°. O5 from coordinated water and Nd$_1$O$_7$N$_1$ display a slightly distorted dodecahedral geometry. The approximate plane made up of a seven-member chelating ring (O2B–C–O3B–Nd1), monodentate-bonding O1A, and coordinated water O5, can be visualized as an equatorial plane with two closely perpendicular planes derived from another two chelating rings, N1–C–O4–Nd1 and O6–C–O7C–Nd1, of which the dihedral angles are 85.951° and 83.750°. The bond angles of O–Nd–O and O–Nd–N vary from 73.39(12)° (O1A, O4) to 151.85(13)° (O2B, O4), and from 64.19(12)° (O4, N1) to 150.57(13)° (O7C, N1). Bond distances of Nd–O involving the central ion range from 2.344(3) to 2.535(4) Å, corresponding to Nd1–O3B$_{\text{carboxylate}}$ and Nd1–O5$_{\text{water}}$, respectively, and the Nd1–N1 distance is 2.661(4) Å.

Adjacent Nd^{3+} ions are bridged by nitrogen and carboxylato oxygen atoms of HPhIDC^{2-} to give a zig-zag 1-D chain (figure 1b). The distance between two alternate metal ions is 6.7510(4) Å and the continuous three metal ions lead to an isosceles triangle with the vertex angle 122.650(1)°. The similar chain presented in figure 1(c) comes from 180° rotation of the original chain in figure 1(b) with the HPhIDC^{2-} ion downwards along the phenyl substituent. Regular chains linked by carboxylato oxygen atoms result in a 2-D layer (figure 1d), which can also be visualized as a sheet composed of the SUBs: Nd$_6$(HPIDC)$_6$(H$_2$O)$_6$. The six Nd ions assemble orderly in a hexacyclic

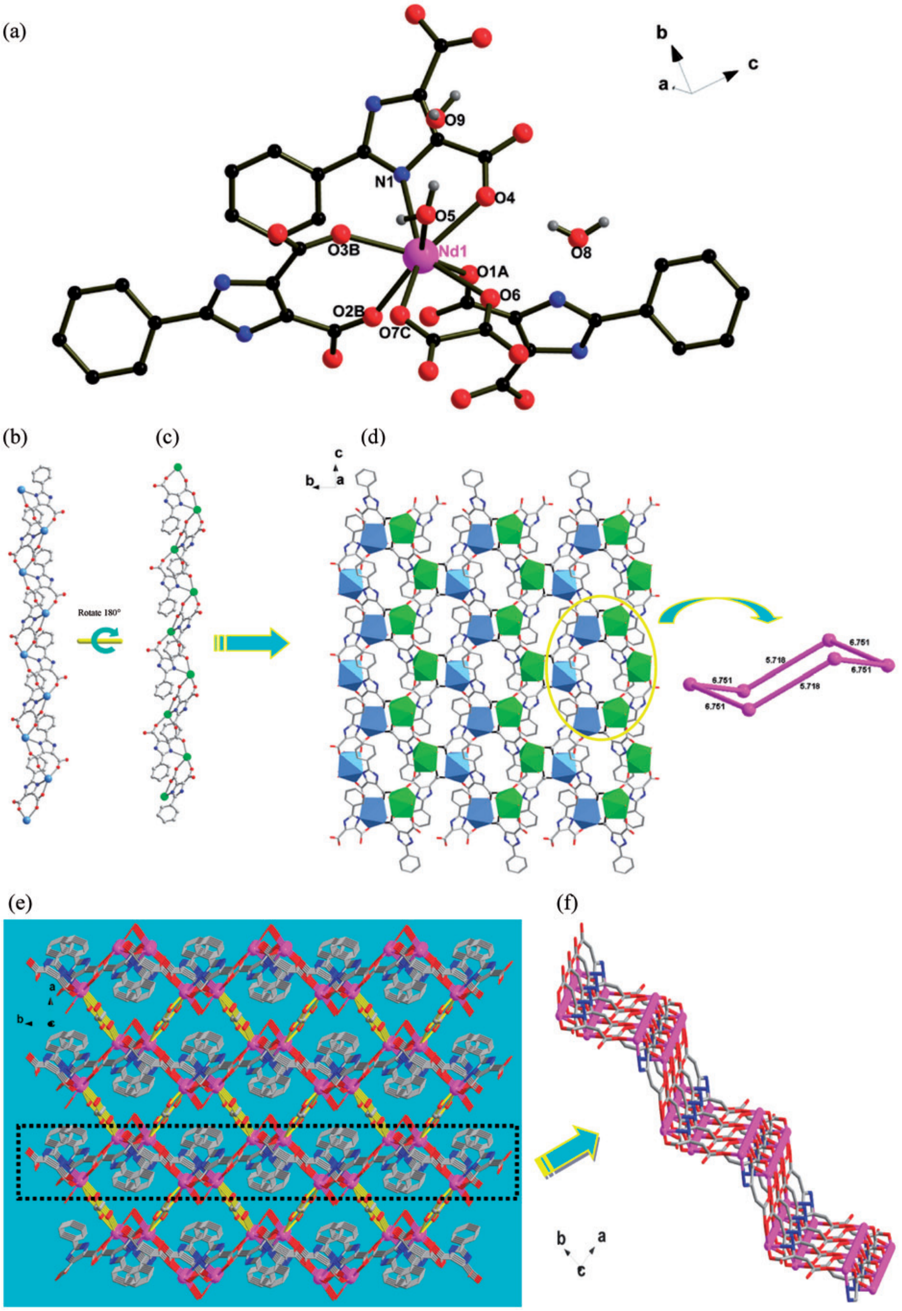

Figure 1. (a) Coordination arrangement of the Nd(III) in **1** (some hydrogen atoms are omitted for clarity); (b) ball-and-stick representation of the 1-D zig-zag chain of Nd1(III) alternately linked by $HPhIDC^{2-}$ anions; (c) view of the infinite chain shown in figure 1(b) after rotation of 180°; (d) polyhedral view of a spectacular 2-D layer in **1** down the *a*-axis assembled by the SUBs, $Nd_6(HPhIDC)_6(H_2O)_6$; (e) perspective view of the 3-D framework for **1** along the *c*-axis built from 2-D layers connected by oxalate; (f) wavelike structure of the 2-D layers in the *ab*-plane simplified by omitting partial $HPhIDC^{2-}$ units and coordinated water.

ring with the chair conformation resembling cyclohexane, which is akin to the reported structure [28]. The distances of two contiguous Nd ions are 5.718 Å and 6.751 Å. Strikingly, the oxalates connect the infinite 2-D layers to constitute the 3-D supramolecular structure (figure 1e). The two parallel eclipsed oxalate planes exhibit the distance of 2.5337 Å and two adjacent oxalates between two layers display perpendicularly with the extended angle of 80.119°. The 2-D sheet in figure 1(d) presents a wave-like diagram down the *c*-axis (figure 1f) and the length of the nearest sticks is 3.239 Å. The bilateral planes forming the valley have a dihedral angle of 83.127°, which makes the sheet close to a stair. A similar wave-like 2-D network can be obtained with linkage of Nd ions by oxalate, which is joined by carboxylate groups of $HPhIDC^{2-}$ to generate the architecture.

The volumes and corresponding bond lengths of **1**–**3** decrease owing to the decreasing ionic radius of metals, a result from the lanthanide contraction. Analysis of the crystal structures of **1**–**3** reveals hydrogen bonds in the three frameworks: (a) the kinds of hydrogen bonds are eight, six, and seven for **1**, **2**, and **3**, respectively (figure 2a–c), which is one difference for their similar structures. The number of hydrogen bonds donated by uncoordinated water molecule is five, three, and four, which may arise from the slight difference in relative spatial location of the uncoordinated water. (b) The distances of N···H and H···O for **1**–**3** are all 0.86 Å and 2.11 Å, several of which the oxygen atoms come from uncoordinated water. (c) All donor oxygen atoms are from (un)coordinated water molecules and acceptors are oxygen atoms from $HPhIDC^{2-}$, oxalate and uncoordinated water. The D···H distances (D is the representative for donor) and A···H (A is the representative for acceptor) range from 0.80 Å to 0.85 Å and 1.85 Å to 2.61 Å for **1**, from 0.84 Å to 0.87 Å and 1.83 Å to 2.48 Å for **2**, from 0.85 Å to 0.89 Å and 1.83 Å to 2.42 Å for **3**.

3.3. *IR spectroscopy and TGA*

The IR spectral data of **1**–**3** are in accord with the values in previous reports [19–21]. TGA were carried out to investigate thermal stabilities of **1**–**3** from 30.0°C to 1100.0°C in air (Supplementary material) and their thermal behaviors are very similar due to similar structures. The TG data for **1** are selected as representative. There are two steps of mass loss with **1** stable to 47.2°C. The initial mass loss of 13.1% from 47.2°C to 258.6°C corresponds to removal of two lattice and one coordinated water molecules (Calcd 11.43%). The solid continues to lose mass to 817.5°C, which is ascribed to decomposition of oxalate and $HPhIDC^{2-}$. The remaining residue accounts for 36.9%, which is consistent with the calculated value of Nd_2O_3 in the crystal unit (Calcd 35.61%).

4. Conclusions

Three new lanthanide–organic coordination polymers have been synthesized under solvothermal reaction by using multidentate H_3PhIDC and oxalate. Polymers **1**–**3** exhibit a 3-D structure constructed from 2-D layer motifs bridged by μ_2-C_2O_4 ions. Utilization of 2-position substituted imidazole dicarboxylato ligands is an effective way to construct functional coordination polymers, particularly for 2-phenyl-1*H*-imidazole-4,5-dicarboxylic. We will continue to explore additional metal complexes with

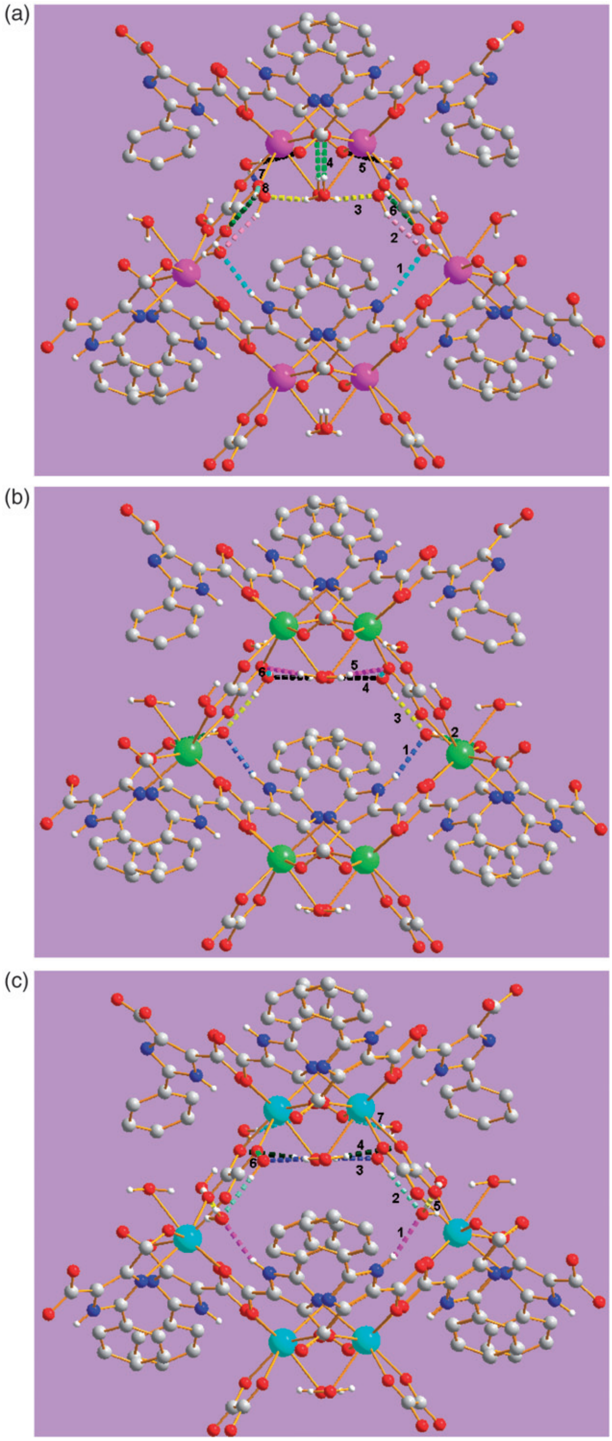

Figure 2. (a) Hydrogen bonds in a selected unit for **1**; (b) six kinds of hydrogen bonds contained in a selected unit for **2**; (c) seven kinds of hydrogen bonds contained in a selected unit for **3**.

interesting structures based on considerations of temperature, solvent, the ratio of water or others, and the ‘‘template’’ ligand.

Supplementary material

Crystallographic data for the structures reported in this article in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC nos. 853633–853635 for **1**–**3**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

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