A New Fluoroaluminophosphate Chain with an Al/P Ratio of Unity

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Received August 4, 2000

A new compound, $Al_2P_2O_8F_2 \cdot [(CH_3)_2CHNH_2CH_2CH_2NH_2CH(CH_3)_2]$ (denoted AlPO-CJ8), with a 1-dimensional fluoroaluminophosphate chain and an Al/P ratio of unity has been synthesized solvothermally by using isopropylamine as an organic additive. It is characterized by X-ray powder diffraction (XRD), inductively coupled plasma (ICP), ion selective electrodes (ISE), and TGA−DTA analyses and structurally determined by single-crystal X-ray diffraction analysis. AlPO-CJ8 crystallizes in the triclinic space group $P\bar{1}$ with $a = 5.0306(8)$ Å, $b = 9.3626(15)$ Å, $c = 10.6131(17)$ Å, $\alpha = 65.949(4)°$, $\beta = 88.218(4)°$, $\gamma = 77.19°$, and $Z = 2$. Its structure is built up by alternation of tetrahedral $PO_3(=O)$ and AlO_3F units to form infinite 1-D $Al_2P_2O_8F_2^{2-}$ macroanionic chains. The inorganic chains are held together by diprotonated *N*,*N*′-diisopropylethylenediamine through H-bonds. The organic species *N*,*N*′-diisopropylethylenediamine is believed to be formed through solvothermal reaction of the organic additive isopropylamine and the solvent ethylene glycol. The existence of terminal P═O and Al−F bond groups in the 1-D chain indicates that it has potential to further set up higher dimensional networks through condensations.

Introduction

Following the discovery of microporous crystalline aluminophosphates $AlPO_4$-*n*, which are built up by strict alternation of tetrahedral AlO_4 and PO_4 to form neutral open frameworks with an Al/P ratio of unity,[1] a number of novel aluminophosphates have been synthesized successfully in hydrothermal systems.[2−4] Recently, through utilizing a solvothermal synthesis technique,[5−7] i.e., using organic solvents instead of water, a variety of organically templated aluminophosphates (AlPOs) with Al/P ratios of nonunity continue to be synthesized, showing vast structural and compositional diversities. The syntheses typically involve the addition of organic amines. It is noted that one template can give rise to many different structures, and that different templates can direct the formation of the same structure. On the other hand, F^- ions are frequently employed in the reaction mixture to promote the formation of large single crystals or novel structures. Three roles for F^- in the synthesis of microporous solids have been described by Guth et al., i.e., (a) mineralizing, (b) structure directing, and (c) templating.[8] In fluoroaluminophosphates, F^- is incorporated into their networks or frameworks.[9−13]

A large number of aluminophosphates, with various dimensionalities and stoichiometries, have been prepared in both hydrothermal and solvothermal systems. There are 3-dimensional (3-D) open framework AlPOs with Al/P ratios of 1/1 ($AlPO_4$-*n*),[1] 12/13 (AlPO-CJB1, the first aluminophosphate molecular sieve with Brönsted acidity),[14] 5/6 (JDF-20 with 20-MR),[15] 4/5 (AlPO-HDA with interconnecting 12- and 8-MR channel system),[16] 3/4 (open-framework with 12-MR cages),[17] 2/3 (AlPO-DETA with 12- and 8-MR channel),[18] and 1/2 (AlPO-CJ4 with propeller-like chiral motifs),[19] a family of 2-D layers with Al/P ratios of 4/5 ($Al_4P_5O_{20}^{3-}$),[20] 3/4 ($Al_3P_4O_{16}^{3-}$),[21−32] 2/3 ($Al_2P_3O_{12}^{3-}$),[33−38] and 1/2 ($AlP_2O_8^{3-}$),[27,39−41] and a series of 1-D chains with Al/P ratios of 2/3,[32] 3/5,[35] and 1/2.[42,43]

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10.1021/ic000879j CCC: $20.00
Published on Web 12/08/2000

Recently, 2-D layered aluminophosphates with an Al/P ratio of 1/1 have been reported.[44−48] It is noted that there are no 1-D aluminophosphates with an Al/P ratio of 1/1. Herein, we report a new compound with a 1-D $Al_2P_2O_8F_2^{2-}$ anionic chain, which represents the first structural type of aluminophosphate chains with an Al/P ratio of unity.

Experimental Section

AlPO-CJ8 was synthesized from an alcoholic system in which ethylene glycol (EG) was used as the solvent and isopropylamine (*i*-$PrNH_2$) as an organic additive. Aluminum triisopropoxide ($Al(PrO^i)_3$) and phosphoric acid (85 wt % in water) were used as the aluminum and phosphorus sources, respectively. Hydrofluoric acid (HF 40 wt % in water) was used in the preparation of AlPO-CJ8. Typically, a reaction mixture with a molar composition of $Al(PrO^i)_3$:2.9 H_3PO_4:5.0 NH_2-$CH(CH_3)_2$:50 EG:1.8 HF:5.8 H_2O was sealed in a Teflon-lined stainless steel autoclave and then heated at 180 °C for 16 days under autogenous pressure. Water was introduced by H_3PO_4 and HF. The resulting long needlelike large single crystals were filtered off, washed with distilled water, and dried in air at ambient temperature.

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air with a heating rate of 20 °C/min.

Table 1. Crystal Data and Structure Refinement for AlPO-CJ8

empirical formula	$AlPO_4FNC_4H_{11}$
fw	214.09
temp	293(2) K
wavelength	0.71073 Å
space group	$P\bar{1}$ (No. 2)
a (Å)	5.0306(8)
b (Å)	9.3626(15)
c (Å)	10.6131(17)
α (deg)	65.949(4)
β (deg)	88.218(4)
γ (deg)	77.19
V (Å^3)	444.14(12)
Z	2
ρ_{calcd} (Mg m^{-3})	1.601
μ (mm^{-1})	0.402
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0646, wR2 = 0.1536
R indices (all data)	R1 = 0.0783, wR2 = 0.1644

[a] $R1 = \sum(\Delta F/\sum(F_o))$; $wR2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o^2)$.

A suitable colorless single crystal with dimensions 0.800 × 0.120 × 0.120 mm was selected for X-ray diffraction analysis. Intensity data were collected on a Siemens SMART diffractometer equipped with a CCD detector using graphite-monochromatized Mo Kα radiation (λ(Mo Kα) = 0.71073 Å) at a temperature of 20 °C ± 2 °C. The total number of measured reflections and observed unique reflections were 2214 and 1279, respectively. The lattice constant was determined by the least-squares procedure applied to the θ values for 25 reflections (2.11−23.27°). Intensity data of 1279 independent reflections ($-5 \le h \le 5$, $-10 \le k \le 10$, $-10 \le l \le 11$) were collected in the ω scan mode. No adsorption correction was applied. The agreement factor between equivalent reflections (R_{int}) was 0.0997. The structure was solved in the space group $P\bar{1}$ by direct methods and refined on F^2 by full-matrix least squares using SHELXTL97.[49] The phosphorus and aluminum atoms were located first. Carbon, nitrogen, oxygen, fluorine, and hydrogen atoms were found in the difference Fourier map. Non-hydrogen atoms were refined with anisotropic thermal parameters. A summary of the crystallographic data is presented in Table 1.

Results and Discussion

AlPO-CJ8 crystallizes from gels with molar composition $Al(PrO^i)_3$:2.9 H_3PO_4:(4.5−6.5) $NH_2CH(CH_3)_2$:50 EG:(1.5−2.0) HF. The F^- ions are necessary for the formation of AlPO-CJ8. Without F^-, no crystalline product is obtained from the reaction mixture. With trace amounts of F^-, aluminophosphate $Al_3P_3O_{12}F{\cdot}C_3H_{10}N$ (denoted AlPO-CJ7, space group $P\bar{1}$, a = 9.186(2) Å, b = 9.2204(2) Å, c = 9.377(2) Å, α = 86.85(3)°, β = 79.86(2)°, and γ = 87.817(15)°) with a structure analogous to AlPO-CHA forms. By increasing the amount of HF to 1.0−1.5 mol, a new phase with an Al/P ratio of 1/1 (Al 13.85, P 16.35, C 10.8, H 3.0, and N 3.99 wt %) crystallizes. AlPO-CJ8 forms when 1.5−2.0 mol of HF is used. Figure 1 shows the measured X-ray powder diffraction pattern for AlPO-CJ8. It is in good agreement with the pattern simulated from the single-crystal structure, proving that the as-synthesized product is a single phase. The differences in reflection intensity are probably due to preferred orientation in the powder sample.

Ion selective electrode (ISE) analysis shows that there exist F atoms in the product of AlPO-CJ8 and that the amount of F atoms is 7.86 wt % (calcd 8.88 wt %). ICP analysis gives the contents of Al as 11.36 wt % (calcd 12.3 wt %) and P as 13.0 wt % (calcd 14.2 wt %), confirming the Al/P ratio of unity. Elemental analysis indicates that the sample contains 21.7, 5.3, and 6.0 wt % (calcd 22.4, 5.1, and 6.5 wt %) of C, H, and N,

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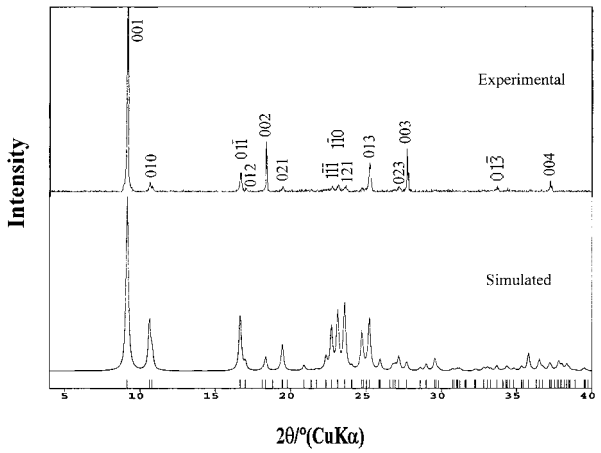

Figure 1. Experimental and simulated X-ray powder diffraction patterns for AlPO-CJ8. The indices in the experimental XRD pattern are given for the main reflections.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for AlPO-CJ8

	x	*y*	*z*	*U*(eq)[a]
P(1)	2834(2)	3919(1)	3853(1)	26(1)
Al(1)	3080(3)	3937(2)	6770(1)	25(1)
F(1)	2834(6)	2371(4)	8187(3)	52(1)
O(1)	−274(6)	4447(4)	3561(4)	36(1)
O(2)	3910(6)	2578(4)	3417(3)	34(1)
O(3)	4047(6)	5384(4)	3087(4)	37(1)
O(4)	3438(7)	3341(4)	5415(3)	41(1)
N(1)	9328(9)	1370(4)	3120(4)	28(1)
C(1)	8210(20)	2911(9)	648(7)	70(2)
C(2)	11847(15)	365(11)	1504(8)	66(2)
C(3)	9144(10)	1229(6)	1757(5)	36(1)
C(4)	10035(12)	−155(6)	4356(5)	34(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

respectively. This is in good agreement with those expected on the basis of the single-crystal structure formula.

Thermogravimetric analysis shows a total weight loss of 41.9 wt % occurring from 210 to 330 °C, which is attributed to the removal of F atoms and the decomposition of the template molecule *N*,*N*′-diisopropylethylenediamine. An obvious endothermal peak is observed at about 300 °C, which may be due to the decomposition of the template molecules.

Single-crystal X-ray diffraction analysis demonstrates that AlPO-CJ8 crystallizes in the space group $P\bar{1}$, $a = 5.0306(8)$ Å, $b = 9.3626(15)$ Å, $c = 10.6131(17)$ Å, $\alpha = 65.949(4)°$, $\beta = 88.218(4)°$, and $\gamma = 77.19°$. The atomic coordinates and selected bond lengths and bond angles are listed in Tables 2 and 3, respectively.

Figure 2 shows one asymmetric unit of AlPO-CJ8. It contains one crystallographically independent P, Al, and F. Tetrahedral P atoms share three oxygen atoms with adjacent Al atoms with the P−O bond lengths of 1.532(3), 1.532(3), and 1.536(4) Å, respectively. There is a terminal P═O group with a bond distance of 1.497(3) Å, which is typical for the P═O bond lengths observed in previously reported aluminophosphates.[14−42] Similarly, tetrahedral Al atoms share three oxygen atoms with adjacent P atoms (Al−O: 1.733(3)−1.748(3) Å) with the fourth position occupied by a terminal F which is confirmed by ISE analysis. The Al−F bond distance is 1.642(3) Å, which is characteristic of the Al−F bond distance in tetrahedral AlO_3F.[12]

The alternation of tetrahedral $PO_3(=O)$ and AlO_3F forms a unique 1-D $Al_2P_2O_8F_2^{2-}$ chain (Figure 3). Diprotonated *N*,*N*′-

Table 3. Selected Bond Lengths (Å) and Angles (deg) for AlPO-CJ8[a]

P(1)−O(2)	1.497(3)	Al(1)−O(1)#2	1.748(3)
P(1)−O(3)	1.532(3)	N(1)−C(4)	1.471(6)
P(1)−O(1)	1.532(3)	N(1)−C(3)	1.513(6)
P(1)−O(4)	1.536(4)	C(1)−C(3)	1.511(8)
Al(1)−F(1)	1.642(3)	C(2)−C(3)	1.497(8)
Al(1)−O(4)	1.733(3)	C(4)−C(4)#3	1.506(10)
Al(1)−O(3)#1	1.737(3)		

O(2)−P(1)−O(3)	112.73(19)	O(4)−Al(1)−O(3)#1	108.14(18)
O(2)−P(1)−O(1)	108.99(19)	F(1)−Al(1)−O(1)#2	112.13(17)
O(3)−P(1)−O(1)	108.28(18)	O(4)−Al(1)−O(1)#2	111.37(18)
O(2)−P(1)−O(4)	110.23(19)	O(3)#1−Al(1)−O(1)#2	106.56(16)
O(3)−P(1)−O(4)	108.7(2)	P(1)−O(1)−Al(1)#2	143.5(2)
O(1)−P(1)−O(4)	107.73(19)	P(1)−O(3)−Al(1)#1	138.6(2)
F(1)−Al(1)−O(4)	107.99(17)	P(1)−O(4)−Al(1)	143.9(2)
F(1)−Al(1)−O(3)#1	110.59(17)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x+1, -y+1, -z+1$; (#2) $-x, -y+1, -z+1$; (#3) $-x+2, -y, -z+1$.

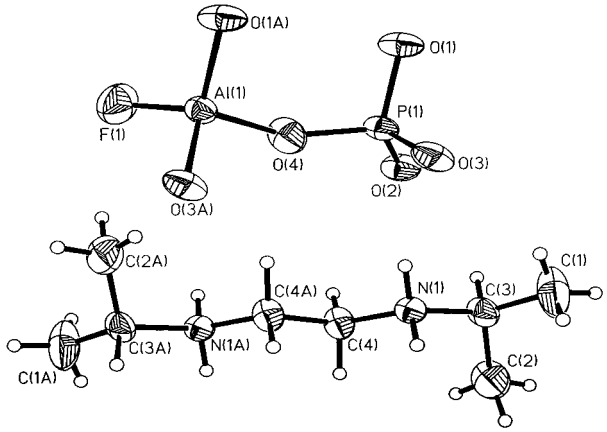

Figure 2. The asymmetric unit of AlPO-CJ8. Thermal ellipsoids at 50% probability.

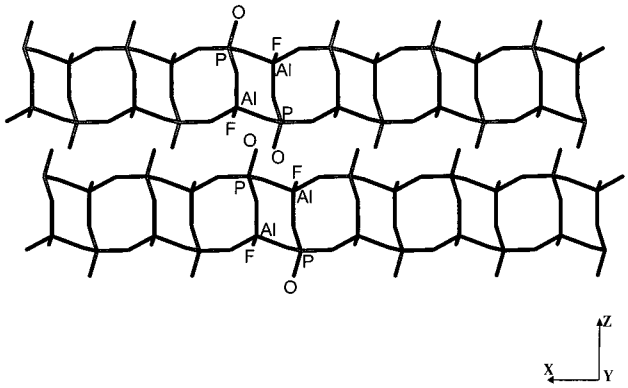

Figure 3. The infinite chain of AlPO-CJ8 parallel to the [010] direction (for clarity the organic templating agent in the interchain region is omitted).

diisopropylethylenediamine resides in the interchain regions. The N···O distances are 2.771(5) and 2.860(5) Å, indicating that there are strong H-bonds between the template molecules and the inorganic chains. Figure 4 shows the H-bonding interaction between the macroionic inorganic chain and the organic amines. Each N atom offers two hydrogen atoms to the terminal P═O group. The hydrogen information is summarized in Table 4.

It is interesting to note that the organic species in AlPO-CJ8 is *N*,*N*′-diisopropylethylenediamine instead of isopropylamine which is added in the initial reaction mixture. It is believed that it is formed by reaction of isopropylamine and the solvent

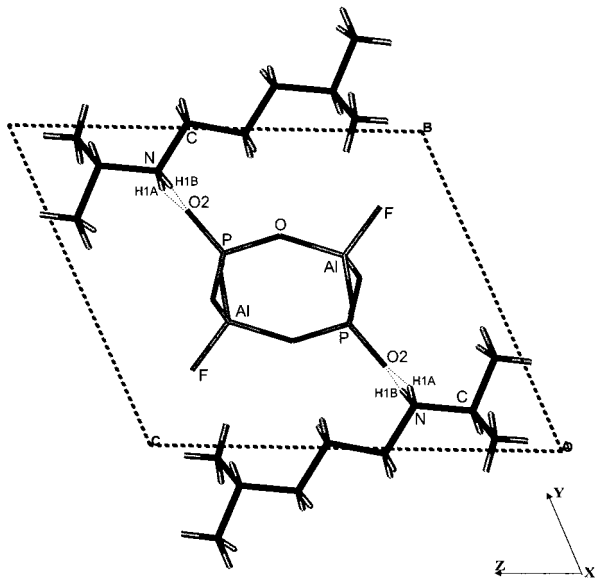

Figure 4. The hydrogen-bonding interaction between the inorganic chain and organic templating agent

Table 4. Hydrogen Bond Information for AlPO-CJ8 (Å and deg)[a]

D−H···A	*d*(D−H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
N(1)−H(1A)···O(2)#4	0.93(6)	1.96(6)	2.860(5)	163(5)
N(1)−H(1B)···O(2)	0.90(6)	1.88(6)	2.771(5)	169(5)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x+1, -y+1, -z+1$; (#2) $-x, -y+1, -z+1$; (#3) $-x+2, -y, -z+1$; (#4) $x+1, y, z$.

ethylene glycol through a dehydration process during the solvothermal crystallization.

$$(CH_3)_2CHNHH{+}HOCH_2CH_2OH{+}HHNCH(CH_3)_2 \xrightarrow{-2H_2O} (CH_3)_2CHNHCH_2CH_2HNCH(CH_3)_2$$

The fragmentation and cyclization of organic additive molecules during hydrothermal or solvothermal processes have been found before, e.g., in the syntheses of $[NH_3(CH_2)_2NH_3][NH_3(CH_2)_3NH_3]_2[Al_2P_4O_{16}]$[50] and $(Al_3P_4O_{16})^{3-}[NH_3(CH_2)_5NH_3]^{2+}(C_5H_{10}NH_2)^+$.[51] In the former case, $C_5N_2H_{12}$ (homopiperazine) is added to the reaction mixture. However, the molecules contained in the structure are ethylenediamine and propylenediamine instead of $C_5N_2H_{12}$. In the case of $(Al_3P_4O_{16})^{3-}[NH_3(CH_2)_5NH_3]^{2+}(C_5H_{10}NH_2)^+$, $NH_2(CH_2)_5NH_2$ is used as an additive. The existence of $C_5H_{10}NH$ in the structure is attributed to the cyclization of $NH_2(CH_2)_5NH_2$ and the elimination of ammonia. However, the reaction between the organic additive and the solvent molecules to produce a new type of templating agent has never been observed before.

Previously reported aluminophosphate[4] chains include $[Al_3P_5O_{20}H]_5[C_5H_9NH_3]$[35] (UT-2) made up of alternating tetrahedral AlO_4 and $P(O-Al)_nO_{4-n}$ units ($n = 1, 2, 3$), $[AlP_2O_8H_2][Et_3NH]$[42] consisting of linear corner-sharing Al_2P_2 four-membered rings, $[AlP_2O_8H_2][H_3NCH_2CH_2NH_3]$[43] consisting of a linear arrangement of fused edge-sharing Al_2P_2 four-membered rings with (PO_4H) side groups, and $Ir(C_6N_2H_{14})_3Al_2P_3O_{12}\cdot 4H_2O$[32] which consists of corner-sharing AlO_4 and PO_4 tetrahedra linked together to form a ribbon made of edge-sharing 4-rings. There are both triply and doubly bridging PO_4 units in this chain. The infinite chain in AlPO-CJ8 consists of a linear arrangement of fused edge-sharing Al_2P_2 four-membered rings without the (PO_4H) side groups found in $[AlP_2O_8H_2][H_3NCH_2CH_2NH_3]$. The existence of terminal P=O and Al−F groups in AlPO-CJ8 indicates that it has potential to condense and form 2-D layers or 3-D frameworks. Figure 5a shows a hypothetical sheet with a 4.4.6-net generated by connecting two adjacent chains through Al−F−Al linkages. Interestingly, a similar topology has been found in a recently reported layered aluminophosphate $Cs_2Al_2P_2O_9$.[52] Instead of the Al−F−Al linkages in Figure 5a, it contains linear Al−O−Al linkages, in violation of Lowenstein's rule as claimed by the authors. Figure 5b shows another hypothetical sheet with a novel 4.4.8-net generated through connecting two adjacent chains via an additional PO_4 tetrahedron replacing two F atoms. This layered structure possesses a stoichiometry of $Al_2P_3O_{12}^{3-}$.

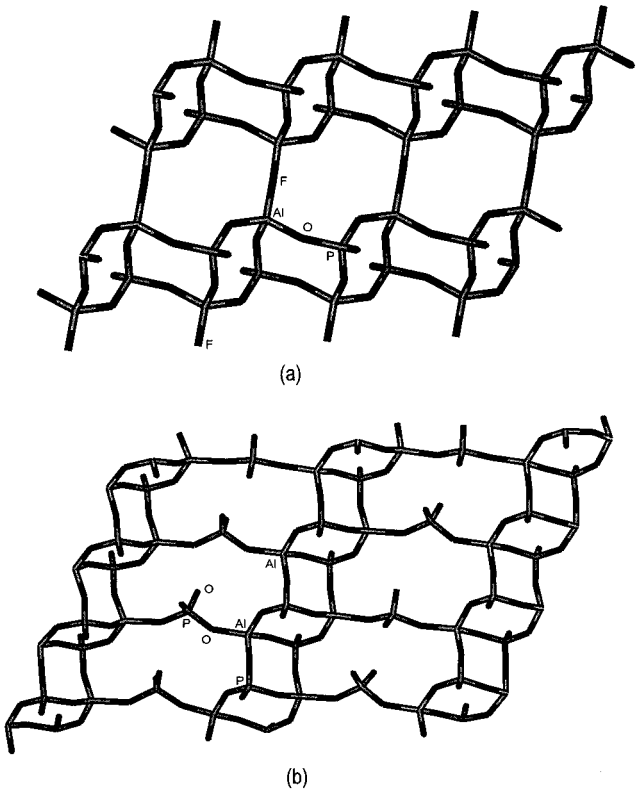

Figure 5. Hypothetical sheet structures with (a) a 4.4.6-net and (b) a 4.4.8-net

Conclusion

AlPO-CJ8 ($Al_2P_2O_8F_2\cdot[(CH_3)_2CHNH_2CH_2CH_2NH_2CH(CH_3)_2]$) has been synthesized in a solvothermal system using isopropylamine as an organic additive in the presence of HF. The presence of F^- in the reaction mixture is necessary for its formation. Its structure consists of an $Al_2P_2O_8F_2^{2-}$ infinite macroanionic chain held together by diprotonated *N*,*N*′-diisopropylethylenediamine through H-bonds. It represents the first 1-D aluminophosphate chain with an Al/P ratio of 1/1. The organic template *N*,*N*′-diisopropylethylenediamine is believed to be formed through a reaction between isopropylamine and the solvent ethylene glycol. Some hypothetical 2-D layered

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networks can be designed by condensation of this 1-D chain. This will further aid the rational design and synthesis of new networks with specific structures.

Acknowledgment. Financial support by the National Natural Science Foundation of China and the State Basic Research Project (of China) (G2000077507) is gratefully acknowledged. J.Y. is thankful for the support by the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE, P.R.C.

Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000879J