

Synthesis and Characterization of a New Layered Aluminophosphate [Al₃P₄O₁₆][(CH₃)₂NHCH₂CH₂NH(CH₃)₂][H₃O]

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DEDICATED TO PROFESSOR G. D. STUCKY IN RECOGNITION AND APPRECIATION OF HIS LIFELONG DEVOTION TO ZEOLITE SCIENCE
AND HIS OUTSTANDING ACHIEVEMENTS IN THE FIELD OF MATERIAL SCIENCES

A new layered aluminophosphate, denoted AIPO-CJ12, has been synthesized in the system Al(OPrⁱ)₃–H₃PO₄–tetramethylethylenediamine–triethyleneglycol and its structure solved by single-crystal X-ray diffraction analysis. It is further characterized by X-ray powder diffraction, ICP, TG, DTA, and elemental analyses. The compound has an empirical formula of [Al₃P₄O₁₆][(CH₃)₂NHCH₂CH₂NH(CH₃)₂][H₃O], and crystallizes in the triclinic space group P-1 (No. 2) with $a = 8.9907(6)$ Å, $b = 9.8359(6)$ Å, $c = 14.5566(8)$ Å, $\alpha = 75.872(3)^\circ$, $\beta = 88.616(3)^\circ$, $\gamma = 63.404(3)^\circ$, $Z = 2$, $R_1 = 0.0451$, and $wR_2 = 0.1094$. The alternation of tetrahedral AlO₄ and PO₃(=O) units forms a sheet structure with a 4 × 6 × 8 network. The inorganic layers stacked in an AAAA sequence are held together by the protonated organic amine and water molecules. The co-templating role of the water molecules is studied by the calculation of the nonbonding host–guest interaction energies through a computational simulation. © 2002 Elsevier Science (USA)

Key Words: layered; aluminophosphate; synthesis; structure; computational simulation.

INTRODUCTION

The discovery of aluminophosphate molecular sieves (AIPO₄-*n*) by scientists at the Union Carbide Corp. in the early 1980s has stimulated many attempts to develop new aluminophosphates by hydrothermal and solvothermal methods (1–7). In recent years, a variety of organically structure-directed aluminophosphates with anionic chains (one-dimensional) (8–12, 56), layers (two-dimensional) (10, 11, 13–43), and frameworks (three-dimensional) (38, 39, 44–47, 57) have been successfully synthesized. Among the two-dimensional layer compounds, six distinct stoichiometries have been found, i.e., Al₁₃P₁₈O₇₂¹⁵⁻ (32), Al₄P₅O₂₀³⁻ (31), Al₃P₄O₁₆³⁻ (11, 13, 21–30, 40–43, 48), Al₂P₃O₁₂³⁻ (10, 16–20), AlP₂O₈³⁻ (13–15), and Al₂P₂O₉²⁻ (33–37). In the case of aluminophosphate layers with an Al/P ratio of 3/4, except for [Al₃P₄O₁₆][C₃N₂H₅]₂ (13), the anionic inorganic

layers are exclusively constructed from tetrahedral AlO₄ and PO₃(=O) units alternately linked to form 4 × 6 (25, 28), 4 × 6 × 8 (21, 22, 27, 40, 41), and 4 × 6 × 12 net (23, 29) stacked in an AAAA (22, 27, 30, 40, 41), ABAB (21, 23), ABCABC (42), or ABCDEFA (43), sequences. These compounds are all structure-directed by the organic amines, which reside in the interlayer region and interact with the inorganic host through H-bonds, van der Waals Forces, and coulombic interactions. Synthetic studies show that the organic additive plays a critical role during the formation of these materials. It is noted that one structure-directing agent can lead to different inorganic sheet structures and that the same inorganic sheet structure can be directed by different structure-directing agents. For example, the 4 × 6 × 8 net sheets can be formed using NH₂(CH₂)₅NH₂ (27), CH₃(CH₂)₂NH₂ (40), CH₃CH₂NH₂ (22), Co(tn)₃Cl₃ (tn = 1,3 diaminopropane) (41), NH₂(CH₂)₂NH₂ (21), or C₄H₇NH₂ (cyclobutylamine) or C₅H₁₀NH (piperidine) (30) as the structure-directing agent. Therefore, an understanding of the templating ability of various organic amines in the formation of these materials is a key to the rational selection of a suitable organic structure-directing agent for a specific inorganic structure. Recently, much progress has been achieved in understanding the role of the organic structure-directing agent by computational simulations (49–52). It shows that understanding the effects of the nonbonding energy of the organic structure-directing agent–zeolite interaction on zeolite phase selectivity will play a fundamental role in the future discovery of new zeolite phases through rational structure-directing agent selection.

In this work, using tetramethylethylenediamine (TME-DA) as a structure-directing agent, we have prepared a new 2-D layered aluminophosphate compound, denoted AIPO-CJ12. The inorganic sheet contains a 4 × 6 × 8 net stacked in an AAAA sequence. Furthermore, the co-templating role of the water molecules is studied via the calculation of the nonbonding interaction energies, including H-bonds,

van der Waals Forces, and coulombic energies between the inorganic layer and the guest species. This will further assist in the rational synthesis of target materials with specific structures.

EXPERIMENTAL DETAILS

AlPO-CJ12 was synthesized from an alcoholic system in which triethylene glycol (tEG) was used as the solvent and tetramethylethylenediamine (TMEDA) as the structure-directing agent. Aluminum triisopropoxide ($Al(OPr^i)_3$) and phosphoric acid (85 wt% in water) were used as the aluminum and phosphorus sources, respectively. Typically, 1.0 g of finely grounded aluminum triisopropoxide was first dispersed in 10 mL of tEG solvent with stirring, followed by the addition of 3.0 mL of TMEDA. Finally 1.1 mL of phosphoric acid (85 wt% in water) was added dropwise to the above mixture with stirring. The reaction mixture was stirred until it was homogeneous and then was sealed in a Teflon-lined stainless steel autoclave and heated under autogenous pressure at 180°C for 8 days. The product, containing large single crystals of AlPO-CJ12 with a plate-like shape, was separated by sonication, washed with deionized water, and dried in air at ambient temperature.

TABLE 1
Crystal Data and Structure Refinement for AlPO-CJ12

Identification code	AlPO-CJ12
Empirical formula	C6 H21 Al3 N2 O17 P4
Formula weight	598.07
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	$a = 8.9907(6)$ Å $\alpha = 75.872(3)^\circ$. $b = 9.8359(6)$ Å $\beta = 88.616(3)^\circ$. $c = 14.5566(8)$ Å $\gamma = 63.404(3)^\circ$.
Volume	1110.85(12) Å ³
Z, Calculated density	2, 1.788 Mg/m ³
Absorption coefficient	0.540 mm ⁻¹
$F(000)$	612
Crystal size	0.40 × 0.20 × 0.10 mm
Theta range for data collection	1.45° to 23.26°.
Limiting indices	$-8 \leq h \leq 9$, $-10 \leq k \leq 10$, $-16 \leq l \leq 15$
Reflections collected/unique	5412/3157 [$R(\text{int}) = 0.0304$]
Completeness to $\theta = 23.26$	99.6%
Absorption correction	Empirical
Max. and min. transmission	0.69 and 0.46
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3157/12/292
Goodness-of-fit on F^2	1.010
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0451$, $wR_2 = 0.1094$
R indices (all data)	$R_1 = 0.0727$, $wR_2 = 0.1232$
Largest diff. peak and hole	0.860 and -0.716 e. Å ⁻³

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

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for AlPO-CJ12: $U(\text{eq})$ Is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor

	x	y	z	$U(\text{eq})$
Al(1)	11,560(2)	4,485(2)	3,879(1)	22(1)
Al(2)	7,234(2)	4,939(2)	2,533(1)	17(1)
Al(3)	8,293(2)	5,460(2)	-1,064(1)	19(1)
P(1)	7,768(2)	6,659(2)	3,901(1)	23(1)
P(2)	10,891(2)	2,429(2)	2,733(1)	18(1)
P(3)	3,662(2)	5,486(2)	2,291(1)	22(1)
P(4)	7,905(2)	6,851(2)	664(1)	18(1)
O(1)	11,284(4)	3,057(4)	3,507(3)	36(1)
O(2)	9,652(4)	6,138(4)	3,819(3)	32(1)
O(3)	7,321(4)	5,511(4)	3,557(2)	26(1)
O(4)	7,512(5)	6,378(5)	4,966(2)	39(1)
O(5)	6,725(5)	8,318(4)	3,374(3)	38(1)
O(6)	8,981(4)	3,179(4)	2,537(3)	32(1)
O(7)	11,619(4)	687(4)	3,022(2)	30(1)
O(8)	11,601(5)	2,937(4)	1,813(2)	38(1)
O(9)	5,575(4)	4,500(4)	2,525(2)	26(1)
O(10)	2,881(5)	5,014(5)	3,183(3)	41(1)
O(11)	3,137(5)	7,195(4)	1,994(3)	46(1)
O(12)	3,197(4)	4,917(5)	1,505(3)	39(1)
O(13)	7,127(4)	6,429(4)	1,570(2)	27(1)
O(14)	7,681(5)	5,967(4)	-13(2)	31(1)
O(15)	9,796(4)	6,211(4)	914(3)	32(1)
O(16)	7,102(4)	8,597(4)	257(2)	30(1)
C(1)	10,430(20)	-916(19)	4962(11)	55(4)
C(1')	10,723(19)	-390(20)	5,258(11)	55(4)
C(2)	13,418(12)	-964(9)	5,384(6)	87(3)
C(3)	13,031(10)	-2,675(8)	4,600(5)	66(2)
C(4)	9,369(9)	736(8)	101(5)	60(2)
C(5)	6,726(9)	1,998(8)	728(6)	71(2)
C(6)	8,978(9)	-315(9)	1,803(5)	61(2)
N(1)	12,248(6)	-1,061(6)	4,750(3)	41(1)
N(2)	8,210(6)	457(5)	801(3)	38(1)
O(1W)	4,288(5)	9,390(5)	1,825(3)	57(1)

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with $CuK\alpha$ radiation ($\lambda = 1.5148$ 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 NETZSCH STA 449C unit was used to carry out the TGA and DTA analyses in air with a heating rate of 10°C/min.

Energy calculations were accomplished using the Burchart1.01-Dreiding2.21 force field with the Cerius² software package (53).

A suitable colorless plate-like single crystal with dimensions 0.40 × 0.20 × 0.10 mm was selected for single-crystal X-ray diffraction analysis. Intensity data were collected on a Siemens SMART diffractometer equipped with a CCD detector using graphite-monochromatized $MoK\alpha$ radiation

($\lambda = 0.71073 \text{ \AA}$) at a temperature of $20 \pm 2^\circ\text{C}$. The total numbers of measured reflections and observed unique reflections were 5412 and 3157, respectively. Intensity data of 3157 independent reflections ($-8 \leq h \leq 9$, $-10 \leq k \leq 10$, $-16 \leq l \leq 15$) were collected in the ω scan mode. An empirical absorption correction was applied using the SADABS program with $T_{\min} = 0.46$ and $T_{\max} = 0.69$ (54). The agreement factor between equivalent reflections (R_{int}) was 0.0304. The structure was solved in the space group P-1 by direct methods and refined on F^2 by full-matrix least squares using SHELXTL97 (55). The phosphorus and aluminum atoms were located first. Carbon, nitrogen, and oxygen were found in the difference Fourier map. C(1) was disordered over two sites. The hydrogen atoms were placed geometrically except for those attached to C(1), N(1), and O1w. The existence of H_3O^+ instead of NH_4^+ was confirmed by the elemental analysis. A summary of the crystallographic data is presented in Table 1.

Single-crystal X-ray diffraction analysis shows that AIPO-CJ12 crystallizes in the triclinic space group P-1, $a = 8.9907(6) \text{ \AA}$, $b = 9.8359(6) \text{ \AA}$, $c = 14.5566(8) \text{ \AA}$, $\alpha = 75.872(3)^\circ$, $\beta = 88.616(3)^\circ$, and $\gamma = 63.404(3)^\circ$. The atomic coordinates and selected bond lengths and bond angles are listed in Table 2 and Table 3, respectively.

RESULTS AND DISCUSSION

AIPO-CJ12 can be crystallized from gels with molar compositions $\text{Al}(\text{OPr}^i)_3 : (2.8\text{--}3.3) \text{ H}_3\text{PO}_4 : (3.8\text{--}5.0) \text{ TME-DA} : 15 \text{ tEG}$ at 180°C for 8 days. The measured X-ray powder diffraction pattern for AIPO-CJ12 is in good agreement with that simulated from single-crystal structural data, proving that the as-synthesized product is a single phase.

ICP analysis gives the contents of Al as 13.3 wt% (calcd 13.6 wt%) and P as 19.4 wt% (calcd 20.7 wt%). Elemental analysis indicates that the sample contains 12.1, 3.4, and 4.7 wt% of C, H, and N, respectively. These are in good agreement with the expected values of 12.04, 3.51, and 4.68 wt% for C, H, and N, respectively, on the basis of the empirical formula given by single-crystal structure analysis.

Thermogravimetric analysis shows two steps of weight loss from 100 to 900°C (Fig. 1). The weight loss of 3.28 wt% for the first step from 100 to 340°C is attributed to the removal of the water molecules (calcd: 3.01 wt%). The weight loss of 18.8 wt% for the second step from 340 to 900°C is attributed to the decomposition of the structure-directing agent molecule (calcd: 19.7 wt%). Accordingly, an endothermal and an exothermal peak are observed on the DTA curve at 130°C and 440°C , respectively, which are due to the removal of the water molecules and the decomposition of the structure-directing agent molecules residing in the interlayer region.

TABLE 3
Selected Bond Lengths [\AA] and Angles [$^\circ$] for AIPO-CJ12

Al(1)–O(10)#1	1.717(4)
Al(1)–O(4)#2	1.726(4)
Al(1)–O(1)	1.738(4)
Al(1)–O(2)	1.741(4)
Al(2)–O(9)	1.729(3)
Al(2)–O(3)	1.732(3)
Al(2)–O(13)	1.732(3)
Al(2)–O(6)	1.739(4)
Al(3)–O(12)#3	1.717(4)
Al(3)–O(8)#4	1.725(4)
Al(3)–O(14)	1.726(4)
Al(3)–O(15)#4	1.736(4)
P(1)–O(5)	1.479(4)
P(1)–O(4)	1.537(4)
P(1)–O(3)	1.542(4)
P(1)–O(2)	1.546(4)
P(2)–O(7)	1.482(3)
P(2)–O(1)	1.526(4)
P(2)–O(6)	1.536(4)
P(2)–O(8)	1.538(4)
P(3)–O(11)	1.476(4)
P(3)–O(12)	1.530(4)
P(3)–O(10)	1.532(4)
P(3)–O(9)	1.546(3)
P(4)–O(16)	1.495(3)
P(4)–O(13)	1.533(3)
P(4)–O(14)	1.534(4)
P(4)–O(15)	1.543(4)
O(4)–Al(1)#2	1.726(4)
O(8)–Al(3)#4	1.725(4)
O(10)–Al(1)#5	1.717(4)
O(12)–Al(3)#3	1.717(4)
O(15)–Al(3)#4	1.736(4)
C(1)–C(1')	0.872(19)
C(1)–C(1')#6	1.204(15)
C(1)–N(1)	1.601(17)
C(1)–C(1)#6	1.64(3)
C(1')–C(1)#6	1.204(15)
C(1')–C(1')#6	1.31(3)
C(1')–N(1)	1.498(16)
C(2)–N(1)	1.465(9)
C(3)–N(1)	1.491(9)
C(4)–C(4)#7	1.479(14)
C(4)–N(2)	1.506(8)
C(5)–N(2)	1.485(8)
C(6)–N(2)	1.489(8)
O(10)#1–Al(1)–O(4)#2	2108.88(19)
O(10)#1–Al(1)–O(1)	109.8(2)
O(4)#2–Al(1)–O(1)	106.3(2)
O(10)#1–Al(1)–O(2)	109.78(19)
O(4)#2–Al(1)–O(2)	111.17(19)
O(1)–Al(1)–O(2)	110.81(19)
O(9)–Al(2)–O(3)	109.12(17)
O(9)–Al(2)–O(13)	114.46(17)
O(3)–Al(2)–O(13)	107.66(17)
O(9)–Al(2)–O(6)	104.25(17)
O(3)–Al(2)–O(6)	110.96(18)
O(13)–Al(2)–O(6)	110.39(18)
O(12)#3–Al(3)–O(8)#4	111.5(2)
O(12)#3–Al(3)–O(14)	107.60(18)
O(8)#4–Al(3)–O(14)	106.16(19)
O(12)#3–Al(3)–O(15)#4	108.1(2)

TABLE 3—Continued

O(8)#4–Al(3)–O(15)#4	110.44(18)
O(14)–Al(3)–O(15)#4	112.97(18)
O(5)–P(1)–O(4)	111.7(2)
O(5)–P(1)–O(3)	112.5(2)
O(4)–P(1)–O(3)	105.0(2)
O(5)–P(1)–O(2)	112.1(2)
O(4)–P(1)–O(2)	107.4(2)
O(3)–P(1)–O(2)	107.8(2)
O(7)–P(2)–O(1)	111.5(2)
O(7)–P(2)–O(6)	110.6(2)
O(1)–P(2)–O(6)	107.9(2)
O(7)–P(2)–O(8)	109.2(2)
O(1)–P(2)–O(8)	109.3(2)
O(6)–P(2)–O(8)	108.4(2)
O(11)–P(3)–O(12)	111.8(2)
O(11)–P(3)–O(10)	112.5(2)
O(12)–P(3)–O(10)	107.7(2)
O(11)–P(3)–O(9)	112.4(2)
O(12)–P(3)–O(9)	105.8(2)
O(10)–P(3)–O(9)	106.3(2)
O(16)–P(4)–O(13)	110.2(2)
O(16)–P(4)–O(14)	113.3(2)
O(13)–P(4)–O(14)	106.21(19)
O(16)–P(4)–O(15)	110.3(2)
O(13)–P(4)–O(15)	108.68(19)
O(14)–P(4)–O(15)	107.9(2)
P(2)–O(1)–Al(1)	151.7(3)
P(1)–O(2)–Al(1)	142.5(2)
P(1)–O(3)–Al(2)	140.1(2)
P(1)–O(4)–Al(1)#2	146.8(3)
P(2)–O(6)–Al(2)	139.0(2)
P(2)–O(8)–Al(3)#4	142.8(3)
P(3)–O(9)–Al(2)	134.7(2)
P(3)–O(10)–Al(1)#5	159.7(3)
P(3)–O(12)–Al(3)#3	144.6(3)
P(4)–O(13)–Al(2)	145.9(2)
P(4)–O(14)–Al(3)	142.5(2)
P(4)–O(15)–Al(3)#4	143.2(2)
C(1')–C(1)–C(1')#6	76(2)
C(1')–C(1)–N(1)	67.3(17)
C(1')#6–C(1)–N(1)	116.8(13)
C(1')–C(1)–C(1)#6	45.4(15)
C(1')#6–C(1)–C(1)#6	31.0(10)
N(1)–C(1)–C(1)#6	97.2(13)
C(1)–C(1')–C(1)#6	104(2)
C(1)–C(1')–C(1')#6	63.3(18)
C(1)#6–C(1')–C(1')#6	40.3(11)
C(1)–C(1')–N(1)	80(2)
C(1)#6–C(1')–N(1)	128.2(11)
C(1')#6–C(1')–N(1)	117.1(17)
C(2)–N(1)–C(3)	108.2(5)
C(2)–N(1)–C(1')	97.5(8)
C(3)–N(1)–C(1')	125.5(8)
C(2)–N(1)–C(1)	126.9(8)
C(3)–N(1)–C(1)	98.4(7)
C(1')–N(1)–C(1)	32.5(7)
C(5)–N(2)–C(6)	111.1(5)
C(5)–N(2)–C(4)	107.6(5)
C(6)–N(2)–C(4)	114.7(5)

Note. Symmetry transformations used to generate equivalent atoms: #1, $x+1, y, z$; #2, $-x+2, -y+1, -z+1$; #3, $-x+1, -y+1, -z$; #4, $-x+2, -y+1, -z$; #5, $x-1, y, z$; #6, $-x+2, -y, -z+1$; #7, $-x+2, -y, -z$.

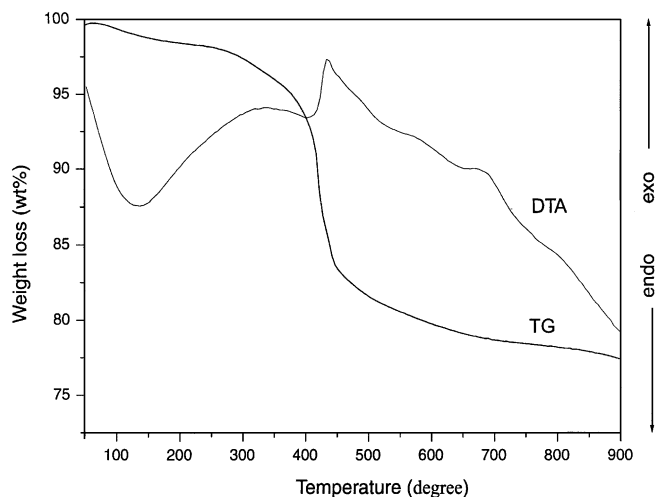


FIG. 1. TG-DTA curves of AlPO-CJ12.

Figure 2 shows the atomic labeling scheme for AlPO-CJ12. There are three crystallographically distinct Al sites. Each aluminium atom is tetrahedrally coordinated to four oxygen atoms, linking adjacent P atoms. The Al–O bond lengths and O–Al–O bond angles are in the range 1.717(4)–1.741(4) Å and 104.3(2)–114.5(2)°, respectively, which are typical for four-coordinated Al in alumin-

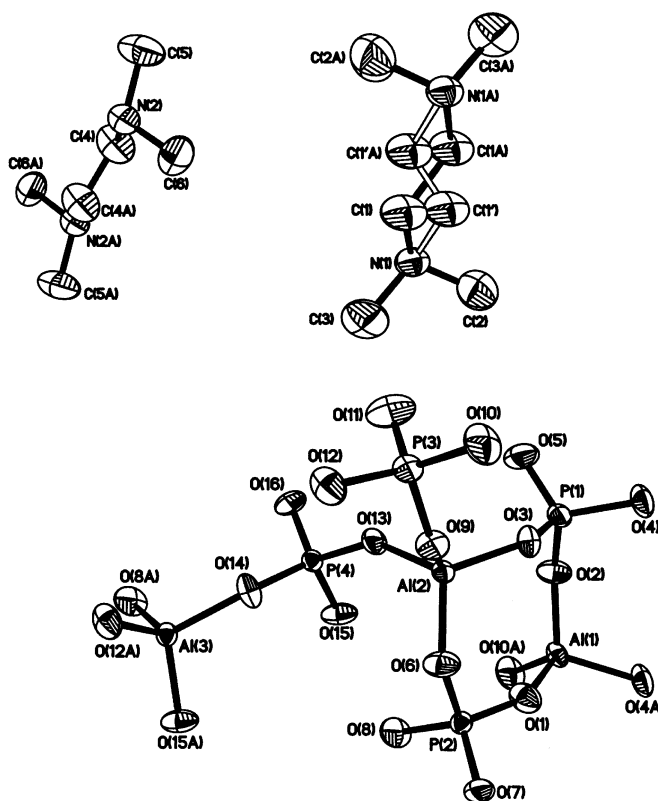


FIG. 2. The atomic labeling scheme for AlPO-CJ12 (thermal ellipsoids at 50% probability).

phosphates (8–43). All the four crystallographically distinct P atoms share three oxygens with adjacent Al atoms, and the P–O bond lengths are in the range 1.526(4)–1.546(3) Å. The fourth P–O bond lengths for each P atom are 1.479(4) Å, 1.482(3) Å, 1.476(4) Å, and 1.495(3) Å, respectively, which are the shortest among the P–O distances. These distances suggest that each crystallographically distinct P atom possesses one P=O group (11, 13, 21–30). From Fig. 2, it is noted that one of the two structure-directing agent molecules is disordered in the position of C(1).

The alternation of AlO_4 and $\text{PO}_3(=\text{O})$ tetrahedra via bridging oxygen atoms forms the 2-D network with a $4 \times 6 \times 8$ net parallel to the *ac* plane as shown in Fig. 3. This $4 \times 6 \times 8$ net has been found in several reported aluminophosphate compounds (21, 22, 27, 30, 40, 41). The sheet structure is featured by a series of capped six-membered rings. The orientation of the capped P=O group in the cap is opposite to those three terminal P=O groups in the capped six-membered ring.

The inorganic sheets are held together by the protonated $(\text{CH}_3)_2\text{NHCH}_2\text{CH}_2\text{NH}(\text{CH}_3)_2$ and water molecules through H-bonds. Figure 4 shows the H-bonding interaction between the macroionic inorganic layer and the guest templating species. It should be mentioned that one disordered position of C(1) is deleted and that the hydrogen atoms attached on C(1), N(1), and O1w are added geometrically in Cerius² followed by energy optimization. As seen in Fig. 4, N(2) forms one strong H-bond to terminal O(16) with the $\text{N} \cdots \text{O}$ separation of 2.710(6) Å. Each N(1) atom offers one hydrogen atom to the capped P=O group in the capped six-membered ring with the $\text{N} \cdots \text{O}$ separation of 2.586 Å. One protonated water molecule forms two H-bonds to two terminal P=O groups in the capped six-membered ring, and forms one H-bond to

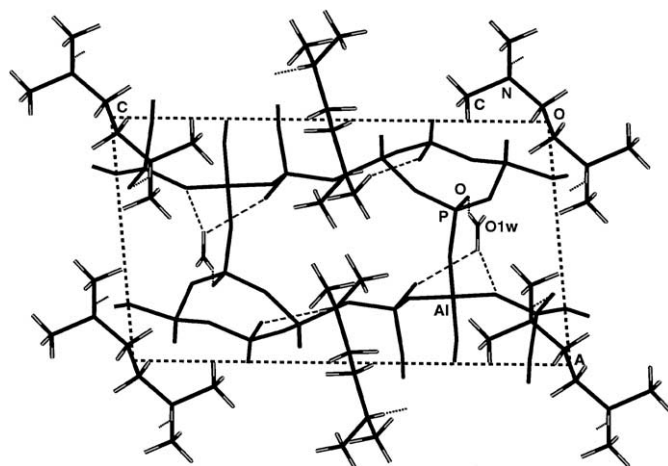


FIG. 4. The H-bonding interactions between the inorganic sheets and the protonated organic amine and water molecules.

one bridging O atom. The $\text{O} \cdots \text{O}$ distances are 2.743, 2.829, and 2.993 Å, respectively. So far, over ten compounds with an Al/P ratio of 3/4 have been prepared with various organic amines in a hydrothermal or solvothermal system. To our knowledge, AlPO-CJ12 is the first example in which water molecules play a co-templating role with the organic amine structure-directing agent.

The reason why water molecules are involved in the structure can be understood by their roles in the aspects of H-bond donors and charge balancing to the inorganic network. The H-bonds of the guest-host are believed to play a dominant role in stabilizing the inorganic network. In previously reported 2-D layered AlPOs with an $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$ stoichiometry, most of the organic structure-directing agents are primary or secondary amines, the protonated species of which can offer at least two hydrogen atoms for per N atom to form H-bonds to the terminal oxygen atoms in the inorganic sheets. In the preparation of AlPO-CJ12, a tertiary amine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ was used as the structure-directing agent. It can only offer one hydrogen atom for per N atom to form a H-bond to the inorganic sheet. This reduces the H-bonding interaction between the inorganic sheet and the organic structure-directing agent. Thus, the introduction of another species that can serve as an extra H-bond donor is necessary. Energy calculations using the Burchart1.01–Dreiding2.21 force field with the Cerius² software package gives that the H-bond energy of the water molecules and the inorganic network is -47.2 kJ/mol for per $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$ unit. Therefore the introduction of water molecules plays a stabilization role to the inorganic sheets. Similarly, in the case of a layered aluminophosphate $[\text{Al}_3\text{P}_4\text{O}_{16}][\text{C}_5\text{N}_2\text{H}_9][\text{NH}_4]$ (26), when a tertiary amine of 1,2-dimethylimidazole was used, the protonated ammonia molecules were also involved into

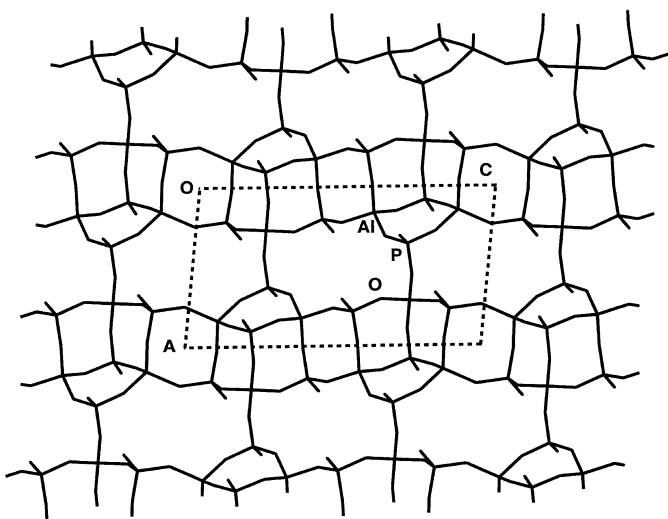


FIG. 3. The inorganic sheet of AlPO-CJ12.

the structure in order to enhance the H-bonding interaction between the inorganic host and the guest species.

On the other hand, the protonated water molecules in AIPO-CJ12 $[Al_3P_4O_{16}][(CH_3)_2NHCH_2CH_2NH(CH_3)_2][H_3O]$ also play a charge balance role to the inorganic network. If only the protonated TMEDA molecules are involved in the structure, the formula should be $[Al_3P_4O_{16}][(CH_3)_2NHCH_2CH_2NH(CH_3)_2]_{1.5}$. Energy calculation shows that the nonbonding interaction between the inorganic host and the guest species including H-bonds, van der Waals Forces, and Coulombic energies is $-420.43 \text{ kJmol}^{-1}$ for $[Al_3P_4O_{16}][(CH_3)_2NHCH_2CH_2NH(CH_3)_2]_{1.5}$ and $-538.9 \text{ kJmol}^{-1}$ for $[Al_3P_4O_{16}][(CH_3)_2NHCH_2CH_2NH(CH_3)_2][H_3O]$ for per $Al_3P_4O_{16}^{3-}$ unit. This result indicates that the introduction of the extra water molecules makes AIPO-CJ12 more energetically favorable.

CONCLUSIONS

A new layered aluminophosphate with an Al/P ratio of 3/4 is synthesized solvothermally and its structure solved by single-crystal X-ray diffraction analysis. Its structure contains $4 \times 6 \times 8$ -net macroanionic sheets stacked in an AAAA sequence. It is the first 2-D aluminophosphate layer co-structure-directed by the organic amines and the protonated water molecules. The protonated water molecules play the following roles: (i) stabilizing the inorganic sheets by acting as an extra H-bond donor to the oxygen atoms in the inorganic sheet and (ii) balancing the negative charge of the inorganic sheets. The co-templating role of the protonated water molecules can be understood through the calculation of the nonbonding interaction energies between the inorganic host and the guest templating species.

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