Hybrid Open Frameworks. 8. Hydrothermal Synthesis, Crystal Structure, and Thermal Behavior of the First Three-Dimensional Titanium(IV) Diphosphonate with an Open Structure: $Ti_3O_2(H_2O)_2(O_3P-(CH_2)-PO_3)_2\cdot(H_2O)_2$, or MIL-22

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$Ti_3O_2(H_2O)_2(O_3P-(CH_2)-PO_3)_2\cdot(H_2O)_2$, or MIL-22, was prepared in a pure form under hydrothermal conditions (4 days, 493 K, autogenous pressure). Its structure was determined from single-crystal X-ray diffraction data. This compound is monoclinic (space group $P2_1/c$ (no. 14)), with $a = 6.3845(2)$ Å, $b = 11.1816(4)$ Å, $c = 11.7003(5)$ Å, $\beta = 99.994(1)°$, $V = 822.60(5)$ Å^3, and $Z = 2$. Its three-dimensional structure is built up from corner-shared trimeric units of titanium(IV) octahedra linked together via diphosphonate groups. This delimits a three-dimensional network with cross-linked 10-, 7-, and 6-membered ring tunnels along *a*, *b*, and *c*, respectively, at the intersection of which free water molecules are interacting with the terminal water bound to the titanium atoms. The thermal behavior, deduced from TGA and X-ray thermodiffractometry, is described.

1. Introduction

Dense titanium phosphates are of great interest in materials science, owing to their interesting properties (ion exchange, ionic conductivity, optical activity, and so forth). However, titanium phosphates with an open framework are very scarce, with only the titanium(IV) solids $Ti_3(PO_4)_4(H_2O)_2\cdot NH_3$, $Ti_2O(PO_4)_2\cdot 2H_2O$, and $(NH_4)((Ti_2O_3)(HPO_4)_2(PO_4)_2)$, reported by Poojary et al.,[1] and, recently, $Ti^{III}Ti^{IV}(PO_4)(HPO_4)_2\cdot(H_2O)_2\cdot 0.5\ H_2N-(CH_2)_3-NH_2$, a mixed valence titanium phosphate templated by 1,3-diaminopropane, described by Sevov et al.[2]

We initiated a systematic study of the titanium fluorophosphate systems and recently reported the two first-layered oxyfluorinated titanium phosphates MIL-6 ($TiPO_4F_2\cdot 0.5N_2C_2H_{10}$ and $TiPO_4F_2\cdot 0.5N_2C_3H_{12}\ 0.5H_2O$),[3] and two new titanium phosphates with an open framework, the mixed valence MIL-15,[4] or $Ti^{III}Ti^{IV}F(PO_4)_2\cdot 2H_2O$, and MIL-18,[5] or $Ti^{IV}{}_6O_3(H_2O)_3(PO_4)_7\cdot(H_3O)_3\cdot H_2O$.

However, all these systems use organic cations as templating agents and their removal very often leads to the collapse of the inorganic framework. Some research groups, including ours, recently developed new routes for synthesizing microporous solids with an accessible porosity. The method used first diphosphonic acids instead of phosphoric acid. The inorganic part of the acid chelates the cationic species while its organic part, acting as a pillar and a spacer, links the inorganic parts together, frequently leading to pillared three-dimensional structures.[6] This method does not need any templating agent and therefore, the porosity becomes readily accessible.

During the past decade, several mono-, di-, or tri-dimensional metal phosphonates have been reported.[6−14] The contribution of our group concerned, first, several series (MIL-*n* for Materials of Institut Lavoisier) of three-dimensional rare earth diphosphonates;[9] the extension to compounds containing 3D transition metals (M = V, Fe, Ti), led to solids with various dimensionalities: open-framework vanadium diphosphonates (MIL-2,[10] -5,[11] and -7[12]), a layered iron diphosphonate (MIL-13),[13] and a monodimensional titanium(IV) or vanadium(IV) diphosphonate (MIL-10).[14] Extending the concept, our group has evidenced for the first time open-framework metallic dicarboxylates.[15−19]

This paper deals with the synthesis, crystal structure, and thermal behavior of the first three-dimensional titanium(IV) diphosphonate with an open structure: $(Ti_3O_2(H_2O)_2(O_3P-(CH_2)-PO_3)_2\cdot(H_2O)_2$ or MIL-22.

2. Experimental Section

Synthesis and Chemical 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 compound was hydrothermally synthesized (autogenous pressure for 3 days) from a mixture of hydrous TiO_2, $H_2O_3P-(CH_2)-PO_3H_2$ (Alfa, 97%), HF (Prolabo Normapur, 40%), and H_2O in the

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Table 1. Crystallographic Data of MIL-22

empirical formula	$Ti_3P_4O_{18}C_2H_{12}$
fw (g)	592
temp (K)	293 (2)
wavelength (Å)	0.71073
space group	$P2_1/c$ (No. 14)
unit cell dimensions (Å)	$a = 6.3845$ (2)
	$b = 11.1816$ (4)
	$c = 11.7003$ (5)
	$\beta(°) = 99.994$ (1)
volume (Å)	822.60 (5)
multiplicity (z)	2
calculated density (mg/cm^3)	2.390
absorption coefficient (cm^{-1})	17.56
final R indices ($I > 2$ (I))[a]	$R_1(F) = 0.0329$
	$wR_2(F^2) = 0.0712$

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

molar ratio 1:0.5:1:500 introduced in this order without stirring in a Teflon-lined steel autoclave. At 463 K, a few parallelepipedic crystals of MIL-22 appeared among a white powder corresponding to a poorly crystallized anatase. The same original mixture, treated during 4 days at 493 K, led to powder and crystals of the pure sample in a 100% yield. The pH remained strongly acidic (<1) during the reaction.

Quantitative elemental analyses indicated P/Ti, C/P, and H/Ti ratios, respectively equal to 1.30(4), 0.58(6), and 4.3(1), which is in good agreement with the theoretical values: 1.33, 0.5, and 4. A TGA experiment performed on a TA-Instrument type 2050 analyzer apparatus, under oxygen atmosphere, indicated a weight loss of 12.26% in the 273−873 K range; this corresponds to the departure of the water molecules. The infrared spectrum of the title compound clearly showed the presence of the vibrational bands characteristic of the −(P−O−Ti)−groups around 1100 cm^{-1}; the bands at 2980 and 2915 cm^{-1} also indicated the presence of CH_2 groups characteristic of the organic part of the diphosphonate agents.

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.

Structure Determination. A parallelepipedic single crystal suitable for data collection was glued with Araldite on a glass fiber. The intensity data were collecteded on a Bruker-Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector. The crystal-to-detector was kept to 45 mm, allowing a data collection up to 65° (2θ). Data were recorded in a bit more than a hemisphere (Table 1). An empirical absorption correction was then applied using the SADABS program,[20] based on the method of Blessing.[21] The cell is monoclinic, space group $P2_1/c$ (No. 14), with $a = 6.3845(2)$ Å, $b = 11.1816(4)$ Å, $c = 11.7003(5)$ Å, $b = 99.994(1)°$, and $V = 822.60(5)$ Å^3. The structure was solved using the SHELXTL package.[22] Titanium and phosphorus atoms were located first, while the oxygen, carbon, and hydrogen atoms were found using difference Fourier maps. The final reliability factors converged to $R_1(F) = 0.033$ and $wR_2(F^2) = 0.071$. The formula deduced from the structure determination $Ti_3O_2(H_2O)_2(O_3P-(CH_2)-PO_3)_2\cdot(H_2O)_2$ agrees well with chemical results. Atomic coordinates are listed in Table 2, while bond distances are given in Table 3. The indexed powder pattern is reported in Table 4.

Table 2. Atomic Coordinates ($^*10\wedge4$) and Equivalent Isotropic Displacement Parameters ($*10\wedge3$) (Å^2) for MIL-22[a]

atom	x	y	z	U(eq)
Ti(1)	7822(1)	7153(1)	−85(1)	9(1)
Ti(2)	0	10000	0	11(1)
P(3)	8982(1)	8440(1)	−2289(1)	12(1)
P(4)	2525(1)	7675(1)	−498(1)	10(1)
O(1)	7595(3)	7566(2)	−1742(2)	13(1)
O(2)	2422(3)	8933(2)	26(2)	13(1)
O(3)	8167(3)	6377(2)	1429(2)	13(1)
O(4)	4753(3)	7174(2)	−230(2)	15(1)
O(5)	10950(3)	6834(2)	−47(2)	13(1)
O(6)	8349(3)	8639(2)	359(2)	12(1)
O(7)	886(3)	10344(2)	1657(2)	12(1)
$O_W(1)$	7397(4)	5390(2)	−759(2)	23(1)
$O_W(2)$	5648(5)	5241(3)	−2978(3)	38(1)
C	11629(4)	7809(3)	−2039(2)	14(1)

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

Table 3. Principal Bond Lengths for MIL-22[a]

Ti(1)−O(6)	1.756(2)	Ti(1)−O(4)	1.938(2)
Ti(1)−O(3)	1.950(2)	Ti(1)−O(1)	1.974(2)
Ti(1)−O(5)	2.021(2)	Ti(1)−O_w(1)	2.124(2)
Ti(2)−O(6)#1	1.939(2) (*2)	Ti(2)−O(2)#3	1.949(2) (*2)
Ti(2)−O(7)#3	1.961(2) (*2)		
P(3)−O(3)#4	1.514(2)	P(3)−O(1)	1.531(2)
P(3)−O(7)#7	1.543(2)	P(3)−C	1.807(3)
P(4)−O(4)	1.510(2)	P(4)−O(5)#2	1.536(2)
P(4)−O(2)	1.541(2)	P(4)−C#2	1.801(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 2, -z$; #2 $x - 1, y, z$; #3 $-x, -y + 2, -z$; #4 $x, -y + 3/2, z - 1/2$; #5 $x, -y + 3/2, z + 1/2$; #6 $x + 1, y, z$.

Table 4. Indexed Powder Pattern of MIL-22[a]

h k l	2θ obs.	2θ calc.	d*hkl* (Å)	int.
0 1 1	11.016	11.016	8.025	56
1 0 0	14.075	14.073	6.388	87
0 0 2	15.359	15.366	5.761	100
0 2 0	15.834	15.838	5.591	52
1 1 0	16.150	16.158	5.481	30
−1 1 1	16.818	16.815	5.268	26
0 1 2	17.291	17.300	5.121	56
0 2 1	17.615	17.617	5.030	28
1 1 1	18.920	18.937	4.682	7
−1 2 1	21.762	21.247	4.178	59
0 2 2	22.136	22.136	4.012	70
−1 2 2	24.824	24.818	3.584	30
0 3 1	25.097	25.089	3.546	19
0 2 3	28.161	28.163	3.166	14
2 0 0	28.346	28.364	3.144	17
−2 1 1	29.204	29.204	3.055	20
−2 1 0	29.507	29.489	3.026	14
−2 0 2	29.912	29.896	2.986	3
1 1 3	30.334	30.344	2.943	9
0 0 4	31.032	31.017	2.881	55
0 1 4	32.008	31.989	2.795	14
2 2 0	32.649	32.650	2.740	23
0 4 1	32.963	32.943	2.717	10
0 3 3	33.506	33.472	2.675	12
−2 2 2	33.973	34.006	2.634	7

[a] The indexing is based on a monoclinic cell with the dimensions: $a = 6.3845$ (2) Å, $b = 11.1816$ (4) Å, $c = 11.7003$ (1) Å, $\beta = 99.994$ (1) SG: $P2_1/c$ (No. 14).

3. Description of the Structure and Discussion

MIL-22 is three-dimensional (Figure 1). The structure is built up from the corner-sharing of TiO_6, $TiO_5(H_2O)$ octahedra, and $(PO_3-CH_2-PO_3)$ groups, with two types of linkage: Ti−O−Ti and Ti−O−P. The titanium octahedral subnetwork consists of trimeric units $Ti_3O_{16}(H_2O)_2$ with an almost regular ($\langle Ti(2)-O\rangle = 1.95$ Å) central $Ti(2)O_6$ octahedron linked by trans vertices O(6) to two $Ti(1)O_5(H_2O)$ octahedra (Figure 2a). In the latter, Ti(1)−O(6) corresponds to the titanyl bond (1.75 Å), opposite to the long Ti(1)−O_w(1) one (2.12 Å), while the others take usual values (1.94 Å). The diphosphonate units share all their oxygen atoms with the titanium ones (P−O distances in the range 1.51−1.54 Å), and the P−C distance is usual (1.81 Å).

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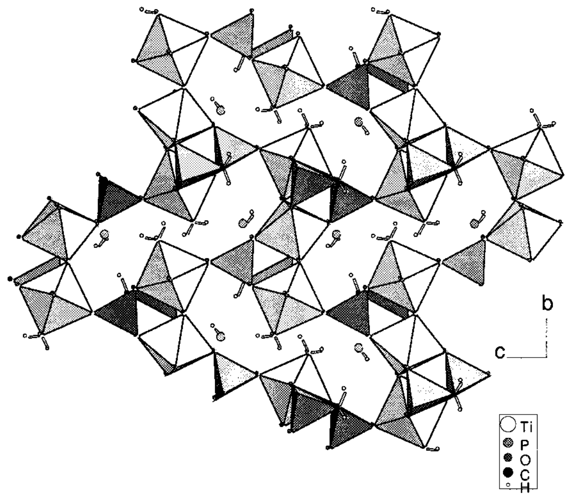

Figure 1. View of the structure of MIL-22 along the *a* axis.

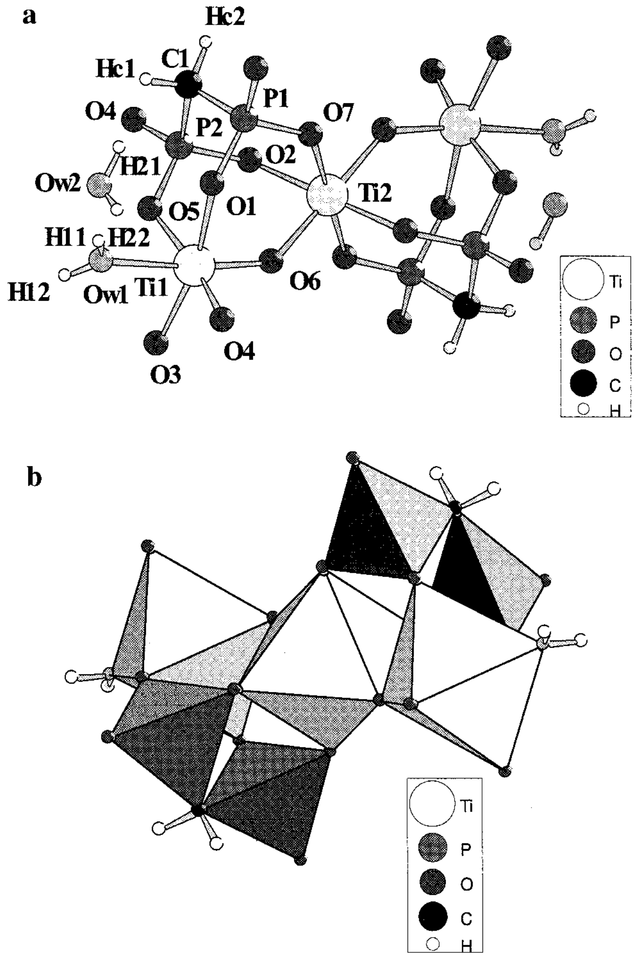

Figure 2. Secondary building unit (SBU) of MIL-22 in a balls-and-stick (a) and polyhedral representation (b).

Two diphosphonic groups, grafted to the trimer, produce the secondary building unit (SBU) of the framework of MIL-22 (Figure 2b). The connection of these SBUs by corners build the framework in such a way that, in the cationic subnetwork, Ti(2) has two Ti(1) and four P(1,2) neighbors, Ti(1) has one Ti(2) and four P(1,2) neighbors, and each phosphorus is surrounded by three Ti and one P. This topology defines three kinds of channels along *a*, *b* and *c*: corrugated S-shaped 10-membered ring channels with six Ti and four P along the (100) axis (Figure 1) and, respectively, seven- (three Ti and four P) and six-membered ring channels (four Ti and two P) along the *b* and *c* axis (Figures 3 and 4). Water molecules $O_w(2)$ are located at the intersection of these channels. They strongly interact (Figure 2a) via hydrogen bonds ($d(H(11)-O_w(2)) = 1.88$ Å) with the terminal water molecules bound to Ti(1), which point toward the tunnels. If free water is located into small cavities, the shortest distances between oxygen or carbon atoms delimiting the tunnels are 4.46, 3.75, and 3.77 Å for each tunnel along the *a*, *b*, and *c* direction, respectively. This indicates a very low porosity for this compound. The departure of water molecules might thus allow the inclusion of small guest molecules.

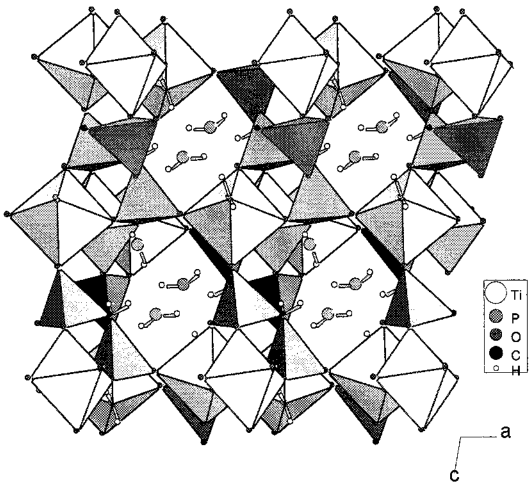

Figure 3. Ti−P network of MIL-22 along the *b* axis, showing the seven-membered rings. Water molecules are represented as gray spheres and hydrogen atoms as small white ones.

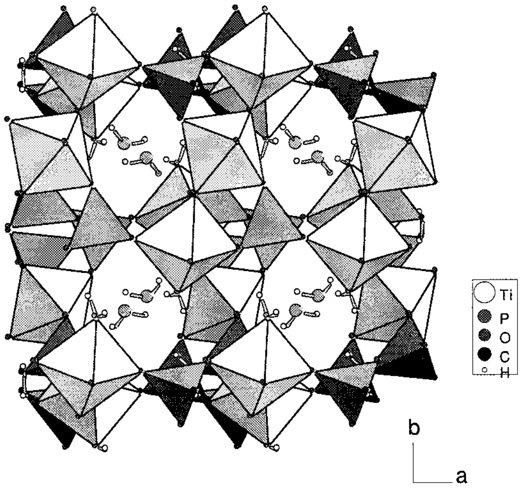

Figure 4. Ti−P network of MIL-22 along the *c* axis, showing the six-membered rings. Water molecules are represented as gray spheres and hydrogen atoms as small white ones.

The thermal stability of MIL-22 is interestingly high compared to other phosphonates. The TGA measurements, performed between 293 and 873 K under oxygen atmosphere, show (inset of Figure 5) a quasi-one-step total weight loss of 12.26%, just achieved at 873 K, which corresponds to the departure of all the water molecules (theor. value: 12.85%). One could expect, however, a two-step decomposition owing to the two different structural situations of the water molecules in the initial solid. This was revealed by the X-ray thermodiffractogram of MIL-22 (Figure 5), performed under oxygen atmosphere up to 1073 K. Indeed, the evolution of the patterns shows several slight structural changes below 873 K. Even if, up to this

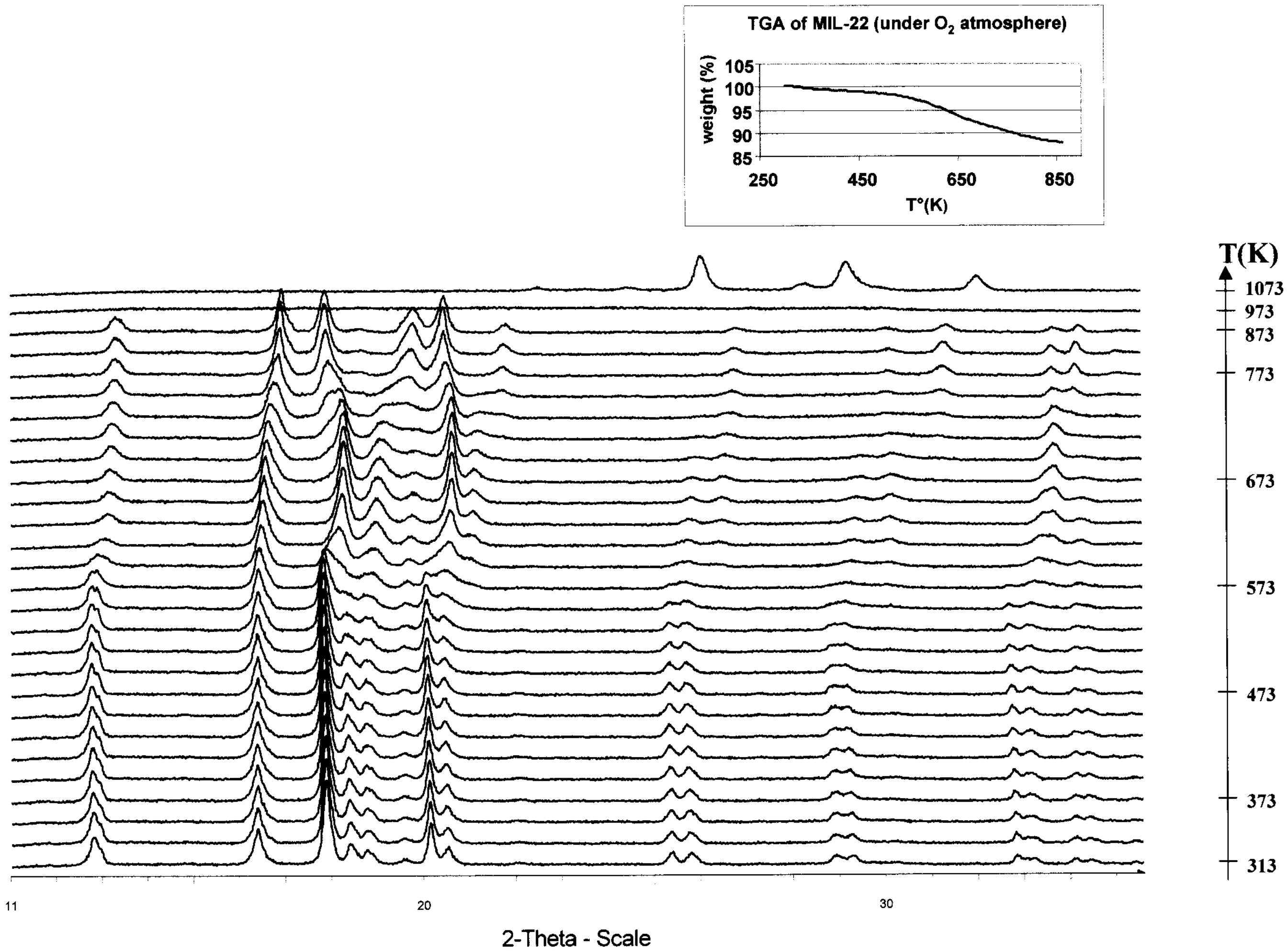

Figure 5. X-ray thermodiffractogram of MIL-22 under O_2 atmosphere. The TGA curve of MIL-22 is represented as an inset.

temperature, the pattern is kept up on the whole, a first structural change occurs above 573 K. It corresponds to the departure of the free water molecules with a slight correlative cell contraction as illustrated by the decrease of d_{110} from 8 to 7.75 Å. Two other structural modifications occur at higher temperatures, between 673 and 773 K, probably related to a two-step departure of the terminal water molecules bound to the titanium atom. The bad quality of the patterns prevents any structural refinement of the high-temperature dehydrated forms. However, it may be assumed that the skeleton is roughly kept during the thermal treatment. In a first step, the water molecules in the tunnels evolve the structure. Their extraction occurs at a rather high temperature, owing to the strong hydrogen bonds evidenced by the structural study. Above 673 K, the second loss of water affects the coordination of Ti(1), which becomes square pyramidal with probably some slight distortions of the framework. Both rehydration steps are slowly reversible. The title compound heated at 573 or 773 K during a few hours and cooled to room temperature still exhibits, 1 day after, the pattern of the dehydrated phase. After 1 month at 300 K, the diagram corresponds to the as-synthesized phase.

At higher temperatures, between 873 and 973 K, MIL-22 collapses. By further heating, the crystallization of the amorphous product leads to the titanium(IV) diphosphate: TiP_2O_7 with no evidence of TiO_2, expected from the formula. The existence of diphosphate groups reveals a certain structural memory. The departure of the carbon between the two P atoms probably occurs at temperatures between 873 and 1073 K, collapsing the structure, but the short-range topology is kept and the further heating under O_2 atmosphere leads to the diphosphate.

MIL-22 is the first three-dimensional titanium(IV) diphosphonate with an open structure characterized up to now. Its good thermal resistance needs to be studied, mainly for testing its porous character at high temperatures. Other, similar compounds have recently been synthesized in our group, and their study is currently in progress to expand the field of microporous hybrid phases based on titanium.

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Supporting Information Available: Tables showing crystallographic data, atomic coordinates and equivalent isotropic displacemtn parameters, anistropic displacement parameters, bond lengths, and intramolecular angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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