Hydrothermal Synthesis and Structure Determination from Powder Data of New Three-Dimensional Titanium(IV) Diphosphonates $Ti(O_3P-(CH_2)_n-PO_3)$ or MIL-25_n ($n = 2, 3$)

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$Ti(O_3P-(CH_2)_n-PO_3)$ or MIL-25_n ($n = 2, 3$) were prepared under hydrothermal conditions (4 days, 463 K, autogenous pressure). Their structures were determined *ab initio* from X-ray diffraction powder data. MIL-25_2 is triclinic (space group *P*-1 (no. 2)), with $a = 5.033(1)$, $b = 5.092(1)$, $c = 6.859(1)$ Å, $\alpha = 95.860(1)°$, $\beta = 99.994(1)°$, $\gamma = 118.217(1)°$, and $Z = 2$. MIL-25_3 exhibits an orthorhombic symmetry (space group *Cm*2*m* (no. 38)), with $a = 5.230(1)$, $b = 8.451(1)$, $c = 17.400(2)$ Å, and $Z = 4$. Their three-dimensional structures are built up from TiO_6 titanium(IV) octahedra linked together via diphosphonate groups. This leads to pillared structures whose inorganic sheets are closely related to those of the αTiP titanium phosphate structure.

Introduction

During the past few years, an alternative pathway to the synthesis of three-dimensional inorganic-based materials with an open structure under hydrothermal conditions has used chelating agents such as diphosphonic acids instead of phosphates.[1−5] In fact, metallophosphates usually retain organic structuring agents in the final solid, and their removal very often leads to the collapse of the inorganic framework.[5] Using instead hybrid chelating diacids usually leads to pillared three-dimensional structures. Since no templating agent is needed then, the porosity becomes readily accessible.

Several mono-, di-, or three-dimensional metal phosphonates have been reported recently.[1−5] Several groups, including ours, extended this pathway to compounds containing either rare earths[6] or 3d transition metals (M = V, Fe, Ti, Co, Ni),[7−11] and this led to solids with various dimensionalities. Further extending this concept, open framework metallic dicarboxylates were synthesized.[12−13]

This paper deals with the synthesis and structure determination from powder data of new three-dimensional titanium(IV) diphosphonates with an open structure: $Ti(O_3P-(CH_2)_n-PO_3)$ or MIL-25_n ($n = 2, 3$). A brief discussion concerning their common features with the αTiP titanium(IV) phosphate is also reported.

Experimental Section

Synthesis and Analysis. Hydrous titanium dioxide 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 were hydrothermally synthesized (autogenous pressure, 4 days at 463 K) from a mixture of hydrous TiO_2, $H_2O_3P-(CH_2)_n-PO_3H_2$ (Alfa 97%) ($n = 2, 3$), HF (Prolabo Normapur 40%), and H_2O, in the molar ratio 1:1:1:500, introduced in this order without stirring in a Teflon-lined steel autoclave. The pH increased from 2 to 3 during the reaction.

Quantitative elemental analyses, performed at the CNRS laboratory of Vernaison (69, France), indicated P/Ti ratios, respectively, of 1.9 and 2.0 for MIL25_2 and MIL25_3, which are in good agreement with the theoretical values (2 and 2). Density measurements, operated on a Micromeretics Accupyc 1330 apparatus, are, respectively, 2.61 and 2.08 g/cm^3 for MIL25_2 and MIL25_3 (theoretical values: 2.55 and 2.14).

TGA experiments performed on a TA-instrument type 2050 analyzer apparatus, under an oxygen atmosphere, indicated a weight loss of 4.2% for MIL25_2 and 12.3% for MIL25_3 in the 273−873 K range; this corresponds to the departure of the CH_2 groups and their replacement by oxygen atoms (theoretical losses: 5.1 and 10.5%). The residual compound is, in both cases, the dense titanium diphosphate TiP_2O_7.[14]

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Table 1. Crystallographic Data of MIL-25_2 and MIL-25_3

phase	MIL-25_2	MIL-25_3
composition	$TiP_2O_6C_2H_4$	$TiP_2O_6C_3H_6$
molar weight (g mol^{-1})	234	248
calculated density (g cm^{-3})	2.53	2.14
symmetry	triclinic	orthorhombic
space group	*P*-1 (n°2)	*Cm*2*m* (n°38)
multiplicity (*Z*)	2	4
a(Å)	5.092 (1)	5.230 (1)
b(Å)	6.859 (1)	8.431 (1)
c(Å)	5.033 (1)	17.400 (2)
α(°)	95.860 (1)	90.0
β(°)	118.217 (1)	90.0
γ(°)	90.745 (1)	90.0
V(Å^3)	153.69 (1)	769.06 (5)
λ (λCu (Å)):Kα1 and Kα2	1.54059, 1.54439	1.54059, 1.54439
range (°2θ)	5−70	7−70
time/step (s)	18	15
step size (°)	0.02	0.02
excluded area (°2θ)	5.0−10.0	10.6−12.0
total no. of reflns	132	115
total no. of points	3251	3151
no. of structural param	15	22
no. of profile param	23	20
no. of atoms refined	6	11
no. of distance constraints	15	14
overall thermal isotropic factor(Å^2)	0.56	0.20
R_p (%)	10.3	14.1
R_{wp} (%)	14.4	19.5
R_{Bragg} (%)	4.85	10.7

^{31}P Spectra were performed using a DSX500 Bruker apparatus with a 11.7 T magnetic field; the 2 mm Teflon-headed MAS probe used a rotation speed of 20 kHz. The field frequency was 202.4156 MHz with a pulse time (P1) of 1.5 μs, and 2s (D1) was used as a repetition time. The reference was H_3PO_4 85% ($\delta = 0$ ppm).

Finally, these results are in close agreement with the formula deduced from structure determination: $Ti(O_3P-(CH_2)_n-PO_3)$ or MIL-25_n ($n = 2, 3$).

Structure Determination. Single crystals could not be obtained for either phases even with an increase in synthesis time, synthesis temperature, or by varying the initial stoechiometry. The powder diffraction patterns were collected on a D5000 ($\theta-2\theta$ mode) Siemens diffractometer with λ_{Cu}(Kα1, Kα2) = 1.54059, 1.54439 Å. The patterns of MIL-25_n ($n = 2, 3$) were indexed with the Ito program.[15] Solutions with adequate figures of merit were found for MIL-25_2 (M(20) = 28 (0.024, 56)) and MIL-25_3 (M(20) = 57 (0.006, 29)). A triclinic solution was found for MIL-25_2, space group *P*1 (no. 1) or *P*-1 (no. 2), while systematic absences were consistent with the space group *Cm*2*m* (no. 38) for MIL-25_3.

The XRD patterns of MIL-25_n ($n = 2, 3$) showed a strong preferred orientation effect, probably due to the lamellar-like structure. Therefore, the powders were pulverized with a Mac Crone grinder in ethanol (Prolabo, 95%) and dried at 373 K. The fine powders were then mounted in a top-loaded Mac Murdie type sample holder, which led to a reduction of the preferred orientation effect.

The pattern matching was performed with Fullprof 97.[16] The direct method used Sirpow97.[17] The structures of MIL-25_n ($n = 2, 3$) were then refined also using Fullprof. One angular domain per phase was excluded during the refinement. For MIL-25_2, the 5−10° 2θ angular range exhibited a strong background that could not be fitted correctly using polynomial parameters and was excluded. Pure MIL-25_3 could not be obtained, an unknown byproduct was present whatever the synthesis conditions; then, the angular domain (10.6−12°) of the most intense characteristic peak of this phase was excluded. Soft distance constraints, overall thermal parameters, and preferred orientation correction parameters were applied during refinements. Preferred orientation vectors were chosen in both cases as the directions perpendicular to the inorganic layers. Details of the structure determinations are summarized in Table 1.

Table 2. Atomic Coordinates

MIL-25_2 Using a Triclinic Cell with a = 5.092 (1), b = 6.859 (2), c = 5.033 (1) Å, α = 95.859 (1), β = 118.217 (1), γ = 90.745 (1); Space Group = *P*-1 (no. 2)

atom	*X*	*Y*	*Z*
Ti	0	0	0
P	−0.633 (1)	0.229 (1)	−0.313(1)
O(1)	−0.820 (2)	0.208 (1)	−0.656 (2)
O(2)	−0.310 (2)	0.169 (1)	−0.222 (2)
O(3)	0.238 (2)	0.110 (1)	−0.161 (2)
C	−0.379 (2)	0.509 (2)	0.168 (2)

MIL-25_3 Using a Orthorhombic Cell with a = 5.230 (1), b = 8.451 (1), c = 17.400 (2) Å; Space Group = *Cm*2*m* (no. 38)

atom	*X*	*Y*	*Z*
Ti(1)	0	0.007 (3)	0.249 (1)
P(1)	0	0.647 (2)	0.337 (1)
P(2)	0.5	0.851 (2)	0.158 (1)
O(1)	−0.225 (3)	0.543 (3)	0.324 (1)
O(2)	0	0.790 (4)	0.285 (3)
O(3)	0.255 (4)	0.945 (3)	0.163 (1)
O(4)	0.5	0.720 (4)	0.217 (2)
C(1)	0	0.733 (2)	0.431 (1)
C(2)	0.5	0.118 (3)	0.5
C(3)	0.5	0.739 (2)	0.069 (1)
C(4)	0.5	0.847 (3)	0.25

Table 3. Interatomic Distances (Å) of MIL-25_2 and MIL-25_3

	MIL-25_2		
Ti−O(1)	1.96 (2)	Ti−O(2)	1.93 (1)
Ti−O(3)	1.93 (1)		
P−O(1)	1.52 (1)	P−O(2)	1.56 (2)
P−O(3)	1.51 (1)	P−C	1.86 (2)
C−C	1.54 (2)		
	MIL-25_3		
Ti(1)−O(1) (*2)	1.96 (2)	Ti(1)−O(3) (*2)	2.07 (3)
Ti(1)−O(2)	1.93 (4)	Ti(1)−O(4)	1.89 (4)
P(1)−O(1) (*2)	1.49 (3)	P(1)−O(2)	1.51 (4)
P(1)−C(1)	1.79 (2)		
P(2)−O(3) (*2)	1.51 (2)	P(2)−O(4)	1.51 (4)
P(2)−C(3)	1.81 (4)		
C(1)−C(2)	1.54 (2)	C(3)−C(4)	1.52 (2)

The final agreement factors are:[18] $R_p = 10.3$, $R_{wp} = 14.4$, and $R_{Bragg} = 4.85\%$ for MIL-25_2, and $R_p = 14.1$, $R_{wp} = 19.5$, and $R_{Bragg} = 10.7\%$ for MIL-25_3. The final Rietveld plots are reported in Figures 1 and 2. Atomic coordinates are given in Table 2 , while bond distances are reported in Table 3.

Discussion

MIL-25_n ($n = 2, 3$) are three-dimensional (Figure 3). Their structures are built up from TiO_6 octahedra and $(PO_3-(CH_2)_n-PO_3)$ groups ($n = 2, 3$) with only Ti−O−P bonds. In the titanium octahedral subnetwork, the TiO_6 octahedra are almost regular and linked to PO_3C tetrahedra.

The inorganic layers of MIL-25_n are very close to those of the lamellar titanium(IV) phosphate αTiP (Figure 4).[19] αTiP or $Ti(HPO_4)_2 \cdot 2H_2O$ crystallizes with $a = 5.006(1)$ (1), $b = 8.630$

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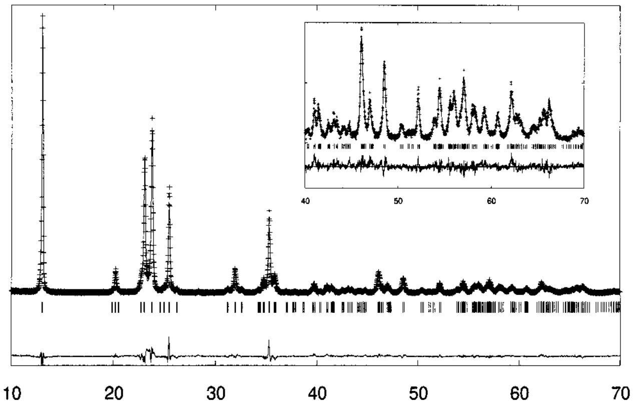

Figure 1. Final Rietveld plot of MIL-25_2. An enlargement of the 40−70° range plot is added at the top right of the figure.

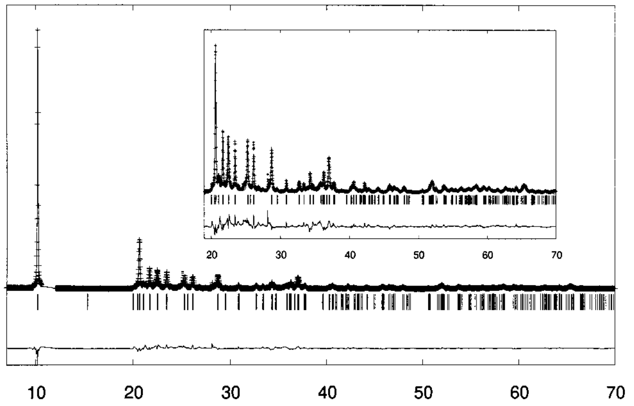

Figure 2. Final Rietveld plot of MIL-25_3. An enlargement of the 20−70° range plot is added at the top right of the figure.

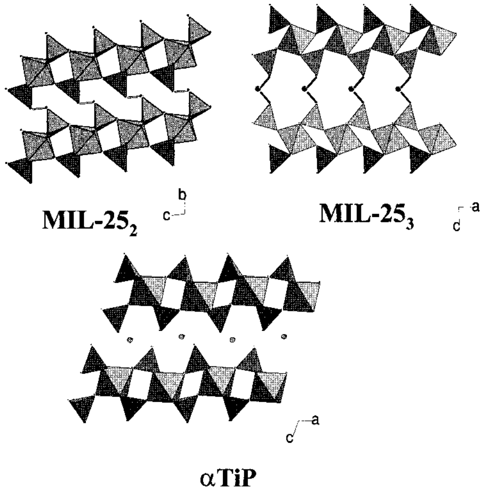

Figure 3. Comparative view of the "interlayer space" of MIL-25_n (n = 2, 3) and αTiP; in the latter case, water molecules are represented as gray circles.

(1), $c = 16.189(3)$ Å, $\beta = 110.20\ (1)°$, and space group = $P2_1/c$ (no. 14). This justifies the cell parameter relations existing between these phases: $a_1 \approx a_2 \approx a_3$ and $c_1\sin\beta_1 \approx b_2/2 \approx b_3/2$ (1 = MIL-25_2, 2 = MIL-25_3, 3 = αTiP). The water molecules located inside the interlayer spacing of αTiP are, in the case of MIL-25_n (n = 2, 3), replaced by the alkyl chains of the diphosphonate groups (Figure 3). These chains link together the inorganic sheets and ensure the three-dimensionality (Figure 3). As the distances between organic groups are short (≈4.5 Å), both compounds are not microporous.

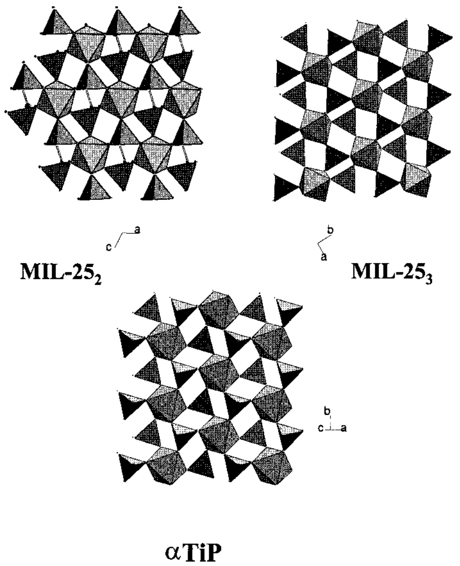

Figure 4. Comparative view of the inorganic sheets of MIL-25_n (n = 2, 3) and αTiP; in the latter case, water molecules are represented as gray circles.

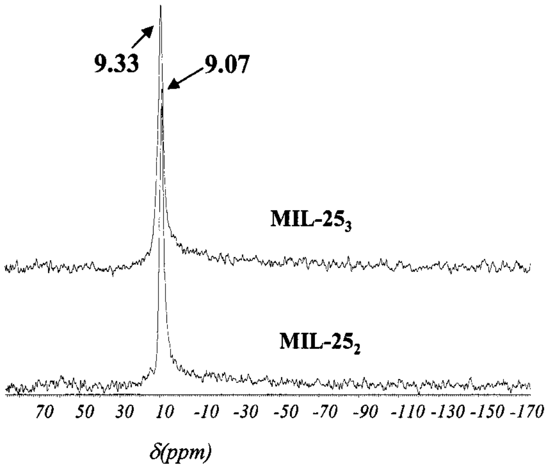

Figure 5. ^{31}P solid-state NMR spectra of MIL-25_n (n = 2, 3).

The interatomic distances are, in both cases, close to those usually reported for titanium phosphates and diphosphonates: Ti−O distances are between 1.89 and 2.07 Å while P−O distances are between 1.49 and 1.56 Å. The P−C and C−C distances are usual (respectively, in the range 1.79−1.86 Å for the former and 1.52−1.54 Å for the latter).

The structure of MIL-25_3 is noncentrosymmetric. This is due to the conformation of the alkyl chains of the diphosphonate groups inside the interlayer spacing; the chains are clearly oriented in the same direction (Figure 3), and this rules out the existence of any mirror perpendicular to the *b* axis and, thus, any center of symmetry.

Solid-state NMR ^{31}P spectra were recorded. Each phase exhibits (Figure 5) only one signal at values close to + 9 ppm; these unexpected values, compared to those usually encountered for titanium phosphates, are probably due to the electron-donor character of the $-CH_2-$ groups of the diphosphonate. Besides, as one phosphorus site is present in both cases, this is in agreement with the corresponding space groups.

MIL-25_n (n = 2, 3) are new examples of three-dimensional titanium(IV) diphosphonates that have been characterized up to now. Their structures are, however, very different from other three-dimensional titanium(IV) diphosphonate $Ti_3O_2(H_2O)_2$-

$(O_3P-CH_2-PO_3)_2\cdot 2H_2O$ or MIL-22.[9b] In case of MIL-22, methylenediphosphonic groups ($O_3P-CH_2-PO_3$) act rather like diphosphate groups, and a three-dimensional pore network is present whereas in case of MIL-25_n ($n = 2, 3$), diphosphonic groups act more like spacers, and this leads to pillared structures.

Finally, Alberti et al. recently synthesized pillared microporous zirconium compounds using phosphite and diphosphonate groups.[20] Then, as the access to pillared titanium(IV) diphosphonates is now open by using adequate chelating agents, this will hopefully lead to new microporous titanium-based materials. Other studies are currently in progress to open more the field of microporous hybrid phases based on titanium.

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