Hybrid Organic−Inorganic Frameworks (MIL-*n*). Hydrothermal Synthesis of a Series of Pillared Lanthanide Carboxyethylphosphonates and X-ray Powder ab Initio Structure Determination of MIL-19, $Pr[O_3P(CH_2)_2CO_2]$

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A series of lanthanide and yttrium carboxyethylphosphonates has been hydrothermally prepared (200 °C, 4 days) from the 1:1 mixture of carboxyethylphosphonic acid and the metal chlorides. The crystal structure of the praesodymium compound $Pr^{III}[O_3P(CH_2)_2CO_2]$ has been determined ab initio from X-ray powder diffraction data and refined by the Rietveld method. The compound crystallizes in the monoclinic space group $P2_1/m$ (No. 11) with cell parameters at 20 °C $a = 8.3617(2)$ Å, $b = 7.1899(2)$ Å, $c = 5.4586(2)$ Å, $\beta = 103.784(2)°$, and $Z = 2$. The final agreement factors converged to the values $R_p = 0.139$, $R_{wp} = 0.177$, Bragg $R = 0.123$, $R_F = 0.055$, and $\chi^2 = 3.50$. The hybrid framework consists of inorganic Pr/O/P/C layers connected by organic groups, with an interlayer spacing of ~8.36 Å. The praesodymium atoms are 7-fold coordinated in this pillared layered structure. Isostructural compounds were prepared for yttrium and the entire series of the lanthanide elements.

Introduction

For the last six years, our work was dedicated to the synthesis and the structural characterization of new series of fluorinated microporous gallophosphates labeled ULM-*n* ($n \leq 19$).[1] The total substitution of Ga by Fe or V induced new structural types, and we showed for the first time the hitherto unknown magnetic microporous iron and vanadium phosphates.[2] The extension of this idea to microporous rare-earth phosphates failed due to the strong affinity of phosphate and fluoride anions toward lanthanide elements which, whatever the chemical conditions, led to the formation of monazite type phosphates $LnPO_4$ and fluoride LnF_3.

The preparation of lanthanide compounds with an open framework required use of other chelating agents which prevent the formation of dense, insoluble inorganic species. Since the pioneering work of Alberti, Dines, and Clearfield, it is well-known that organic species such as phosphonates react with inorganic compounds.[3] Most of the papers cited in the literature concern nonfunctionalized monophosphonates with the aim of synthesizing layered compounds,[4] but some attempts with diphosphonates[5] or functionalized monophosphonates[6] led to a few three-dimensional compounds. We have already hydrothermally synthesized and determined ab initio the structure of lanthanide and yttrium propylene-, ethylene-, and methylene-diphosphonates with general formula $LnH[O_3P(CH_2)_nPO_3]$ ($n = 1-3$), which all present a pillared layered structure.[7] More recently, we have prepared a new series of lanthanide dicarboxylates $[Ln(H_2O)]_2[O_2C(CH_2)_2CO_2]_3 \cdot H_2O$ and $[Ln(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$ which present an open hybrid organic−inorganic framework with weakly bonded water molecules in the tunnels.[8] We present here a new series of compounds $Ln[O_3P(CH_2)_2CO_2]$ which are structurally close to the lanthanide diphosphonates.

Experimental Section

Preparation of Lanthanide and Yttrium Carboxyethylphosphonates. $LnCl_3 \cdot xH_2O$ ($x = 6$ or 7) (Aldrich 99.9%) and 2-carboxyethylphosphonic acid (Aldrich 94%) were used as received with no further

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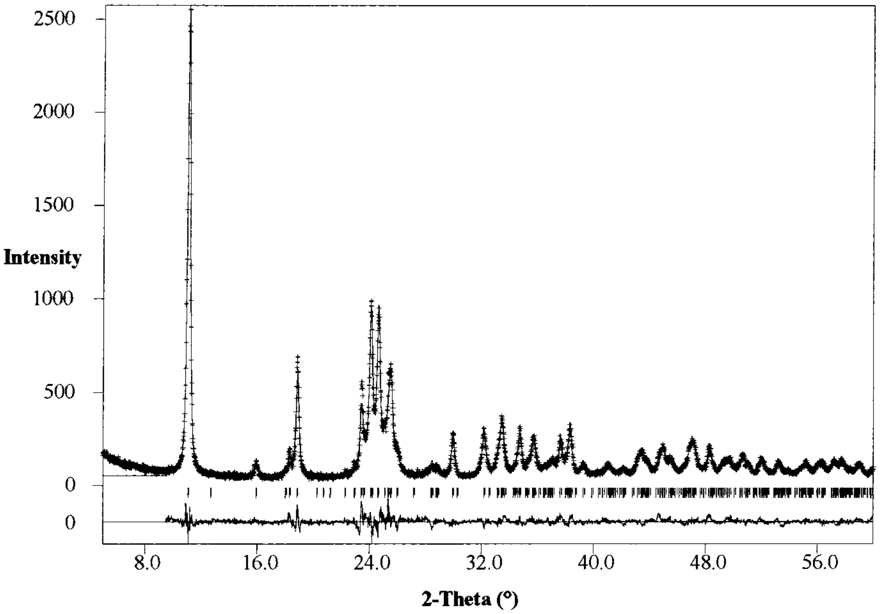

Figure 1. Observed, calculated, and difference Rietveld diagrams for $Pr[O_3P(CH_2)_2CO_2]$.

Table 1. Crystallographic Data for $Pr[O_3P(CH_2)_2CO_2]$

formula weight (g)	291.94
crystallographic system	monoclinic
space group	$P2_1/m$ (No. 11)
a (Å)	8.3617(2)
b (Å)	7.1899(2)
c (Å)	5.4586(2)
β (deg)	103.784(2)
V (Å^3)	318.72(1)
Z	2
$d_{calculated}$ (g cm^{-3})	3.02
λ (Cu Kα_1, Kα_2) (Å)	1.5406/1.5444
T (°C)	room temperature
no. of reflections	1030
no. of fitted parameters	34
R_p[a]	13.9
R_{wp}[a]	17.7
Bragg R[a]	12.3
R_F[a]	5.5
χ^2 [a]	3.5

[a] See ref 11 for definitions.

Table 2. Positional Parameters for $Pr[O_3P(CH_2)_2CO_2]$

atom	x	y	z	occupancy factor
Pr	0.4238(2)	$^1/_4$	0.8345(5)	$^1/_2$
P	0.6718(9)	$^1/_4$	0.376(2)	$^1/_2$
O1	0.6416(7)	$^1/_4$	0.638(4)	$^1/_2$
O2	0.602(1)	0.087(2)	0.209(2)	
O3	0.174(2)	$^1/_4$	0.006(4)	$^1/_2$
O4	0.227(2)	$^1/_4$	0.429(4)	$^1/_2$
C1	0.917(2)	$^1/_4$	0.452(6)	$^1/_2$
C2	−0.060(2)	$^1/_4$	0.176(6)	$^1/_2$
C3	0.121(3)	$^1/_4$	0.231(6)	$^1/_2$

purification. The starting mixture, with molar ratio 1 $LnCl_3 \cdot xH_2O$:1 $H_2O_3P(CH_2)_2CO_2H$:y base:100 H_2O, was placed in a Teflon-lined stainless steel autoclave and heated at 200 °C for 4 days. The carboxyethylphosphonic acid presents three different acidities: two phosphonic acidities and one carboxylic acidity, with respective pK_a values of 2.2, 4.6, and 7.7.[9] The base (1,3-diaminopropane, NH_3 20%, or NaOH 20%) was added to adjust the initial pH at a value between 2 and 8 (final pH = 2). A green powder of the praesodymium compound was collected by filtration, washed with distilled water, and air-dried. Analoguous compounds were prepared for Y and the entire lanthanide series.

Table 3. Interatomic Distances (Å) in $Pr[O_3P(CH_2)_2CO_2]$

atom	atom	distance
Pr	O1	2.32(2)
Pr	O2[a]	2.51(1)
Pr	O2[b]	2.44(1)
Pr	O2[c]	2.51(1)
Pr	O2[d]	2.44(1)
Pr	O3[a]	2.48(2)
Pr	O4	2.42(2)
P	O1	1.51(2)
P	O2	1.51(1)
P	O2[e]	1.51(1)
P	C1	1.99(3)
C1	C2[f]	1.56(4)
C2	C3	1.47(4)
C3	O3	1.40(4)
C3	O4	1.23(4)

[a] Atom related by $x, y, z + 1$. [b] Atom related by $-x + 1, y + {}^1/_2, -z + 1$. [c] Atom related by $x, -y + {}^1/_2, z + 1$. [d] Atom related by $-x + 1, -y, -z + 1$. [e] Atom related by $x, -y + {}^1/_2, z$. [f] Atom related by $x + 1, y, z$.

X-ray Data Collection. Due to the pseudo-lamellar character of the compounds, the powder was first milled using a McCrone micronizing mill in order to reduce the size of the particles and to prevent preferred orientation. Step-scanned X-ray powder data for the sample (side-loaded into a flat McMurdie type aluminum sample holder) were realized on the finely ground sample by means of a Siemens-D5000 computer-automated diffractometer (Cu Kα, 40 kV, 30 mA). Data were collected between 5 and 60° in 2θ with a step size of 0.02° and a count time of 18 s step^{-1}. The powder pattern was indexed using DICVOL91[10] on the basis of the first 20 observed lines.

For the praesodymium compound, the best solution which indexed all the lines (figure of merit FOM = 30) indicated a monoclinic unit cell with parameters $a = 8.36(1)$ Å, $b = 7.19(1)$ Å, $c = 5.46(1)$ Å, and $\beta = 103.8(1)°$. The systematic absences ($0k0$: $k = 2n$) were consistent with the space groups $P2_1/m$ (No. 11) or $P2_1$ (No. 4). The structure was solved in the centric group.

Structure Solution and Refinement of $Pr[O_3P(CH_2)_2CO_2]$. For a better precision about the position and the intensity of the peaks, new data were collected between 7 and 60° and between 60.02° and 100° in 2θ with a step size of 0.02° and a count time of 26 and 52 s step^{-1}, respectively. Initially, background, profile and unit cell parameters were

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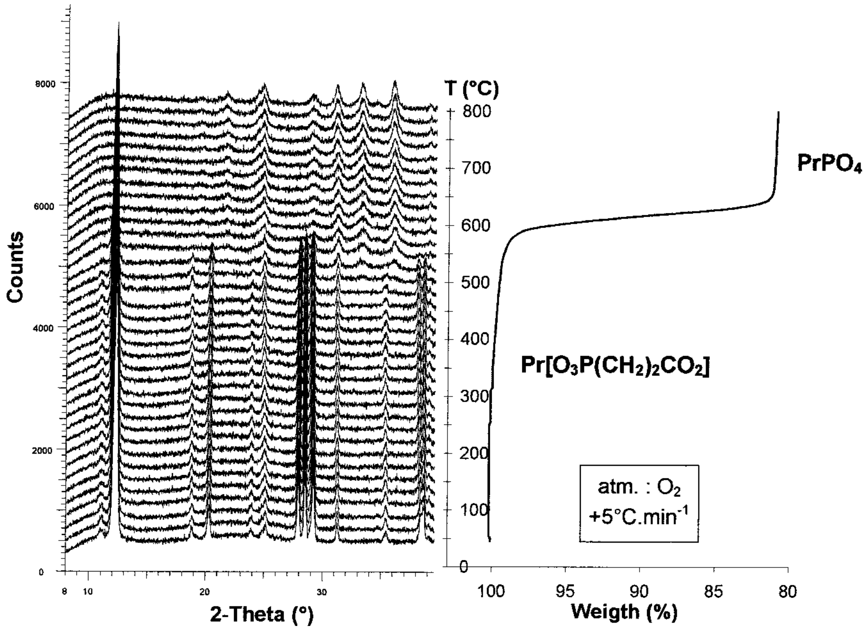

Figure 2. Thermodiffractogram (left) and TG curve (right) for Pr[$O_3P(CH_2)_2CO_2$] showing a remarkable thermal stability until 500 °C.

Table 4. Intramolecular Bond Angles (deg) in Pr[$O_3P(CH_2)_2CO_2$]

atom	atom	atom	angle
O1	Pr	O2[a]	89.9(9)
O1	Pr	O2[b]	90.8(7)
O1	Pr	O2[c]	89.9(9)
O1	Pr	O2[d]	90.8(7)
O1	Pr	O3[a]	175(1)
O1	Pr	O4	91(1)
O2[a]	Pr	O2[b]	124.2(8)
O2[a]	Pr	O2[c]	55.5(5)
O2[a]	Pr	O2[d]	68.8(6)
O2[a]	Pr	O3[a]	94.6(7)
O2[a]	Pr	O4	152(1)
O2[b]	Pr	O2[c]	68.8(6)
O2[b]	Pr	O2[d]	166.9(9)
O2[b]	Pr	O3[a]	88.6(7)
O2[b]	Pr	O4	83.5(8)
O2[c]	Pr	O2[d]	124.2(8)
O2[c]	Pr	O3[a]	94.6(8)
O2[c]	Pr	O4	152(1)
O2[d]	Pr	O3[a]	88.6(7)
O2[d]	Pr	O4	83.5(8)
O3[a]	Pr	O4	84(1)
O1	P	O2	116(2)
O1	P	O2[e]	116(2)
O1	P	C1	101(2)
O2	P	O2[e]	101(1)
O2	P	C1	111(2)
O2[e]	P	C1	111(2)
P	C1	C2[f]	99(2)
C1[f]	C2	C3	99(3)
O3	C3	O4	117(3)
O3	C3	C2	110(3)
O4	C3	C2	133(3)

[a] Atom related by $x, y, z + 1$. [b] Atom related by $-x + 1, y + {}^1/_2, -z + 1$. [c] Atom related by $x, -y + {}^1/_2, z + 1$. [d] Atom related by $-x + 1, -y, -z + 1$. [e] Atom related by $x, -y + {}^1/_2, z$. [f] Atom related by $x + 1, y, z$.

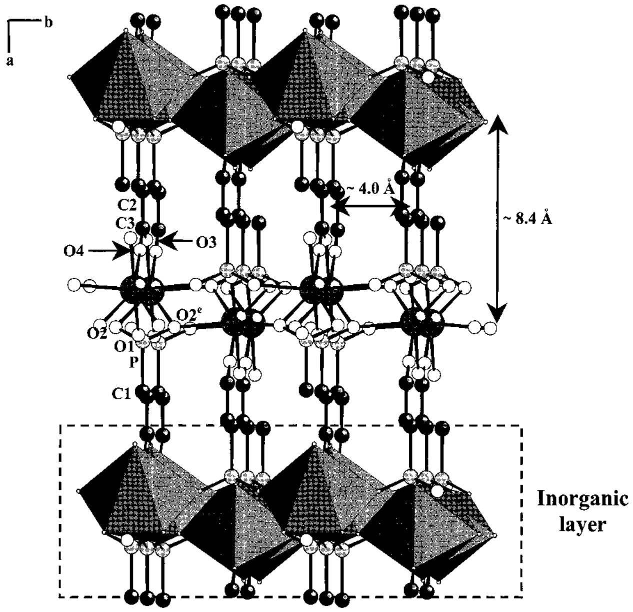

Figure 3. Mixed polyhedral and ball-and-stick projection of the pillared layered structure of Pr[$O_3P(CH_2)_2CO_2$] along the *c* axis. Large dark gray balls, Pr; small light gray balls, P; small open balls, O; small dark balls, C.

refined using the whole fitting Rietveld method in the FULLPROF program package.[11] The praesodymium atom was first located by calculation of a difference Fourier map using SHELXS program.[12] Phosphorus, oxygen and carbon atoms were then revealed by using FULLPROF and SHELXL altogether. The structure was refined with Rietveld method without any constraints and with an overall isotropic temperature factor. A correction was made for preferred orientation effect using the usual Rietveld function, with a diffraction vector along the *a** axis. A final Rietveld refinement plot is given in Figure 1.

Thermogravimetric and Thermodiffractometric Analysis. TG analysis under O_2 (heating rate = +5 °C min^{-1}) was carried out for the product. The TG curve (Figure 2) indicates that the compound is anhydrous and begins to decompose at 500 °C. This remarkable thermal stability is confirmed by thermodiffractometry (in air, heating rate = +5 °C min^{-1}) which shows that the crystalline structure of the compound is kept until ~500 °C (Figure 2). According to X-ray data, the residue (900 °C) is well-crystallized monazite type $PrPO_4$.

Structure Description and Discussion. Structure of Pr[$O_3P(CH_2)_2CO_2$]. Crystallographic data are given in Table 1, final positional parameters in Table 2, and bond lengths and angles in Tables 3 and 4, respectively. The structure shown in Figure 3 is pillared layered, as encountered in the lanthanide diphosphonates.[7] Like in the latter, both

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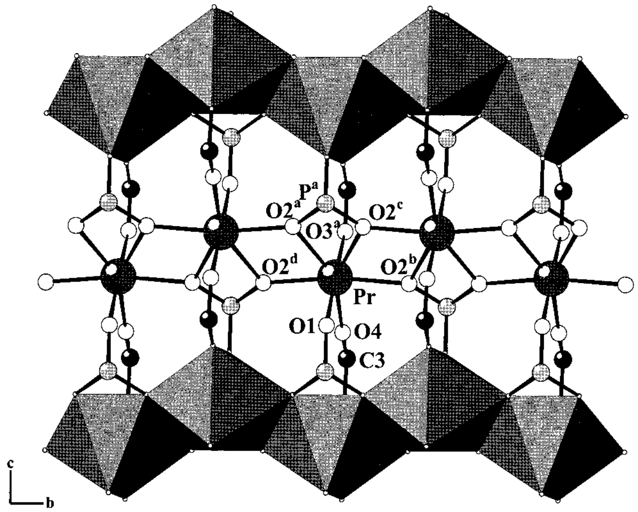

Figure 4. Mixed polyhedral and ball-and-stick representation of the layer arrangement in the structure of $Pr[O_3P(CH_2)_2CO_2]$ showing the 7-fold coordination of the praesodymium atoms. See Figure 3 for symbol key.

phosphonic and carboxylic groups participate in the formation of layers and allows them to connect. Nevertheless, due to the substitution of a phosphonic group by a carboxylic group, differences in the connection in the inorganic layer and the rare-earth environment are observed. As evidenced in Figure 4, praesodymium atoms are 7-fold coordinated (eight-fold coordination in the diphosphonates) by five oxygens from four phosphonic groups and two oxygens from carboxylic groups. Three phosphonic groups are bridging while the fourth one chelates the rare-earth atom; both carboxylic groups are purely bridging. The environment around the rare-earth atom is a pentagonal bipyramid, as shown in Figure 5. The phosphonic group chelates a praesodymium atom and shares the chelating oxygen atoms with two close praesodymium atoms (Pr−Pr = 4.09(1) Å) in order to form chains of edge-sharing rare-earth polyhedra along the [010] direction. The phosphonic group shares its third oxygen O1 with a rare-earth atom of an adjacent file in order to bridge the rows and form an inorganic layer in the (100) plane. The carboxylic group completes this linkage by sharing its O3 and O4 oxygens. The phosphonic and the carboxylic groups are opposite to each other in the layer and point out on each side of the layer. Moreover, Figure 4 shows that on both sides of the layer the carboxylic and phosphonic groups strictly alternate in the [010] direction between the rare-earth rows while just one type of acidic group is repeated in the [001] direction.

Discussion

This new series presents some common features with both the diphosphonate and dicarboxylate series: (i) the three types of structures contain edge-sharing rare-earth polyhedra chains which lead to a common unit-cell parameter roughly corresponding to twice the Ln−Ln distance in the chain (8.348(1) Å for $PrH[O_3P(CH_2)_3PO_3]$, 8.132(1) Å for $[Pr(H_2O)]_2[O_2C(CH_2)_3CO_2]_3\cdot 4H_2O$, and 7.190(1) Å for $Pr[O_2C(CH_2)_2CO_2]$); (ii) each unit cell exhibits a larger unit-cell parameter directly related to the length of the carbon chain of the organic molecule between two files (2 × 9.556(1) Å for $PrH[O_3P(CH_2)_3PO_3]$, 2 × 9.938(1) Å for $[Pr(H_2O)]_2[O_2C(CH_2)_3CO_2]_3\cdot 4H_2O$, and 8.362(1) Å for $Pr[O_2C(CH_2)_2CO_2]$). But while the rare-earth files are also well separated in the third direction in the dicarboxylates, they are directly connected by the small $-PO_3^{2-}$ and $-CO_2^-$ groups in the diphosphonates and the carboxyphosphonates. This leads to a dense pillared layered structure and does not allow the formation of an open framework as in dicarboxylates. Moreover, the distance between adjacent lanthanide atoms in the inorganic layers ($d_{min} = \sim 4.0$ Å) and therefore between the carbon chains in the interlamellar space is too short to give rise to any porosity. In both diphosphonates and carboxyphosphonate cases, a solution would be the coprecipitation of small monofunctionalized groups (phosphate, phosphite, formate) and the bisfunctionalized organic molecules, as previously described by Alberti.[5a,b] In this way, the small groups could act as spacers between the pillared organic agents in order to generate the desired porosity. Attempts in this way are currently in progress.

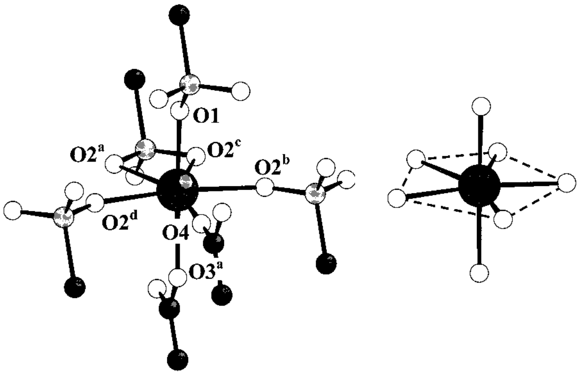

Figure 5. 7-Fold coordination of the praesodymium atom in $Pr[O_3P(CH_2)_2CO_2]$ leading to a PrO_7 pentagonal bipyramid.

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