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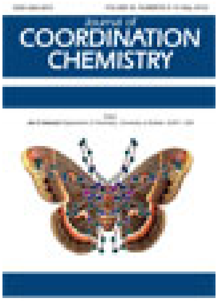

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

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Published online: 18 Apr 2012.

To cite this article: Mengwei Guo, Nan Chen, Yong-Chao Gao, Hui-Jie Lu & Gang Li (2012) A series of lanthanide-organic frameworks constructed by 2-methyl imidazole dicarboxylate and oxalate: synthesis, structures, and properties, Journal of Coordination Chemistry, 65:10, 1724-1739, DOI: 10.1080/00958972.2012.680590

To link to this article: http://dx.doi.org/10.1080/00958972.2012.680590

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Journal of Coordination Chemistry
Vol. 65, No. 10, 20 May 2012, 1724–1739

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A series of lanthanide-organic frameworks constructed by 2-methyl imidazole dicarboxylate and oxalate: synthesis, structures, and properties

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(*Received 11 July 2011; in final form 28 February 2012*)

Five lanthanide(III) coordination polymers with 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3MIDC) and ammonium oxalate, $\{[(Ln1)_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot 3H_2O\}_n$ (Ln1 = Nd (**1**), Sm (**2**)), $\{[Eu_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot 0.5EtOH\cdot 3H_2O\}_n$ (**3**), $\{[Ce_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot EtOH\cdot 3H_2O\}_n$ (**4**), and $\{[Gd_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot MeOH\cdot 3H_2O\}_n$ (**5**), have been prepared and structurally characterized. Single-crystal X-ray diffraction analyses reveal that **1** and **2** are isostructural, as are **3**, **4**, and **5**. Each exhibits a 3-D open framework, which is built by a regular 2-D grid connected by $HMIDC^{2-}$ and Ln(III). The luminescence and thermal properties of these complexes have been investigated as well.

Keywords: Coordination polymer; Lanthanide; Imidazole dicarboxylate; Crystal structure; Properties

1. Introduction

Considering the strong coordination abilities and various coordination modes of 4,5-imidazoledicarboxylic acid [1–17] and its 2-position substituent derivatives, such as 2methyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3MIDC) [18–20], 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid [21, 22], 2-propyl-1*H*-imidazole-4,5-dicarboxylic acid [23–25], 2-(hydroxymethyl)-1*H*-imidazole-4,5-dicarboxylic acid [26], 2-pyridyl-1*H*-imidazole-4, 5-dicarboxylic acid [27, 28], and 2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid [29–31], they have been used to prepare many metal–organic frameworks (MOFs) with intriguing structures and properties. Most of the reported imidazole dicarboxylate-based MOFs are of transition metal ions and MOFS of lanthanides are limited [4, 6, 23]. This may be due to lanthanide ions usually having higher coordination numbers and more flexible coordination geometries compared with transition metal ions, making it even more difficult to control the final structures. Thus, it is still a challenge to design and construct lanthanide coordination polymers with imidazole dicarboxylate ligands.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.680590

Herein, H_3MIDC was reacted with lanthanide ions in the presence of ammonium oxalate under hydro(solvo)thermal conditions. Five lanthanide(III) coordination polymers, $\{[(Ln1)_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot 3H_2O\}_n$ (Ln1 = Nd (**1**), Sm (**2**)), $\{[Eu_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot 0.5EtOH\cdot 3H_2O\}_n$ (**3**), $\{[Ce_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot EtOH\cdot 3H_2O\}_n$ (**4**), and $\{[Gd_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot MeOH\cdot 3H_2O\}_n$ (**5**), have been prepared and structurally characterized. Luminescence and thermal properties of these complexes have been investigated as well.

2. Experimental

2.1. *Materials*

All chemicals were of reagent grade quality obtained from commercial sources and used without purification. H_3MIDC was prepared according to literature procedure [32].

C, H, and N microanalyses were carried out on a FLASH EA 1112 analyzer. Infrared (IR) spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets from 400 cm^{-1} to 4000 cm^{-1}. TG-DSC measurements were performed by heating the crystalline sample from 20°C to 800°C at a rate of 10°C min^{-1} in air on a Netzsch STA 409PC differential thermal analyzer. Fluorescence spectra were characterized at room temperature by an F-4500 fluorescence spectrophotometer (240 nm min^{-1}).

2.2. *Preparation of $\{[Nd_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot 3H_2O\}_n$ (1)*

A mixture of $Nd(NO_3)_3\cdot 6H_2O$ (87.6 mg, 0.2 mmol), H_3MIDC (34.0 mg, 0.2 mmol), $(NH_4)_2C_2O_4$ (15.2 mg, 0.1 mmol), NaOH (4.0 mg, 0.1 mmol), CH_3CH_2OH/H_2O (2/3, 7.5 mL), and Et_3N (0.028 mL, 0.2 mmol) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 155°C for 4 days, and then cooled to room temperature. Block-shaped rose red crystals of **1** were isolated, washed with distilled water, and dried in air (53% yield). Anal. Calcd for $C_{14}H_{20}N_4O_{18}Nd_2$ (%): C, 20.26; H, 2.35; N, 6.67. Found (%): C, 20.47; H, 2.44; N, 6.82. IR (cm^{-1}, KBr): 3311 (s), 1618 (s), 1576 (s), 1516 (m), 1406 (m), 1314 (m), 1248 (m), 1119 (m), 869 (w), 806 (m), 791 (m), 653 (m), 435 (w).

2.3. *Preparation of $\{[Sm_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot 3H_2O\}_n$ (2)*

Compound **2** was synthesized by a method similar to that of **1**, except that $Nd(NO_3)_3\cdot 6H_2O$ was replaced by $Sm(NO_3)_3\cdot 6H_2O$. Block-shaped cyan crystals of **2** were isolated, washed with distilled water, and dried in air (68% yield). Anal. Calcd for $C_{14}H_{14}N_4O_{18}Sm_2$ (%): C, 20.19; H, 1.61; N, 6.67. Found (%): C, 20.31; H, 1.69; N, 6.77. IR (cm^{-1}, KBr): 3404 (s), 1593 (s), 1586 (s), 1406 (m), 1374 (m), 1314 (m), 1119 (w), 1045 (w), 806 (m), 792 (m), 655 (m), 419 (w).

2.4. *Preparation of $\{[Eu_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot 0.5EtOH\cdot 3H_2O\}_n$ (3)*

Compound **3** was synthesized by a method similar to that of **1**, except that $Nd(NO_3)_3\cdot 6H_2O$ was replaced by $Eu(NO_3)_3\cdot 6H_2O$. Block-shaped oyster colorless crystals of **3** were isolated, washed with distilled water, and dried in air (57% yield). Anal. Calcd for $C_{15}H_{23}N_4O_{18.50}Eu_2$ (%): C, 20.81; H, 2.57; N, 6.61. Found (%): C, 20.95; H, 2.68; N, 6.52. IR (cm^{-1}, KBr): 3423 (s), 2924 (m), 2851(m), 1618 (s), 1571 (s), 1384(s), 1341 (m), 1253 (m), 1120 (w), 1046 (w), 807 (m), 789 (m), 672 (w), 435 (w).

2.5. *Preparation of* $\{[Ce_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot EtOH\cdot 3H_2O\}_n$ *(4)*

Compound **4** was synthesized by a method similar to that of **1**, except that $Nd(NO_3)_3\cdot 6H_2O$ was replaced by $Ce(NO_3)_3\cdot 6H_2O$. Block-shaped light pink crystals of **4** were isolated, washed with distilled water, and dried in air (62% yield). Anal. Calcd for $C_{16}H_{26}N_4O_{19}Ce_2$ (%): C, 22.28; H, 3.01; N, 6.46. Found (%): C, 22.36; H, 3.03; N, 6.52. IR (cm^{-1}, KBr): 3386 (s), 1652 (s), 1570 (s), 1528 (s), 1405 (s), 1334 (m), 1251 (m), 1117 (m), 1034 (w), 792 (m), 673 (m), 480 (m).

2.6. *Preparation of* $\{[Gd_2(HMIDC)_2(C_2O_4)(H_2O)_3]\cdot MeOH\cdot 3H_2O\}_n$ *(5)*

Compound **5** was synthesized by a method similar to that of **1**, except that $Nd(NO_3)_3\cdot 6H_2O$ was replaced by $Gd(NO_3)_3\cdot 6H_2O$ and 1 mL of methanol was added to the reaction solution. Block-shaped yellowish pink crystals of **5** were isolated, washed with distilled water, and dried in air (47% yield). Anal. Calcd for $C_{15}H_{24}N_4O_{19}Gd_2$ (%): C, 20.39; H, 2.68; N, 6.28. Found (%): C, 20.48; H, 2.73; N, 6.37. IR (cm^{-1}, KBr): 3422 (s), 1637 (s), 1579 (s), 1577 (s), 1384 (s), 1253 (m), 1122 (w), 1047 (w), 808 (m), 734 (w), 672 (w), 478 (w).

2.7. *Crystal structure determinations*

Suitable single crystals of **1**–**5** were selected for single-crystal X-ray diffraction analyses. The intensity data were measured on a Bruker Smart APEXII CCD imaging plate area detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Single crystals of **1**–**5** were 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 five 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. All calculations were performed using the SHELX-97 crystallographic software package [33]. Crystallographic data of the five complexes are given in table 1. Selected bond lengths are listed in table 2.

3. Results and discussion

3.1. *Hydrothermal syntheses*

Initially, we tried to synthesize the complexes with the evaporation method at room temperature utilizing sodium hydroxide to adjust pH, but we cannot obtain suitable crystals. Hydrothermal synthesis has been widely used to produce novel and diverse

Table 1. Crystal data and structure refinement information for **1–5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{14}H_{20}N_4Nd_2O_{18}$	$C_{14}H_{20}N_4Sm_2O_{18}$	$C_{15}H_{23}N_4Eu_2O_{18.5}$	$C_{16}H_{26}N_4Ce_2O_{19}$	$C_{15}H_{24}N_4Gd_2O_{19}$
Formula weight	820.82	833.05	859.29	858.65	878.87
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$
Unit cell dimensions (Å, °)					
a	10.3246(15)	10.255(3)	10.2289(5)	10.416(2)	10.190(3)
b	11.3359(17)	11.268(4)	11.2526(5)	11.440(3)	11.232(3)
c	22.316(3)	22.194(7)	22.1877(11)	22.457(5)	23.240(6)
α	90	90	90	90	90
β	97.290(2)	97.061(4)	96.9670(10)	97.695(2)	108.943(10)
γ	90	90	90	90	90
Volume (Å^3), Z	2590.7(7), 4	2545.2(15), 4	2535.0(2), 4	2651.9(11), 4	2515.9(12), 4
Calculated density (Mg m^{-3})	2.104	2.158	2.252	2.151	2.246
Absorption coefficient (mm^{-1})	4.051	4.657	4.997	3.484	5.320
Crystal size (mm^3)	0.35 × 0.21 × 0.18	0.18 × 0.16 × 0.14	0.20 × 0.20 × 0.18	0.30 × 0.20 × 0.18	0.20 × 0.18 × 0.17
Reflections collected	17,881	18,485	18,875	19,610	18,564
Independent reflection	4823 [R(int) = 0.0499]	4490 [R(int) = 0.0745]	4457 [R(int) = 0.0360]	4665 [R(int) = 0.0241]	4420 [R(int) = 0.0795]
Data/restraints/parameters	4823/0/345	4490/0/343	4457/22/394	4665/5/391	4420/6/354
Goodness-of-fit on F^2	1.044	1.040	1.073	1.078	0.946
R	0.0352	0.0580	0.0249	0.0195	0.0479
R_w	0.0969	0.1435	0.0640	0.0450	0.1247

Table 2. Selected bond distances (Å) and angles (°) for **1–5**.

1[a]			
Nd(1)–O(1)	2.448(4)	Nd(1)–O(8)#1	2.453(4)
Nd(1)–O(12)	2.480(4)	Nd(1)–O(9)#2	2.490(4)
Nd(1)–O(6)#1	2.526(4)	Nd(1)–N(1)	2.649(4)
Nd(1)–O(5)	2.479(4)	Nd(1)–O(7)	2.517(3)
Nd(1)–N(3)#2	2.672(4)	Nd(2)–O(2)#3	2.366(4)
Nd(2)–O(10)	2.349(4)	Nd(2)–O(4)#4	2.404(4)
Nd(2)–O(14)	2.457(4)	Nd(2)–O(11)	2.457(4)
Nd(2)–O(3)#3	2.412(4)	Nd(2)–O(15)	2.509(5)
Nd(2)–O(13)	2.490(4)	O(8)#1–Nd(1)–O(5)	71.25(12)
O(1)–Nd(1)–O(8)#1	124.07(13)	O(1)–Nd(1)–O(5)	127.02(12)
O(1)–Nd(1)–O(12)	104.74(13)	O(8)#1–Nd(1)–O(12)	131.19(14)
O(1)–Nd(1)–O(9)#2	151.16(12)	O(8)#1–Nd(1)–O(9)#2	67.52(13)
O(12)–Nd(1)–O(9)#2	69.07(13)	O(1)–Nd(1)–O(7)	68.38(12)
O(5)–Nd(1)–O(7)	65.44(12)	O(12)–Nd(1)–O(7)	68.19(13)
O(5)–Nd(1)–O(12)	80.92(13)	O(5)–Nd(1)–O(9)#2	80.84(12)
O(9)#2–Nd(1)–O(7)	128.57(13)	O(8)#1–Nd(1)–O(7)	128.07(12)
O(5)–Nd(1)–O(6)#1	132.95(12)	O(7)–Nd(1)–O(6)#1	134.76(14)
O(1)–Nd(1)–O(6)#1	70.58(13)	O(8)#1–Nd(1)–O(6)#1	64.76(12)
O(5)–Nd(1)–N(1)	76.33(14)	O(7)–Nd(1)–N(1)	70.18(13)
O(12)–Nd(1)–O(6)#1	142.15(14)	O(9)#2–Nd(1)–O(6)#1	96.67(14)
O(8)#1–Nd(1)–N(3)#2	106.01(13)	O(9)#2–Nd(1)–N(3)#2	63.03(13)
O(1)–Nd(1)–N(1)	64.62(13)	O(8)#1–Nd(1)–N(1)	73.00(13)
O(12)–Nd(1)–N(1)	137.87(14)	O(9)#2–Nd(1)–N(1)	138.96(13)
O(6)#1–Nd(1)–N(1)	75.73(14)	O(1)–Nd(1)–N(3)#2	88.15(13)
O(5)–Nd(1)–N(3)#2	140.49(14)	O(12)–Nd(1)–N(3)#2	71.99(14)
O(7)–Nd(1)–N(3)#2	125.54(13)	O(6)#1–Nd(1)–N(3)#2	70.35(14)
N(1)–Nd(1)–N(3)#2	142.11(14)	O(13)–Nd(2)–O(15)	135.29(17)
O(10)–Nd(2)–O(2)#3	138.64(15)	O(10)–Nd(2)–O(4)#4	87.92(17)
O(2)#3–Nd(2)–O(4)#4	107.13(15)	O(4)#4–Nd(2)–O(3)#3	72.21(14)
O(10)–Nd(2)–O(3)#3	75.42(15)	O(2)#3–Nd(2)–O(3)#3	73.24(13)
O(10)–Nd(2)–O(11)	72.09(14)	O(2)#3–Nd(2)–O(11)	148.15(13)
O(4)#4–Nd(2)–O(11)	76.45(14)	O(2)#3–Nd(2)–O(14)	83.05(15)
O(3)#3–Nd(2)–O(11)	135.12(13)	O(10)–Nd(2)–O(14)	110.13(19)
O(4)#4–Nd(2)–O(14)	139.92(15)	O(3)#3–Nd(2)–O(14)	145.73(15)
O(11)–Nd(2)–O(14)	75.84(15)	O(4)#4–Nd(2)–O(13)	72.01(14)
O(10)–Nd(2)–O(13)	148.76(16)	O(2)#3–Nd(2)–O(13)	71.70(15)
O(3)#3–Nd(2)–O(13)	118.37(15)	O(11)–Nd(2)–O(13)	79.90(14)
O(14)–Nd(2)–O(13)	75.07(16)	O(4)#4–Nd(2)–O(15)	147.89(17)
O(10)–Nd(2)–O(15)	72.6(2)	O(2)#3–Nd(2)–O(15)	75.09(19)
O(3)#3–Nd(2)–O(15)	78.19(18)	O(11)–Nd(2)–O(15)	119.04(18)
2[b]			
Sm(1)–O(12)#1	2.416(7)	Sm(1)–O(2)#2	2.436(7)
Sm(1)–O(3)	2.439(7)	Sm(1)–O(1)	2.506(7)
Sm(1)–O(5)	2.451(7)	Sm(1)–O(8)#3	2.452(7)
Sm(1)–N(1)#3	2.645(9)	Sm(1)–N(3)#1	2.611(8)
Sm(1)–O(4)#2	2.509(7)	Sm(2)–O(9)	2.388(8)
Sm(2)–O(7)	2.318(8)	Sm(2)–O(11)	2.346(8)
Sm(2)–O(10)#4	2.390(8)	Sm(2)–O(14)	2.442(8)
Sm(2)–O(13)	2.466(8)	Sm(2)–O(6)	2.416(8)
Sm(2)–O(15)	2.516(10)	O(2)#2–Sm(1)–O(3)	71.4(2)
O(12)#1–Sm(1)–O(2)2	128.0(2)	O(12)#1–Sm(1)–O(3)	125.1(2)
O(12)#1–Sm(1)–O(5)	103.3(2)	O(2)#2–Sm(1)–O(5)	80.6(2)
O(3)–Sm(1)–O(5)	131.6(2)	O(12)#1–Sm(1)–O(8)#3	150.9(2)
O(5)–Sm(1)–O(8)#3	69.8(2)	O(3)–Sm(1)–O(1)	65.2(2)
O(12)#1–Sm(1)–O(4)#2	68.2(2)	O(2)#2–Sm(1)–O(8)#3	79.8(2)
O(5)–Sm(1)–O(4)#2	67.9(2)	O(12)#1–Sm(1)–O(1)	70.6(2)
O(12)#1–Sm(1)–N(3)#1	65.5(2)	O(5)–Sm(1)–O(1)	142.0(3)
O(5)–Sm(1)–N(3)#1	137.5(3)	O(2)#2–Sm(1)–O(4)#2	65.8(2)

(*Continued*)

Table 2. Continued.

O(4)#2–Sm(1)–N(3)#1	70.0(3)	O(8)#3–Sm(1)–O(4)#2	128.6(3)
O(3)–Sm(1)–N(1)#3	105.9(3)	O(2)#2–Sm(1)–N(3)#1	77.1(3)
O(1)–Sm(1)–N(1)#3	70.1(3)	O(8)#3–Sm(1)–N(3)#1	138.7(2)
O(5)–Sm(1)–N(1)#3	72.2(3)	O(12)#1–Sm(1)–N(1)#3	87.3(2)
O(4)#2–Sm(1)–N(1)#3	125.7(3)	O(3)–Sm(1)–O(8)#3	67.1(2)
O(8)#3–Sm(1)–O(1)	97.2(3)	O(2)#2–Sm(1)–O(1)	133.7(2)
O(3)–Sm(1)–O(4)#2	128.1(2)	O(1)–Sm(1)–O(4)#2	134.3(3)
O(3)–Sm(1)–N(3)#1	73.2(3)	O(1)–Sm(1)–N(3)#1	75.7(3)
O(8)#3–Sm(1)–N(1)#3	63.6(2)	O(2)#2–Sm(1)–N(1)#3	139.9(3)
N(3)#1–Sm(1)–N(1)#3	141.9(3)	O(13)–Sm(2)–O(15)	135.6(3)
O(7)–Sm(2)–O(11)	139.1(3)	O(7)–Sm(2)–O(9)	75.6(3)
O(7)–Sm(2)–O(10)#4	88.1(3)	O(11)–Sm(2)–O(10)#4	107.4(3)
O(7)–Sm(2)–O(6)	72.1(3)	O(11)–Sm(2)–O(6)	147.5(3)
O(10)#4–Sm(2)–O(6)	76.3(3)	O(7)–Sm(2)–O(14)	109.6(3)
O(9)–Sm(2)–O(14)	146.4(3)	O(10)#4–Sm(2)–O(14)	139.6(3)
O(7)–Sm(2)–O(13)	148.5(3)	O(11)–Sm(2)–O(13)	71.7(3)
O(10)#4–Sm(2)–O(13)	72.0(3)	O(6)–Sm(2)–O(13)	79.4(3)
O(7)–Sm(2)–O(15)	72.5(3)	O(11)–Sm(2)–O(15)	75.1(3)
O(10)#4–Sm(2)–O(15)	147.5(3)	O(6)–Sm(2)–O(15)	119.5(3)
O(11)–Sm(2)–O(9)	73.9(3)	O(9)–Sm(2)–O(10)#4	72.1(3)
O(9)–Sm(2)–O(6)	135.0(3)	O(11)–Sm(2)–O(14)	83.1(3)
O(6)–Sm(2)–O(14)	75.3(3)	O(9)–Sm(2)–O(13)	118.6(3)
O(14)–Sm(2)–O(13)	75.0(3)	O(9)–Sm(2)–O(15)	77.9(4)
3^c			
Eu(1)–O(3)	2.320(3)	Eu(1)–O(6)#1	2.338(3)
Eu(1)–O(8)#2	2.368(3)	Eu(1)–O(14)	2.415(4)
Eu(1)–O(7)#1	2.388(3)	Eu(1)–O(1)	2.409(3)
Eu(1)–O(13)	2.437(4)	Eu(1)–O(15)	2.471(4)
Eu(2)–O(10)#3	2.431(3)	Eu(2)–O(11)	2.434(3)
Eu(2)–O(5)	2.411(3)	Eu(2)–O(2)#4	2.434(3)
Eu(2)–O(4)	2.450(3)	Eu(2)–O(12)#3	2.496(3)
Eu(2)–O(9)	2.498(3)	Eu(2)–N(1)	2.634(4)
Eu(2)–N(3)	2.587(4)	O(3)–Eu(1)–O(6)#1	139.31(13)
O(3)–Eu(1)–O(8)#2	88.51(14)	O(6)#1–Eu(1)–O(8)#2	106.89(13)
O(6)#1–Eu(1)–O(7)#1	74.17(11)	O(8)#2–Eu(1)–O(7)#1	72.11(13)
O(3)–Eu(1)–O(1)	72.59(12)	O(3)–Eu(1)–O(7)#1	75.40(12)
O(6)#1–Eu(1)–O(1)	146.92(12)	O(8)#2–Eu(1)–O(1)	76.48(12)
O(7)#1–Eu(1)–O(1)	135.16(11)	O(8)#2–Eu(1)–O(14)	139.56(14)
O(3)–Eu(1)–O(14)	109.96(17)	O(6)#1–Eu(1)–O(14)	83.63(14)
O(3)–Eu(1)–O(13)	148.47(13)	O(7)#1–Eu(1)–O(13)	118.76(13)
O(7)#1–Eu(1)–O(14)	146.60(14)	O(1)–Eu(1)–O(14)	74.75(13)
O(6)#1–Eu(1)–O(13)	71.46(13)	O(8)#2–Eu(1)–O(13)	71.64(13)
O(3)–Eu(1)–O(15)	72.47(16)	O(7)#1–Eu(1)–O(15)	77.77(15)
O(1)–Eu(1)–O(13)	78.94(12)	O(14)–Eu(1)–O(13)	75.41(16)
O(6)#1–Eu(1)–O(15)	75.18(15)	O(8)#2–Eu(1)–O(15)	147.64(14)
O(13)–Eu(1)–O(15)	135.63(14)	O(14)–Eu(1)–O(15)	72.54(16)
O(1)–Eu(1)–O(15)	119.89(15)	O(10)#3–Eu(2)–O(11)	71.08(11)
O(5)–Eu(2)–O(10)#3	128.35(10)	O(5)–Eu(2)–O(11)	125.59(11)
O(5)–Eu(2)–O(2)#4	103.17(11)	O(10)#3–Eu(2)–O(2)#4	80.78(12)
O(11)–Eu(2)–O(2)#4	131.20(11)	O(11)–Eu(2)–O(4)	66.95(11)
O(5)–Eu(2)–O(4)	150.79(11)	O(10)#3–Eu(2)–O(4)	79.49(11)
O(10)#3–Eu(2)–O(12)#3	66.36(10)	O(4)–Eu(2)–O(12)#3	128.40(11)
O(2)#4–Eu(2)–O(4)	69.31(11)	O(5)–Eu(2)–O(12)#3	67.92(10)
O(11)–Eu(2)–O(12)#3	128.63(11)	O(2)#4–Eu(2)–O(12)#3	68.01(11)
O(11)–Eu(2)–O(9)	65.64(10)	O(12)#3–Eu(2)–O(9)	133.64(11)
O(5)–Eu(2)–O(9)	70.18(11)	O(10)#3–Eu(2)–O(9)	133.55(11)
O(2)#4–Eu(2)–O(9)	142.08(12)	O(4)–Eu(2)–O(9)	97.95(12)
O(11)–Eu(2)–N(3)	73.35(12)	O(12)#3–Eu(2)–N(3)	70.26(12)
O(5)–Eu(2)–N(3)	65.96(11)	O(10)#3–Eu(2)–N(3)	76.98(12)

(*Continued*)

Table 2. Continued.

O(2)#4–Eu(2)–N(3)	137.76(12)	O(4)–Eu(2)–N(3)	138.59(11)
O(9)–Eu(2)–N(3)	75.35(12)	O(5)–Eu(2)–N(1)	86.58(11)
O(10)#3–Eu(2)–N(1)	140.14(11)	O(4)–Eu(2)–N(1)	63.95(11)
O(11)–Eu(2)–N(1)	105.84(12)	O(2)#4–Eu(2)–N(1)	72.17(12)
O(12)#3–Eu(2)–N(1)	125.19(12)	O(9)–Eu(2)–N(1)	70.23(12)
4[d]			
Ce(1)–O(3)	2.485(2)	Ce(1)–O(10)#1	2.487(2)
Ce(1)–O(8)#2	2.511(2)	Ce(1)–O(5)	2.527(2)
Ce(1)–O(9)	2.537(2)	Ce(1)–O(12)	2.506(2)
Ce(1)–O(11)#1	2.553(2)	Ce(1)–N(2)	2.702(2)
Ce(1)–N(3)	2.704(3)	Ce(2)–O(1)#1	2.445(2)
Ce(2)–O(6)	2.384(2)	Ce(2)–O(4)#3	2.404(2)
Ce(2)–O(2)#3	2.450(2)	Ce(2)–O(7)	2.489(2)
Ce(2)–O(13)	2.501(3)	Ce(2)–O(15)	2.548(3)
Ce(2)–O(14)	2.523(2)	O(3)–Ce(1)–O(10)#1	122.85(7)
O(3)–Ce(1)–O(12)	125.83(7)	O(10)#1–Ce(1)–O(12)	71.49(7)
O(3)–Ce(1)–O(8)#2	106.63(7)	O(3)–Ce(1)–O(5)	151.56(7)
O(10)#1–Ce(1)–O(8)#2	130.52(7)	O(12)–Ce(1)–O(8)#2	80.39(8)
O(10)#1–Ce(1)–O(5)	67.70(7)	O(12)–Ce(1)–O(5)	81.94(7)
O(8)#2–Ce(1)–O(5)	68.71(8)	O(12)–Ce(1)–O(9)	64.71(7)
O(3)–Ce(1)–O(9)	68.58(8)	O(10)#1–Ce(1)–O(9)	127.63(7)
O(8)#2–Ce(1)–O(11)#1	142.70(8)	O(3)–Ce(1)–N(2)	63.57(7)
O(10)#1–Ce(1)–O(11)#1	64.32(7)	O(12)–Ce(1)–O(11)#1	132.67(7)
O(12)–Ce(1)–N(3)	140.80(7)	O(9)–Ce(1)–N(3)	126.07(8)
O(5)–Ce(1)–O(11)#1	95.91(8)	O(9)–Ce(1)–O(11)#1	135.06(8)
O(3)–Ce(1)–N(3)	89.35(7)	O(10)#1–Ce(1)–N(3)	105.92(8)
O(8)#2–Ce(1)–N(3)	72.36(8)	O(5)–Ce(1)–N(3)	62.30(7)
O(10)#1–Ce(1)–N(2)	72.75(8)	N(2)–Ce(1)–N(3)	142.41(8)
O(8)#2–Ce(1)–O(9)	68.61(8)	O(5)–Ce(1)–O(9)	129.07(8)
O(11)#1–Ce(1)–N(3)	70.45(8)	O(6)–Ce(2)–O(4)#3	138.44(9)
O(6)–Ce(2)–O(1)#1	88.31(10)	O(4)#3–Ce(2)–O(1)#1	107.11(8)
O(6)–Ce(2)–O(2)#3	76.23(8)	O(6)–Ce(2)–O(7)	71.39(8)
O(4)#3–Ce(2)–O(2)#3	72.40(7)	O(1)#1–Ce(2)–O(2)#3	72.54(8)
O(4)#3–Ce(2)–O(7)	149.05(8)	O(1)#1–Ce(2)–O(7)	76.15(8)
O(2)#3–Ce(2)–O(7)	135.07(8)	O(1)#1–Ce(2)–O(13)	140.33(9)
O(6)–Ce(2)–O(13)	109.77(11)	O(4)#3–Ce(2)–O(13)	82.85(8)
O(2)#3–Ce(2)–O(13)	144.79(9)	O(7)–Ce(2)–O(13)	76.87(8)
O(6)–Ce(2)–O(14)	149.20(9)	O(2)#3–Ce(2)–O(14)	118.02(8)
O(4)#3–Ce(2)–O(14)	71.57(9)	O(1)#1–Ce(2)–O(14)	72.25(8)
O(7)–Ce(2)–O(14)	80.70(8)	O(13)–Ce(2)–O(14	75.13(9)
O(6)–Ce(2)–O(15)	72.19(12)	O(14)–Ce(2)–O(15)	135.20(10)
O(4)#3–Ce(2)–O(15)	75.03(11)	O(1)#1–Ce(2)–O(15)	147.61(10)
O(7)–Ce(2)–O(15)	119.09(10)	O(13)–Ce(2)–O(15)	71.83(10)
5[e]			
Gd(1)–O(11)	2.398(6)	Gd(1)–O(4)	2.405(6)
Gd(1)–O(6)#1	2.435(6)	Gd(1)–O(12)	2.491(6)
Gd(1)–O(10)	2.425(6)	Gd(1)–O(2)	2.437(6)
Gd(1)–N(1)	2.616(7)	Gd(1)–N(3)	2.567(7)
Gd(1)–O(9)	2.488(6)	Gd(2)–O(8)#3	2.357(6)
Gd(2)–O(1)	2.316(7)	Gd(2)–O(5)#2	2.328(6)
Gd(2)–O(15)	2.437(6)	Gd(2)–O(14)	2.396(7)
Gd(2)–O(7)#2	2.368(7)	Gd(2)–O(3)	2.400(6)
Gd(2)–O(13)	2.432(7)	O(11)–Gd(1)–O(4)	128.7(2)
O(11)–Gd(1)–O(10)	71.3(2)	O(4)–Gd(1)–O(10)	125.7(2)
O(11)–Gd(1)–O(6)#1	80.6(2)	O(11)–Gd(1)–O(2)	79.2(2)
O(4)–Gd(1)–O(6)#1	102.8(2)	O(10)–Gd(1)–O(6)#1	131.5(2)
O(6)#1–Gd(1)–O(2)	69.6(2)	O(11)–Gd(1)–O(9)	66.5(2)
O(4)–Gd(1)–O(2)	150.7(2)	O(10)–Gd(1)–O(2)	66.8(2)

(*Continued*)

Table 2. Continued.

O(4)–Gd(1)–O(12)	70.1(2)	O(10)–Gd(1)–O(12)	65.73(19)
O(10)–Gd(1)–O(9)	128.81(19)	O(11)–Gd(1)–N(3)	77.2(2)
O(4)–Gd(1)–O(9)	67.89(19)	O(6)#1–Gd(1)–O(9)	67.9(2)
O(2)–Gd(1)–O(9)	128.5(2)	O(11)–Gd(1)–O(12)	134.1(2)
O(10)–Gd(1)–N(3)	73.3(2)	O(9)–Gd(1)–N(3)	70.2(2)
O(4)–Gd(1)–N(3)	66.3(2)	O(6)#1–Gd(1)–N(3)	133.6(2)
O(2)–Gd(1)–N(3)	138.4(2)	O(12)–Gd(1)–N(3)	75.7(2)
O(6)#1–Gd(1)–N(1)#2	72.1(2)	O(12)–Gd(1)–N(1)#2	70.0(2)
O(11)–Gd(1)–N(1)	140.2(2)	O(4)–Gd(1)–N(1)	86.0(2)
O(10)–Gd(1)–N(1)	106.2(2)	O(2)#2–Gd(1)–N(1)#2	64.6(2)
O(9)–Gd(1)–N(1)	124.7(2)	N(3)–Gd(1)–N(1)	141.6(2)
O(1)–Gd(2)–O(8)#3	89.6(3)	O(5)#2–Gd(2)–O(8)#3	106.3(2)
O(1)–Gd(2)–O(7)#2	75.4(2)	O(1)–d(2)–O(5)#2	139.2(2)
O(5)#2–Gd(2)–O(7)#2	74.4(2)	O(8)#3–Gd(2)–O(7)#2	71.9(2)
O(1)–Gd(2)–O(3)	73.4(2)	O(8)#3–Gd(2)–O(14)	139.2(3)
O(1)–Gd(2)–O(14)	109.0(3)	O(5)#2–Gd(2)–O(14)	83.4(3)
O(7)#2–Gd(2)–O(14)	147.0(3)	O(3)–Gd(2)–O(13)	120.2(3)
O(1)–Gd(2)–O(13)	72.1(3)	O(7)#2–Gd(2)–O(15)	118.7(2)
O(5)#2–Gd(2)–O(13)	75.3(3)	O(8)#3–Gd(2)–O(15)	70.8(2)
O(3)–Gd(2)–O(13)	120.2(3)	O(14)–Gd(2)–O(13)	72.7(3)
O(1)–Gd(2)–O(15)	148.3(2)	O(7)#2–Gd(2)–O(15)	118.7(2)
O(5)#2–Gd(2)–O(15)	71.8(2)	O(8)#3–Gd(2)–O(15)	70.8(2)
O(3)–Gd(2)–O(15)	77.9(2)	O(14)–Gd(2)–O(15)	75.2(3)

[a] Symmetry codes for **1**: 1: $-x+1/2$, $y+1/2$, $-z+1/2$; #2: $-x-1/2$, $y+1/2$, $z+1/2$; #3: $-x$, $-y+1$, $-z$; #4: $x-1$, y, z. [b] For **2**: #1: $-x+1$, $-y$, $-z$; #2: $-x+3/2$, $y+1/2$, $-z+1/2$; #3: $-x+1/2$, $y-1/2$, $-z+1/2$; #4: $-x$, $-y$, $-z$. [c] For **3**: #1: $x-1/2$, $-y+3/2$, $z+1/2$; #2: $-x+3/2$, $y-1/2$, $-z+1/2$; #3: $-x+3/2$, $y+1/2$, $-z+1/2$; #4: $-x+1/2$, $y+1/2$, $-z+1/2$. [d] For **4**: #1: $-x+3/2$, $y+1/2$, $-z+1/2$; #2: $-x+1/2$, $y-1/2$, $-z+1/2$; #3: $x-1/2$, $-y+3/2$, $z+1/2$. [e] For **5**: #1: $-x+1$, $y+1/2$, $-z+3/2$; #2: $x-1$, $-y+3/2$, $z-1/2$; #3: $-x+2$, $y-1/2$, $-z+3/2$.

architectures due to relatively high temperature and pressure improving ligand solubility and the reactivity to obtain suitable crystals. Thus, we adopted the hydrothermal synthesis to prepare lanthanide(III) coordination polymers. Fortunately, five lanthanide(III) coordination polymers, **1**–**5**, have been prepared.

As discussed in our recent publication [34], introduction of methyl into H_3MIDC affects the natural bond orbital charge distributions of oxygen and nitrogen. H_3MIDC shows strong coordination ability. In order to continuously explore the methyl substituent effects in such a ligand, we prepare lanthanide(III) polymers. Our findings confirm that H_3MIDC has strong coordination ability in **1**–**5**.

During the experiment, lanthanide nitrate salts reacted with H_3MIDC in mixed solvents CH_3CH_2OH/H_2O (2 : 3), CH_3CN/H_2O (2 : 3) or pure H_2O; crystalline products were found only in CH_3CH_2OH/H_2O (2 : 3). Solvent effects are significant in hydrothermal processes. The stoichiometry of the starting materials is also important for formation of products. Only 1 : 1 molar ratio of lanthanide salts and H_3MIDC produced crystals. Temperature may affect the crystal shape of final products. We chose temperatures between 140°C and 180°C. Only at 155°C we can acquire suitable crystals readily. The pH is also vital; using sodium hydroxide, potassium hydroxide, and triethylamine independently to adjust the pH, no crystals were obtained. Only when sodium hydroxide and triethylamine were employed together could target products be formed.

By controlling over synthetic conditions such as solvent, pH, metal/ligand molar ratio, and temperature, the reproducibility of our experiments is good.

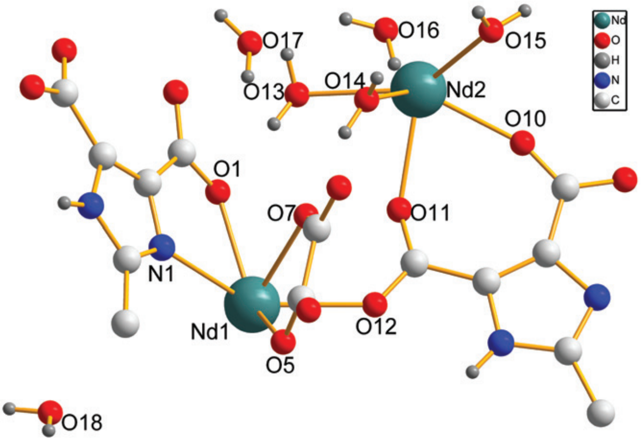

Figure 1. The segment of **1** showing the local coordination environment of Nd(III) ions.

To confirm the existence of solvent guests in crystals of **1**–**5**, we first heated crystalline samples of **1**–**5** from room temperature to 158°C, 162°C, 207°C, 211°C, and 200°C according to their thermal analysis data, respectively, then determined their elemental analysis. The elemental analysis (EA) results for heated samples of **1** (C, 21.59; H, 1.68; N, 7.28%), **2** (C, 21.36; H, 1.84; N, 7.23%), **3** (C, 20.89; H, 1.58; N, 7.08%), **4** (C, 22.39; H, 1.76; N, 7.48%), and **5** (C, 22.49; H, 1.47; N, 6.67%) are consistent with the calculated values of **1**–**5** without solvent guests (For **1**: C, 21.93; H, 1.84; N, 7.31%. For **2**: C, 21.59; H, 1.81; N, 7.19%. For **3**: C, 20.74; H, 1.60; N, 7.41%. For **4**: C, 22.14; H, 1.99; N, 7.38%. For **5**: C, 22.33; H, 2.00; N, 6.94%).

3.2. *Descriptions of crystal structures of 1–5*

The crystal structures determined by X-ray diffraction reveal that **1**–**5** exhibit 3-D frameworks consisting of lanthanide-organic layers pillared by oxalate anions. Polymers **1** and **2** are isostructural, as are **3**, **4**, and **5**. They crystallize in the monoclinic space group *P*2(1)/*n*. The only structural difference is the number and type of lattice solvent. Therefore, only the structure of **1** will be discussed in detail as a representative. Crystallographic data and structural refinements for **1**–**5** are summarized in table 1. According to EA data, thermal analyses, and experimental diffraction data, we ascertain the kinds of solvent and their occupancy factors of **1**–**5**. However, thermal ellipsoids of ethanol are large, which may be due to disordered solvents included as guests in porous hosts being difficult to identify.

As shown in figure 1, the asymmetric unit contains two Nd(III), two independent deprotonated HMIDC^{2-}, one oxalate which is lying on an inversion center, three coordinated water molecules, and three lattice water molecules. There are two crystallographically unique Nd(III) centers in the asymmetric unit, which show different coordination environments. Nd1(III) is nine-coordinate in a slightly distorted dodecahedron, with two nitrogen atoms (N3, N3B) from two individual μ_3-HMIDC^{2-}, three carboxylate oxygen atoms (O1, O9B, O12) from three individual μ_3-HMIDC^{2-}, and four other oxygen atoms (O5, O7, O6A, O8A) from two oxalate anions (figure 2a).

The Nd2(III) is eight-coordinate by five oxygen atoms (O10, O11, O3C, O4D, O15) from three individual μ_3-HMIDC^{2-} and three other oxygen atoms (O13, O14, O15) from three coordinated water molecules, forming a slightly distorted square-antiprism (figure 2b). The Nd1–O bond lengths vary from 2.448(4) to 2.526(4) Å and Nd1–N bond lengths are 2.649(4)–2.672(4) Å. The bond distances of Nd2–O range from 2.349(4) to 2.509(5) Å, close to those of Nd1–O distances. The bond angles around each Nd(III) vary from 63.03(13)° to 151.16(12)°, similar to those reported in several related species [4, 6].

In **1**, HMIDC^{2-} adopt μ_3-kN, O : kO′, O′: kO′ mode to bridge three Nd(III) ions and the seven carboxylates adopt bis(bridging) bidentate and monodentate modes to connect two Nd(III) ions. In the cationic layer, a dimer is formed by μ_3-HMIDC^{2-} linking two adjacent Nd(III) ions, another alternate dimer is generated through two adjacent Nd(III) ions connected by oxo-bridged ligand, then three adjacent dimers are arranged alternately in an Nd6 hexagonal ring (figure 3). Six Nd(III) ions are almost coplanar and the pairwise Nd(III)···Nd(III)···Nd(III) angles are 100.376(5)°, 119.479(5)°, and 139.617(6)° successively, while the adjacent Nd(III)···Nd(III) distances are 6.4018(8)–6.9139(7) Å.

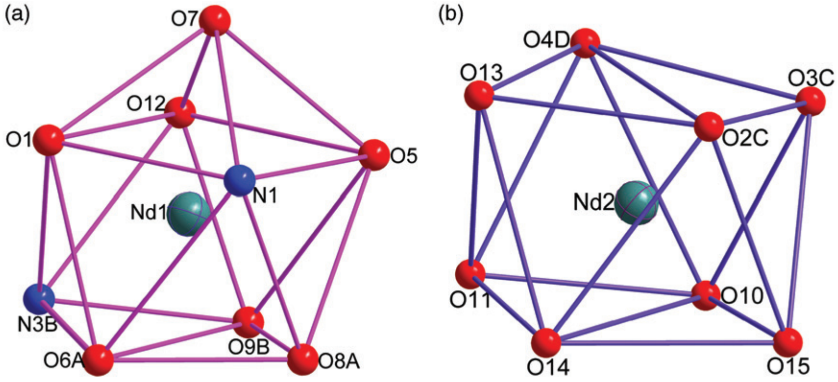

Figure 2. View of the coordination geometry around Nd1(III) or Nd2(III) sites.

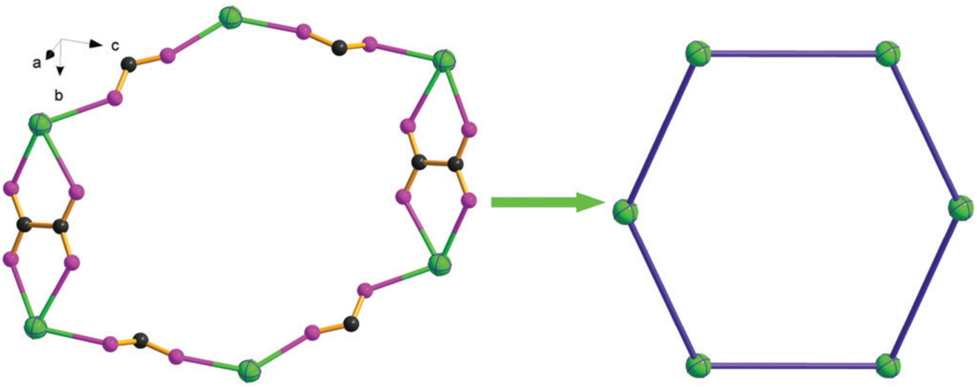

Figure 3. An individual Nd6 hexagonal ring viewed approximately in **1**.

Central Nd1(III) has no coordinated water molecules so that an infinite L–Nd1–L (L = oxalate ion) right-hand (P) helical chain was formed (figure 4a); the nearest distance of two adjacent Nd1(III) is 5.6633(6) Å. A regular 2-D grid was formed through these parallel infinite chains connected by carboxylate of $HMIDC^{2-}$ and Nd2(III) (figure 4b). Finally, a 3-D framework was acquired by adjacent sheets connecting through oxalate (figure 5). Water molecules reside in the channels and there

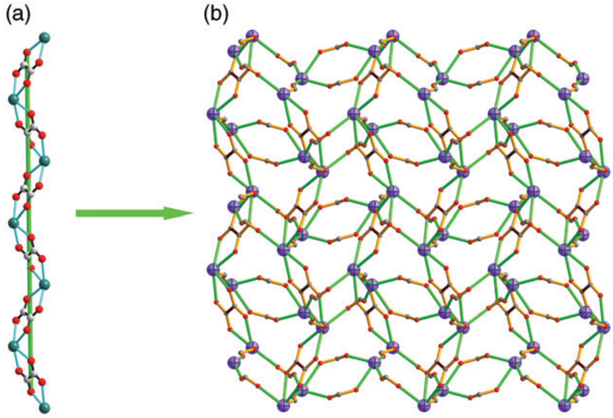

Figure 4. (a) View of the 1-D helical chain by Nd1(III) ions and oxalic. (b) 2-D layer constructed from μ_3-$HMIDC^{2-}$ and Nd(III) ions.

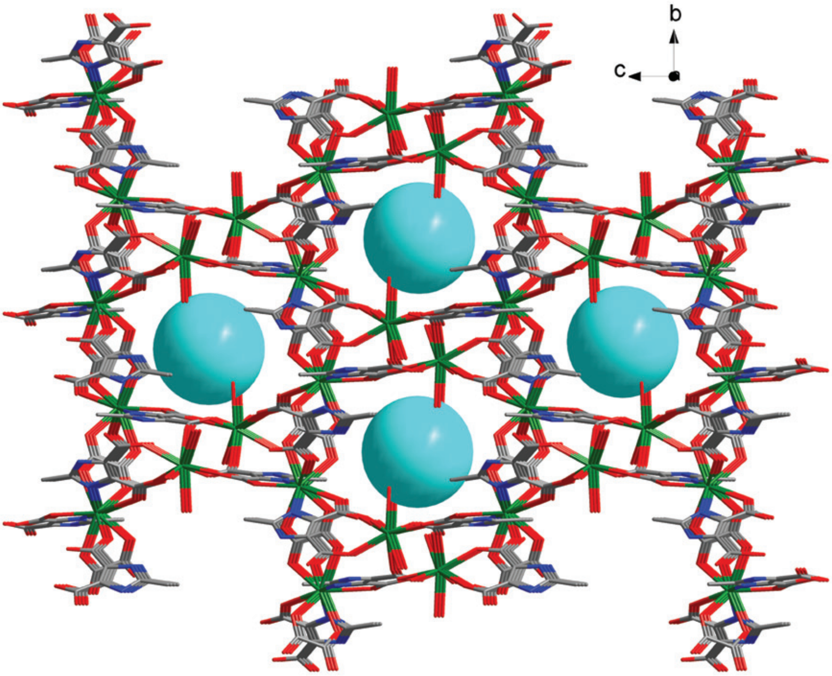

Figure 5. Perspective view of the 3-D framework of **1** with the cricoid 1-D tunnels encapsulating water molecules.

Table 3. Hydrogen-bond distances (Å) and angles (°) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(13)–H(1W)···O(1)	0.85	1.99	2.841(6)	178.3
O(13)–H(1W)···O(2)	0.85	2.47	2.997(5)	120.9
O(13)–H(2W)···O(2)#3	0.85	2.35	2.845(6)	117.4
O(14)–H(3W)···O(7)	0.85	1.90	2.735(6)	169.2
O(14)–H(4W)···O(16)	0.85	2.01	2.848(7)	170.5
O(15)–H(6W)···O(18)#6	0.85	2.33	2.923(10)	127.6
O(16)–H(7W)···O(5)#6	0.85	2.11	2.893(7)	153.7
O(16)–H(8W)···O(17)	0.85	2.00	2.745(9)	146.0
O(17)–H(9W)···O(9)#5	0.85	2.17	2.985(7)	162.0
O(17)–H(10W)···O(4)#8	0.85	2.17	3.016(8)	179.6
O(17)–H(10W)···O(3)#8	0.85	2.57	3.142(8)	125.1
O(18)–H(11W)···O(9)#1	0.85	2.14	2.956(7)	159.4
O(18)–H(11W)···O(10)#1	0.85	2.65	3.159(8)	119.2
N(2)–H(2)···O(11)#5	0.86	2.37	3.181(6)	156.6
N(4)–H(4)···O(18)#4	0.86	2.00	2.842(7)	167.1

Symmetry codes: #1: $-x+1/2,\ y+1/2,\ -z+1/2$; #3: $-x,\ -y+1,\ -z$; #4: $x-1,\ y,\ z$; #5: $x+1,\ y,\ z$; #6: $-x+1/2,\ y-1/2,\ -z+1/2$; #8: $-x+1,\ -y+1,\ -z$.

are numerous strong H-bonding interactions among coordinated water molecules, lattice water molecules, nitrogen atoms of μ_3-HMIDC^{2-} ligands, and oxygen atoms of HMIDC^{2-} with an O···O(N) distance of 2.735(6)–3.181(6) Å (table 3), completing the 3-D framework splendidly.

3.3. *IR spectra*

Compounds **1**–**5** show very similar absorption bands owing to their similar structural features. The absorptions for water, carboxylate, and imidazolyl units are observed in IR spectra. The strong and broad absorptions at 3400–3500 cm^{-1} indicate the presence of ν(N–H) and ν(O–H) of imidazole and coordinated water. The coordination of the carboxylate can be seen from absorptions in the frequency range 1340–1610 cm^{-1} in **1**–**5** due to ν_{as}(COO$^-$) and ν_s(COO$^-$). The features at 1610–1570 cm^{-1} in **1**–**5** are associated with C=N and C=C stretches of imidazole in HMIDC^{2-}.

3.4. *Thermal properties*

Thermogravimetric analyses (TGA) for **1**–**5** with TG and differential scanning calorimetry (DSC) curves are reported in "Supplementary material."

TG data show that **1** has two weight losses; the first with 25.02% is from room temperature to 419.8°C corresponding to loss of three lattice water molecules, three coordination water molecules, and one oxalate. Subsequently, weight loss of 35.03% occurs from 419.8°C to 795°C corresponding to decomposition of the μ_3-HMIDC^{2-}. A plateau is observed from 795°C to 810°C. The final residue is Nd_2O_3 (observed 39.95%, Calcd 40.99%). There are strong endothermic peaks at 472.3°C and 576.3°C and two weak exothermic peaks at 165.9°C and 216.0°C on the DSC curve.

There are two weak exothermic peaks (167.6°C and 208.1°C) and two strong endothermic peaks (464.6°C and 577.7°C) in the DSC curve of **2**. It first loses the three free water molecules, three coordination water molecules, and part of $C_2O_4^{2-}$ from 30°C to 258.9°C (observed 15.38%, Calcd 15.52%). Second, polymer **2** loses weight from 258.9°C to 676°C (observed 43.11%) corresponding to the decomposition of $HMIDC^{2-}$ and residual $C_2O_4^{2-}$. Finally, a plateau is observed from 676°C to 800°C. The final white residue is Sm_2O_3 (observed 41.24%, Calcd 42.07%).

Polymer **3** also indicates two steps of weight lost, first water and part of $C_2O_4^{2-}$ at 32°C to 224.9°C (observed 14.93%, Calcd 15.01%); second from 224.9°C to 763°C (observed 43.90%) corresponding to decomposition of $HMIDC^{2-}$ and residual $C_2O_4^{2-}$. The final pale-yellow residue is Eu_2O_3 (observed 41.17%, Calcd 40.96%). There are one weak endothermic peak at 451.3°C and one weak exothermic peak at 210.8°C on the DSC curve of **3**.

Two main steps of weight loss in **4** are 13.57% from room temperature to 249.9°C corresponding to removal of three lattice water molecules and one ethanol, and subsequently 44.21% corresponding to loss of coordinated water, oxalate, and the decomposition of μ_3-$HMIDC^{2-}$. It keeps constant weight after 485°C. The final residue is Ce_2O_3 (observed 42.22%, Calcd 41.23%). There is one strong endothermic peak at 388.0°C and two weak exothermic peaks at 149.0°C and 210.8°C on the DSC curve of **4**.

There are one weak exothermic peak (212.2°C) and two strong endothermic peaks (496.4°C and 615.8°C) in the DSC curve of **5**. It first loses solvents from 25°C to 271.9°C (observed 14.10%, Calcd 13.98%) and then from 271.9°C to 716.9°C (observed 43.06%) corresponding to decomposition of $HMIDC^{2-}$ and $C_2O_4^{2-}$. The final white residue is Gd_2O_3 (observed 42.93%, Calcd 42.61%).

3.5. *Photoluminescence property*

Population of the excited states of lanthanide(III) ions may be increased by coordination to organic ligands, which act as sensitizers [35]. Thus, the solid-state photoluminescence properties of **1**–**5** were investigated at room temperature; **1** and **4** have no fluorescence emission.

Polymers **2** and **3** (figure 6a and b) show characteristic emission of lanthanide ions. Complex **2** has peaks at 560 nm and 594 nm corresponding to $^4G_{5/2}$–$^6H_{5/2}$ and $^4G_{5/2}$–$^6H_{7/2}$ transitions of Sm^{3+} [36] under excitation of 320 nm (figure 6). The emission spectrum of free ligand disappeared (figure 6) with the energy completely passed to the center metal by H_3MIDC. H_3MIDC has a better role on Sm^{3+} in sensitized luminescence. For Eu(III) complex **3**, two apparent emission peaks under excitation at 340 nm are observed at room temperature, typical of Eu(III) [37, 38]. The $^5D_0$–$^7F_1$ transition (591 nm) corresponds to a magnetic dipole transition, and the intensity of this emission for **3** is medium–strong. The most intense emission in the luminescence spectrum is the $^5D_0$–$^7F_2$ transition at 613 nm, a hypersensitive transition responsible for the brilliant-red emission of **3** [39].

As previously reported, free H_3MIDC displays luminescence, with the emission maximum at 430 nm by selective excitation at 300 nm, which is attributed to the $\pi^* \rightarrow n$ transition [34]. As shown in figure 6(c), **5** also exhibits a broad emission at 450 nm upon excitation at 380 nm. Compared with free H_3MIDC, blue shift of 20 nm in **5** is observed, and the strength of peak in **5** is stronger than H_3MIDC. The emission can be assigned to the ligand-to-metal charge transfer, rather than the $\pi^* \rightarrow n$ transition of the ligand.

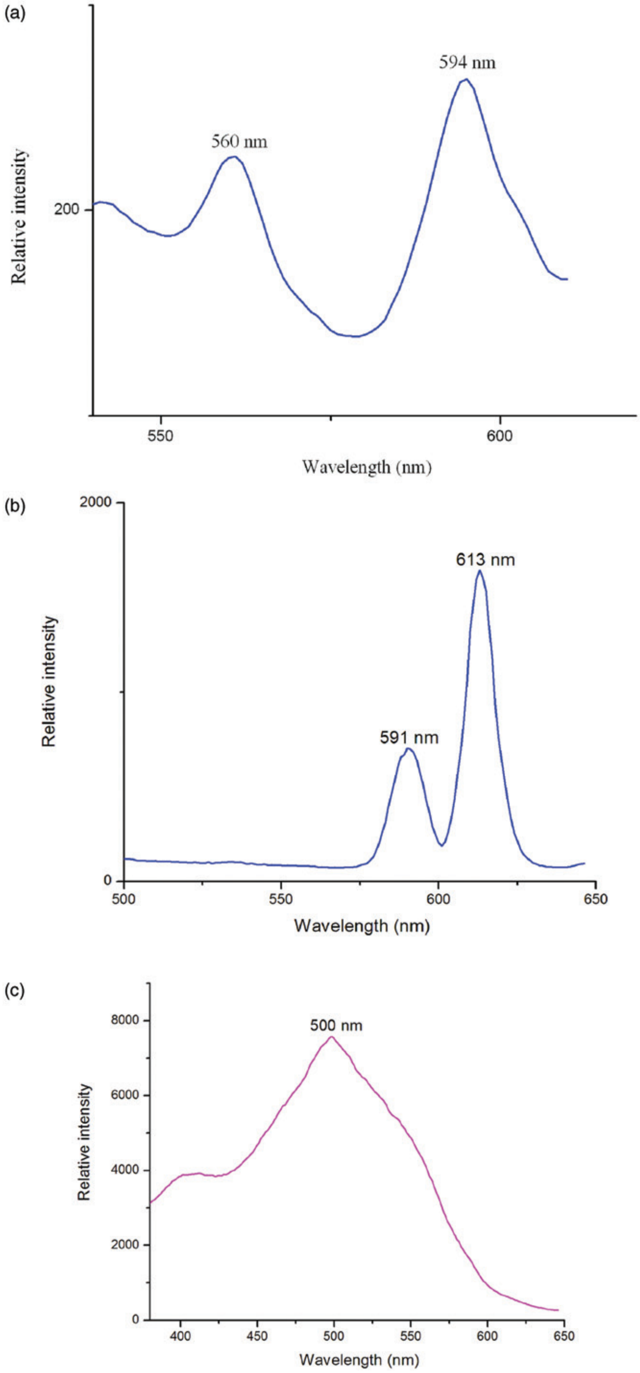

Figure 6. Solid-state photoluminescent spectra of **2** (a), **3** (b), and **5** (c) at room temperature.

4. Conclusions

Five lanthanide(III) architectures have been synthesized under solvothermal conditions by reactions of H_3MIDC and ammonium oxalate with lanthanide(III) nitrate anions. They all exhibit interesting 3-D networks. The luminescence of **2**, **3**, and **5** at room temperature suggest potential applications as luminescent materials.

Supplementary material

Crystallographic data for these structures reported in this article in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 782692 for **1**, 797066 for **2**, 797067 for **3**, 797068 for **4**, and 782691 for **5**. Copies of these 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).

Acknowledgments

We gratefully acknowledge the financial support by the National Natural Science Foundation of China (21071127, 20501017, and J0830412), and Program for New Century Excellent Talents in University (NCET-10-0139) and the Natural Science Foundation of Henan Education Department (2009A150028 and 2011A150029).

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