

# Syntheses and Structures of Two Reduced Open-framework Titanophosphates

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Using metallic Ti powder as raw materials and 1,2-diaminocyclohexane (DACH) as the trial template, two novel reduced titanophosphate open-structures were hydrothermally isolated by varying the H<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O ratio to adjust the pH value. TiPO-1 crystallizes in orthorhombic *Pbca* space group with cell parameters  $a = 21.956(3)$  Å,  $b = 8.6268(11)$  Å,  $c = 7.2883(9)$  Å,  $V = 1380.5(3)$  Å<sup>3</sup>,  $Z = 4$ . TiPO-2 crystallizes in triclinic space group  $P\bar{1}$  with parameters  $a = 5.1620(10)$  Å,  $b = 8.815(2)$  Å,  $c = 10.655(3)$  Å,  $\alpha = 99.45^\circ$ ,  $\beta = 102.94^\circ$ ,  $\gamma = 91.06^\circ$ ,  $V = 465.34$  Å<sup>3</sup>. TiPO-1 is constructed by infinite -Ti-O-Ti-O- linkage that is capped by PO<sub>4</sub> groups to form a chain structure with protonated DACH molecules occupying the interchain spaces. TiPO-2 represents a rare 3-D reduced titanophosphate with 12-MR channels. The structure of TiPO-2 is a neutral framework with water molecules located in the channels.

**Key Words :** Hydrothermal synthesis. Open-structure. Single crystal structure. Titanophosphate

## Introduction

Transition metal phosphate open-structures are of great interest due to their wide applications in redox catalysis, ion-exchange, photochemistry and magnetism.<sup>1-3</sup> The structural diversity that stemmed from the variable coordination geometry and oxidation states has directed to the extensive expansion of open-framework transition metal phosphates, including Zn, Co, Zr, Fe, Ni, and V phosphates, with large dimensions, unique topologies and novel polyhedral connectivities.<sup>4-13</sup> Titanium phosphates have shown important properties in materials science, such as the second harmonic generation crystal KTiOPO<sub>4</sub>, the excellent ion-exchange and adsorptive properties of layered  $\alpha$ -Ti(HPO<sub>4</sub>)<sub>2</sub>,  $\gamma$ -Ti(H<sub>2</sub>PO<sub>4</sub>)(PO<sub>4</sub>)·H<sub>2</sub>O, and the NASICON-type MTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> as fast ionic conductors or low thermal expansion ceramics.<sup>14-18</sup> However, the open-structured titanophosphates are still limited in literature up to date. Rb<sub>2</sub>Ti<sub>3</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub> was the first synthetic example with 12-ring channels for the pursuit of new KTP-related compound.<sup>19</sup> Two layered structures and an anhydrous form of  $\gamma$ -Ti(H<sub>2</sub>PO<sub>4</sub>)(PO<sub>4</sub>)·H<sub>2</sub>O were reported in the early 1990s.<sup>20-22</sup> Clearfield and co-workers contributed three porous structures, which contain monomeric, dimeric and trimeric TiO<sub>6</sub> octahedra respectively.<sup>23</sup> Several new titanophosphate and titanophosphonate compounds were isolated by Ferey's group and Pang's group in the past few years.<sup>24-29</sup> The first templated microporous mixed-valent Ti<sup>III</sup>Ti<sup>IV</sup> titanophosphate were reported by Sevov.<sup>30</sup> Of the known titanophosphate compounds, reduced materials are rare and interesting for catalytic, magnetic properties. Recently, two reduced titanium gallophosphates were synthesized, including a novel microporous phase possessing 10-MR channels and reversible oxidation state of Ti<sup>III</sup> and Ti<sup>IV</sup>, showing potential redox catalytic property.<sup>31,32</sup> A new

mixed valent titanophosphate open-structure with intersecting 12-ring channels, TiPO-2, was recently reported by using zinc cations as the mineralizer. By Using 1,2-diaminocyclohexane (DACH) as the trial template, two new reduced titanophosphate open-structures [H<sub>2</sub>DACH]H<sub>0.5</sub>[TiO(HPO<sub>4</sub>)<sub>2</sub>]·H<sub>2</sub>O (denoted as TiPO-1) and [Ti<sup>III</sup>Ti<sub>0.5</sub><sup>IV</sup>(H<sub>2</sub>O)<sub>0.5</sub>(PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>0.5</sub>]·H<sub>2</sub>O (denoted as TiPO-2) were isolated. Here we report their syntheses and structures.

## Experimental

TiPO-1 was synthesized from 0.25 g metallic Ti powder, 3 mL H<sub>3</sub>PO<sub>4</sub>, 7 mL H<sub>2</sub>O and 1 g DACH as a template. Typically, Ti powder, H<sub>3</sub>PO<sub>4</sub> and water was sealed in an autoclave and reacted at 180 °C for two days. After cooled to room temperature, DACH was injected and stirred to homogeneity. The final mixture with pH value of 2.5 was heated at 180 °C for 8 days. 1.39 g blue plate-like crystals precipitated at the bottom with 68% yield based on titanium metal. A similar procedure was performed for isolating compound TiPO-2 with different compositions of 0.25 g metallic Ti powder, 7 mL H<sub>3</sub>PO<sub>4</sub>, 3 mL H<sub>2</sub>O and 1 g DACH. The pH value of the starting mixture for TiPO-2 was -0.25. Reddish brown polyhedral crystals formed with very low yield. These crystals are stable in air for several months. The blue and brown colours of TiPO-n indicate the existence of Ti<sup>3+</sup> species in these compounds. The Ti:P ratio were measured by energy dispersive X-ray analysis on three crystals of each sample with the average results of 10.78:5.97 for TiPO-1 and 10.56:6.24 for TiPO-2 respectively, which were close to the theoretical values.

Single crystals of TiPO-1 and TiPO-2 were mounted on glass fibers. The data were collected on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW

**Table 1.** Crystal data and structural refinement for TiPO-1 and TiPO-2

Compound Name	TiPO-1	TiPO-2
Formula weight	390.99	1237.38
Temperature	293(2) K	
Crystal system, space group	orthorhombic, <i>Pbca</i>	triclinic, $P\bar{1}$
<i>a</i> , $\alpha$	21.956(3) Å, 90°	5.1620(10) Å, 99.45°
<i>b</i> , $\beta$	8.6268(11) Å, 90°	8.815(2) Å, 102.94°
<i>c</i> , $\gamma$	7.2883(9) Å, 90°	10.655(3) Å, 91.06°
Volume	1380.5(3) Å <sup>3</sup>	465.34
Z, Calculated density (gcm <sup>-3</sup> )	4, 1.824	1, 2.379
Absorption coefficient (mm <sup>-1</sup> )	0.904	1.800
Theta range for data collection	1.86° to 28.31°	1.99° to 25.00°
Reflections collected/unique	8373 / 3270 [ <i>R</i> <sub>int</sub> = 0.0247]	1808/1609 [ <i>R</i> <sub>int</sub> = 0.0695]
Goodness of fit	1.090	1.069
R indices (all data)	<i>R</i> <sub>1</sub> = 0.0663, <i>wR</i> <sub>2</sub> = 0.1478	<i>R</i> <sub>1</sub> = 0.0868, <i>wR</i> <sub>2</sub> = 0.1978

sealed tube X-ray source. The structure was solved by directed method. The titanium and phosphorous and oxygen atoms were first located and the carbon, nitrogen and part of hydrogen atoms were found in the final difference Fourier maps. Structure solution and refinement were performed by using SHELXTL (Ver. 5.01) program. Crystal data and details of structure refinement are given in Table 1. The atomic positions are listed in Table 2 and Table 3 for TiPO-1 and TiPO-2 respectively.

### Results and Discussion

TiPO-1 and TiPO-2 were synthesized by varying the H<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O ratio to adjust the pH value of the starting mixtures. The speciation of titanium in solution has been claimed depending on several factors. In the present system, the pH value plays the key role. Studies on the hydrolysis of Ti<sup>3+</sup> cation indicate the tendency of formation Ti<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup> dimer and containing significant amount of Ti<sup>4+</sup> cations in the system even at very low pH value.<sup>33</sup> This makes it more difficult to understand the hydrolysis behavior and the formation mechanism of TiPO-*n*. Ferey's group has systematically investigated the deprotonation of Ti<sup>4+</sup> to study the formation mechanism of Ti<sup>IV</sup> titanophosphates.<sup>34</sup> Deprotonation lead to condensation through phosphate bridges. The dimensionality of the crystal is affected by the protonation of phosphate group. When the acidity decreases, condensation of TiO<sub>6</sub> occurs through the formation of Ti-O-Ti bond including clusters and chains. The phenomenon in the formation of TiPO-*n* is similar to Ferey's observations, which suggests the hydrolysis of Ti<sup>4+</sup> cations at different acidity directed the structural variation of TiPO-*n*. The comparison between the experimental and simulated powder XRD patterns indicates both of TiPO-1 and TiPO-2 are isolated as pure phase

**Table 2.** Atomic coordinates and equivalent isotropic displacement parameters for TiPO-1

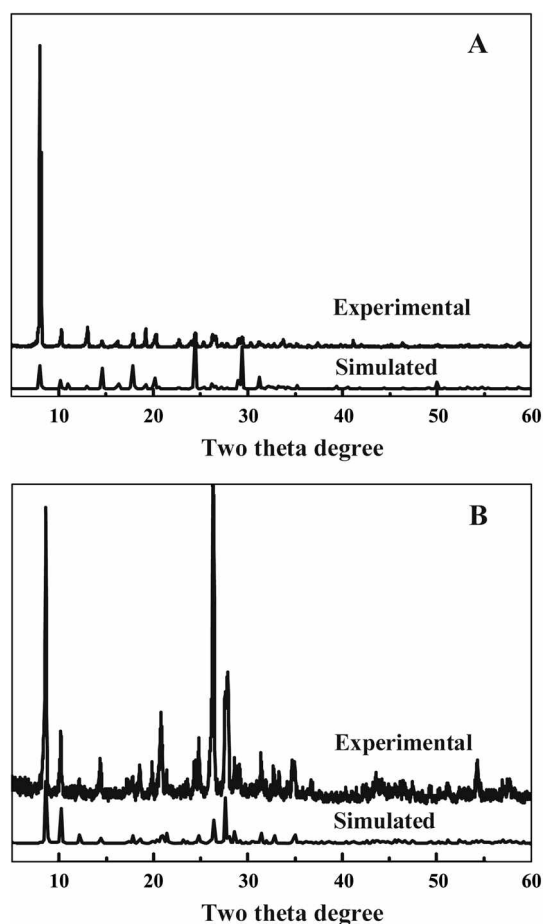
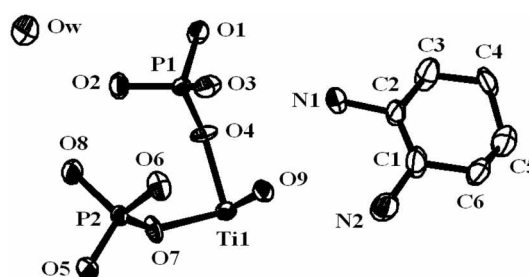
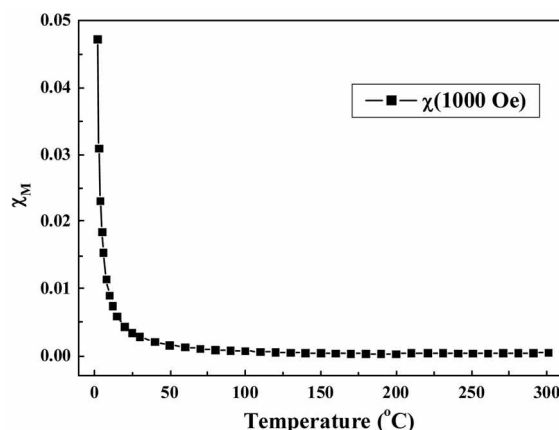
	x	y	z	U <sub>eq</sub>
P1	0.39129(4)	0.34864(10)	0.2087(4)	0.0164(2)
P2	0.43029(4)	0.76983(10)	0.2099(4)	0.0155(2)
Ti1	0.49836(8)	0.5002(2)	0.4689(3)	0.0257(2)
O1	0.36582(14)	0.1796(4)	0.2059(12)	0.0240(7)
O2	0.33555(12)	0.4518(3)	0.2120(12)	0.0296(7)
O3	0.4309(2)	0.3747(8)	0.0356(7)	0.0264(13)
O4	0.4301(2)	0.3697(8)	0.3771(6)	0.0226(13)
O5	0.43957(12)	0.9418(3)	0.2109(12)	0.0250(6)
O6	0.4587(3)	0.6925(7)	0.0359(7)	0.0246(13)
O7	0.4539(3)	0.6953(7)	0.3807(7)	0.0239(13)
O8	0.35963(13)	0.7430(4)	0.2040(13)	0.0310(7)
O9	0.53654(12)	0.4796(3)	0.2084(10)	0.0209(5)
OW	0.2384(2)	0.5427(5)	0.0065(8)	0.0500(15)
HWA	0.2119	0.5584	0.1113	0.060
HWB	0.2117	0.5584	-0.0981	0.060
N1	0.53937(15)	0.1245(4)	0.2057(13)	0.0230(7)
H11	0.5112	0.0503	0.2071	0.034
H12	0.5357	0.1799	0.1033	0.034
H13	0.5343	0.1860	0.3025	0.034
N2	0.6514(2)	0.3148(5)	0.226(2)	0.0551(19)
H21	0.6896	0.3493	0.2221	0.083
H22	0.6344	0.3433	0.3321	0.083
H23	0.6303	0.3548	0.1336	0.083
C1	0.6513(2)	0.1510(6)	0.213(3)	0.061(2)
H1A	0.6498	0.1580	0.0791	0.073
C2	0.6003(2)	0.0538(6)	0.213(3)	0.085(3)
H2A	0.6015	0.0501	0.0783	0.103
C3	0.6023(2)	-0.1091(5)	0.219(2)	0.0423(15)
H3A	0.5762	-0.1488	0.1228	0.051
H3B	0.5848	-0.1418	0.3354	0.051
C4	0.6635(2)	-0.1847(5)	0.2003(17)	0.0351(13)
H4A	0.6720	-0.2013	0.0712	0.042
H4B	0.6626	-0.2852	0.2599	0.042
C5	0.7141(3)	-0.0881(8)	0.2836(10)	0.0428(16)
H5A	0.7532	-0.1359	0.2578	0.051
H5B	0.7091	-0.0832	0.4157	0.051
C6	0.71264(19)	0.0765(6)	0.2029(17)	0.0319(10)
H6A	0.7417	0.1405	0.2683	0.038
H6B	0.7253	0.0720	0.0755	0.038
H1	0.383(3)	0.124(7)	0.179(12)	0.03(2)
H2	0.3505(18)	0.653(5)	0.251(6)	0.000(11)

(Figure 1).

Single crystal structure refinement reveals that TiPO-1 crystallizes in the orthorhombic space group *Pbca*. The asymmetric unit of TiPO-1 contains 21 non-hydrogen atoms, one Ti, two P, ten O, two N and six C atoms (Figure 2). The Ti atom is hexagonally coordinated by six O atoms with the bond lengths of 1.914(7)-2.083(7) Å. The bond angles range from 87.07(18)° to 179.63(12)°. Four coordinated oxygen atoms of Ti are connected to P1 [O3, O4] and P2 [O6, O7] atoms. The O9 atom bridges the titanium atoms into an infinite linear -Ti-O-Ti-O-Ti- linkage with O9-Ti-O9 bond

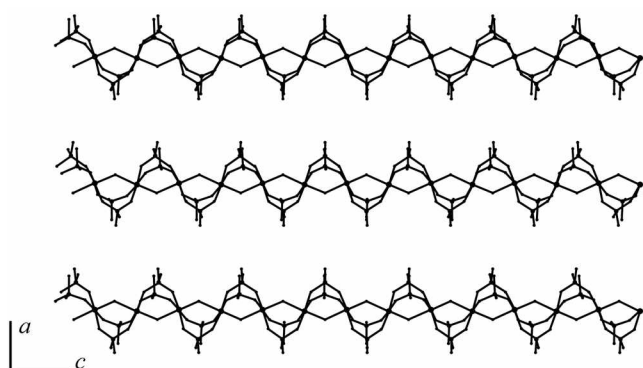
**Table 3.** Atomic coordinates and equivalent isotropic displacement parameters for TiPO-2

	x	y	z	U
Ti1	0.5000	0.5000	0.0000	0.0111(5)
Ti2	-0.1390(2)	1.06236(14)	0.20608(12)	0.0095(4)
P3	-0.6046(3)	1.3098(2)	0.23393(18)	0.0105(5)
P4	0.2983(3)	0.8492(2)	0.09600(18)	0.0090(5)
P5	0.0580(9)	0.9158(5)	0.4735(4)	0.0241(10)
O1	0.1560(11)	0.4293(6)	-0.1497(5)	0.0216(12)
O2	0.3519(12)	0.3742(7)	0.1077(6)	0.0308(15)
O3	0.3031(11)	0.6750(6)	0.0692(6)	0.0247(14)
O4	-0.5899(17)	1.4448(8)	0.3509(7)	0.0451(19)
O5	-0.3436(11)	1.2338(6)	0.2614(6)	0.0237(13)
O6	0.1658(10)	1.2013(7)	0.2344(6)	0.0246(14)
O7	-0.2449(10)	1.0834(7)	0.0306(5)	0.0221(13)
O8	-0.4370(10)	0.9178(6)	0.1853(5)	0.0146(11)
O9	0.0732(10)	0.8889(6)	0.1660(5)	0.0154(11)
O10	-0.0338(10)	1.0371(6)	0.3897(4)	0.0179(12)
O10'	0.0338(10)	0.9629(6)	0.6103(4)	0.0179(12)
O11	-0.115(4)	0.7662(13)	0.4127(14)	0.065(6)
O12	0.338(3)	0.857(3)	0.4609(18)	0.114(11)
OW1	0.0000	0.5000	-0.5000	0.118(7)
OW2	-0.347(8)	0.705(3)	0.386(2)	0.132(13)

**Figure 1.** The experimental and simulated XRD patterns of TiPO-1 (A) and TiPO-2 (B).**Figure 2.** The ORTEP view of TiPO-1 with the labelling scheme.**Figure 3.** The magnetic curve of TiPO-1.

angel of  $179.63^\circ$ . The  $\text{PO}_4$  groups have the geometry of the monophosphate with the bond lengths ranging from  $1.494(6)$  Å to  $1.569(3)$  Å and the bond angles of  $105.06(17)$ - $112.4(4)^\circ$ . Two oxygen atoms of each P atom are joint to Ti atoms, with the rest pending to the interchain spaces. O1 of P1 and O8 of P2 are hydroxy groups with the elongated P-O distances [P1-O1,  $1.562(3)$  Å; P2-O8,  $1.569(3)$  Å]. Magnetic curve was measured to determine the oxidation state of Ti in TiPO-1. The experimental curve (Figure 3) is fitted with  $\chi_m = C_m/(T-\theta) + \text{TIP}$ , where  $C_m$  and  $\theta$  are the Curie and Weiss constants respectively, and TIP is the temperature independent paramagnetism originated from mixing of low-lying empty states. The Curie constant indicates the magnetic moments of  $0.867 \mu_B$ . This is consistent with half unpaired electron per formula unit. Bond valence sum calculation gives the oxidation state of Ti atoms of 3.51, which is in agreement with the magnetic result. For the charge balance, half proton is required. Hence TiPO-1 is formulated as  $[\text{H}_2\text{DACH}]\text{H}_{0.5}[\text{TiO}(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$ .

$\text{TiO}_6$  octahedral and  $\text{PO}_4$  tetrahedral are held together forming an anionic  $[\text{TiO}(\text{HPO}_4)_2]^{-2.5}$  chain structure (Figure 4). The negative charges are compensated by protonated DACH molecules. The  $\text{TiO}_6$  octahedral is slightly distorted along the chain direction with the difference of Ti-O bond lengths [Ti-O9#1 and Ti-O9] of  $0.169$  Å, which is different from those in compounds JTP-A [a  $\text{Ti}^{\text{IV}}$  titanophosphate chain with similar topology of TiPO-1], TP-J1 and KTP type structures. The differences maybe originate from the existence of  $\text{Ti}^{\text{III}}$ . The interchain spaces are filled with protonated DACH and water molecules. The structure of TiPO-1 is

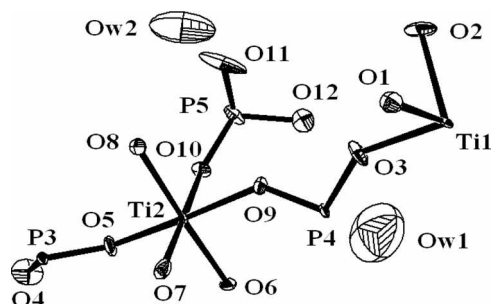


**Figure 4.** Structure of TiPO-1 along [010] direction. The H atoms, water and DACH molecules are omitted for clarity.

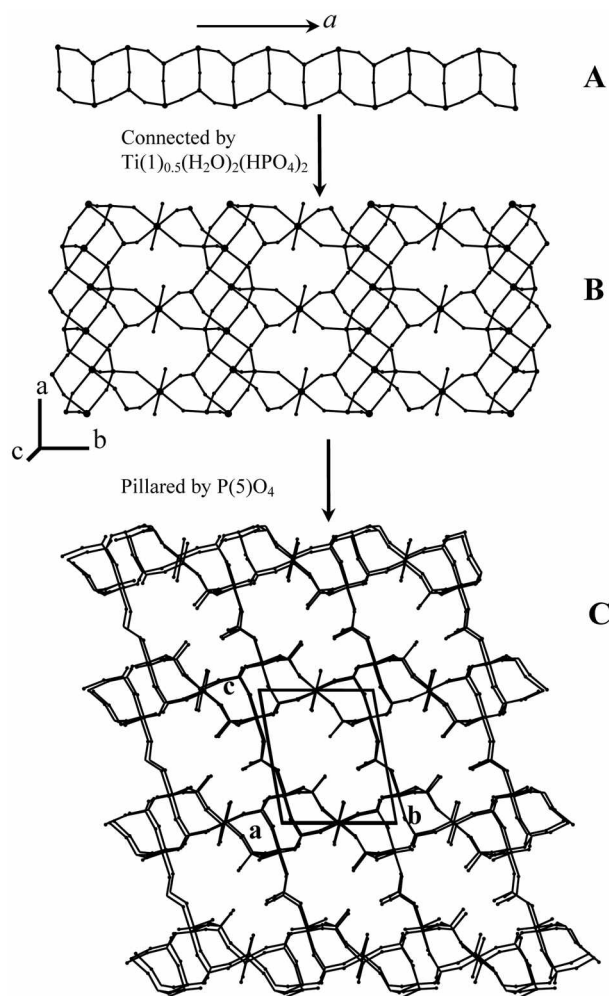
stabilized by complex H-bonds [N1-H...O5, 2.70 Å, N1-H...O6, 2.87 Å, N1-H...O7, 2.84 Å, N1-H...O9, 3.06 Å; N2-H...Ow1, 2.79 Å, N2-H...O9, 2.90 Å; O1-H...O5, 2.61 Å; O8-H...O2, 2.57 Å].

TiPO-1 is a structural analogue to AlPO-CJ10 (a chain structure of fluoroaluminophosphate),<sup>35,36</sup>  $\text{LiNa}_2\text{HAl}(\text{PO}_4)_2 \cdot (\text{OH})$ ,  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  and  $\text{Na}_3\text{Al}(\text{OH})(\text{HPO}_4)(\text{PO}_4)$ ,<sup>37,38</sup>  $\text{Ti}^{\text{IV}}$  titanophosphate JTP-A and mineral tancoite.<sup>28</sup> Similar chain structures also occur in two gallophosphates.<sup>39</sup> These reveal some relationship between aluminophosphate, gallophosphate and titanophosphate. In JTP-A, the  $-\text{Ti}^{\text{IV}}-\text{O}-\text{Ti}^{\text{IV}}-\text{O}-$  linkage is in *cis-cis-trans* configuration. Due to the flexibility of ethylenediamine molecules, the bending of the chains gives rise to helices. However, the  $\text{TiO}_6$  octahedral in TiPO-1 are all *trans*-linked similar to the  $-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$  linkages in TP-J1 and  $\alpha\text{-NaTiOPO}_4$ .<sup>24</sup> The rigid DACH template directs to a linear chain structure.

Compound TiPO-2 crystallizes in the triclinic space group  $P\bar{1}$ . The asymmetric unit contains eighteen non-hydrogen atoms, two Ti, three P and thirteen O (Figure 5). Both of the two Ti atoms are coordinated by six O atoms with the bond lengths of 1.974(6)-2.109(6) Å for Ti1 and 1.863(6)-1.972(5) Å for Ti2 respectively. Four oxygen atoms attached to Ti1 are joints to P3 and P4 atoms. The rest of two oxygen atoms belong to coordinated water molecules with elongated Ti-O bond of 2.114 Å. All of the oxygen atoms attached to Ti2 bond to P atoms. The  $\text{PO}_4$  groups have the geometry of the monophosphate with the bond lengths ranging from 1.479(6) to 1.570(9) Å and the bond angles of 98.3(13)-117.8(8)°. O4 of P3 and O11 and O12 of P5 are hydroxy



**Figure 5.** The ORTEP plot of TiPO-2 with the labeling scheme.



**Figure 6.** Illustration of the formation scheme of TiPO-2 showing the 4-MR chains (A), the 8-MR channels along *c* direction (B) and 12-MR channels along *a* direction (C).

groups with the elongated P-O bond lengths. Bond valence sum calculation shows that the oxidation state of Ti atoms are 3.23 for Ti1 and 4.17 for Ti2 respectively. The ratio of  $\text{Ti}^{\text{III}}$  to  $\text{Ti}^{\text{IV}}$  is 0.5. Hence, TiPO-2 can be formulated as  $[\text{Ti}_{10.5}^{\text{III}}(\text{H}_2\text{O})_2\text{Ti}^{\text{IV}}(\text{PO}_4)(\text{HPO}_4)(\text{H}_2\text{PO}_4)_{0.5}] \cdot \text{H}_2\text{O}$ .

The extended structure of TiPO-2 is a neutral network constructed by  $\text{TiO}_6$  and  $\text{PO}_4$  groups without Ti-O-Ti and P-O-P linkages. The structure could be illustrated as the following steps as shown in Figure 6.  $\text{Ti}_2\text{O}_6$  and  $\text{P}_4\text{O}_4$  groups fuse together to form 4-MR rings. The edge linking of these 4-MR rings generates infinite chains running along *a* direction. These chains are connected by  $[\text{Ti}_1(\text{H}_2\text{O})_2(\text{HPO}_4)_2]$  bridges, giving rise to a layer structure in *ab* plane with 8-MR windows along *c* axis. Using  $\text{P}_5\text{O}_4$  groups as pillars, stacking of these layers produces a complex 3-D tunnel architecture with 12-MR channels along *a* direction (Figure 6C) and 8-MR tunnels along *b* directions (Figure 7). The 12-MR channels show a dimension of 10.6 Å (O8-O9)  $\times$  6.6 Å (O5-O6). The channel spaces are occupied by water molecules.

The thermogravimetric curves of TiPO-1 and TiPO-2 are

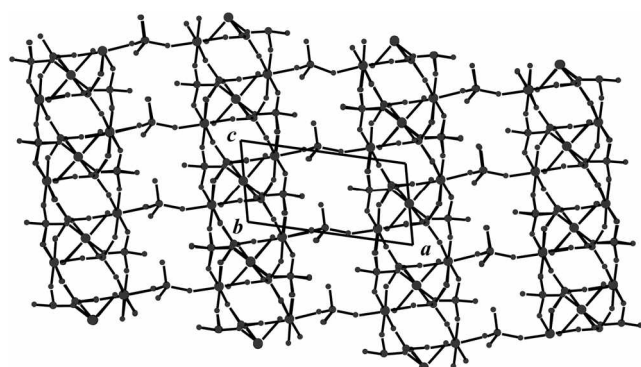


Figure 7. Structure of TiPO-2 along *b* direction showing the 8-MR ring channels.

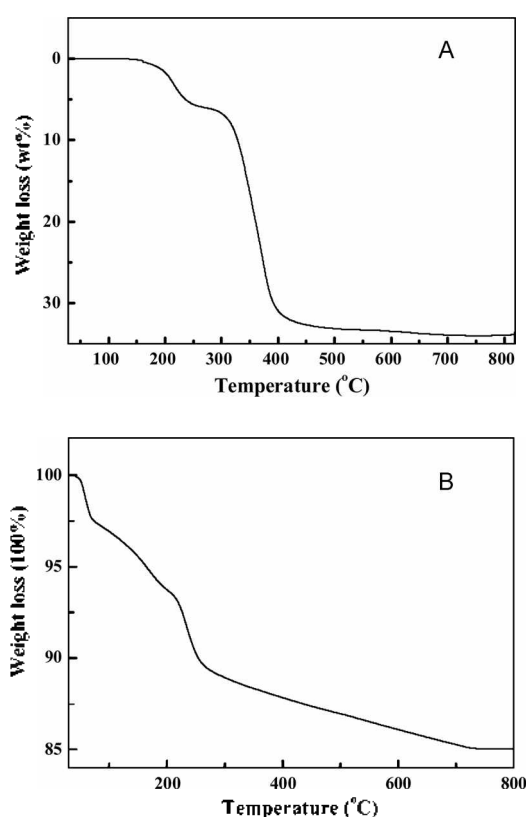


Figure 8. The TG curves for TiPO-1 (A) and TiPO-2 (B).

shown in Figure 8. Thermogravimetric analysis of TiPO-1 shows a two-step weight loss. The 6.05% weight loss at 150–290 °C is assigned to the emission of water. 27.35% of mass loss between 290 °C and 600 °C is attributed to the loss of DACH molecules and hydroxyl groups. Heating TiPO-1 at 220 °C for two hours results in deep blue crystals. Indicated by the powder XRD data, the first peak of the heated crystal slightly shifted to low angle compared with the as-prepared sample. Attempts on determining the structure of the annealed sample failed. The total 14.96% weight loss of TiPO-2 between 40 °C and 800 °C was in agreement with the calculated result of 15.2% [2.4%, 40–70 °C; 4.0%, 70–200 °C; 8.56%, 200–720 °C]. These mass losses are stemmed from removing water molecules.

## Conclusions

The present study shows that various topologies of titanophosphates could be formed by adjusting the starting compositions under the assistance of organoamine. Two novel mix-valent titanophosphate open-structures have been successfully isolated under hydrothermal conditions. The structures varied from 1-D chain of TiPO-1 to 3-D tunnel structure of TiPO-2 by changing the  $H_3PO_4/H_2O$  ratio. TiPO-2 is a rare example of three-dimensional reduced titanophosphate with intersecting 12-MR apertures, which indicates that large dimensions could be accessed in the family of reduced titanophosphates.

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