Inorg. Chem. **2006**, *45*, 5399–5406

Inorganic Chemistry
Article

Synthesis, Crystal Structure, and Porosity Estimation of Hydrated Erbium Terephthalate Coordination Polymers

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Received February 13, 2006

The reaction of the Er^{3+} ion with polycarboxylate ligands in gel media leads to coordination polymers exhibiting various structural types and dimensionalities. Five Er^{3+}/1,4-benzenedicarboxylate-based coordination polymers have been obtained in such conditions. Four out of the five are new. Their crystal structures are reported and compared herein. Compound **1**, namely, $Er_2Ter_3(H_2O)_6$, where H_2Ter symbolizes the terephthalic acid, crystallizes in the space group $P\bar{1}$ (No. 2) with $a = 7.8373(10)$ Å, $b = 9.5854(2)$ Å, $c = 10.6931(2)$ Å, $\alpha = 68.7770(8)°$, $\beta = 70.8710(8)°$, and $\gamma = 75.3330(12)°$. It has already been reported elsewhere. The last four compounds are new. Compound **2**, namely, $Er_2Ter_3(H_2O)_6{\cdot}2H_2O$, crystallizes in the space group $P121/a1$ (No. 14) with $a = 6.7429(2)$ Å, $b = 22.4913(7)$ Å, $c = 9.6575(3)$ Å, and $\beta = 91.6400(18)°$. Compound **3**, namely $Er_2Ter_3(H_2O)_8{\cdot}2H_2O$ crystallizes in the space group $P\bar{1}$ (No. 2) with $a = 7.5391(2)$ Å, $b = 10.0533(3)$ Å, $c = 10.4578(3)$ Å, $\alpha = 87.7870(10)°$, $\beta = 82.5510(11)°$, and $\gamma = 86.2800(16)°$. Compound **4**, namely, $Er_2Ter_3(H_2O)_6{\cdot}2H_2O$ crystallizes in the space group $C2/c$ (No. 15) with $a = 38.5123(13)$ Å, $b = 11.1241(4)$ Å, $c = 7.0122(2)$ Å, and $\beta = 98.634(2)°$. Compound **5**, namely, $Er_2Ter_3(H_2O)_6{\cdot}H_2O$, crystallizes in the space group $P\bar{1}$ (No. 2) with $a = 6.8776(10)$ Å, $b = 11.0420(2)$ Å, $c = 18.5675(3)$ Å, $\alpha = 84.7240(6)°$, $\beta = 81.8380(6)°$, and $\gamma = 84.1770(8)°$. A computational method has also been developed to evaluate the potential porosity of the coordination polymers. This method is described and then applied to the different $Er_2Ter_3(H_2O)_n$ coordination polymers previously described.

Introduction

The synthesis of coordination polymers has developed rapidly in recent years.[1−4] Work along this line is motivated by their interesting molecular topologies[5,6] and crystal packing motifs, along with their potential applications as functional materials. Indeed, partly because of the emergence of nanotechnologies, there is currently a renewal of interest in the field. Actually, the design of nanoporous open frameworks is a factor of this revival because these compounds are anticipated to exhibit good efficiency as far as size selective separation, catalysis, and gas storage are concerned.[2,7−17] As compared to the reports of d-block

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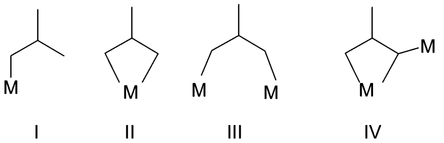
10.1021/ic060241t CCC: $33.50

transition metal coordination polymers, lanthanide polymeric complexes are less common because, unlike the d orbitals of the transition elements, the f orbitals of the lanthanide ions do not contribute significantly to complex formation. Actually, bonding between lanthanide ions and coordinating ligands depends essentially on the electronegativity of the bonding atoms of the ligands, and the lanthanide ions show very little structuring effect.[18,19] However, there has been an upsurge in the synthesis of lanthanide-based polymeric complexes becaue of their fascinating coordination geometry and their unique physical properties.[13,20−34] Benzene-polycarboxylate ligands, especially, have drawn much attention[33,35−45] because these ligands are chemically and thermally reasonably stable, present a structuring effect thanks to π-stacking, and their carboxylato functional groups allow one to expect a structural diversity resulting from their numerous possible coordination modes (see Scheme 1).

Scheme 1. Coordination Modes Presented by the Carboxylato Groups



Scheme 2. Terephthalate Ligand (Ter^{2-})

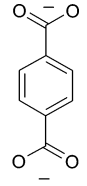


Table 1. List of Lanthanide-Based Coordination Polymers with the 1,4-Benzene-dicarboxylate Ligand

chemical formula	lanthanide ion	dimensionality	ref
$Er_2(Ter)_3(H_2O)_6$	Er	3D	37
$Er_2(Ter)_3(H_2O)_3$	Er	3D	46
$Ln_2(Ter)_3(H_2O)_4$	Tb and Er	3D	46, 47, 49
$TbTer(NO_3)(DMF)_2$	Tb	3D	47, 48

Table 2. Summary of Synthesis Results[a]

gel	gel density	chemical formula
agar−agar	0.1%	$Er_2Ter_3(H_2O)_6\cdot 2H_2O$ (**2**)
TEOS	17.5/2.5	$Er_2Ter_3(H_2O)_6$ (**1**)
TEOS	18.5/1.5	$Er_2Ter_3(H_2O)_6\cdot H_2O$ (**5**)
TMOS	18.5/0.5	$Er_2Ter_3(H_2O)_8\cdot 2H_2O$ (**3**)
TMOS	18.5/1.5	$Er_2Ter_3(H_2O)_6\cdot 2H_2O$ (**4**)

[a] Density of gel is expressed in weight percent for the agar−agar gel, while it is expressed as the ratio of water/ortho silicate (vol/vol) for the TEOS and TMOS gels.

For almost a decade some of us have been focusing our attention on the construction of new lanthanide-containing coordination framework exhibiting porosity after removal of the crystallization water molecules. One of the major challenges in that field is to maintain the host framework integrity in the absence of the guest molecules to allow reversible access to the cavities within the host. Obviously, three-dimensional coordination frameworks are needed for such a purpose. However, despite the high coordination numbers presented by the lanthanide ions, three-dimensional coordination polymers are rather uncommon, and the choice of the organic binding ligand seems to be a key point.

The terephthalic acid (1,4-benzenedicarboxylic acid), hereafter symbolized by H_2Ter, is represented in Scheme 2. It presents some interesting characteristics: (i) its two carboxylato groups have a good affinity for lanthanide ions, (ii) its rodlike topology induces low steric hindrance and allows binding of numerous ligands to a given lanthanide ion, (iii) its chemical and thermal stabilities are high, and (iv) it has a high structuring effect becausr of its π-system and its donor oxygen atoms that can be involved in hydrogen bonds. This is an important asset for obtaining lanthanide-containing well-crystallized compounds.

Actually several lanthanide coordination polymers involving the terephthalate ion as a bridging ligand have already been reported.[37,46−50] Most of them were obtained by hy-

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Table 3. Crystallographic Data for Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
chemical formula	$Er_2C_{24}H_{24}O_{18}$	$Er_2C_{24}H_{28}O_{20}$	$Er_2C_{24}H_{32}O_{22}$	$Er_2C_{24}H_{28}O_{20}$	$Er_2C_{24}H_{24}O_{18}$
system	triclinic	monoclinic	triclinic	monoclinic	triclinic
a (Å)	7.83730(10)	6.7429(2)	7.5391(2)	38.5123(13)	6.87760(10)
b (Å)	9.5854(2)	22.4913(7)	10.0533(3)	11.1241(4)	11.0420(2)
c (Å)	10.6931(2)	9.6575(3)	10.4578(3)	7.0122(2)	18.5675(3)
α (deg)	68.7770(8)		87.7870(10)		84.7240(6)
β (deg)	70.8710(8)	91.6400(18)	82.5510(11)	98.634(2)	81.8380(6)
γ (deg)	75.3330(12)		86.2800(16)		84.1770(8)
V (Å^3)	699.17(2)	1464.02(8)	783.92(4)	2970.08(17)	1384.26(4)
Z	2	4	2	4	2
fw (g mol^{-1})	935	971	1007	971	935
space group	$P\bar{1}$ (No. 2)	$P121/a$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
D_{calcd} (g cm^{-3})	2.221	2.203	2.158	2.171	2.252
μ (mm^{-1})	6.047	5.785	6.022	5.703	6.112
R	3.42	4.78	3.63	6.33	3.45
R_w	8.65	11.93	8.15	16.58	9.10

drothermal methods. The compounds containing only terephthalate as the coordinating ligand are listed in Table 1.

As one see in this table, all the reported compounds are three-dimensional, but none of them can really be considered to be a porous material. On the basis of this observation, we have reinvestigated the $Er^{3+}-H_2O-Ter^{2-}$ system in gel media. This synthetic route has proven its efficiency in leading to unprecedented crystal structures.[19,51−52] Indeed, altering with the density and the nature of the gel allows us to control the kinetics of the reaction and thus to take advantage of the great chemical flexibility of the lanthanide ions. Five different compounds were obtained in this manner. To the best of our knowledge, they have never been obtained by other synthetic routes. In this paper, we report the synthesis and crystal structure of these five compounds. Compound **1**, $Er_2Ter_3(H_2O)_6$, has already been reported,[37] while compounds **2**, $Er_2Ter_3(H_2O)_6{\cdot}2H_2O$, **3**, $Er_2Ter_3(H_2O)_8{\cdot}2H_2O$, **4**, $Er_2Ter_3(H_2O)_6{\cdot}2H_2O$, and **5**, $Er_2Ter_3(H_2O)_6{\cdot}(H_2O)$, have never been described.

Experimental Section

Syntheses. Hydrated erbium salts were prepared from the oxide according to literature methods.[53] Erbium oxide was furnished by Rhôdia Electronics and Catalysis. The gels were purchased from Accros Organics and gelified according established procedures.[54,55] The sodium salt of the terephthalic acid was purchased from Accros Organics and used without further purification.

Single crystals of each phase were obtained by reaction of the same reactants (erbium chloride hexahydrate and sodium terephthalate) with crystallization occurring in different gel media. Three different gels were used, namely, agarose gel (agar−agar), tetraethyl ortho-silicate gel (TEOS), and tetramethyl ortho-silicate gel (TMOS). The first one is a physical gel, while the latter two are chemical gels.

Dilute solutions of Er(III) chloride (0.1 mol L^{-1}) and sodium terephatlate (0.1 mol L^{-1}) were allowed to slowly diffuse through a gel medium in a U-shaped tube. After a few weeks, single crystals were obtained. Details of the different syntheses are listed in Table 2.

Anal. Calcd (found) for $Er_2Ter_3(H_2O)_6$ (**1**): Er, 35.78 (35.5); C, 30.8 (31.0); H, 2.62 (2.5); O, 30.8 (31.0). Anal. Calcd (found) for $Er_2Ter_3(H_2O)_6{\cdot}H_2O$ (**5**): Er, 35.10 (35.0); C, 30.22 (30.3); H, 2.78 (2.7); O, 31.9 (32.0). Anal. Calcd (found) for $Er_2Ter_3(H_2O)_6{\cdot}2H_2O$ (**2**): Er, 34.45 (34.5); C, 29.66 (29.7); H, 2.93 (2.8); O, 32.96 (33.0). Anal. Calcd (found) for $Er_2Ter_3(H_2O)_6{\cdot}2H_2O$ (**4**): Er, 34.45 (34.4); C, 29.66 (29.8); H, 2.93 (2.8); O, 32.96 (33.0). Anal. Calcd (found) for $Er_2Ter_3(H_2O)_8{\cdot}2H_2O$ (**3**): Er, 33.22 (33.0); C, 28.6 (29.0); H, 3.22 (3.0); O, 34.96 (35.0).

The same IR spectrum is observed for the five complexes. It clearly shows the presence of the vibration bands characteristic of the −(O−C−O)− groups around 1560 and 1490 cm^{-1}, confirming the presence of carboxylate groups.

Single-Crystal X-ray Diffraction Data. All crystals were sealed in glass capillaries for X-ray single-crystal data collection to avoid potential dehydration. Single crystals were mounted on a Nonius KappaCCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal data collection was performed at room temperature.

A crystal-to-detector distance of 25.0 mm was used, and the data collection strategy (determination and optimization of the detector and goniometer positions) was performed with the help of the COLLECT program[56] to measure Bragg reflections of the unique volume in reciprocal space.

Unique reflections were indexed, Lorentz-polarization corrected, and then integrated by the DENZO program of the KappaCCD software package.[57]

Absorption corrections were performed using the facilities[58−62] included in the WinGX program suite.[63]

Structure determinations were performed with SIR97,[64] which revealed all the non-hydrogen atoms. All non-hydrogen atoms were

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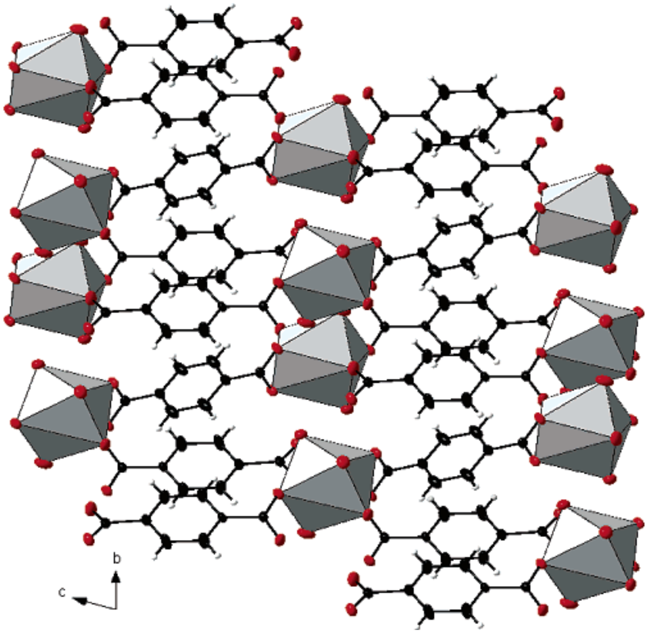

Figure 1. Projection view along the $\vec{a}$ axis of compound $Er_2Ter_3(H_2O)_6$. Er coordination polyhedrons have been drawn.

refined anisotropically using the SHELXL program.[65−67] Hydrogen atoms bound to the organic ligand were localized at ideal positions. The hydrogen atoms of the water molecules have not been localized. Crystal and final structure refinement data of the five compounds are listed in Table 3.

Full details of the X-ray structure determination of compounds **1**−**5** have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC-188931 (**1**), CCDC-194824 (**2**), CCDC-188932 (**3**), CCDC-297191 (**4**), and CCDC-297192 (**5**) and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK. Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk.), on request from the authors and in reference to this publication.

Results and Discussion

Structural Description of $Er_2Ter_3(H_2O)_6$ (1). This crystal structure was reported some time ago.[37] This compound crystallizes in the triclinic system, space group $P\bar{1}$ (No. 2) with $a = 7.8373(1)$ Å, $b = 9.5854(2)$ Å, $c = 10.6931(2)$ Å, $\alpha = 687770(8)°$, $\beta = 70.8710(8)°$, $\gamma = 75.3330(12)°$, and $Z = 2$. This structure is three-dimensional, and the organic−inorganic planes spread parallel to the ($\vec{b}$, $\vec{c}$) plane (Figure 1). The Er atom is eight-coordinated and presents a dodecahedral coordination polyhedron made of three oxygen atoms from three coordination water molecules and five oxygen atoms from carboxylate groups. All in all, four different terephthalate ligands are connected to each lanthanide ion. No crystallization water molecule has been found because the channels created along the $\vec{c}$ axis are not large enough for water molecules.

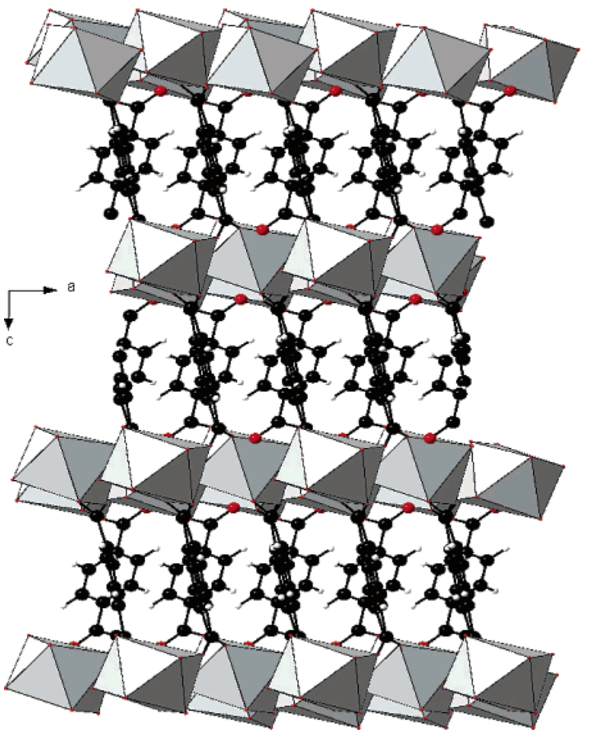

Figure 2. Projection view along the $\vec{b}$ axis of the framework of the compound $Er_2Ter_3(H_2O)_6 \cdot 2H_2O$. Er coordination polyhedrons have been represented.

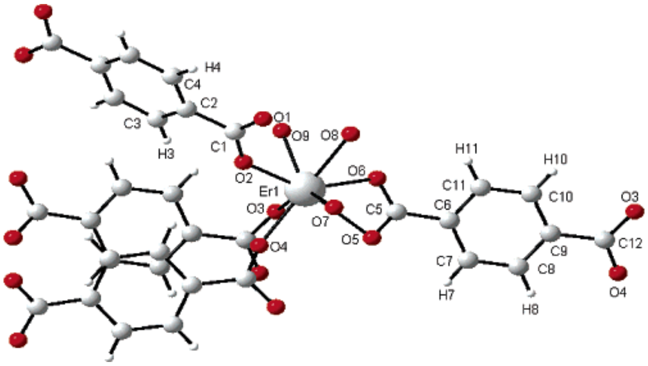

Figure 3. Extended asymmetric unit along with the numbering scheme of compound $Er_2Ter_3(H_2O)_6 \cdot 2H_2O$.

Structural Description of $Er_2Ter_3(H_2O)_6 \cdot 2H_2O$ (2). This compound crystallizes in the monoclinic system, space group *P*121/*a* (No. 14) with $a = 6.7429(2)$ Å, $b = 22.4913(7)$ Å, $c = 9.6575(3)$ Å, $\beta = 91.6400(18)°$, and $Z = 4$. The crystal structure is three-dimensional. As can be seen in Figure 2, the crystal structure can be described as inorganic planes spreading in the ($\vec{a}$,$\vec{b}$) plane made of Er coordination polyhedrons linked together by terephthalate ligands.

The Er atom is eight-coordinated by 3 oxygen atoms from the coordination water molecules and five oxygen atoms from the carboxylate groups, thus forming a distorted dodecaedron. Each Er atom is bounded to four different terephthalate

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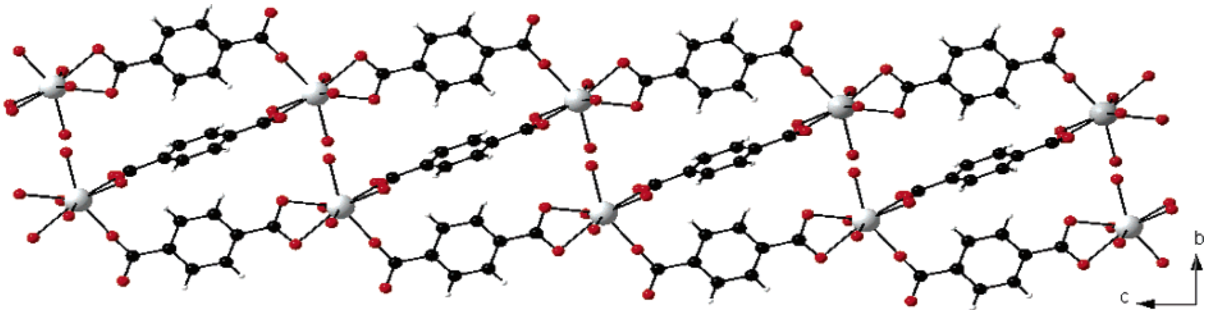

Figure 4. Projection view along the $\vec{a}$ axis of a molecular ribbonlike motif of compound $Er_2Ter_3(H_2O)_8 \cdot 2H_2O$.

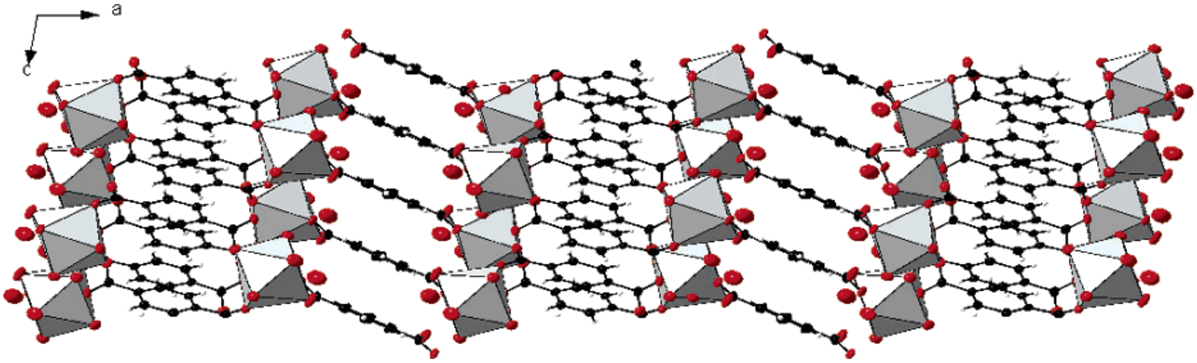

Figure 5. Projection view along the $\vec{b}$ axis of compound $Er_2Ter_3(H_2O)_6 \cdot 2H_2O$. The coordination polyhedrons of the Er atoms have been represented.

ligands (Figure 3). There is only one crystallization water molecule per asymmetric unit localized inside the inorganic planes.

Structural Description $Er_2Ter_3(H_2O)_8 \cdot 2H_2O$ (3). This compound crystallizes in the triclinic system, space group $P\bar{1}$ (No. 2) with $a = 7.5391(2)$ Å, $b = 10.0533(3)$ Å, $c = 10.4578(3)$ Å, $\alpha = 87.7870(10)°$, $\beta = 82.5510(11)°$, $\gamma = 86.2800(16)°$, and $Z = 2$. The crystal structure is one-dimensional. The crystal structure can be described as the juxtaposition of molecular ribbonlike motifs spreading along the $\vec{c}$ axis (see Figure 4).

The Er atom is eight-coordinated by four oxygen atoms from coordination water molecules and four oxygen atoms from carboxylate groups; thus it forms a distorted dodecahedron. Each Er atom is bound to three different terephthalate ligands (see Figure 4). There is only one crystallization water molecule per asymmetric unit, which is localized between adjacent ribbons.

Structural Description $Er_2Ter_3(H_2O)_6 \cdot 2H_2O$ (4). This compound crystallizes in the monoclinic system, space group $C2/c$ (No. 15) with $a = 38.5123(13)$ Å, $b = 11.1241(4)$ Å, $c = 7.0122(2)$ Å, $\beta = 98.634(2)°$, and $Z = 4$. The crystal structure is three-dimensional. As can be seen in Figure 5, the crystal structure can be described as inorganic planes spreading in the $(\vec{b},\vec{c})$ plane linked by terephthalate groups.

The Er atom is eight-coordinated by three oxygen atoms from coordination water molecules and five oxygen atoms from carboxylate groups, thus forming a distorted square antiprism. Each Er atom is bound to four terephthalate ligands (see Figure 6).

As shown on Figure 7, the crystallization water molecules are localized inside channels that spread along the $\vec{c}$ axis. They are bound to the molecular three-dimensional motif via hydrogen bounds.

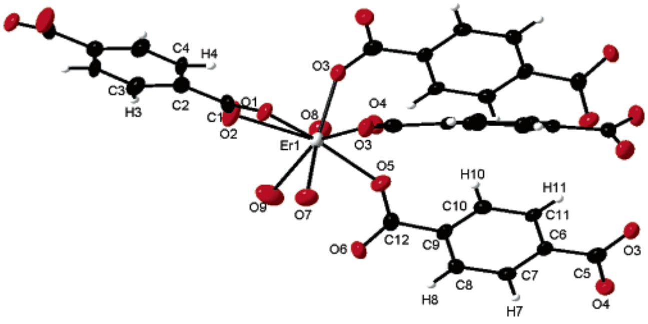

Figure 6. Projection view along with the numbering scheme of an extended asymmetric unit of compound $Er_2Ter_3(H_2O)_6 \cdot 2H_2O$.

Structural Description $Er_2Ter_3(H_2O)_6 \cdot H_2O$ (5). This compound crystallizes in the triclinic system, space group $P\bar{1}$ (No. 2) with $a = 6.8776(10)$ Å, $b = 11.0420(2)$ Å, $c = 18.5675(3)$ Å, $\alpha = 84.7240(6)°$, $\beta = 81.8380(6)°$, $\gamma = 84.1770(8)°$, and $Z = 2$. The crystal structure is three-dimensional.

The two independent Er atoms are both eight-coordinated. One of them is coordinated by two oxygen atoms from coordination water molecules and six oxygen atoms from carboxylate groups, while the second one is coordinated by four oxygen atoms from coordination water molecules and four oxygen atoms from carboxylate groups. Both coordination polyhedra can be best described as distorted square antiprisms. The Er1 atom is bound to five terephthalate ligands, while the Er2 atom is bound to only three (Figure 8).

As shown in Figure 9, the structure can be described as a juxtaposition of inorganic planes bound by terephthalates

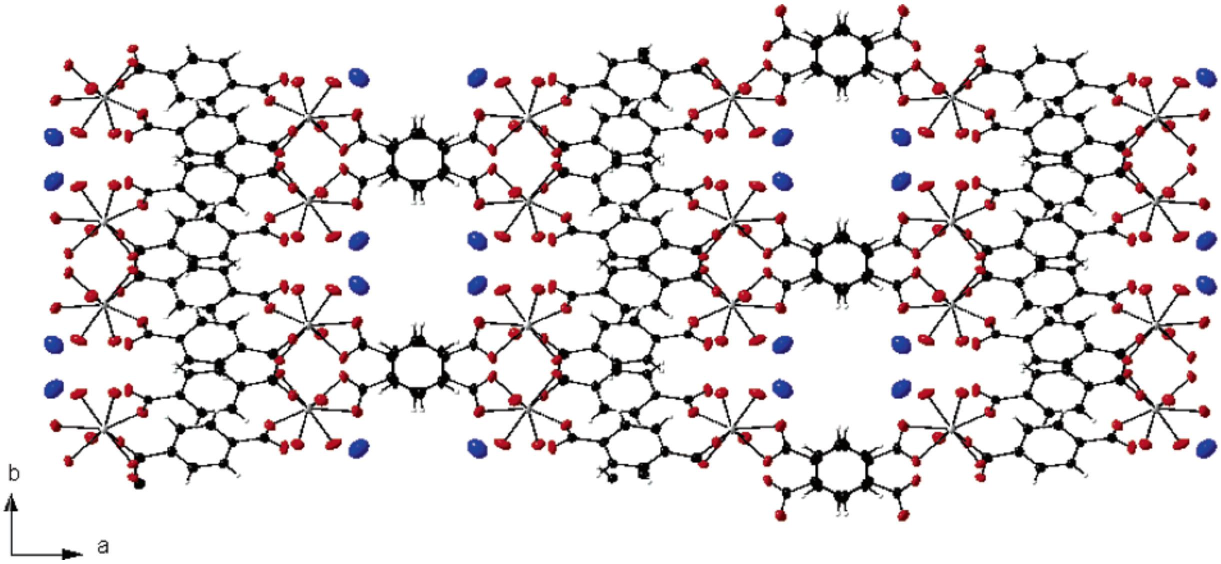

Figure 7. Projection view along the $\vec{c}$ axis of compound $Er_2Ter_3(H_2O)_6 \cdot 2H_2O$. The oxygen atoms from the crystallization water molecules have been represented in blue.

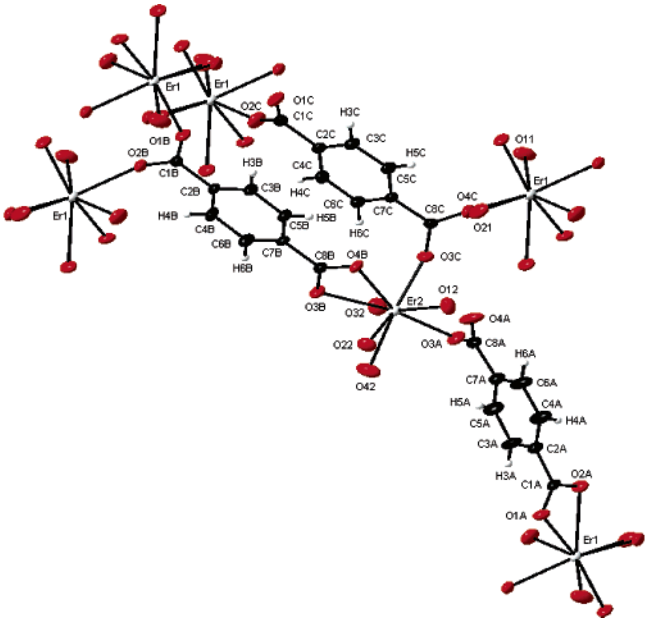

Figure 8. Projection view, along with numbering scheme, of an extended asymmetric unit of compound $Er_2Ter_3(H_2O)_6 \cdot H_2O$.

ligands. The crystallization water molecules are linked to the molecular framework via hydrogen bounds.

Comparison of the Different Crystal Structures. As one can notice from Table 1, all the crystal structures already reported were compact and present no crystallization solvent molecule. In contrast, our synthetic route has lead to four new compounds (**2**−**5**) exhibiting one or two crystallization water molecules. Furthermore, three out of these four compounds are three-dimensional (**2**, **4**, and **5**). These three compounds fill the two requirements of our approach: they are three-dimensional and present some easy to remove guest molecules. These three compounds have been obtained under different experimental conditions. They present very similar chemical formulas (compounds **2** and **4** even have the same one) and different crystal structures. Actually, in the crystal structures of both **2** and **4**, the Er ions are eight-coordinated by three oxygen atoms from coordination water molecules and five oxygen atoms from carboxylate groups from four terephthalate ligands. Similarly, the coordination modes of the carboxylate are identical. In both compounds, there is one bidentate carboxylato group (mode II), one bridging carboxylato group (mode III), and one monodentate carboxylato group (mode I) per asymmetric unit. The main difference between these crystal structures is in the way that the terephthalate ligands interact with each other. This structural diversity is usual and mainly the result of the synthetic route, which involves slow diffusion of the reactants through gel media.

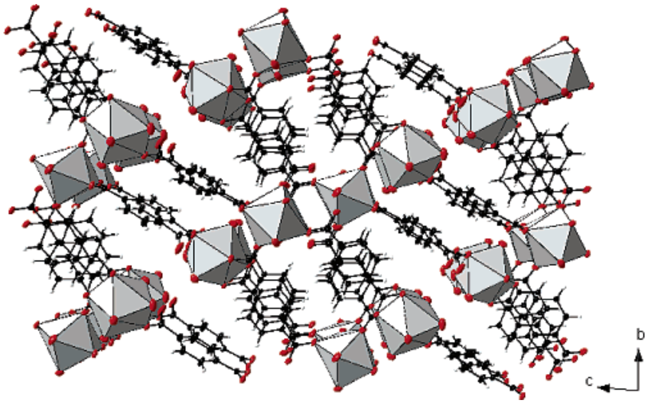

Figure 9. Perspective view along the $\vec{a}$ axis of compound $Er_2Ter_3(H_2O)_6 \cdot H_2O$. The coordination polyhedrons of the Er atoms have been represented.

Computational Method. Gas adsorption is the usual way to characterize a material's porosity. However, it is sometimes difficult to implement this method. This is especially the case for coordination polymers that often collapse or decompose during the preceding desorption treatment. Even more, when measurements are possible, the obtained porosity depends highly on the theoretical model used and on the sample's granulometry.[68]

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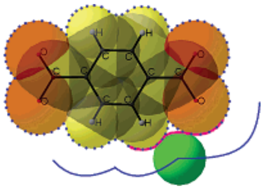
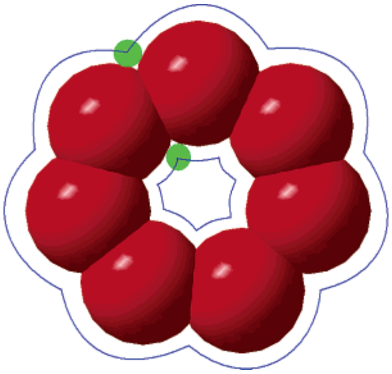
Scheme 3. Schematic Representation of the Van Der Waal's Surface (blue dotted line), the Solvent-Accessible Surface (blue line), and the Molecular Surface or Connolly's Surface (pink line) for a Terephthalate Anion[a]



[a] The probe sphere is represented in green.

Scheme 4. Internal and External Solvent Accessible Surfaces for a Cycle



We thus developed a computational method that allows us to estimate the potential porosity of any coordination polymer. This method, based only on crystallographic data, leads to a value which does not depend on sample geometry. It is particularly useful for studying coordination polymers with low thermal stability. It is also useful for comparing the potential porosity of materials with complex networks of interconnected channels.

The software package developed by Michael L. Connolly in 1983[69] is used in this method to calculate the solvent accessible surface and the molecular surface (or Connolly's surface) of the proteins. The solvent accessible area is defined and computed as the area traced out by the center of a probe sphere representing a solvent molecule as it is rolled over the surface of the interesting molecule. The molecular surface consists of the part of the van der Waals surface of the atoms that is accessible to the probe sphere (contact surface) connected by a network of concave and saddle-shaped surfaces that smoothes over the crevices and pits between the atoms as shown in Scheme 3.

The infinite character of coordination polymers causes some difficulties. Indeed, for a given sphere radius, if we apply the Connolly's algorithm to a crystallographic cell, we obtain

$$S^{1*1*1} = S^{1*1*1}_{\text{internal}} + S^{1*1*1}_{\text{external}}$$

where S^{1*1*1} is the solvent-accessible surface calculated by Connolly's program, $S^{1*1*1}_{\text{internal}}$ is the internal solvent-accessible surface of the molecular content of the cell, and $S^{1*1*1}_{\text{external}}$ is the external solvent-accessible surface of the content of the cell as defined in Scheme 4.

Obviously, only $S^{1*1*1}_{\text{internal}}$ is interesting for our purpose. If we apply Connolly's algorithm to a molecular fragment corresponding to the content of $n*n*n$ cells, we obtain S^{n*n*n} with

$$S^{n*n*n} = n^3 S^{111}_{\text{internal}} + n^2 S^{111}_{\text{external}}$$

Thus by plotting $(S^{n*n*n}/M_w{}^{1*1*1} \times n^3) \times N_A$ versus $1/n$, where N_A is the Avogadro constant, $M_w{}^{1*1*1}$ is the unit cell weight, we obtain a straight line. The specific accessible surface of the material expressed in square meters per gram is the origin ordinate of this line.

Table 4. Specific Accessible Surfaces ($m^2\ g^{-1}$) Calculated for the $Er_2Ter_3(H_2O)_6$ Compounds Exhibiting Crystal Structures **2**, **4**, and **5** with Various Values of Probe Sphere Radius, r_0, Corresponding Respectively to the Kinetic Radii of He, H_2, and N_2[72]

	$Er_2Ter_3(H_2O)_6$ type **2**	$Er_2Ter_3(H_2O)_6$ type **4**	$Er_2Ter_3(H_2O)_6$ type **5**-
$r_0 = 1.3$ Å (He)	0	248.0	0
$r_0 = 1.45$ Å (H_2)	0	176.6	0
$r_0 = 1.8$ Å (N_2)	0	43.5	0

To test the validity of our approach, we have calculated the porosity of Faujasite ($Na_{5.12}Al_{52.35}Si_{139}O_{362.88}(OH)_{32}H_{39.594}$). For this purpose, we have chosen a probe sphere radius of 1.8 Å, which is often considered to be the kinetic radius of N_2.[70] The calculations lead to 960 $m^2\ g^{-1}$. This value is in fairly good agreement with reported values.[71]

We then applied this method to coordination polymers **2**, **4**, and **5**. All these compounds are thermally stable below 100 °C, and it is possible, by cold drying, to remove the crystallization water molecules without destroying the molecular framework. For all of them, we have formally removed all the crystallization water molecules and calculated the specific accessible surface assuming that the crystal structure was globally unchanged. Only the partially dehydrated compound (**4**), $Er_2Ter_3(H_2O)_6$, exhibits some porosity. In Table 4, we have reported the results of these calculations.

A further development of the method is to calculate a "profile" of the material's porosity. This can be obtained by calculating the molecular surface (or Connolly's surface), S'^{n*n*n}, for various probe sphere radii, r. In Figure 10**,** we have plotted S'^{2*2*2} versus r.

The S'^{2*2*2} value for $r = 0$ Å is the van der Waals surface (internal + external) of the molecular content of the 2*2*2 cells. Then, S'^{2*2*2} decreases when r increases and reaches a plateau. The sudden decrease at 2.5 Å is representative of the channel's radius. Indeed, when r is bigger than the radius of the channels, the probe sphere cannot penetrate the framework and the S'^{2*2*2} becomes equal to the $S'^{2*2*2}_{\text{external}}$ value. When r increases more, $S'^{2*2*2}_{\text{external}}$ tends toward the value of the 2*2*2 cell surface.

Once again, we have checked the validity of this calculation with Faujasite, and once again, the results are in good agreement with literature values.

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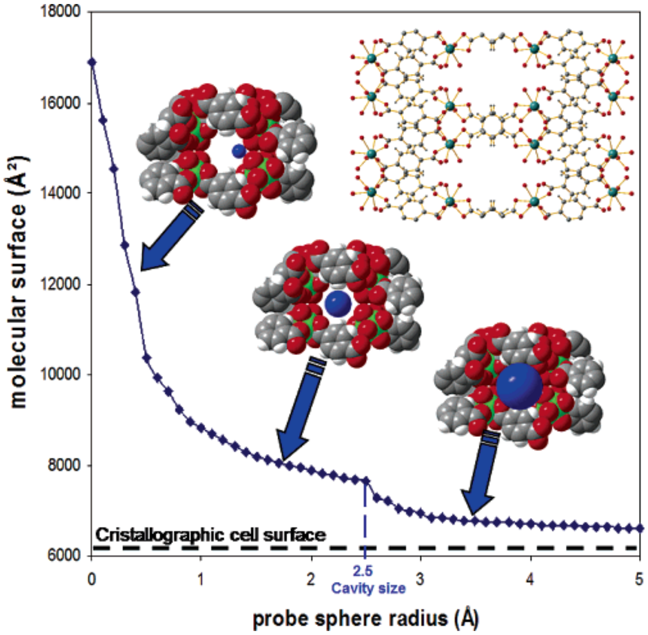

Figure 10. Representation of the profile of compound $Er_2Ter_3(H_2O)_6$ (**4**).

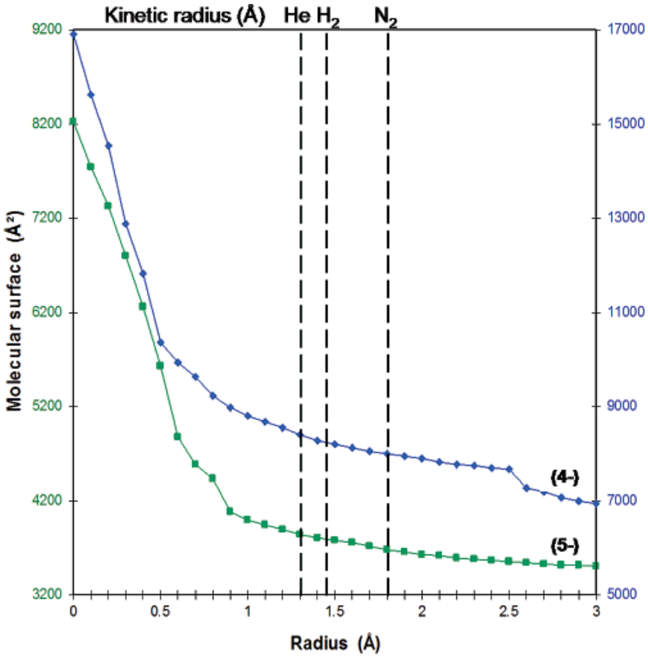

Figure 11. Profiles of partially dehydrated compounds **4** and **5**.

The profiles calculated for partially dehydrated $Er_2Ter_3(H_2O)_6$ compounds **4** and **5** are represented in Figure 11.

In this figure, the kinetic radii corresponding to He, H_2, and N_2 have also been reported. It appears that only the crystal structure of **4** has channels large enough to host one of these gaseous molecules. This is in perfect agreement with the zero internal accessible surface that was calculated for crystal structure **5**.

This profile may be the most interesting development of this computational model. Indeed, it gives information that is particularly difficult to obtain otherwise: (i) information about the channel diameters, even when they spread in a zigzag manner and (ii) information about the open character of the cavities inside the structure.

Conclusions and Outlook

We have reported five coordination polymers with the general chemical formula $Er_2Ter_3(H_2O)_n$. Four out of the five are three-dimensional, and three out of those four host crystallization water molecules. This confirms the validity of our approach that rodlike ligands with low steric hindrance are good promoters of three-dimensional lanthanide-based coordination polymers. However, we have also demonstrated here that this rodlike topology is not sufficient for obtaining the molecular precursors of porous solids. Actually, the terephthalate ligand can lead to very dense phases exhibiting no porosity. This can be attributed to the small size of the ligand and to the carboxylate-coordinating modes. Indeed, some coordinating modes (modes II and IV for instance), by bridging two different metal ions, lead to very short intermetallic distances and very high densities. We are currently studying new coordination polymers involving bigger rodlike ligands.

In this paper, we also presented a computational method that makes the evaluation of the accessible surface presented by a polymer for a given host molecule possible. This method also gives an estimate of the channel sizes. The aim of this method is not to replace porosity measurements but to make an evaluation of the porosity of solids with low thermal stability or complex networks of interconnected channels possible. This can be interesting for the study of compounds devoted to potential applications that do not require high thermal stability. This is the case, for instance, for biological applications or domestic depollution. For example, compound **4**, $Er_2ter_3(H_2O)_6{\cdot}2H_2O$, once dehydrated presents some porosity (98 $m^2\ g^{-1}$) as far as CO_2 adsorption is concerned ($r_0 = 1.65$ Å).

Acknowledgment. The authors thank the Region Bretagne for financial support. The Center of Crystallography of the Université de Rennes is acknowledged for recording the crystallographic data. M. M. Xavier Le Guillou and Thomas Bourdin are also warmly acknowledged for their help in the development of the computational method.

IC060241T