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Hydrothermal Synthesis and Structural Characterization of Three Organically Templated Titanium Phosphates: $Ti_2(HPO_4)_2(PO_4)_2{\cdot}C_2N_2H_{10}$, $Ti_3(H_2PO_4)(HPO_4)_{3.5}(PO_4)_2{\cdot}C_2N_2H_{10}$, and $Ti_7(HPO_4)_6(PO_4)_6{\cdot}C_3N_2H_{12}$

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Three organically templated titanium phosphates with the formulas $Ti_2(HPO_4)_2(PO_4)_2{\cdot}C_2N_2H_{10}$ (**1**), $Ti_3(H_2PO_4)(HPO_4)_{3.5}(PO_4)_2{\cdot}C_2N_2H_{10}$ (**2**), and $Ti_7(HPO_4)_6(PO_4)_6{\cdot}C_3N_2H_{12}$ (**3**) have been prepared hydrothermally from titanium powder, phosphoric acid, and structure-directing organic amines. The as-synthesized products are characterized by powder X-ray diffraction, ^{31}P MAS NMR spectroscopy, IR spectroscopy, and thermogravimetric and differential thermal analyses (TG-DTA). The structures have been solved by single-crystal X-ray diffraction analysis. Crystal data for **1**: triclinic, $P\bar{1}$, $a = 6.3066(17)$ Å, $b = 10.181(4)$ Å, $c = 12.644(3)$ Å, $\alpha = 102.14(2)°$, $\beta = 102.49(3)°$, $\gamma = 90.00(2)°$, $Z = 2$. Crystal data for **2**: triclinic, $P\bar{1}$, $a = 10.3183(9)$ Å, $b = 10.7501(10)$ Å, $c = 10.8315(10)$ Å, $\alpha = 73.436(2)°$, $\beta = 79.648(2)°$, $\gamma = 83.260(2)°$, $Z = 2$. Crystal data for **3**: trigonal, $R\bar{3}$, $a = 16.4993(15)$ Å, $b = 16.4993(15)$ Å, $c = 12.704(3)$ Å, $Z = 3$. Their frameworks are all built up with TiO_6 octahedra and PO_4, $PO_2(OH)_2$, $PO_3(OH)$, and/or $PO_2({=}O)(OH)$ tetrahedral units. Compound **1** is an ethylenediamine intercalated layered titanium phosphate in which the layers are similar to that of γ-type titanium phosphate. Both **2** and **3** are of open-framework type, and the diprontonated organic amine molecules are entrapped in 12-membered-ring channels for **2** and 8-membered-ring channels for **3**.

Introduction

Since Clearfield and co-workers first prepared layered titanium phosphates,[1,2] titanium phosphates have been extensively studied with respect to their potential applications in ion exchange, intercalation, proton conduction, catalysis, molecular sorption, etc. For example, layered and framework titanium phosphates show promising ion-exchange and intercalation properties.[3a] Recently, Inagaki reported a novel mesoporous titanium phosphate molecular sieves with ion-exchange capacity and high catalytic activity.[3b] Potassium titanyl phosphate ($KTiOPO_4$) has been studied extensively as a nonlinear optical material as well as a structural archetype from which numerous related structures have been derived.[4] NASICON-type phosphates such as $MTi_2(PO_4)_3$ ($M = Li^+, Na^+, K^+$, etc.) have been shown to be fast ionic conductors and low thermal expansion ceramics.[5]

Table 1. Crystallographic Data for 1−3

	1	2	3
empirical formula	$C_2H_{12}N_2O_{16}P_4Ti_2$	$C_2H_{15.5}N_2O_{26}P_{6.5}Ti_3$	$C_3H_{18}N_2O_{48}P_{12}Ti_7$
formula weight	539.82	828.67	1557.12
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)
T (K)	293(2)	293(2)	293(2)
a (Å)	6.3066(17)	10.3183(9)	16.4993(15)
b (Å)	10.181(4)	10.7501(10)	16.4993(15)
c (Å)	12.644(3)	10.8315(10)	12.704(3)
α (deg)	102.14(2)	73.436(2)	90
β (deg)	102.49(3)	79.648(2)	90
γ (deg)	90.00(2)	83.260(2)	120
V (Å^3)	774.0(4)	1130.07(18)	2995.1(7)
Z	2	2	3
ρ_{calc} (g cm^{-3})	2.316	2.435	2.590
μ (mm^{-1})	1.537	1.621	1.962
crystal size (mm)	0.10 × 0.05 × 0.02	0.15 × 0.15 × 0.05	0.16 × 0.14 × 0.06
R_1 [$I > 2\sigma(I)$]^a	0.0612	0.0681	0.0374
wR_2 [$I > 2\sigma(I)$]^b	0.1714	0.1278	0.0907

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

Recently, a large number of titanium phosphates with various structural and compositional diversities have

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10.1021/cm0109894 CCC: $22.00

Table 2. Summary of Titanium Phosphates Templated by en with Ti/P Ratios and Dimensionalities

no.	formula	Ti/P ratio, dimension	primary building unit	synthesis method	reference
1	$[Ti_3P_6O_{27}]\cdot5[NH_3CH_2CH_2NH_3]\cdot2[H_3O]$	1/2, 1-D	TiO_6, PO_4	solvothermal	12
2	$[TiO(HPO_4)_2]\cdot[NH_3CH_2CH_2NH_3]$	1/2, 1-D	TiO_6, HPO_4	solvothermal	13
3	$[TiOPO_4]\cdot[H_2NCH_2CH_2NH_3]$	1/1, 2-D	TiO_5N, HPO_4	solvothermal	10a
4	$[TiOPO_4]\cdot[H_2NCH_2CH_2NH_3]$	1/1, 2-D	TiO_5N, HPO_4	hydrothermal	10b
5	$[Ti(OH)PO_4]\cdot[H_2NCH_2CH_2NH_3]$	1/1, 2-D	TiO_5N, HPO_4	hydrothermal	10c
6	$[Ti_2(PO_4)_2F_4]\cdot[N_2C_2H_{10}]$	1/1, 2-D	TiO_4F_2, PO_4	hydrothermal	11
7	$[Ti_2(HPO_4)_2(PO_4)_2]\cdot[N_2C_2H_{10}]$	1/2, 2-D	TiO_6, HPO_4, PO_4	hydrothermal	this work, 1
8	$[Ti^{III}Ti^{IV}(HPO_4)_4]\cdot[C_2N_2H_9]\cdot[H_2O]$	1/2, 3-D	TiO_6, HPO_4	hydrothermal	9
9	$[Ti_3(H_2PO_4)(HPO_4)_{3.5}(PO_4)_2]\cdot[N_2C_2H_{10}]$	3/6.5, 3-D	TiO_6, H_2PO_4, HPO_4, PO_4	hydrothermal	this work, 2
10	$[Ti_4(HPO_4)_2(PO_4)_4F_2]\cdot[N_2C_2H_{10}]\cdot[H_2O]$	2/3, 3-D	TiO_6, TiO_5F, HPO_4, PO_4	hydrothermal	7

been synthesized in both hydrothermal and solvothermal systems by using the organic amines as templates. Up to now, there are 3-dimensional (3-D) open-framework TiPOs with Ti/P ratios of 2/3 $Ti^{III}Ti^{IV}(PO_4)(HPO_4)_2(H_2O)_2\cdot0.5NH_2CH_2CH_2CH_2NH_2$,[6] $Ti_4(HPO_4)_2(PO_4)_4F_2\cdot C_4N_2H_{12}\cdot H_2O$,[7] 7/12 $Ti_7(HPO_4)_6(PO_4)_6\cdot C_6N_2H_{14}$,[8] and 1/2 $Ti^{III}Ti^{IV}(HPO_4)_4\cdot C_2N_2H_9\cdot H_2O$,[9] $Ti_2(HPO_4)_3(PO_4)\cdot0.5C_4N_2H_{12}$.[8] 2-D layers with Ti/P ratio of 1/1 $(H_3NC_2H_4NH_2)TiOPO_4$,[10] $Ti_2(PO_4)_2F_4\cdot C_2N_2H_{10}$,[11] $Ti_2(PO_4)_2F_4\cdot C_3N_2H_{12}\cdot H_2O$,[11] and 1-D chains with Ti/P ratios of 1/2 $Ti_3P_6O_{27}\cdot5NH_3CH_2CH_2NH_3\cdot2H_3O$,[12] and $TiO(HPO_4)_2\cdot C_2N_2H_{10}$.[13]

Herein, we reported three titanium phosphates, in which compound **1** is an extended γ-titanium phosphate intercalated with ethylenediamine. Although the structure of the γ-TiP phase has been proposed by Christensen,[14] the current work can be presented as the first single-crystal confirmation of the γ-TiP structure. Another interesting aspect of this compound is the direct preparation in single-crystal form of an intercalation compound. Generally, the amine-intercalated compounds were prepared by placing the crystals (α-TiP, γ-TiP, etc.) in an atmosphere saturated with amine vapors at room temperature, and the final products were in a powder form. The other two compounds are of three-dimensional frameworks and represent the unique Ti/P ratio of 6/13 and 7/12, respectively.

Experimental Section

Synthesis. All reagents were of analytical grade. Three compounds were hydrothermally prepared from a starting mixture containing ethylenediamine (for compounds **1** and **2**) and 1,3-diaminopropane (for compound **3**) as the structure-directing agent. The compounds were obtained as a pure single-phase material by adjusting the synthetic conditions. For **1**, titanium powder, phosphoric acid (85 wt %), ethylene-

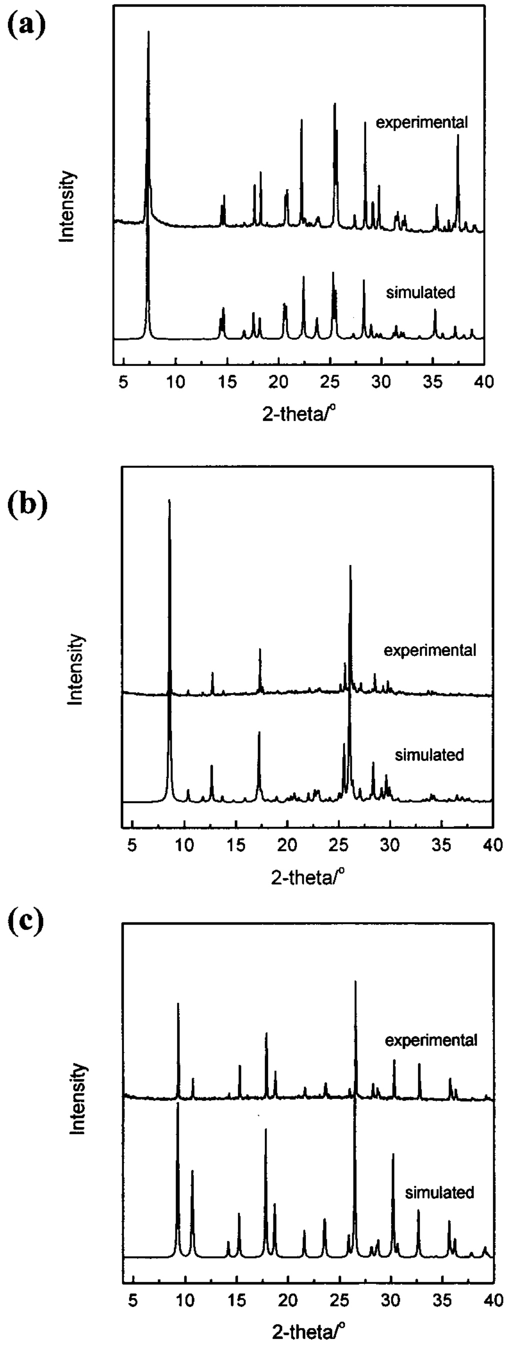

Figure 1. Experimental and simulated powder X-ray diffraction patterns of (a) **1**, (b) **2**, and (c) **3**.

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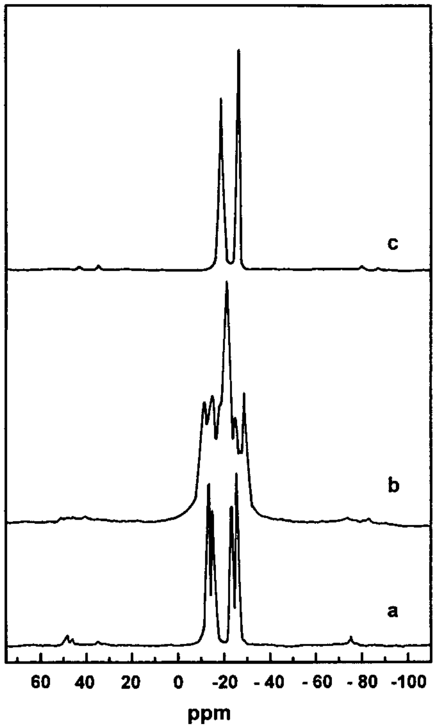

Figure 2. ^{31}P MAS NMR spectra for (a) **1**, (b) **2**, and (c) **3**.

diamine, and distilled water were mixed in the molar ratio of 1.0:15:2.2:27. The mixture was sealed in a 16 mL Teflon-lined stainless steel autoclave with a filling capacity of ~80% and heated at 513 K for 5 days under autogenous pressure. For **2**, titanium powder was dissolved in the phosphoric acid beforehand by heating, followed addition of distilled water and ethylenediamine. The molar ratio of the mixture was 1.0Ti:15H_3PO_4:22H_2O:1.5en. Then the mixture was transferred into autoclave and heated at 513 K for 3 days. Compound **3** was synthesized in a manner similar to **2** described above. The molar ratio of the mixture was 1.0Ti:15H_3PO_4:22H_2O:1.8(1,3-diaminopropane). The mixture was heated at 453 K for 5 days and then at 513 K for 13 days. The resulting products 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 by using Cu Kα radiation (λ = 1.5418 Å) with a graphite monochromator. The step size was 0.02°, and the count time was 4 s. The ^{31}P MAS NMR spectrum was acquired at a ^{31}P frequency of 161.97 MHz on a Infinity Plus spectrometer. A pulse length of 2.5 s and repetition time of 30 s were used. The ^{31}P chemical shifts were reported relative to 85% H_3PO_4 as an external reference. 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 pellet. The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were conducted on a NETZSCH STA 449C analyzer in air with a heating rate of 20 °C min^{-1}.

Determination of Crystal Structures. A suitable single crystal for each compound was selected and mounted on a glass fiber by 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, λ = 0.710 73 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.[15] The structure was solved by direct methods (for **1** and **2**) and patterson method (for **3**) and refined by full-matrix least-squares on F^2 using SHELXTL version 5.1.[16] For **1**, on the difference Fourier map, atom P(4) splits into two positions (P(4) and P(4′)) with equal occupancy for each, indicative of statistical disorder. As a result, atom O(16) is located at two sites (O(16) and O(16′)) with equal occupancy for each also. Similar statistical disorders of P and O atoms among two positions in an indium phosphate have also been observed previously.[17] All non-hydrogen atoms except for O(16) and O(16′) were refined anisotropically. The hydrogen atoms of the amine were placed geometrically (d_{N-H} = 0.89 Å, d_{C-H} = 0.97 Å) and

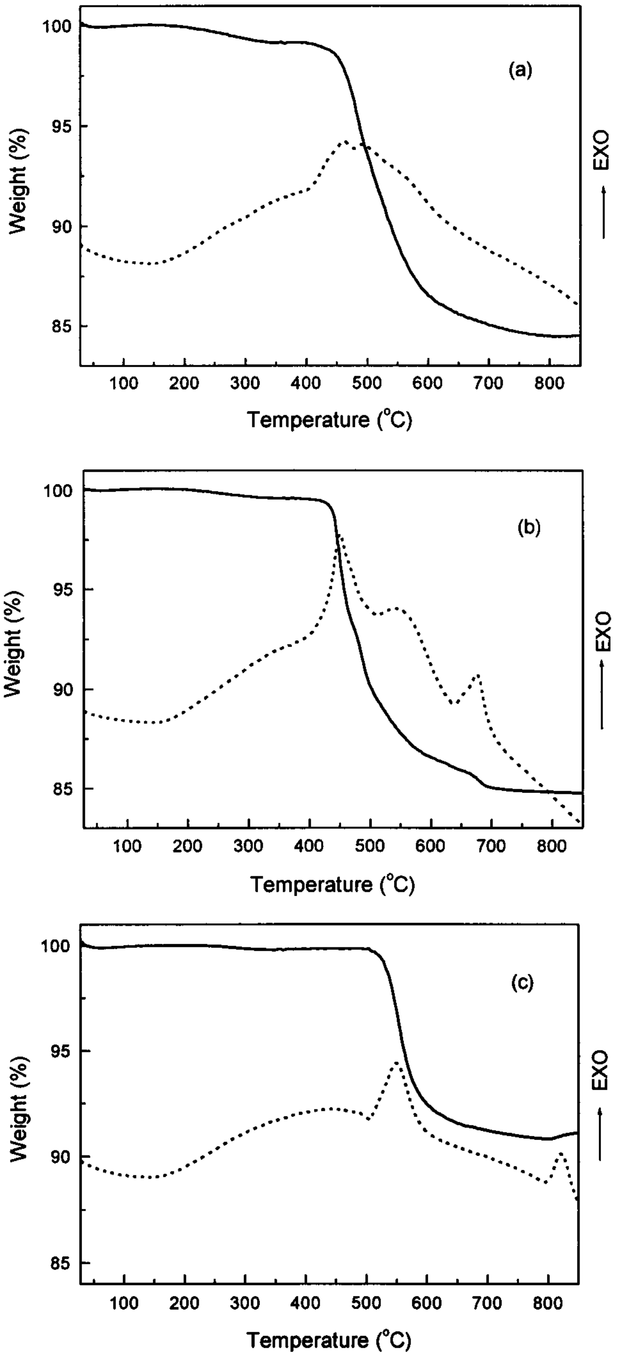

Figure 3. TGA (—) and DTA (- - -) curves for (a) **1**, (b) **2**, and (c) **3**.

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

atom	*x*	*y*	*z*	*U*(eq)[a]
Ti(1)	1993(3)	5816(2)	3734(1)	13(1)
Ti(2)	1947(3)	870(2)	3732(1)	12(1)
P(1)	2744(4)	8751(2)	5526(2)	12(1)
P(2)	7235(4)	6220(2)	4452(2)	12(1)
P(3)	1795(5)	2944(2)	1943(2)	16(1)
P(4)[b]	1438(12)	−2090(6)	1980(4)	23(1)
P(4′)	81(10)	−1994(5)	2149(4)	12(1)
O(1)	2630(11)	7253(6)	5043(5)	16(2)
O(2)	−1034(11)	5769(6)	3788(5)	19(2)
O(3)	1397(12)	7124(6)	2798(5)	25(2)
O(4)	5009(11)	5879(6)	3629(5)	18(2)
O(5)	2599(11)	4504(6)	4603(5)	13(2)
O(6)	1260(11)	4409(6)	2360(5)	15(2)
O(7)	3948(12)	2860(7)	1622(6)	25(2)
O(8)	−98(12)	2342(6)	920(5)	26(2)
O(9)	1595(11)	2133(6)	2807(5)	18(2)
O(10)	4979(11)	814(6)	3730(5)	19(2)
O(11)	2230(11)	−478(6)	4602(5)	20(2)
O(12)	−1155(11)	905(6)	3698(5)	18(2)
O(13)	2494(11)	2262(6)	5094(5)	14(2)
O(14)	1228(11)	−577(6)	2383(5)	15(2)
O(15)	−436(15)	−2579(7)	918(6)	45(3)
O(16)	3830(30)	−2342(17)	1754(14)	53(5)
O(16′)	−2270(20)	−1892(13)	2648(11)	25(3)
N(1)	6518(15)	724(9)	1454(7)	35(3)
N(2)	6540(15)	4963(9)	1446(7)	35(3)
C(1)	5340(20)	−285(12)	487(10)	53(4)
C(2)	6150(20)	4827(13)	220(10)	40(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] P(4), P(4′), O(16), and O(16′) are with half-occupancies.

allowed to ride on the atoms to which they were attached with fixed isotropic thermal parameters. For **2**, P(7) is found disordered with half-occupancy. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed geometrically and held in the riding mode. For **3**, 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 were refined anisotropically. The experimental X-ray data for structures **1**, **2**, and **3** are listed in Table 1.

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

atom	*x*	*y*	*z*	*U*(eq)[a]
Ti(1)	881(1)	1835(1)	2945(1)	10(1)
Ti(2)	4873(1)	4168(1)	3062(1)	11(1)
Ti(3)	−1097(1)	6409(1)	3207(1)	11(1)
P(1)	−698(2)	−838(2)	3723(2)	11(1)
P(2)	1582(3)	3194(3)	−190(2)	38(1)
P(3)	4014(2)	1160(2)	3192(2)	14(1)
P(4)	1623(2)	4534(2)	3496(2)	10(1)
P(5)	7942(2)	3370(2)	3562(2)	13(1)
P(6)	5661(2)	6868(2)	3628(2)	11(1)
P(7)	4509(8)	5677(5)	94(5)	44(1)
O(1)	348(5)	126(5)	3039(5)	14(1)
O(2)	−683(6)	−1365(5)	5179(5)	19(1)
O(3)	−2061(5)	−123(6)	3465(5)	20(1)
O(4)	−407(5)	−1936(5)	3044(5)	17(1)
O(5)	987(6)	2248(6)	1037(5)	21(1)
O(6)	3104(12)	2925(16)	−380(11)	68(3)
O(7)	1292(14)	4637(14)	−68(10)	64(3)
O(8)	963(6)	3048(6)	−1289(5)	22(1)
O(9)	2696(5)	1105(5)	2779(5)	17(1)
O(10)	4373(6)	2535(7)	2926(8)	32(1)
O(11)	3946(6)	408(8)	4632(6)	33(2)
O(12)	5139(5)	472(5)	2406(6)	22(1)
O(13)	1435(5)	3496(5)	2820(5)	15(1)
O(14)	3067(5)	4885(5)	3160(6)	20(1)
O(15)	771(5)	5776(5)	2986(5)	16(1)
O(16)	1220(6)	3991(5)	4966(5)	21(1)
O(17)	6713(5)	3402(6)	2945(5)	18(1)
O(18)	7623(6)	2733(8)	5078(6)	34(2)
O(19)	9036(5)	2533(6)	2982(6)	21(1)
O(20)	8374(5)	4730(6)	3346(6)	23(1)
O(21)	5471(5)	5790(6)	3019(6)	23(1)
O(22)	5300(7)	6380(9)	5104(6)	38(2)
O(23)	7112(5)	7173(5)	3287(5)	19(1)
O(24)	4765(7)	8041(6)	3122(9)	36(2)
O(25)	5077(7)	4746(8)	1167(6)	31(1)
O(26)	3008(16)	5903(19)	378(17)	44(3)
O(27)	4920(20)	7020(20)	−10(20)	52(4)
N(1)	2539(12)	8017(16)	1877(10)	55(3)
N(2)	2305(19)	8325(15)	−1095(10)	65(4)
C(1)	2670(20)	9127(18)	740(20)	66(4)
C(2)	1690(20)	9160(30)	−180(20)	81(6)

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

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for 3

atom	*x*	*y*	*z*	*U*(eq)[a]
Ti(1)	0	0	5000	9(1)
Ti(2)	3189(1)	1010(1)	8357(1)	10(1)
P(1)	2537(1)	−186(1)	10515(1)	12(1)
P(2)	1957(1)	407(1)	6260(1)	9(1)
O(1)	3380(1)	−263(1)	10850(1)	18(1)
O(2)	2524(1)	−41(1)	9335(1)	15(1)
O(3)	1624(1)	−1057(1)	10789(1)	15(1)
O(4)	1895(1)	−513(1)	5943(1)	15(1)
O(5)	2821(1)	1230(1)	5756(1)	14(1)
O(6)	2060(1)	523(1)	7464(1)	13(1)
O(7)	1073(1)	419(1)	5925(1)	15(1)
O(8)	2540(2)	634(2)	11133(2)	28(1)
C(2)	0	0	10000	119(6)
C(1)	−274(7)	−190(50)	9019(7)	49(6)
N(1)	0	0	8040(5)	121(4)

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

Results and Discussion

Synthesis and Characterization. Ethylenediamine (en), which has been discussed in the synthesis of aluminum phosphates and gallium phosphates with an open-framework in many published papers, is one of the best structure-directing agents (SDA). The synthesis of organo-templated titanium phosphates also demonstrates the diversity of en in directing the formation of new structures. When ethylenediamine is used as the template, a series of titanium phosphates can be obtained by varying the solvents and the compositions of the reaction mixture (as shown in Table 2). In the solvothermal system using 1-butanol as the reaction medium, we have prepared three novel titanium phosphates which include a layered structure (TP-J1)[10a] and two 1-D chains (JTP-A, JTP-B)[12,13] by varying the concentration of phosphoric acid. Fjellvåg and Férey also reported the hydrothermal synthesis of similar 2-D titanium phosphate with ULM-11 topology.[10b,c] These studies indicate that TP-J1 (or UiO-19) can be synthesized under both solvothermal and hydrothermal conditions. Recently, Férey and Sevov reported an ethylenediamine-templated mixed-valence titanium phosphate obtained under hydrothermal conditions.[9] However, in a similar hydrothermal system, we obtained an extended γ-titanium phosphate (compound **1**) intercalated with ethylenediamine by treating the Ti/H_3PO_4/H_2O/en directly. Interestingly, if titanium powder was dissolved in the phosphoric acid beforehand by heating, the second new phase compound **2** was obtained. Especially, the existence of HF in the mixture gave rise to two new

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

Ti(1)−O(5)	1.891(6)	Ti(2)−O(9)	1.894(6)
Ti(1)−O(2)	1.927(7)	Ti(2)−O(10)	1.913(7)
Ti(1)−O(1)	1.933(6)	Ti(2)−O(11)	1.918(6)
Ti(1)−O(4)	1.937(7)	Ti(2)−O(12)	1.948(7)
Ti(1)−O(3)	1.946(6)	Ti(2)−O(13)	1.952(6)
Ti(1)−O(6)	1.972(6)	Ti(2)−O(14)	1.974(6)
P(1)−O(1)	1.515(6)	P(3)−O(7)	1.496(8)
P(1)−O(11)#1	1.519(7)	P(3)−O(9)	1.527(7)
P(1)−O(12)#2	1.539(7)	P(3)−O(6)	1.537(6)
P(1)−O(10)#3	1.544(7)	P(3)−O(8)	1.572(7)
P(2)−O(5)#3	1.516(7)	P(4)−O(3)#5	1.438(9)
P(2)−O(13)#3	1.526(6)	P(4)−O(14)	1.533(8)
P(2)−O(2)#4	1.529(7)	P(4)−O(15)	1.574(9)
P(2)−O(4)	1.546(7)	P(4)−O(16)	1.60(2)
O(5)−Ti(1)−O(2)	91.7(3)	O(9)−Ti(2)−O(10)	90.4(3)
O(5)−Ti(1)−O(1)	91.3(3)	O(9)−Ti(2)−O(11)	177.0(3)
O(2)−Ti(1)−O(1)	90.8(3)	O(10)−Ti(2)−O(11)	90.4(3)
O(5)−Ti(1)−O(4)	90.0(3)	O(9)−Ti(2)−O(12)	89.2(3)
O(2)−Ti(1)−O(4)	178.0(3)	O(10)−Ti(2)−O(12)	178.7(3)
O(1)−Ti(1)−O(4)	90.2(3)	O(11)−Ti(2)−O(12)	90.0(3)
O(5)−Ti(1)−O(3)	178.1(3)	O(9)−Ti(2)−O(13)	93.3(3)
O(2)−Ti(1)−O(3)	89.1(3)	O(10)−Ti(2)−O(13)	91.8(3)
O(1)−Ti(1)−O(3)	90.4(3)	O(11)−Ti(2)−O(13)	89.5(3)
O(4)−Ti(1)−O(3)	89.1(3)	O(12)−Ti(2)−O(13)	89.5(3)
O(5)−Ti(1)−O(6)	91.2(2)	O(9)−Ti(2)−O(14)	88.4(3)
O(2)−Ti(1)−O(6)	88.1(3)	O(10)−Ti(2)−O(14)	91.4(3)
O(1)−Ti(1)−O(6)	177.3(2)	O(11)−Ti(2)−O(14)	88.7(3)
O(4)−Ti(1)−O(6)	90.9(3)	O(12)−Ti(2)−O(14)	87.3(3)
O(3)−Ti(1)−O(6)	87.1(3)	O(13)−Ti(2)−O(14)	176.3(3)
O(1)−P(1)−O(11)#1	110.2(4)	O(5)#3−P(2)−O(13)#3	109.9(3)
O(1)−P(1)−O(12)#2	110.5(4)	O(5)#3−P(2)−O(2)#4	110.9(4)
O(11)#1−P(1)−O(12)#2	110.2(4)	O(13)#3−P(2)−O(2)#4	109.6(4)
O(1)−P(1)−O(10)#3	109.7(4)	O(5)#3−P(2)−O(4)	110.5(4)
O(11)#1−P(1)−O(10)#3	110.9(4)	O(13)#3−P(2)−O(4)	109.3(3)
O(12)#2−P(1)−O(10)#3	105.2(4)	O(2)#4−P(2)−O(4)	106.5(4)
O(7)−P(3)−O(8)	111.1(4)	O(3)#5−P(4)−O(14)	114.6(5)
O(9)−P(3)−O(8)	104.3(4)	O(3)#5−P(4)−O(15)	111.3(6)
O(6)−P(3)−O(8)	106.3(4)	O(14)−P(4)−O(15)	107.2(5)
O(7)−P(3)−O(9)	113.9(4)	O(3)#5−P(4)−O(16)	101.5(8)
O(7)−P(3)−O(6)	111.6(4)	O(14)−P(4)−O(16)	108.8(8)
O(9)−P(3)−O(6)	109.1(4)	O(15)−P(4)−O(16)	113.5(8)

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

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 2[a]

Ti(1)−O(13)	1.899(5)	Ti(2)−O(22)#3	1.885(6)
Ti(1)−O(2)#1	1.928(5)	Ti(2)−O(21)	1.902(6)
Ti(1)−O(9)	1.941(5)	Ti(2)−O(14)	1.928(5)
Ti(1)−O(1)	1.949(5)	Ti(2)−O(10)	1.938(6)
Ti(1)−O(19)#2	1.960(5)	Ti(2)−O(25)	1.948(7)
Ti(1)−O(5)	1.971(5)	Ti(2)−O(17)	1.976(5)
Ti(3)−O(16)#4	1.886(5)	Ti(3)−O(4)#5	1.943(5)
Ti(3)−O(20)#2	1.904(5)	Ti(3)−O(15)	1.964(5)
Ti(3)−O(23)#2	1.929(5)	Ti(3)−O(8)#6	1.975(5)
P(1)−O(2)	1.518(5)	P(4)−O(15)	1.529(6)
P(1)−O(1)	1.525(5)	P(4)−O(16)	1.529(6)
P(1)−O(4)	1.535(5)	P(4)−O(14)	1.535(5)
P(1)−O(3)	1.553(5)	P(4)−O(13)	1.545(5)
P(2)−O(8)	1.501(6)	P(5)−O(19)	1.519(6)
P(2)−O(5)	1.504(6)	P(5)−O(20)	1.521(6)
P(2)−O(6)	1.550(12)	P(5)−O(17)	1.527(5)
P(2)−O(7)	1.583(16)	P(5)−O(18)	1.579(7)
P(3)−O(10)	1.501(7)	P(6)−O(24)	1.503(7)
P(3)−O(9)	1.519(5)	P(6)−O(22)	1.524(6)
P(3)−O(11)	1.532(6)	P(6)−O(23)	1.527(5)
P(3)−O(12)	1.557(6)	P(6)−O(21)	1.534(6)
P(7)−O(25)	1.462(9)	P(7)−O(26)	1.529(18)
P(7)−O(27)	1.518(19)		
O(13)−Ti(1)−O(2)#1	91.6(2)	O(2)−P(1)−O(1)	113.4(3)
O(13)−Ti(1)−O(9)	91.5(2)	O(2)−P(1)−O(4)	111.1(3)
O(2)#1−Ti(1)−O(9)	92.8(2)	O(1)−P(1)−O(4)	105.3(3)
O(13)−Ti(1)−O(1)	178.6(2)	O(2)−P(1)−O(3)	110.1(3)
O(2)#1−Ti(1)−O(1)	89.3(2)	O(1)−P(1)−O(3)	107.2(3)
O(9)−Ti(1)−O(1)	87.5(2)	O(4)−P(1)−O(3)	109.6(3)
O(13)−Ti(1)−O(19)#2	90.9(2)	O(8)−P(2)−O(5)	107.5(3)
O(2)#1−Ti(1)−O(19)#2	91.2(3)	O(8)−P(2)−O(6)	113.5(6)
O(9)−Ti(1)−O(19)#2	175.3(2)	O(5)−P(2)−O(6)	109.1(5)
O(1)−Ti(1)−O(19)#2	90.0(2)	O(8)−P(2)−O(7)	109.8(5)
O(13)−Ti(1)−O(5)	91.5(2)	O(5)−P(2)−O(7)	110.4(5)
O(2)#1−Ti(1)−O(5)	176.3(2)	O(6)−P(2)−O(7)	106.7(8)
O(9)−Ti(1)−O(5)	89.2(2)	O(10)−P(3)−O(9)	111.8(3)
O(1)−Ti(1)−O(5)	87.6(2)	O(10)−P(3)−O(11)	112.7(5)
O(19)#2−Ti(1)−O(5)	86.7(3)	O(9)−P(3)−O(11)	108.1(3)
O(22)#3−Ti(2)−O(21)	91.5(3)	O(10)−P(3)−O(12)	106.5(4)
O(22)#3−Ti(2)−O(14)	90.8(3)	O(9)−P(3)−O(12)	110.3(3)
O(21)−Ti(2)−O(14)	91.0(2)	O(11)−P(3)−O(12)	107.4(4)
O(22)#3−Ti(2)−O(10)	93.8(4)	O(15)−P(4)−O(16)	110.3(3)
O(21)−Ti(2)−O(10)	173.9(3)	O(15)−P(4)−O(14)	107.3(3)
O(14)−Ti(2)−O(10)	91.8(2)	O(16)−P(4)−O(14)	111.3(3)
O(22)#3−Ti(2)−O(25)	179.1(3)	O(15)−P(4)−O(13)	109.8(3)
O(21)−Ti(2)−O(25)	87.8(3)	O(16)−P(4)−O(13)	108.5(3)
O(14)−Ti(2)−O(25)	89.8(3)	O(14)−P(4)−O(13)	109.6(3)
O(10)−Ti(2)−O(25)	86.8(3)	O(19)−P(5)−O(20)	110.7(3)
O(22)#3−Ti(2)−O(17)	89.7(3)	O(19)−P(5)−O(17)	108.4(3)
O(21)−Ti(2)−O(17)	90.2(2)	O(20)−P(5)−O(17)	111.6(3)
O(14)−Ti(2)−O(17)	178.7(2)	O(19)−P(5)−O(18)	108.7(4)
O(10)−Ti(2)−O(17)	87.0(3)	O(20)−P(5)−O(18)	108.1(4)
O(25)−Ti(2)−O(17)	89.7(3)	O(17)−P(5)−O(18)	109.2(3)
O(16)#4−Ti(3)−O(20)#2	90.6(3)	O(24)−P(6)−O(22)	109.5(5)
O(16)#4−Ti(3)−O(23)#2	91.1(3)	O(24)−P(6)−O(23)	111.8(4)
O(20)#2−Ti(3)−O(23)#2	93.0(2)	O(22)−P(6)−O(23)	109.3(4)
O(16)#4−Ti(3)−O(4)#5	89.7(2)	O(24)−P(6)−O(21)	108.9(4)
O(20)#2−Ti(3)−O(4)#5	175.2(3)	O(22)−P(6)−O(21)	108.8(4)
O(23)#2−Ti(3)−O(4)#5	91.8(2)	O(23)−P(6)−O(21)	108.6(3)
O(16)#4−Ti(3)−O(15)	92.7(2)	O(25)−P(7)−O(27)	108.1(11)
O(20)#2−Ti(3)−O(15)	90.8(2)	O(25)−P(7)−O(26)	113.6(8)
O(23)#2−Ti(3)−O(15)	174.6(2)	O(27)−P(7)−O(26)	100.2(12)
O(4)#5−Ti(3)−O(15)	84.4(2)	O(23)#2−Ti(3)−O(8)#6	87.8(2)
O(16)#4−Ti(3)−O(8)#6	176.1(3)	O(4)#5−Ti(3)−O(8)#6	86.6(2)
O(20)#2−Ti(3)−O(8)#6	93.1(3)	O(15)−Ti(3)−O(8)#6	88.1(2)

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

phases, layered MIL-6[11] and three-dimensional $[Ti_4(HPO_4)_2(PO_4)_2F_2]\cdot[N_2C_2H_{10}]\cdot[H_2O]$.[7]

The powder XRD patterns of the as-synthesized compounds **1**−**3** with that simulated on the basis of the single-crystal structure are presented in Figure 1. For three compounds, the diffraction peaks on both patterns correspond well in position, indicating the phase purity of the as-synthesized sample. 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, 17.73; P, 22.97; C, 4.45; H, 2.22; N, 5.19. Found: Ti, 17.10; P, 22.20; C, 4.32; H, 1.94; N, 5.06. Calcd for **2**: Ti, 17.34; P, 24.32; C, 2.90; H, 1.87; N, 3.38. Found: Ti, 17.41; P, 24.01; C, 2.86; H, 1.91; N, 3.40. Calcd for **3**: Ti, 21.53; P, 23.89; C, 2.31; H, 1.16; N, 1.80. Found: Ti, 21.40; P, 23.62; C, 2.29; H, 1.08; N, 1.75.

^{31}P MAS NMR spectra of as-synthesized compounds are shown in Figure 2. ^{31}P NMR data of various titanium phosphates and oxophosphates have been reported. In studies of a series of layered Ti, Zr, and Al phosphates by MAS NMR spectroscopy, Nakayama et al. reported that the isotropic ^{31}P chemical shifts of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} groups appear around −10, −20, and −30 ppm, respectively.[18] ^{31}P MAS NMR spectra of **1** show four peaks at −13.8, −16.0, −24.2, and −26.6 ppm with a relative intensity ratio of 1:1:1:

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Table 8. Selected Bond Lengths (Å) and Angles (deg) for 3[a]

Ti(1)−O(7)	1.9407(17)	Ti(2)−O(5)#6	1.8594(17)
Ti(1)−O(7)#1	1.9407(17)	Ti(2)−O(1)#7	1.9234(18)
Ti(1)−O(7)#2	1.9407(17)	Ti(2)−O(4)#8	1.9307(17)
Ti(1)−O(7)#3	1.9407(17)	Ti(2)−O(3)#9	1.9392(17)
Ti(1)−O(7)#4	1.9407(17)	Ti(2)−O(2)	1.9621(17)
Ti(1)−O(7)#5	1.9407(17)	Ti(2)−O(6)	1.9775(17)
P(1)−O(3)	1.5125(18)	P(2)−O(4)	1.5237(17)
P(1)−O(1)	1.5200(19)	P(2)−O(7)	1.5296(18)
P(1)−O(2)	1.5206(18)	P(2)−O(5)	1.5330(18)
P(1)−O(8)	1.562(2)	P(2)−O(6)	1.5395(19)
O(7)−Ti(1)−O(7)#1	180.00(8)	O(5)#6−Ti(2)−O(1)#7	94.51(8)
O(7)−Ti(1)−O(7)#2	87.17(8)	O(5)#6−Ti(2)−O(4)#8	89.12(8)
O(7)#1−Ti(1)−O(7)#2	92.83(8)	O(1)#7−Ti(2)−O(4)#8	91.50(7)
O(7)−Ti(1)−O(7)#3	92.83(8)	O(5)#6−Ti(2)−O(3)#9	89.11(7)
O(7)#1−Ti(1)−O(7)#3	87.17(8)	O(1)#7−Ti(2)−O(3)#9	175.36(8)
O(7)#2−Ti(1)−O(7)#3	92.83(8)	O(4)#8−Ti(2)−O(3)#9	91.46(8)
O(7)−Ti(1)−O(7)#4	92.83(8)	O(5)#6−Ti(2)−O(2)	172.71(7)
O(7)#1−Ti(1)−O(7)#4	87.17(8)	O(1)#7−Ti(2)−O(2)	91.72(7)
O(7)#2−Ti(1)−O(7)#4	180.00(8)	O(4)#8−Ti(2)−O(2)	86.93(7)
O(7)#3−Ti(1)−O(7)#4	87.17(8)	O(3)#9−Ti(2)−O(2)	84.87(7)
O(7)−Ti(1)−O(7)#5	87.17(8)	O(5)#6−Ti(2)−O(6)	93.49(8)
O(7)#1−Ti(1)−O(7)#5	92.83(8)	O(1)#7−Ti(2)−O(6)	88.77(7)
O(7)#2−Ti(1)−O(7)#5	87.17(8)	O(4)#8−Ti(2)−O(6)	177.35(7)
O(7)#3−Ti(1)−O(7)#5	180.00(9)	O(3)#9−Ti(2)−O(6)	88.11(7)
O(7)#4−Ti(1)−O(7)#5	92.83(8)	O(2)−Ti(2)−O(6)	90.42(7)
O(3)−P(1)−O(1)	112.01(10)	O(4)−P(2)−O(7)	110.42(10)
O(3)−P(1)−O(2)	106.87(10)	O(4)−P(2)−O(5)	109.94(10)
O(1)−P(1)−O(2)	112.01(10)	O(7)−P(2)−O(5)	110.08(10)
O(3)−P(1)−O(8)	106.12(12)	O(4)−P(2)−O(6)	109.57(9)
O(1)−P(1)−O(8)	108.94(11)	O(7)−P(2)−O(6)	108.77(9)
O(2)−P(1)−O(8)	110.73(11)	O(5)−P(2)−O(6)	108.01(10)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x, -y, -z + 1$; #2: $-y, x - y, z$; #3: $x - y, x, -z + 1$; #4: $y, -x + y, -z + 1$; #5: $-x + y, -x, z$; #6: $-x + {}^{2}/_{3}, -y + {}^{1}/_{3}, -z + {}^{4}/_{3}$; #7: $-y + {}^{1}/_{3}, x - y - {}^{1}/_{3}, z - {}^{1}/_{3}$; #8: $-x + y + {}^{2}/_{3}, -x + {}^{1}/_{3}, z + {}^{1}/_{3}$; #9: $x - y, x, -z + 2$.

1. Compound **2** shows six signals at −10.2, −15.0, −18.7, −21.2, −24.7, and −29.3 ppm with an intensity ratio of about 1:1:0.5:2: 1:1. Compound **3** shows two peaks at −17.6 and −25.7 ppm with equal intensities. On the basis of the previous studies in titanium phosphates,[19−22] we assigned the NMR peaks at −13.8, −16.0 ppm to the HPO_4 group and −24.2, −26.6 ppm to the PO_4 group for compound **1**. For **2**, the −10.2 ppm signal can be assigned to the H_2PO_4 group, the −15.0, −18.7, −21.2 ppm ones to the HPO_4 group, and the −24.7, −29.3 ppm ones to the PO_4 group. For **3**, the signal at −17.6 ppm can be attributed to the HPO_4 group and the one of −25.7 ppm to the PO_4 group. These assignments are also in good agreement with the structures derived from the single-crystal X-ray diffraction.

The TGA/DTA curves of compounds are shown in Figure 3; the three compounds are thermally stable up to ∼400 °C and revealed a mass loss over the range 400−750 °C. The stage is corresponding to the removal of the organic template (calcd 11.86% for **1**, 8.25% for **2**, and 5.27% for **3**) and the dehydration of HPO_4^{2-} and $H_2PO_4^{-}$ groups (calcd 1.67% for **1**, 2.17% for **2**, and 3.47% for **3**). The observed mass losses are consistent with the expected losses corresponding to the removal of the templates and hydroxyls.

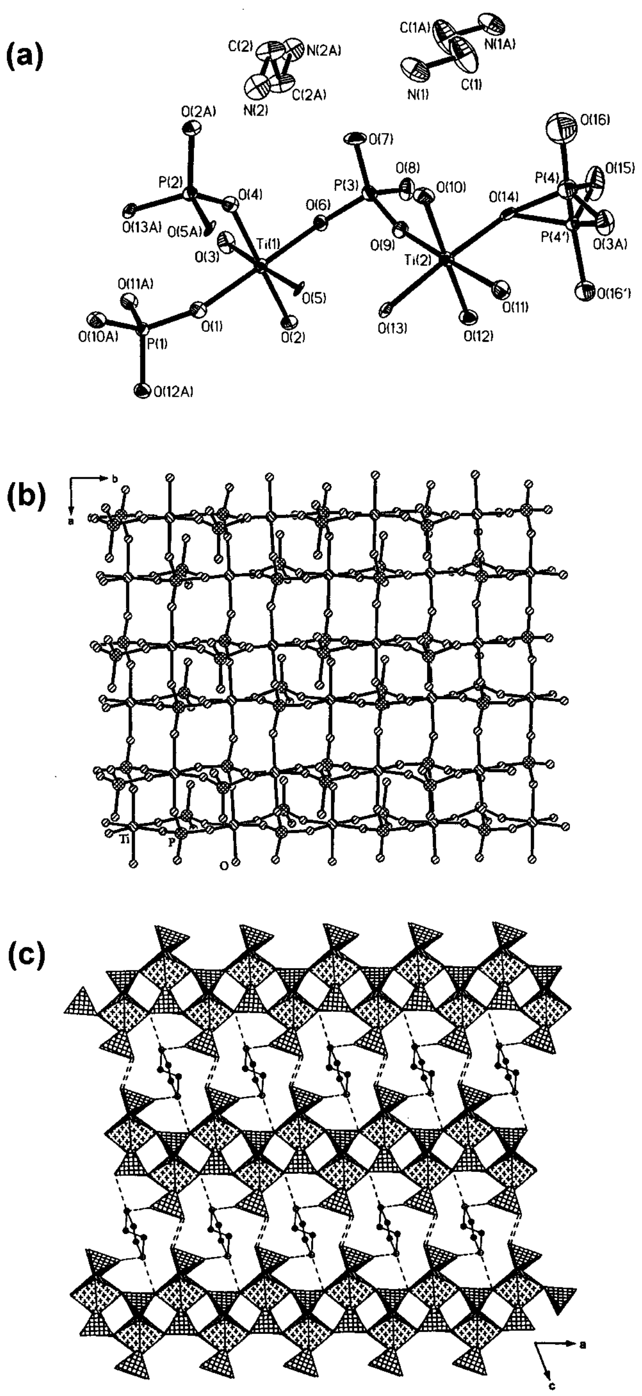

Figure 4. (a) ORTEP view of the structure of **1** showing the atom-labeling scheme (50% thermal ellipsoids). (b) The framework structure of **1** viewed along the [001] direction. (c) Polyhedral presentation of the structure down the *b*-axis. Hydrogen bonds involving the organic amine molecules and hydroxyl groups are marked.

Structural Description. The atomic coordinates with isotropic temperature factors are listed in Tables 3−5, and selected bond lengths and angles are given in Tables 6−8.

The atom-labeling scheme of **1** is shown in Figure 4a, and it contains two crystallographically distinct Ti sites with each being coordinated to six O atoms. The Ti−O bond lengths and O−Ti−O bond angles are in the range 1.891(6)−1.974(6) Å and 87.1(3)−178.7(3)°, which are

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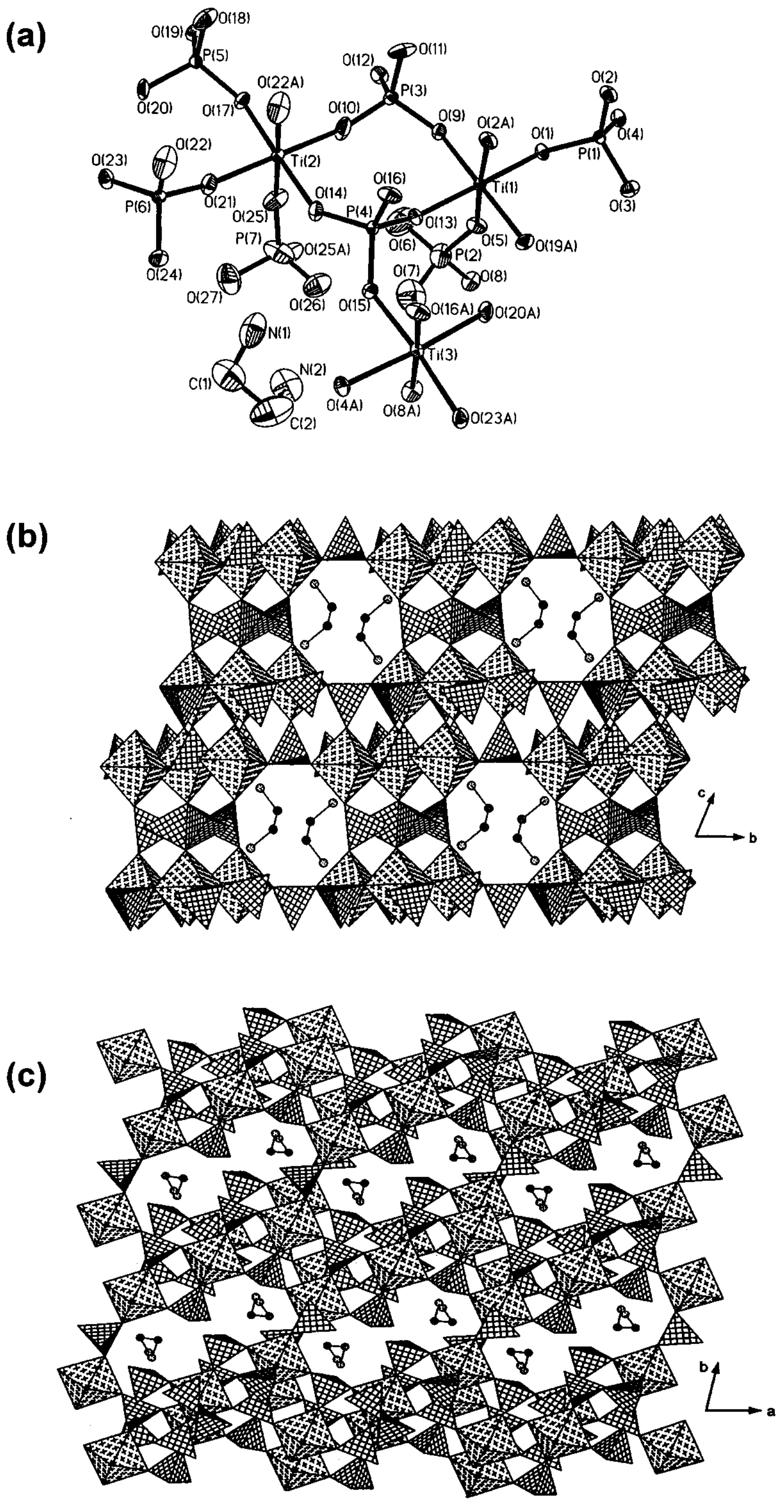

Figure 5. (a) ORTEP view of the structure of **2** showing the atom-labeling scheme (50% thermal ellipsoids). (b) A polyhedral representation of the structure of compound **2** down the *a*-axis, showing the eight-membered-ring channels and the ethylenediamine molecules. Hydrogens on the amine molecule are not shown for clarity. (c) Polyhedral representation of the structure of compound **2** as viewed down the *c*-axis.

in good agreement with those reported previously for other titanium phosphates. Of the four crystallographically distinct P sites, P(1) and P(2) atoms share four oxygens with adjacent Ti atoms with the P$-$O distances varying between 1.515(6) and 1.546(7) Å. The P(3) atom is connected to Ti(1) and Ti(2) through bridging O atoms and has one hydroxyl group and one P$=$O group attached on it. The P(3)$-$O(8)H distance is 1.572(7) Å, and that for P(3)$=$O(7) is much shorter (1.496(8) Å). P(4) shares two oxygens with adjacent Ti atoms, leaving two oxygens on it terminal. The longer distances of P(4)$-$O(15) and P(4)$-$O(16) bonds (1.574(9) and 1.60(2) Å, respectively) indicate that an H atom might be bound to each of O(15) and O(16) atoms, as also requested by charge balance.

The individual $[Ti_2(HPO_4)_2(PO_4)_2]^{2-}$ macroanionic layer is constructed from infinite corner-sharing 4-ring chains formed by PO_4 tetrahera and TiO_6 octahedra alternatively. These chains are linked together by sharing oxygen atoms as to form a 2-dimensional network (Figure 4b). All the terminal P−O groups in the tetrahedral P(3) and P(4) units protrude into the interlayer space up and down the sheet. The diprotonated ethylenediamine cations $[NH_3CH_2CH_2NH_3]^{2+}$ reside in the interlayer regions between the inorganic layers (Figure 4c), and there are extensive H-bonds between the organic cations and the framework oxygens. Each $[NH_3CH_2CH_2NH_3]^{2+}$ cation supplies six H atoms to form H-bonds with six oxygens attached to the phosphate groups. The O(7) atom attached to P(3) accepts two H atoms from two crystallographically distinct organic cations. In addition, there is a strong intralayer H-bond between O(8)−H(8)···O(15), and the O(8)···O(15) distance is 2.480(11) Å.

The inorganic layer of compound **1** is isostructural to the γ-type of titanium phosphate and zirconium phosphate.[23] Although the structure of the γ-TiP phase has been proposed by Christensen,[14] the current work can be regarded as the first single-crystal confirmation of the γ-TiP structure.

Unlike compound **1** with a layered structure, compounds **2** and **3** are of three-dimensional frameworks with channel systems. Figure 5a shows the asymmetric unit of **2**. The structure consists of three independent Ti atoms and seven phosphorus atoms. Although the compound is phosphorus-rich (Ti:P = 3:6.5), there is no P−O−P bonding. All three titanium atoms are octahedrally coordinated to six oxygen atoms. The Ti−O bond lengths and the O−Ti−O bond angles are in the range of 1.885(6)−1.976(5) Å and 86.6(2)−179.1(3)°, respectively. Of the seven crystallographically distinct phosphate groups, P(4) and P(6) are present as PO_4^{3-} and P(2) as $H_2PO_4^-$. The two oxygens of the P−OH groups in P(2) phosphate groups are O(6) and O(7), respectively [P(2)−O(6) = 1.550(12) Å and P(2)−O(7) = 1.583(16) Å]. The P(1), P(3), P(5), and P(7) (P7 has 0.5 occupancy) groups are present as HPO_4^{2-}; the terminal hydroxyl groups are characterized by the longer P−O distances [P(1)−O(3) = 1.553(5) Å, P(3)−O(12) = 1.557(6) Å, P(5)−O(18) = 1.579(7) Å, and P(7)−O(26) = 1.529(18) Å].

A polyhedral representation of the structure viewed down the *a*-axis is shown in Figure 5b. It is constructed from strictly alternating TiO_6 octahedra, PO_4, $PO_3(OH)$, and $PO_2(OH)_2$ tetrahedra. There are eight-membered-ring (8-MR) channels along the *a* direction of the structure. The structure also consists of large elliptical 12-membered-ring channels along the *c*-axis (Figure 5c). The diprotonated ethylenediamine molecules are trapped in these channels, and they interact with oxygens attached to the framework through H-bondings. Some of the possible hydrogen-bonding contacts are N(1)···O(24) = 2.871(12) Å, N(2)···O(3) = 2.771(12) Å, and N(2)···O(26) = 2.73(2) Å; all other contacts are above 3 Å. The hydroxyl groups are hydrogen-bonded to the framework oxygens with O(3)···O(19) = 3.066(8) Å, O(6)···O(21) = 2.993(12) Å, O(6)···O(25) = 3.135(16) Å, and O(12)···O(24) = 2.559(9) Å.

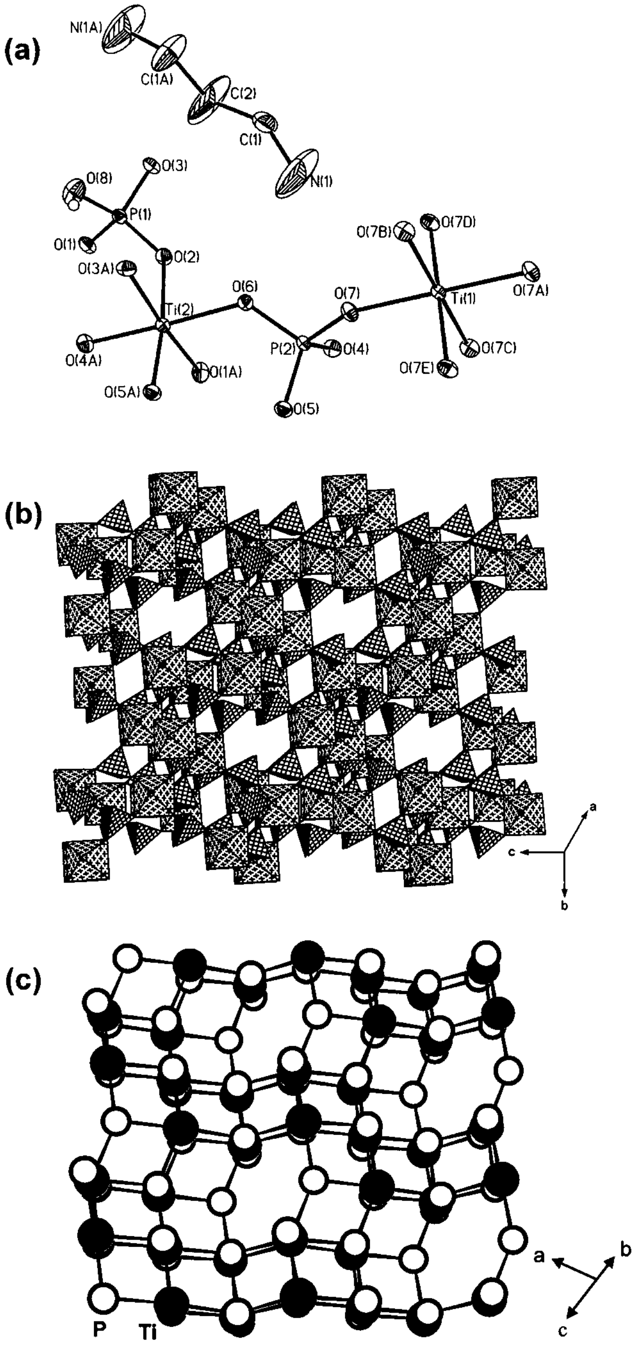

Figure 6. (a) ORTEP view of the structure of **3** showing the atom-labeling scheme (50% thermal ellipsoids). (b) The framework structure of **3** viewed along the labeled direction. (c) Section of a triple 4,8-net layer in the framework of **3**. (The oxygens are omitted for clarity.)

The atom-bonding scheme of **3** is shown in Figure 6a. 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 1.8594(17)−1.9775(17) Å, and the O−Ti−O bond angles are in the range 84.87(7)°−180.00(9)°. Of the two crystallographically distinct P atoms, P(2) shares four oxygens with adjacent Ti atoms with the P−O distances varying between 1.5237(17) and 1.5395(19) Å. The P(1) 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(1)−

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(23) Poojary, D. M.; Shpeizer, B.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1995**, 111.

O(8) = 1.562(2) Å. The framework of **3** is three-dimensional and is made of corner-sharing TiO_6 octahedra and PO_4, $PO_3(OH)$ tetrahedra (Figure 6b). It has a one-dimensional eight-membered ring channel along the labeling direction, and the diprotonated 1,3-diaminopropane cations are located in the channels. The structure of **3** can be viewed as constructed from a series of layers: the TiO_6 octahedra and the PO_4 and $PO_3(OH)$ tetrahedra connect together to form zigzag triple infinite 4,8-net layers (Figure 6c); a series of this type of triple layers are linked together through P(1) and P(2) tetrahedra by sharing oxygens to build the open framework.

In conclusion, three new organically templated titanium phosphates have been synthesized under hydrothermal conditions. Structural analyses indicate that all the compounds are constructed from strictly alternating TiO_6 octahedra and PO_4 and $PO_3(OH)$ tetrahedra. This study has demonstrated that, by controlling the hydrothermal conditions (such as the template, prior treatment, solvent), the new titanium phosphates with different structures can be synthesized. The preparation of new open-framework titanium phosphates along this line is in progress.

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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, 2**, and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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