DALTON
COMMUNICATION

A new layered aluminophosphate $[Al_2P_4O_{16}][C_6H_{22}N_4][C_2H_{10}N_2]$ with 4.12-net porous sheets

Bo Wei, Jihong Yu,* Zhan Shi, Shilun Qiu* and Jiyang Li

Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jilin University, Changchun 130023, P. R. China. E-mail: jihong@mail.jlu.edu.cn; sqiu@mail.jlu.edu.cn

Received 19th April 2000, Accepted 23rd May 2000

Employing phenol, an aromatic and acidic organic solid, as the solvent, and triethylene tetramine as the template, a new two-dimensional layered aluminophosphate $[Al_2P_4O_{16}][C_6H_{22}N_4][C_2H_{10}N_2]$ has been solvothermally synthesized for the first time, which contains novel 4.12-net porous sheets.

Since the first report of microporous aluminophosphates ($AlPO_4$-*n*) in 1982,[1] much study has been focused on the exploration of new microporous aluminophosphate (AlPO) compounds. This is not only for their potential applications in sorption, catalysis, and host–guest assembly chemistry,[2–4] but also for the diversity of their arrangements of AlO_4 (and/or AlO_5, AlO_6) and PO_4 tetrahedral building units forming one-dimensional (1-D) chain, two-dimensional (2-D) layer, and three-dimensional (3-D) open-framework structures with Al/P ratios of 1/1, 1/2, 2/3, 3/5, 3/4, 4/5, 5/6, *etc.*[5–7]

So far, three distinct aluminophosphate networks have been found to have a stoichiometry of $[AlP_2O_8]^{3-}$ with an Al/P ratio of 1/2. Two of them are based upon a chain network built up by corner-sharing and edge-sharing Al_2P_2 4-membered rings (MRs), respectively.[8–11] The third one is based upon a 2-D sheet built up solely by 8-MRs.[12,13] Here, we report a new layered aluminophosphate $[Al_2P_4O_{16}][C_6H_{22}N_4][C_2H_{10}N_2]$ (denoted **1**) with an Al/P ratio of 1/2. Compared to previous layered AlPOs with 4.6-, 4.8-, 4.6.8-, 4.6.12-, and 8-nets,[7] **1** is the first 2-D layered AlPO constructed of 4.12-net porous sheets.

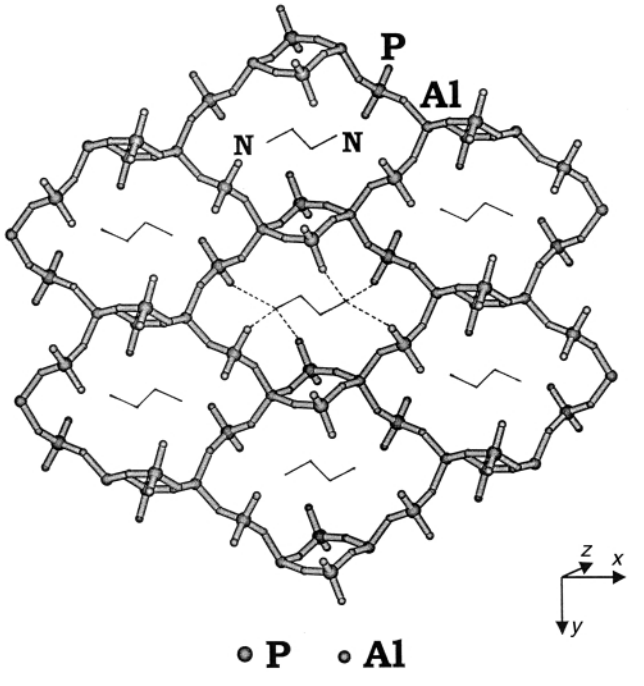

Fig. 1 The 4.12-net porous sheet of **1** parallel to the [−101] plane, with ethylene diammonium cations located inside the 12-MR openings (H-bonds are represented by dotted lines).

In this work, we employ phenol (melting point is 41°C) as an aromatic and acidic solvent in the synthesis, and use triethylenetetramine (TETA) as the template. Large platelike single crystals were formed from a gel mixture with the molar ratio $1.0Al_2O_3:1.8P_2O_5:10.0TETA:65$ PhOH heated at 185 °C for 12 days.[14] The experimental powder X-ray diffraction pattern of **1** is in agreement with the simulated one, proving that the as-synthesized product is a single phase. Inductively coupled plasma (ICP) analysis gives the Al and P content as 8.6 and 19.7 wt%, respectively, showing an Al/P molar ratio of 1/2. A suitable single crystal with dimensions of 0.3 × 0.3 × 0.2 mm was selected for single-crystal X-ray diffraction analysis.[15] Single crystal analysis showed that **1** crystallizes in the monoclinic space group *P*2(1)/*n* (no. 14) with lattice parameters $a = 10.826(1)$ Å, $b = 8.143(8)$ Å, $c = 13.770(1)$ Å, and $\beta = 95.104(2)°$.

Each asymmetric unit of **1** contains one crystallographically distinct Al atom and two crystallgraphically distinct P atoms. All AlO_4 tetrahedra are vertex linked with PO_4 tetrahedra with the Al–O bond lengths in the range of 1.7277–1.7415 Å, but only two vertices of the PO_4 tetrahedra are linked with adjacent AlO_4 tetrahedra with P–O bond lengths in the range of 1.5142–1.5512 Å, with the remaining vertex being a terminal P=O group. The bond lengths of P(1)=O(2) and P(2)=O(8) are 1.505 and 1.508 Å, respectively.

The structure of **1** consists of macroanion $[AlP_2O_8]^{3-}$, which is charge balanced by the tetraprotonated TETA molecule $^{+}H_3N(CH_2)_2NH_2^{+}(CH_2)_2NH_2^{+}(CH_2)_2NH_3^{+}$, and diprotonated ethylenediamine $^{+}H_3N(CH_2)_2NH_3^{+}$. The ethylenediamine

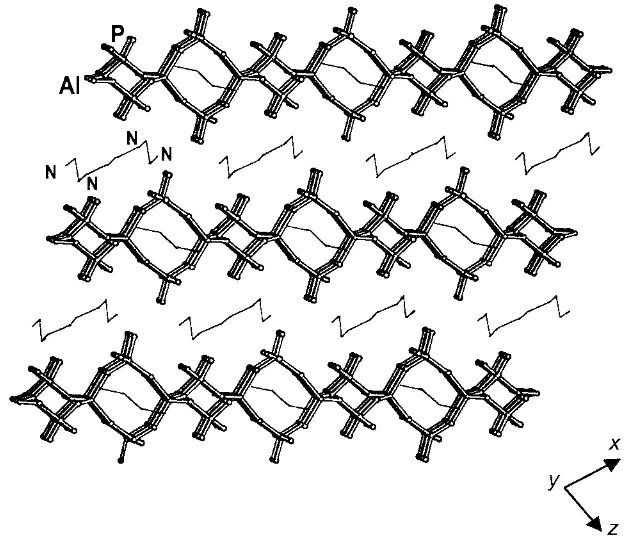

Fig. 2 Packing of the sheets along the [−101] direction in an AAAA sequence, with TETA molecules intercalated in the interlayer region.

DOI: 10.1039/b003153o

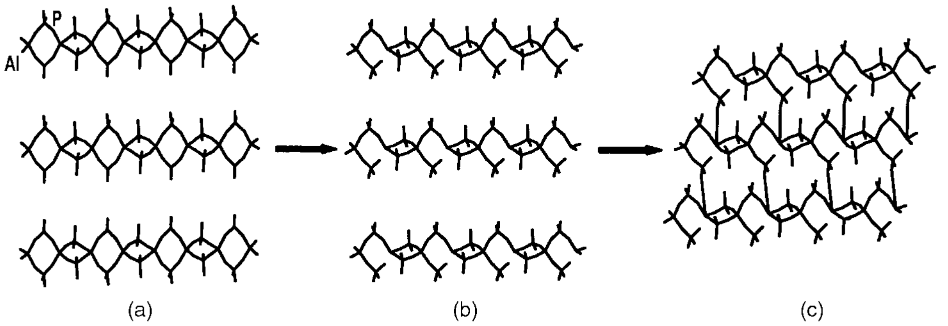

Fig. 3 Structural relationship between the 1-D $AlP_2O_8^{3-}$ chain and the 2-D $AlP_2O_8^{3-}$ sheet in **1**, (a) 1-D $AlP_2O_8^{3-}$ chain with corner-sharing 4-MRs; (b) breaking the P–O · · · Al bond in the 1-D chain; (c) relinking the P–O · · · Al bond with adjacent chains to form a 4.12-net sheet as in **1**.

molecules are believed to be generated during the course of solvothermal synthesis through fragmentation of the TETA molecules, as in the case of the previously reported 1-D chain $[Al_2P_4O_{16}][NH_3(CH_2)_2NH_3][NH_3(CH_2)_3NH_3]_2$.[16] The network of **1**, as shown in Fig. 1, is constructed of 4.12-net porous sheets parallel to the (−101) plane. This novel 4.12-net was first found in layered AlPO compounds.

Diprotonated ethylenediammonium cations $^+H_3N(CH_2)_2NH_3^+$ exist in the 12-MR openings. Each 12-MR traps one ethylenediamine molecule, which interacts with six adjacent terminal P=O groups through strong H-bonds with N · · · O separation in the range of 2.757–2.859 Å. Energy calculation by Cerius[2] using a Burchart1.01-Dreiding 2.21 force field[17,18] gives the the H-bonding interaction energy between the sheets and occluded ethylenediamine molecules as −10.25 kcal mol^{-1} per unit of $[AlP_2O_8]^{3-}$. It is believed that the ethylenediamine molecules play an important role in the stabilization of the 12-MR in the porous sheet.

The macroanionic sheets are stacked in an AAAA sequence along the [−101] direction (Fig. 2), and intercalated by tetraprotonated $^+H_3NCH_2CH_2{}^+NH_2CH_2CH_2NH^+{}_2CH_2CH_2NH_3^+$ cations. The distance between two layers is *ca.* 9.13 Å (atom to atom). Each tetraprotonated TETA cation provides a total of ten H-bonds to terminal P=O groups protruding into the interlayer region, with both ^+H_3N-groups each providing three H-bonds, and the middle H_2N^+-groups each providing two H-bonds.

Thermogravimetric analysis shows that the template molecules decompose in the region 280–430 °C with a weight loss of 30.2% (theoretical value: 32.8%), which is correlated to the decomposition of occluded TETA and ethylenediamine molecules. Elemental analysis gives the C, H and N content as 15.3, 5.2 and 13.6%, respectively, which is in agreement with the theoretical values of 14.9, 4.95 and 13.0%, respectively.

Further insight into the sheet structure of **1**, a structural relationship between **1** and a corner-sharing $AlP_2O_8^{3-}$ 1-D chain[9] (Fig. 3a) can be found. This 1-D $AlP_2O_8^{3-}$ chain is proposed to be a parent chain for the formation of a family of 1-D chain, 2-D layer and 3-D open-framework AlPOs through an hydrolysis–condensation self-assembly pathway by Ozin and co-workers.[19] As shown in Fig. 3b,c, through breaking the P–O · · · Al bonds in the 1-D chain, and relinking the Al–O · · · group with the dangling P atoms in the adjacent chain, the 4.12-net sheet of **1** can be transformed from the 1-D $AlP_2O_8^{3-}$ chain (Fig. 3c). It is noteworthy that both the 1-D $AlP_2O_8^{3-}$ chain and the 4.12-net $AlP_2O_8^{3-}$ sheets of **1** can be stabilized by the ethylenediamine cations. Further investigation of the crystallization of **1** might yield some information on the formation of this 2-D layer compound.

Acknowledgements

We are grateful for financial support from National Natural Science Foundation and Pandeng Project of China.

Notes and references

1 S. T. Wilson, B. M. Lok, C. A. Messian, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146; S. T. Wilson, B. M. Lok and E. M. Flanigen, US Pat. 4 310 440, 1982.

2 O. Terasaki, *J. Phys. Condens. Matter*, 1990, **2**, 5209.

3 G. A. Ozin, *Adv. Mater.*, 1992, **4**, 612.

4 J. Chen and J. M. Thomas, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 603; Z. K. Tang, M. M. T. Loy, J. Chen and R. Xu, *Appl. Phys. Lett.*, 1997, **70**, 34.

5 J. M. Bennett, W. J. Dytrych, J. J. Pluth, J. W. Richardson Jr. and J. V. Smith, *Zeolites*, 1986, **6**, 349.

6 J. Chen, W. Pang and R. Xu, *Top. Catal.*, 1999, **9**, 93.

7 J. Yu, R. Xu and J. Li, *Solid State Sci.*, 2000, 2, 181.

8 R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, Y. Xu, A. K. Cheetham and D. Bieber, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1170.

9 Q. Gao, J. Chen, S. Li and R. Xu, *J. Solid State Chem.*, 1996, **127**, 145.

10 I. D. Williams, J. Yu, Q. Gao, J. Chen and R. Xu, *Chem. Commun.*, 1997, 1273.

11 A. M. Chippindale and C. Turner, *J. Solid State Chem.*, 1997, **128**, 318.

12 J. Yu and I. D. Williams, *J. Solid State Chem.*, 1998, **136**, 141.

13 M. A. Leech, A. R. Cowley, K. Prout and A. M. Chippindale, *Chem. Mater.*, 1998, **10**, 451.

14 In a typical experiment, 1.0 g of aluminium triisopropoxide was first dispersed into 30 g of phenol at 50 °C under reflux conditions with stirring, and then 0.6 mL of H_3PO_4 (85wt% in water) was added dropwise to form a gel. Finally, 4.0 mL of TETA was added to the above mixture. The reaction mixture was further stirred until homogenous and then was sealed in a Teflon-lined stainless steel autoclave and heated at 185 °C for 12 days under autogenous pressure. The resulting product containing pure large platelike single crystals of up to 1 mm was filtered and washed thoroughly with ethanol and deionized water, and dried at ambient temperature.

15 Crystal structure data: $F_w = 323.12$, monoclinic, space group $P2(1)/n$ (no. 14), $a = 10.826(1)$ Å, $b = 8.143(8)$ Å, $c = 13.770$ (1) Å, and $\beta = 95.104(2)°$, $V = 1029.2(2)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\rho_{calcd} = 1.775$ Mg m^{-3}, $F(000) = 672$, μ(Mo-Kα) = 0.471 mm^{-1}, $\theta_{max} = 23.26°$. Goodness-of-fit on F^2 was 1.083, R_1[for $I > 2\sigma(I)$] = 0.0285, $wR_2 = 0.0836$, Data/restraints/parameters = 1679/0/227. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite–monochromated Mo-Kα radiation (λ(Mo-Kα) = 0.71073 Å). The data were collected at 20 ± 2 °C. Data processing was accomplished with the SAINT processing program (SMART and SAINT (software packages), Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1996.). Direct methods were used to solve the structure using the SHELXTL crystallographic software package (SHELXL, version 5.1; Siemens Industral Automation, Inc., 1997.). Hydrogen atoms were located by a difference Fourier map, and were added to the structure factor calculation. All non-hydrogen atoms were refined anisotropically. CCDC reference number 186/2002. See http://www.rsc.org/suppdata/dt/b0/b003153o/ for crystallographic files in .cif format.

16 K. Sugiyama, K. Hiraga, J. Yu, S. Zheng, S. Qiu and O. Terasaki, *Acta Crystallogr.*, *Sect. C*, 1999, **55**, 1615.

17 Cerius2, Molecular simulations/Biosym corporation, San Diego, CA, 1995.

18 J. Li, J. Yu, W. Yan, Y. Xu, W. Xu, S. Qiu and R. Xu, *Chem. Mater.*, 1999, **11**, 2600.

19 S. Oliver, A. Kuperman and G. A. Ozin, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 46.