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A New Organo-Directed Titanium Phosphate Phase Containing Zigzag Chains of Corner-Sharing TiO_6 Octahedra

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Abstract: A new organo-directed titanium phosphate, $[NH_3CH_2CH_2NH_3]\cdot[TiO(HPO_4)_2]$, was synthesized by the solvothermal method and its structure was determined by single crystal X-ray diffraction. The structure consists of 1-D zigzag chains built up from *trans*-corner-sharing titanium oxo octahedra running along the b axis, with fused Ti_2P three-membered rings being attached to the – Ti – O – Ti – O – backbone.

Keywords: Titanium compound, 1-D chain structure, solvothermal synthesis.

The chemistry of titanium phosphates has attracted considerable interests because of their applications in ion exchange, redox catalysis and outstanding non-linear optical materials. However, only a few titanium compounds have been reported, and fewer reports deal with single-crystal structure determinations due to the difficulty in obtaining large single crystals of titanium phosphates. The synthesis of titanium phosphates often leads to two-dimensional layered phases[1-3], and several titanium phosphates with open-framework structure have recently been reported[4-5]. In order to search for new titanium-based material, we have undertaken a systematic study of the titanium phosphates in the system TiO_2-P_2O_5-en-BuOH by solvothermal method. In this work, we report the first organo-directed titanium phosphate, $[NH_3CH_2CH_2NH_3]\cdot[TiO(HPO_4)_2]$ (denoted JTP-B), with 1-D zigzag chain architecture.

Compound JTP-B was synthesized by solvothermal reaction of $Ti(OC_4H_9)_4$ (TBOT), H_3PO_4, $NH_2CH_2CH_2NH_2$ (en) in butanol (BuOH) solution, with a gel composition of 1.0 TBOT: 6.2 H_3PO_4: 6.4 en: 20 BuOH. The crystals of JTP-B suitable for a single crystal X-ray structure determination were obtained after heating the mixture in a Teflon-lined stainless steel autoclave at 453 K for 6 days. The product formed is essentially phase-pure based on X-ray powder diffraction.

Single crystal structural analysis of JTP-B reveals that it crystallizes in the space group $P2(1)/n$ with lattice parameters a = 8.670(5) Å, b = 7.253(2) Å, c = 16.601(7) Å, β = 102.69(3)°. The asymmetric unit, as shown in **Figure 1**, contains one crystallographically distinct Ti atom and two crystallographically distinct P atoms. The structure of the title compound represents a fundamental structural type for metal phosphates. It is a 1-D chain inorganic polymer shown in **Figure 2**. It consists of

infinite chains of *trans*-corner-sharing TiO_6 octahedra running parallel to the b axis. There are two TiO_6 octahedra per chain of unit cell length along the [010] direction. Each of two equivalent TiO_6 octahedra has a short Ti – O bond of 1.694 Å, *trans* to a long Ti – O bond of 2.214 Å. The octahedra sharing the opposed corners form a zigzag chain along the – Ti – O – Ti – O – backbone. The bond angle at the shared O atom between two Ti atoms is 136.4 (3)°. Other Ti – O bond lengths are in the range 1.990 – 2.021 Å.

Figure 1 Thermal ellipsoid plot (50 % probability) and atomic labeling scheme for an asymmetric unit of JTP-B

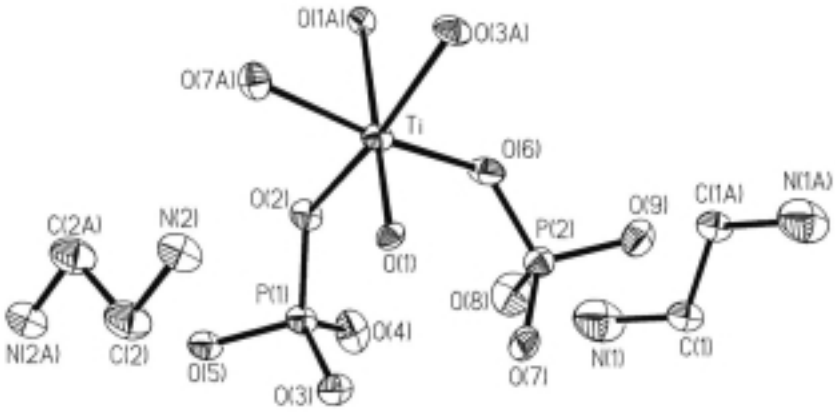
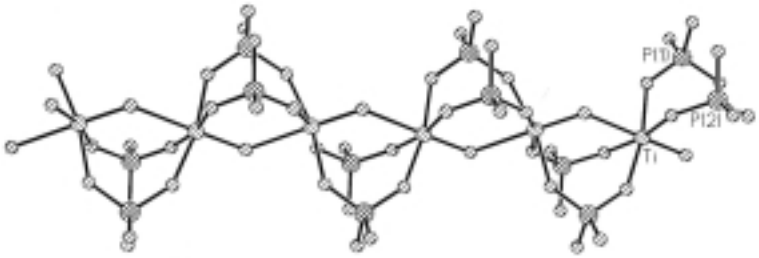


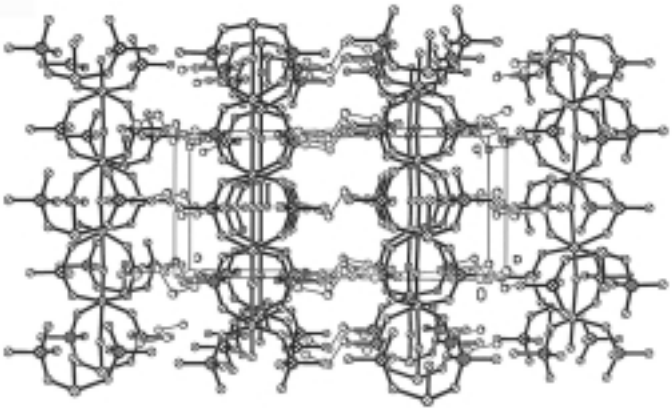
Figure 2 The zigzag chain of *trans*-corner-sharing titanium oxo octahedra linked with phosphorus oxo tetrahedra running along the [010] direction



Adjacent octahedra are bridged by two phosphate tetrahedra with sharing two corners of each tetrahedron. Two bridging phosphate groups connect two Ti atoms, thus a series of Ti-P-Ti three-membered rings are attached to the – Ti – O – Ti – O – backbone as shown in **Figure 2**. The P-O (bridging) distances are 1.512 – 1.526 Å and slightly

shorter than the P-O (terminal) bond lengths of 1.534 – 1.548 Å. Although the esd's are higher, the terminal P-O bond lengths would seem to support the formulation $[TiO(HPO_4)_2]$ for the inorganic component, with scrambling-disorder of terminal P-OH and $P\text{-}O^-$/ P=O functionalities. The ^{31}P MAS NMR spectrum of the sample has only one signal at 1.2 ppm, clearly indicating that the various phosphates are effective in similar structural environments.

Figure 3 view of the structure, showing the 1-D chains separated by organic cations



The (enH_2) cations physically separate the 1-D TiPO chains, and view of the structure showing the separation of the 1-D chains is given in **Figure 3**. The titanium phosphate chains are linked to organic cations by hydrogen bonds, thus the organic cations also help to stabilize the structure. On the basis of the O···O distances, all oxygen atoms are involved in hydrogen bonding. Two short O···O distances O(5)···O(5)#5 and O(9)···O(9)#6 of 2.499 and 2.630 Å respectively, indicate the existence of strong H-bonds between the chains. The organic cations are also nested *via* a hydrogen-bonded network.

The existence of the PO_4H side-groups in JTP-B indicates a low level of polyhedral condensation, which may have implications for the mechanism of build-up of TiPO polymers with higher levels of complexity. Interestingly, the structure showing a short – long bond alternation along the – Ti – O – Ti – O – backbone often emerges in the 3-D frameworks of outstanding non-linear optical materials KTP $(KTiOPO_4)$[6]. To our knowledge, however, the chain architecture of JTP-B has not been seen previously for polymeric TiPO systems. Further investigation of titanium phosphate compounds with novel stoichiometries and dimensionalities in solvothermal system is in progress.

References and notes

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7. Crystallographic data of $[NH_3CH_2CH_2NH_3]\cdot[TiO(HPO_4)_2]$: monoclinic, space group *P*2(1)/*n*; *a* = 8.670(5) Å, *b* = 7.253(2) Å, *c* = 16.601(7) Å, β = 102.69(3)°, Z = 4; Measurement temperature 293(2)K; Mo (Kα) = 0.71073 Å; R ($I>2\sigma(I)$) = 0.0651, *w*R2 = 0.1390.
   The numbers of collected reflections and independent reflections were 2215 and 1381, respectively. Structure solved by direct methods and refined by full-matrix least-squares. All calculation was performed using SHELXTL program system. Crystallographic parameters have been deposited in the editorial office of CCL.

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