Hydrothermal Synthesis, Structure Determination, and Thermal Behavior of New Three-Dimensional Europium Terephthalates: MIL-$51_{LT,HT}$ and MIL-52 or $Eu_2^n(OH)_x(H_2O)_y(O_2C-C_6H_4-CO_2)_z$ (n = III, III, II; x = 4, 0, 0; y = 2, 0, 0; z = 1, 1, 2)

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Three-dimensional europium terephthalates have been obtained under hydrothermal conditions and their structures solved using either X-ray powder diffraction or single-crystal data. MIL-51_{LT} or $Eu_2^{III}(H_2O)_2(OH)_4(O_2C-C_6H_4-CO_2)$ and MIL-51_{HT} or $Eu_2^{III}(OH)_4(O_2C-C_6H_4-CO_2)$ contain only trivalent europium, while MIL-52 or $Eu^{II}(O_2C-C_6H_4-CO_2)$ involves only europium(II) metallic centers. Their structures are built up from eight- or nine-coordinated europium polyhedra and terephthalate anions, creating pillared structures. Inorganic layers of MIL-$51_{LT,HT}$ are closely related to those of europium hydroxide. Oxygen atoms of the inorganic sheets are either water molecules, hydroxyl groups, or oxygen atoms of the dicarboxylates. In the case of MIL-52, anions are oxygen atoms from the organic moities. In both structures, elongated hydrophobic channels are present but with no real porosity. Thermogravimetric analysis and X-ray thermodiffractometry have shown that MIL-51_{LT} and MIL-51_{HT} are correlated. Crystal data for MIL-51_{LT} and MIL-51_{HT}: triclinic space group $P\bar{1}$ (No. 2) with a = 13.190(1) Å, b = 7.185(1) Å, c = 3.718(1) Å, α = 120.452(1)°, β = 87.630(1)°, γ = 97.650(1)°, V = 300.96(1) Å^3 and a = 11.9691(1) Å, b = 6.2569(1) Å, c = 3.6773(2) Å, α = 91.03(1)°, β = 97.53(1)°, γ = 91.01(1)°, V = 273.6(1) Å^3. Crystal data for MIL-52: orthorhombic space group *Pbca* (No. 61) with a = 7.4052(2) Å, b = 10.1144(3) Å, c = 18.7512(1) Å, V = 1404.45(7) Å^3.

1. Introduction

The synthesis of hybrid inorganic−organic porous solids has recently grown exponentially, giving a new dimension to the domain of porous compounds.[1−4] The association of the huge variety of possible organic linkers and the multiple physical properties of inorganic solids allow a wide modulation of both the dimensions of the pores and the properties of the final porous materials. In such structures, organic species can act as either pillars or linkers and arrange respectively inorganic layers, chains, or clusters of transition or rare earth metals.

In the field of rare earth hybrid solids, our group reported recently series of diphosphonates,[5] carboxyphosphonates,[6] and dicarboxylates.[7] If the first two series led only to pillared structures with no porosity, linear dicarboxylic acids led to microporous compounds built up from a 1-D inorganic framework connected through diacids. Using rigid dicarboxylic acids, several groups characterized also three-dimensional solids;[8] although a porosity is sometimes present, these solids are however coordination polymers with isolated, or clustered rare earth polyhedra connected through dicarboxylic acids. Wang et al. reported also a porous lanthanide coordination polymer using a saturated tricarboxylic acid.[9] Using bypiridine dioxide, Schröder et al. reported also a large pore coordination polymer lanthanide solid with an unusual topology.[10] Finally, an original approach was developed recently using lanthanide cubane-like clusters as precursors to microporous hybrid solids.[11]

This paper deals with the synthesis, the crystal structure, and the thermal behavior of new three-dimensional europium(III) or europium(II) dicarboxy-

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lates obtained using terephthalic acid: MIL-$51_{LT,HT}$ and MIL-52 or $Eu_2^n(OH)_x(H_2O)_y(O_2C-C_6H_4-CO_2)_z$ (n = III, III, II; x = 4, 4, 0; y = 2, 0, 0; z = 1, 1, 2).

2. Experimental Section

Synthesis and Chemical Analysis. MIL-$51_{LT,HT}$ were hydrothermally synthesized (autogenous pressure for 4 days) from a mixture of europium nitrate $Eu(NO_3)_3 \cdot 5H_2O$ (Aldrich, 98%), terephthalic acid $HO_2C-(C_6H_4)-CO_2H$ (Alfa 97%), sodium hydroxide NaOH (Prolabo, 99%), and H_2O in the molar ratio 1:0.5:2:400. Reactants were introduced in this order and stirred approximately 10 min before the resulting suspensions were introduced into a Teflon-lined steel autoclave. MIL-51_{LT} was obtained pure after 4 days at 453 K, while MIL-51_{HT} was synthesized at higher temperatures (523 K, 4 days). The final pH evolved from 7 to 5 in both syntheses which led to white crystalline powders on which chemical analyses were performed. All attempts for getting crystals of MIL-51_{LT} failed. On the contrary, during the course of the study of synthetic parameters, tiny plateletlike crystals of MIL-51_{HT} appeared among other phases and allowed the structure determination of MIL-51_{HT} from single-crystal data.

The synthesis of MIL-52 was made using metallic europium (Aldrich, 99.9%), terephthalic acid, and water in the 1:1:200 ratios. Without any stirring, the suspension was placed in a Teflon-lined steel autoclave and the temperature set at 423 K for one night (15 h); a small proportion (5−10%) of platelet orange crystals was isolated among a white powder corresponding to MIL-51_{LT}. The final pH was about 7.

Quantitative elemental analyses indicated C:Eu ratios respectively equal to 3.8 and 4.05 for MIL-51_{LT} and MIL-51_{HT}, which is in good agreement with the theoretical value: 4. No quantitative analysis could be performed with MIL-52 due to the impossibility of separating the crystals of MIL-52 from the powder of MIL-51_{LT}.

Thermogravimetric analysis (TGA) experiments, performed under air atmosphere on MIL-$51_{LT,HT}$ using a TA-Instrument type 2050 analyzer apparatus have shown several weight losses in the 373−873 K range. The residual solid has been identified as europium oxide Eu_2O_3. MIL-51_{LT} exhibits three weight losses of 5.3, 5.1, and 19.4% at 423, 623, and 723 K, corresponding respectively to the departures of bonded water, half of the hydroxyl groups, and the organic moieties followed by their partial replacement by oxygen atoms to form europium oxide at higher temperatures (see thermal behavior section). These losses are in agreement with the theoretical values (5.5, 5.5, and 21%). MIL-51_{HT} exhibits similar weight losses (5.1 and 20%), at 623 and 723 K, except that no water loss is present.

The infrared spectra of the title compounds clearly shows the presence of the vibrationnal bands characteristic of the −(O−C−O)− groups around 1550 and 1430 cm^{-1}, confirming the presence of the dicarboxylate within the solids; no band at 1700 cm^{-1} characteristic of a free C−O groups is observed for MIL-51_{LT}, which seems at first sight in disagreement with its structure determination; this latter point will be discussed further in the article. Bands around 3500 cm^{-1} also confirmed the presence of OH and/or H_2O groups in MIL-$51_{LT,\ HT}$.

X-ray thermodiffractometry, performed in the furnace of a Siemens D-5000 diffractometer in the $\theta-\theta$ mode, shows several steps in the decomposition for MIL-51_{LT} (see thermal behavior section).

Finally, these analyses are on the whole in agreement with the results of the structure determination.

Structure Determination. *(a) MIL-51_{LT} (Powder Data).* It was already mentioned that all the attempts for getting single crystals of MIL-51_{LT} failed. So, its powder X-ray diffraction pattern was collected on a D5000 ($\theta-2\theta$ mode) Siemens diffractometer with λ(Cu Kα) = 1.5406, 1.5444 Å. The pattern of MIL-51_{LT} was indexed with the Dicvolgv program,[12] and a triclinic solution with adequate figures of merit was found (see Table 1). The XRD pattern of MIL-51_{LT} shows a strong preferred orientation effect due to the pillared structure. Therefore, the powder was pulverized with a Mac Crone grinder in ethanol (Prolabo, 95%) and dried at 373 K. The fine powder was then mounted in a top-loaded Mac Murdie Type sample holder,[13] which led to a reduction of the preferred orientation effect. The pattern matching was performed with Fullprof2k using the Winplotr software package.[14] Structure determination was performed using the EXPO package, which combines a full pattern decomposition program EXTRA and a direct method program SIR97 optimized for powder diffraction data.[15] The structure of MIL-51_{LT} was then refined using also Fullprof2k. Twenty-six experimental point values were introduced during the refinement to adjust the background. The peak profile was determined using a Pseudo-Voigt function and two asymmetry parameters. Soft distance constraints, an overall thermal parameter, and a preferred orientation vector corresponding to the direction perpendicular to the inorganic layers were also introduced during the refinement. Details of the structure determination are summarized in Table 1 and the indexed powder pattern in Table 2. Bond valence calculation gives a value of 3.13 for the valence of europium atoms.[16]

Table 1. Crystal Data and Structure Refinement Parameters for MIL-51_{LT} or $Eu_2^{III}(H_2O)_2(OH)_4(O_2C-C_6H_4-CO_2)$

empirical formula	$Eu^{III}_2(H_2O)_2(OH)_4(O_2CC_6H_4CO_2)$
fw ($g \cdot mol^{-1}$)	572.09
calcd dens ($g \cdot cm^{-3}$)	3.15
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	13.190(1)
b (Å)	7.185(1)
c (Å)	3.718(1)
α (deg)	120.452(1)
β (deg)	87.630(1)
γ (deg)	97.650(1)
V (Å^3)	300.96(1)
figures of merit	M_{20} = 47; F_{20} = 97
Z	1
radiation λ(Cu Kα) (Å)	1.5406, 1.5444
2θ range (deg)	580
no. of reflections	475
no. of atoms	10
no. of intens params	31
no. of profile params	14
R_P	0.114
R_{WP}	0.149
R_B	0.105
R_F	0.056

[a] Overall thermal parameter: 1.9(1) Å^2.

The formula deduced from the structure determination for MIL-51_{LT} is: $Eu_2^{III}(OH)_4(H_2O)_2(O_2C-C_6H_4-CO_2)$. The final agreement factors are satisfactory:[17] R_p = 11.4%, R_{wp} = 14.9% and R_{Bragg} = 10.5%, R_F = 5.6%. The corresponding Rietveld plot is reported in Figure 1. Atomic coordinates and principal bond distances are reported in Table 3.

(b) MIL-51_{HT} and MIL-52 (Single Crystal). Platelet-like single crystals of MIL-51_{HT} and MIL-52 suitable for data collection were glued on a glass fiber. The intensity data were collected respectively on a Enraf Nonius CAD-4 four-circle

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Table 2. Indexed Powder Pattern of MIL-51$_{LT}$[a]

h k l	$2\theta_{obs}$	$2\theta_{calc}$	d_{hkl} (Å)	intens
1 0 0	6.760	6.759	13.066	100
2 0 0	13.535	13.541	6.533	18
0 0 2	14.393	14.411	6.141	3
$\bar{1}$ 1 0	15.105	15.108	5.859	1
1 1 0	16.710	16.717	5.297	11
$\bar{2}$ 1 0	18.470	18.479	4.797	8
3 0 0	20.382	20.372	4.355	1
2 1 0	21.088	21.087	4.209	7
$\bar{3}$ 1 0	23.413	23.431	3.793	9
0 $\bar{1}$ 1	23.391	23.938	3.714	1
1 $\bar{1}$ 1	24.608	24.611	3.614	5
$\bar{1}$ $\bar{1}$ 1	25.161	25.187	3.533	1
3 1 0	26.566	26.564	3.353	3
4 0 0	27.283	27.277	3.267	1
0 0 1	27.800	27.824	3.204	3
1 $\bar{2}$ 1	28.360	28.396	3.140	5
$\bar{1}$ 2 0	28.932	28.967	3.080	10
$\bar{4}$ 1 0	29.195	29.221	3.054	4
$\bar{1}$ $\bar{2}$ 1	29.782	29.802	2.995	1
2 $\bar{2}$ 1	30.109	31.140	2.963	1
$\bar{2}$ 2 0	30.459	30.486	2.930	1
1 2 0	30.715	30.740	2.906	3
$\bar{3}$ $\bar{1}$ 1	32.308	32.319	2.767	3
4 1 0	32.649	32.655	2.740	2
3 $\bar{2}$ 1	33.301	33.277	2.690	2
2 2 0	33.760	33.780	2.649	1
$\bar{3}$ 0 1	34.211	34.205	2.619	1
$\bar{5}$ 1 0	35.478	35.501	2.526	2
$\bar{4}$ $\bar{1}$ 1	37.397	37.409	2.402	2
1 $\bar{3}$ 1	38.035	38.067	2.362	1

[a] The indexing is based on a triclinic cell with the following dimensions: a = 13.190(1) Å, b =7.185(1) Å, c =3.718(1) Å, α = 120.452(1)°, β = 87.630(1)°, γ = 97.650(1)°, space group $P\bar{1}$ (No. 2).

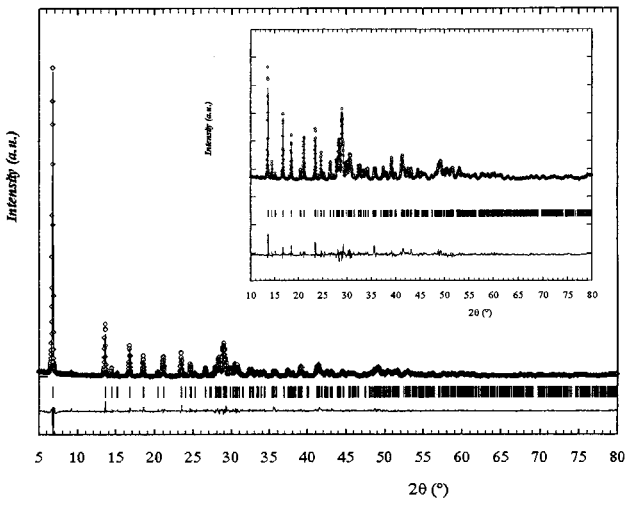

Figure 1. Final Rietveld plot of MIL-51$_{LT}$. An enlargement of the high-angle range is represented as in insert at the top of the figure.

diffractometer (MIL-51$_{HT}$) and on a Bruker-Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector (MIL-52), using the Mo Kα radiation in both cases. The reflections were corrected for Lorentz and polarization effects and absorption. The cell of MIL-51$_{HT}$ is triclinic, space group $P\bar{1}$ (No. 2), while MIL-52 is orthorhombic, space group *Pbca* (No. 61). Details of the structure determination are given in Table 4.

In both cases, the structures were solved using the SHELX-TL package.[18] Europium, oxygen atoms, and most of the carbon atoms were first located, while the remaining carbon atoms were found using difference Fourier maps. Hydrogen atoms of the benzene ring were fixed using distance and angle constraints. The final reliability factors[18] converged to $R_1(F)$ = 0.0461 and $R_{w2}(F^2)$ = 0.099 for MIL-51$_{HT}$ and $R_1(F)$ = 0.0263 and $R_{w2}(F^2)$ = 0.0572 for MIL-52. Bond valence calculations give values of 3.19 and 2.07 for europium atoms in MIL-51$_{HT}$ and MIL-52, respectively.[16] Finally, the formulas deduced from the structure determination were respectively $Eu_2^{III}(OH)_4(O_2C{-}C_6H_4{-}CO_2)$ and $Eu^{II}(O_2C{-}C_6H_4{-}CO_2)$ for MIL-51$_{HT}$ and MIL-52, which agree well with chemical results. Atomic coordinates are listed in Table 5a,b and the principal bond distances given in Table 6a,b.

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Table 3. Atomic Coordinates and Principal Bond Lengths (Å) for MIL-51$_{LT}$

atom	*x*	*y*	*z*
Eu	0.4367(2)	0.2345(5)	−0.005(1)
O(1)	0.317(2)	0.053(3)	0.348(8)
O(2)	0.471(2)	0.838(3)	0.582(7)
O(3)	0.413(2)	0.467(3)	−0.289(6)
O(4)	0.228(1)	0.314(3)	0.137(7)
O(5)	0.235(1)	0.658(3)	0.257(6)
C(1)	0.203(1)	0.503 (3)	0.306(12)
C(2)	−0.048(2)	0.315(3)	0.513(11)
C(3)	0.096(2)	0.490(3)	0.347(11)
C(4)	0.035(2)	0.295(3)	0.292(11)

Eu−O(1)	2.56(2)	Eu−O(1)	2.63(3)
Eu−O(2)	2.56(2)	Eu−O(2)	2.28(2)
Eu−O(2)	2.32(2)	Eu−O(3)	2.44(3)
Eu−O(3)	2.35(2)	Eu−O(3)	2.52(2)
Eu−O(4)	2.85(2)		
O(5)−C(1)	1.23(4)	O(4)−O(1)	1.26(4)
C(1)−C(3)	1.41(2)	C(2)−C(3)	1.45(4)
C(3)−C(4)	1.43(4)	C(4)−C(2)	1.32(4)

Table 4. Crystallographic Data of MIL-51$_{HT}$ and MIL-52

compd	MIL-51$_{HT}$	MIL-52
empirical formula	$Eu_2O_8C_8H_8$	$Eu_2O_8C_{16}H_8$
fw (g)	536.06	632.14
temp (K)	293 (2)	293 (2)
wavelength (Å)	0.71073	0.71073
space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
unit cell dimens (Å)		
a	3.6773(7)	7.4052 (2)
b	6.2569(13)	10.1144 (3)
c	11.969(2)	18.7512 (5)
α (deg)	91.01(3)	
β (deg)	97.53(3)	
γ (deg)	91.03(3)	
vol (Å^3)	272.91(9)	1404.45 (7)
multiplicity (Z)	1	4
calcd dens (mg/cm^3)	3.262	2.990
F(000):	246	1176
cryst size (μm)	100 × 80 × 20	240 × 160 × 40
range for data collecn (deg)	3.26−44.99	2.17−29.60
limiting indices	$-7 < h < +7$, $-12 < k < +12$, $0 < l < +23$	$-9 < h < +9$, $-13 < k < +8$, $-25 < l < +25$
reflcns collected	4056	9027
independ reflcns	3925 (R_{int} = 0.0577)	1872 (R_{int} = 0.0529)
refinement method	full-matrix least-squares on F^2	
data/restraints/params	3925/0/83	1872/0/119
goodness-of-fit on F^2	1.005	0.976
extincn coeff	0.0036(19)	0.00096(11)
largest diff peak and hole (e^{-3})	+5.530 and −6.762	+2.073 and −1.306
absorp coeff (cm^{-1})	11.416	8.900
final R indices ($I > 2\sigma(I)$)[a]		
$R_1(F)$	0.0461	0.0263
$R_{w2}(F^2)$	0.0990	0.0572

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{w2}(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\times 10^3$ Å^2) for MIL-51$_{HT}$ and MIL-52

atom	*x*	*y*	*z*	*U*(eq)[a]
		(a) For MIL-51$_{HT}$		
Eu	0.0658(1)	0.7545(1)	−0.2220(1)	8(1)
O(1)	0.0490(4)	0.1351(7)	−0.228(1)	10(1)
O(2)	−0.0902(4)	0.502(1)	−0.299(1)	12(1)
O(3)	0.1930(4)	0.913(1)	0.328 (1)	15(1)
O(4)	0.2703(4)	0.676(1)	−0.012(1)	18(1)
C(1)	0.393(1)	0.914(1)	0.374(2)	15(1)
C(2)	0.405(1)	0.115(1)	0.543(2)	19(1)
C(3)	0.280 (1)	0.827(1)	0.226(2)	15(1)
C(4)	0.489(1)	0.799(1)	0.332(2)	19(1)
		(b) For MIL-52		
Eu	0.0310(1)	0.6992(1)	0.0190(1)	15(1)
O(1)	0.3279(4)	0.5984(2)	−0.0327(1)	18(1)
O(2)	0.0504(4)	0.4780(3)	0.0804(2)	20(1)
O(3)	−0.2050(4)	0.7077(3)	−0.0968(2)	22(1)
O(4)	−0.3118(3)	0.6185(2)	0.0576(2)	18(1)
C(1)	0.4460(5)	0.4629(4)	−0.2719(2)	18(1)
C(2)	0.4405(5)	0.4389(4)	−0.1992(2)	19(1)
C(3)	0.3636(5)	0.5307(3)	−0.1530(2)	16(1)
C(4)	0.2981(5)	0.6496(4)	−0.1813(2)	18(1)
C(5)	0.2038(5)	0.3295(4)	0.2464(2)	18(1)
C(6)	0.3673(5)	0.5770(4)	−0.3003(2)	17(1)
C(7)	−0.1320(5)	0.6026(4)	−0.1209(2)	18(1)
C(8)	0.3350(5)	0.5011(4)	−0.0753(2)	16(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Principal Bond Lengths (Å) for MIL-51$_{HT}$ and MIL-52

	(a) For MIL-51$_{HT}$		
Eu−O(1)	2.410(4)	Eu−O(1)	2.385(4)
Eu−O(1)	2.394(4)	Eu−O(2)	2.412(4)
Eu−O(2)	2.409(4)	Eu−O(2)	2.511(4)
Eu−O(3)	2.589(5)	Eu−O(3)	2.543(5)
Eu−O(4)	2.528(5)		
O(3)−C(3)	1.279(8)	O(4)−C(3)	1.265(8)
C(1)−C(3)	1.48(1)	C(1)−C(2)	1.39(1)
C(1)−C(4)	1.39(1)	C(2)−C(4)	1.39(2)
	(b) For MIL-52		
Eu−O(2)	2.520(3)	Eu−O(1)	2.554(3)
Eu−O(1)	2.611(3)	Eu−O(4)	2.611(3)
Eu−O(3)	2.614(3)	Eu−O(2)	2.655(3)
Eu−O(4)	2.763(3)	Eu−O(3)	2.789(3)
O(1)−C(8)	1.269(4)	O(2)−C(7)	1.268(5)
O(3)−C(7)	1.276(4)	O(4)−C(8)	1.266(4)
C(1)−C(2)	1.39(1)	C(1)−C(6)	1.40(1)
C(2)−C(3)	1.39(1)	C(3)−C(4)	1.40(1)
C(3)−C(8)	1.50(1)	C(4)−C(5)	1.37(1)
C(5)−C(6)	1.39 (1)	C(6)−C(7)	1.50(1)

3. Results and Discussion

MIL-51$_{LT,HT}$ and MIL-52 exhibit three-dimensional structures built up from nine- (MIL-51$_{LT,HT}$) or eight-coordinated (MIL-52) europium monocapped antiprims and square antiprims polyhedra and terephthalate ions. MIL-51$_{LT,HT}$ contain trivalent europium, while MIL-52 possesses divalent europium atoms. Unlike in the case of the rare earth terephthalate coordination polymer obtained previously by Yaghi et al.,[8a] these structures are made from two-dimensional europium inorganic networks related together via organic diacids creating pillared frameworks (Figure 2).

These inorganic layers are built-up from chains of europium polyhedra which are made from face-sharing europium polyhedra linked through μ_3-hydroxyl groups or oxygen atoms from dicarboxylates (Figures 2 and 3). However, these chains are related together differently within the layer: through face-sharing polyhedra in the case of MIL-51$_{LT,HT}$ and through edges in the case of MIL-52 (Figure 4). These differences come from the number of terephthalate or hydroxyl ions present in each phase. In the case of MIL-51$_{LT,HT}$, there is only one terephthalate anion per two europium atoms and half of the oxygen atoms of the inorganic sheets come from the organic linkers and half from hydroxyl groups. In the case of MIL-52, there is twice as much terephthalate anions per europium atom as in MIL-51$_{LT,HT}$; thus, no hydroxyl group is present, and anions from inorganic sheets are oxygen atoms of the organic acid. In the case of MIL-51$_{LT,HT}$, the presence of hydroxyl groups is

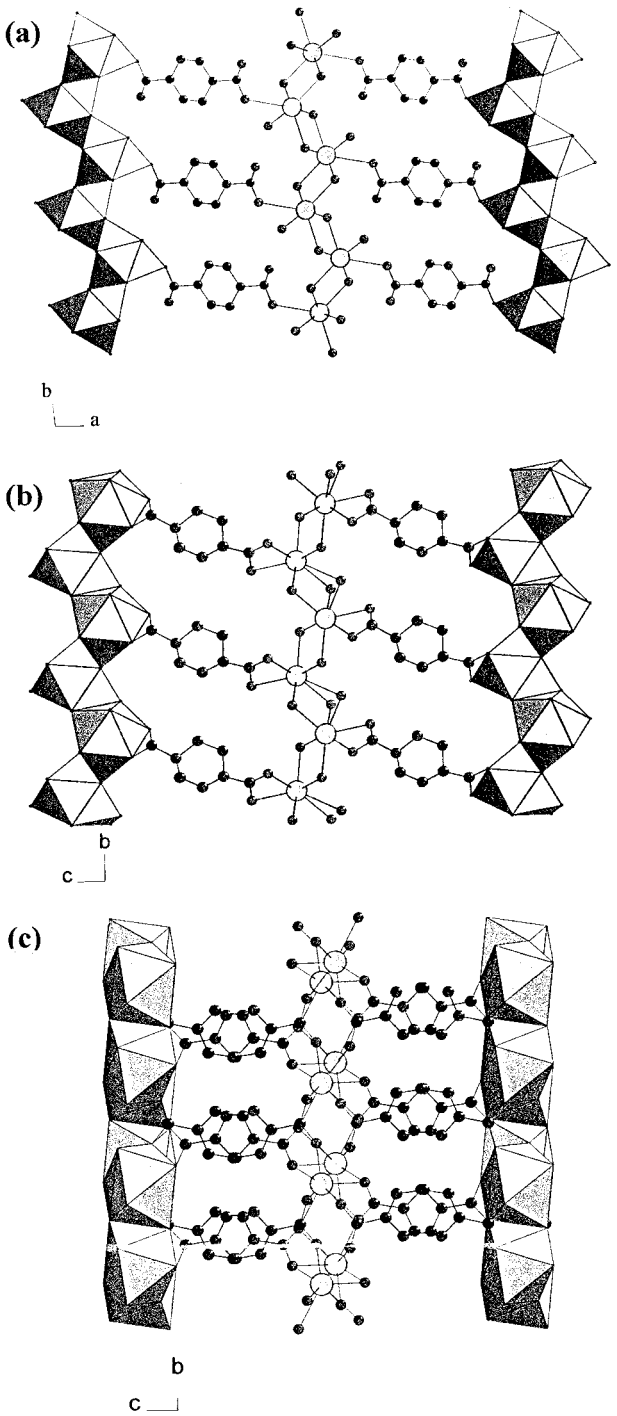

Figure 2. View of the "interlayer spacing" of (a) MIL-51$_{LT}$ along the (100) direction, (b) MIL-51$_{HT}$ along the (100) direction, and (c) MIL-52 along the (001) direction.

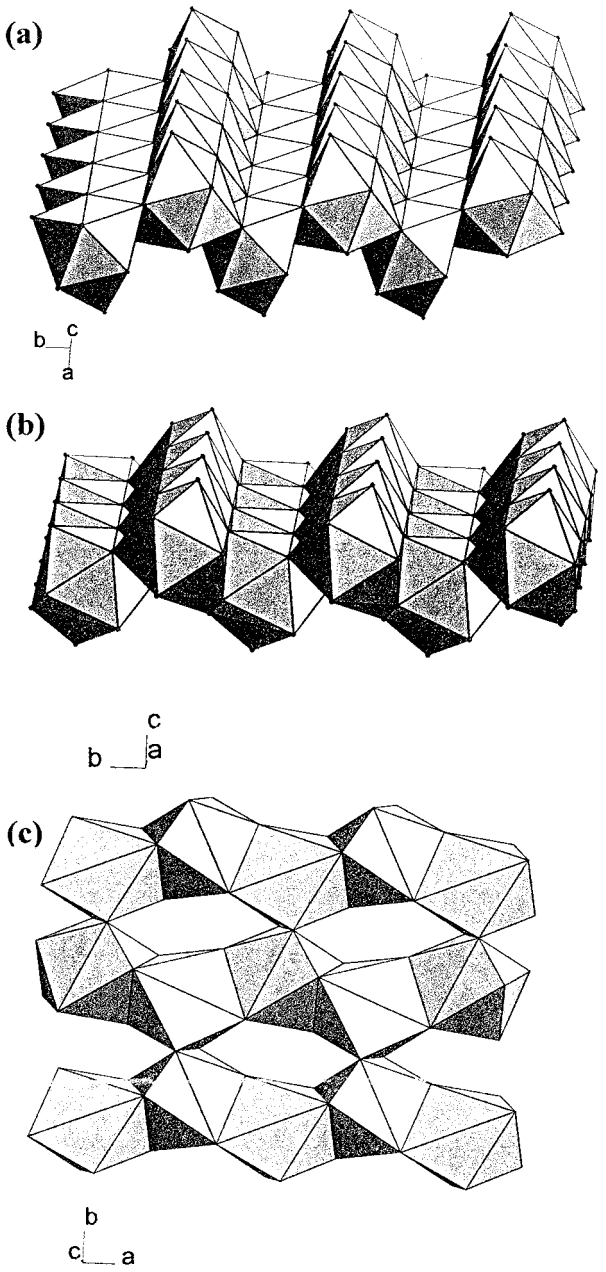

Figure 3. View of an inorganic layer of (a) MIL-51_{LT}, (b) MIL-51_{HT}, and (c) MIL-52.

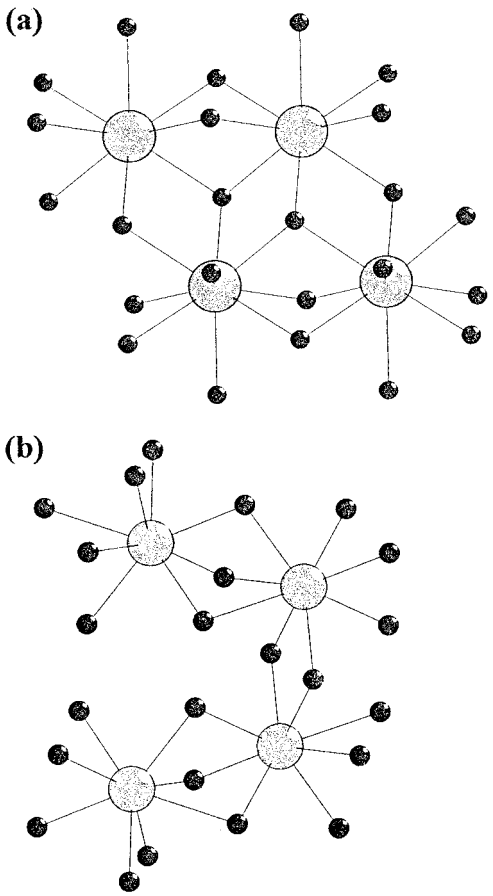

Figure 4. Schematic "ball and stick" representation of the connection mode of europium polyhedra within the inorganic layers of (a) MIL-$51_{LT,HT}$ and (b) MIL-52.

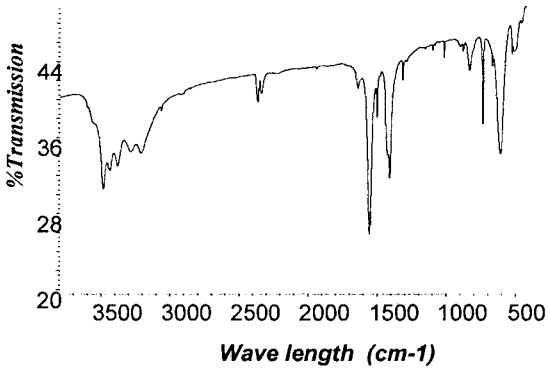

Figure 5. Infrared spectrum of MIL-51_{LT}.

obvious since inorganic sheets are very similar to those of europium hydroxide $Eu(OH)_3$; cell parameters of inorganic layers of MIL-$51_{LT,HT}$ and those of $Eu(OH)_3$ (a = 6.352 Å, c = 3.653 Å, space group $P6_3/m$)[19] are related: $b_1 \sin \alpha_1 \approx b_2 \approx b_3$ and $c_1 \approx c_2 \approx c_3$ (1, MIL-51_{LT}; 2, MIL-51_{HT}; 3, $Eu(OH)_3$). Bond valence calculations for MIL-$51_{LT,HT}$ are in agreement with the presence of hydroxyl groups in these structures since values within the 0.9−1.3 range are obtained for these oxygen atoms.

Each europium of MIL-51_{HT} is surrounded by seven μ_3-OH and two oxygen atoms of the dicarboxylate; europium atoms from MIL-51_{LT} exhibit almost the same environment but since terephthalate ions are in this case monodendate, europium atoms complete their coordination with a μ_2-O water molecule (O(1)). Bond valence calculation gives a value of +0.49 for this oxygen atom, which is correct for a water molecule. In the case of MIL-52, dicarboxylate anions are bidendate and europium atoms eight-coordinated, surrounded only by the μ_3-oxygen atoms of the dianions.

The interatomic distances are on the whole close to those usually reported for europium dicarboxylates: Eu−O interatomic distances are between 2.28 and 2.63 Å for MIL-$51_{LT,HT}$ (Eu^{III}) and within the 2.52−2.79 Å range for MIL-52 (Eu^{II}). The only exception concerns an oxygen atom of MIL-51_{LT}, O(4), which belongs to the

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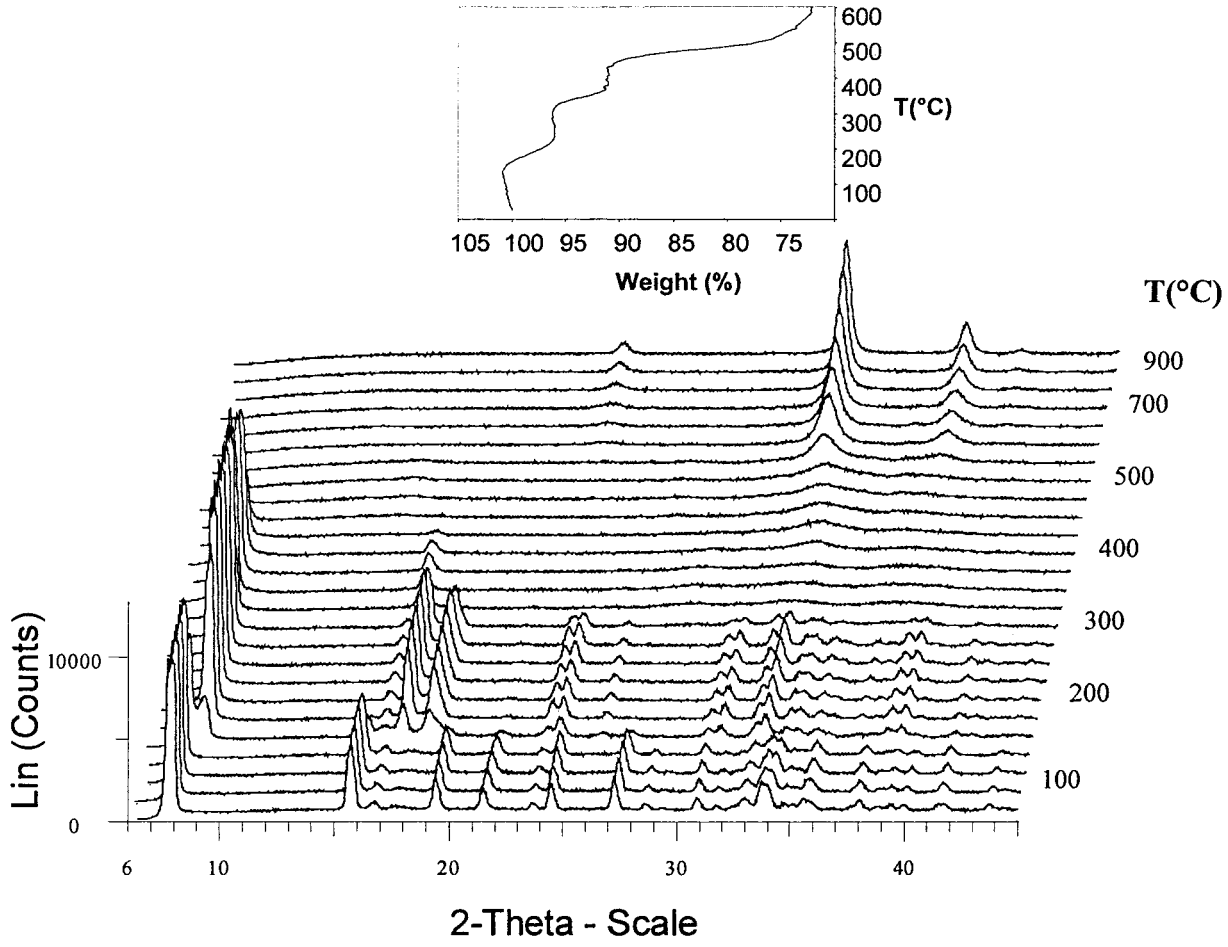

Figure 6. X-ray thermodiffractogram of MIL-51_{LT} under air atmosphere. A TGA of MIL-51_{LT} performed under air is represented as in insert at the top of the figure.

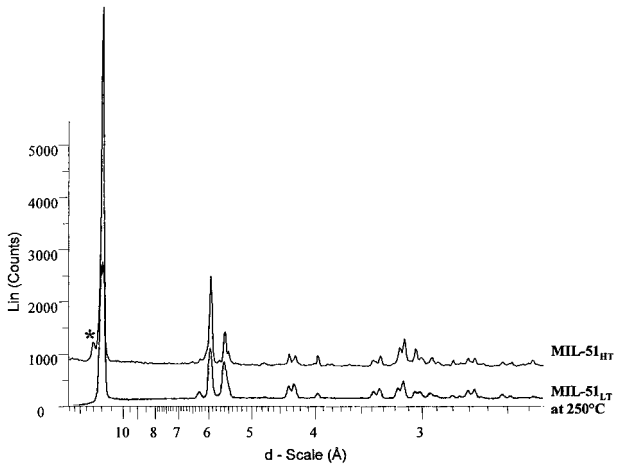

Figure 7. Comparative view of the X-ray diffraction patterns of MIL-51_{LT}, performed at 250 °C, and of MIL-51_{HT} realized at room temperature. In the latter case, MIL-51_{LT} is present as an impurity, and its strongest diffraction peak is denoted with an asterisk on the pattern.

monodendate dicarboxylate and is bonded to the europium atoms; a Eu−O distance of 2.85 Å is observed, indicating that terephthalate anions are weakly bonded to the europium atoms. The water molecule of MIL-51_{LT} (O(1)) interacts strongly with the free −C−O− group of the dicarboxylate (d(O(1)−O(4)) = 2.77 Å), and this might explain the absence of the infrared band at 1700 cm^{-1} (Figure 5), characteristic of a free C−O group. Besides, C−O and C−C distances are, in both cases, usual, within the ranges 1.23−1.28 and 1.32−1.51 Å, respectively.

Finally, the steric hindrance of the benzyl groups of the dicarboxylate leaves no porosity even if small elongated hydrophobic channels exist for MIL-$51_{LT,HT}$.

Thermal Study of MIL-51_{LT} and Comparison with MIL-51_{HT}. Since MIL-51_{LT} contains water molecules, structural changes were expected for this compound. An X-ray thermodiffractometry experiment was performed under air atmosphere between room temperature and 900 °C (1173 K).

As shown in Figure 6, MIL-51_{LT} is stable up to 400 °C and three major structural changes occur respectively at 150, 350, and 450 °C. These changes, which are in agreement with TGA results (see insert in Figure 6), are attributed to the departure of water molecules (150 °C), the loss of half the hydroxyl groups (350 °C), and the departure of the organic diacid, respectively. This corresponds to the following scheme:

$$Eu_2(H_2O)_2(OH)_4(O_2C{-}C_6H_4{-}CO_2) \xrightarrow{T = 150\ °C,\ -2H_2O} Eu_2(OH)_4(O_2C{-}C_6H_4{-}CO_2) \quad (1)$$

$$Eu_2(OH)_4(O_2C{-}C_6H_4{-}CO_2) \xrightarrow{T = 350\ °C,\ -2H_2O} Eu_2O_2(O_2C{-}C_6H_4{-}CO_2) \quad (2)$$

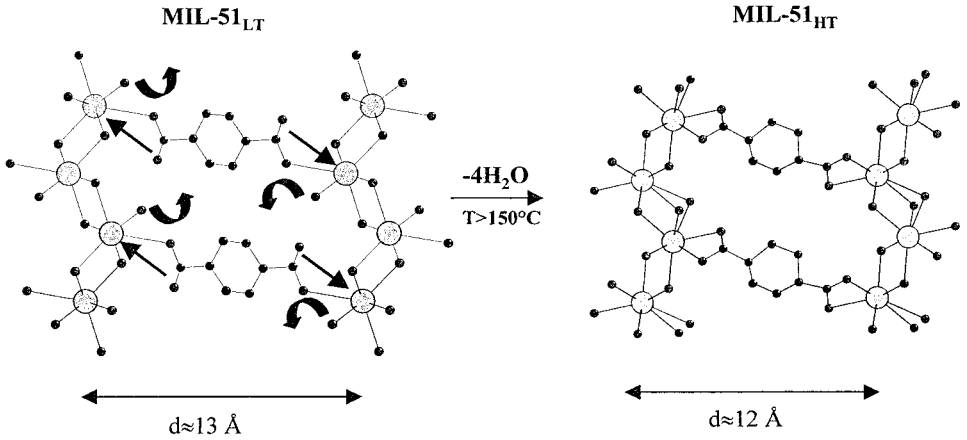

Figure 8. Schematic representation of the dehydration under air of MIL-51_{LT} and its transformation into MIL-51_{HT}.

$$Eu_2O_2(O_2C{-}C_6H_4{-}CO_2) \xrightarrow{\substack{T > 400\ °C,\\ -(O_2C{-}C_6H_4{-}CO_2) + 0.5O_2}} \text{amorphous } Eu_2O_3 \quad (3)$$

$$\text{amorphous } Eu_2O_3 \xrightarrow{T > 500\ °C} \text{cristallized } Eu_2O_3 \quad (4)$$

The crystallinity of MIL-51_{LT} is kept after the first structural change (1) despite a decrease in *d* spacing, from 13 to 12 Å, approximately. Interestingly, the pattern of dehydrated MIL-51_{LT} corresponds exactly to those of MIL-51_{HT} (Figure 7). Thus, the departure of the water molecules from MIL-51_{LT} is followed by the connection of the free −C−O− groups to the inorganic sheets to form MIL-51_{HT} (see scheme in Figure 8). This structural change is not reversible. The second phase transition, (2), occurring at 350 °C, leads to a poorly crystallized solid; however, since both intensity and position of the first peak remain unchanged, it suggests that the framework of MIL-51_{LT} is on the whole kept. Above 400 °C, the departure of the organic diacid, (3), leads to a amorphous powder which crystallizes at higher temperature, (4), into europium oxide Eu_2O_3.[19]

Finally, MIL-51_{LT} and MIL-51_{HT} exhibit the same structural type: layers of europium hydroxide related with terephthalate dianions but with two different ways of connection of the carboxylate groups: a weakly monodendate, MIL-51_{LT}, or a strongly bidendate, MIL-51_{HT}, bonded dicarboxylate. The denser form, MIL-51_{HT}, can be obtained using two different synthetic ways: either through direct synthesis by increasing the synthetic temperature above 220 °C or by heating under air at 200 °C MIL-51_{LT}, synthesized at lower temperatures (T < 220 °C).

4. Conclusion and Outlooks

The study of the europium−terephthalic acid systems under hydrothermal conditions led only to new pillared structures, made from di- or trivalent europium, which do not exhibit a significant porosity. The two europium(III) structures are topologically equivalent, MIL-51_{LT} being hydrated with monodendate dicarboxylic bridges and MIL-51_{HT}, the denser dehydrated form with bidendate diacids. This latter can be obtained either by changing the synthesis temperature or by dehydration under air of MIL-51_{LT}.

Since the previous use of linear dicarboxylate led to microporous solids built-up from 1D inorganic lanthanide chains related with organic diacids,[7] the formation of pillared solids using terephthalate anions might come from the stabilizing $\pi-\pi$ effect favoring the stacking of the phenyl groups. This was observed previously with transition metals (Co, Zn) where similar structures built-up from layers of metal hydroxide pillared by terephthalate anions were obtained.[21] Finally, even if our europium dicarboxylates exhibit no porosity, the presence of π electrons might however lead to interesting optical or magnetic properties. Such studies are currently in progress, and first results will be soon reported.

Acknowledgment. The authors gratefully acknowledge Dr. André Leclaire of CRISMAT, ISMRA, CNRS URA 1318, Université de Caen, Caen Cedex, France, for collecting the X-ray data of MIL-51_{HT}.

Supporting Information Available: Tables listing crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for MIL-51_{HT} and MIL-52 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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