

Na[H₂TETA]_{0.5}[ZnPO₄]₂·0.5H₂O or TJPU-1: A New Zincophosphate Open-structure Co-templated by Sodium and Organoamine

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Received September 4, 2006

Key Words : Co-template synthesis, Single crystal structure, Zeolite, Zinc phosphate

Synthetic open-structured materials attract increasing attention for wide applications in catalysis, ion-exchange or intercalation. Metal phosphates are possibly the fastest expanding group of open-framework inorganic materials in the past decade.¹ The structural diversity that stemmed from the variable coordination number and oxidation states has directed to the extensive expansion of open-framework metal phosphates. Since the bivalent metal phosphates (+2, +5) are associated with the same total charge as aluminosilicate zeolites (+3, +4), phosphate-based framework structures containing bivalent metals are considerably pursued. After the discovery of the first open-framework zincophosphate with zeolite topologies reported by G. D. Stucky,² a great deal of effort has been devoted to isolating novel open-structures within this system. And this compound group has experienced extraordinary expansion in terms of the diversity of their structures and compositions. Zincophosphates with zero-, one-, two-, and three-dimensional architectures have been isolated,³ in which an eye-catching result is the gigantic pore structure with 24-membered rings in ND-1.⁴ This variety was achieved by varying a number of factors that can influence the structure, including template, pH, solvent, reaction temperature, additives, zinc source and others. On the other hand, the pursuit of chiral molecular sieves is of great interest with respect to the applications in enantioselective separation and syntheses. However, only a few inorganic chiral frameworks were known up to now.⁵

For the syntheses of open-structured crystals, both alkali cations and organoamine are used as structure directing reagent separately in the literatures. Although there are some compound containing both of them,⁶ systematically investigation of the co-template effect of alkali cations and organoamines is seldom. Our group has focused on metal phosphate open-structures for many years.⁷ Recently, we are interest in exploring new open-framework metal phosphates co-templated by alkali cation and organoamine. This approach has successfully yielded a new zincophosphate open-structure, Na[H₂TETA]_{0.5}[ZnPO₄]₂·0.5H₂O (TETA = triethylenetetraamine) or TJPU-1 (TJPU = Tianjin Polytechnic University), with the zeolite CZP topology. This compound contains left-handed chiral channels along its *c* axis. Here we report its synthesis and crystal structure.

Experimental Section

Synthesis and initial characterizations. TJPU-1 was hydrothermally synthesized from a mixture of zinc acetate dihydrate, boric acid, phosphorous acid (85%), sodium chloride, TETA and distilled water. All reagents were used as received. Typically, 0.44 g Zn(ac)₂·2H₂O, 2 mL H₃PO₄, 1 g H₃BO₃ and 0.7 g NaCl were dissolved in 20 mL H₂O under stirring. Then 1.7 g TETA was injected. After stirred to homogeneity, the final mixture was sealed in a 40 mL TEFLON-lined stainless steel autoclave and heated statically at 120 °C for 3 days. The hydrothermal reaction produced large polyhedral transparent crystals that were washed by water and dried at room temperature. The EDAX analysis gave the Zn : P : Na ratio of 2 : 2 : 1. The boric acid is used as pH adjustment. No attempt is performed to isolate TJPU-1 in the absence of boric acid. The well matched experimental and simulated XRD patterns indicated the monophasic feature of the product.

Structure determination. A polyhedron crystal was mounted on a glass fiber. The data were collected on a Siemens Smart CCD diffractometer equipped with a normal focus 2.4 KW sealed tube X-ray source. Intensities were recorded in 1271 frames with ω -scan (0.3°/min). Data were collected at room temperature in the range of 2.25–24.99 with $-12 \leq h \leq 12$, $-8 \leq k \leq 12$, $-17 \leq l \leq 15$. Of the total 7317 reflections measured, 1633 were unique. The structure was solved by directed method. The sodium, zinc and phosphorous atoms were first located by direct phase determination. The carbon and nitrogen atoms were found in the final successive difference Fourier maps. No attempt was performed for locating the hydrogen atoms due to the highly disordered template molecules of TETA. Structure solution and refinement were performed using SHELXTL (Ver. 5.01) program. The final full-matrix least-square refinement on F^2 converged with $R_1 = 0.0497$ and $wR_2 = 0.1362$ for observed reflections [$I \geq 2\sigma(I)$]. The final difference electron density map showed no features. Details of crystal parameters, data collection and structure refinement are given in Table 1. Atomic positions are listed in Table 2.

Results and Discussion

Single crystal structure determination reveals that TJPU-1

Table 1. Details of data collection and structure refinement of TJPU-1

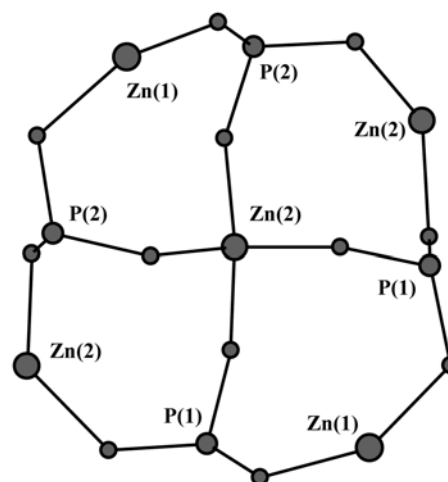
Empirical formula	C ₃ H ₁₂ N ₂ NaO _{8.50} P ₂ Zn ₂
Formula weight	427.82
Temperature	293(2) K
Wavelength	0.71073
Unit cell dimensions <i>a</i> (Å)	10.4713(6)
<i>b</i> (Å)	10.4713(6)
<i>c</i> (Å)	15.0533(16)
γ (°)	120
Volume (Å ³)	1429.43(19)
Z, calculated density	6, 2.982 g/cm ³
Absorption coefficient	5.462 mm ⁻¹
F(000)	1272
Crystal size	0.16 × 0.14 × 0.08 mm
Theta range for data collection	2.25–24.99°
Limiting indices	–12 ≤ <i>h</i> ≤ 10, –8 ≤ <i>k</i> ≤ 12, –17 ≤ <i>l</i> ≤ 15
Reflections collected / unique	7317 / 1633 [R(int) = 0.0368]
Completeness to theta = 24.99	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.496636
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.044
Final R indices [I > 2σ(I)]	R1 = 0.0503, wR2 = 0.1373
R indices (all data)	R1 = 0.0509, wR2 = 0.1377
Absolute structure parameter	0.09(4)
Largest diff. peak and hole	0.671 and –0.982 e.Å ⁻³

crystallizes in hexagonal space group P6₅. The asymmetric unit contains 35 non-hydrogen atoms [two Zn, two P, two Na, nine O, eight N, twelve C], of which twelve belong to the framework and the rest atoms belong to inclusive molecules and cations. Each of two distinct zinc atoms is coordinated by four oxygen atoms with bond lengths ranging from 1.909(5) Å to 1.964(5) Å and bond angles in the range of 95.7(2)°–122.5(2)°, which are typical data for Zn in tetrahedral coordination. Both of the two unique phosphorous atoms are in slightly distorted tetrahedral geometry with bond lengths of 1.519(6) Å–1.549(6) Å and bond angles of 107.5(3)°–112.3(3)°. The sodium cations are coordinated by six O atoms including a water molecule. The connections of zinc and phosphorous tetrahedral generate a three-dimensional anionic framework of [ZnPO₄]_n. The organoamines are highly distorted. Charge balance requires diprotonation of the TETA molecules. Hence, TJPU-1 is formulated in Na[H₂TETA]_{0.5}[ZnPO₄]₂·0.5H₂O.

The extended structure of this anionic framework is a chiral tetrahedral network without Zn–O–Zn or P–O–P linkages. The feature of this tetrahedral connectivity is the presence of squares of 4-rings that are formed by the linkages of ZnO₄ and PO₄ tetrahedral (Figure 1). In each of the squares, a central ZnO₄ tetrahedron is surrounded by an 8-ring of alternately connected ZnO₄ and PO₄ groups. In this building unit, the Zn(2) atom makes four 4-rings with its neighbor atoms. The propagation of the square moieties generate a

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for TJPU-1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U
Zn1	0.48981(9)	0.97971(8)	0.24954(6)	0.01265(17)
Zn2	0.68048(8)	0.84017(9)	0.41641(9)	0.01702(18)
P1	0.5884(2)	0.75330(19)	0.22529(13)	0.0185(4)
P2	0.5878(2)	0.83463(19)	0.60717(13)	0.0176(5)
O1	0.5702(6)	0.8774(6)	0.1829(4)	0.0276(13)
O2	0.7508(6)	0.7966(6)	0.2210(4)	0.0267(15)
O3	0.4905(6)	0.6109(6)	0.1754(4)	0.0302(15)
O4	0.5355(6)	0.7305(6)	0.3231(4)	0.0254(14)
O5	0.5351(6)	0.8057(6)	0.5091(4)	0.0255(15)
O6	0.4927(6)	0.8807(6)	0.6587(4)	0.0341(15)
O7	0.5681(7)	0.6910(5)	0.6472(4)	0.0254(15)
O8	0.7506(6)	0.9533(6)	0.6112(4)	0.0308(17)
N1	0.6622(14)	0.6558(8)	–0.0628(15)	0.0920(8)
C1	0.6900(10)	0.7997(7)	–0.0918(8)	0.0804(8)
C2	0.6538(13)	0.8953(7)	–0.0306(12)	0.0515(8)
N2	0.7502(17)	1.0540(6)	–0.0263(5)	0.0756(8)
C3	0.7615(11)	1.1548(12)	0.0431(6)	0.0718(8)
C4	0.8754(15)	1.2000(10)	0.1183(7)	0.0703(8)
N3	0.9295(8)	1.3386(10)	0.1651(8)	0.0802(8)
C5	1.0476(6)	1.4540(11)	0.2169(9)	0.0810(8)
C6	1.2023(6)	1.4708(14)	0.2183(9)	0.0860(8)
N4	1.2477(13)	1.412(2)	0.2913(14)	0.0689(8)
O9	1.0090(12)	1.4016(11)	0.1645(9)	0.0237(7)
N5	0.9251(14)	0.9720(15)	–0.1405(7)	0.0748(8)
C7	0.895(2)	1.0528(16)	–0.0781(4)	0.0793(8)
C8	0.868(2)	1.0145(15)	0.0214(4)	0.0622(8)
N6	0.9465(13)	1.1131(14)	0.0901(4)	0.0547(8)
C9	0.9992(18)	1.0739(14)	0.1646(4)	0.0369(8)
C10	1.0392(17)	1.1572(14)	0.2537(4)	0.0549(8)
N7	1.0626(8)	1.1010(19)	0.3329(4)	0.0664(8)
C11	1.1934(11)	1.136(3)	0.3772(4)	0.0769(8)
C12	1.2204(11)	1.170(4)	0.4771(4)	0.0899(8)
N8	1.1120(17)	1.102(5)	0.5427(6)	0.0818(8)
Na1	0.3825(9)	0.7135(9)	0.0726(7)	0.055(2)
Na2	0.2868(9)	0.6164(9)	0.0976(7)	0.056(2)

**Figure 1.** The 4-ring square in TJPU-1 with Zn and P atoms labeled.

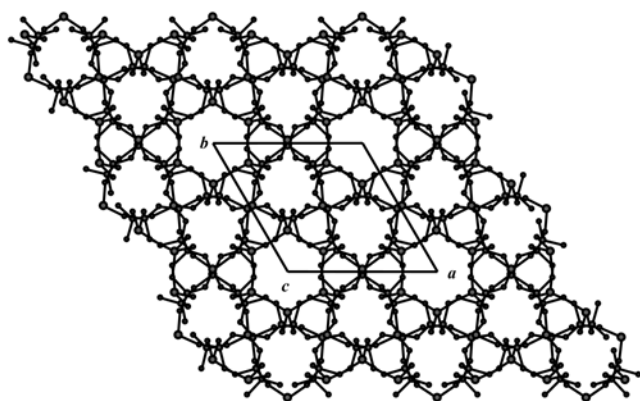


Figure 2. The structure of TJPU-1 showing the 12-ring and 8-ring channels viewed along *c* axis. The inclusive cations and molecules of Na^+ , TETA and H_2O are omitted for clarity.

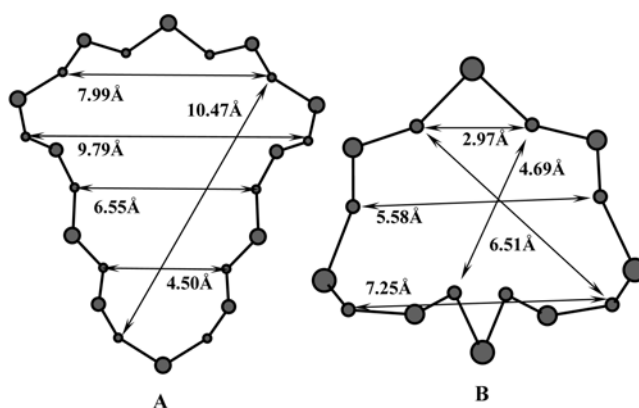


Figure 3. The dimensions of 12-ring (A) and 8-ring (B) windows in TJPU-1 showing the selected $\text{O}\cdots\text{O}$ distances.



Figure 4. The left-handed helix of TETA molecules linked by complex H-bonds along the *c* direction.

helical chain running along the *c* axis. Linking these helices give rise to a three-dimensional architecture with 8- and chiral 12-ring channels along the *c* axis (Figure 2). The dimensions of the channels are shown in Figure 3.

The channel spaces are occupied by diprotonated TETA molecules, sodium cations and water. The TETA molecules that locate in the 12-ring tunnels form a left-handed helix through complex H-bonds (Figure 4). No attempts are performed to elucidate possible H-bond configurations due to the high degree of disorder of the organoamines. The helical chains of TETA also manifest the left-handed feature of the 12-ring apertures. The sodium cations and water reside in the 8-ring channels that surround the 12-ring tunnels.

Thermal analysis on TJPU-1 shows two step mass loss between room temperature (rt) to 800 °C. The total weight loss of 13.29 wt% [rt–350 °C, 3.91 wt%, 350–800 °C, 9.38 wt%] is ascribed to the emission of water and TETA molecules.

In summary, a new zincophosphate open-structure was hydrothermally isolated under the co-template effect of Na^+ and TETA. The linkages of Zn and P tetrahedral generate a three-dimensional architecture with left-handed chiral channels along the *c* axis. The tunnel spaces are occupied by sodium cations and diprotonated TETA molecules. The TETA molecules form left-handed helix by complex H-bonds, which verified the left-handed chirality of the 12-ring tunnels. The synthesis of TJPU-1 indicates the co-template effect of alkali cations and organoamine on developing new open-structures. This approach is believed to induce more novel structures in the field of open-structured materials.

Acknowledgement. The authors are grateful to the financial support by SRF for ROCS, SEM and Nature Science Foundation of Tianjin (05YFJMJC13500).

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