

# Hydrothermal synthesis, thermal behaviour and structure determination from powder data of a porous three-dimensional europium trimesate: $\text{Eu}_3(\text{H}_2\text{O})(\text{OH})_6[\text{C}_6\text{H}_3(\text{CO}_2)_3]\cdot 3\text{H}_2\text{O}$ or MIL-63

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Received 18th April 2002, Accepted 29th July 2002

First published as an Advance Article on the web 29th August 2002

A new three-dimensional microporous europium carboxylate has been obtained under hydrothermal conditions using trimesic acid and its structure solved from X-ray powder diffraction data. MIL-63 or  $\text{Eu}_3(\text{H}_2\text{O})(\text{OH})_6[\text{C}_6\text{H}_3(\text{CO}_2)_3]\cdot 3\text{H}_2\text{O}$  crystallises in monoclinic symmetry with  $a = 17.640(1)$ ,  $b = 3.689(2)$ ,  $c = 12.385(1)$  Å,  $\beta = 91.245(1)^\circ$ ,  $V = 805.74(4)$  Å<sup>3</sup>, space group  $P2_1$  ( $n^\circ 4$ ). Its structure is built up from nine-coordinate monocapped square antiprism europium polyhedra and trimesate anions, creating pillared structures. The inorganic layers of MIL-63 are similar to those of europium hydroxide, but with a periodic oscillation that leaves within the interlayer space two types of pores along the  $b$  axis that contain both free and bound water molecules. The thermal behaviour of MIL-63 has been investigated using TGA and X-ray thermodiffraction, and indicates that MIL-63 is stable up to 723 K and exhibits zeolitic behaviour.

## Introduction

The synthesis of hybrid inorganic–organic porous solids continues to be a very active area of research<sup>1–4</sup> because of the wide range of their potential applications in catalysis, shape-selective absorption, non-linear optical (NLO) devices or molecular-based magnetism. The association of modulable functionalised organic moieties (*i.e.* moieties that can be tailored to give new topologies or structures by changing the organic spacer between the complexing groups linked to it, *e.g.* carboxylic, phosphonic or sulfonic groups) with transition or rare-earth metals allows the creation of a large number of porous solids with original pore shape and dimensions, and sometimes, unique physical properties.<sup>5</sup> In such structures, organic species can act either as pillars, linkers associated with inorganic layers, chains or clusters of transition or rare earth metals.

In the field of rare earth hybrid solids, our group reported recently diphosphonates,<sup>6</sup> carboxyphosphonates<sup>7</sup> and dicarboxylates.<sup>8,9</sup> While the use of the first two series led only to pillared structures, linear dicarboxylic acids provided microporous compounds incorporating a 1-D inorganic network. Using rigid unsaturated carboxylic acids, several groups also characterised three-dimensional solids,<sup>10–18</sup> however, these solids are coordination polymers with isolated, or clusters of rare earth polyhedra connected through dicarboxylic acids. Wang *et al.* also reported a porous lanthanide coordination polymer using a saturated tricarboxylic acid.<sup>19</sup> Using other organic linkers such as bipyridine dioxide, Schröder *et al.* characterised a porous lanthanide coordination polymer with an unusual topology.<sup>20</sup> Finally, an alternative approach was recently developed using lanthanide cubane-like clusters as precursors to porous hybrid solids.<sup>21</sup>

We recently undertook a global study of the europium system in water using rigid carboxylic acids. This led to the first three-dimensional lanthanide terephthalates that exhibit a two-dimensional inorganic network: MIL-51 and MIL-52.<sup>22</sup> This paper deals with the synthesis, crystal structure and thermal behaviour of a new porous three-dimensional europium(III) carboxylate obtained using trimesic acid: MIL-63 or  $\text{Eu}_3(\text{H}_2\text{O})(\text{OH})_6[\text{C}_6\text{H}_3(\text{CO}_2)_3]\cdot 3\text{H}_2\text{O}$ .

## Experimental

### Synthesis and chemical analysis

MIL-63 was hydrothermally synthesised (autogenous pressure for 5 days) at 443 K from a mixture of europium nitrate  $\text{Eu}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  (Aldrich, 98%), trimesic acid [ $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$ ; Alfa, 98%], sodium hydroxide (Prolabo, 99%) and  $\text{H}_2\text{O}$  in the molar ratio 1:0.33:2.75:400. Reactants were introduced in this order and stirred for a few minutes before the resulting suspensions were introduced into a Teflon-lined steel autoclave. The final pH evolved from 8 to 6, which led to a white crystalline powder on which chemical analyses were performed. All attempts to obtain crystals of MIL-63 failed.

Quantitative elemental analyses indicated C/Eu and H/Eu ratios equal to 3.02 and 5.06, respectively, which are in agreement with the theoretical values deduced from the structure, 3 and 5. The density measurement, performed on a Micromeritics Accupyc 1330 apparatus, gave a value of  $3.68(4)$  g.cm<sup>-3</sup> (calcd: 3.42).

A TGA experiment on MIL-63, performed under air atmosphere using a TA-Instrument type 2050 analyser apparatus, revealed several weight losses in the 273–873 K range. The residual solid was identified as europium oxide  $\text{Eu}_2\text{O}_3$ . MIL-63 exhibits five weight losses of 4.3%, 2.2, 2.2, 6.2 and 19% at 373, 423, 523, 623 and 673 K, corresponding, respectively, to the departure of free water (in two steps), bound 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. These losses are in agreement with the theoretical values (4.35, 2.17, 2.17, 6.16 and 22.1%). These results will be discussed in detail in the Results and discussion section.

The infrared spectrum of the title compound clearly shows the presence of the vibrational bands characteristic of the  $-(\text{O}-\text{C}-\text{O})-$  groups around 1550 and 1430 cm<sup>-1</sup>, confirming the presence of the carboxylate within the solids. Bands around 3500 cm<sup>-1</sup> also confirm the presence of OH and/or  $\text{H}_2\text{O}$  groups in MIL-63.

X-Ray thermodiffraction, performed in the furnace of a

Siemens D-5000 diffractometer in the  $\theta$ - $\theta$  mode, shows several steps in the decomposition for MIL-63 (see below).

Finally, these analyses are, on the whole, in agreement with the results deduced from the structure determination of MIL-63,  $\text{Eu}_3(\text{H}_2\text{O})(\text{OH})_6[\text{C}_6\text{H}_3(\text{CO}_2)_3]\cdot 3\text{H}_2\text{O}$ .

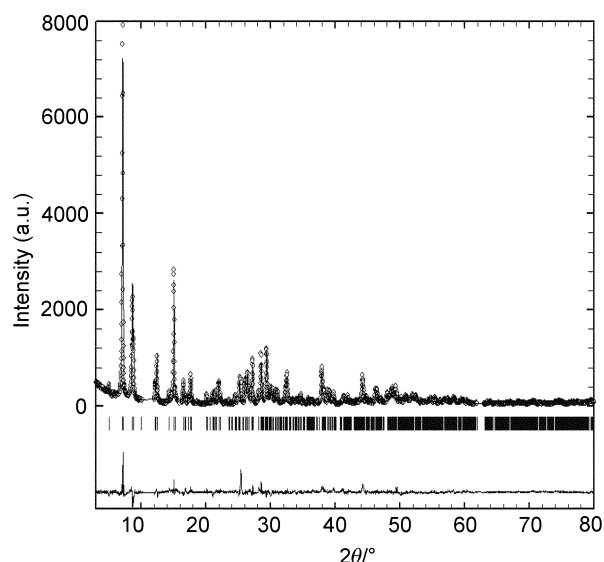
### Structure determination

Single crystals could not be obtained, even by increasing the synthesis time and synthesis temperature, or by varying the stoichiometry. To minimise the preferred orientation effect on the XRD pattern of MIL-63, the powder was mounted in a top-loaded Mac Murdie-type sample holder. The powder diffraction pattern of MIL-63 was collected on a D5000 ( $\theta$ - $2\theta$  mode) Siemens diffractometer with  $\lambda_{\text{Cu}}(\text{K}\alpha_1, \text{K}\alpha_2) = 1.54059, 1.54439$  Å. Its pattern was indexed with the DICVOLGV program.<sup>23</sup> A monoclinic solution with adequate figures of merit was found [ $M_{20}, F_{20} = 35, 90$  (0.007, 38)]. Systematic absences were consistent with the space group  $P2_1$  or  $P2_1/m$  ( $n^\circ 4$ ).

The pattern matching was performed with Fullprof2k using the WinPLOT package.<sup>24,25</sup> Structure determination was performed using the EXPO package, which combines a full pattern decomposition program (EXTRA) and a direct method program (SIR97) optimised for powder diffraction data.<sup>26</sup> The europium atoms and most of the oxygen and carbon atoms were found using the direct method and a Fourier difference was performed, *via* the SHELXTL94 program,<sup>27</sup> to locate the missing atoms. The structure of MIL-63 was also refined using Fullprof. Forty-nine experimental points were used to adjust the background, with a Pseudo-Voigt function to determine the peak profile. Two asymmetry parameters, two thermal parameters, one for the heavy (Eu) and one for the light atoms (O, C), and a preferred orientation correction parameter were also applied during refinements. The preferred orientation vector was chosen as the direction parallel to the pores. Distance and angle constraints were used during the refinement, especially to refine the trimesate anion as a rigid body. As the origin in the space group  $P2_1$  is along the screw axis, the origin of the  $y$  value was set by fixing the  $y$  coordinates of the heavy atoms. Three excluded areas were used to remove the two most intense reflections of an impurity present in small amounts, and a reflection of the sample holder. This impurity can be isolated pure using different synthesis conditions, and analyses (IR, TGA, elemental analysis) show that this solid is another europium trimesate. Details of the structure determination are summarised in Table 1.

**Table 1** Crystal data and structure refinement parameters for MIL-63

Formula	$\text{Eu}_3\text{O}_{16}\text{C}_9\text{H}_{17}$
Formula weight/g mol <sup>-1</sup>	828.5
Calculated density/g cm <sup>-3</sup>	3.42
Crystal system	Monoclinic
Space group	$P2_1$
$a/\text{Å}$	17.640(1)
$b/\text{Å}$	3.689(2)
$c/\text{Å}$	12.385(1)
$\beta/^\circ$	91.247(4)
$V/\text{Å}^3$	805.74(2)
$Z$	2
Figures of merit	$M_{20} = 35; F_{20} = 90$
$2\theta$ range/ $^\circ$	3–80
Excluded areas/ $^\circ$	10.2–12; 15.9–16.3; 62–63
Reflections	665
Atoms	28
Intensity-dependent parameters	83
Profile parameters	13
$R_p$	0.101
$R_{wp}$	0.141
$R_B$	0.099
$R_F$	0.089



**Fig. 1** Final Rietveld plot of MIL-63.

The final agreement factors are satisfactory:  $R_p = 10.1$ ,  $R_{wp} = 14.1$  and  $R_{Bragg} = 9.9\%$ . The final Rietveld plot is reported in Fig. 1. Atomic coordinates are given in Table 2, while the principal bond distances are reported in Table 3.

### Results and discussion

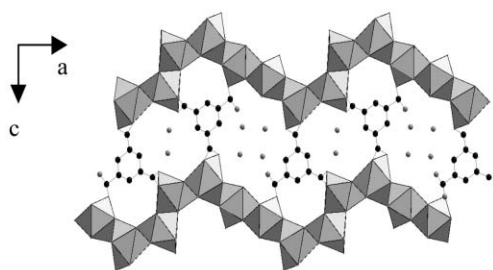
MIL-63 exhibits a three-dimensional structure built up from nine-coordinate europium(III) monocapped square antiprisms polyhedra and trimesate ions. As in the case of the previously reported terephthalate europium solids, MIL-51 and MIL-52, these structures are made from two-dimensional europium inorganic networks connected together *via* organic acids, creating pillared frameworks (Fig. 2). However, within two consecutive layers, the trimesic acids alternatively connect the inorganic layers twice and once; this creates two kinds of

**Table 2** Atomic coordinates for MIL-63

Atom	$x$	$y$	$z$
Eu(1)	0.0949(3)	0.25	0.5515(5)
Eu(2)	0.2673(3)	-0.25	0.7095(4)
Eu(3)	0.4592(3)	0.25	0.6312(4)
O(1)	-0.048(2)	0.265(10)	-0.446(3)
O(2)	0.404(2)	-0.250(10)	0.719(3)
O(3)	0.171(2)	0.245(10)	-0.284(3)
O(4)	0.187(2)	-0.235(12)	0.544(3)
O(5)	0.315(2)	0.245(10)	0.606(3)
O(6)	0.543(1)	-0.305(7)	0.701(3)
O(7)	0.051(3)	-0.240(18)	0.678(4)
O(8)	0.206(2)	0.810(12)	0.925(2)
O(9)	0.151(1)	0.340(11)	0.391(1)
O(10)	0.553(2)	0.220(8)	0.779(3)
O(11)	0.439(2)	-0.250(13)	0.504(3)
O(12)	0.286(2)	0.205(9)	0.870(1)
O(13)	-0.088(2)	0.895(14)	-0.240(2)
Ow(1)	0.076(3)	0.470(17)	-0.088(5)
Ow(2)	-0.059(3)	0.465(18)	-0.087(5)
Ow(3)	0.504(3)	-0.325(24)	-0.089(3)
C(1)	0.274(1)	0.360(17)	0.282(2)
C(2)	0.588(1)	-0.045(6)	0.733(2)
C(3)	0.138(1)	0.230(10)	0.303(2)
C(4)	0.274(1)	0.170(9)	0.059(1)
C(5)	0.337(2)	0.270(16)	0.114(1)
C(6)	0.205(1)	0.130(17)	0.130(2)
C(7)	0.213(1)	0.146(7)	0.241(1)
C(8)	0.336(1)	0.415(9)	0.219(1)
C(9)	0.262(2)	0.020(13)	-0.041(1)

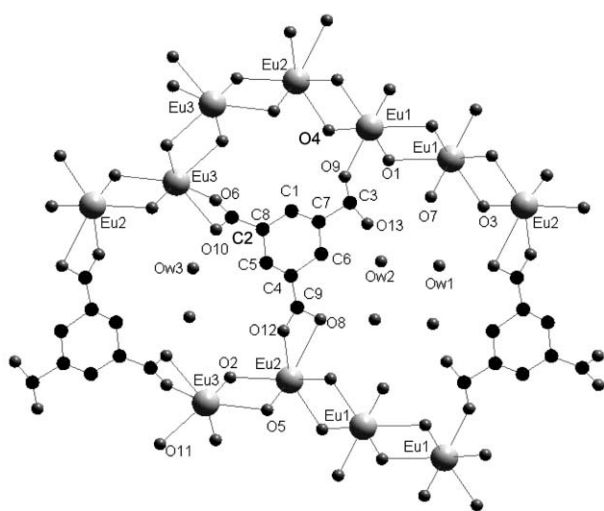
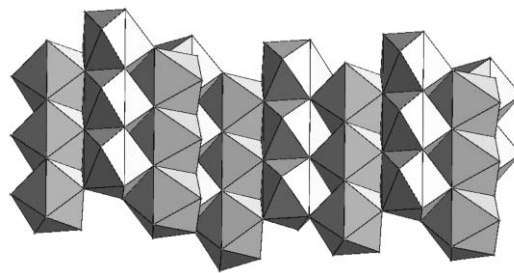
**Table 3** Principal bond lengths (Å) for MIL-63

Eu(1)–O(1)	2.35(3)	Eu(1)–O(1)	2.52(4)
Eu(1)–O(1)	2.45(4)	Eu(1)–O(3)	2.41(3)
Eu(1)–O(4)	2.42(4)	Eu(1)–O(4)	2.50(4)
Eu(1)–O(7)	2.53(5)	Eu(1)–O(7)	2.58(6)
Eu(1)–O(9)	2.26(6)		
Eu(2)–O(2)	2.41(3)	Eu(2)–O(3)	2.52(4)
Eu(2)–O(3)	2.49(4)	Eu(2)–O(4)	2.46(4)
Eu(2)–O(5)	2.42(4)	Eu(2)–O(5)	2.39(4)
Eu(2)–O(8)	2.90(4)	Eu(2)–O(12)	2.84(3)
Eu(2)–O(12)	2.62(3)		
Eu(3)–O(2)	2.36(4)	Eu(3)–O(2)	2.37(4)
Eu(3)–O(5)	2.55(4)	Eu(3)–O(6)	2.65(3)
Eu(3)–O(6)	2.37(3)	Eu(3)–O(10)	2.44(4)
Eu(3)–O(11)	2.44(4)	Eu(3)–O(11)	2.45(4)
Eu(3)–O(11)	2.49(4)		
C(2)–O(6)	1.29(4)	C(2)–O(10)	1.30(4)
C(3)–O(9)	1.18(3)	C(3)–O(13)	1.32(4)
C(9)–O(8)	1.33(5)	C(9)–O(12)	1.36(4)
C(1)–C(7)	1.42(4)	C(1)–C(8)	1.37(2)
C(2)–C(8)	1.46(2)	C(3)–C(7)	1.58(2)
C(4)–C(5)	1.34(2)	C(4)–C(6)	1.52(3)
C(4)–C(9)	1.37(2)	C(5)–C(8)	1.41(2)
C(6)–C(7)	1.38(2)		
Ow(1)–O(8)	2.62(7)	Ow(2)–O(13)	2.52(7)
Ow(3)–O(6)	2.71(6)	Ow(3)–O(10)	2.51(7)
Ow(3)–O(10)	2.75(8)		

**Fig. 2** Polyhedral representation of the structure of MIL-63 along the *b* axis. Carbon atoms, oxygen atoms and water molecules are represented as black and grey circles, respectively.

channels along the *b* axis with two and four water molecules per channel, respectively (Fig. 2 and 3).

Two of the three europium atoms of MIL-63 [Eu(2) and Eu(3)] are surrounded by seven  $\mu_3$ -OH and two oxygen atoms of the dicarboxylate (Fig. 3); the third europium atom [Eu(1)]

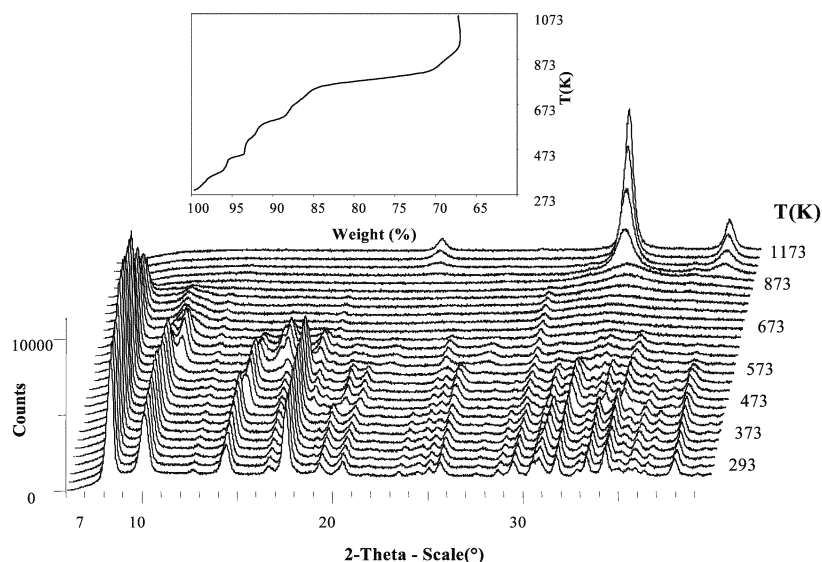
**Fig. 3** Ball and stick representation of MIL-63 along the *b* axis; some atom labels have been added for clarity.**Fig. 4** Polyhedral representation of an inorganic layer of MIL-63.

exhibits almost the same environment, but the carboxylate group of the trimesate close to this europium atom is monodentate; this europium atom completes its coordination with a  $\mu_2$ -O water molecule [O(7)]. This phenomenon was previously observed with MIL-51<sub>LT</sub>. Bond valence calculation gives a value of about +0.6 for this oxygen atom, which is correct for a water molecule. The interatomic distances are very well defined for a structure based on laboratory powder diffraction data: Eu–O distances are within the usual 2.35–2.80 Å range, while the C–C and C–O distances lie within the 1.18–1.54 Å range.

The inorganic layers are built up from chains of europium polyhedra, which are made from face-sharing europium polyhedra linked through  $\mu_3$ -hydroxyl groups or oxygen atoms from dicarboxylates (Fig. 4).

As in the case of europium terephthalate MIL-51, the inorganic sheets are related to those of europium hydroxide, Eu(OH)<sub>3</sub>; the cell parameters of the inorganic layers of MIL-63 and those of Eu(OH)<sub>3</sub> ( $a = 6.352$ ,  $c = 3.653$ , space group  $P6_3/m$ )<sup>28</sup> are related:  $(a_1 \sin \alpha_1)/3 \approx b_2$  and  $b_1 \approx c_2$  [1: MIL-63, 2: Eu(OH)<sub>3</sub>]. The *a* parameter is tripled in case of MIL-63 because of the constraints imposed by the mode of connection of the three carboxylate groups to the layers (Fig. 2 and 3); this creates a periodic oscillation of the inorganic sheets and a tripling of the periodicity along the *a* axis. Bond valence calculation for MIL-63 are in agreement with the presence of hydroxyl groups in these structures, since values within the 1–1.4 range are obtained for these oxygen atoms. The non-centrosymmetry of MIL-63 comes from the position of the –CO<sub>2</sub> groups and the free water molecules. If the benzene ring lies almost within the (010) plane, the –CO<sub>2</sub> groups rotate along their corresponding –C–C– axis and are not located within or perpendicular to the (010) plane. The free water molecules, which interact with the carboxylate groups, are also not located in the (010) plane. This rules out the existence of any mirror plane perpendicular to the screw axis. The free oxygen [O(13)] of the monodentate trimesic acid points alternatively up and down the (010) plane and the water molecules, Ow(1) and Ow(2), are located alternatively above or below this terminal oxygen (Fig. 3). These water molecules interact through hydrogen bonds with oxygens of the framework (see Table 3): the bound water molecule and the free oxygen of the carboxylate group [O(13)]. The interaction between Ow(2) and O(13) is particularly strong  $\{d[\text{Ow}(2)\text{--O}(13)] = 2.52 \text{ \AA}\}$ , which probably explains why the departure of the free water occurs in two steps (see TGA results in Experimental section): Ow(1) and Ow(3) below 373 K and Ow(2) around 423 K.

The thermal stability of MIL-63 has been studied using TGA and X-ray thermodiffraction. The TGA measurements, performed between 293 and 1273 K under oxygen atmosphere, showed several weight losses in the whole temperature range, corresponding to the departure of the free water, the bound water, half of the hydroxyl groups and the organic acid (see Experimental section). The X-ray thermodiffraction under air atmosphere of MIL-63 (Fig. 5), indicates that MIL-63 is stable up to 723 K and that several structural changes occur, in agreement with the TGA results.



**Fig. 5** X-Ray thermodiffractograms of MIL-63 under air atmosphere. For greater clarity, a  $2\theta$  offset has been applied. The TGA under air of MIL-63 is shown in the inset at the top of the figure.

First, the departure of the free water leads to a slight phase transition below 473 K; the loss of bound water leads to a more significant structural change between 523 and 573 K, as indicated by the shift at higher angles of most of the reflections. At higher temperatures, the departure of some of the hydroxyl groups leads to an additional phase transition, together with an important decrease in crystallinity but as the intensity of the first reflection is maintained, the framework is probably retained for the most part. Finally, the destruction of the framework occurs at 773 K, producing an amorphous solid which crystallises into europium(III) oxide at higher temperatures.

The reversibility of the dehydration of MIL-63 has been studied using X-ray thermodiffractometry. This showed that the departure of the free and bound water molecules is reversible with no loss of crystallinity (Fig. 6).

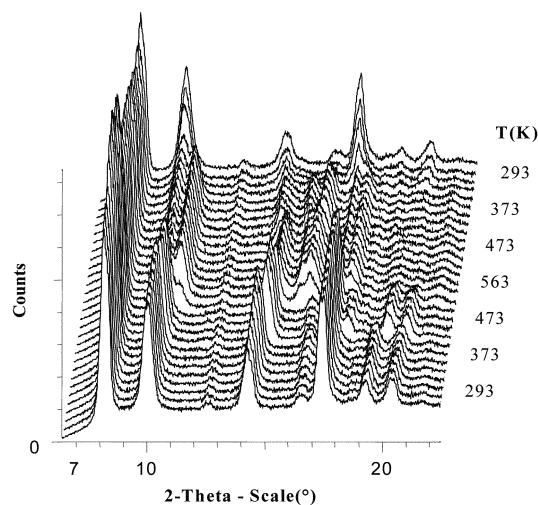
The reversibility of the departure of the bound water indicates that, unlike in the case of the terephthalate solid MIL-51, no irreversible connection of the free oxygen atom of the carboxylic acid to the layers occurs when the water molecules leave the structure. This is probably due to the topological constraints created by the mode of connection of the rigid tricarboxylate to the inorganic sheets; the carboxylate functions connect alternately twice and once the upper and lower

layers, unlike MIL-51; relating the free oxygen [O(13)] of the monodendate carboxylate group to the layers is thus more difficult since the trimesic acid is strongly bound to the framework by three carboxylate groups instead of two. Finally, the porosity of MIL-63 can be estimated through the interatomic distances between atoms delimiting the pores taking into account their van der Waals radii. This gives estimated  $3.1 \times 4$  and  $4 \times 5.6 \text{ \AA}^2$  free apertures for the two types of pores present in MIL-63. However, a BET nitrogen adsorption measurement performed on the solid dehydrated at 523 K revealed a low surface area ( $\approx 15 \text{ m}^2 \text{ g}^{-1}$ ) probably because of pore contraction occurring upon dehydration.

In conclusion, MIL-63 is the first example of a porous three-dimensional europium carboxylate characterised up to now that exhibits both a two-dimensional inorganic framework, zeolitic behaviour and high thermal stability. Other similar compounds are currently under study to enlarge the field of microporous hybrid phases based on rare earth metals.

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**Fig. 6** X-Ray thermodiffractograms under air atmosphere of MIL-63 heated from 293 to 563 K, and then cooled back down to 293 K.

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