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Article

Self-Assembly of Lanthanide Helicate Coordination Polymers into 3D Metal-Organic Framework Structures

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Pyridine-2,6-dicarboxylic acid ($pdcH_2$) reacts with nitrate salts of La(III), Ce(III), and Nd(III) under hydrothermal conditions to form three-dimensional network structures, **1**–**4**. All the compounds crystallize in the monoclinic space group $P2_1/c$ with the following lattice parameters: $\{La_2(pdc)_3\cdot 3H_2O\}$ **1**, $a = 10.966(3)$ Å, $b = 17.534(4)$ Å, $c = 13.578(2)$ Å, $\beta = 100.23(3)°$, $V = 2569.3(9)$ Å^3, $Z = 4$, R1 = 0.052, wR2 = 0.143, $S = 1.06$; $\{Ce_2(pdc)_3\cdot 3H_2O\}$ **2**, $a = 12.701(3)$ Å, $b = 9.979(1)$ Å, $c = 19.401(4)$ Å, $\beta = 97.73(2)°$, $V = 2436.6(8)$ Å^3, $Z = 4$, R1 = 0.039, wR2 = 0.117, $S = 1.30$; $\{Ce_2(pdc)_3\cdot 3H_2O\}$ **3**, $a = 10.961(5)$ Å, $b = 17.523(5)$ Å, $c = 13.505(2)$ Å, $\beta = 100.89(3)°$, $V = 2547.2(8)$ Å^3, $Z = 4$, R1 = 0.040, wR2 = 0.103, $S = 1.08$; $\{Nd_2(pdc)_3\cdot 3H_2O\}$ **4**, $a = 10.944(3)$ Å, $b = 17.448(5)$ Å, $c = 13.397(2)$ Å, $\beta = 101.19(3)°$, $V = 2569.3(9)$ Å^3, $Z = 4$, R1 = 0.052, wR2 = 0.143, S = 1.06. Compounds **1**, **3**, and **4** form infinite single helical chains with large widths and pitches containing four metal ions per turn while **2** forms a different helix with smaller width and pitch containing two metal ions per turn. Each helix is further bonded on either side via carboxylate bridging producing three-dimensional metal-organic framework structures.

Introduction

Modular synthesis of metal-organic framework (MOF) structures is of great interest, as these structures are likely to afford new materials[1−6] such as molecular magnets, optoelectronic devices, sensors, catalysts, and so on. These MOF structures can be rapidly, accurately, and efficiently synthesized from relatively simple subunits, where the metal ions, multidentate organic ligands, and coordinate bonding are the parameters for directing the self-assembly processes. Lanthanide ions generally adopt higher than six coordination[7] and, therefore, can become important building blocks in designing different MOF structures. With lanthanides, the metal−ligand coordination bonds are mostly ionic and the nature of the coordination sphere is controlled, by a subtle interplay between metal−ligand interactions and interligand steric constraints. A number of lanthanide containing MOFs have been reported that include square catenate,[8] cyclic tetranuclear,[9] cubane,[10] interpenetrating networks,[11] and other[12] 3D structures. Interest in the synthesis of lanthanide MOFs stems from the fact that these structures can be potentially useful as luminescent materials,[13] catalysts,[14] radiopharmaceuticals,[15] MRI contrast agents,[16] etc. In this work, we have used pyridine-2,6-dicarboxylic acid ($pdcH_2$) to construct MOFs with lanthanides under hydrothermal conditions. This ligand forms discrete complexes[17] at room

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Table 1. Crystal Data and Structure Refinement for **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{21}H_9N_3O_{15}La_2$	$C_{21}H_9N_3O_{15}Ce_2$	$C_{21}H_9N_3O_{15}Ce_2$	$C_{21}H_9N_3O_{15}Nd_2$
fw	827.18	829.60	829.60	837.14
temp	293(2) K	293(2) K	293(2) K	293(2) K
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*21/*c*	*P*21/*c*	*P*21/*c*	*P*21/*c*
a, Å	10.966(3)	12.701(3)	10.961(5)	10.944(3)
b, Å	17.534(4)	9.979(1)	17.523(5)	17.448(5)
c, Å	13.578(2)	19.401(4)	13.505(2)	13.397(2)
β, deg	100.23(3)	97.73(2)	100.89(3)	101.19(3)
V, Å^3	2569.3(9)	2436.6(8)	2547.2(8)	2509.5(9)
Z	4	4	4	4
ρ_{calc}, Mg/m^3	2.123	2.289	2.163	2.202
μ, mm^{-1}	3.362	3.775	3.611	4.17
F(000)	1584	1592	1592	1608
reflns collected	3354	3188	3328	3259
indep reflns	2775	2739	2349	2535
refinement meth	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.062	1.299	1.083	1.323
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0522 wR2 = 0.1431	R1 = 0.039 wR2 = 0.117	R1 = 0.040 wR2 = 0.103	R1 = 0.085 wR2 = 0.267
R indices (all data)	R1 = 0.0687 wR2 = 0.1544	R1 = 0.052 wR2 = 0.126	R1 = 0.087 wR2 = 0.117	R1 = 0.112 wR2 = 0.297

temperature and is also known to form coordination polymers[18,19] under hydrothermal conditions with several lanthanides. The La(III) structure reported[19] is identical to that of **1** although presence of any helical pattern in the structure was not mentioned. We describe here four MOF structures (**1**−**4**) of La(III), Ce(III), and Nd(III) with pyridine-2,6-dicarboxylate which form infinite single-strand helicates. The propensity for helication depends[20b] on the stereoelectronic molecular information encoded in the components (i.e., the ligand and the metal) and the external conditions used for reading this information. Interestingly, compounds **2** and **3** have the same empirical formula, but they form two distinctly different helicates, due to different experimental conditions applied during synthesis. The importance of helicate chemistry is related[20] to the development and understanding of self-assembly processes. It also provides for new supramolecular architectures, endowed with functional properties, like directional light-harvesting devices,[21] allosteric ionophores,[22] and MOFs in the form[23−25] of racks, ladders, grids, knots, etc. Moreover, influence of noncovalent interactions on supramolecular stereo- or regiochemistry can be studied by using helicates as models.[26] Hence, the study of helical complexes[27] resulting from metal ions and coordinated organic receptors has become one of the most rapidly expanding fields of supramolecular chemistry. A large number of transition metal helicates of different nuclearity have been synthesized[28−32] using multidentate ligands partitioned into a number of discrete metal-binding sites suitable for the formation of helical complexes. Discrete helicates of pure lanthanides[33,34] or in combination with transition metals[35] are reported by Piguet and co-workers although formation of infinite helicates by lanthanides remains largely unexplored.[36]

Experimental Section

Materials and Methods. The metal salts and pyridine-2,6-dicarboxylic acid were acquired from Aldrich and used as received.

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) in **1** and **2**

		1		
La1 O1 2.500(7)	La2 O10 2.556(7)	La2 N3 2.642(8)	La1 O9 2.498(6)	La1 OW1 2.640(8)
La1 O5 2.575(7)	La2 O12 2.398(7)	La1 O3 2.566(7)	La2 O8 2.400(7)	La2 OW3 2.600(7)
La1 O7 2.520(7)	La2 OW2 2.510(9)	La1 O5′ 2.596(7)	La2 O11 2.510(7)	La1 N2 2.683(8)
La2 O4 2.427(8)	La1 N1 2.646(8)			
O9 La1 O1 87.5(2)	O5 La1 N1 85.5(2)	O8 La2 OW3 69.4(2)	O9 La1 OW1 70.5(2)	O4 La2 O11 89.6(3)
O1 La1 O7 78.1(3)	O9 La1 N2 70.1(2)	O11 La2 OW3 94.8(2)	O7 La1 OW1 141.6(2)	O8 La2 OW2 133.1(3)
O1 La1 O3 121.9(2)	O7 La1 N2 61.0(2)	O10 La2 OW3 130.8(2)	O5 La1 OW1 79.9(2)	O11 La2 OW2 73.9(3)
O9 La1 O5 83.1(2)	O5 La1 N2 59.4(2)	O8 La2 N3 77.7(3)	O9 La1 N1 141.4(2)	O8 La2 O10 78.4(2)
O7 La1 O5 120.3(2)	OW1 La1 N2 125.5(2)	O11 La2 N3 61.4(2)	O7 La1 N1 72.8(2)	O11 La2 O10 122.1(2)
O9 La1 O5 128.5(2)	O12 La2 O8 100.4(3)	O10 La2 N3 60.7(2)	O5 La1 N1 134.1(2)	O12 La2 OW3 77.6(3)
O7 La1 O5 150.4(2)	O8 La2 O4 153.5(3)	O9 La1 O7 79.5(2)	OW1 La1 N1 118.5(2)	O4 La2 OW3 137.0(3)
O5 La1 O5 62.5(3)	O8 La2 O11 90.2(3)	O9 La1 O3 141.0(2)	O1 La1 N2 135.7(2)	OW2 La2 OW3 68.4(3)
O1 La1 OW1 77.3(2)	O12 La2 OW2 89.8(3)	O7 La1 O3 82.3(3)	O3 La1 N2 70.8(2)	O12 La2 N3 132.9(3)
O3 La1 OW1 135.9(2)	O4 La2 OW2 72.0(3)	O1 La1 O5 157.1(2)	O5 La1 N2 114.7(2) 3	O4 La2 N3 79.0(3)
O5 La1 OW1 66.7(2)	O12 La2 O10 72.7(2)	O3 La1 O5 76.8(2)	N1 La1 N2 115.9(3)	OW2 La2 N3 126.1(3)
O1 La1 N1 61.2(2)	O4 La2 O10 79.3(3)	O1 La1 O5 109.2(2)	O12 La2 O4 86.4(3)	OW3 La2 N3 139.3(2)
O3 La1 N1 60.8(2)	OW2 La2 O10 147.2(3)	O3 La1 O5 69.4(2)	O12 La2 O11 163.6(3)	
		2		
Ce1 O1 2.532(7)	Ce2 O10 2.477(7)	Ce2 N3 2.606(8)	Ce1 O9 2.550(7)	Ce1 OW1 2.534(7)
Ce1 O5 2.558(6)	Ce2 O12 2.473(7)	Ce1 O3 2.522(7)	Ce2 O7 2.459(7)	Ce2 OW3 2.620(7)
Ce1 O8 2.582(7)	Ce2 OW2 2.545(7)	Ce1 O5′ 2.570(6)	Ce2 O11 2.475(6)	Ce1 N2 2.635(8)
Ce2 O4 2.430(7)	Ce1 N1 2.605(8)			
O3 Ce1 OW1 79.8(2)	O8 Ce1 N2 61.7(2)	C7 O4 Ce2 142.1(6)	O1 Ce1 O8 81.5(2)	O12 Ce2 OW2 149.2(2)
OW1 Ce1 O1 141.1(2)	O4 Ce2 O7 138.2(2)	C8 O5 Ce1 106.1(6)	O5 Ce1 O8 122.9(2)	O4 Ce2 N3 77.1(2)
OW1 Ce1 O9 71.0(2)	O7 Ce2 O11 71.5(2)	C14 O7 Ce2 110.7(6)	O3 Ce1 N1 62.3(2)	O11 Ce2 N3 137.5(2)
O3 Ce1 O5 156.3(2)	O7 Ce2 O12 118.5(2)	C15 O10 Ce2 126.9(6)	O1 Ce1 N1 61.4(2)	O10 Ce2 N3 61.5(2)
O1 Ce1 O5 76.8(2)	O4 Ce2 O10 87.8(2)	C21 O11 Ce2 135.1(7)	O5 Ce1 N1 131.6(2)	O4 Ce2 OW3 147.1(2)
O3 Ce1 O5 108.8(2)	O11 Ce2 O10 148.1(2)	C1 N1 Ce1 119.5(6)	O8 Ce1 N1 75.7(2)	O11 Ce2 OW3 134.0(2)
O1 Ce1 O5 72.3(2)	O4 Ce2 OW2 71.1(2)	C9 N2 Ce1 121.1(6)	OW1 Ce1 N2 119.9(2)	O10 Ce2 OW3 70.7(2)
O5 Ce1 O5 61.7(2)	O11 Ce2 OW2 80.0(2)	C20 N3 Ce2 120.4(6)	O9 Ce1 N2 70.2(2)	N3 Ce2 OW3 70.8(2)
OW1 Ce1 O8 137.2(2)	O10 Ce2 OW2 68.7(2)	O3 Ce1 O1 122.9(2)	O5 Ce1 N2 116.0(2)	C7 O3 Ce1 123.9(6)
O9 Ce1 O8 70.5(2)	O7 Ce2 N3 144.2(2)	O3 Ce1 O9 81.0(2)	N1 Ce1 N2 117.7(2)	C8 O5 Ce1 125.2(6)
O5 Ce1 O8 151.7(2)	O12 Ce2 N3 62.3(2)	O1 Ce1 O9 137.8(2)	O4 Ce2 O11 76.2(2)	Ce1 O5 Ce1 118.3(2)
OW1 Ce1 N1 122.3(2)	OW2 Ce2 N3 121.0(2)	OW1 Ce1 O5 76.5(2)	O4 Ce2 O12 80.9(2)	C14 O8 Ce1 123.0(6)
O9 Ce1 N1 134.8(2)	O7 Ce2 OW3 73.4(2)	O9 Ce1 O5 92.3(2)	O11 Ce2 O12 81.1(2)	C15 O9 Ce1 142.1(7)
O5 Ce1 N1 82.3(2)	O12 Ce2 OW3 90.6(2)	OW1 Ce1 O5 70.2(2)	O7 Ce2 O10 106.3(2)	C21 O12 Ce2 126.7(6)
O3 Ce1 N2 134.9(2)	OW2 Ce2 OW3 120.0(2)	O9 Ce1 O5 137.3(2)	O12 Ce2 O10 123.8(2)	C5 N1 Ce1 120.3(6)
O1 Ce1 N2 68.8(2)	C6 O1 Ce1 123.3(6)	O3 Ce1 O8 76.4(2)	O7 Ce2 OW2 77.7(2)	C16 N3 Ce2 120.4(6)
O5 Ce1 N2 61.2(2)				

The X-ray powder patterns were obtained on a Siefert X-ray generator (model ISODEBYEFLEX-2002) with Cu Kα radiation at a scan rate of 3°/min at room temperature. Thermogravimetric analyses were carried out on a Perkin-Elmer Pyris 6, TGA analyzer in N_2 atmosphere at the heating rate of 20 °C/min.

Synthesis. Synthesis of the compounds was achieved by the hydrothermal technique, in a Teflon-lined autoclave and under synthetic reaction conditions determined empirically.

$La_2(pdc)_3 \cdot 3H_2O$, 1. This compound was synthesized by reacting 1 mmol of $La(NO_3)_3 \cdot 6H_2O$ and 2 mmol of pyridine-2,6-dicarboxylic acid ($pdcH_2$) in 5 mL of water. The autoclave was heated under autogenous pressure to 180 °C for 2 days and then kept at 60 °C for a further 12 h period. Upon cooling to RT, the desired product appeared as long colorless rectangular parallelopipeds in ∼60% yield. Anal. Calcd for $C_{21}H_{15}N_3O_{15}La_2$: C, 30.05; H, 1.83; N, 5.08%. Found: C, 30.16; H, 1.79; N, 5.01%.

$Ce_2(pdc)_3 \cdot 3H_2O$, 2. This compound could be isolated in ∼55% yield as pale yellow rectangular crystals, on hydrothermal reaction of $Ce(NO_3)_3 \cdot 6H_2O$ with the ligand in a 1:2 molar ratio in 5 mL of H_2O and under experimental conditions identical to those above. Anal. Calcd for $C_{21}H_{15}N_3O_{15}Ce_2$: C, 30.40; H, 1.81; N, 5.01%. Found: C, 30.31; H, 1.89; N, 4.98%.

$Ce_2(pdc)_3 \cdot 3H_2O$, 3. In an attempt to construct a different MOF, a mixture containing $Ce(NO_3)_3 \cdot 6H_2O$, the ligand, and sodium oxalate was taken in 1:2:2 molar ratio. The experimental conditions were slightly different from those above. The mixture was heated at 180 °C under hydrothermal conditions for 3 days and then allowed to cool to RT over a period of 8 h. Single crystals of **3** were isolated as the sole product, in ∼45% yield as pale yellow rectangular parallelopipeds. Anal. Calcd for $C_{21}H_{15}N_3O_{15}Ce_2$: C, 30.40; H, 1.81; N, 5.01%. Found: C, 30.51; H, 1.79; N, 5.07%. Absence of sodium oxalate in the reaction mixture did not afford **3** although the role of this salt is not understood at present.

$Nd_2(pdc)_3 \cdot 3H_2O$, 4. The metal salt, $Nd(NO_3)_3 \cdot 6H_2O$, and the ligand, taken in a 1:2 molar ratio with 5 mL of water, were heated at 160 °C for 3 days followed by heating at 80 °C for 12 h.On cooling to room temperature over a period of 10 h, the desired product was obtained in ∼70% yield as violet rectangular parallelopipeds. Anal. Calcd for $C_{21}H_{15}N_3O_{15}Nd_2$: C, 30.11; H, 1.80; N, 5.01%. Found: C, 29.96; H, 1.87; N, 4.97%.

X-ray Structural Studies. Single-crystal X-ray data on the compounds were collected at RT, on an Enraf-Nonius CAD4 Mach2 X-ray diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). In each case, cell parameters were determined by least-squares refinement of the diffractometer setting angles, from 25 centered reflections in the range $18° \leq 2\theta \leq 24°$. Three standard reflections were measured every hour to monitor instrument and crystal stability. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography*.[37] The structures were solved by the direct method using SIR92[38] and refined on F^2 by full-matrix least-squares techniques

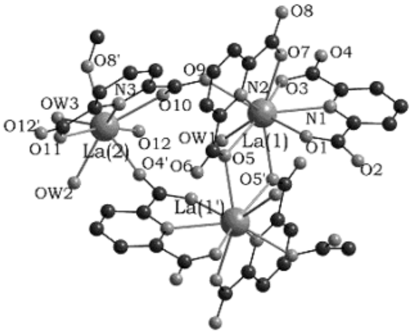

Figure 1. Three La(III) ions are shown with the ligands to illustrate the coordination mode in **1**. The H atoms are omitted for clarity.

using the SHELXL-97[39] program package. All the non-hydrogen atoms were refined anisotropically except in **4**, where two pyridine N and two carboxylate O atoms were disordered and so refined isotropically. The H atom positions or thermal parameters were not refined but included in the structure factor calculations. The crystal data for the two structures are collected in Table 1.

Results and Discussion

All of the compounds are stable in air and insoluble in water or in common organic solvents. High yields of the products indicate that these compounds are thermodynamically stable under the prevailing reaction conditions. The IR spectra of the compounds are similar, each showing strong absorption bands between 1350 and 1550 cm^{-1} that are diagnostic of coordinated carboxylates.[40]

The asymmetric unit of **1** consists of $\{La_2(pdc)_3(H_2O)_3\}$ as the building block (Figure 1). There are two independent La(III) ions where La(1) is nine-coordinated with N_2O_7 donor and La(2) is eight-coordinated with NO_7 donor sets. The two La(III) ions are well-separated with the nonbonding distance at 6.326(4) Å. The La(1) is bonded to a single water molecule while La(2) is bound to two water molecules. The rest of the donor atoms come from the pdc^{2-} units. Both carboxylate groups of the ligand units are bridged forming the MOF structure.

Selective bond distances and bond angles for **1** are collected in Table 2. The La(III)−O and La(III)−N distances are similar to those found in other La(III) complexes.[7,19] The bond distances and bond angles in the ligand moiety are within normal ranges. The structure shows that the La(III) ions are arranged in infinite single helices (Figure 2a) with intervening pdc^{2-} ligands although the ligand has no intrinsic tendency to form helical structures. Known lanthanide helicates are usually discrete with low nuclearity and are formed with multidentate ligands acting as molecular threads, containing metal binding domains at certain optimum intervals. In the case of **1**, the helical structure is, therefore, a result of metal−ligand interactions coupled with stereoelectronic characteristics of the ligand and the conditions prevailing during the synthesis. Once the helical structure is initiated, it continues infinitely along the coordination polymeric chain. The width of the helix is calculated to be 21.6 Å and the pitch is 19.7 Å containing four La(III) ions per turn. The helix has two La···La distances of 6.87 and 10.98 Å. The stability of the final helical structure relies on the coordinate bonds that each metal makes with the ligand. Known structures of lanthanide helicates[33] are double- or triple-stranded with long polydentate ligands. These ligands are able to wrap around lanthanide ions forming compact helical structures with lower pitch and narrower width. The helices in **1** are further organized into metal-organic framework structures through interhelix bridging of the carboxylates (Figure 3a). The view of **1** approximately down the crystallographic *c* axis shows void spaces which constitute less than 10% of the structure and, hence, may not be suitable for gas absorption or catalytic studies.

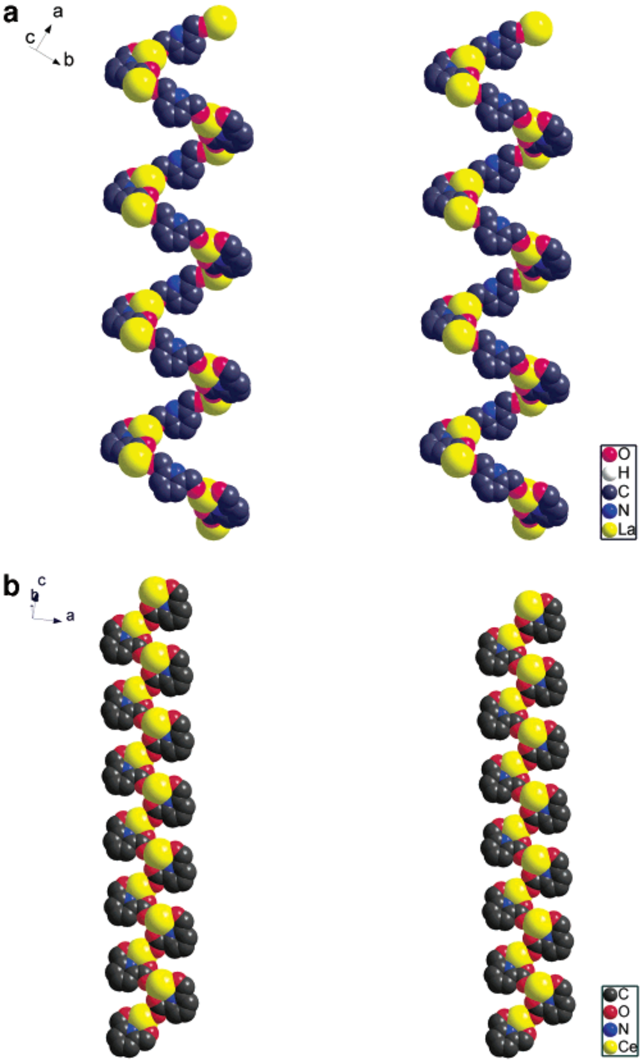

Figure 2. (a) Single helical stereoview of **1**, **3**, and **4**. Other atoms have been omitted for clarity. Color code: C, black; N, blue; O, red; metal, yellow. (b) Single helical stereoview of **2**. Other atoms have been omitted for clarity. Color code: C, black; N, blue; O, red; metal, yellow.

The structure of **2** and **3** contains the entity $\{Ce_2(pdc)_3(H_2O)_3\}$ in the asymmetric unit as in **1**. In both of the

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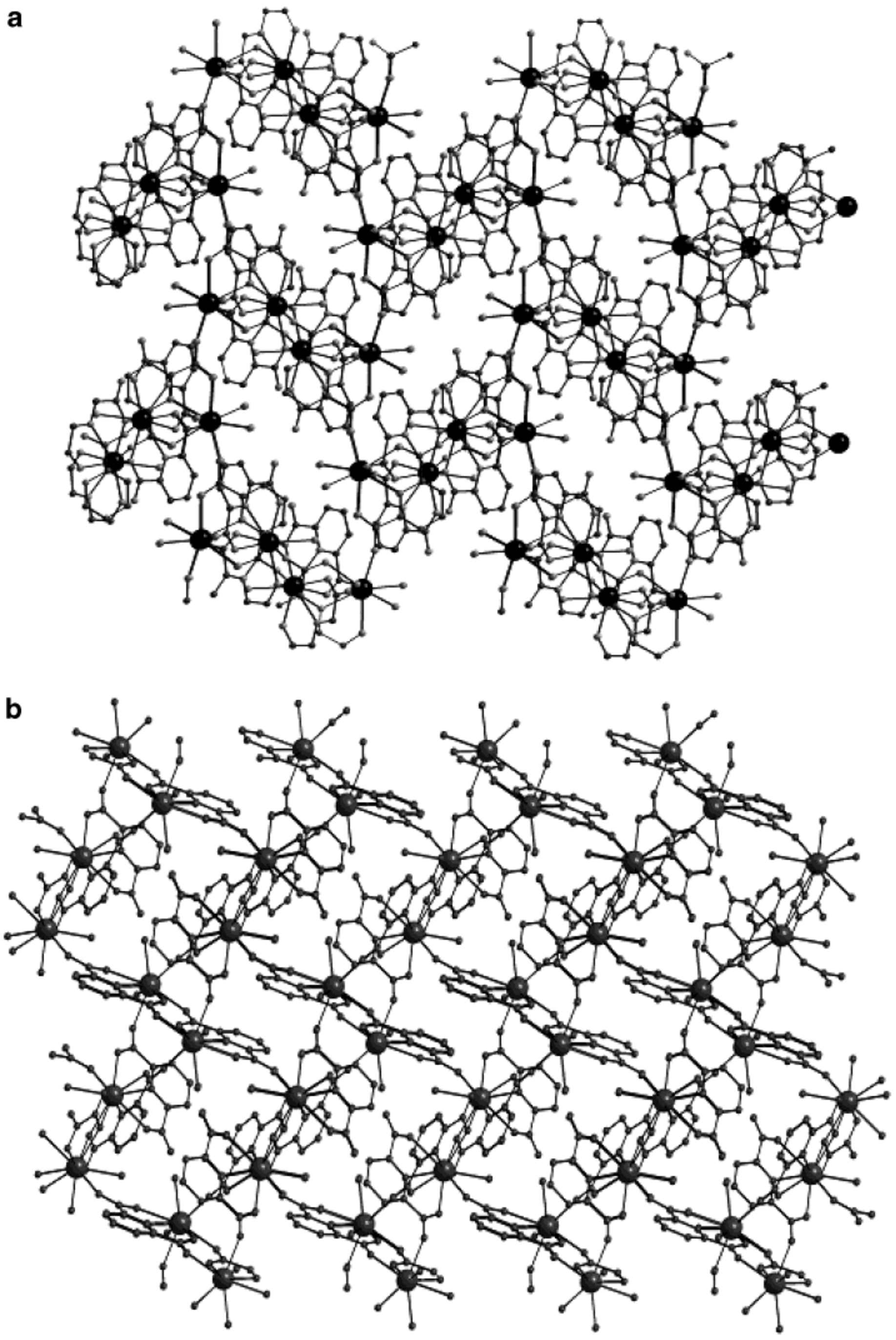

Figure 3. (a) The MOF structure of **1** viewed approximately down the *c* axis. H atoms are omitted for clarity. Structures of both **3** and **4** are similar to that of **1**. (b) The MOF structure of **2** viewed approximately down the *c* axis. H atoms are omitted for clarity.

structures, Ce(1) shows 9-coordination with the N_2O_7 donor set and Ce(2) shows 8-coordination with the NO_7 donor set. All of the carboxylate groups are bridged. The Ce(III)−O and Ce(III)−N distances are within the normal range found in other reported[19] Ce(III) complexes. All of the bond distances and bond angles in the pdc^{2-} units are also within normal ranges. The nonbonding distance between Ce(1) and Ce(2) is 6.752 (5) Å in **2** while this distance is 6.833(5) Å in **3**, both of which are slightly longer compared to the distance found in **1**. The helical structure in **2** is very different from those found in **1**, **3**, and **4**. Here, both the width (15.5 Å) and the pitch (10.0 Å) are much smaller and only two Ce(III) ions are present per turn (Figure 2b). The framework structure of **2** results from connection of the individual helix (Figure 3b) on both sides through bridging carboxylates. The open framework structure in **2** shows slight differences in terms of the shape of the voids and its overall dimension. However, like in other cases, the voids are small.

In spite of having the same empirical formula, the helical structure in **3** is distinctly different from that of **2** and compares well with that of **1** and **4**. The helix in **3** gives a width of 21.5 Å and a pitch of 19.7 Å with four Ce(III) ions per turn. The valence orbitals in lanthanides are buried inside, and hence these metal ions do not have a preference for a coordination geometry. Therefore, under different external conditions applied for the synthesis of **2** and **3**, the recognition and its expression differ in the final supramolecular structures. The role of sodium oxalate present in the synthesis of **3** is presently difficult to comment on given the paucity of data. However, we have not been able to isolate **3** by varying the temperature or time of the hydrothermal synthesis carried out in the absence of sodium oxalate.

Compound **4** exhibits a structure very similar to that of **1** and **3** with identical donor sets around each metal ion. The asymmetric unit consists of the entity $\{Nd_2(pdc)_3(H_2O)_3\}$. All of the Nd(III)−O and Nd(III)−N distances are similar to those found in Nd(III) complexes reported earlier.[41] The nonbonding distance between Nd(1) and Nd(2) is found to be 6.505(7) Å. The helical structure present in **4** is very similar to that of **1** and **3**, showing a width of 21.4 Å and a pitch of 19.5 Å. The MOF structure of this compound is also very similar to that of **1** and **3**.

Thermal gravimetric analyses show that the onset of weight loss occurs above ∼150 °C for each compound and all of the H_2O molecules are lost before ∼220 °C. This shows that the H_2O molecules are tightly held to the metal ion. Complete decomposition is achieved only above 450 °C in each case. Powder X-ray diffraction studies of the compound before and after water expulsion showed only minor changes in the diffraction patterns pointing to the robustness of the MOFs to the exclusion of water.

Conclusion. We report here, for the first time, single infinite helical arrays of La(III), Ce(III), and Nd(III) ions. The accepted model for helication requires a long multidentate ligand as a molecular thread, containing a number of discrete metal-binding sites separated by spacer units. Such a molecular thread can twist around several metal ions controlled by their coordination behavior. However, synthesis of only discrete helicates can be achieved with such molecular threads. The structures of the four compounds reported here show that infinite single helical chains can be constructed with simpler ligands. Here, the driving force for helication is the metal−ligand interactions coupled with stereoelectronic characteristics of the ligand and the reaction conditions. Of particular interest is the fact that different helical structures can sometimes result by applying different experimental conditions in the synthesis. This shows that the valence orbitals in lanthanides are buried inside and hence these metal ions do not have preference for a coordination geometry. The nature of coordination modes is, therefore, controlled by a subtle interplay between metal−ligand and interligand steric interactions. Each compound is further organized into metal-organic framework structures through interhelix bridging of the carboxylates. Although these structures have voids, the percentage of the void space present in each compound is low. We are presently engaged in using different ligands with proper spacer units to form framework structures with large voids for possible gas absorption and catalytic studies.

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Supporting Information Available: X-ray crystallographic files in CIF format for structures of **1**, **2**, **3**, and **4**, some structural figures, X-ray powder diffraction patterns, and TGA curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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