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Synthesis and Characterization of New Lamellar Templated Titanium(IV) Phosphates with Perforated Layers: MIL-28$_n$ or $Ti_3O_2X_2(HPO_4)_x(PO_4)_y\cdot(N_2C_nH_{2n+6})_z\cdot(H_2O)_2$ ($n = 2, 3; x = 0, 2; y = 4, 2; z = 3, 2; X = F, OH$)

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The title compounds (MIL-28$_n$) were prepared hydrothermally (3−4 days, 453−473 K, autogenous pressure) in the presence of organic bases ($NH_2-(CH_2)_n-NH_2$ ($n = 2, 3$)). The structure of MIL-28$_3$ or $[Ti_3O_2(OH)_2(HPO_4)_2(PO_4)_2]\cdot(NH_3-(CH_2)_3-NH_3)_2\cdot(H_2O)_2$ has been determined ab initio from powder diffraction data and was refined in the orthorhombic space group *Fm*2*m* (no. 42). Its unit cell is $a = 18.331(2)$ Å, $b = 18.943(3)$ Å, $c = 7.111(1)$ Å, $V = 2469.2(2)$ Å^3, $z = 4$. MIL-28$_3$ is two-dimensional. Its inorganic layers are made of trans-linked corner-sharing TiO_6 octahedra chains connected with tetrahedral phosphate groups and related via isolated $TiO_4(OH)_2$ octahedra. This creates 10-member-ring apertures within the inorganic layers in which diamine molecules are present. Both water molecules, located in the interlayer space, and organic agents interact with terminal OH groups and ensure the stability of the structure. MIL-28$_2$ or $[Ti_3O_2F_2(PO_4)_4]\cdot(NH_3-(CH_2)_2-NH_3)_3\cdot(H_2O)_2$ crystallizes in a triclinic space group (*P*1 (no. 1)) with the following parameters: $a = 10.071(5)$ Å, $b = 18.920(2)$ Å, $c = 7.107(4)$ Å, $\alpha = 89.88(2)$, $\beta = 106.23(2)°$, $\gamma = 100.45(1)°$, and $V = 1273.5(3)$ Å^3. Although the structure of compound MIL-28$_2$ has not been determined, a brief study will show that it shares strong features with those of MIL-28$_3$.

1. Introduction

Metallophosphates have attracted a lot of interest in the past decade. Among them, titanium phosphates such as α-TiP,[1] γ-TiP,[2] KTP,[3] or the $M_2Ti_2(PO_4)_3$[4−5] compounds (M = Li, Na, ...) are very attractive materials for their applications in ion conductivity, ion exchange, and nonlinear optics. However, if a large number of three-dimensional solids containing metals such as Zn, Ni, Co, Al, Ga, Fe, Zr, V, ... have been characterized to date,[6] partially due to the recent progress in structure determination from X-ray powder diffraction, most of the titanium solids characterized to date exhibit lamellar structures.[7−9] Only a few years ago Poojary et al. reported the first three-dimensional titanium phosphates with an open structure:[10] $Ti_3(PO_4)_4(H_2O)_2\cdot NH_3$, $Ti_2O(PO_4)_2\cdot 2H_2O$, or ρ-TiP, and another solid of formula $NH_4\cdot Ti_2O_3(HPO_4)_2(PO_4)_2$. Sevov et al. also characterized the first templated mixed-valence three-dimensional titanium phosphate, $Ti^{III}Ti^{IV}(PO_4)(HPO_4)_2\cdot(NH_2-(CH_2)_3-NH_2)_{0.5}\cdot 2H_2O$,[11] and the first thermally

Table 1. Experimental and Theoretical (in Parentheses) Stoichiometries for Phases MIL-28$_n$ (n = 2, 3)

	ratio		
phase	Ti/P	C/P	F/P
MIL-28$_2$	0.97 (0.75)	1.60 (1.50)	0.60 (0.50)
MIL-28$_3$	0.92 (0.75)	1.45 (1.50)	traces (0)

Table 2. Experimental and Theoretical (in Parentheses) TGA Losses for Phases MIL-28$_n$ (n = 2, 3)

	loss (%)	
phase	H_2O	diamine/HX (X = F, OH)
MIL-28$_2$[a]	5.1 (4.35)	24.5 (22.6)/4.2 (4.6)
MIL-28$_3$	3.15 (4.25)	25 (23.9)

[a] For phase MIL-28$_2$, only the total diamine + HX loss is reported.

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10.1021/cm011058v CCC: $22.00

Table 3. Cell Parameters and Space Groups for Phases MIL-28$_n$ (n = 2, 3)

phase	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	V (Å^3)	space group
MIL-28$_2$	10.071(5)	18.920(2)	7.107(4)	89.88(1)	106.23(2)	100.45(1)	1273.5(3)	$P1$ or $P-1$
MIL-28$_3$	18.331(2)	18.943(1)	7.111(3)	90.0	90.0	90.0	2469.3(2)	$Fm2m$

Table 4. Indexed Powder Pattern of MIL-28$_3$[a,b]

hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_{max} (%)	hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_{max} (%)
020	9.46	9.471	9	222	3.131	3.129	4
200	9.18	9.166	100	531	2.896	2.896	5
220	6.59	6.586	1L	042	2.845	2.843	14
111	6.26	6.257	3	402	2.810	2.809	5
040	4.77	4.736	30	422	2.692	2.693	1L
311	4.50	4.502	10	460	2.597	2.600	1
240	4.21	4.207	4	640	2.568	2.567	4
420	4.13	4.125	11	171	2.506	2.505	5
331	3.736	3.736	2	711	2.437	2.437	1
002	3.559	3.556	16	062	2.354	2.361	3
022	3.330	3.329	10	371	2.336	2.337	1
440	3.294	3.289	10	731	2.290	2.290	2
511	3.213	3.211	21	133	2.203	2.203	1
060	3.159	3.157	2	313	2.105	2.104	1

[a] Indexing is based on a orthorhombic cell with the following parameters: a = 18.331 Å, b = 18.943 Å, c = 7.111 Å; L refers to a very low intensity reflection ($\ll$1). [b] Only the first reflections are reported.

stable three-dimensional titanium phosphate with an open structure, $Ti^{III}Ti^{IV}(HPO_4)_4\cdot(NH_2-(CH_2)_2-NH_3)\cdot H_2O$.[12] Recently, new templated titanium phosphates synthesized from nonaqueous media have been reported;[13] among them, two are three-dimensional with an open structure.

Our group has meanwhile initiated a systematic study of the titanium system, and we recently reported new titanium phosphates. Some of them exhibit layered structures, such as $Ti_2(PO_4)_2F_4$, $N_2C_nH_{2n+6}$, or MIL-6$_n$ (MIL, Material of Institut Lavoisier; n = 2, 3),[14] while others are three-dimensional solids with an open structure, such as $Ti^{III}Ti^{IV}F(PO_4)_2\cdot 2H_2O$ or MIL-15[15] and $Ti_6O_3(H_2O)_3(PO_4)_7\cdot(H_3O)_3\cdot H_2O$ or MIL-18.[16]

We present here the synthesis and the structure determination of a new lamellar titanium phosphate: $[Ti_3O_2(OH)_2(HPO_4)_2(PO_4)_2]\cdot(NH_3-(CH_2)_3-NH_3)_2\cdot(H_2O)_2$ or MIL-28$_3$. Similar compounds (MIL-28$_n$ (n = 2, 4)) have been synthesized with other diamines, and their chemical and structural parameters are also discussed.

2. Experimental Section

Hydrous titanium dioxide ($TiO_2\cdot H_2O$) was prepared from the reaction of strongly acidic solutions of $TiCl_4$ (Aldrich, 99%) in HCl (Prolabo, 36%) with ammonia (Prolabo, 20%) at room temperature. The precipitate was washed with demineralized water and dried at 373 K.

The title compounds MIL-28$_n$ (n = 2, 3), were hydrothermally synthesized from either titanium dioxide (Aldrich, 99%) (n = 2) or hydrous titanium dioxide (n = 3), H_3PO_4 (Prolabo Normapur 85%), HF (Prolabo Normapur 40%), ethylenediamine (n = 2), or 1,3-diaminopropane (n = 3) (Aldrich 99%) and H_2O in the molar ratio 1:1:1:1.0 (n = 2) or 0.5 (n = 3):80. A similar synthesis was also performed with 1,4-diaminobutane (Aldrich 99%) using the same ratios as MIL-28$_3$. Mixtures were placed without stirring in a Teflon-lined steel autoclave under autogenous pressure for 4 days at 453 K. The final synthesis pH is close to 4 in all cases. The resulting white powders were washed with demineralized water and dried at room temperature.

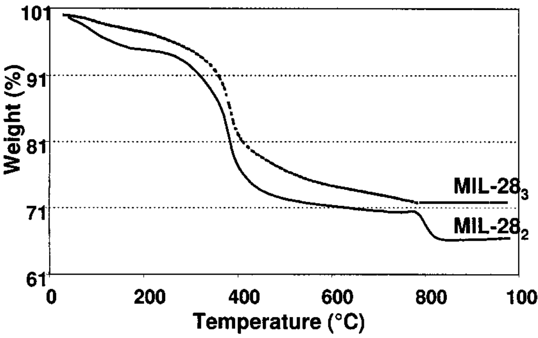

Figure 1. TGA of phases MIL-28$_n$ (n = 2, 3) under air atmosphere.

Elementary analysis gave ratios Ti/P and C/P, respectively, close to the theoretical values (see Table 1), Ti/P being higher than expected due to the presence of residual titanium precursor in the final product. A calculation based on quantitative analysis results gives an estimate of less than 9% and 7% of anatase, respectively, for MIL-28$_2$ and MIL-28$_3$. The F/Ti ratio is about 0.6 for MIL-28$_2$ (theoretical value 0.5), and only traces of fluorine were detected for MIL-28$_3$, confirming the absence of fluorine atoms inside this solid.

TGA experiments, operated with a Texas Instrument TA 2050 apparatus under oxygen flow, were performed and showed several weight losses between 30 and 900 °C (Figure 1 and Table 2) for all compounds. The first loss, between 30 and 250 °C, corresponds to the departure of the water molecules, and the experimental values correspond to the calculated values (Table 2). The departure of the template occurs between 250 and 600 °C and is followed by fluorine loss between 750 and 850 °C for MIL-28$_2$. Such departures at high temperatures have been observed previously for other titanium fluorophosphates.[14] In the case of MIL-28$_3$, the template and hydroxyl group departure are not well separated. However, in both cases, the total losses (diamine + HX) are in good agreement with the theoretical values (see Table 2). The residual calcined solids are a mixture of anatase and the dense titanium(IV) phosphate TiP_2O_7.

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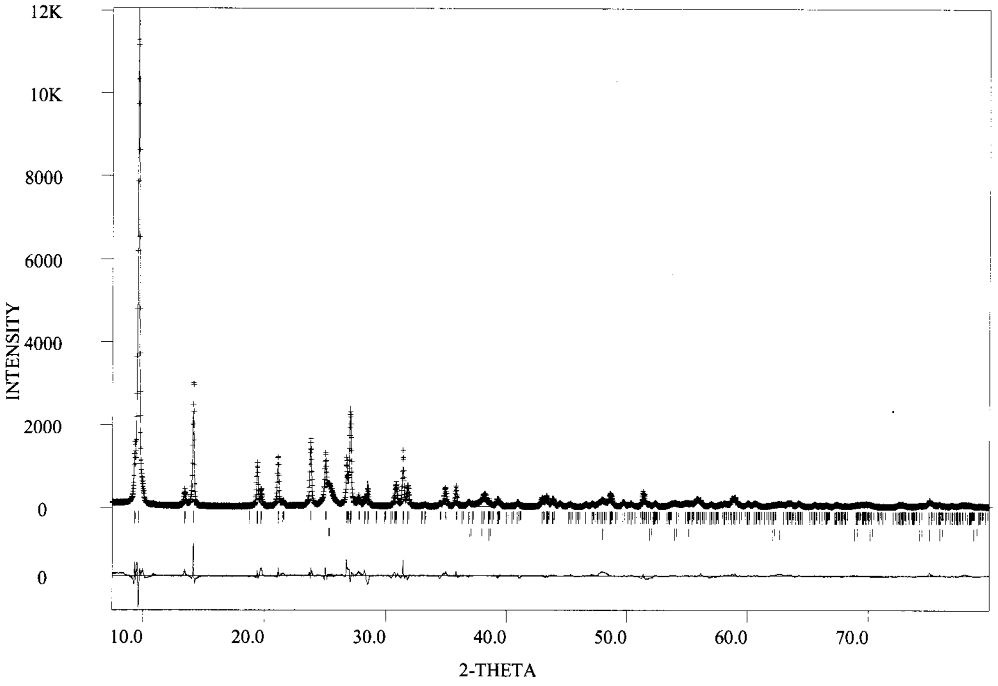

Figure 2. Final Rietveld plot of MIL-28_3 using TiO_2 anatase as a secondary phase. The corresponding reflections are pointed out using two different sets of vertical bars.

Table 5. Crystallographic Data of MIL-28_3[a]

composition	$Ti_3P_4O_{22}N_4C_6H_{32}$
molar mass (g·mol^{-1})	780
calcd volumic mass (g·cm^{-3})	2.19
crystallographic system	orthorhombic
space group	$Fm2m$ (no. 42)
multiplicity (Z)	4
a (Å)	18.342(2)
b (Å)	18.950(2)
c (Å)	7.115(1)
V (Å^3)	2473.1(1)
radiation (λ_{Cu} (Å)): Kα_1, Kα_2	1.540 59, 1.544 39
angular ranges (deg 2θ)	7.5−35.0 and 35.02−80
step time (s)	35 (range 1) and 70 (range 2)
step (deg)	0.02
excluded areas (deg 2θ)	37.2−38.9 and 44.2−44.8
no. of reflections	225
profile points no.	3453
no. of structural parameters	39
no. of constraints	30
no. of profile parameters	33
no. of independent atoms	21
R_p (%)	13.4
R_{wp} (%)	18.7
R_{Bragg} (%)	8.95
R_F (%)	9.95
B_{iso} (Å^2)	1.95

[a] Cell parameters are deduced from the Rietveld refinement.

Table 6. Atomic Coordinates for MIL-28_3

atom	x	y	z
Ti(1)	0.5	0.1503(15)	0
Ti(2)	0.5	−0.999(11)	−0.2195(16)
P(1)	−0.1092(9)	−0.2042(10)	0
P(2)	0.6035(8)	0.0074(10)	0
O(1)	0.581(2)	0.084(1)	0
O(2)	0	−0.082(2)	0
O(3)	0.082(1)	−0.171(1)	0.817(3)
O(4)	−0.185(1)	−0.197(3)	0
O(5)	0	−0.148(2)	0.5
O(6)	0	0.140(3)	0.765(3)
O(7)	0.575(1)	−0.036(2)	−0.152(3)
O(8)	−0.090(1)	−0.284(1)	0
O(9)	0.693(1)	0.017(3)	0
Ow(1)	−0.25	−0.090(5)	−0.25
Ow(2)	0.25	−0.394(2)	0.75
N(1)	0.141(1)	−0.304(2)	0.5
N(2)	−0.142(1)	−0.461(2)	0.5
C(1)	0	0.199(2)	0
C(2)	0.068(1)	0.236(2)	0
C(21)	0	−0.467(2)	0.5
C(22)	689(8)	757(18)	0

The density measurements, performed on a Micromeritics apparatus Accupyc 1330, were respectively 2.24 and 2.26 g/cm^{-3} for MIL-28_2 and MIL-28_3, which correspond well to the theoretical values (2.31 and 2.14).

Solid state ^{31}P NMR experiments used a DSX500 Bruker apparatus with an 11.7 T magnetic field with a 2 mm Teflon-headed MAS probe at a rotation speed of 20 kHz; spectrum were recorded at 202.4156 MHz with a pulse time (P1) of 1.5 μs and 2 s (D1) as a repetition time. H_3PO_4 (85%) was used as reference ($\delta = 0$ ppm). The X-ray thermodiffractometry, performed in the furnace of a Siemens D-5000 diffractometer in the $\theta-\theta$ mode, showed several steps in the decomposition. This point will be discussed further in this paper.

Finally, these analyses confirmed the formula deduced from the structure determination for MIL-28_3: $[Ti_3O_2(OH)_2(HPO_4)_2(PO_4)_2]\cdot(NH_3-(CH_2)_3-NH_3)_2\cdot(H_2O)_2$. A proposed formula could also be given for MIL-28_2: $[Ti_3O_2F_2(PO_4)_4]\cdot(NH_3-(CH_2)_2-NH_3)_3\cdot(H_2O)_2$.

3. Structure Determination

No single crystal could be obtained even with increasing synthesis times. The powder diffraction patterns were collected on a D5000 ($\theta-2\theta$) mode Siemens diffractometer with λ_{Cu} (Kα_1, Kα_2) = 1.54059, 1.54439 Å. The patterns of MIL-28_n (n = 2, 3) were indexed with the Ito program.[17] Solutions with adequate figures of merit were found for MIL-28_2 ($M(20) = 27$ (0.017, 45)) and MIL-28_3 ($M/F(20) = 67$ (0.012, 31)) (see Table 3). Systematic absences were consistent with the space groups $Fm2m$ (no. 42) for MIL-28_3 and $P-1$ or $P1$ (no. 1) for MIL-28_2. The indexed powder pattern of MIL-28_3 is reported in Table 4.

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Table 7. Selected Interatomic Distances (Å) for MIL-28$_3$

Ti(1)−O(1) (*2)	1.95(3)	Ti(1)−O(6) (*2)	1.89(2)
Ti(1)−O(8) (*2)	2.06(3)		
Ti(1)−O(1)	1.96(2)	Ti−O(4)	1.96(2)
Ti(2)−O(2)	2.02(2)	Ti(2)−O(3) (*2)	2.13(3)
Ti(2)−O(5)	1.81(3)	Ti(2)−O(7) (*2)	1.90(3)
P(1)−O(3) (*2)	1.53(3)	P(1)−O(4)	1.40(3)
P(1)−O(8)	1.56(3)		
P(2)−O(1)	1.51(3)	P(2)−O(7) (*2)	1.46(3)
P(2)−O(9)	1.65(3)		
N(1)−C(2)	1.53(3)	N(2)−C(22)	1.51(3)
C(1)−C(2)	1.43(3)	C(21)−C(22)	1.51(3)
N(1)−Ow(2) (*2)	3.19(3)	N(2)−Ow(2) (*2)	2.95(3)
N(1)−O(6) (*2)	3.25(3)	N(2)−O(9)	3.06(3)
N(1)−N(2)	2.98(3)		

Table 8. Selected Interatomic Angles (deg) for MIL-28$_3$

O(1)−Ti(1)−O(1)	99(2)	O(1)−Ti(1)−O(6)	86(2)
O(1)−Ti(1)−O(8)	176(2)	O(1)−Ti(1)−O(8)	78(3)
O(6)−Ti(1)−O(6)	168(2)	O(6)−Ti(1)−O(8)	93(2)
O(8)−Ti(1)−O(8)	106(2)		
O(2)−Ti(2)−O(3)	78(2)	O(2)−Ti(2)−O(5)	160(2)
O(2)−Ti(2)−O(7)	98(1)	O(3)−Ti(2)−O(3)	90(2)
O(3)−Ti(2)−O(5)	88(1)	O(3)−Ti(2)−O(7)	88(2)
O(3)−Ti(2)−O(7)	176(2)	O(5)−Ti(2)−O(7)	96(2)
O(7)−Ti(2)−O(7)	94(2)		
O(3)−P(1)−O(3)	117(3)	O(3)−P(1)−O(4)	106(3)
O(3)−P(1)−O(8)	109(3)	O(4)−P(1)−O(8)	108(2)
O(1)−P(2)−O(7)	117(3)	O(1)−P(2)−O(9)	100(1)
O(7)−P(2)−O(7)	96(3)	O(7)−P(2)−O(9)	115(2)
N(1)−C(2)−C(1)	121(2)	N(2)−C(22)−C(21)	120(2)
C(2)−C(1)−C(2)	121(2)	C(22)−C(21)−C(22)	114(2)

The XRD pattern of MIL-28$_n$ ($n = 2, 3$) showed a strong preferred orientation effect, probably due to the lamellar structure. Therefore, the powders were pulverized with a MacCrone grinder in ethanol (Prolabo, 95%) and dried at 373 K. The fine powders were then introduced vertically in a MacMurdie type sample holder, which led to a reduction of the preferred orientation effect.

The pattern matching were performed with Fullprof 97.[18] The direct method used Sirpow97.[19] MIL-28$_3$ data led to acceptable solutions while the low symmetry of MIL-28$_2$ ($P1$ or $P{-}1$) combined with its large cell volume (~1273 Å^3) ruled out any satisfactory solutions. Titanium, phosphorus, and most of the oxygen atoms were first located, while atoms of the organic molecule and water molecules were found using Fourier difference maps. The structure of MIL-28$_3$ was then refined using Fullprof. Because MIL-28$_3$ (and MIL-28$_2$) could not be obtained pure without the presence of residual TiO_2 anatase, the structure of MIL-28$_3$ was refined using anatase as a secondary phase. Soft distance constraints, an overall thermal parameter, and a preferred orientation correction parameter were applied during the refinement for MIL-28$_3$. Two angular areas corresponding to the aluminum sample holder reflections were also excluded. Details of the structure determination are summarized in Table 5.

The final agreement factors are $R_p = 13.4\%$, $R_{wp} = 18.7\%$, $R_{Bragg} = 8.95\%$, and $R_F = 9.95\%$. The final Rietveld plot is reported on Figure 2. Atomic coordinates are given in Table 6, while principal bond distances and angles are reported in Tables 7 and 8.

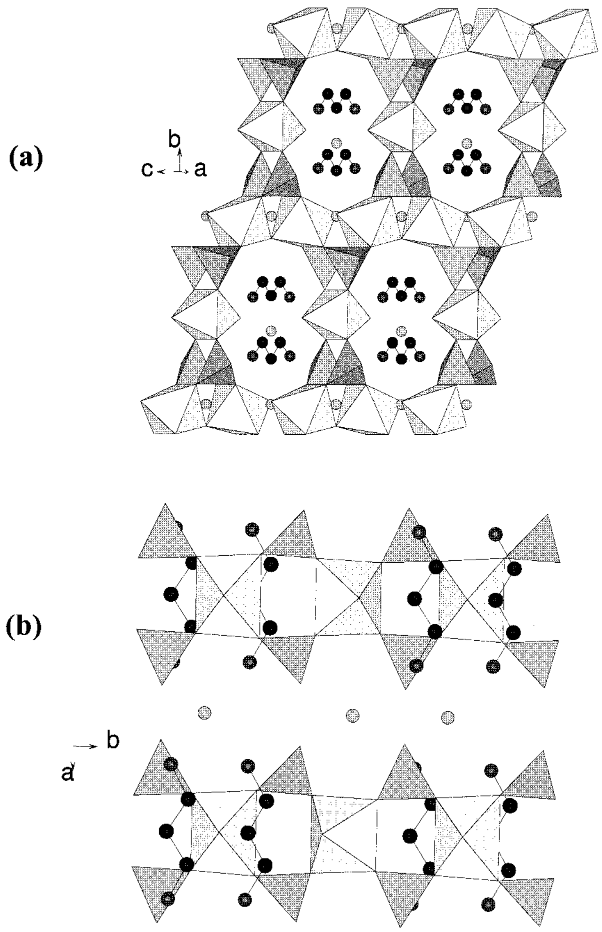

Figure 3. View of the structure of MIL-28$_3$: (a) view along the [101] axis; (b) view along the [100] axis.

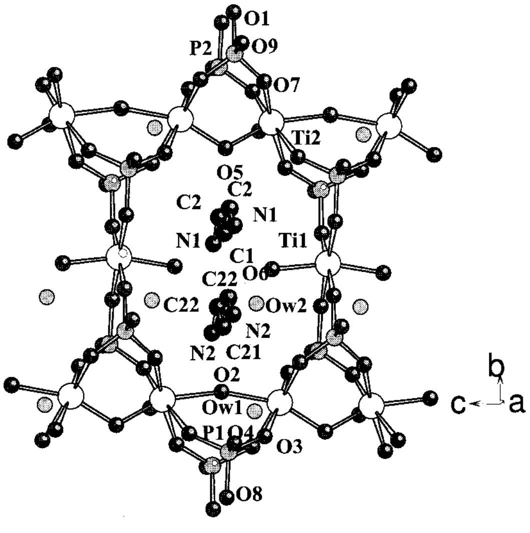

Figure 4. Asymmetric unit of MIL-28$_3$.

4. Discussion

MIL-28$_3$ is two-dimensional (Figure 3). The inorganic layers are made of TiO_6 and $TiO_4(OH)_2$ octahedra and PO_4 or HPO_4 tetrahedra. These units are related together to produce Ti(2)O_6 of trans-linked corner-sharing octahedra chains on which phosphate groups are connected. These chains have the same topology as the mineral Tancoïte.[20] These units are related via Ti(1)-$O_4(OH)_2$ isolated octahedra creating 10-member-ring perforated layers (Figure 3a). MIL-28$_3$ framework can

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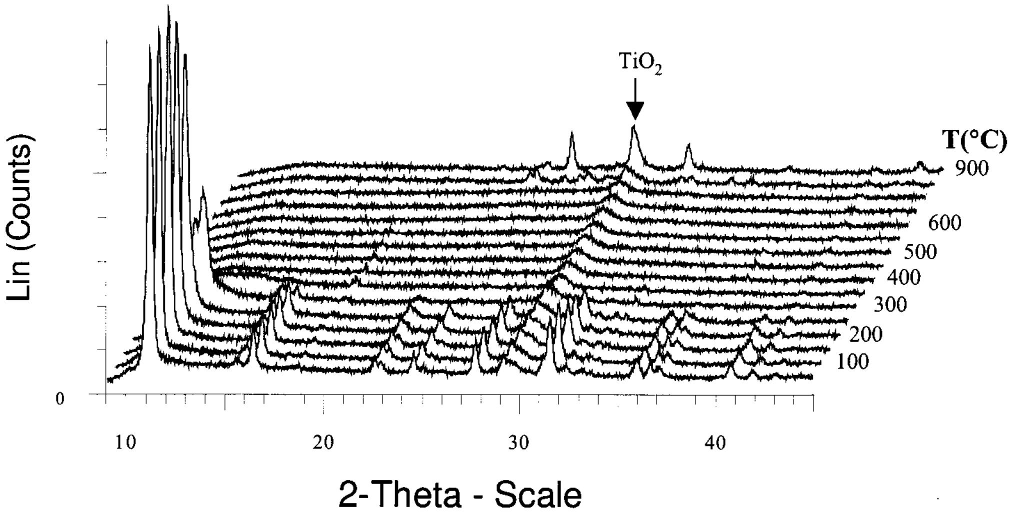

Figure 5. X-ray thermodiffractogram of MIL-28_3 under air atmosphere.

also be described using SBU (secondary building units), of formula $Ti_3O(OH)_2(HPO_4)_2(PO_4)_2$, built from three titanium octahedra and four phosphate groups.

The organic structuring agents are unusually located within the layers inside the 10-member rings instead of the interlayer space (Figure 3b). Here, only water molecules are present between the layers. They ensure the cohesion of the inorganic sheets via hydrogen bonds.

The ligands around the two octahedrally coordinated titanium atoms are different (Figure 4). Ti(1) has four bridging oxygens and two terminal hydroxyl groups. Only bridging oxygens surrounds Ti(2); four of them relate titanium and phosphorus atoms while the two others are bound to titanium atoms. The two phosphorus atoms have three bridging oxygens and one terminal group. Due to powder data, the accurate nature of the terminal groups (O(4), O(6), O(9)), bound to the phosphorus and titanium atoms, cannot be determined using only distance considerations. In addition, considering the acidity of the synthesis medium, amino groups would be better described as protonated. Thus, MIL-28_3 could be described either with two OH groups, two HPO_4, and two PO_4 groups (formula $[Ti_3O_2(OH)_2(HPO_4)_2(PO_4)_2]{\cdot}(NH_3{-}(CH_2)_3{-}NH_3)_2{\cdot}(H_2O)_2)$ or with two terminal water molecules and four PO_4 groups (formula $[Ti_3O_2(H_2O)_2(PO_4)_4]{\cdot}(NH_3{-}(CH_2)_3{-}NH_3)_2{\cdot}(H_2O)_2)$. As no terminal water losses could be deduced from TGA results, the best formula for MIL-28_3 is $[Ti_3O_2(OH)_2(HPO_4)_2(PO_4)_2]{\cdot}(NH_3{-}(CH_2)_3{-}NH_3)_2{\cdot}(H_2O)_2)$.

Interatomic distances on the whole agree with those usually observed for titanium phosphates: Ti−O distances are between 1.81 and 2.06 Å except for Ti(2)−O(3), which is 2.13 Å, a value too high for a bridging oxygen. As in every distorted titanium oxo chain observed previously, Ti−O distances for oxygens bridging titanium atoms are alternatively short and long (1.81 and 2.02 Å). P−O distances are between 1.46 and 1.65 Å except for P(1)−O(4), which is 1.40 Å. The diamine N−C and C−C distances also are in agreement with those usually reported: between 1.43 and 1.53 Å. These discrepancies are related to the difficulty of resolution from powder data of two-dimensional solids of large volume (~2500 Å^3).

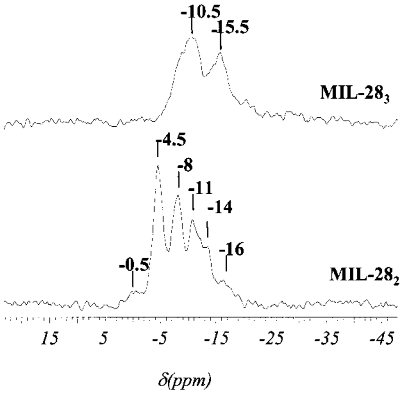

Figure 6. Solid state ^{31}P NMR spectra of phases MIL-28_n ($n = 2, 3$).

Water molecules interact differently. Ow(1) molecules exhibit hydrogen bonds mostly with terminal P−OH (or P=O) groups (d(Ow(1)−O(4)) = 2.96 Å) while Ow(2) molecules interact both with amino groups (d((Ow(2)−N(1)) = 3.19 Å and d(Ow(2)−N(2)) = 2.95 Å) and with Ti−OH groups (d(Ow(2)−O(6)) = 3.09 Å). This may explain the late departure of water, unfinished at 200 °C, observed by TGA for MIL-28_3 (Figure 1).

The two crystallographically independent diamines also interact differently with the inorganic framework. The first diamine (1) interacts less with the framework (d(N(1)−O(6)) = 3.25 Å (*2)) than the second structuring agent (d(N(2)−O(9)) = 3.06 Å and d(N(2)−O(7)) = 3.11 Å); this may explain the departure of the organic template which occurs in a wide range of temperature (250−650 °C). Amino groups are in cis position, and diamines are oriented along the same direction (Figure 4). This does not allow the existence of any m mirror perpendicular to the b-axis and justifies the choice of the noncentrosymmetric space group $Fm2m$.

The thermal behavior of MIL-28_3 has been investigated using X-ray thermodiffractometry (Figure 5). Below 250 °C, the water departure leads to no significant change. Above 250 °C, the structure of MIL-28_3 starts collapsing because of the departure of the organic template. Above 350 °C, an amorphous solid is formed and higher temperatures lead to the crystallization of a mixture of TiO_2 anatase and the dense titanium phosphate TiP_2O_7.

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(20) Hawthorne, F. C. *Acta Crystallogr.* **1994**, *B50*, 481.

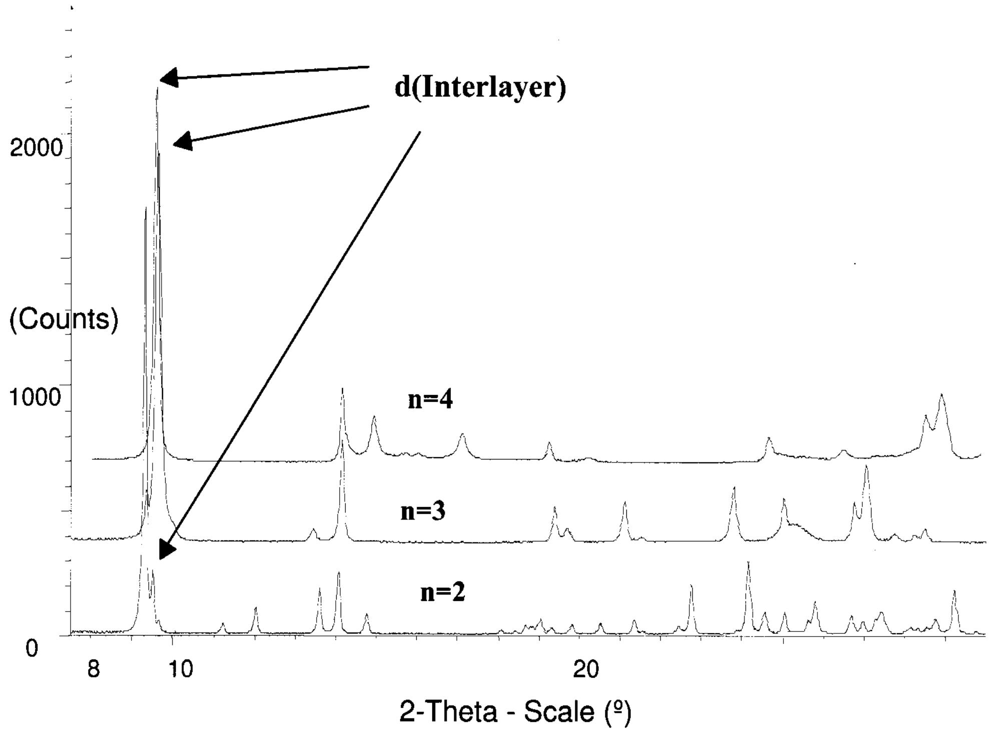

Figure 7. X-ray powder diffraction patterns of phases MIL-28_n ($n = 2, 3, 4$).

Finally, similar syntheses have been conducted with ethylenediamine and 1,4-diaminobutane (Aldrich, 99%), and white crystalline solids or MIL-28_n ($n = 2, 4$), has been obtained in both cases. The composition and thermal behavior of MIL-28_2 or $[Ti_3O_2F_2(PO_4)_4]\cdot(NH_3-(CH_2)_2-NH_3)_3\cdot(H_2O)_2$ are, except for the presence of fluorine, very close to those of MIL-28_3. The cell parameters of MIL-28_2 and MIL-28_3 are related (see Table 3); *b* and *c* are almost identical while $a \sin \gamma$ nearly doubles from MIL-28_2 to MIL-28_3. Even if MIL-28_2 or $[Ti_3O_2F_2(PO_4)_4]\cdot(NH_3-(CH_2)_2-NH_3)_3\cdot(H_2O)_2$ possesses three diamines per four phosphate groups instead of two per four for MIL-28_3, these two solids exhibit probably isostructural inorganic layers. Admitting that two of the three diamines of MIL-28_2 are located, as for MIL-28_3, within the 10-member rings, the third organic molecule can only be present inside the interlayer space. If one considers the distance between two consecutive amino groups in MIL-28_3 (~5.35 Å) and the fact that ethylenediamine molecules are shorter than 1,3-diaminopropane molecules, this allows enough room for an additional diamine between the layers. This supplementary molecule would create new interactions with the framework, and this would explain the lower symmetry observed for MIL-28_2 (triclinic) compared with MIL-28_3 (orthorhombic F). Solid state ^{31}P NMR spectrum confirms the lower symmetry of MIL-28_2 (Figure 6): only two peaks are present at −10.5 and −15.5 ppm for MIL-28_3 while at least six peaks are observed between −0.5 and −16 ppm for MIL-28_2. This latter solid is also probably noncentrosymmetric.

The composition of MIL-28_4 is close to $[Ti_3O_2F_2(PO_4)_4]\cdot(NH_3-(CH_2)_4-NH_3)_2\cdot(H_2O)_2]$, according to TGA and quantitative analysis. Its composition and thermal behavior are similar to those of MIL-28_2 and MIL-28_3. However, no cell indexing could be performed due to an insufficient crystallinity. However, the interlayer spacing distance, which corresponds to the *d*(020) reflection for both MIL-28_2 and MIL-28_3, corresponds to the first and strongest peak of the X-ray diffraction pattern of MIL-28_4 (Figure 7). Then MIL-28_4 probably shares strong structural features with those of MIL-28_2 and MIL-28_3.

These solids possess, like $KTiOPO_4$,[3] distorted chiral titanyl chains and are interesting candidates for second harmonic generation measurements that could result in nonlinear optical properties. The compounds are also potential candidates for ion-exchange reactions.

In conclusion, a series of new templated titanium(IV) phosphates, exhibiting strong structural features and with potential optical and ion-exchange properties, has been characterized. Further experiments are currently in progress and will hopefully lead to new titanium-based solids with interesting applications.

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