

# Template synthesis and characterization of a new 2-D layered titanium phosphate

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Received 17th June 1999, Accepted 25th October 1999

A new titanium phosphate  $[\text{H}_3\text{NC}_2\text{H}_4\text{NH}_2]\text{TiOPO}_4$  has been prepared under solvothermal conditions. It crystallized in the monoclinic space group  $P2_1/c$  with cell parameters  $a=9.2457(19)$ ,  $b=7.3465(16)$ ,  $c=9.929(2)$  Å,  $\beta=100.702(5)^\circ$ ,  $V=662.7(2)$  Å<sup>3</sup>,  $Z=4$ ,  $M_w=219.98$  g mol<sup>-1</sup>,  $D_c=2.205$  g cm<sup>-3</sup>; the final residual factors were  $R=0.0337$  and  $R_w=0.0804$ . The structure is two-dimensional and consists of infinite zigzag  $\text{TiO}_5\text{N}$  octahedra in chains corner-linked by  $\text{PO}_4$  tetrahedra; the  $\text{TiO}_5\text{N}$  octahedra are all *trans*-linked with Ti–O bonds being alternately short and long. The monoprotonated ethylenediamine is intercalated between the layers with one end coordinated to Ti. Thermogravimetric analysis implied N–C scission upon calcination.

## 1 Introduction

Metal phosphates have been extensively studied, especially since the discovery of microporous aluminophosphates,<sup>1</sup> with respect to their diverse structures and applications in catalysis, adsorbents, ion-exchange and molecular recognition. Introducing transition metals into phosphates has received increasing attention owing to their variable coordination number and oxidation states, which give rise to potential applications in ionic conductivity, redox catalysis and magnetic studies. A large number of transition metal phosphates with open frameworks have been prepared for vanadium, zinc, zirconium, iron, *etc.*<sup>2</sup> Titanium phosphates show important properties, such as the second harmonic generation properties of KTP ( $\text{KTiOPO}_4$ ) and its analogues as non-linear optical (NLO) materials<sup>3</sup> and layered  $\alpha\text{-Ti}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$ ,  $\gamma\text{-Ti}(\text{H}_2\text{PO}_4)(\text{PO}_4)\cdot 2\text{H}_2\text{O}$  and their pillared derivatives which display ion exchange and absorptive properties.<sup>4</sup> However, very few synthesized examples have been reported to date. The hydrothermal synthesis of two layered titanium phosphates,  $\text{TiO}(\text{OH})(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$  and  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$ , was reported in the early 1990s<sup>5</sup> and the synthesis of  $\beta\text{-Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4)$ , the anhydrous form of  $\gamma\text{-Ti}(\text{H}_2\text{PO}_4)(\text{PO}_4)\cdot 2\text{H}_2\text{O}$ , followed.<sup>6</sup> Recently, Clearfield and coworkers reported the hydrothermal synthesis and powder X-ray structure of three porous titanium phosphates,  $[\text{Ti}_3(\text{PO}_4)_4(\text{H}_2\text{O})_2]\cdot\text{NH}_3$ ,  $[\text{Ti}_2\text{O}(\text{PO}_4)_2(\text{H}_2\text{O})]$  and  $(\text{NH}_3)_2[(\text{Ti}_3\text{O}_2)(\text{HPO}_4)_2(\text{PO}_4)_2]$ .<sup>7</sup> A mixed titanium phosphate phosphonate  $\text{Ti}(\text{H}_2\text{PO}_4)_{1.25}(\text{HPO}_4)_{0.12}(\text{PhPO}_3)_{1.25}\cdot 0.3\text{H}_2\text{O}$  has also been reported recently.<sup>8</sup> The first organically templated microporous mixed valent  $\text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}$  phosphate  $\text{Ti}_2(\text{PO}_4)(\text{HPO}_4)_2(\text{H}_2\text{O})_2\cdot 0.5\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  and its interesting magnetic properties have been recently reported by Ekambaram and Sevov.<sup>9</sup> The synthesis and *ab initio* structure determination of two novel layered oxyfluorinated titanium phosphates,  $\text{Ti}_2(\text{PO}_4)_2\text{F}_4\cdot\text{N}_2\text{C}_2\text{H}_{10}$  and  $\text{Ti}_2(\text{PO}_4)_2\text{F}_4\cdot\text{N}_2\text{C}_3\text{H}_{12}\cdot\text{H}_2\text{O}$ , have also been reported very recently.<sup>10</sup>

In the past decade, solvothermal synthesis promoted by organic amines has proved to be an exciting and promising method to prepare materials with new structures.<sup>11</sup> Using this method, notable achievements have been obtained in our laboratory, including the synthesis of JDF-20,<sup>12</sup> a microporous aluminophosphate with 20-member rings, as well as a series of 1-, 2- and 3-D aluminophosphates.<sup>13</sup> Herein, we report the first solvothermal synthesis and characterization of a new layered

titanium phosphate denoted TP-J1 (J=Jilin University) templated by ethylenediamine.

## 2 Experimental

### 2.1 Synthesis and analysis

Chemicals used were tetrabutyltitanium (TBOT, 98%, Aldrich), phosphoric acid ( $\text{H}_3\text{PO}_4$ , 85 wt%, Beijing chemical reagent factory), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, Beijing chemical reagent factory), butanol (BuOH, 99%, Beijing chemical reagent factory), ammonia ( $\text{NH}_3\cdot\text{H}_2\text{O}$ , 25%, Beijing chemical reagent factory) and ethylenediamine (en, 99%, Beijing chemical reagent factory). In a typical synthesis, 4.76 g of TBOT was dispersed in 20 mL of BuOH under vigorous stirring, then 4.16 mL of  $\text{H}_3\text{PO}_4$  was added and an orange gel formed. Subsequent addition of 3.6 mL of ethylenediamine and *ca.* 5 mL of  $\text{NH}_3\cdot\text{H}_2\text{O}$  raised the pH to *ca.* 9 and the gel changed to a yellow sol. The final mixture with molar composition 1.4 TBOT : 6  $\text{H}_3\text{PO}_4$  : 5 en : 22 BuOH was transferred into a 40 mL Teflon-lined autoclave and crystallized at 180 °C for five days. The products were filtered off, washed with water and dried at room temperature.

Powder X-ray diffraction patterns were recorded on Rigaku D/max III and Siemens D5005 diffractometers with Ni-filtered  $\text{Cu-K}\alpha$  radiation over the range  $2\theta$  4–40°. Raman spectra were collected on a JOBIN YVON T64000 instrument over the range 200–1200  $\text{cm}^{-1}$ . Excitation was accomplished with the 488 nm line of an argon-ion laser, and the incident power was 300 mW. Chemical analyses were carried out on a Plasma-SPEC (1) ICP-AES instrument which gave a Ti : P ratio of 1 : 1. Thermal analyses were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer and a Perkin Elmer DTA 1700 differential thermal analyzer in nitrogen with a heating rate of 10 °C min<sup>-1</sup>. Scanning electron microscopy (SEM) was performed on a Hitachi X-650B instrument.

### 2.2 Structure determination

A single crystal of TP-J1 was glued to a fine glass fiber and mounted on a three-circle fixed Siemens diffractometer fitted with a Siemens SMART CCD detector. Cell dimensions and intensity data were collected on a Siemens SMART system using graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda=0.71073$  Å) at 298 K. Unit cell data and the experimental

**Table 1** Crystal data and structure refinement for  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2]\text{TiOPO}_4$ 

Empirical formula	$[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2]\text{TiOPO}_4$
Formula weight	219.98
$\lambda/\text{nm}$	0.071073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
$a/\text{\AA}$	9.2457(19)
$b/\text{\AA}$	7.3465(16)
$c/\text{\AA}$	9.929(2)
$\beta/^\circ$	100.702(5)
$V/\text{\AA}^3$	662.7(2)
$Z$ ( $D_f \text{ g cm}^{-3}$ )	4(2.205)
$\mu/\text{mm}^{-1}$	1.509
$F(000)$	448
Crystal size/mm	$0.13 \times 0.08 \times 0.02$
$\theta$ range for data collection/ $^\circ$	3.47–23.25
Limiting indices	$-9 \leq h \leq 6, -8 \leq k \leq 8, -3 \leq l \leq 11$
Reflections collected/unique ( $R_{\text{int}}$ )	1310/803 (0.0430)
Completeness to $\theta = 23.25$ (%)	84.7
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	803/0/100
Goodness-of-fit on $F^2$	1.038
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0337, wR2 = 0.0804$
$R$ indices (all data)	$R1 = 0.0489, wR2 = 0.0847$
Largest diff. peak, hole/e $\text{\AA}^{-3}$	0.375, $-0.391$

conditions for data collection are summarized in Table 1. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Refinements were performed using the SHELXTL (version 5.1, Siemens Automation, Inc., Madison, WI 53719, USA, 1997) crystallographic software package. Atomic positional parameters and isotropic temperature factors for TP-J1 are given in Table 2, while selected bond lengths and angles are listed in Table 3.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/191. See <http://www.rsc.org/suppdata/jm/a9/a904837e/> for crystallographic data in .cif format.

### 3 Results and discussion

#### 3.1 Synthesis and analysis

TP-J1 formed in the solvothermal system was obtained as single crystals with a thin plate-like shape. The value of the pH affects the product substantially. Products with good quality only formed after addition of 3.16 mL of ethylenediamine and *ca.* 5 mL of  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . The role of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  is solely to adjust the pH value, while too much ethylenediamine led to an unknown phase (Fig. 1). The experimental powder XRD pattern and the simulated XRD pattern of TP-J1 based on single crystal X-ray diffraction analysis are shown in Fig. 2.

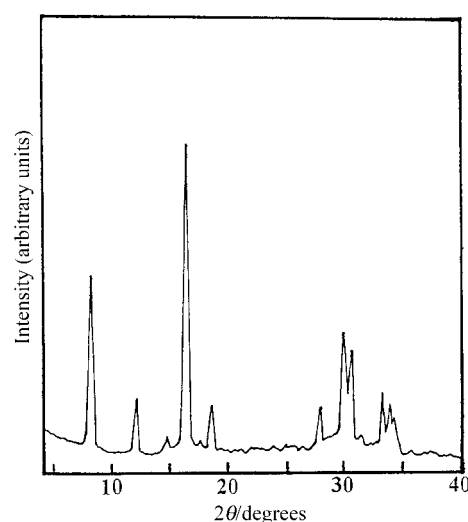
**Table 2** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2]\text{TiOPO}_4$ .  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

Atom	$x$	$y$	$z$	$U_{\text{eq}}$
Ti(1)	4933(1)	1460(1)	2321(1)	14(1)
P(1)	2918(2)	1320(2)	-872(1)	12(1)
O(1)	3487(4)	1977(4)	3489(4)	17(1)
O(2)	6448(4)	421(4)	1365(4)	18(1)
O(3)	1245(4)	1293(4)	-1248(4)	18(1)
O(4)	4483(4)	-1353(4)	2757(3)	16(1)
O(5)	3351(4)	1450(4)	698(3)	19(1)
N(1)	6498(5)	1025(5)	4262(5)	20(1)
N(2)	10073(5)	2903(5)	6240(5)	20(1)
C(1)	7961(6)	1875(7)	4452(5)	21(1)
C(2)	8831(6)	1875(7)	4452(5)	21(1)

**Table 3** Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2]\text{TiOPO}_4^a$ 

Ti(1)–O(4)#1	1.701(3)	Ti(1)–O(5)	1.965(4)
Ti(1)–O(1)	1.970(3)	Ti(1)–O(2)	1.984(3)
Ti(1)–O(4)	2.168(3)	Ti(1)–N(1)	2.208(5)
P(1)–O(3)	1.522(4)	P(1)–O(2)#2	1.525(3)
P(1)–O(1)#3	1.534(3)	P(1)–O(5)	1.539(4)
O(4)–Ti(1)#4	1.701(3)	O(2)–P(1)#2	1.525(3)
O(1)–P(1)#5	1.534(3)	N(1)–C(1)	1.469(7)
N(2)–C(2)	1.504(7)	C(2)–C(1)	1.504(8)
O(4)#1–Ti(1)–O(5)	99.22(16)	O(4)#1–Ti(1)–O(1)	95.78(14)
O(5)–Ti(1)–O(1)	90.21(15)	O(4)#1–Ti(1)–O(2)	94.79(14)
O(5)–Ti(1)–O(2)	95.17(15)	O(1)–Ti(1)–O(2)	167.22(13)
O(4)#1–Ti(1)–O(4)	169.66(7)	O(5)–Ti(1)–O(4)	91.11(14)
O(1)–Ti(1)–O(4)	83.61(13)	O(2)–Ti(1)–O(4)	84.70(13)
O(4)#1–Ti(1)–N(1)	90.82(16)	O(5)–Ti(1)–N(1)	169.36(14)
O(1)–Ti(1)–N(1)	85.24(16)	O(2)–Ti(1)–N(1)	87.44(16)
O(4)–Ti(1)–N(1)	78.84(14)	O(3)–P(1)–O(2)#2	110.1(2)
O(3)–P(1)–O(1)#3	108.68(19)	O(2)#2–P(1)–O(1)#3	111.83(18)
O(3)–P(1)–O(5)	108.1(2)	O(2)#2–P(1)–O(5)	109.49(19)
O(1)#3–P(1)–O(5)	108.52(19)	P(1)–O(5)–Ti(1)	147.7(2)
Ti(1)#4–O(4)–Ti(1)	144.80(19)	P(1)–O(2)–Ti(1)	145.4(2)
P(1)#5–O(1)–Ti(1)	136.14(19)	C(1)–N(1)–Ti(1)	119.3(3)
N(2)–C(2)–C(1)	112.4(4)	N(1)–C(1)–C(2)	112.1(4)

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

**Fig. 1** Powder XRD pattern of the unknown phase.

Their peak positions are in good agreement with each other, demonstrating the phase purity of the as-synthesized compound. The differences in intensity may be explained by a preferred orientation effect on the observed XRD pattern. An SEM image shows the plate-shape morphology of a typical crystal with dimensions of *ca.*  $0.15 \times 0.08 \times 0.03$  mm (Fig. 3).

The Raman spectrum (Fig. 4) shows a strong sharp band at

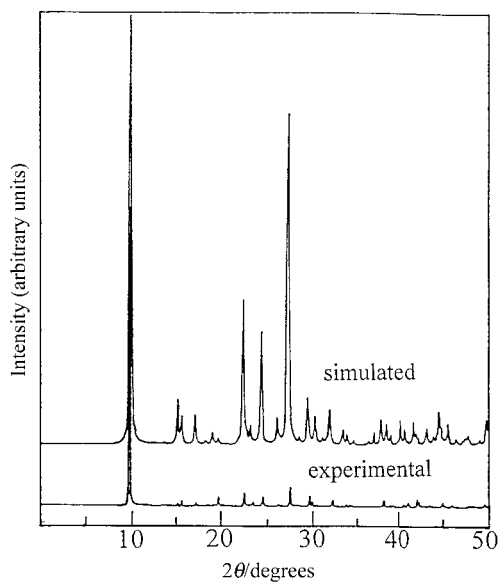


Fig. 2 Experimental and simulated XRD patterns of TP-J1.



Fig. 3 SEM of TP-J1.

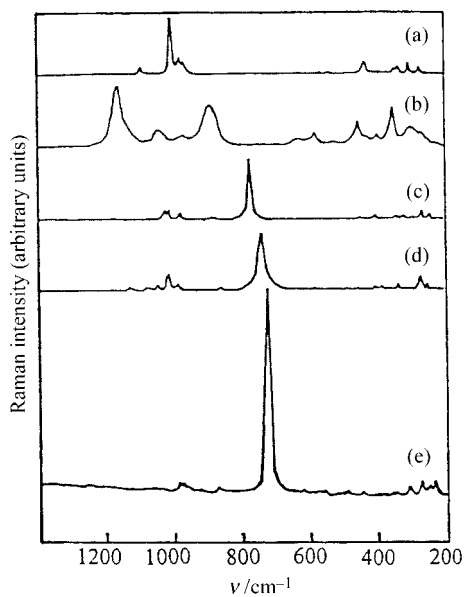


Fig. 4 Raman spectra of TP-J1 and some other titanium phosphates: (a)  $\text{NaTi}_2(\text{PO}_4)_3$ , (b)  $\text{Na}_4\text{Ca}_{0.5}\text{Ti}(\text{PO}_4)_3$ , (c)  $\text{LiTiOPO}_4$ , (d)  $\text{Ni}_{0.5}\text{TiOPO}_4$  and (e) TP-J1.

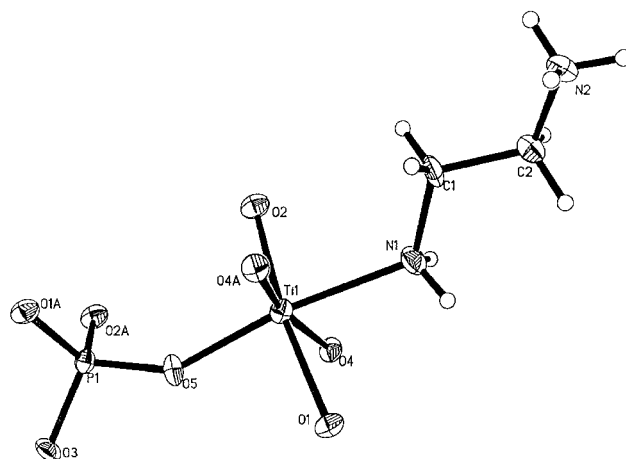


Fig. 5 The co-ordination environments around the Ti and P atoms with the atomic labeling scheme for TP-J1.

*ca.*  $735\text{ cm}^{-1}$  and several weak bands at  $200\text{--}400$  and  $800\text{--}1100\text{ cm}^{-1}$ . By comparison with other titanium phosphates,<sup>14</sup> the strong sharp peak is assigned to the vibration of Ti–O–Ti

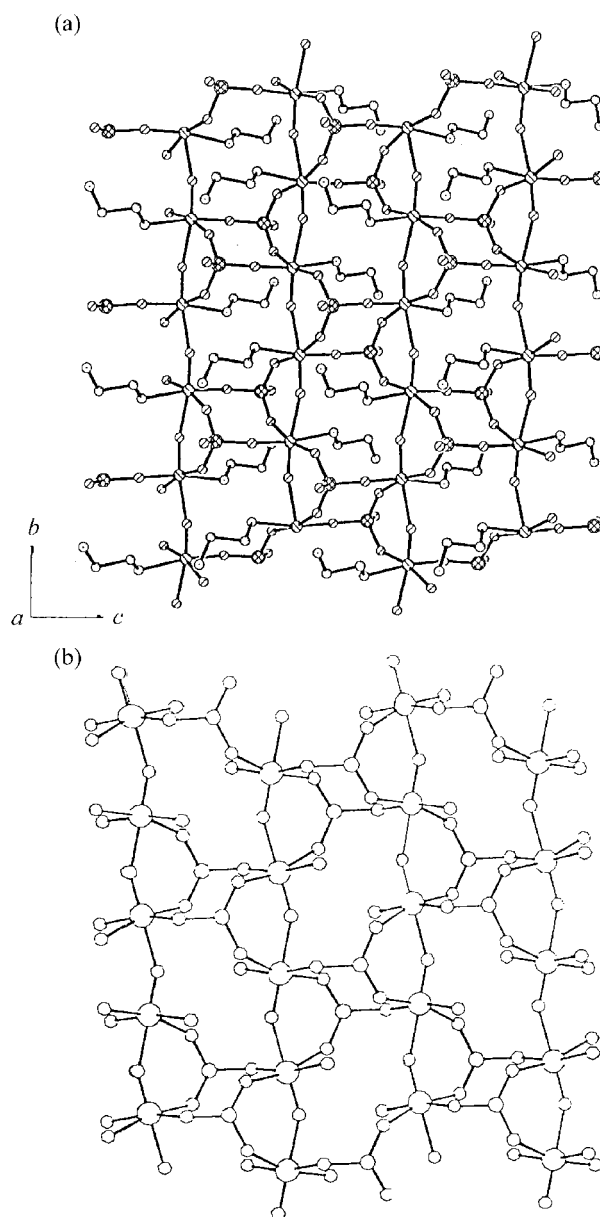


Fig. 6 The layered structures of (a) TP-J1 and (b)  $\text{VO}(\text{PhPO}_3)\cdot\text{H}_2\text{O}$ .

chains. Bands between 350 and 600  $\text{cm}^{-1}$  are attributed to O–P–O deformations ( $\nu_2$  and  $\nu_4$   $\text{PO}_4$  modes) and the vibrations of Ti–O bands. Peaks in the 1000  $\text{cm}^{-1}$  region are due to the symmetric and antisymmetric stretching vibrations,  $\nu_1$  and  $\nu_3$ , of isolated phosphate groups. Bands observed below 300  $\text{cm}^{-1}$  are attributed to lattice vibrations.

### 3.2 Description of the structure of TP-J1

The asymmetric unit of TP-J1 contains 11 non-hydrogen atoms (Fig. 5). The crystallographically independent Ti atoms are octahedrally coordinated ( $\text{TiO}_5\text{N}$ ). Three of the coordinated oxygen atoms are bridged to the adjacent  $\text{PO}_4$  tetrahedron, the other two oxygen atoms are connected to a neighboring  $\text{TiO}_5\text{N}$  octahedron while the N atom is the unprotonated end of the ethylenediamine molecule. The  $\text{PO}_4$  tetrahedra have the geometry observed for monophosphates, being corner-linked to three neighboring  $\text{TiO}_5\text{N}$  octahedra by O(5), O(1) and O(2) with the terminal P–O(3) group lying alternately above and below the chain into the interlayer space perpendicular to the sheet. The  $\text{TiO}_5\text{N}$  octahedra are significantly distorted with Ti–O bond lengths ranging from 1.701 to 2.168 Å while the Ti–N bond length is 2.208 Å. Compared to other Ti complexes, the Ti–N bond of TP-J1 is comparatively strong.<sup>15</sup> The Ti–O distances are distinctly different from those of typical layered titanium phosphates such as the  $\alpha$ - and  $\beta$ -layered phases (Ti–O 1.95–1.98 Å). However, the present Ti–O bond lengths are similar to those in KTP ( $\text{KTiOPO}_4$ ) type structures. The layer structure of TP-J1 is composed of infinite zigzag corner-shared  $\text{TiO}_5\text{N}$  octahedral chains connected by phosphate tetrahedra along the *b*-axis with Ti(1)#4–O(4)–Ti(1) and O(4)#1–Ti–O(4) angles of 144.80(19) and 169.66(7)°. Each chain is separated from the next by phosphate tetrahedra, which bond to two adjacent titanium octahedra in one chain and a single  $\text{TiO}_5\text{N}$  octahedron in a neighboring chain and a net-like framework is formed [Fig. 6(a)]. The  $\text{TiO}_5\text{N}$  octahedra are all *trans*-linked as in  $\alpha$ - $\text{NaTiOPO}_4$  (Fig. 7).<sup>3</sup> Like most KTP analogues, one shorter (<1.75 Å) ‘titanyl’ Ti–O bond and one longer (>2.10 Å) bond (Ti–O(4)#1 1.701 Å, Ti–O(4) 2.168 Å) alternating between the octahedra are seen in the structure of TP-J1. The difference in the Ti–O distances (0.467 Å) is larger in

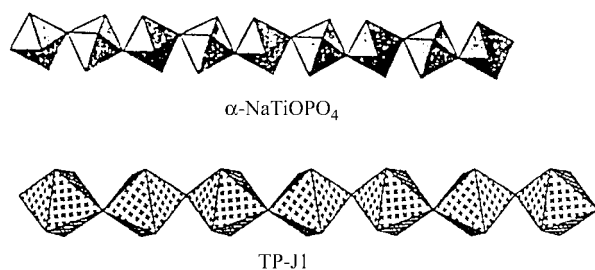


Fig. 7 The *trans*-linked octahedral chains of TP-J1 and  $\alpha$ - $\text{NaTiOPO}_4$ .

comparison with most KTP-type compounds (Table 4). In addition, compared with the KTP structure, the  $\text{TiO}_5\text{N}$  octahedra are substantially distorted owing to the coordination of N in place of O along the *a*-axis, with the Ti atom lying off-centre in the octahedron.

TP-J1 has the same topology as the layered vanadium phenyl phosphonate  $\text{VO}(\text{PhPO}_3)\cdot\text{H}_2\text{O}$ ,<sup>16</sup> which crystallizes in the monoclinic space group  $C2/c$ . In the latter, the octahedral chain can be described as  $\text{V}=\text{O}-\text{V}=\text{O}$  and a water molecule is coordinated to V, similarly to the N bound to Ti in TP-J1 [Fig. 6(b)], while the phosphate is replaced by phenyl phosphonate.

The protonated ethylenediamine molecules are sandwiched between the sheets (Fig. 8). In most organic–inorganic solid compounds, organic amines exist as charge-balanced cations in the diprotonated state and serve as H-bond donors to the nearest framework oxygen. In the structure of TP-J1, however, one end [N(2)] of the ethylenediamine molecule is protonated (charge-balanced) as well as acting as an H-bond donor interacting with a terminal O atom of  $\text{PO}_4$  from a neighboring sheet [N(2)–H(2A)⋯O(3A), 2.791 Å, N(2)–H(2B)⋯O(3B), 2.774 Å, N(2)–H(3C)⋯O(3C), 2.936 Å]. The other (unprotonated) nitrogen [N(1)] is coordinated directly to the Ti atom

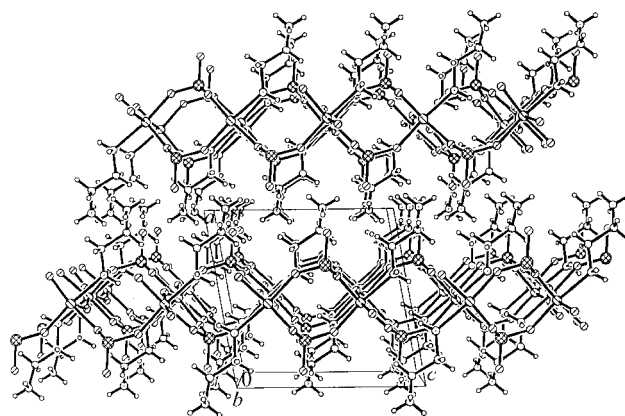


Fig. 8 Structure of TP-J1 viewed down the *b*-axis.

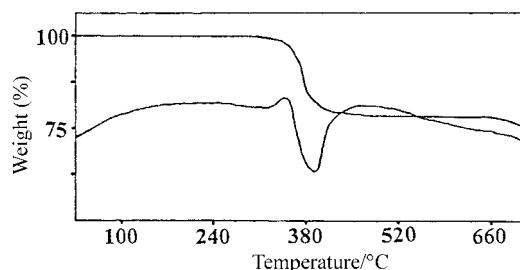


Fig. 9 TGA–DTA curves of TP-J1.

Table 4 Comparison of Ti–O distances (Å) in TP-J1 with KTP-type compounds

Compound	Ti(1)–O(1)	Ti(1)–O(9)	Ti(1)–O(10)	$\Delta$ (Ti–O)	Ti(2)–O(9)	Ti(2)–O(10)	$\Delta$ (Ti–O)
$\text{KTiOPO}_4$	2.161(4)	1.993(4)	1.718(4)	0.443(6)	1.738(4)	2.101(4)	0.363(6)
$\text{NH}_4\text{TiOPO}_4$	2.148(4)	1.967(3)	1.717(3)	0.438(5)	1.742(4)	2.096(4)	0.354(6)
$\text{TlTiOPO}_4$	2.154(5)	1.961(5)	1.725(5)	0.429(7)	1.747(5)	2.076(5)	0.329(7)
$\text{RbTiOPO}_4$	2.148(5)	1.967(4)	1.722(5)	0.426(7)	1.750(5)	2.094(5)	0.344(7)
$\text{AgTiOPO}_4$	2.228(11)	1.998(11)	1.709(11)	0.519(16)	1.783(12)	2.073(11)	0.290(16)
$\beta$ - $\text{NaTiOPO}_4$	2.229(6)	2.007(6)	1.714(6)	0.515(8)	1.755(6)	2.102(6)	0.347(8)
$(\text{NH}_4)_{0.5}\text{H}_{0.5}\text{TiOPO}_4$	1.947(4)	2.012(4)	1.901(4)	0.046(6)	2.114(5)	1.746(5)	–0.350(7)
$\text{NH}_4\text{H}_3\text{OTi}_2(\text{PO}_5)_2$	2.15(3)	2.04(2)	1.70(2)	0.45(4)	1.79(2)	2.04(2)	0.25(3)
$\text{KTiOAsO}_4$	2.138(15)	1.957(16)	1.735(16)	0.403(22)	1.770(19)	2.097(19)	0.327(27)
$\text{KTiO}(\text{P}_{0.5}\text{As}_{0.5})\text{O}_4$	2.153(7)	1.975(8)	1.727(7)	0.426(11)	1.759(8)	2.091(8)	0.332(11)
$\text{K}_{0.5}(\text{NH}_4)_{0.5}\text{TiOAsO}_4$	2.153(11)	1.984(11)	1.731(11)	0.422(16)	1.763(11)	2.123(11)	0.360(16)
$\text{TlTiOPO}_4$	2.054(10)	1.823(9)	1.823(9)	0.231(13)	1.901(7)	1.901(7)	0.000(10)
TP-J1	Ti(1)–O(4)	Ti(1)–O(4)#1		0.467			
	2.168(3)	1.701(3)					

with a Ti–N distance of 2.208 Å. Imobility of the ethylenediamine molecule is thus predicted.

Thermogravimetric analysis (Fig. 9) shows a *ca.* 21% weight loss from 330 to 400 °C and is inconsistent with the calculated mass of ethylenediamine in TP-J1 (27.8 wt%), but in accord with the loss of C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> (20.5 wt%). This result may be caused by a weakened C–N bond resulting from the Ti–N interaction. When heated, C–N bond scission occurs with the formation of C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>. In agreement with the TGA curve, a weak exothermic peak is observed in the DTA curve at *ca.* 330 °C which may correspond to C–N bond scission. At higher temperatures, the main strong endothermic peak is assigned to the loss of organoamine. Samples calcined in air at 380 °C for 2 h collapse and are converted to an amorphous phase. Titanium oxide phosphate [Ti<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>] forms upon calcination at 800 °C (JCPDS: 36-699).

#### 4 Conclusion

A novel organically templated titanium phosphate TP-J1 with a layered structure has been synthesized under solvothermal conditions. In contrast to most layered titanium phosphates, the structure of TP-J1 is similar to that of KTP. The layers are constructed from infinite Ti–O–Ti chains connected by PO<sub>4</sub> tetrahedra with alternate short and long terminal Ti–O bonds while the organic amine is unusually monoprotonated. The protonated end of the amine acts as an H-bond donor to a terminal O of PO<sub>4</sub> in a neighboring sheet, while deprotonated N is directly bonded to Ti. The unique structure of TP-J1 increases our understanding of titanium phosphates. Systematic investigation of the TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>–amine system under solvothermal conditions should lead to the synthesis of further titanium phosphates.

#### Acknowledgements

The authors acknowledge the financial support of the National Natural Science Foundation of China and the Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University.

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Paper a904837e