A New Porous Three-Dimensional Lanthanide Coordination Polymer

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Introduction

Of contemporary interest is the assembly of metal−organic infinite frameworks via coordination of metal ions with multifunctional organic ligands.[1] Work along this line has been motivated by the concept that molecular-based coordination polymers have potential technological applications such as optoelectronic devices and microporous materials for shape- and size-selective separations and catalysis.[2]

The synthetic strategy for metal−organic framework polymers allows the choice from a variety of parameters, including diverse electronic properties and coordination geometries of metal ions as well as versatile functions and topologies of organic ligands. Thus, specific structural and physicochemical characteristics at the molecular level can be translated into prescribed bulk properties for solid-state materials. In this context, there has been current interest in using polycarboxylates as anionic linking groups to support neutral, stable polymeric coordination open frameworks.[1a] For example, the use of rigid organic ring carboxylates, such as 1,3,5-benzenetricarboxylate, has led to several 3-D porous coordination polymers.[3] In this work, we used *cis*,*cis*-1,3,5-cyclohexanetricarboxylate ($C_9H_9O_6^{3-}$ or CTC), a saturated ring analogue to 1,3,5-benzenetricarboxylate, to synthesize 3-D lanthanide coordination polymers under hydrothermal conditions. Saturated ring carboxylates remain largely unexplored for sustaining 3-D coordination networks, and incorporating them into a framework may provide pore shapes and properties different from those supported by rigid aromatic ring templates. At the outset of this work, there has been only one reported, 2-D metal−CTC framework, which was prepared from a room-temperature reaction of zinc(II) with *cis*,*cis*-1,3,5-cyclohexanetricarboxylic acid (H_3CTC) in pyridine and dimethylformamide.[4] Ancillary ligation of pyridine and dimethylformamide to two coordination sites per octahedral zinc(II) ion is supposedly the cause for low dimensionality. The control of dimensionality is a principal issue that requires thorough investigation within the rapidly growing metal−organic framework field. Recent reports have demonstrated the effectiveness of solvothermolysis[5] in generating crystalline metal−organic frameworks of higher dimensionality, presumably through the entire or partial loss of ancillary terminal ligands at elevated temperatures.[3a,6] In our exploration of hydrothermal reactions of H_3CTC with lanthanide ions, we reasoned that the unique lanthanide nature (e.g., large size and high coordination number) and the reaction conditions would work in synergy to produce new 3-D porous open-framework coordination polymers. Herein we report the synthesis and structure of the compound $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ that represents the first lanthanide−CTC coordination polymer as well as the second 3-D open-framework metal−carboxylate network with nine-coordinate lanthanide centers.[7] We also describe the generation of porous frameworks from $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ by removing guest and coordinated water molecules.

Experimental Section

Materials and Methods. Erbium(III) nitrate hydrate and *cis,cis*-1,3,5-cyclohexanetricarboxylic acid were purchased from commercial suppliers and were used without further purification. Infrared spectra (IR) were recorded from KBr pellets on a Midac Prospect IR spectrometer. Thermogravimetric analyses (TGA) were performed under N_2 at a scan rate of 1 °C/min using a TA 2050 system. X-ray powder diffraction (XRPD) data were recorded on a Rigaku D/M-2200T automated diffractometer. The simulated XRPD patterns were calculated with the SHELXTL-XPOW program using the single-crystal data. Elemental analysis was performed by Atlantic Microlab in Norcross, GA.

Synthesis of $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$. A mixture of $Er(NO_3)_3\cdot 5H_2O$ (0.353 g, 0.80 mmol) and H_3CTC (0.216 g, 1.0 mmol) was placed in a Teflon-lined Parr bomb containing 15 mL of deionized water. The bomb was sealed, heated at 170 °C for 24 h, and allowed to cool to room temperature. Large, pink crystals were isolated by decanting the supernatant, washed thoroughly with deionized water, ethanol, and acetone, and air-dried to give 0.370 g of product (80%). Main IR absorption bands (cm^{-1}): 3413 (s, br), 2940 (w), 2867 (w), 1624 (m), 1544 (s), 1433 (s), 743 (m), 591 (m). A single-crystal X-ray analysis (see below) reveals the existence of both coordinated water ligands ($2H_2O/Er$) and noncoordinated water guests ($2.5H_2O$ per formula unit). The bulk-phase purity of this compound was confirmed by comparing its observed and simulated XRPD patterns. The results of elemental analysis were consistently high in C and low in H, suggesting that the crystals lose guest water molecules after prolonged isolation from the mother liquor.

Removal of Guest and Coordinated Water. A freshly isolated sample of $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ (246 mg) was evacuated under 2×10^{-3} Torr for 2 h at room temperature. The measured weight loss (23.2 mg) was equivalent to the loss of 2.5 water molecules per formula unit (calcd 24.1 mg). Elemental analysis of the desolvated compound

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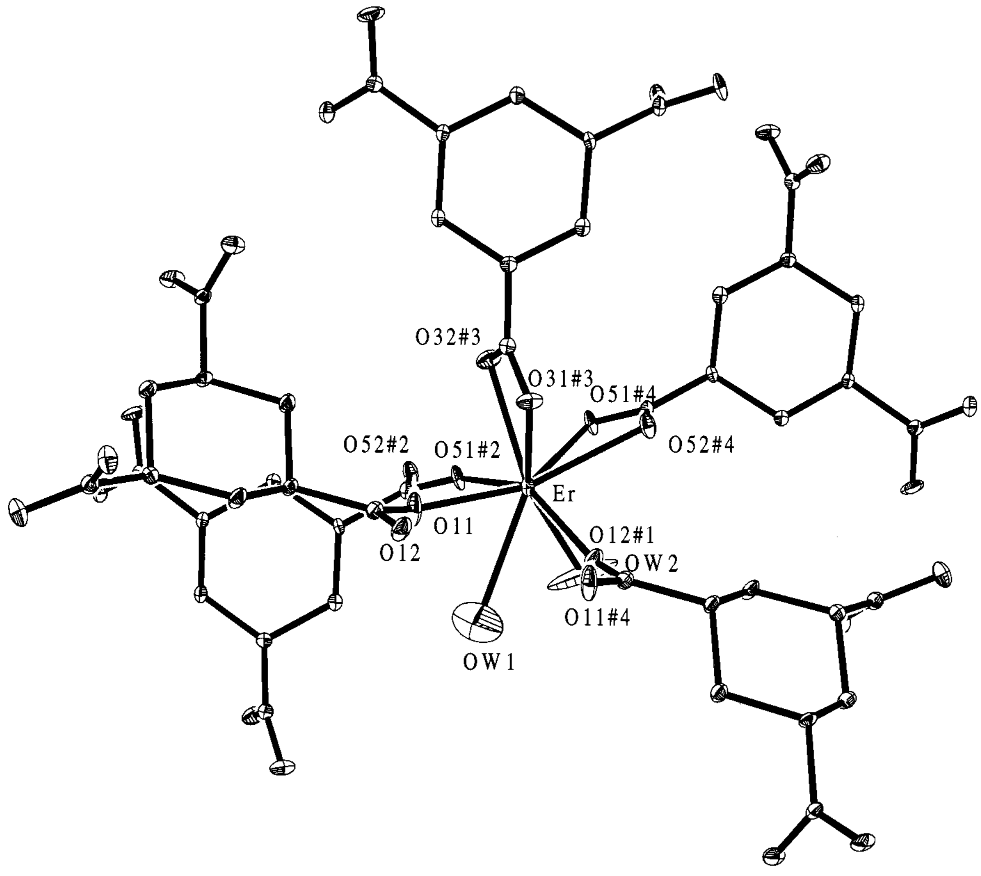

Figure 1. Coordination environment of [Er($C_9H_9O_6$)(H_2O)$_2$]·2.5H_2O. Thermal ellipsoids at 35% probability. Atoms with additional labels #1−#4 are related to each other by symmetry operations specified in Table 2.

supports its formulation as [Er($C_9H_9O_6$)(H_2O)$_2$]. Calcd (found) for $C_9H_{13}O_8Er$: C, 25.96 (25.83); H, 3.15 (3.12). The IR absorption bands of [Er($C_9H_9O_6$)(H_2O)$_2$] are similar to those of [Er($C_9H_9O_6$)(H_2O)$_2$]·2.5H_2O. Compared with that of [Er($C_9H_9O_6$)(H_2O)$_2$]·2.5H_2O, the XRPD pattern of [Er($C_9H_9O_6$)(H_2O)$_2$] is considerably broadened with only two sharp lines. Reintroduction of guest water molecules into the evacuated sample was effected by immersing 178.9 mg of [Er($C_9H_9O_6$)(H_2O)$_2$] in water. After 12 h, the solid was isolated, washed thoroughly with acetone, and air-dried until its weight stabilized at 197.6 mg. The increase in weight (18.7 mg) was equivalent to the gain of 2.5 water molecules per formula [Er($C_9H_9O_6$)(H_2O)$_2$] (calcd 19.3 mg). This resolvated material shows an identical XRPD with that of the original [Er($C_9H_9O_6$)(H_2O)$_2$]·2.5H_2O. Exposure of [Er($C_9H_9O_6$)(H_2O)$_2$] to water vapor for 2 days also regenerates [Er($C_9H_9O_6$)(H_2O)$_2$]·2.5H_2O.

TGA performed on [Er($C_9H_9O_6$)(H_2O)$_2$] showed continuous weight loss above 65 °C, and the curve had a discernible inflection point where the temperature was approximately 150 °C and the weight loss (4.36%) corresponded to the loss of one coordinated water molecule per formula unit (calcd 4.32%). Another weight loss (4.38%) was observed between 150 and 440 °C, suggesting the loss of the second equivalent of coordinated water (calcd 4.32%). The decomposition of the Er−CTC framework occurred above 480 °C, as indicated by a significant weight loss (43.42%). No attempt was made to identify the products of decomposition. A sample of [Er($C_9H_9O_6$)(H_2O)$_2$] (130.7 mg) was heated at 150 °C under vacuum for 3 h and recorded a weight loss of 5.4 mg, corresponding to the loss of one water molecule per formula [Er($C_9H_9O_6$)(H_2O)$_2$] (calcd 5.6 mg). The resulting solid appeared amorphous, showing no sharp peaks in its XRPD pattern. However, after being immersed in water for 12 h, this material reverted to the original [Er($C_9H_9O_6$)(H_2O)$_2$]·2.5 H_2O, as confirmed by comparing the XRPD patterns.

X-ray Crystallography. A flake-shaped single crystal of [Er($C_9H_9O_6$)(H_2O)$_2$]·2.5H_2O (dimensions 0.12 × 0.10 × 0.04 mm) was sealed in a glass capillary with a small amount of the mother liquor and was mounted on a Siemens CCD SMART diffractometer. Data were collected at 293 K with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and *ω−2θ scan* mode (2.25° < 2θ < 27.91°). The structure was solved by direct methods using the program SIR97[8] and was refined by full-matrix least-squares techniques using the program SHELXL 5.0. A summary of the crystallographic data and structure refinement is presented in Table 1.

Table 1. Crystal Data and Structure Refinement for [Er($C_9H_9O_6$)(H_2O)$_2$]·2.5H_2O

empirical formula	$ErC_9H_{18}O_{10.5}$
a, Å	13.4186(2)
b, Å	12.2468(2)
c, Å	15.9193(3)
β, deg	92.1430(10)
V, Å^3	2614.27(8)
Z	8
formula weight	461.49
space group	$C2/c$
T, °C	20(2)
λ(Mo Kα), Å	0.710 73
ρ_{calc}, g cm^{-3}	2.345
μ, cm^{-1}	64.72
final R indices* [$I > 2\sigma(I)$]	R1 = 0.0356, wR2 = 0.0822
R indices[a] (all data)	R1 = 0.0384, wR2 = 0.0837

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Results and Discussion

[Er($C_9H_9O_6$)(H_2O)$_2$]·2.5H_2O was synthesized from a hydrothermal reaction of Er(NO_3)$_3$·H_2O with H_3CTC. The IR spectrum shows strong, diagnostic absorption bands at 1544 and 1433 cm^{-1} for the coordinated carboxylate groups;[9] the absence

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$[a]

Er−O(12)#1	2.222(4)	Er−O(52)#4	2.415(4)
Er−O(11)	2.235(4)	Er−O(31)#3	2.443(4)
Er−O(51)#2	2.330(4)	Er−O(51)#4	2.563(4)
Er−OW2	2.336(7)	Er−OW1	2.577(11)
Er−O(32)#3	2.398(4)		
O(12)#1−Er−O(11)	95.23(17)	OW2−Er−O(31)#3	151.1(3)
O(12)#1−Er−O(51)#2	148.96(17)	O(32)#3−Er−O(31)#3	53.54(14)
O(11)−Er−O(51)#2	81.96(16)	O(52)#4−Er−O(31)#3	73.19(16)
O(12)#1−Er−OW2	76.2(2)	O(12)#1−Er−O(51)#4	120.97(15)
O(11)−Er−OW2	120.5(4)	O(11)−Er−O(51)#4	143.75(16)
O(51)#2−Er−OW2	78.7(2)	O(51)#2−Er−O(51)#4	66.34(16)
O(12)#1−Er−O(32)#3	132.79(16)	OW2−Er−O(51)#4	71.4(3)
O(11)−Er−O(32)#3	84.16(19)	O(32)#3−Er−O(51)#4	72.78(15)
O(51)#2−Er−O(32)#3	77.91(16)	O(52)#4−Er−O(51)#4	51.55(13)
OW2−Er−O(32)#3	142.8(2)	O(31)#3−Er−O(51)#4	108.11(15)
O(12)#1−Er−O(52)#4	78.61(16)	O(12)#1−Er−OW1	70.3(3)
O(11)−Er−O(52)#4	150.84(18)	O(11)−Er−OW1	62.4(3)
O(51)#2−Er−O(52)#4	117.67(14)	O(51)#2−Er−OW1	81.3(3)
OW2−Er−O(52)#4	86.0(4)	OW2−Er−OW1	59.3(4)
O(32)#3−Er−O(52)#4	79.75(16)	O(32)#3−Er−OW1	142.7(3)
O(12)#1−Er−O(31)#3	80.09(16)	O(52)#4−Er−OW1	137.5(3)
O(11)−Er−O(31)#3	77.68(18)	O(31)#3−Er−OW1	126.5(3)
O(51)#2−Er−O(31)#3	128.56(16)	O(51)#4−Er−OW1	125.2(3)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + {}^3/_2$, $-y + {}^1/_2$, $-z$; #2, $-x + 1$, y, $-z - {}^1/_2$; #3, $-x + {}^3/_2$, $y - {}^1/_2$, $-z - {}^1/_2$; #4, x, $-y$, $z + {}^1/_2$; #5, $-x + {}^3/_2$, $y + {}^1/_2$, $-z - {}^1/_2$; #6, x, $-y$, $z - {}^1/_2$.

of the strong and broad −COOH absorption band at 1702 cm^{-1} for H_3CTC indicates the complete deprotonation of H_3CTC. The structure of $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ was determined by single-crystal X-ray analysis. The crystallographic unit cell contains eight chemically equivalent Er ions and CTC ligands, and Figure 1 shows the coordination environment of an Er center. Among the nine oxygen atoms bound to an Er ion, two are from water molecules, four from two bidentate COO$^-$ groups, and three from three monodentate COO$^-$ groups. Note that the oxygen atom labeled O51#2 is ligated to another Er ion (not shown). The carboxylic O−Er bond distances range from 2.222(4) to 2.563(4) Å and those of the H_2O−Er bonds from 2.336(7) to 2.577(11) Å, all of which are comparable to those reported for other nine-coordinate erbium−oxygen donor complexes.[10] More data on selected bond distances and angles are presented in Table 2. Each multifunctional CTC unit acts as a bridging ligand connecting five Er ions through its three COO$^-$ groups, and the detailed binding modes are shown in Figure 2. Two COO$^-$ groups chelate to two Er ions in a bidentate fashion, and the third COO$^-$ binds to another two Er ions through its two oxygen atoms in a monodentate fashion. The fifth Er is bound to one of the bidentate COO$^-$ groups through O51 at a distance of 2.330 Å.

In the infinite 3-D solid-state structure, CTC templates form 1-D channels parallel to the crystallographic *a*, *b*, and *c* axes, respectively. Figure 3 is a representation of the polymeric structure viewed down the *b* axis. The channels along *c* have the largest cavity size at about 4.7 Å, as measured by the shortest H···H distance between two diametrically opposing CTC rings (Figure 4). The noncoordinated water molecules are enclathrated in these channels as guest molecules apparently because of the available room for inclusion. The diameters of the channels along the *a* and *b* axes are approximately 2.7 Å. In consideration of the van der Waals radii of the host framework atoms, such channels are too small in size to accommodate guest water molecules. The X-ray crystallographic analysis did not observe hydrogen bonds involving coordinated or guest water molecules.

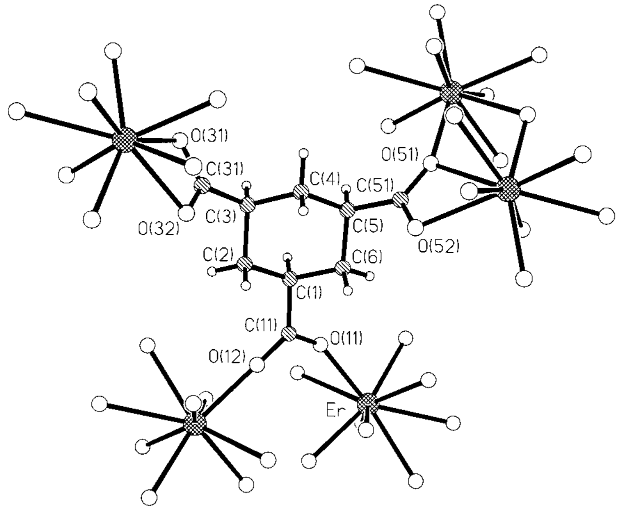

Figure 2. Binding modes of the carboxylate groups in a CTC unit. The crosshatched and shaded circles represent Er and C, respectively, and the open circles with decreasing size represent O and H, respectively.

The open channels in the 3-D network of $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ make it possible to generate porous frameworks by removing the guest water and/or bound water molecules. Evacuation of $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ at room temperature removes quantitatively the guest water molecules. The XRPD of the resulting $[Er(C_9H_9O_6)(H_2O)_2]$ shows significant broadening, which indicates a degradation of long-range crystallinity. Nonetheless, the similarity between the IR spectra of $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ and $[Er(C_9H_9O_6)(H_2O)_2]$ suggests the retention of a stable framework in the latter. This observation is corroborated by the fact that $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ can be regenerated from $[Er(C_9H_9O_6)(H_2O)_2]$ via reintroducing guest water molecules into the channels, as confirmed by comparing the XRPD patterns. The mobility of the channel water molecules in $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$ appears to suggest possible absence of hydrogen bonding that would otherwise hold them more tightly.

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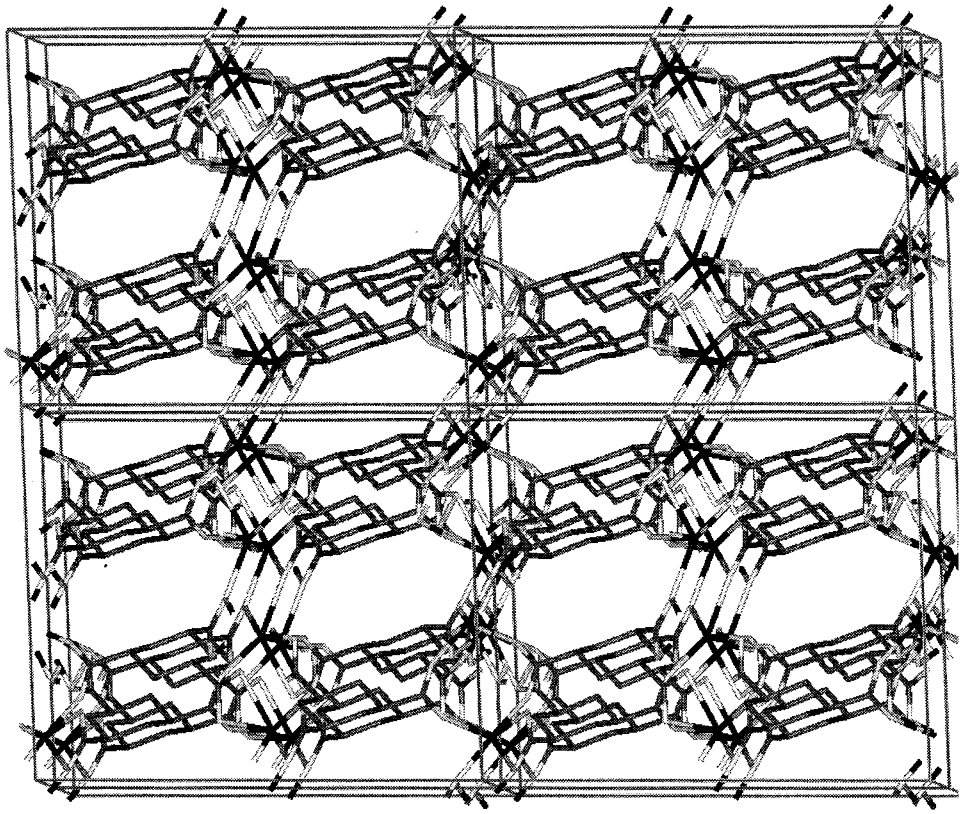

Figure 3. [$Er(C_9H_9O_6)(H_2O)_2$] polymer framework viewed along the *b* axis.

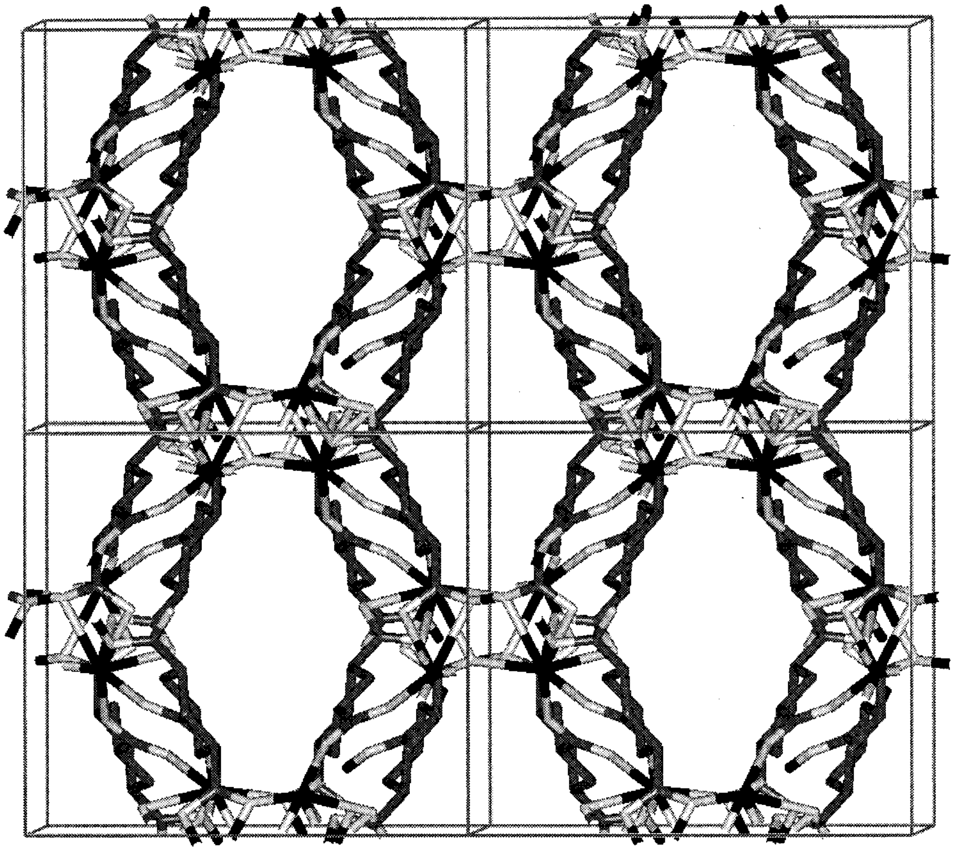

Figure 4. Illustration of the channels along the *c* axis. Guest water molecules are omitted for clarity.

Removal of the coordinated water molecules in [$Er(C_9H_9O_6)(H_2O)_2$] is intended for the study of the robustness of its framework. Assisted by TGA measurements, a preparative-scale sample of [$Er(C_9H_9O_6)(H_2O)_2$] was heated at 150 °C under vacuum to lose 1 equiv of coordinated water. The integrity of the Er−CTC framework remains in the resulting solid which, after being treated with water, exhibits the same XRPD as does the original [$Er(C_9H_9O_6)(H_2O)_2$]·$2.5H_2O$. According to a TGA measurement, the loss of the second coordinated water molecule spanned a wide temperature range (150−440 °C). Although this intriguing result is not well understood at present, it is tempting to hypothesize that reorganization of the Er−CTC framework may accompany this dehydration process probably to realize eight- or nine-coordination for the Er(III) ions. The CTC ring flexibility at the elevated temperatures should facilitate such structural change. Immersion into water of a sample, presumably $Er(C_9H_9O_6)$, taken from the TGA experiment, yielded an unidentified solid exhibiting an XRPD different from that of $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$. These experiments demonstrate that complete dehydration of $[Er(C_9H_9O_6)(H_2O)_2]$ irreversibly changes the Er−CTC framework structure.

In conclusion, we have synthesized $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$, a novel 3-D lanthanide coordination polymer supported by the anionic linking group *cis*,*cis*-1,3,5-cyclohexanetricarboxylate.[11] The open framework structure of this compound is utilized to generate the porous material $[Er(C_9H_9O_6)(H_2O)_2]$ via removing the guest water molecules. Removal of one equivalent of coordinated water in $[Er(C_9H_9O_6)(H_2O)_2]$ does not irreversibly change the infinite metal−organic framework. We are currently investigating similar metal−ligand systems.

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Supporting Information Available: XRPD patterns and a complete X-ray crystallographic file in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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(11) We have sought to synthesize analogues with other trivalent lanthanide ions but have not been successful.