Journal of Solid State Chemistry **161,** 259–265 (2001)
doi:10.1006/jssc.2001.9307, available online at http://www.idealibrary.com on IDEAL®

Synthesis and Characterization of a New Fluoroaluminophosphate Chain

Wenfu Yan, Jihong Yu, Zhan Shi, Yu Wang, Yongcun Zou, and Ruren Xu[1]

State Key Lab of Inorganic Synthesis and Preparation Chemistry, Jilin University, Changchun 130023, People's Republic of China

Received March 29, 2001; in revised form July 6, 2001; accepted July 12, 2001

A new fluoroaluminophosphate chain, denoted AlPO-CJ10, has been synthesized in the system $Al(PrO^i)_3$–H_3PO_4–hexamethyleneimine–HF–TEG and its structure solved by single-crystal X-ray diffraction analysis. It is characterized by X-ray powder diffraction (XRD), ion-selective electrodes (ISE), inductively coupled plasma (ICP), thermogravimetric (TG), and elemental analyses. The compound has an empirical formula of $[AlP_2O_5(OH)_3F]\cdot[C_6H_{12}NH_2]$ and crystallizes in the orthorhombic space group *Pnma* (No. 62) with $a = 25.547(10)$ Å, $b = 6.915(2)$ Å, $c = 7.179(2)$ Å, $Z = 4$, $R_1 = 0.0550$, and $wR_2 = 0.1382$. Its structure is built up by alternation of tetrahedral $PO_3(OH)$ and $PO_2(OH)_2$ units and octahedral AlO_4F_2 units to form one-dimensional $AlP_2O_8H_3F^-$ macroanionic chains containing an infinite –Al–F–Al– linkage. The inorganic chains are held together by protonated hexamethyleneimine through H bonds. © 2001 Academic Press

Key Words: **fluoroaluminophosphate; chain; synthesis; solvothermal.**

INTRODUCTION

Since 1982, a series of microporous aluminophosphates, $AlPO_4$-*n*, where AlO_4 and PO_4 tetrahedra are alternated through vertex oxygen atoms, have been hydrothermally synthesized in the presence of various organic templates (1–7). These materials have potential applications in adsorption and catalysis, like aluminosilicate zeolites. Recently, through use of a solvothermal synthesis technique, i.e., use of organic solvents instead of water, a variety of organically templated aluminophosphates (AlPOs) with anionic networks or open frameworks continue to be synthesized. There are three-dimensional (3-D) open-framework AlPOs with Al/P ratios of 12/13 (22), 11/12 (23), 5/6 (24), 4/5 (25), 3/4 (26), 2/3 (27), and 1/2 (28), a family of 2-D layers with Al/P ratios of 4/5 (29), 3/4 (30–41), 2/3 (42–47), and 1/2 (36, 48–49), and a series of 1-D chains with Al/P ratios of 1/1 (50), 2/3 (41), 3/5 (44), and 1/2 (51–53). The organic amines are incorporated in the interchains, interlayers, and channels or cages voids (8–10), playing templating and charge-balancing roles. In addition, it is noted that the addition of fluoride ions to the reaction mixture allows the formation of new compounds (11) because of the effects of mineralizing, structure directing, and templating of F^-. By this method, a series of fluoroaluminophosphates have been prepared in the system Al_2O_3–P_2O_5–HF–amine–H_2O (12) with 1-D chains (50), 2-D layers (13–16), and 3-D open frameworks (17–21).

In this work, using hexamethyleneimine as a template and with the addition of HF in the reaction mixture, we have prepared a new type of 1-D fluoroaluminophosphate chain with an Al/P ratio of 1/2, which is the second type of 1-D fluoroaluminophosphate chains. Its structure consists of tetrahedral $PO_3(OH)$ and $PO_2(OH)_2$ units and octahedral AlO_4F_2 units to form a unique 1-D chain architecture.

EXPERIMENTAL

AlPO-CJ10 was synthesized from an alcoholic system in which tetraethylene glycol (TEG) was used as the solvent and hexamethyleneimine ($(CH_2)_6NH$) as the organic template. Aluminium triisopropoxide 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-CJ10. A reaction mixture with a molar composition of 1:6.0:5.0:14:1.9:8.9 of $Al(PrO^i)_3 : H_3PO_4 : (CH_2)_6NH : TEG : HF : H_2O$ was sealed in a Teflon-lined stainless steel autoclave and then heated at 180°C for 15 days under autogenous pressure. The resulting long needle-like 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$K\alpha$ radiation

[1] To whom correspondence should be addressed. Fax: 86-431-5671974. E-mail: rrxu@mail.jlu.edu.cn.

0022-4596/01 $35.00

TABLE 1
Crystal Data and Structure Refinement for AlPO-CJ10

Empirical formula	$AlP_2O_8FNC_6H_{17}$
Formula weight	339.13
Temperature	293(2) K
Wavelength	0.71073 Å
Space group	*Pnma* (No. 62)
a (Å)	25.547(10)
b (Å)	6.915(2)
c (Å)	7.179(2)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1268.3(7)
Z	4
ρ_{calcd} (mg m^{-3})	1.776
μ (mm^{-1})	0.4460
Final R indices [$I > 2\sigma(I)$]*	$R_1 = 0.0550$, $wR_2 = 0.1382$
R indices (all data)	$R_1 = 0.0806$, $wR_2 = 0.1509$

Note. $R_1 = \sum(\Delta F/\sum(F_o))$; $wR_2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o^2)$.

($\lambda = 1.5418$ Å). The elemental analysis was 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 10°C/min.

A suitable colorless single crystal with dimensions $0.6 \times 0.08 \times 0.08$ mm was glued to a thin glass fiber with epoxy resin and mounted on a Siemens Smart CCD diffractometer equipped with a normal-focus, 2.4-kW sealed-tube X-ray source (graphite-monochromatic Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Intensity data were collected at a temperature of 20 ± 2°C. The total number of measured reflections and observed unique reflections were 5885 and 992, respectively. The lattice constant was determined by the least-squares procedure applied to the θ values for 25 reflections (1.59°–23.21°). Intensity data of 992 independent reflections ($-28 \le h \le 28$, $-7 \le k \le 7$, $-7 \le l \le 6$) were collected in the ω scan mode. An empirical absorption correction was applied using the SADABS program with $T_{min} = 0.1697$ and $T_{max} = 0.2641$ (58). The structure was solved in the space group *Pnma* by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97 (54). The phosphorus and aluminum atoms were located first. Carbon, nitrogen, and oxygen were found in the difference Fourier map. The F atoms between two Al atoms were suggested by the ISE determination. Hydrogen atoms were placed geometrically. All non-hydrogen atoms were refined with anisotropic thermal parameters. A summary of the crystallographic data is presented in Table 1.

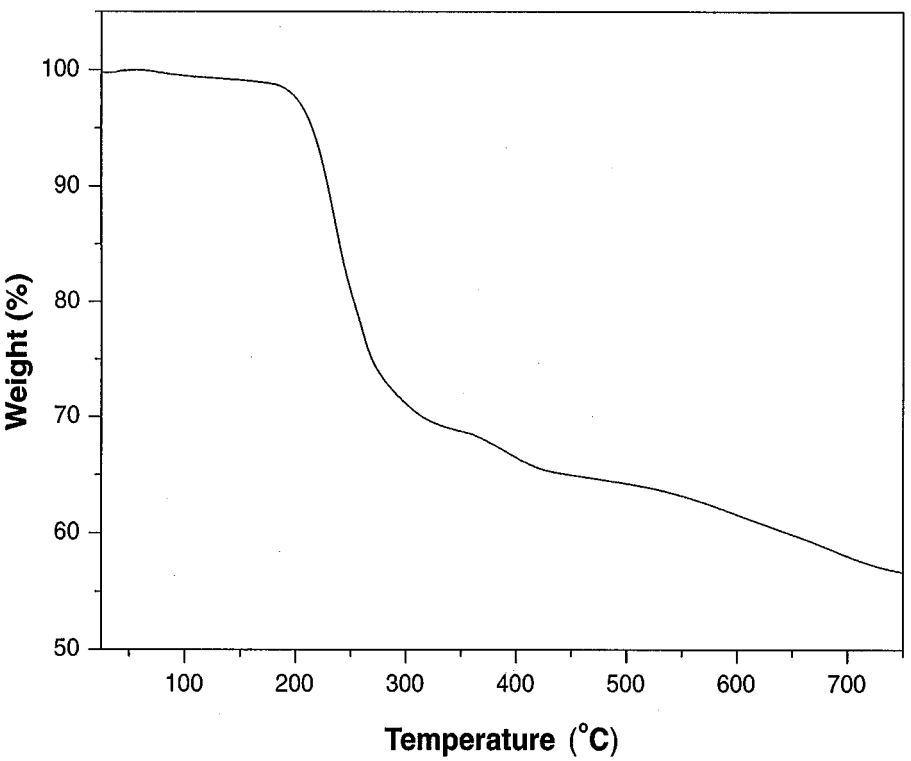

FIG. 1. Thermogravimetric (TG) analysis curve of AlPO-CJ10.

RESULTS AND DISCUSSION

AlPO-CJ10 crystallizes from a gel with molar composition 1:6.0:5.0:14:1.9:8.9 of $Al(PrO^i)_3 : H_3PO_4 : (CH_2)_6NH : TEG : HF : H_2O$. Water molecules are introduced by H_3PO_4 and HF. The addition of F^- is critical for the synthesis of AlPO-CJ10. Without F^-, a compound with structure analogous to AlPO-CJB1 (22) is obtained in the above reaction mixture. When the amount of HF is increased to 1.5 mol, small needle-like single crystals of AlPO-CJ10 are obtained as a pure phase. When the amount of HF is increased to 1.9 mol, large single crystals of AlPO-CJ10 are formed. With a HF amount between trace and 1.5 mol, AlPO-CJB1 and AlPO-CJ10 co-exist in the product. The measured X-ray powder diffraction pattern for AlPO-CJ10 is in good agreement with the XRD pattern simulated from single-crystal structural data, proving that the as-synthesized product is a single phase.

Ion-selective electrode (ISE) analysis shows that there exists F atoms in the product of AlPO-CJ10 and that the amount of F atoms is 5.4 wt% (calcd. 5.6 wt%). ICP analysis gives the contents of Al as 9.8 wt% (calcd. 10.7 wt%) and P as 20.4 wt% (calcd. 21.0 wt%), indicating an Al/P ratio of 1/2. Elemental analysis indicates that the sample contains 20.73, 5.02, and 4.22 wt% of C, H, and N, respectively. These are in good agreement with the expected values of 21.2, 5.0, and 4.1 wt% of C, H, and N, respectively, on the basis of the empirical formula given by the single-crystal structure analysis.

Thermogravimetric analysis shows three steps of weight loss from 200 to 750°C (Fig. 1). The weight loss of 30 wt% for the first step from 200 to 340°C is attributed to the decomposition of the template molecule (calcd: 29.5 wt%). The weight loss of 6.0 wt% for the second step from 340 to 480°C is in accord with the removal of HF (calcd: 5.9%). The weight loss of 8.1 wt% for the third step is attributed to the removal of –OH as H_2O (calcd: 7.96 wt%). XRD study shows that the degree of crystallinity of AlPO-CJ10 dramatically decreases when the sample is heated at 270°C for 3 h, and the sample becomes amorphous when heated at 350°C for 3 h.

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for AlPO-CJ10

	x	*y*	*z*	*U* (eq)
P(1)	974(1)	2500	3936(2)	20(1)
P(2)	369(1)	2500	8423(3)	17(1)
Al(1)	0	0	5000	15(1)
F(1)	244(1)	− 2500	5430(5)	17(1)
O(1)	652(1)	707(5)	4070(6)	39(1)
O(2)	1409(2)	2500	5464(8)	56(2)
O(3)	1321(2)	2500	2167(6)	23(1)
O(4)	211(2)	708(5)	7394(5)	52(1)
O(5)	945(2)	2500	8840(7)	69(3)
O(6)	66(2)	2500	10300(7)	29(1)
N(1)	3923(3)	2500	3455(12)	61(3)
C(1)	3546(4)	2500	1944(16)	63(3)
C(2)	3036(7)	2500	2210(30)	241(16)
C(3)	2703(6)	2500	3620(30)	182(12)
C(4)	2837(6)	2500	5430(30)	159(9)
C(5)	3328(6)	2500	6242(15)	80(4)
C(6)	3793(5)	2500	5300(20)	136(8)

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

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for AlPO-CJ10

P(1)–O(1)	1.492(4)
P(1)–O(1)#1	1.492(4)
P(1)–O(3)	1.549(5)
P(1)–O(2)	1.561(6)
P(2)–O(4)	1.498(4)
P(2)–O(4)#1	1.498(4)
P(2)–O(5)	1.501(6)
P(2)–O(6)	1.555(5)
Al(1)–O(1)#2	1.860(3)
Al(1)–O(1)	1.860(3)
Al(1)–F(1)	1.8633(14)
Al(1)–F(1)#2	1.8633(14)
Al(1)–O(4)#2	1.867(4)
Al(1)–O(4)	1.867(4)
F(1)–Al(1)#3	1.8633(14)
O(1)–P(1)–O(1)#1	112.4(3)
O(1)–P(1)–O(3)	111.66(19)
O(1)#1–P(1)–O(3)	111.66(19)
O(1)–P(1)–O(2)	110.34(19)
O(1)#1–P(1)–O(2)	110.34(19)
O(3)–P(1)–O(2)	99.7(3)
O(4)–P(2)–O(4)#1	111.6(3)
O(4)–P(2)–O(5)	111.2(2)
O(4)#1–P(2)–O(5)	111.2(2)
O(4)–P(2)–O(6)	107.0(2)
O(4)#1–P(2)–O(6)	107.0(2)
O(5)–P(2)–O(6)	108.5(3)
O(1)#2–Al(1)–O(1)	180.00(9)
O(1)#2–Al(1)–F(1)	89.76(16)
O(1)–Al(1)–F(1)	90.24(16)
O(1)#2–Al(1)–F(1)#2	90.24(16)
O(1)–Al(1)–F(1)#2	89.76(16)
F(1)–Al(1)–F(1)#2	180.0(2)
O(1)#2–Al(1)–O(4)#2	90.2(2)
O(1)–Al(1)–O(4)#2	89.8(2)
F(1)–Al(1)–O(4)#2	90.34(16)
F(1)#2–Al(1)–O(4)#2	89.66(16)
O(1)#2–Al(1)–O(4)	89.8(2)
O(1)–Al(1)–O(4)	90.2(2)
F(1)–Al(1)–O(4)	89.66(16)
F(1)#2–Al(1)–O(4)	90.34(16)
O(4)#2–Al(1)–O(4)	180.000(1)
Al(1)#3–F(1)–Al(1)	136.2(2)
P(1)–O(1)–Al(1)	137.4(3)
P(2)–O(4)–Al(1)	138.5(3)

Note. Symmetry transformations used to generate equivalent atoms: (#1) $x, -y+\frac{1}{2}, z$; (#2) $-x, -y, -z+1$; (#3) $-x, y-\frac{1}{2}, -z+1$.

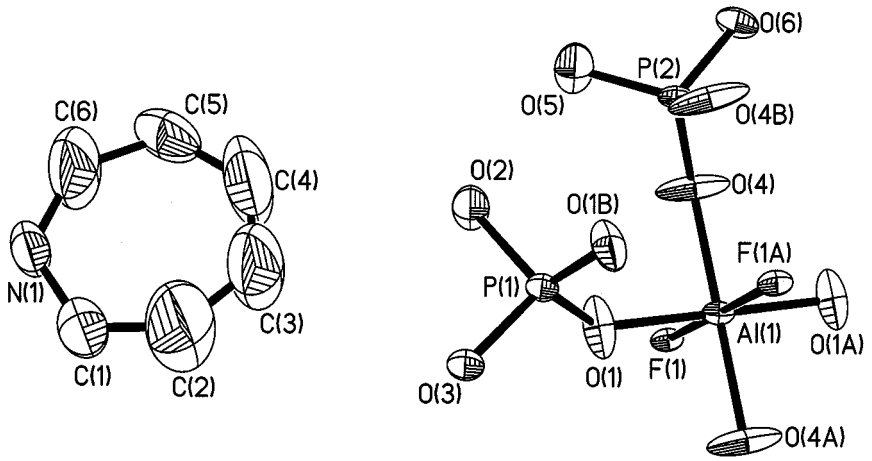

FIG. 2. The atomic labeling scheme for AlPO-CJ10 (thermal ellipsoids at 50% probability).

Single-crystal X-ray diffraction analysis shows that AlPO-CJ10 crystallizes in the space group *Pnma* (No. 62) with $a = 25.547(10)$ Å, $b = 6.915(2)$ Å, $c = 7.179(2)$ Å, and $Z = 4$. The atomic coordinates and selected bond lengths and bond angles are listed in Tables 2 and 3, respectively.

Figure 2 shows the atomic labeling scheme for AlPO-CJ10. Each asymmetric unit contains one crystallographically independent Al and F atoms and two crystallographically independent P atoms. The tetrahedral P(1) atom shares two oxygen atoms with adjacent Al atoms with the P–O bond lengths of 1.492(4) Å, leaving the other two oxygen atoms as terminal P–OH groups (bond lengths: 1.549(5) and 1.561(6) Å). The tetrahedral P(2) atom shares two oxygen atoms with adjacent Al atoms with the P–O bond lengths of 1.498(4) Å, with the other two oxygen atoms as a terminal P=O group (bond length: 1.501(6) Å) and P–OH group (bond length: 1.555(5) Å). It is noted that the bond distances of $P–O_{bridging}$ of 1.492(4) and 1.498(4) Å are slightly shorter than the normal $P–O_{bridging}$ bond in previously reported aluminophosphates (17–47). This can be understood upon consideration that the bond valence sum for the bridging oxygen is constant. As the Al–O bond becomes longer, the P–O bond must become shorter. The Al atom lies in the reversion center and coordinates to four oxygen atoms and two fluorine atoms to form a regular octahedron. The F–Al–F bond angle for two fluorine atoms in a *trans* position is 180°. The bond angles for O(1)–Al–(1)# and O(4)–Al–(4)# in the plane are also 180°. The Al–O bond lengths of 1.860(3) and 1.867(4) Å are typical for octahedral Al units. The bond distance of Al–F is 1.863(1) Å, which is characteristic of the Al–F bond distances in octahedral AlO_4F_2 units (12–21).

Alternation of tetrahedral $PO_2(=O)(OH)$ and $PO_2(OH)_2$ units and AlO_4F_2 units forms a unique 1-D $AlP_2O_5(OH)_3F^-$ chain with the Al/P ratio of 1/2 (Fig. 3). Protonated hexamethyleneimines reside in the interchain regions. The $N(1)\cdots O(4)$ distances are 3.224(7) Å, indicating that there are weak H bonds between the template molecules and the inorganic chains. The distances of $O(2)\cdots O(5)$, $O(3)\cdots O(5)$, and $O(6)\cdots O(4)$ are 2.697(8), 2.575(7), and

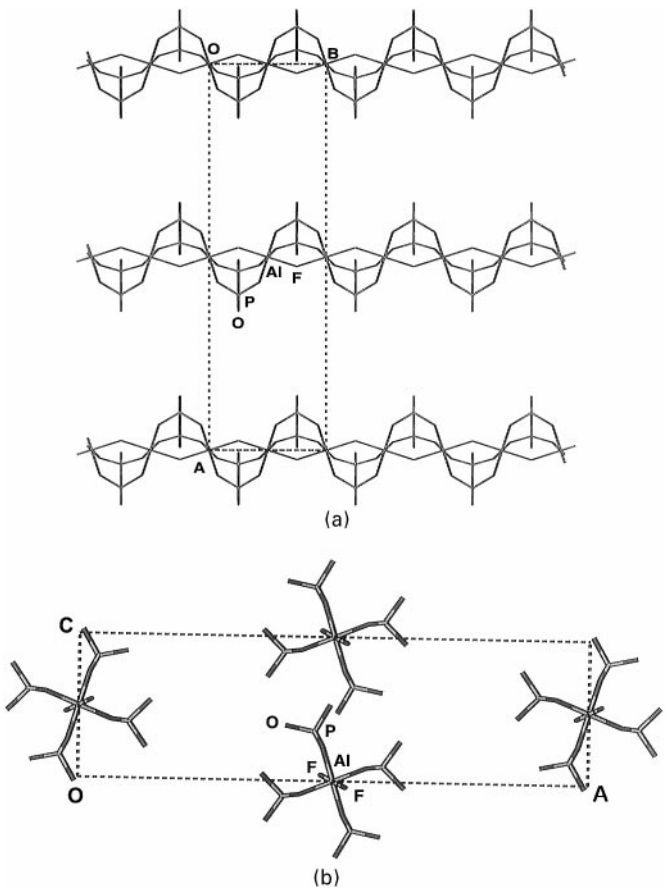

FIG. 3. The inorganic chain structure of AlPO-CJ10 viewed along the [001] (a) and [010] (b) directions.

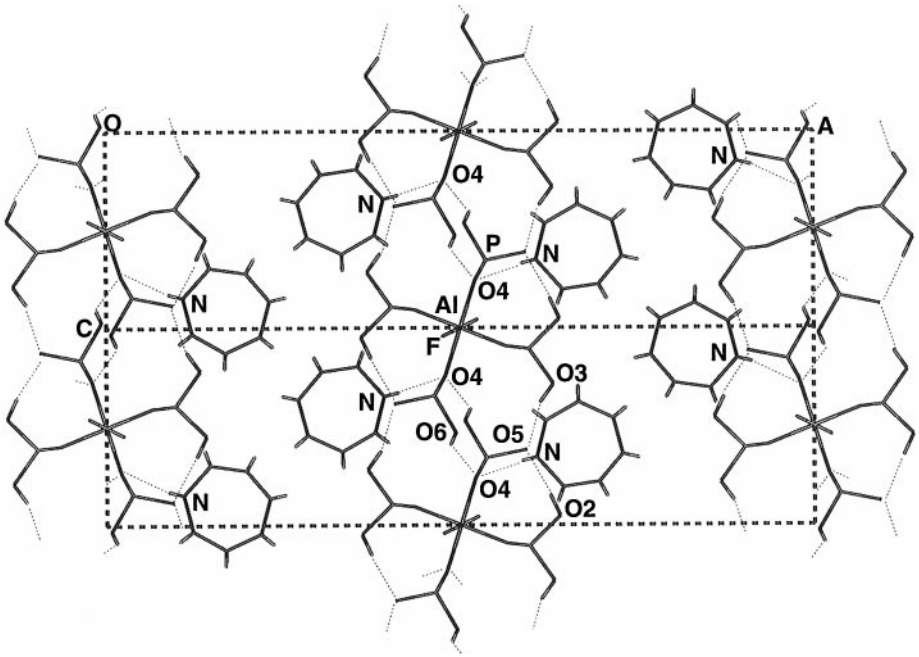

FIG. 4. The hydrogen-bonding interactions among the inorganic chains and the organic templating molecules (viewed along the *b* direction).

2.857(5) Å, respectively, indicating that there are relatively strong H bonds among the inorganic chains. Each $-NH_2$ group of the template offers two H atoms to two O(4) atoms in the chain to form H bonds, while each O(4) atom forms two H bonds with one N atom of the template and one O(6) atom in the adjacent chain. Each O(5) atom forms two H bonds to O(2) inside the chain and O(3) in the adjacent chain. Figure 4 shows the H-bonding interactions among the macroanionic inorganic chains and the organic amines. The hydrogen bond information is summarized in Table 4.

1-D chains with an Al/P ratio of 1/2 have been found in two distinct structures. One is $[AlP_2O_8H_2][Et_3NH]$ (51, 53), consisting of linear corner-sharing Al_2P_2 four-membered rings. The other is $[AlP_2O_8H_2][H_3NCH_2CH_2NH_3]$ (52), consisting of linear edge-sharing Al_2P_2 four-membered rings with (PO_4H) side groups. The chain structure of AlPO-CJ10 resembles the 1-D chain containing corner-sharing four-membered rings upon removal of –Al–F–Al– linkages.

TABLE 4
Hydrogen Bonds for AlPO-CJ10 (Å and °)

D–H ⋯ A	*d*(D–H) (Å)	*d*(H ⋯ A) (Å)	*d*(D ⋯ A) (Å)	∠(DHA) (°)
O(2)–H(2) ⋯ O(5)	0.82	1.88	2.697(8)	176.4
O(3)–H(3) ⋯ O(5)#4	0.82	1.79	2.575(7)	159.6
O(6)–H(6) ⋯ O(4)#5	0.82	2.17	2.857(5)	141.3
N(1)–H(1A) ⋯ O(4)#6	0.90	2.34	3.224(7)	165.7
N(1)–H(1B) ⋯ O(4)#7	0.90	2.34	3.224(7)	165.7

Note. Symmetry transformations used to generate equivalent atoms: (#4) $x, y, z-1$; (#5) $-x, -y, -z+2$; (#6) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$; (#7) $-x+\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$.

In a natural mineral of tancoite, $LiNa_2HAl(PO_4)_2(OH)$ (55), two synthetic 1-D aluminophosphates $Na_4Al(PO_4)_2(OH)$ (56), and $Na_3Al(OH)(HPO_4)(PO_4)$ (57), there exist as a similar 1-D chain structure as AlPO-CJ10. The differences are that the charge-compensating species are alkali metal cations and that there exists –Al–OH–Al– infinite linkages in these aluminophosphates instead of –Al–F–Al– linkages in AlPO-CJ10. A similar architecture had been found in two gallium phosphate chains (59), both of which contain infinite –Ga–F–Ga– linkages.

So far, a number of fluoroaluminophosphates have been prepared in the presence of HF (13–21, 50), wherein F^- are incorporated into the networks or frameworks and exclusively bonded to Al atoms to form an Al-centered AlOF polyhedron including a tetrahedron, octahedron, and trigonal bipyramid. There are three bond types of Al–F in fluoroaluminophosphates including terminal Al–F bonds (14, 15, 17, 50) and bridging Al–F–Al bonds in which there exist μ_2-F (13, 15, 16, 18–21) and μ_3-F (21) bridging two and three Al atoms, respectively. Terminal Al–F bonds are found in tetrahedral AlO_3F_t (t: terminal) (50), octahedral AlO_4F_{2t} (14), $AlO_4F_bF_t$ (b: bridging) (14, 15), and AlO_5F_t (17), with the bond distances ranging from 1.642 to 1.839 Å. Bringing Al–F–Al bonds are found in octahedral $AlO_3F_{2b}N$ (13), $AlO_4F_bF_t$ (14, 15), AlO_4F_{2b} (18–21), and trigonal bipyramid AlO_4F_b (21), with the Al–F distances of 1.802 to 1.964 Å. ULM-6 is the only example containing μ_3-F atoms,

with the bond distances of the F atom to three Al atoms being 1.953(3), 1.964(3), and 2.297(3) Å, respectively, which are longer than normal Al–F bond distances. This can be easily understood as bond valence calculations. The higher the coordination of F, the longer the distance to keep the valence sum equal to 1. Normally, when F atom acts as a bridging atom, two Al atoms are connected by one F atom. However, in the case of some 3-D fluoroaluminophosphates, e.g., gismondine (GIS) (18), chabazite (CHA) (19, 20), and ULM-6 (21), two Al atoms are connected by two F atoms, which causes a short distance of 2.97 Å between these two Al atoms. It is interesting to note that an infinite –Al–F–Al– linkage is found in AlPO-CJ10, which is also featured in two layered fluoroaluminophosphates (13, 16). The existence of various Al–F bonds and AlOF polyhedra greatly enriches the structural chemistry of fluoroaluminophosphates.

CONCLUSION

AlPO-CJ10 ($[AlP_2O_5(OH)_3F]\cdot[(CH_2)_6NH_2]$) has been synthesized in a solvothermal system using hexamethyleneimine as an organic template in the presence of HF. The presence of F^- in the reaction mixture is necessary for its formation. Its structure consists of $AlP_2O_5(OH)_3F^-$ infinite macroanionic chains held together by protonated hexamethyleneimine through H bonds. There exists an infinite –Al–F–Al– linkage in the chain. Various Al–F bonds and AlOF polyhedra in the family of fluoroaluminophosphates have been discussed. It is believed that fluoroaluminophosphates with various structural architectures would be continuously synthesized under suitable conditions.

ACKNOWLEDGMENTS

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

REFERENCES

1. S. T. Wilson, B. M. Lok, C. A. Messian, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.* **104,** 1146 (1982); S. T. Wilson, B. M. Lok, and E. M. Flanigen, U.S. Patent 4 310 440, 1982.
2. E. M. Flanigen, B. M. Lok, R. L. Patton, and S. T. Wilson, *in* "New Developments in Catalysis" (Y. Murakami, A. Ijima, and J. W. Ward, Eds.), p. 103. Elsevier, New York, 1986.
3. J. M. Bennett, W. J. Dytrych, J. J. Pluth, J. W. Richardson, Jr., and J. V. Smith, *Zeolites* **6,** 349 (1986).
4. E. M. Flanigen, R. L. Patton, and S. T. Wilson, *in* "Studies in Surface Science and Catalysis" (P. J. Grobet, W. J. Mortier, E. F. Vansant, and G. Schulz-Ekloff, Eds.), p. 13. Elsevier, New York, 1988.
5. M. E. Davis, C. Saldarriage, C. Montes, J. Garces, and C. Crowder, *Nature* **331,** 698 (1988).
6. W. H. Meier, D. H. Olson, and Ch. Baerlocher, "Atlas of Zeolite Structure Types." Elsevier, London, 1996.
7. J. Yu, R. Xu, and J. Li, *Solid State Sci.* **2,** 181 (2000).
8. D. M. Bibby and M. R. Dale, *Nature* **317,** 157 (1985).
9. R. Xu, Q. Huo, and W. Pang, *in* "Proceedings of the Ninth International Zeolites Conference" (von V. Ballmoos, J. B. Higgins, and M. M. J. Treacy, Eds.), Vol. 1, p. 271. Butterworth-Heinemann, Toronto, 1992.
10. R. Morris and S. L. Weigel, *Chem. Soc. Rev.* **26,** 309 (1997).
11. J. L. Guth, H. Kessler, and R. Wey, *Stud. Surf. Sci. Catal.* **28,** 121 (1986).
12. G. Férey, *J. Fluorine Chem.* **72,** 187 (1995).
13. D. Riou, T. Loiseau, and G. Férey, *J. Solid State Chem.* **102,** 4 (1993).
14. J. Renaudin and G. Férey, *J. Solid State Chem.* **120,** 197 (1995).
15. N. Simon, T. Loiseau, and G. Férey, *J. Mater. Chem.* **9,** 585 (1999).
16. N. Simon, N. Guillou, T. Loiseau, F. Taulelle, and G. Férey, *J. Solid State Chem.* **147,** 92 (1999).
17. L. Yu, W. Pang, and L. Li, *J. Solid State Chem.* **87,** 241 (1990); G. Férey, T. Loiseau, P. Lacorre, and F. Taulelle, *J. Solid State Chem.* **105,** 179 (1993).
18. J. L. Paillaud, B. Marler, and H. Kessler, *Chem. Commun.* 1293 (1996).
19. M. M. Harding and B. M. Kariuki, *Acta Crystallogr. C* **50,** 852 (1994).
20. S. Oliver, A. Kuperman, A. Lough, and G. A. Ozin, *J. Mater. Chem.* **7,** 807 (1997).
21. N. Simon, T. Loiseau, and G. Férey, *J. Chem. Soc., Dalton Trans.* 1147 (1999).
22. W. Yan, J. Yu, R. Xu, G. Zhu, F. Xiao, Y. Han, K. Sugiyama, and O. Terasaki, *Chem. Mater.* **12,** 2517 (2000).
23. W. Yan, J. Yu, Z. Shi, P. Miao, K. Wang, and R. Xu, submitted for publication.
24. Q. Huo, R. Xu, S. Li, Z. Ma, J. M. Thomas, R. H. Jones, and A. M. Chippindale, *J. Chem. Soc., Chem. Commun.* 875 (1992).
25. J. Yu, K. Sugiyama, S. Zheng, S. Qiu, J. Chen, R. Xu, Y. Sakamoto, O. Terasaki, K. Hiraga, M. Light, M. B. Hursthouse, and J. M. Thomas, *Chem. Mater.* **10,** 1208 (1998).
26. Y. Xu, B. Zhang, X. Chen, S. Liu, C. Duan, and X. You, *J. Solid State Chem.* **145,** 220 (1999).
27. B. Wei, G. Zhu, J. Yu, S. Qiu, and O. Terasaki, *Chem. Mater.* **11,** 3417 (1999).
28. W. Yan, J. Yu, Z. Shi, and R. Xu, *Chem. Commun.* 1431 (2000).
29. L. Vidal, V. Gramlich, J. Patarin, and Z. Gabelica, *Eur. J. Solid State Chem.* **35,** 345 (1998).
30. R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, A. K. Cheetham, and A. V. Powell, *J. Chem. Soc., Chem. Commun.* 1266 (1991).
31. Q. Gao, B. Li, J. Chen, S. Li, and R. Xu, *J. Solid State Chem.* **129,** 37 (1997).
32. J. M. Thomas, R. H. Jones, R. Xu, J. Chen, A. M. Chippindale, S. Natarajan, and A. K. Cheetham, *J. Chem. Soc., Chem. Commun.* 929 (1992).
33. A. M. Chippindale, A. R. Cowley, Q. Huo, R. H. Jones, and A. D. Law, *J. Chem. Soc., Dalton. Trans.* 2639 (1997).
34. I. D. Williams, Q. Gao, J. Chen, L. Ngai, Z. Lin, and R. Xu, *Chem. Commun.* 1781 (1996).
35. J. Yu, J. Li, K. Sugiyama, N. Togashi, O. Terasaki, K. Hiraga, B. Zhou, S. Qiu, and R. Xu, *Chem. Mater.* **11,** 1727 (1999).
36. J. Yu and I. D. Williams, *J. Solid State Chem.* **136,** 141 (1998).
37. R. H. Jones, A. M. Chippindale, S. Natarajan, and J. M. Thomas, *J. Chem. Soc., Chem. Commun.* 565 (1994).
38. K. Morgan, G. Gainsford, and N. Millestone, *J. Chem. Soc., Chem. Commun.* 425 (1995).
39. P. A. Barrett and R. H. Jones, *J. Chem. Soc., Chem. Commun.* 1979 (1995).
40. S. Oliver, A. Kuperman, A. Lough, and G. A. Ozin, *Inorg. Chem.* **35,** 6373 (1996).
41. D. J. Williams, J. S. Kruger, A. F. McLeroy, A. P. Wilkinson, and J. C. Hanson, *Chem. Mater.* **11,** 2241 (1999).

42. J. Yu, K. Sugiyama, K. Hiraga, N. Togashi, O. Terasaki, Y. Tanaka, S. Nakata, S. Qiu, and R. Xu, *Chem. Mater*. **10,** 3636 (1998).
43. A. M. Chippindale, A. V. Powell, L. M. Bull, R. H. Jones, A. K. Cheetham, J. M. Thomas, and R. Xu, *J. Solid State Chem.* **96,** 199 (1992).
44. S. Oliver, A. Kuperman, A. Lough, and G. A. Ozin, *Chem. Mater*. **8,** 2391 (1996).
45. S. Oliver, A. Kuperman, A. Lough, and G. A. Ozin, *Chem. Commun.* 1761 (1996).
46. P. Lightfoot, Z. A. D. Lethbridge, R. E. Morris, D. S. Wragg, P. A. Wright, Å. Kvick, and G. B. M. Vaughan, *J. Solid State Chem.* **143,** 74 (1999).
47. A. M. Chippindale and R. I. Walton, *J. Solid State Chem.* **145,** 731 (1999).
48. K. R. Morgan, G. J. Gainford, and N. B. Milestone, *Chem. Commun.* 61 (1997).
49. M. A. Leech, A. R. Cowley, K. Prout, and A. M. Chippindale, *Chem. Mater*. **10,** 451 (1998).
50. W. Yan, J. Yu, Z. Shi, and R. Xu, *Inorg. Chem.* **40,** 379 (2001).
51. R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, Y. Xu, A. K. Cheetham, and D. Bieber, *J. Chem. Soc., Chem. Commun.* 1170 (1990).
52. I. D. Williams, J. Yu, Q. Gao, J. Chen, and R. Xu, *Chem. Commun.* 1273 (1997).
53. A. A. Ayi, A. Choudhury, and S. Natarajan, *J. Solid State Chem.* **156,** 185 (2001).
54. G. M. Sheldrick, SHELXTL-NT, Version 5.1, Brucker Axs Ainc., Madison, WI, 1997.
55. R. A. Ramik, B. D. Sturman, P. J. Dunn, and A. S. Poverennykh, *Can. Mineral.* **18,** 185 (1980).
56. M. P. Attfield, R. E. Morris, I. Burshtein, C. F. Campana, and A. K. Cheetham, *J. Solid State Chem.* **118,** 412 (1995).
57. K. Lii and S. Wang, *J. Solid State Chem.* **128,** 21 (1997).
58. G. M. Sheldrick, A Program for the Siemens Area Detector Absorption Correction, University of Göttingen, Göttingen, Germany, 1997.
59. R. I. Walton, F. Millange, and D. O'Hare, *Chem. Mater*. **12,** 1977 (2000).