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Hydrothermal Synthesis and Characterization of Two New Three-Dimensional Titanium Phosphates

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Two new three-dimensional titanium phosphates with the formulas $Ti_2(HPO_4)_3(PO_4)\cdot 0.5C_4N_2H_{12}$ (**1**) and $Ti_7(HPO_4)_6(PO_4)_6\cdot C_6N_2H_{14}$ (**2**) have been prepared hydrothermally from titanium powder, phosphoric acid, and structure-directing organic amines. The as-synthesized products were characterized by powder X-ray diffraction, IR spectroscopy, thermogravimetric, and differential thermal analyses (TG-DTA). The structures were solved by single-crystal X-ray diffraction analysis. Crystal data are as follows: $Ti_2(HPO_4)_3(PO_4)\cdot 0.5C_4N_2H_{12}$ (**1**), monoclinic, space group $P2_1/n$ (no. 14), $a = 10.7455(11)$ Å, $b = 6.3469(6)$ Å, $c = 20.4800(19)$ Å, $\beta = 104.286(3)°$, $V = 1353.6(2)$ Å^3, $Z = 4$; $Ti_7(HPO_4)_6(PO_4)_6\cdot C_6N_2H_{14}$ (**2**), trigonal, space group R-3 (no. 148), $a = 16.8640(14)$ Å, $b = 16.8640(14)$ Å, $c = 12.334(2)$ Å, $V = 3037.7(6)$ Å^3, $Z = 3$. Both structures are of the open-framework type, and the frameworks are built from TiO_6 octahedra and PO_4, $PO_3(OH)$, and/or $PO_2({=}O)(OH)$ tetrahedral units. There exist eight-membered ring channels, in which the diprotonated organic amine molecules are entrapped along the [010] direction for **1** and along the [001] direction for **2**.

Introduction

During the past decade, considerable efforts have been directed toward the preparation of open-framework metal phosphates that might find applications in catalysis, adsorption, ionic conduction, ion exchange, electronics and optoelectronics. After the discovery of microporous crystalline aluminophosphates,[1−3] a large number of new metal phosphates with open frameworks have appeared in the literature, with metals including gallium,[4] indium,[5,6] zinc,[7,8] iron,[9] tin,[10] vanadium,[11−13] and molybdenum.[14]

The titanium phosphate compounds are of special interest. For example, the well-known α-$Ti(HPO_4)_2\cdot H_2O$[15,16] and γ-$Ti(H_2PO_4)(PO_4)\cdot 2H_2O$[17] compounds have been investigated extensively for their ion-exchange properties and for their use in preparing organically or inorganically pillared materials. Potassium titanyl phosphate ($KTiOPO_4$, KTP) has attracted considerable attention because of its high nonlinear optical coefficient, high optical damage threshold, and low phase matching temperature sensitivity.[18,19] However, only a few titanium phosphate compounds with open-framework structures have been synthesized and structurally characterized. Three new layered titanium phosphates with the formulas $TiO(OH)(H_2PO_4)\cdot 2H_2O$,[20] $Ti_2O_3(H_2PO_4)_2\cdot 2H_2O$,[21] and β-$Ti(PO_4)(H_2PO_4)$[22] were recently prepared. Clearfield and co-workers reported the synthesis and structures of three porous titanium phosphates,[23] and recently, two organically templated mixed-valent Ti^{III}/Ti^{IV} phosphates with open-framework structures were also discovered.[24,25] Férey and co-workers reported the

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synthesis and ab initio structure determination of a new three-dimensional mixed-valence oxyfluorinated titanium phosphate MIL-15 and two layered oxyfluorinated titanium phosphates.[26,27]

In recent years, we have devoted effort toward hydrothermal and solvothermal syntheses in titanium-containing systems to obtain possible new types of materials with valuable properties.[28−31] We have prepared two novel titanosilicates, JDF-L1 (a layered titanosilicate with five-coordinate Ti atoms)[28] and JLU-1 (a novel microporous titanosilicate),[29] as well as a novel titanium phosphate TP-J1 (a layered titanium phosphate prepared under solvothermal conditions, with a structure consisting of infinite Ti−O−Ti chains).[30] In this paper, we describe the hydrothermal syntheses and X-ray crystal structures of two new three-dimensional titanium phosphates.

Experimental Section

Synthesis. All reagents were of analytical grade. The two compounds were hydrothermally prepared from a starting mixture containing piperazine (for compound **1**) and 1,4-diazabicyclo[2.2.2]octane (Dabco) (for compound **2**) as the structure-directing agent. For **1**, titanium powder, phosphoric acid (85 wt %), piperazine, and distilled water were mixed in the molar ratio 1:10.5:1:40. For **2**, titanium powder, phosphoric acid, 1,4-diazabicyclo[2.2.2]octane, and distilled water were mixed in the molar ratio 1:45:1.2:14. The mixture was sealed in a 40-mL Teflon-lined stainless steel autoclave with a filling capacity of ~70% and heated at 513 K for 5 days for **1** and for 6 days for **2** under autogenous pressure. The resulting platelike crystals for compound **1** and cubic crystals for compound **2** were recovered by filtration, washed thoroughly with distilled water, and dried at room temperature.

Characterization. The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) with a graphite monochromator. The step size was 0.02°, and the count time was 4 s. The element analyses were performed on a Perkin-Elmer 2400 element analyzer, and the inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300 DV ICP spectrometer. The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were conducted on a Perkin-Elmer TGA 7 thermogravimetric analyzer and a Perkin-Elmer DTA 1700 differential thermal analyzer, respectively, in air with a heating rate of 10 °C min^{-1}.

Determination of Crystal Structures. A suitable single crystal for each compound was selected and mounted on a glass fiber using cyanoacrylate. The data collection and the structural analysis were performed on a Bruker Smart CCD diffractometer equipped with a normal-focus, 2.4-kW sealed-tube X-ray source (graphite-monochromated Mo Kα radition, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° and exposure time of 30 s per frame). The data processing was accomplished with the SAINT processing program.[32] The structure was solved by direct methods and refined by a full-matrix least-squares approach on F^2 using SHELXTL, version 5.1.[33] For compound **1**, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the amine molecule were placed geometrically ($d_{N-H} = 0.90$ Å, $d_{C-H} = 0.97$ Å) and allowed to ride on the atoms to which they were attached with fixed isotropic thermal parameters. For **2**, because of the disordering of the carbon and nitrogen atoms of the amine molecule, hydrogen atoms attached to the nitrogen and carbon atoms were not located. All non-hydrogen atoms except for C and N were refined anisotropically. The experimental X-ray data for structures **1** and **2** are listed in Table 1, atomic coordinates with isotropic temperature factors are listed in Tables 2 and 3, and selected bond lengths and angles are given in Tables 4 and 5.

Table 1. Summary of Crystal Data for $Ti_2(HPO_4)_3(PO_4)\cdot 0.5C_4N_2H_{12}$ and $Ti_7(HPO_4)_6(PO_4)_6\cdot C_6N_2H_{14}$

	1	2
empirical formula	$C_2H_9NO_{16}P_4Ti_2$	$C_6H_{20}N_2O_{48}P_{12}Ti_7$
formula weight	522.78	1595.18
crystal system	monoclinic	trigonal
space group	$P2_1/n$	$R3$
a (Å)	10.7455(11)	16.8640(14)
b (Å)	6.3469(6)	16.8640(14)
c (Å)	20.4800(19)	12.334(2)
α (°)	90	90
β (°)	104.286(3)	90
γ (°)	90	120
V (Å^3)	1353.6(2)	3037.7(6)
Z	4	3
D_{calc} (g cm^{-3})	2.565	2.616
λ (Å)	0.71073	0.71073
μ (mm^{-1})	1.752	1.938
crystal size (mm)	0.10 × 0.08 × 0.02	0.25 × 0.25 × 0.25
θ range (°)	1.97−23.24	2.16−23.19
data/restraints/parameters	1929/0/226	966/0/112
final R indices [$I > 2\sigma(I)$] R_1,[a] wR_2[b]	0.0501, 0.0971	0.0425, 0.1215

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

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 1

	x	y	z	U (equiv)[a]
Ti(1)	8906(1)	351(2)	2003(1)	11(1)
Ti(2)	10967(2)	−4570(2)	3935(1)	11(1)
P(1)	11723(2)	1716(3)	1777(1)	17(1)
P(2)	8838(2)	−4623(3)	2430(1)	9(1)
P(3)	10252(2)	−9512(3)	3665(1)	11(1)
P(4)	8202(2)	−4184(3)	4468(1)	10(1)
O(1)	8884(5)	−2704(7)	1990(3)	14(1)
O(2)	8022(5)	289(8)	1056(3)	16(1)
O(3)	8877(5)	3429(7)	2005(3)	12(1)
O(4)	9971(5)	310(8)	2915(3)	18(1)
O(5)	7347(5)	380(7)	2300(3)	13(1)
O(6)	10497(5)	460(8)	1710(3)	19(1)
O(7)	10025(5)	−4597(7)	3028(3)	14(1)
O(8)	10865(6)	−1517(8)	4012(3)	17(2)
O(9)	11878(5)	−4681(8)	4889(3)	15(1)
O(10)	11138(5)	−7644(7)	3919(3)	15(2)
O(11)	12557(6)	−4301(8)	3701(3)	17(1)
O(12)	9344(5)	−4868(8)	4218(3)	17(1)
O(13)	12534(6)	1757(8)	2509(3)	24(2)
O(14)	11458(6)	4013(7)	1572(3)	21(2)
O(15)	8976(6)	−9155(8)	3870(3)	25(2)
O(16)	8245(6)	−1816(7)	4631(3)	21(2)
N(1)	11338(7)	5353(12)	254(4)	33(2)
C(1)	10403(10)	7065(13)	234(5)	31(3)
C(2)	10833(11)	3798(15)	−281(6)	40(3)

[a] U (equiv) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Synthesis and Characterization. The formation of titanium phosphates has been shown sensitive to the

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2

	x	*y*	*z*	*U* (equiv)[a]
Ti(1)	3241(1)	1016(1)	8376(1)	14(1)
Ti(2)	0	0	5000	20(1)
P(1)	1948(1)	453(1)	6304(1)	14(1)
P(2)	2580(1)	−732(1)	10049(1)	15(1)
O(1)	2109(2)	599(2)	7529(3)	17(1)
O(2)	3899(2)	2101(2)	7595(3)	20(1)
O(3)	2862(2)	1680(2)	9332(3)	19(1)
O(4)	2577(2)	−30(2)	9291(3)	22(1)
O(5)	3633(3)	366(3)	7468(3)	26(1)
O(6)	4321(2)	1437(2)	9327(3)	20(1)
O(7)	1069(2)	434(2)	5963(3)	21(1)
O(8)	2644(3)	−1463(3)	9343(4)	35(1)
C(1)	592(12)	855(12)	276(15)	58(4)
C(2)	964(11)	280(11)	607(15)	58(4)
N(1)	0	0	1320(60)	420(40)

[a] *U* (equiv) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected Bond Lengths (Å) and Angles (°) for 1

Ti(1)−O(5)	1.918(5)	Ti(2)−O(7)	1.884(6)
Ti(1)−O(4)	1.936(6)	Ti(2)−O(11)	1.893(6)
Ti(1)−O(2)	1.937(6)	Ti(2)−O(8)	1.949(5)
Ti(1)−O(1)	1.939(5)	Ti(2)−O(9)	1.959(6)
Ti(1)−O(6)	1.948(5)	Ti(2)−O(10)	1.961(5)
Ti(1)−O(3)	1.954(5)	Ti(2)−O(12)	1.978(5)
P(1)−O(6)	1.517(6)	P(2)−O(5)^b	1.509(5)
P(1)−O(14)	1.524(5)	P(2)−O(3)^c	1.518(5)
P(1)−O(11)^a	1.532(5)	P(2)−O(1)	1.523(5)
P(1)−O(13)	1.538(6)	P(2)−O(7)	1.535(6)
P(3)−O(4)^c	1.495(6)	P(4)−O(12)	1.505(6)
P(3)−O(8)^c	1.525(6)	P(4)−O(2)^b	1.516(6)
P(3)−O(10)	1.528(5)	P(4)−O(9)^d	1.522(5)
P(3)−O(15)	1.546(6)	P(4)−O(16)	1.538(5)
O(5)−Ti(1)−O(4)	92.8(2)	O(7)−Ti(2)−O(11)	92.8(2)
O(5)−Ti(1)−O(2)	93.8(2)	O(7)−Ti(2)−O(8)	93.5(2)
O(4)−Ti(1)−O(2)	173.1(2)	O(11)−Ti(2)−O(8)	90.2(2)
O(5)−Ti(1)−O(1)	90.3(2)	O(7)−Ti(2)−O(9)	176.5(2)
O(4)−Ti(1)−O(1)	90.1(2)	O(11)−Ti(2)−O(9)	89.7(2)
O(2)−Ti(1)−O(1)	88.0(2)	O(8)−Ti(2)−O(9)	88.8(2)
O(5)−Ti(1)−O(6)	177.3(2)	O(7)−Ti(2)−O(10)	90.2(2)
O(4)−Ti(1)−O(6)	86.7(2)	O(11)−Ti(2)−O(10)	89.5(2)
O(2)−Ti(1)−O(6)	86.8(2)	O(8)−Ti(2)−O(10)	176.3(2)
O(1)−Ti(1)−O(6)	92.3(2)	O(9)−Ti(2)−O(10)	87.4(2)
O(5)−Ti(1)−O(3)	88.5(2)	O(7)−Ti(2)−O(12)	89.4(2)
O(4)−Ti(1)−O(3)	90.9(2)	O(11)−Ti(2)−O(12)	177.7(2)
O(2)−Ti(1)−O(3)	91.1(2)	O(8)−Ti(2)−O(12)	90.0(2)
O(1)−Ti(1)−O(3)	178.5(2)	O(9)−Ti(2)−O(12)	88.0(2)
O(6)−Ti(1)−O(3)	88.9(2)	O(10)−Ti(2)−O(12)	90.2(2)
O(6)−P(1)−O(14)	112.3(3)	O(5)^b−P(2)−O(3)^c	110.9(3)
O(6)−P(1)−O(11)^a	106.5(3)	O(5)^b−P(2)−O(1)	111.7(3)
O(14)−P(1)−O(11)^a	108.4(3)	O(3)^c−P(2)−O(1)	107.6(3)
O(6)−P(1)−O(13)	111.6(3)	O(5)^b−P(2)−O(7)	108.6(3)
O(14)−P(1)−O(13)	106.0(3)	O(3)^c−P(2)−O(7)	109.3(3)
O(11)^a−P(1)−O(13)	112.1(4)	O(1)−P(2)−O(7)	108.8(3)
O(4)^c−P(3)−O(8)^c	111.7(3)	O(12)−P(4)−O(2)^b	109.5(3)
O(4)^c−P(3)−O(10)	111.0(3)	O(12)−P(4)−O(9)^d	112.5(3)
O(8)^c−P(3)−O(10)	109.2(3)	O(2)^b−P(4)−O(9)^d	106.4(3)
O(4)^c−P(3)−O(15)	108.8(3)	O(12)−P(4)−O(16)	111.9(3)
O(8)^c−P(3)−O(15)	107.8(3)	O(2)^b−P(4)−O(16)	110.1(3)
O(10)−P(3)−O(15)	108.3(3)	O(9)^d−P(4)−O(16)	106.3(3)

[a−d] The following symmetry transformations were used to generate equivalent atoms: (a) $-x + {}^5/_2, y + {}^1/_2, -z + {}^1/_2$; (b) $-x + {}^3/_2, y - {}^1/_2, -z + {}^1/_2$; (c) $x, y - 1, z$; (d) $-x + 2, -y - 1, -z + 1$.

Table 5. Selected Bond Lengths (Å) and Angles (°) for 2

Ti(1)−O(2)	1.865(4)	Ti(2)−O(7)^a	1.969(4)
Ti(1)−O(5)	1.903(4)	Ti(2)−O(7)	1.969(4)
Ti(1)−O(4)	1.915(4)	Ti(2)−O(7)^b	1.969(4)
Ti(1)−O(3)	1.940(4)	Ti(2)−O(7)^c	1.969(4)
Ti(1)−O(1)	1.971(4)	Ti(2)−O(7)^d	1.969(4)
Ti(1)−O(6)	1.976(4)	Ti(2)−O(7)^e	1.969(4)
P(1)−O(2)^f	1.518(4)	P(2)−O(4)	1.509(4)
P(1)−O(7)	1.526(4)	P(2)−O(5)^h	1.515(4)
P(1)−O(6)^g	1.530(4)	P(2)−O(3)^i	1.521(4)
P(1)−O(1)	1.534(4)	P(2)−O(8)	1.557(4)
O(2)−Ti(1)−O(5)	93.06(17)	O(7)^a−Ti(2)−O(7)	180.00(16)
O(2)−Ti(1)−O(4)	174.74(16)	O(7)^a−Ti(2)−O(7)^b	87.33(16)
O(5)−Ti(1)−O(4)	91.57(16)	O(7)−Ti(2)−O(7)^b	92.67(16)
O(2)−Ti(1)−O(3)	87.38(15)	O(7)^a−Ti(2)−O(7)^c	87.33(16)
O(5)−Ti(1)−O(3)	178.48(16)	O(7)−Ti(2)−O(7)^c	92.67(16)
O(4)−Ti(1)−O(3)	87.92(15)	O(7)^b−Ti(2)−O(7)^c	87.33(16)
O(2)−Ti(1)−O(1)	94.13(15)	O(7)^a−Ti(2)−O(7)^d	92.67(16)
O(5)−Ti(1)−O(1)	92.07(15)	O(7)−Ti(2)−O(7)^d	87.33(16)
O(4)−Ti(1)−O(1)	88.17(15)	O(7)^b−Ti(2)−O(7)^d	180.00(18)
O(3)−Ti(1)−O(1)	89.35(15)	O(7)^c−Ti(2)−O(7)^d	92.67(16)
O(2)−Ti(1)−O(6)	87.97(15)	O(7)^a−Ti(2)−O(7)^e	92.67(16)
O(5)−Ti(1)−O(6)	91.87(15)	O(7)−Ti(2)−O(7)^e	87.33(16)
O(4)−Ti(1)−O(6)	89.40(15)	O(7)^b−Ti(2)−O(7)^e	92.67(16)
O(3)−Ti(1)−O(6)	86.69(15)	O(7)^c−Ti(2)−O(7)^e	180.00(18)
O(1)−Ti(1)−O(6)	175.43(15)	O(7)^d−Ti(2)−O(7)^e	87.33(16)
O(2)^f−P(1)−O(7)	110.3(2)	O(5)^h−P(2)−O(8)	108.3(2)
O(2)^f−P(1)−O(6)^g	108.7(2)	O(3)^i−P(2)−O(8)	109.5(2)
O(7)−P(1)−O(6)^g	109.8(2)	O(4)−P(2)−O(5)^h	111.2(2)
O(2)^f−P(1)−O(1)	107.6(2)	O(4)−P(2)−O(3)^i	108.0(2)
O(7)−P(1)−O(1)	111.5(2)	O(5)^h−P(2)−O(3)^i	112.0(2)
O(6)^g−P(1)−O(1)	108.8(2)	O(4)−P(2)−O(8)	107.7(2)

The following symmetry transformations were used to generate equivalent atoms: (a) $-x, -y, -z + 1$; (b) $y, -x + y, -z + 1$; (c) $x - y, x, -z + 1$; (d) $-y, x - y, z$; (e) $-x + y, -x, z$; (f) $-x + {}^2/_3, -y + {}^1/_3, -z + {}^4/_3$; (g) $-y + {}^1/_3, x - y - {}^1/_3, z - {}^1/_3$; (h) $-x + y + {}^2/_3, -x + {}^1/_3, z + {}^1/_3$; (i) $y, -x + y, -z + 2$.

organic templates. When diamines such as ethylenediamine, 1,2-diaminopropane, 1,4-diaminobutane, piperazine, 1,4-diazabicyclo[2.2.2]octane, and imidazole are used as the templates, a series of open-framework titanium phosphates can be obtained. A number of monoamines such as ethylamine, isopropylamine, triethylamine, and diisopropylamine were also tried in our synthetic system, but no organically templated titanium phosphates were prepared. Several other open-framework titanium phosphates were also prepared in the presence of diamines.[24−26] It seems that the presence of diamines is crucial for the formation of open-framework titanium phosphates. Crystallization temperature (180−240 °C) has no obvious influence on the products; it only affects the crystallization time. Interestingly, the use of titanium powder is essential to the synthesis of the titanium phosphates. When we used tetrabutyltitanium (TBOT), $TiCl_3$, or $TiCl_4$ as the titanium source, we could not obtain the titanium phosphate products. This phenomenon has been noted in the preparation of another two organically templated mixed-valence titanium phosphates.[24,25]

The powder XRD patterns of the as-synthesized compounds **1** and **2** with those simulated on the basis of the single-crystal structure are presented in Figure 1. For **1** and **2**, the diffraction peaks on both patterns correspond well in position, indicating the phase purity of the as-synthesized sample. The differences in reflection intensity are probably due to preferred orientation in the powder samples. The ICP and elemental analysis results are also in good agreement with the values based on the single-crystal structure analysis. Calcd for **1**: Ti, 18.32; P, 23.72; C, 4.59; H, 1.72; N, 2.68. Found: Ti, 18.10; P, 23.50; C, 4.55; H, 1.63; N, 2.61. Calcd for **2**: Ti, 21.00; P, 23.32; C, 4.51; H, 1.25; N, 1.75. Found: Ti, 20.41; P, 23.01; C, 4.70; H, 1.17; N, 2.03.

The IR spectrum of **1** (Figure 2) clearly shows two typical sharp peaks for piperazine at 1602 and 1464 cm^{-1}, and the broad bands at 920 and 1045 cm^{-1} are associated with the asymmetric stretching vibrations of

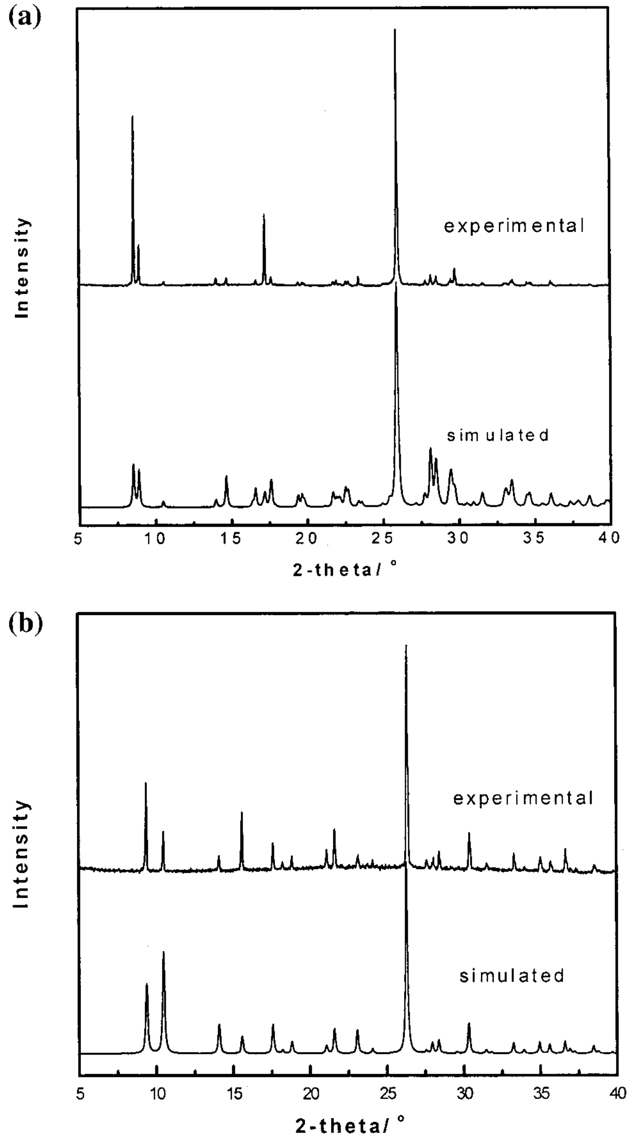

Figure 1. Experimental and simulated powder X-ray diffraction patterns of (a) **1** and (b) **2**.

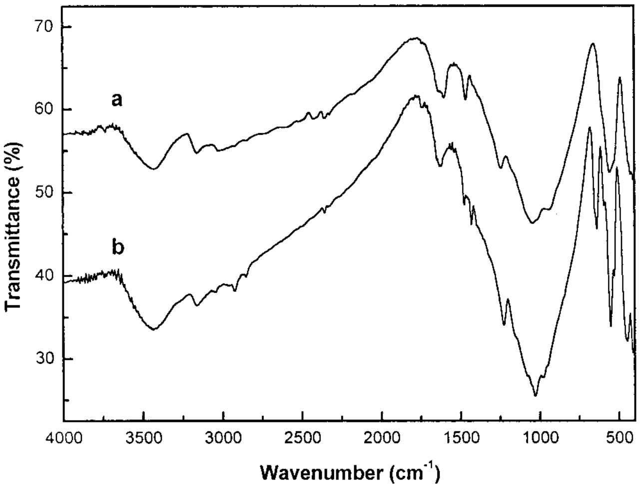

Figure 2. IR spectra of (a) **1** and (b) **2**.

PO_4 units. An absorption at 558 cm^{-1} appears as well, which is due to bending vibrations of phosphate groups. The broad bands observed at 3430, 3161, and 3023 cm^{-1} correspond to the combination and overlapping of the stretching vibrations of NH_2^+ and CH_2 groups. The

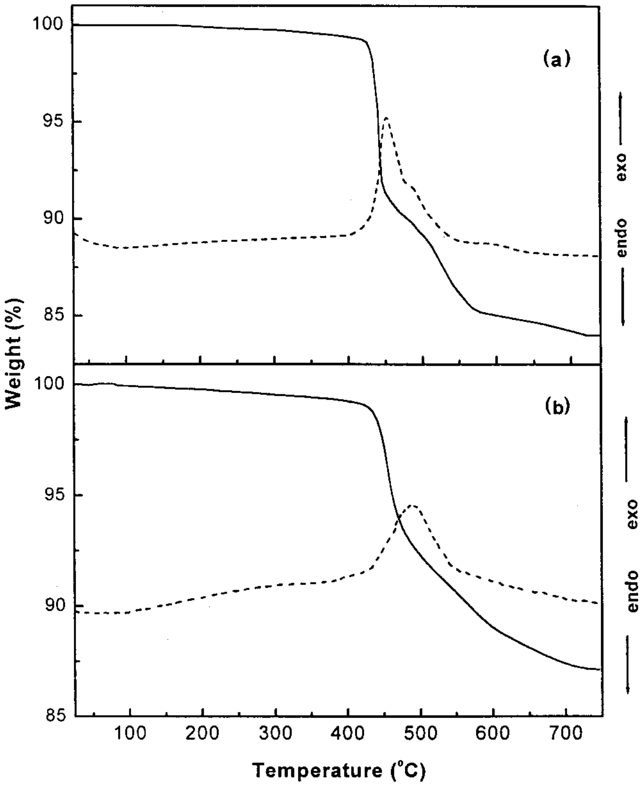

Figure 3. TGA (—) and DTA (- - -) curves for (a) **1** and (b) **2**.

absorption bands of compound **2** appear at 3439, 3163, 1629, 1430, 1227, 1029, 639, 553, and 447 cm^{-1}. They include characteristic bands of amine molecules, phosphate groups, and OH groups. The assignment of these bands is similar to that for compound **1**.

The TGA of compound **1** (Figure 3) shows that the piperazine molecules decompose at 370−480 °C, corresponding to a weight loss of 9.65%, and the further weight loss of 5.3% at 480−660 °C is consistent with the dehydroxylation of the compound. The DTA curve exhibits two exothermic peaks at ca. 440 and 490 °C corresponding to the decomposition of the template and the dehydroxylation. The structure of **1** collapses and converts to an amorphous phase after calcination at 600 °C for 2 h. At 800 °C, the amorphous phase recrystallizes to form a TiP_2O_7 phase (JCPDS: 38-1468), as confirmed by powder X-ray diffraction. For compound **2**, the TGA−DTA results indicate two steps. A mass loss of 8.10% in the range of 405−535 °C corresponds to the loss of the amine molecules (calcd 7.2%); the loss of 3.6% in the region 535−700 °C corresponds to the loss of the OH groups (calcd 3.4%).

Structural Description. The atom-labeling scheme of **1** is shown in Figure 4a, and it contains two crystallographically distinct Ti atoms, with each atom being coordinated to six O atoms. The Ti−O bond lengths and O−Ti−O bond angles are in the ranges of 1.884(6)−1.978(5) Å and 86.7(2)−177.3(2)°, respectively, which are in good agreement with those reported previously for other titanium phosphates. Of the four crystallographically distinct P atoms, P(2) shares four oxygens with adjacent Ti atoms, with the P−O distances varying between 1.509(5) and 1.535(6) Å. The P(3) and P(4) atoms, each of which has one terminal hydroxyl group characterized by the longer P−O bond distances [P(3)−O(15) = 1.546(6) Å and P(4)−O(16) = 1.538(5) Å], are

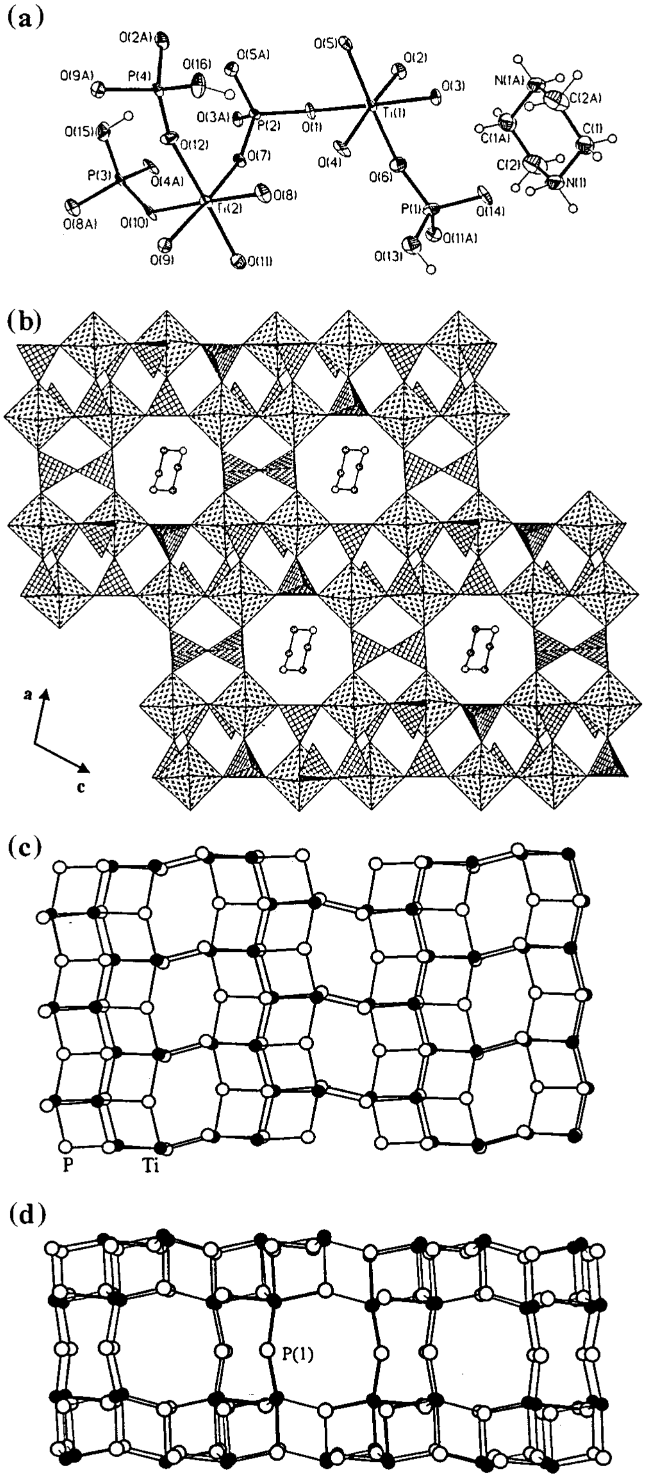

Figure 4. (a) ORTEP view of the structure of **1** showing the atom-labeling scheme (50% thermal ellipsoids). (b) Framework structure of **1** viewed along the [010] direction, showing the eight-membered ring channels and the piperazine molecules. Hydrogens on the amine molecule are not shown for clarity. (c) 4,8-net double layer along the *a* direction. (d) 4,8-net layers connected through P(1) to form the 8-MR channels along the [010] direction. (The oxygens and templates are omitted for clarity.)

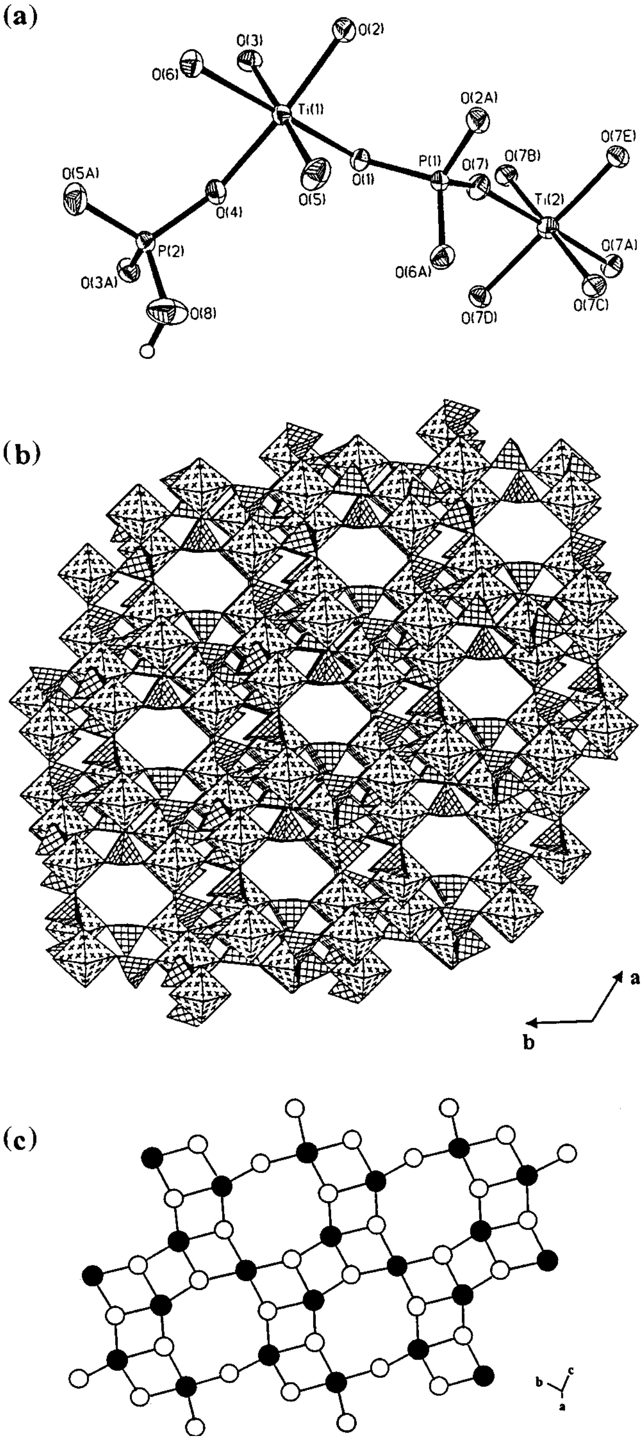

Figure 5. (a) ORTEP view of the structure of **2** showing the atom-labeling scheme (50% thermal ellipsoids). (b) Framework structure of **2** viewed along the [001] direction. (c) Section of a 4,8-net layer in the framework of **2**.

also connected to Ti(1) and Ti(2) through three bridging O atoms. P(1) shares only two oxygens with adjacent Ti atoms, leaving two terminal P−O bonds, of which the longer one [P(1)−O(13)] has a bond distance of 1.538(6) Å, while the shorter one [P(1)−O(14)] has a bond distance of 1.524(5) Å. The longer P−O bond is that of a P−OH group, whereas the shorter one might be regarded as a mixture of P=O and P−O⁻.

The framework structure of **1** is shown in Figure 4b. It is constructed from strictly alternating TiO_6 octahedra and PO_4 and $PO_3(OH)$ tetrahedra. There are eight-membered-ring (8-MR) channels along the *b* direction of the structure. The three-dimensional open-framework structure of **1** can be viewed as constructed from two-dimensional layers: (i) the TiO_6 octahedra and the PO_4 and $PO_3(OH)$ tetrahedra connect together to form two infinite 4,8-net layers along the *a* direction; (ii) the two layers are linked together by sharing oxygens to form a double layer (Figure 4c); (iii) a series of this type of double layers is further connected together through P(1) tetrahedra to build the three-dimensional framework with the 8-MR channels along the [010] direction (Figure 4d).

The diprotonated piperazine molecules are trapped in the main 8-MR channels, and they interact with the oxygens attached to the framework through H bonds. The N(1)−H(1A) group supplies one H to form a H bond with the terminal O(14) atom attached to P(1) atom, with the N(1)···O(14) separation being 2.802(9) Å. The N(1)−H(1B) group tends to form two H bonds with one terminal oxygen O(16) attached to P(4) and one bridging oxygen O(10), the N(1)···O(16) and N(1)···O(10) distances being 2.825(9) and 3.095(10) Å, respectively. The terminal O(16) atom attached to P(4) also forms a strong H bond to the terminal oxygen O(15) attached to P(3), and the O(16)···O(15) separation is 2.551(7) Å. In addition, O(16) also forms a H bond with O(12) through H(15), and the O(16)···O(12) distance is 2.816(7) Å.

The atom-bonding scheme of **2** is shown in Figure 5a. It contains two crystallographically distinct titanium sites and two distinct phosphorus sites. Although the two titanium atoms are coordinated octahedrally by oxygen atoms, they have different occupancies. Ti(1) has an occupancy of 1, and Ti(2) has one of $^1/_6$ only. The Ti−O distances are in the range 1.865(4)−1.976(4) Å, and the O−Ti−O bond angles are in the range 86.69(15)−180.00(16)°. Of the two crystallographically distinct P atoms, P(1) shares four oxygens with adjacent Ti atoms, with the P−O distances varying between 1.518(4) and 1.534(4) Å. The P(2) atom is bonded to three TiO_6 octahedra via the three nonprotonated oxygen vertexes and has one terminal hydroxyl group characterized by the longer P−O bond distance, P(2)−O(8) = 1.557(4) Å. The framework of **2** is three-dimensional and is made of corner-sharing TiO_6 octahedra and PO_4 and $PO_3(OH)$ tetrahedra (Figure 5b). It has a one-dimensional eight-membered ring channel along the *c* direction, and the diprotonated Dabco cations are located in the channels. Similarly, the structure of **2** can be viewed as being built from the layers parallel to the (101) plane that are composed of a series of finite 4,8-net layers (as shown in Figure 5c). The layers are further connected together through P(1) and P(2) tetrahedra to build the open-framework.

The two compounds described here are Ti(IV) compounds. The bond valence sum calculation for the titanium position in **1** is 4.16, whereas this value for **2** is 4.06.[34] The calculated valence sums are somewhat exaggerated; the same problem was encountered in two other templated titanium phosphates.[24,25]

Conclusions

Two new organically templated titanium phosphates with a three-dimensional open-framework have been synthesized under hydrothermal conditions. Both of the compounds are constructed from strictly alternating TiO_6 octahedra and PO_4 and $PO_3(OH)$ tetrahedra. There are 8-MR channels in the framework structures, and the diprotonated organic amine molecules are trapped in these channels. The three-dimensional open-framework structure of **1** can be described as formed from two-dimensional layers. The successful preparation of **1** and **2** demonstrates that, by varying the reaction conditions, titanium phosphates with new structural features can be crystallized.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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