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Synthesis and Characterization of a New Layered Fluoroaluminophosphate $(C_4H_{11}NOH)_{3.5}[Al_4(PO_4)_5F]\cdot 0.5H_3O$ with Extra-Large 16-Rings

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A new two-dimensional-layered fluoroaluminophosphate $(C_4H_{11}NOH)_{3.5}[Al_4(PO_4)_5F]\cdot 0.5H_3O$ (denoted as AlPO-CJ20) with an Al/P ratio of 4:5 has been synthesized solvothermally by using 2-amino-2-methyl-1-propanol as the structure-directing agent. Its structure was determined by single-crystal X-ray diffraction analysis and further characterized by solid-state NMR techniques, including ^{27}Al, $^{19}F \rightarrow {}^{27}Al$ cross-polarization, and ^{31}P magic angle spinning NMR. The alternation of Al-centered tetrahedra (AlO_4 and AlO_3F) and $PO_3(=O)$ tetrahedra gives rise to a new type of 4.6.16-net sheet. The inorganic sheets are stacked in an ABAB sequence along the [010] direction and further held together through strong H bonds between protonated template molecules and P=O groups in the inorganic layers. Except for Mu-4, AlPO-CJ20 is the second layered aluminophosphate with an Al/P ratio of 4:5, and it contains the largest pore opening of 16-rings in the known layered aluminophosphates. Furthermore, the coordination of Al and P of fluoroaluminophosphates is summarized. Crystal data: $(C_4H_{11}NOH)_{3.5}[Al_4(PO_4)_5F]\cdot 0.5H_3O$, monoclinic, $C2/c$ (No. 15), $a = 32.678(7)$ Å, $b = 12.956(3)$ Å, $c = 21.045(4)$ Å, $\beta = 115.17(3)°$, $V = 8064(3)$ Å^3, $Z = 8$, R1 = 0.0837 [$I > 2\sigma(I)$], and wR2 = 0.2428 (all data).

Introduction

Since the first discovery of aluminophosphate molecular sieves $AlPO_4$-n (n denotes a specific structure type) in 1982,[1] there has been considerable interest in developing new aluminophosphate (denoted as AlPO) compounds with novel framework structures because of their potential applications in catalysis, adsorption, and separation.[2−15] A large number of open-framework aluminophosphates with various structure architectures have been synthesized that display rich structural chemistry, including neutral zeolite-like open frameworks $AlPO_4$-n and anionic frameworks with three-dimensional (3D) open-framework, 2D layer, 1D chain, and 0D cluster structures.[2,3]

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2D AlPO layers show diverse stoichiometries, sheet structures, and sheet stacking sequences.[16−26] The known stoichiometries of 2D-layered AlPO compounds are found as $AlPO_4(OH)^-$, $AlP_2O_8^{3-}$, $Al_2P_3O_{12}^{3-}$, $Al_3P_4O_{16}^{3-}$, $Al_4P_5O_{20}^{3-}$, $Al_{13}P_{18}O_{72}^{15-}$, and so forth. The inorganic network is composed of porous sheets with 4.6, 4.8, 4.6.8, and 4.6.12 nets (4, 6, 8, and 12 stand for *n*-rings), and the stacking sequences of these inorganic sheets include AAAA, ABAB, ABCABC, ABCDABCD, and ABCDEFABCDEF, etc. Up to now, the pore openings in the layered AlPO compounds have been limited to 12-rings.[16,21]

Organic templates or structure-directing agents play a significant role in the formation of open-framework AlPO compounds, which interact with the host inorganic frameworks through H bonds.[27] In addition, F^- ions are sometimes added in the reaction mixture, acting as mineralizing, structure-directing, or templating agents.[28,29]

In this work, a new layered fluoroaluminophosphate $(C_4H_{11}NOH)_{3.5}[Al_4(PO_4)_5F]\cdot 0.5H_3O$, denoted as AlPO-CJ20, with an Al/P ratio of 4:5 has been solvothermally synthesized successfully by using 2-amino-2-methyl-1-propanol as the template in the presence of F^- ions. Its structure consists of a novel 4.6.16-net sheet. To the best of our knowledge, it contains the largest pore opening of 16-rings in the known layered aluminophosphates. It is a novel member in the fluoroaluminophosphate family.[30−42] In addition, solid-state ^{27}Al, $^{19}F \rightarrow {}^{27}Al$ cross-polarization (CP), and ^{31}P magic angle spinning (MAS) NMR experiments have been utilized to characterize the coordination of Al and P atoms.

Table 1. Crystal Data and Structure Refinement for AlPO-CJ20

formula	$H_{43.5}Al_4N_{3.5}O_{24}P_5C_{14}F$
fw	926.79
temp (K)	293(2)
cryst size (mm^3)	$0.24 \times 0.21 \times 0.17$
wavelength (Å)	0.710 73
cryst syst, space group	monoclinic, *C*2/*c*
a (Å)	32.678(7)
b (Å)	12.956(3)
c (Å)	21.045(4)
β (deg)	115.17(3)
V (Å^3)	8064(3)
Z	8
D_c (g cm^{-3})	1.527
F(000)	3840
θ range (deg)	3.00−27.48
reflns collected	37 971
unique reflns	9035
R_{int}	0.0707
GOF	1.104
R1,^{a} wR2^b [$I > 2\sigma(I)$]	0.0837, 0.2428
R1,^{a} wR2^b	0.1219, 0.2834
max, min $\Delta\rho$ (e Å^{-3})	1.708, −0.843

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

Experimental Section

Synthesis and Characterization. AlPO-CJ20 was synthesized from the reaction mixture of $Al(OPr^i)_3/H_3PO_4$ (85%)/2-amino-2-methyl-1-propanol/triethylene glycol/hydrofluoric acid (HF) (40%) with an optimized molar composition of 1.0:2.0−7.0:3.0−7.0:55:0.5. Typically, 0.4 g of finely ground aluminum triisopropoxide was dispersed into 9 mL of triethylene glycol solvent with stirring, followed by the addition of 0.97 mL of 2-amino-2-methyl-1-propanol. H_3PO_4 and HF were then added dropwise to the above reaction mixture with stirring. The reaction mixture was stirred until it was homogeneous, and then it was sealed in a 15-mL Teflon-lined stainless steel autoclave and heated under autogenous pressure at 170 °C for 3−6 days. The resulting product containing plate-shaped single crystals was separated using sonication, washed with deionized water, and dried in air. The yield of the product was about 70% based on the amount of $Al(OPr^i)_3$.

X-ray powder diffraction (XRD) collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) was used to confirm the phase purity by a comparison with the calculated diffraction pattern. Inductively coupled plasma analysis was performed on a Perkin-Elmer Optima 3300Dv spectrometer, which gives the contents of Al and P as 12.1 and 15.9 wt %, respectively (calcd: Al, 11.65; P, 16.71). Elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer, which give the contents of C, H, and N as 18.10, 4.62, and 5.22 wt %, respectively (calcd: C, 18.14; H, 4.73; N, 5.29). The compositional analysis results are in agreement with the empirical formula, $(C_4H_{11}NOH)_{3.5}(H_3O)_{0.5}\cdot[Al_4(PO_4)_5F]$, given by single-crystal structure analysis. Powder XRD analysis indicates that the AlPO-CJ20 framework collapses upon calcinations at 300 °C for 3 h.

All NMR experiments were performed on a Varian Infinity-plus 400 spectrometer operating at a magnetic field strength of 9.4 T.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for AlPO-CJ20[a]

Al(1)−O(3)	1.720(4)	Al(3)−O(12)	1.723(4)	Al(1)−O(2)	1.721(4)	Al(3)−O(11)	1.732(4)
Al(1)−O(4)	1.729(4)	Al(3)−O(9)	1.734(4)	Al(1)−O(1)	1.743(4)	Al(3)−O(10)	1.735(4)
Al(2)−O(7)	1.728(4)	Al(4)−F(1)	1.657(5)	Al(2)−O(5)	1.730(4)	Al(4)−O(14)	1.696(5)
Al(2)−O(8)	1.733(4)	Al(4)−O(13)	1.709(4)	Al(2)−O(6)	1.738(5)	Al(4)−O(15)	1.713(5)
P(1)−O(16)	1.485(4)	P(3)−O(4)#1	1.539(4)	P(1)−O(11)#1	1.523(4)	P(3)−O(9)	1.540(4)
P(1)−O(5)	1.534(4)	P(4)−O(19)	1.485(4)	P(1)−O(1)	1.535(4)	P(4)−O(13)	1.520(4)
P(2)−O(17)	1.476(4)	P(4)−O(7)	1.523(4)	P(2)−O(6)	1.522(4)	P(4)−O(12)#1	1.524(4)
P(2)−O(2)	1.534(4)	P(5)−O(10)	1.522(4)	P(2)−O(8)#2	1.547(4)	P(5)−O(20)	1.493(5)
P(3)−O(18)	1.490(4)	P(5)−O(14)#3	1.529(6)	P(3)−O(3)	1.535(4)	P(5)−O(15)#1	1.533(5)
O(21)−C(2)	1.328(13)	O(23)−C(10)	1.407(8)	O(21)−H(21)	0.8200	O(23)−H(23)	0.8200
O(22)−C(6)	1.252(13)	O(24)−C(14)	1.352(18)	O(22)−H(22)	0.8200	O(24′)-C(14)	1.464(18)
N(1)−C(1)	1.497(7)	N(3)−C(9)	1.514(7)	N(2)−C(5)	1.506(8)	N(4)−C(13)	1.480(15)
C(1)−C(2)	1.472(11)	C(9)−C(11)	1.509(9)	C(1)−C(4)	1.504(12)	C(9)−C(10)	1.529(8)
C(1)−C(3)	1.527(10)	C(9)−C(12)	1.543(9)	C(5)−C(7)	1.499(10)	C(13)−C(14)	1.402(16)
C(5)−C(6)	1.532(12)	C(13)−C(16)	1.414(15)	C(5)−C(8)	1.547(12)	C(13)−C(15)	1.459(15)

O(3)−Al(1)−O(2)	104.9(2)	O(3)−Al(1)−O(4)	112.9(2)	O(18)−P(3)−O(3)	112.9(2)	O(18)−P(3)−O(4)#1	111.3(2)
O(2)−Al(1)−O(4)	110.8(2)	O(3)−Al(1)−O(1)	108.8(2)	O(3)−P(3)−O(4)#1	108.0(2)	O(18)−P(3)−O(9)	111.1(2)
O(2)−Al(1)−O(1)	109.7(2)	O(4)−Al(1)−O(1)	109.6(2)	O(3)−P(3)−O(9)	105.3(2)	O(4)#1−P(3)−O(9)	108.0(2)
O(7)−Al(2)−O(5)	112.3(2)	O(7)−Al(2)−O(8)	106.9(2)	O(19)−P(4)−O(13)	109.8(3)	O(19)−P(4)−O(7)	111.3(3)
O(5)−Al(2)−O(8)	108.1(2)	O(7)−Al(2)−O(6)	108.2(2)	O(13)−P(4)−O(7)	106.9(3)	O(19)−P(4)−O(12)#1	111.7(2)
O(5)−Al(2)−O(6)	110.8(2)	O(8)−Al(2)−O(6)	108.2(2)	O(13)−P(4)−O(12)#1	108.3(2)	O(7)−P(4)−O(12)#1	108.6(2)
O(12)−Al(3)−O(11)	110.0(2)	O(12)−Al(3)−O(9)	108.3(2)	O(20)−P(5)−O(10)	112.6(3)	O(20)−P(5)−O(14)#3	111.4(4)
O(11)−Al(3)−O(9)	110.6(2)	O(12)−Al(3)−O(10)	113.6(2)	O(10)−P(5)−O(14)#3	104.1(3)	O(20)−P(5)−O(15)#1	110.9(3)
O(11)−Al(3)−O(10)	108.0(2)	O(9)−Al(3)−O(10)	106.3(2)	O(10)−P(5)−O(15)#1	107.7(3)	O(14)#3−P(5)−O(15)#1	109.9(3)
F(1)−Al(4)−O(14)	106.3(4)	F(1)−Al(4)−O(13)	108.2(3)	P(1)−O(1)−Al(1)	139.8(3)	P(2)−O(2)−Al(1)	143.3(3)
O(14)−Al(4)−O(13)	108.9(3)	F(1)−Al(4)−O(15)	109.2(3)	P(3)−O(3)−Al(1)	149.3(3)	P(3)#1−O(4)−Al(1)	142.6(3)
O(14)−Al(4)−O(15)	111.3(3)	O(13)−Al(4)−O(15)	112.7(2)	P(1)−O(5)−Al(2)	150.1(3)	P(2)−O(6)−Al(2)	144.3(3)
O(16)−P(1)−O(11)#1	111.9(2)	O(16)−P(1)−O(5)	112.3(2)	P(4)−O(7)−Al(2)	145.1(3)	P(2)#2−O(8)−Al(2)	137.6(3)
O(11)#1−P(1)−O(5)	108.4(2)	O(16)−P(1)−O(1)	108.2(2)	P(3)−O(9)−Al(3)	136.0(2)	P(5)−O(10)−Al(3)	138.5(3)
O(11)#1−P(1)−O(1)	108.6(2)	O(5)−P(1)−O(1)	107.3(3)	P(1)#1−O(11)−Al(3)	148.4(3)	P(4)#1−O(12)−Al(3)	155.7(3)
O(17)−P(2)−O(6)	112.4(3)	O(17)−P(2)−O(2)	109.5(2)	P(4)−O(13)−Al(4)	151.0(3)	P(5)#4−O(14)−Al(4)	155.3(4)
O(6)−P(2)−O(2)	108.5(3)	O(17)−P(2)−O(8)#2	112.3(3)	P(5)#1−O(15)−Al(4)	153.4(4)		
O(6)−P(2)−O(8)#2	107.8(3)	O(2)−P(2)−O(8)#2	105.9(2)				

Hydrogen Bonds

D−H···A	d(D···A)	∠(DHA)	D−H···A	d(D···A)	∠(DHA)
O(21)−H(21)···O(1W)#1	2.985(15)	136.3	N(2)−H(2C)···O(19)#7	2.782(7)	174.8
O(22)−H(22)···N(4)	3.050(19)	126.9	N(3)−H(3A)···O(19)	2.774(6)	161.1
O(23)−H(23)···O(18)#1	2.659(6)	123.6	N(3)−H(3B)···O(1)#8	3.102(6)	139.8
N(1)−H(1A)···O(16)	2.768(6)	154.4	N(3)−H(3B)···O(16)#8	3.178(6)	147.0
N(1)−H(1B)···O(23)#5	2.782(7)	174.5	N(3)−H(3C)···O(18)#8	2.819(6)	175.4
N(1)−H(1C)···O(17)#2	2.724(7)	170.1	N(4)−H(4C)···O(24′)	2.41(4)	111.6
N(2)−H(2A)···O(16)#1	2.910(6)	148.3	N(4)−H(4C)···O(22)	3.050(19)	129.3
N(2)−H(2B)···O(20)#6	3.054(8)	165.1			

[a] Symmetry transformations used to generate equivalent atoms are as follows: #1, $-x + 1/2, -y + 1/2, -z$; #2, $-x + 1/2, -y - 1/2, -z$; #3, $x - 1/2, y + 1/2, z$; #4, $x + 1/2, y - 1/2, z$; #5, $x, -y, z + 1/2$; #6, $-x, y, -z - 1/2$; #7, $-x + 1/2, y + 1/2, -z - 1/2$; #8, $x, -y, z - 1/2$.

Table 3. Fluoroaluminophosphates with Various Dimensionalities, Framework Al/P Ratios, and Al and P Coordinations[a]

dimensionality	no.	Al/P ratio	Al coordinations	P coordinations	ref
1D	1	1:2	$AlO_{4b}F_{2b}$	$PO_{3b}O_t$, $PO_{2b}O_{2t}$	30
	2	1	$AlO_{3b}F_t$	$PO_{3b}O_t$	31
2D	3	1	$AlO_{3b}F_{2b}N_t$	$PO_{3b}O_t$	32
	4	1	$AlO_{3b}F_t$, $AlO_{4b}F_{2t}$, $AlO_{4b}F_bF_t$	PO_{4b}, $PO_{3b}O_t$	33
	5	2:3	$AlO_{4b}F_bF_t$, $AlO_{5b}F_b$	$PO_{3b}O_t$	34
	6	2	$AlO_{2b}(X)_{2b}(X)_{2t}$, $AlO_{2b}(X)_{4b}$[b]	PO_{4b}	35
	7	1	$AlO_{3b}O_tF_{2b}$	$PO_{3b}O_t$	36
	8	4:5	$AlO_{3b}F_t$, AlO_{4b}	$PO_{3b}O_t$	this work
3D	9	1	AlO_{5b}, $AlO_{5b}F_t$	PO_{4b}	37, 38
	10	1	AlO_{4b}, $AlO_{4b}F_{2b}$	PO_{4b}	39
	11	1	AlO_{4b}, $AlO_{4b}F_{2b}$	PO_{4b}	40
	12	1	AlO_{4b}, $AlO_{4b}F_{2b}$	PO_{4b}	41
	13	1	$AlO_{4b}O_t$, $AlO_{4b}F_b$, $AlO_{4b}F_{2b}$	PO_{4b}	42

[a] b: bridging. t: terminal. [b] X = OH or F. OH^- and F^- ions are statistically distributed.

The resonance frequencies at this field strength were 161.9, 104.2, and 376.4 MHz for ^{31}P, ^{27}Al, and ^{19}F, respectively. A Chemagnetics 5-mm triple-resonance MAS probe was employed to acquire ^{31}P and ^{27}Al NMR spectra with a spinning rate of 6 kHz. A $^{19}F \rightarrow {}^{27}Al$ CP MAS spectrum was acquired in a 4-mm double-resonance MAS probe with a spinning rate of 6 kHz. ^{27}Al MAS NMR spectra were acquired using a one-pulse sequence with a short radio-frequency (rf) pulse of 0.5 μs (corresponding to a $\pi/15$ flip angle) and a pulse delay of 1.0 s. Single-pulse ^{31}P MAS NMR experiments with ^1H decoupling were performed with a 90° pulse width of 4.9 μs, a recycle delay of 180 s, and a ^1H decoupling strength of 40 kHz. The Hartmann−Hahn matching conditions for $^{19}F \rightarrow {}^{27}Al$ CP MAS experiments were as follows: $\omega F = 16$ kHz, $\omega Al = 5.5$ kHz (where ωF and ωAl were the rf field strengths applied on the ^{31}P and ^{27}Al channels, respectively), and the contact time for CP was 0.3 ms. The ^{31}P and ^{27}Al chemical shifts were referenced to a 85% H_3PO_4 and 1 M $Al(NO_3)_3$ solution, respectively.

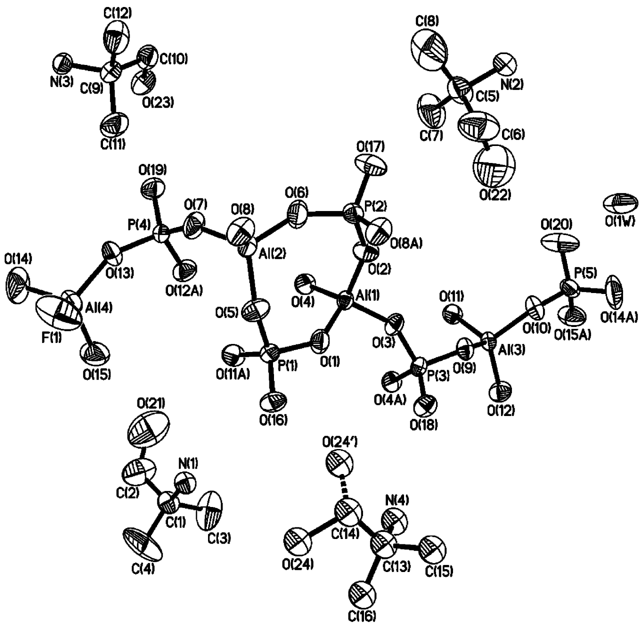
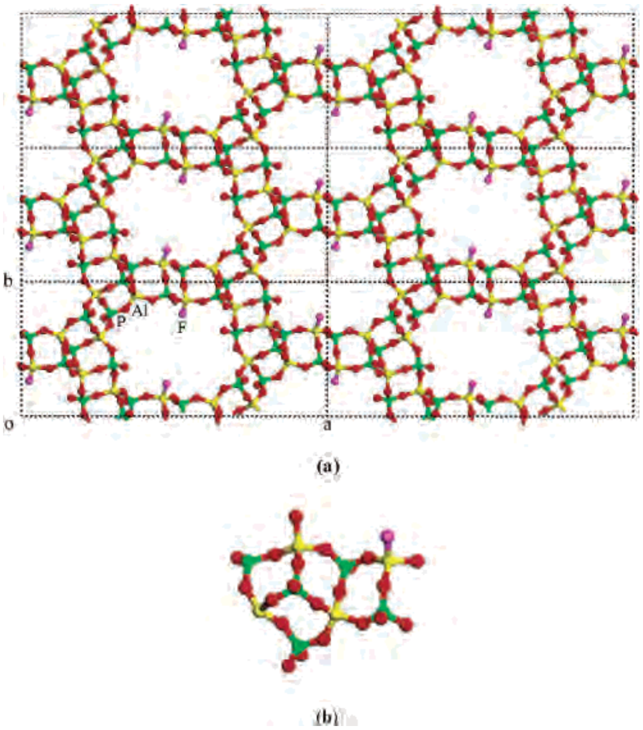


Figure 1. Thermal ellipsoid plot (50% probability) and atomic labeling scheme of AlPO-CJ20.

Structure Determination. A suitable colorless single crystal with dimensions of 0.24 × 0.21 × 0.17 mm^3 was selected for single 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 = 0.710 73 Å) at a temperature of 20 ± 2 °C. Data processing was accomplished with the SAINT processing program.[43] The structure was solved in the space group $C2/c$ by direct methods and refined on F^2 by full-matrix least squares using the *SHELXTL* crystallographic software package.[44] All framework Al, P, and O atoms could be unambiguously located, and the C, N, and F atoms were subsequently located from the difference Fourier map. The coordination of the F atom to Al was confirmed by a solid-state $^{19}F \rightarrow {}^{27}Al$ CP MAS NMR experiment. Diprotonation of 2-amino-2-methyl-1-propanol and H_2O molecules with occupancies of 3.5 and 0.5 was suggested by charge balance, as well as elemental analyses. All H atoms were added geometrically and refined in a riding model. The non-H atoms were refined anisotropically. A summary of the crystallographic data is presented in Table 1. The selected bond lengths and angles are listed in Table 2.

Results and Discussion

The structure of AlPO-CJ20 contains $[Al_4P_5O_{20}F]^{4-}$ anionic layers, which are charge-balanced by the protonated H_2O and 2-amino-2-methyl-1-propanol molecules located in the interlayer regions. As seen in Figure 1, each asymmetric unit contains four crystallographically distinct Al sites, five crystallographically distinct P sites, and one crystallographically distinct F site. Al atoms are all tetrahedrally coordinated. Al(1), Al(2), and Al(3) each share four vertex O atoms with adjacent P atoms with Al−O bond distances in the range of 1.720(4)−1.743(4) Å. Al(4) shares three O atoms with adjacent P atoms, with the fourth vertex being a terminal F atom. The Al−F bond distance is 1.657(5) Å, which is characteristic of the Al atom and terminal F atom in a tetrahedral $AlO_{3b}F_t$ unit and appears to confirm the location of the F atom at this site.[31,33] Of the five crystallographically distinct P atoms, all share three O atoms with adjacent Al atoms, leaving a terminal P═O bond. The P−O distance of 1.520(4)−1.547(4) Å and the P═O distance of 1.476(4)−1.493(5) Å are typical for P−O and P═O bond lengths of known AlPO compounds, respectively. The existence of terminal P═O and Al−F groups results in the interrupted structure of AlPO-CJ20 and the deviation of the Al/P ratio from 1.



(a)

(b)

Figure 2. 4.6.16-net sheet parallel to the (001) plane (a) and the SBU (b) of AlPO-CJ20 (yellow, Al; green, P; pink, F; red, O).

The linkage of AlO_4, AlO_3F, and $PO_3({=}O)$ tetrahedra via Al−O−P bonds forms a novel 4.6.16-net sheet parallel to the (001) plane (Figure 2). All six rings in the layer are capped with a P atom, with P═O groups pointing alternately up and down the layers. Such capped 6-rings are well-known in the 2D AlPO compounds with $Al_3P_4O_{16}{}^{3-}$ stoichiometries.[16,20,21,45−47] Upon investigation of the structure of AlPO-CJ20, a new type of secondary building unit (SBU) composed of the combination of a branched 4-rings and capped 6-rings through edge sharing can be found. The connection of these SBUs through bridging O atoms results in the 2D-layered structure of AlPO-CJ20. The 4.6.16-net sheet possesses the largest 16-rings in known 2D-layered AlPO structures. The only other known layered AlPO with an Al/P ratio of 4:5 is Mu-4.[25]

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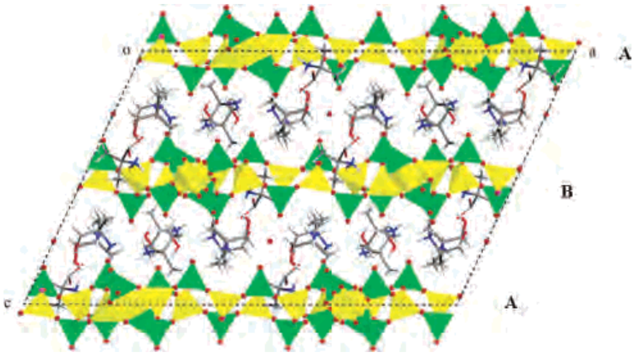

Figure 3. Packing of the inorganic sheets in an ABAB sequence (yellow, Al; green, P; pink, F; red, O; gray, C; blue, N; white, H).

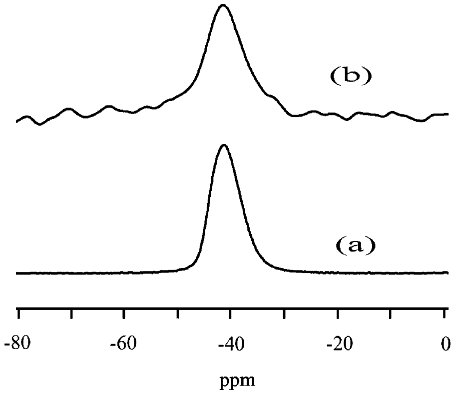

Figure 4. ^{27}Al MAS NMR (a) and $^{19}F \rightarrow ^{27}Al$ CP MAS NMR (b) spectra of AlPO-CJ20.

The inorganic layers are stacked in an ABAB sequence along the [010] direction (Figure 3) and further held together through strong H bonds formed between diprotonated 2-amino-2-methyl-1-propanol molecules and P=O groups. The organic molecules reside not only between the inorganic sheets but also within the extra-large 16-ring windows, acting as space fillers and charge balancers, as well as structure-directing agents, for the anionic inorganic framework. The H-bonding information is listed in Table 2.

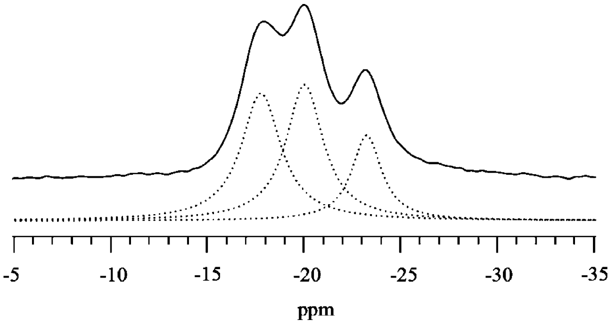

Figure 5. ^{31}P MAS NMR spectrum of AlPO-CJ20 (the dashed lines indicate the decomposition of the ^{31}P NMR spectrum).

The chemical environments of Al and P atoms in AlPO-CJ20 were further investigated by MAS NMR experiments. Figure 4a shows the ^{27}Al MAS NMR spectrum, in which a resonance peak at ca. −44 ppm is observed, which falls in the range of tetrahedral Al environments.[48,49] To probe the connectivity between Al and F atoms, a $^{19}F \rightarrow ^{27}Al$ CP MAS NMR experiment was employed. It shows a relatively broader signal at ca. −44 ppm (Figure 4b), which is generated by the polarization transferred from a nearby ^{19}F atom. Thus, a specific F−Al bond is clearly established in the corresponding tetrahedral AlO_3F unit. The ^{31}P MAS NMR spectrum of AlPO-CJ20 (Figure 5) exhibits three peaks at −17.8, −20.0, and −23.1 ppm, respectively, which are within the chemical shift range of $P(OAl)_3$ species in known AlPO compounds.[48,50] Deconvolution with Gaussian lines gives an integrated intensity ratio of 2:2:1, which is consistent with the five crystallographically distinct P sites, as given by the single-crystal XRD, where two pairs of P atoms have very similar crystallographic environments.

Up to now, a number of microporous fluoroaluminophosphates with 1D chain, 2D layer, and 3D open-framework structures have been synthesized under hydrothermal or solvothermal conditions in the presence of F^- ions. Fluoride sources include HF and NH_4F. Al and F atoms can form various Al-centered AlOF polyhedra, including tetrahedra, octahedra, and trigonal bipyramids, with F atoms being terminal or bridging. There exist two types of bridging F atoms, connecting two and three Al atoms. The coordinations of Al and P of fluoroaluminophosphates reported have been summarized in Table 3. Different combinations of Al and P coordinations result in the diverse framework Al/P ratios and structures. AlPO-CJ20 exhibits a new type of combination of Al and P coordinations with an Al/P ratio of 4:5.

Conclusions

A new fluoroaluminophosphate layer $(C_4H_{11}NOH)_{3.5}[Al_4(PO_4)_5F]\cdot 0.5H_3O$ (Al:P = 4:5) has been synthesized under solvothermal conditions. The alternation of AlO_4, AlO_3F, and $PO_3(=O)$ tetrahedra forms an unusual 2D anionic 4.6.16-net sheet with extra-large 16-rings. These sheets stack in an ABAB sequence, and diprotonated 2-amino-2-methyl-1-propanol molecules reside in the interlayer regions and 16-ring windows, forming extensive H bonds with inorganic layers. ^{27}Al and $^{19}F \rightarrow ^{27}Al$ MAS NMR studies have confirmed the coordination of F atoms to Al. Various coordinations of Al and P of fluoroaluminophosphates have been summarized. It is believed that many more fluoroaluminophosphates with novel structural architectures can be synthesized employing F^- in the reaction system under suitable conditions.

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Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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