

# Solvothermal Synthesis and Characterization of a New Titanium Phosphate with a One-Dimensional Chiral Chain

Yanghong Guo, Zhan Shi, Jihong Yu, Jidong Wang, Yunling Liu, Ni Bai, and Wenqin Pang\*

Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jilin University, Changchun 130023, China

Received August 7, 2000. Revised Manuscript Received October 17, 2000

A new titanium phosphate,  $[\text{Ti}_3\text{P}_6\text{O}_{27}] \cdot 5[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3] \cdot 2[\text{H}_3\text{O}]$ , denoted JTP-A (Jilin-titanium phosphate-A), has been synthesized under solvothermal conditions and its structure determined by single-crystal X-ray diffraction. It crystallizes in an enantiomorphic space group  $P2_12_12_1$  with lattice parameters  $a = 10.1800(6)$  Å,  $b = 15.8992(9)$  Å,  $c = 23.2271(12)$  Å,  $V = 3759(4)$  Å<sup>3</sup>, and  $Z = 4$ . The structure consists of one-dimensional chiral chains built up from corner-sharing titanium oxo octahedra running along the  $2_1$ -screw axis, with the adjacent titanium oxo octahedra being bridged by phosphate tetrahedra. The Ti–O bond lengths along the backbone of the chain are alternately short and long. The results of TGA, IR, <sup>31</sup>P MAS NMR, and second harmonics generation measurements are also presented.

## Introduction

The search for chiral materials is highly active with respect to their applications in enantioselective separations and syntheses.<sup>1</sup> It is known that chiral silica (large crystals of *l* and *d* quartz) adsorbs derivatives of (*R*)- and (*S*)-alanine enantioselectively.<sup>2</sup> For the aspects of zeolites with chiral open frameworks, only zeolite  $\beta$ <sup>3,4</sup> and titanosilicate ETS-10<sup>5</sup> have been found with one of their polymorphic forms present in the intergrowth being chiral. Recently, some research work is focusing on the syntheses of the chiral open frameworks of metal phosphate compounds. Although a large number of metal phosphates including three-dimensional (3-D) open framework, two-dimensional (2-D) layer, and one-dimensional (1-D) chain structures have been prepared,<sup>6,7</sup> the occurrence of chiral framework materials are still rare. So far, there are only a few examples that have been reported for  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ ,<sup>8</sup>  $\text{KIn}(\text{OH})\text{PO}_4$ ,<sup>9</sup>  $\text{RbIn}(\text{OH})\text{PO}_4$ ,<sup>10</sup> a series of UCSB-*n* compounds, etc.<sup>11</sup> Full control of framework chirality has not been achieved

yet because the syntheses of such materials involve complex reaction mechanisms, which are poorly understood.

For the synthesis of chiral frameworks, one useful approach is templated syntheses using chiral templating molecules. Successful examples are the zinc phosphate phase formed with chiral *d*-glucosamine molecules and a gallophosphate compound containing a chiral amine<sup>12,13</sup> as well as a family of layered alumino- and gallophosphates templated by chiral metal complexes.<sup>14–16</sup> On the other hand, it is interesting to note that the chiral materials can be formed by nonchiral templating agents to construct the self-assembly of chiral inorganic frameworks. Such metal phosphate compounds are known for  $[(\text{CH}_3)_2\text{NH}_2]\text{K}_4[\text{V}_{10}\text{O}_{10}(\text{H}_2\text{O})_2(\text{OH})_4(\text{PO}_4)_7] \cdot 4\text{H}_2\text{O}$ ,<sup>17</sup> ULM-5,<sup>18</sup> and UCSB-7EDA.<sup>11</sup>

Our work is focusing on the family of organic-templated titanium phosphates. The synthesis of titanium phosphate compounds is of interest because of their applications in ion exchange, redox catalysis, and nonlinear optical materials. However, few phases have been reported because of the difficulty in obtaining large single crystals. The synthesis of titanium phosphates often leads to two-dimensional layered phases, which is clearly shown by the works of Clearfield and Ferey's group.<sup>19,20</sup> Recently, some titanium phosphates with 3-D open-framework structures have been reported.<sup>21–24</sup>

\* To whom correspondence should be addressed. Fax: +86-431-5671974. E-mail: wqpang@mail.jlu.edu.cn.

- (1) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.
- (2) Kavasmannick, P. R.; Bonner, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 44.
- (3) Treacy, M. M. J.; Newsam, J. M. *Nature* **1988**, *332*, 249.
- (4) Newsam, J. M.; Treacy, M. M. J.; Koetsier, W. T.; De Gruyter, C. B. *Proc. R. Soc. London A* **1988**, *420*, 375.
- (5) Anderson, M. W.; Terasaki, O.; Ohsuna, T.; Philippou, A.; MacKay, S. P.; Ferreira, A.; Rocha, J.; Lidin, S. *Nature* **1994**, *367*, 347.
- (6) Oliver, S.; Kuperman, A.; Ozin, G. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 46.
- (7) Cheetham, A. K.; Ferey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.
- (8) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D.; Broach, R. W.; Bedard, R. A. *Chem. Mater.* **1996**, *8*, 145.
- (9) Hriljac, J. A.; Grey, C. P.; Cheetham, A. K. *J. Solid State Chem.* **1996**, *123*, 243.
- (10) Lii, K. H. *J. Chem. Soc., Dalton Trans.* **1996**, 815.
- (11) Gier, T. E.; Bu, X. H.; Feng, P. Y.; Stucky, G. D. *Nature* **1998**, *395*, 154.

(12) Nenoff, T. M.; Thoma, S. G.; Provencio, P.; Maxwell, R. S. *Chem. Mater.* **1998**, *10*, 3077.

- (13) Lin, H. M.; Lii, K. H. *Inorg. Chem.* **1998**, *37*, 4220.
- (14) Bruce, D. A.; Wilkinson, A. P.; White, M. G.; Bertrand, J. A. *J. Solid State Chem.* **1996**, *125*, 228.
- (15) Stalder, S. M.; Wilkinson, A. P. *Chem. Mater.* **1997**, *9*, 2168.
- (16) Gray, M. J.; Jasper, J. D.; Wilkinson, A. P. *Chem. Mater.* **1997**, *9*, 976.
- (17) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1596.
- (18) Francis, R. J.; O'Brien, S.; Fogg, A. M.; Halasyamani, P. S.; Loiseau, D. T.; Ferey, G. *J. Am. Chem. Soc.* **1999**, *121*, 1002.

However, to our knowledge, there is no report on the synthesis of chiral titanium phosphate. In this work, we report the first organic-templated titanium phosphate,  $[\text{Ti}_3\text{P}_6\text{O}_{27}] \cdot 5[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3] \cdot 2[\text{H}_3\text{O}]$  (denoted JTP-A, J = Jinlin University), with 1-D chiral chain architecture. The structure of the title compound will represent a new fundamental structural type.

### Experimental Section

**Synthesis and Characterization.** Single crystals of JTP-A were synthesized from a 1-butanol system with a gel composition of 1.0:3.2:6.4:25/TBOT:H<sub>3</sub>PO<sub>4</sub>:en:BuOH. The typical synthesis procedure was as follows: 3.78 g of tetrabutyltitanium (TBOT, 98%) was dispersed in 20 mL of 1-butanol (BuOH, 99%) under vigorous stirring and then 4.16 mL of orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85 wt % in water) was added dropwise. An orange gel formed and was stirred at room temperature for 1 day, and then 4.27 mL of ethylenediamine (en, 99%) was added. The final reaction mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 453 K for 6 days. The product was separated by ultrasonication and filtration, washed with distilled water, and dried at ambient temperature. During this procedure, the amorphous phase and crystalline powder were removed. The yield of large colorless cuneiform crystals was  $\approx 80\%$  for the typical synthesis batch.

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Elemental analyses were conducted on a Perkin-Elmer 240C element analyzer. Inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer 2400 Elemental Anal. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 thermal analyzer in the air at a heating rate of 10 °C/min. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer (KBr pellet). <sup>31</sup>P MAS NMR spectra were obtained on a Bruker MSL-300 spectrometer. The second harmonic generation (SHG) response was measured in the reflection mode. A Q-switch pulsed Nd:YAG laser operating at 1064 nm with a 2-Hz repetition rate and an 8-ns pulse width was used as the radiation source. Second harmonic light was collected in reflectance from samples with crystalline sizes of 1–3  $\mu\text{m}$ , and intensities were measured relative to quartz standards.

**Single-Crystal Structure Analysis.** A colorless cuneiform crystal of dimensions 0.25  $\times$  0.05  $\times$  0.05 mm was mounted on a glass fiber on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4-kW sealed-tube X-ray source using monochromated Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Systematic absences and the statistics of intensity distribution resulted in the space group  $P2_12_12_1$ . The structure was solved by direct methods. The Ti and P atoms were first located, and the C, N, and O atoms were found in difference Fourier maps, with the exception of the hydrogen atoms residing on the amine molecules and the extra-chain water, which were placed by geometrical considerations with  $d(\text{N-H}) = 0.89 \text{ \AA}$  and  $d(\text{C-H}) = 0.97 \text{ \AA}$ . The protonation of ethylenediamine molecules was suggested by IR analysis and the protonated water molecules were proven by TGA analysis with the water loss around 170 °C. The full-matrix least-squares refinements were against  $F^2$  and included secondary extinction correction and anisotropic displacement parameters for non-hydrogen atoms. The C(2), N(1), and N(5) of en occupy two split positions: C(2)–C(2'), N(1)–N(1'), and N(5)–N(5'). Each split atom had fixed

**Table 1. Crystal Data and Structure Refinement for JTP-A**

empirical formula	N <sub>10</sub> C <sub>10</sub> H <sub>56</sub> Ti <sub>3</sub> P <sub>6</sub> O <sub>29</sub>
formula weight	1110.17
temperature for data collection	293(2)K
crystal system	orthorhombic
space group	$P2_12_12_1$
unit-cell dimensions	$a = 10.1800(6) \text{ \AA}$ $b = 15.8992(9) \text{ \AA}$ $c = 23.2271(12) \text{ \AA}$
volume	3759.4(4) $\text{\AA}^3$
Z	4
density	1.961 g/cm <sup>3</sup>
F(000)	2296
crystal size	0.250 $\times$ 0.050 $\times$ 0.050 mm
absorption coefficient	99.3 mm <sup>-1</sup>
$\theta$ range for data collection	1.55°–23.29°
index ranges	$-11 \leq h \leq 7$ $-17 \leq k \leq 17$ $-25 \leq l \leq 25$
reflections collected	18 584
unique reflections	5413 ( $R(\text{int}) = 0.1035$ )
completeness to $\theta = 23.29(\%)$	99.7
refinement method	full-matrix least-squares on $F^2$
data/restraints/parameters	5413/0/521
goodness-of-fit on $F^2$	1.074
R indices [ $I > 2\sigma(I)$ ] <sup>a</sup>	$R1 = 0.0452$ , $wR2 = 0.1132$
R indices (all data)	$R1 = 0.0595$ , $wR2 = 0.1199$
absolute structure parameter	0.41(5)
largest difference map	0.710 and $-0.498 \text{ e \AA}^{-3}$
peak and hole	

<sup>a</sup>  $R1 = \Sigma(\Delta F/\Sigma(F_o))$ ;  $wR2 = (\Sigma[w(F_o^2 - F_c^2)])/\Sigma[w(F_o^2)^2]^{1/2}$ ,  $w = 1/\sigma^2(F_o^2)$ .

occupancy of 0.5. The structure solution and refinement were performed using the SHELXTL program system (version 5.1).<sup>25</sup> We had tested the possibility of racemic twinning and had refined the Flack parameter to 0.41(5), indicating that racemic twinning was present. So the single crystal used was a mixture of both hands. The crystallographic data are summarized in Table 1, and the selected bond distances and angles are listed in Table 2.

### Results and Discussion

JTP-A is synthesized in the system  $\text{Ti}(\text{OBU})_4/\text{H}_3\text{PO}_4/\text{en}/\text{BuOH}$ . The synthesis conditions are summarized in Table 3. It is found that one of the controlling factors in the synthesis is the concentration of phosphoric acid in the reaction mixture. When the concentration of phosphoric acid is  $\approx 3 \text{ M}$ , JTP-A is formed. An increase in the concentration of phosphoric acid to 2 times the former results in the formation of another new type of 1-D titanium phosphate,  $[\text{Ti}(\text{HPO}_4)_2] \cdot [\text{C}_2\text{N}_2\text{H}_{10}]$  (JTP-B,  $a = 8.670(5) \text{ \AA}$ ,  $b = 7.253(2) \text{ \AA}$ ,  $c = 16.601(7) \text{ \AA}$ , space group  $P2(1)/n$ ). When the concentration of phosphoric acid is decreased to  $\approx 2 \text{ M}$ , a layered titanium phosphate,  $\text{TiOPO}_4[\text{C}_2\text{N}_2\text{H}_9]$  (TP-J1),<sup>26</sup> is formed. The type of solvent also affects the synthesis products. The water brought by the phosphoric acid (85% in water) in the system does not affect the synthesis result very much. However, when a significant amount of water is added to the reaction system, an unknown phase with a Ti/P of unity instead of JTP-A crystallizes.

Figure 1 shows the X-ray powder diffraction pattern of JTP-A, which is in good agreement with the simulated X-ray diffraction pattern, proving a single phase of the

(19) Bortun, A. I.; Bortun, L. N.; Clearfield, A.; Villa-Garcia, M. A.; Garcia, J. R.; Rodriguez, J. *J. Mater. Res.* **1996**, *11*, 2490.

(20) Serre, C.; Ferey, G. *J. Mater. Chem.* **1999**, *9*, 579.

(21) Ekambaram, S.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 372.

(22) Serre, C.; Guillou, N.; Ferey, G. *J. Mater. Chem.* **1999**, *9*, 1185.

(23) Bortun, A. I.; Khainakov, S. A.; Bortun, L. N.; Poojary, D. M.; Rodriguez, J.; Garcia, J. R.; Clearfield, A. *Chem. Mater.* **1997**, *9*, 1805.

(24) Ekambaram, S.; Serre, C.; Ferey, G.; Sevov, S. C. *Chem. Mater.* **2000**, *12*, 444.

(25) Sheldrick, G. M. *SHELXTL-NT*, Version 5.1; Bruker Axis Inc.: Madison, WI, 1997.

(26) Zhao, Y. N.; Zhu, G. S.; Jiao, X. L.; Pang, W. Q. *J. Mater. Chem.* **2000**, *10*, 463.

Table 2. Selected Bond Lengths (Å) and Angles (deg)<sup>a</sup>

Selected Bond Lengths (Å)					
Ti(1)–O(1)	1.831(5)	Ti(3)–O(18)	1.963(5)	P(4)–O(19)	1.530(5)
Ti(1)–O(6)	1.851(5)	Ti(3)–O(21)	2.003(5)	P(4)–O(20)	1.537(5)
Ti(1)–O(2)	1.985(5)	Ti(3)–O(22)	2.018(5)	P(4)–O(21)	1.542(5)
Ti(1)–O(5)	1.990(5)	P(1)–O(8)	1.496(5)	P(4)–O(15)	1.547(5)
Ti(1)–O(4)	2.043(5)	P(1)–O(5)	1.532(5)	P(5)–O(24)	1.512(5)
Ti(1)–O(3)	2.061(5)	P(1)–O(9)	1.542(5)	P(5)–O(3)#1	1.527(5)
Ti(2)–O(13)	1.759(4)	P(1)–O(7)	1.556(4)	P(5)–O(22)	1.528(5)
Ti(2)–O(6)	1.955(5)	P(2)–O(11)	1.511(4)	P(5)–O(25)	1.555(5)
Ti(2)–O(14)	1.959(5)	P(2)–O(4)	1.528(5)	P(6)–O(27)	1.501(6)
Ti(2)–O(15)	2.003(5)	P(2)–O(10)	1.531(5)	P(6)–O(23)	1.518(5)
Ti(2)–O(9)	2.030(5)	P(2)–O(12)	1.566(4)	P(6)–O(26)	1.545(5)
Ti(2)–O(10)	2.125(5)	P(3)–O(16)	1.523(5)	P(6)–O(2)#1	1.545(5)
Ti(3)–O(1)#1	1.858(5)	P(3)–O(17)	1.525(5)	O(1)–Ti(3)#2	1.858(5)
Ti(3)–O(13)	1.957(4)	P(3)–O(14)	1.543(5)	O(2)–P(6)#2	1.545(5)
Ti(3)–O(23)	1.962(5)	P(3)–O(18)	1.552(5)	O(3)–P(5)#2	1.527(5)

Selected Bond Angles (deg)					
Ti(1)–O(1)–Ti(3)#2	140.3(3)	Ti(1)–O(6)–Ti(2)	140.3(2)	Ti(2)–O(13)–Ti(3)	137.5(3)
P(6)#2–O(2)–Ti(1)	135.0(3)	P(3)–O(18)–Ti(3)	138.8(3)	P(3)–O(14)–Ti(2)	137.2(3)
P(5)#2–O(3)–Ti(1)	138.9(3)	P(4)–O(21)–Ti(3)	138.4(3)	P(4)–O(15)–Ti(2)	137.7(3)
P(2)–O(4)–Ti(1)	138.8(3)	P(1)–O(9)–Ti(2)	140.4(3)	P(5)–O(22)–Ti(3)	136.2(3)
P(1)–O(5)–Ti(1)	137.9(3)	P(2)–O(10)–Ti(2)	138.8(3)	P(6)–O(23)–Ti(3)	139.4(3)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: (#1)  $-x, y + 1/2, -z + 3/2$ ; (#2)  $-x, y - 1/2, -z + 3/2$ .

Table 3. Synthesis Conditions for JTP-A

no.	gel composition (molar ratio)					temp. (°C)	time (days)	product
	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	en <sup>a</sup>	BuOH <sup>b</sup>	H <sub>2</sub> O			
1	1.0	1.6	6.4	20	5.3	180	6	JTP-A
2	1.0	1.0	6.4	21	3.7	180	5	TP-J1
3	1.0	3.1	6.4	20	6.2	180	6	JTP-B
4	1.0	1.6	3.2	20	5.3	180	6	TP-J1+ JTP-A
5	1.0	1.2	6.4	20	5.3	180	6	JTP-A+ am
6	1.0	1.6	6.4	0	25	180	6	unknown phase

<sup>a</sup> en, ethylenediamine. <sup>b</sup> BuOH, 1-butanol; am, amorphous.

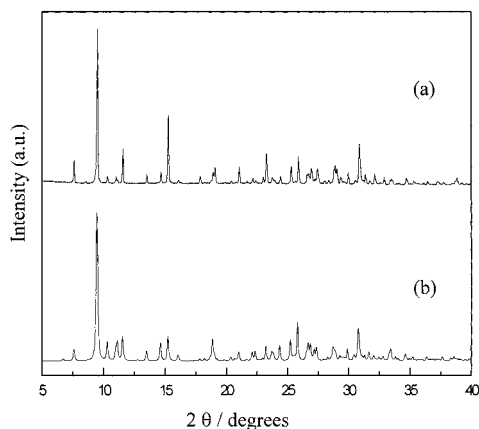


Figure 1. Experimental (a) and simulated (b) X-ray powder diffraction patterns of JTP-A.

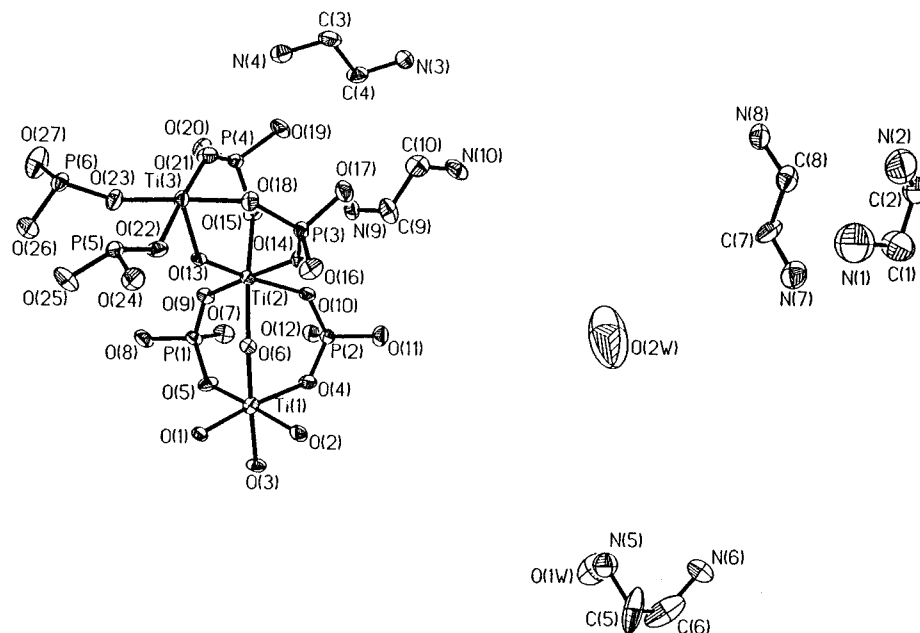
product of JTP-A. Chemical analysis shows the contents of Ti and P as 12.90 and 16.68 wt % (calculated: 12.94 and 16.74 wt %), giving the Ti/P molar ratio of 1:2. The C, H, and N contents are 10.49, 4.93, and 12.41 wt % (calculated: 10.81, 5.08, and 12.62 wt %), respectively; thus, the molar ratio of C:H:N is 1.0:5.6:1.0. These results are in accordance with the formula of JTP-A given by single-crystal structure analysis.

Single-crystal structural analysis of JTP-A reveals that it crystallizes in the enantiomorphic space group  $P2_12_12_1$  with lattice parameters  $a = 10.1800(6)$  Å,  $b = 15.8992(9)$  Å, and  $c = 23.2271(12)$  Å. Therefore, the unit-cell contents are chiral. The asymmetric unit, as shown in Figure 2, contains three crystallographically distinct Ti atoms and six crystallographically distinct P atoms.

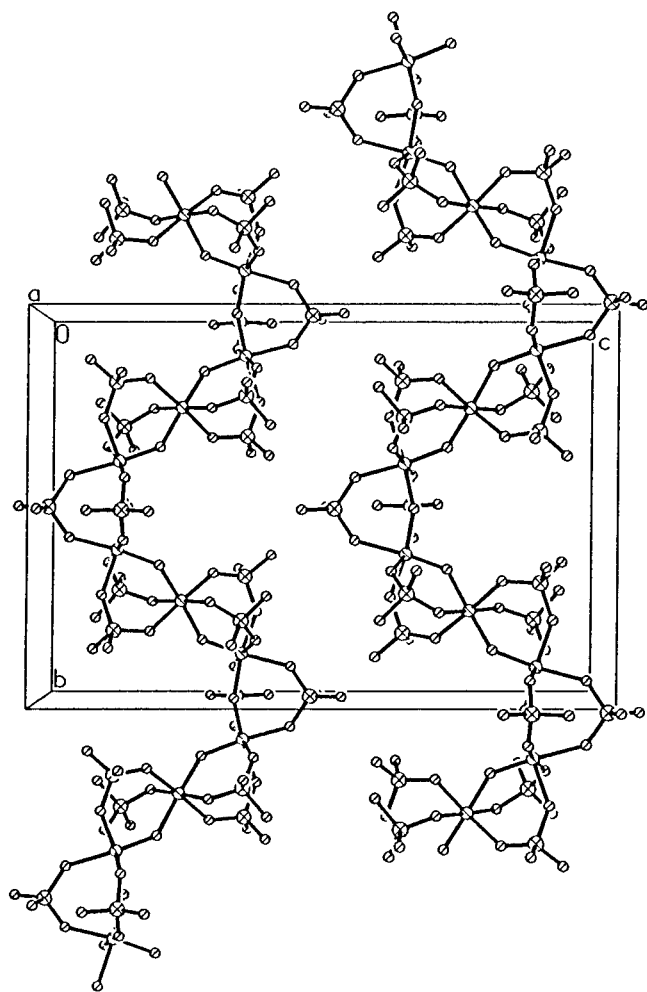
The structure consists of infinite spirals of titanium oxo octahedra running along the [010] direction in the order of  $-\text{Ti}(1)-\text{O}(6)-\text{Ti}(2)-\text{O}(13)-\text{Ti}(3)-\text{O}(1\text{A})-\text{Ti}(1)-$  through a  $-\text{cis}-\text{cis}-\text{trans}-$  corner-sharing connection, as indicated in Figure 3. There are six TiO<sub>6</sub> octahedra per spiral of unit-cell length. The central axis of each spiral is a 2<sub>1</sub>-screw axis. The distortions of titanium oxo octahedra from ideal symmetry are obvious from inspection of the bond angles and distances. The Ti(2)O<sub>6</sub> octahedra is extremely distorted with the deviation of  $\approx 0.18$  Å from the centroid of its Ti–O octahedron. Like most KTP analogues,<sup>27</sup> the  $-\text{Ti}(1)-\text{O}(6)-\text{Ti}(2)-\text{O}(13)-\text{Ti}(3)-$  backbone of titanium oxo octahedra spirals shows a short–long bond alternation (Ti(1)–O(6), 1.851 Å; Ti(2)–O(6), 1.955 Å; Ti(2)–O(13), 1.759 Å; and Ti(3)–O(13), 1.957 Å). The second harmonics signal is clearly generated at 532 nm in a powder sample, indicating that the structure has no center of symmetry. SHG intensity is about 8 times that of quartz. In comparison with the outstanding nonlinear optical crystal KTiOPO<sub>4</sub>, which has the difference 0.443 Å between the short and long Ti–O bonds, JTP-A has the difference of 0.198 Å between the short and highly polarizable titanyl Ti=O bonds. It is known that the short and highly polarizable titanyl Ti=O bonds play a key role in defining nonlinear optical properties.<sup>27</sup> Therefore, KTiOPO<sub>4</sub> produces a large SHG intensity, whereas the observed SHG response for the title compound is small.

The adjacent titanium oxo octahedra are bridged by phosphate tetrahedra, each of which shares two oxygen atoms with two adjacent Ti atoms. Two bridging phosphate groups connect two Ti atoms; thus, a series of Ti–P–Ti three-membered rings are attached to the  $-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$  backbone as shown in Figure 3. There are 12 terminal oxygens attached to the phosphorus atoms, with the P–O bond lengths in the range of 1.496(5)–1.566(4) Å. The <sup>31</sup>P MAS NMR spectrum of the sample has only one signal at 2.4 ppm, clearly indicating that

(27) Phillips, M. L. F.; Harrison, W. T. A.; Stucky, G. D.; McCarron III, E. M.; Calabrese, J. C.; Gier, T. E. *Chem. Mater.* **1992**, *4*, 222.



**Figure 2.** Thermal ellipsoid plot (50% probability) and atomic labeling scheme for an asymmetric unit of JTP-A.



**Figure 3.** The spirals of the titanium oxo octahedra linked with phosphorus oxo tetrahedra running along the [010] direction.

the various phosphates are effective in structurally similar environments. This similarity of the phosphate functional groups can be connected with the similar pattern in their extensive hydrogen bonding with an

organic amine, which has been found by A. I. Bortum and A. Clearfield et al.<sup>19</sup>

The IR spectrum of JPT-A contains the characteristic bands for protonated amines at around 3000–2800 and 2175  $\text{cm}^{-1}$ , which correspond to the stretching and combination bands of  $\text{NH}_3^+$ ,<sup>28</sup> suggesting the ethylenediamine molecules are protonated. Figure 4 presents the structure viewed along the [010] direction, showing the positions of organic cations and water molecules in the interchain region. There are five organic cations and two water molecules at general positions in an asymmetric unit. The  $\text{O}\cdots\text{N}$  distances in the range of 2.70–3.10 Å indicates that the amino groups of the templates form extensive hydrogen bonds with the terminal oxygen atoms attached to the phosphates. The organic cations physically separate the 1-D TiPO chains and hold these inorganic chains together by extensive H bonds.

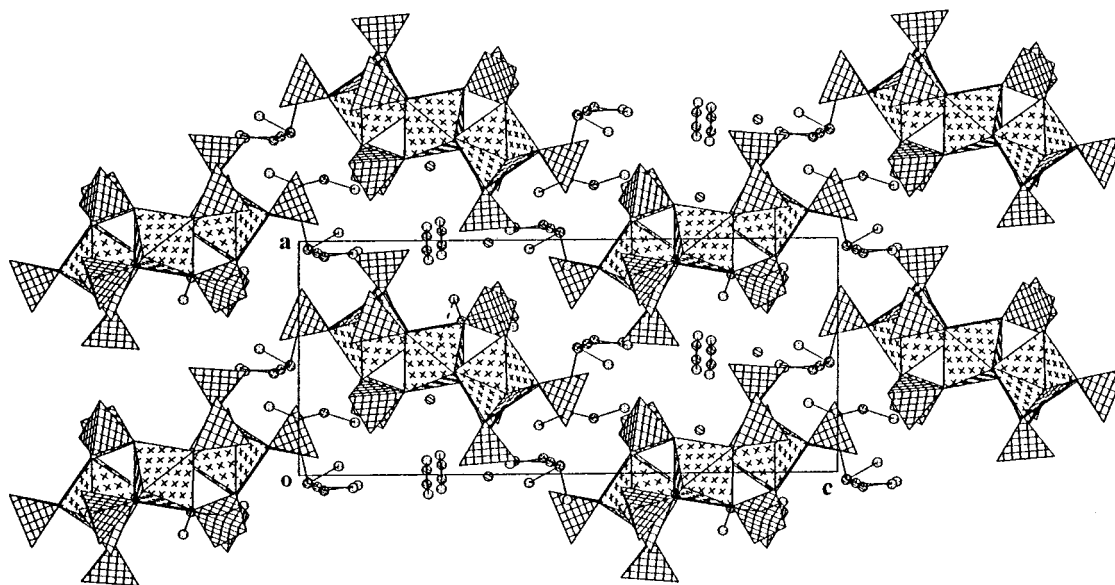
Thermogravimetric analysis of the sample shows a total weight loss of  $\approx 30.6$  wt %. About 3.4% weight loss occurred around 100–210 °C, in agreement with loss of two molecules of water per formula unit. Loss of the water at high temperature is consistent with the hydroxonium ion formulation that we propose. Decomposition of five templating molecules corresponds to a weight loss of 28%, which fits well with the loss of 27% over the range 210–380 °C. After calcination at 400 °C for 4 h, the structure of JTP-A collapses and converts into an amorphous phase. Above 800 °C, the product of the thermal decomposition is composed basically of cubic  $\text{TiP}_2\text{O}_7$ .<sup>29</sup>

Infinite titanium oxo octahedra chains have been found in various higher dimensional TiPOs, such as 3-D KTP ( $\text{KTiOPO}_4$ ) and its analogues<sup>27</sup> and 2-D  $\text{TiO}(\text{OH})(\text{H}_2\text{PO}_4)$ <sup>30</sup> and  $\text{TiOPO}_4[\text{C}_2\text{N}_2\text{H}_9]$ .<sup>26</sup> In these compounds, the tetrahedral coordination of phosphorus is fairly regular,

(28) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*; Aldrich: Milwaukee, WI, 1981.

(29) Levi, G. R.; Peyronel, G. *Thermochim. Acta* **1982**, *58*, 179.

(30) Li, Y. J.; Whittingham, M. S. *Solid State Ionics* **1993**, *63–65*, 391.



**Figure 4.** View of the structure down the chain axis, showing the 1-D chains separated by organic cations and water molecules.

while the octahedral coordination of titanium is often distorted, and the bond lengths show a short–long alternation along the  $-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$  backbone. However, unlike the arrangement of the titanium oxo chains in higher dimensional  $\text{MTiOPO}_4$ , that is, *cis*–*trans* connectivity of  $\text{Ti}-\text{O}$  octahedra chains in  $\text{KTiOPO}_4$  and  $\beta\text{-NaTiOPO}_4$ ,<sup>27</sup> all-*trans* configuration in  $\alpha\text{-NaTiOPO}_4$ <sup>27</sup> and  $\text{TiOPO}_4[\text{C}_2\text{N}_2\text{H}_9]$ ,<sup>26</sup> and all-*cis* mode in  $\gamma\text{-NaTiOPO}_4$ ,<sup>27</sup> the  $\text{Ti}-\text{O}$  chains of JTP-A are linked in a unique configuration of *cis*–*cis*–*trans* corner-sharing titanium oxo octahedra, which may result in the formation of the titanium phosphate with a 1-D chiral chain. This chiral chain architecture in JTP-A has never been observed in those  $[\text{M}(\text{PO}_4)_2\phi']$  chains ( $\phi'$ , O, OH, F) in phosphate minerals,<sup>31</sup> and any other 1-D chain structures of the  $[\text{M}(\text{H}_x\text{PO}_4)_2\phi']$  ( $\text{M} = \text{Al, Ga, Fe, V; } \phi' = \text{O, OH}$ ) series.<sup>32–35</sup>

In summary, the solvothermal synthesis and crystal structure of JPT-A,  $[\text{Ti}_3\text{P}_6\text{O}_{27}] \cdot 5[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3] \cdot$

$2[\text{H}_3\text{O}]$ , the first organic-templated titanium phosphate compound with 1-D chiral chains, are described. Although the structure shows interesting 1-D chiral chains of corner-sharing titanium oxo octahedra, the title compound has a small SHG response because the differences between the short and long  $\text{Ti}-\text{O}$  bonds distance are smaller than that of  $\text{KTiOPO}_4$ . Recent exploratory syntheses of titanium phosphate in a solvothermal system reveal a rich structural chemistry. Further investigation of chiral TiPO compounds is in progress.

**Acknowledgment.** The authors acknowledge the financial support from the State Basic Research Project of China (G2000077507) and the National Natural Science Foundation of China.

**Supporting Information Available:** Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and hydrogen bonds for JTP-A (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM000642L

(31) Hawthorne, F. C. *Acta Crystallogr., Sect. B* **1994**, *50*, 481.

(32) Lii, K. L.; Wang, S. L. *J. Solid State Chem.* **1997**, *128*, 21.

(33) Attfield, M. P.; Morris, R. E.; Burshtein, I.; Campana, C. F.; Cheetham, A. K. *J. Solid State Chem.* **1995**, *118*, 412.

(34) Liu, L. M.; Wang, X. Q.; Bontchev, R.; Ross, K.; Jacobson, A. J. *J. Mater. Chem.* **1999**, *9*, 1585.

(35) Lethbridge, Z. A. D.; Lightfoot, P.; Morris, R. E.; Wragg, D. S.; Wright, P. A.; Kvik, A.; Vaughan, G. *J. Solid State Chem.* **1995**, *142*, 455.