Layered Aluminophosphate

Hydrogen-Bonded Helices in the Layered Aluminophosphate $(C_2H_8N)_2[Al_2(HPO_4)(PO_4)_2]$**

Yu Song, Jihong Yu, Yi Li, Guanghua Li, and Ruren Xu**

Following the discovery of microporous aluminophosphates $AlPO_4$-*n* (*n* denotes a specific structure type),[1] there is considerable interest in developing new aluminophosphate compounds with novel framework structures because of their potential application in catalysis, adsorption, and separation.[2–5] The aluminophosphate family encompasses a rich structural variety enhanced by the employment of organic amines as structure-directing agent under hydrothermal/solvothermal conditions. The diverse arrangements of AlO_n polyhedral units ($n = 4$–6) and $P(O_b)_n(O_t)_{4-n}$ tetrahedral units (b: bridging, t: terminal, $n = 1$–4) form zero-dimensional (0D) cluster, one-dimensional (1D) chain, two-dimensional (2D) layer, and three-dimensional (3D) open-framework structures with various stoichiometries, such as $AlPO_4$, $AlP_4O_{16}^{9-}$, $AlP_2O_8^{3-}$, $Al_2P_3O_{12}^{3-}$, $Al_3P_4O_{16}^{3-}$, $Al_3P_5O_{20}^{6-}$, $Al_4P_5O_{20}^{3-}$, $Al_5P_6O_{24}^{3-}$, $Al_{11}P_{12}O_{48}^{3-}$, $Al_{12}P_{13}O_{52}^{3-}$, and $Al_{13}P_{18}O_{72}^{15-}$.[5] Notable examples are the extra-large-pore materials VPI-5[6] and JDF-20.[7] For the anionic 2D layered compounds with $Al_2P_3O_{12}^{3-}$ stoichiometry, six unique structures exist in $[(BuNH_3)_2][Al_2(HPO_4)(PO_4)_2]$,[8] $[(C_6H_{14}N)_2][Al_2(HPO_4)(PO_4)_2]$,[9] $[(C_6H_{14}N)_2][Al_2(HPO_4)(PO_4)_2]$,[9] $[(pyH)][Al_2(HPO_4)_2(PO_4)]$,[8] $[(C_6H_8N)][Al_2(HPO_4)_2(PO_4)]$,[10] and

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[*] Y. Song, Prof. J. Yu, Y. Li, G. Li, Prof. R. Xu
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry
College of Chemistry, Jilin University
Changchun 130023 (P.R. China)
Fax: (+86) 431-567-1974
E-mail: jihong@mail.jlu.edu.cn
rrxu@mail.jlu.edu.cn

[**] This work is supported by the National Natural Science Foundation of China and the State Basic Research Project of China (G2000077507).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200353118

$[(C_9H_{20}N)][Al_2(HPO_4)_2(PO_4)]$.[11] Their 2D sheets are stabilized by protonated organic amines through hydrogen-bonding interactions with the inorganic network.

Multiple hydrogen bonds are known to cooperatively exert dramatic influences on the control of molecular self-assembly in chemical and biological systems.[12] Our recent studies also found that hydrogen bonds play a significant role in determining stereospecificity between the template and the host framework in open-framework metal phosphates.[13] Herein we describe a distinctive hydrogen-bonded helix formed by the organic amine template and the inorganic network in a new 2D layered aluminophosphate with $Al_2P_3O_{12}^{3-}$ stoichiometry.

Single-crystal structural analysis showed that the title compound **1** has the empirical formula $(C_2H_8N)_2[Al_2(HPO_4)(PO_4)_2]$. The protonated dimethylamine cations compensating the negative charge of the anionic network are believed to result from decomposition of the DMF solvent under solvothermal conditions. Such a phenomenon was observed in the previously reported $Ga_3(PO_4)F_3{\cdot}N_2C_3H_{12}{\cdot}NC_2H_7$.[14] Each asymmetric unit contains two crystallographically distinct Al atoms and three crystallographically distinct P atoms. Each Al atom shares four oxygen atoms with adjacent P atoms with Al–O bond lengths in the range of 1.730(3)–1.749(3) Å. P(1) shares two oxygen atoms with adjacent Al atoms and has one terminal P–OH group (P(1)–(12)H 1.563(4) Å) and one terminal P=O group (P(1)=O(1) 1.470(3) Å), while P(2) and P(3) each share three oxygen atoms with adjacent Al atoms and have one terminal P=O group (P(2)=O(2) 1.493(3) Å, P(3)=O(5) 1.489(3) Å). The $P-O_b$ bond lengths are in the range of 1.531(3)–1.549(3) Å. The macroanionic $[Al_2(HPO_4)(PO_4)_2]^{2-}$ sheet is based on strictly alternating AlO_4 tetrahedra and PO_4 tetrahedra [$PO_2(OH)(=O)$ and $PO_3(=O)$] linked through vertex oxygen atoms.

The inorganic layer (Figure 1) is a new type of 4.8-net porous sheet parallel to the (001) plane. This 4.8-net with $Al_2P_3O_{12}^{3-}$ stoichiometry was previously predicted as a hypothetical network by Yu and Xu et al. on the basis of the construction of $Al_2P_3O_{12}^{3-}$ layers from secondary building units.[15] It features a 1D $AlP_2O_8^{3-}$ chain composed of fused Al_2P_2 four-membered ring ladders with pendant HPO_4 side groups.[16] Such a 1D chain, denoted AlPO-ESC, is believed to be a fundamental chain, like AlPO-CSC[17] (corner-sharing Al_2P_2 four-membered ring linear chain), in the formation of complex aluminophosphate compounds.[18,19] The 4.8-net sheet can be viewed as arising from condensation of AlPO-ESC chains with the loss of HPO_4^{2-} groups.

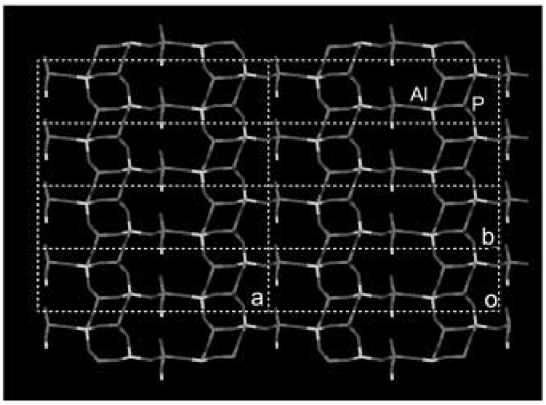

Figure 1. The 4.8-net sheet of **1** parallel to the (001) plane

In contrast to previously reported layered aluminophosphates with $Al_2P_3O_{12}^{3-}$ stoichiometry, which exhibit AAAA or ABAB layer-stacking sequences,[8–11] **1** shows an intriguing ABCD sheet-stacking sequence along the *c* axis (Figure 2). The $(CH_3)_2NH_2^+$ cations in two crystallographically distinct sites reside in the interlayer region and interact with the inorganic network through hydrogen bonds. Strikingly, those $(CH_3)_2NH_2^+$ cations packed between the AB layers and between CD layers interact with the terminal P=O groups in such a way that a hydrogen-bonded helix is created that follows the 2_1 screw axis along the *b* axis. The helical chains within the AB layers are exclusively right-handed, and those within the CD layers are exclusively left-handed. Figure 3a shows a view of the left- and right-handed helical chains formed by hydrogen bonds between the organic templates and the inorganic network. Each N atom forms two hydrogen bonds to two terminal oxygen atoms in adjacent layers. The

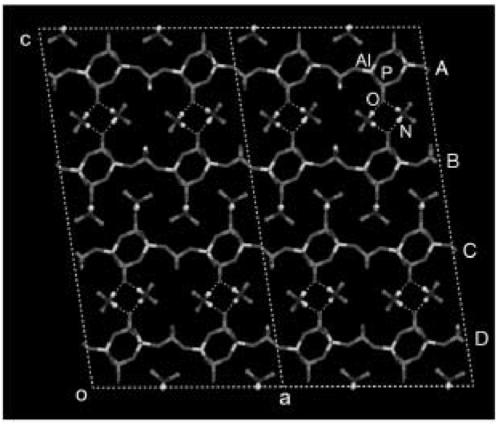

Figure 2. Packing of the anionic layers of **1** in an ABCD stacking sequence (H atoms of C–H bonds are omitted)

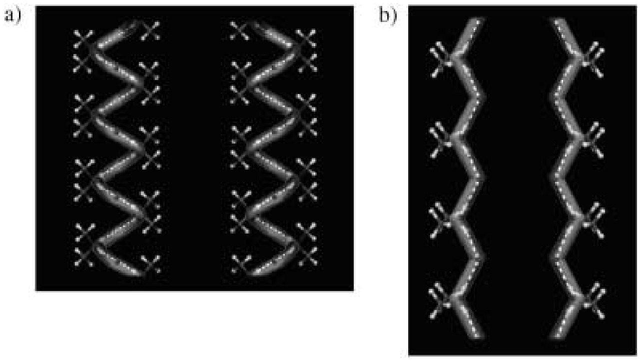

Figure 3. Hydrogen-bonded chains formed by the organic amine templates and the inorganic layers. a) Left- and right-handed hydrogen-bonded helical chains. b) Hydrogen-bonded zig-zag chains (O: black ball, O···H–N hydrogen bonds are indicated by dotted lines)

N···O separation is 2.732(5) Å. Such distinctive hydrogen-bonded helical chains are particularly rare in organically templated inorganic open-framework materials. They resemble the intriguing triple helix in the extra-large-pore aluminophosphate molecular sieve VPI-5, in which a chain of hydrogen-bonded water molecules following the 6_3 screw axis links the octahedrally coordinated Al atoms and forms a triple helix of water molecules inside the 18-ring channel.[20]

The $(CH_3)_2NH_2^+$ cations packed between the BC layers also form hydrogen bonds with the inorganic layers. The hydrogen-bonded chains are arranged in a zig-zag fashion along the *b* axis, as shown in Figure 3b. Each N atom forms three hydrogen bonds to two terminal P=O groups (N···O 2.779(5) and 2.907(5) Å) and one bridging oxygen atom (N···O 3.096 (5) Å) within one layer.

Our previous studies on the layered aluminophosphates with $Al_3P_4O_{16}^{3-}$ stoichiometry have shown that hydrogen-bonding host–guest interaction plays a dominant role in stabilizing the inorganic network.[21] Compound **1** exhibits distinctive hydrogen-bonded chains formed by the organic templates and the inorganic network, which are believed to be responsible for the intriguing packing mode of the inorganic–organic assembly.

Experimental Section

Synthesis and characterization: The synthesis was carried out by the solvothermal combinatorial approach, which is a rapid method for the discovery of new materials.[22–25] The multiautoclave consists of a stainless steel block with 64 Teflon holes (0.7 cm diameter, 3.0 cm in depth, 800 μL per hole). The reaction was carried out in the system 1.0 Al(O*i*Pr)$_3$–*x* H_3PO_4–*y* tri-*n*-propylamine (Pr_3N)–60 DMF with a fixed DMF volume of 450 μL for each crystallization. Finely ground Al(O*i*Pr)$_3$ was first dosed into each Teflon hole, then DMF was added by using a Tecan CH Miniprep 75 pipette robot, followed by the addition of Pr_3N and H_3PO_4 (85%). The reaction mixtures were shaken for 2 h for homogenization. The multiautoclave was placed in an oven for 5 d at 180°C. An optimized range for the crystallization of **1** was found to be 1.0 Al(O*i*Pr):(2.4–4.0) H_3PO_4:(3.0–6.0) Pr_3N:60 DMF. Et_3N could also be used instead of Pr_3N, and the fact that neither was included in the product, suggested that they played a role in adjusting the basicity of the reaction mixture. The array of Teflon chambers was placed in a Hermle 2300 centrifuge apparatus for sample separation. The dried samples were transferred to a sample holder for X-ray analysis. Automated X-ray diffraction analysis was carried out with a computer-controlled xyz stage GADDS microdiffractomer from Bruker D8 Discover with a CCD detector using $Cu_{K\alpha}$ radiation. The X-ray diffraction (XRD) pattern of **1** was in agreement with the simulated pattern generated on the basis of single-crystal structural data, proving the phase purity. Inductively coupled plasma (ICP) analysis indicated an Al/P molar ratio of 2:3.

Structure determination: A suitable single crystal with dimensions of 0.15 × 0.10 × 0.10 mm was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The data were collected at 20 ± 2°C. Data were processed with the SAINT program.[26] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL97.[27] All Al, P, and O atoms were easily located. The hydroxyl H atom was found in the difference Fourier map, and the others were placed geometrically and refined in a riding model. The non-hydrogen atoms were refined anisotropically.

Crystal data: $(C_2H_8N)_2[Al_2(HPO_4)(PO_4)_2]$: $M_r = 432.07$, monoclinic, space group *C*2/*c* (No. 15), $a = 18.4872(15)$, $b = 5.0148(4)$, $c = 35.466(3)$ Å, $\beta = 98.244(6)°$, $V = 3254.0(5)$ Å^3, $Z = 8$, $\mu = 0.534$ mm^{-1}, $\rho_{calcd} = 1.764$ g cm^{-3}, 8472 reflections measured, of which 2859 were unique ($R_{int} = 0.0897$). Final $wR(F^2) = 0.0977$ (all data) and $R(F) = 0.0470$ ($I > 2\sigma(I)$). CCDC 222127 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: October 20, 2003 [Z53118]

Keywords: aluminophosphates · combinatorial chemistry · hydrogen bonds · layered compounds · template synthesis

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