

Synthesis and Structural Characterization of a New Layered Aluminophosphate Intercalated with Triply-Protonated Triethylenetetramine $[C_6H_{21}N_4][Al_3P_4O_{16}]$

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A new layered aluminophosphate $[C_6H_{21}N_4][Al_3P_4O_{16}]$ has been synthesized solvothermally by using triethylenetetramine (*tetam*) as the structure-directing agent and ethylene glycol as the solvent. The structure of the compound was solved by single-crystal X-ray diffraction analysis. $[C_6H_{21}N_4][Al_3P_4O_{16}]$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.550(1)$, $b = 24.064(1)$, $c = 9.601(1)$ Å, $\beta = 97.99(1)^\circ$, $V = 2184.9(1)$ Å³ and $Z = 4$ ($R = 0.057$ and $R_w = 0.052$), and its structure consists of $[Al_3P_4O_{16}]^{3-}$ macroanionic sheets stacked in an *AAAA* sequence. As primary building units in the individual sheet, alternating PO_4 with terminal $P=O$ and AlO_4 tetrahedra are corner-shared to form elliptical eight-membered rings as well as four- and six-membered rings. The macroanionic sheets are held together through H bonds between the terminal $P=O$ groups in the inorganic layers and the N atoms of the *tetam* molecules, which are triply-protonated. © 1999 Academic Press

INTRODUCTION

Since the successful synthesis of a series of microporous crystalline aluminophosphates $AlPO_4-n$ (1), much interest has been focused on the exploration of new three-dimensional phosphates (2, 3). These phosphate materials may be used as shape-selective catalysts (4) or may find themselves in new applications such as nanochemistry and host-guest assembly (5, 6). Most of the microporous aluminophosphates were obtained from a hydrothermal synthetic system, whereas as an alternative route, nonaqueous synthesis, has also proved successful for the formation of 3D framework aluminophosphates (7). Occasionally, novel open-framework aluminophosphates, among which are JDF-20 (8) and $AlPO-HDA$ (9), can form from a nonaqueous reaction system.

Besides the three-dimensional compounds, a large number of layered aluminophosphates with different P/Al ratios such as 2/1 (10, 11), 3/2 (12–14), and 4/3 (15–21) have also been synthesized. Due to the diversity of the arrangements

of AlO_4 and PO_4 tetrahedral units, the sheet structures of these layered aluminophosphates differ to a great extent, and the stacking sequence of the same sheets varies for different structure-directing templates. New layered aluminophosphates have been obtained by using complex templates (22, 23) and by involving fluoride ions in the reaction system (24). Here we present the synthesis and structural characterization of a new layered aluminophosphate with a P/Al ratio of 4:3, which is formed solvothermally from an aluminophosphate gel containing triethylenetetramine (*tetam*) as the structure-directing agent (template) and ethylene glycol as the predominant solvent.

EXPERIMENTAL

To obtain the title compound, aluminum triisopropoxide ($Al(iPrO)_3$) and phosphoric acid (85 wt% aqueous solution) were used as the aluminum and phosphorus sources. Aluminum triisopropoxide (2.04 g) was first added to ethylene glycol (EG) (33 g) and stirred until a homogenous gel was formed. To the mixture was added dropwise phosphoric acid (1.03 ml) and triethylenetetramine (2.0 ml) successively. Finally, NH_4F (0.18 g) was added to the system with stirring. The final reaction gel with a molar composition of $Al(iPrO)_3 : 1.51H_3PO_4 : 1.34tetam : 0.49NH_4F : 53EG : 1.04 H_2O$ was sealed in a Teflon-lined stainless-steel autoclave and heated at 453 K under autogenous pressure for 3 days. The solid product was collected by filtration, washed copiously with distilled water, and dried at ambient temperature. Besides ethylene glycol, a number of other solvents such as diethylene glycol, triethylene glycol, and tetraethylene glycol were also used for the synthesis of the title compound, and the molar compositions of the reaction gels were the same as those for ethylene glycol. To inspect the effect of heteroatoms on the crystallization of the title compound, $Mg(Ac)_2 \cdot 4H_2O$ and $Co(Ac)_2 \cdot 4H_2O$ were introduced into the reaction system with an M/Al ($M = Mg$ or Co) molar ratio of about 0.02.

The inductive coupled plasma (ICP) analysis was conducted on a Jarrzall-ash 800 Mark-II ICP instrument and the elemental analysis on a Perkin–Elmer 240C element analyzer. A Perkin–Elmer DTA 1700 differential thermal analyzer (DTA) and a Perkin–Elmer TGA 7 thermogravimetric analyzer (TGA) were used to obtain the DTA–TGA curves in air with a temperature increasing rate of 10°C/min.

A suitable plate-like single crystal with dimensions 100 × 100 × 40 μm of the title compound was selected from the solid product for structure analysis. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoK α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected at room temperature in 1321 frames with ω scans (width of 0.03° and exposure time of 10 s per frame). The final unit cell constants were determined by a least-squares fit of 4413 reflections for the title compound in the range 5° < 2 θ < 46°. Pertinent experimental details for the structure determination are presented in Table 1. The structure was solved by direct methods using SHELXS-86 (25) and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using SADABS (26) program. Other effects such as absorption by glass fiber were simultaneously corrected. The hydrogen atoms were initially located from

difference Fourier maps, and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all atoms and anisotropic thermal parameters for all nonhydrogen atoms. Full-matrix least-squares structure refinement against |F| was carried out using the CRYSTALS (27) package of programs. The applied weighting scheme was based on Tukey and Prince with a three-term-modified Chebyshev polynomial.

RESULTS AND DISCUSSION

The synthetic systems are predominantly nonaqueous since the amount of water brought from the sources is minute. Although ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol can all be used for the synthesis of the title compound, it seems that ethylene glycol is preferable because other solvents tend to lead to the formation of AlPO₄-tridymite as impurity coexisting with the title compound. The effect of divalent metal cations on the crystal morphology is demonstrated by the fact that the addition of Mg²⁺ cations into the reaction gel increases the thickness of the crystals by one-third without changing the length and width, whereas the existence of Co²⁺ cations apparently decreases the crystal size of the title compound. This phenomenon suggests that the divalent metal cations play a role in the growth of the crystals and the nature of the cations affects the growth habit of the crystals. ICP analysis indicates that Mg and Co are present in the crystals from the divalent metal cation-containing reaction systems. No F atoms can be detected by the ICP analysis, indicating that the fluoride ions introduced into the reaction systems do not enter the structure of the title compound. But without F[−] ions, we failed to synthesize the title compound. Fluoride ions may act as a mineralizer necessary for the formation of the compound.

The ICP analysis also gives a P/Al ratio of about 1.4 for the title compound. This value is close to an integer ratio of 4:3, which is confirmed by the single-crystal analysis described below. The elemental analysis shows that the C, H, and N contents for the title compound are 10.48, 3.54, and 7.97 wt%, corresponding to a molar ratio of C:H:N = 1.53:6.22:1.00 (A triply protonated *tetam* molecule has a calculated C:H:N ratio of 1.50:5.25:1.00). The observed C:N ratio is in good agreement with the value calculated on the basis of the template molecule, suggesting that the backbone of the template remains intact after entering the structure of the compound. The H content based on the element analysis exceeds the value calculated for the triply-protonated template molecule. This is probably due to the existence of disordered water molecules adsorbed in the eight-membered ring channels formed by stacking of the layers as seen from the single-crystal structure analysis. Presence of water molecules in channels of layered

TABLE 1
Crystallographic Data and Conditions of Collection
for [C₆H₂₁N₄][Al₃P₄O₁₆]

Empirical formula	Al ₃ P ₄ O ₁₆ C ₆ H ₂₁ N ₄
Crystal color	Colorless
Crystal size	0.1 × 0.1 × 0.04 mm
Crystal system	Monoclinic
Space group	P2 ₁ /c (No. 14)
Unit cell dimensions	
<i>a</i>	9.550(1) Å
<i>b</i>	24.064(1) Å
<i>c</i>	9.601(1) Å
β	97.99(1)°
Volume	2184.9(1) Å ³
<i>Z</i>	4
Formula weight	610.1
Density (calc.)	1.85 g/cm ³
λ (MoK α)	0.71073 Å
μ	5.4 mm ^{−1}
2 θ range	5.0–46.0°
Total data collected	8601
Index ranges	−10 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 26, 0 ≤ <i>l</i> ≤ 10
Unique data	3080
Observed data (<i>I</i> > 3 σ (<i>I</i>))	1810
<i>R</i>	0.057
<i>R</i> _w	0.052
Refinement method	Full matrix least-squares on F
No. of variables	300
$\Delta\rho$ min/max	−0.64/0.61 e Å ^{−3}

aluminophosphates is not unusual (16). TGA-DTA analyses show that the template is lost within an endothermic effect at about 320°C, indicating that there are strong interactions between the template molecules and the inorganic part of the compound. The TGA curve exhibits a distinct weight loss of about 21.0% corresponding to the decomposition of the template *tetam*. After heating at 350°C for one hour, the sample becomes amorphous, indicative of structural collapse upon decomposition of template molecules.

The atomic coordinates with the equivalent thermal parameters for the title compound are listed in Table 2. In the asymmetric unit (Fig. 1) there are four independent P and three independent Al atoms. These P and Al atoms are all tetrahedrally coordinated by oxygen atoms. Whereas all the four O atoms bonded to each Al are shared by P atoms, only three-fourths bonded to each P are linked to Al atoms, leaving one terminal P=O bond for each PO₄ group. The length of the terminal P=O bond for the PO₄ units varies within the range of 1.480–1.504 Å (Table 3), close to that for the terminal P=O bonds in H₃PO₄·0.5H₂O (1.485 and 1.495 Å) (28) and other layered aluminophosphates reported in the literature (15–21). The length of the P–O single bond for the PO₄ groups is 1.538 Å on average, in agreement with that observed for berlinite (29). The values of the O–P–O bond angles are distributed in the range from 105.7 to 112.4° (Table 4). The Al–O bond length varies within 1.727–1.763 Å with the average value being 1.740 Å, very close to that (1.734 Å) found in berlinite. Like the O–P–O bond angle, the O–Al–O angle changes within a narrow range (106.8 to 113.8°), indicating that the AlO₄ tetrahedral units are rather regular.

All the AlO₄ units are fully corner-shared by PO₄ groups to form a macroanionic network with the empirical formula [Al₃P₄O₁₆]³⁻, and the terminal P=O bonds of the PO₄ groups point upward and downward alternately on either side of the layer which is undulated along the *b* axis. The macroanionic layers are held together in an *AAAA* stacking sequence with intercalated template molecules (Fig. 2). From the single-crystal structure analysis, three H atoms are found on each terminal N atom of the *tetam* molecule, implying that both terminal –NH₂ groups are protonated. There are three H bonds between each terminal N atom and three respective O atoms in the macroanionic aluminophosphate layers (Table 5). Besides the hydrogen-bonds observed for the two terminal N atoms, there should be another strong H-bond between N(3) of the template molecule and O(9) of the inorganic layer since the N(3)···O(9) distance is only 2.668 Å. Therefore, a proton, although not found crystallographically, must exist between these two atoms. This proton cannot be H(13) on N(3) since H(13) is too far away from O(9) (the distance of H(13)···O(9) is 3.316 Å). On the other hand, no hydrogen-bond is observed between N(2) and the O atoms of the inorganic layers (the nearest N(2)···O distance is that

TABLE 2
Atomic Coordinates and Equivalent Thermal Parameters (Å²) with Estimated Standard Deviations in Parentheses for [C₆H₂₁N₄][Al₃P₄O₁₆]

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (equiv)
Al(1)	0.4148(2)	0.57100(8)	1.0729(2)	0.0091
Al(2)	0.3067(2)	0.60655(8)	0.6279(2)	0.0106
Al(3)	0.2253(2)	0.75095(9)	0.8884(2)	0.0107
P(1)	0.0735(2)	0.69253(7)	0.6272(2)	0.0112
P(2)	0.4822(2)	0.66900(7)	0.8792(2)	0.0119
P(3)	0.3171(2)	0.50003(7)	0.8172(2)	0.0122
P(4)	0.3652(2)	0.63705(8)	1.3231(2)	0.0150
O(1)	0.0884(5)	0.7178(2)	0.7768(5)	0.0159
O(2)	–0.0778(5)	0.6878(2)	0.5669(5)	0.0231
O(3)	0.1416(5)	0.6347(2)	0.6381(5)	0.0209
O(4)	0.1560(5)	0.7693(2)	1.0409(5)	0.0210
O(5)	0.3661(6)	0.7057(2)	0.9248(6)	0.0250
O(6)	0.4333(5)	0.6478(2)	0.7293(5)	0.0181
O(7)	0.5021(6)	0.6194(2)	0.9812(5)	0.0212
O(8)	0.6188(5)	0.6994(2)	0.8842(5)	0.0219
O(9)	0.2082(5)	0.4548(2)	0.7892(5)	0.0218
O(10)	0.2963(5)	0.5340(2)	0.9502(5)	0.0180
O(11)	0.5322(5)	0.5235(2)	1.1611(5)	0.0189
O(12)	0.3097(5)	0.5390(2)	0.6892(5)	0.0188
O(13)	0.3161(6)	0.6006(2)	1.1931(5)	0.0181
O(14)	0.2688(6)	0.6879(2)	1.3097(5)	0.0242
O(15)	0.3377(6)	0.6038(2)	1.4545(5)	0.0225
O(16)	0.5163(6)	0.6520(3)	1.3301(7)	0.0342
N(1)	–0.2658(9)	0.9035(3)	–0.0316(8)	0.0431
N(2)	–0.150(1)	0.9240(4)	0.268(1)	0.0635
N(3)	–0.1457(7)	0.8717(3)	0.5462(7)	0.0277
N(4)	–0.2842(7)	0.7530(3)	0.6488(7)	0.0281
C(1)	–0.318(1)	0.9441(5)	0.066(1)	0.0505
C(2)	–0.208(1)	0.9679(5)	0.168(1)	0.0626
C(3)	–0.069(1)	0.9421(5)	0.387(1)	0.0608
C(4)	–0.023(1)	0.8959(5)	0.485(1)	0.0424
C(5)	–0.097(1)	0.8263(4)	0.646(1)	0.0326
C(6)	–0.212(1)	0.8015(4)	0.721(1)	0.0420
H(1)	–0.3461(9)	0.8878(3)	–0.0959(8)	0.0300
H(2)	–0.2003(9)	0.9226(3)	–0.0872(8)	0.0300
H(3)	–0.2149(9)	0.8732(3)	0.0239(8)	0.0300
H(4)	–0.369(1)	0.9741(5)	0.009(1)	0.0300
H(5)	–0.384(1)	0.9247(5)	0.120(1)	0.0300
H(6)	–0.133(1)	0.9814(5)	0.116(1)	0.0300
H(7)	–0.245(1)	0.9992(5)	0.219(1)	0.0300
H(8)	–0.090(1)	0.8987(4)	0.219(1)	0.0300
H(9)	0.015(1)	0.9617(5)	0.362(1)	0.0300
H(10)	–0.126(1)	0.9681(5)	0.436(1)	0.0300
H(11)	0.020(1)	0.8669(5)	0.431(1)	0.0300
H(12)	0.048(1)	0.9091(5)	0.563(1)	0.0300
H(13)	–0.2139(7)	0.8561(3)	0.4691(7)	0.0300
H(14)	–0.056(1)	0.7964(4)	0.594(1)	0.0300
H(15)	–0.023(1)	0.8420(4)	0.718(1)	0.0300
H(16)	–0.284(1)	0.8305(4)	0.729(1)	0.0300
H(17)	–0.170(1)	0.7895(4)	0.817(1)	0.0300
H(18)	–0.3584(7)	0.7386(3)	0.7017(7)	0.0300
H(19)	–0.3276(7)	0.7645(3)	0.5535(7)	0.0300
H(20)	–0.2134(7)	0.7235(3)	0.6411(7)	0.0300

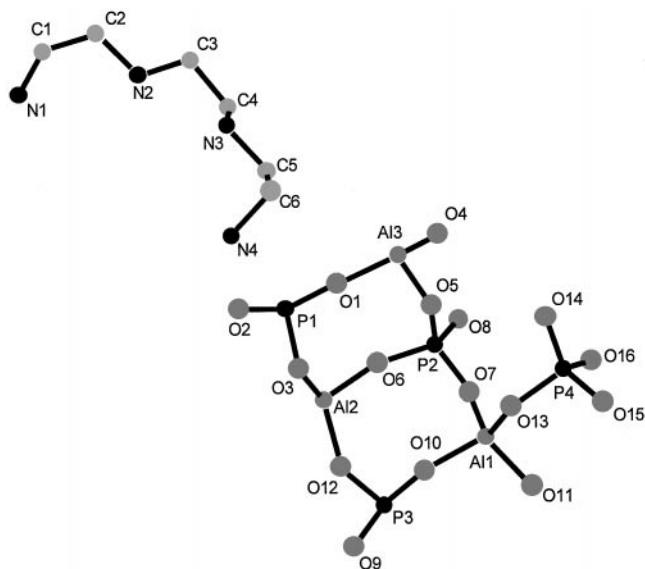


FIG. 1. Asymmetric unit for $[\text{C}_6\text{H}_{21}\text{N}_4][\text{Al}_3\text{P}_4\text{O}_{16}]$.

(3.459 Å) for N(2) ... O(2)). The existence of the extra proton between N(3) and O(9) is also in agreement with the requirement of charge balance for the title compound, that is, the template molecule is triply-protonated to form a trivalent cation. Triply-protonated template molecules are rather unusual for framework and layered aluminophosphates. The N(3)-H ... O(9) hydrogen bond affects the P=O(9) double bond to a certain degree by elongating it from the typical value of ca 1.485 Å found for other P=O bonds in the structure to 1.504 Å (see Table 3).

The macroanionic inorganic sheet viewed along the [100] direction is shown in Fig. 3. The sheet structure

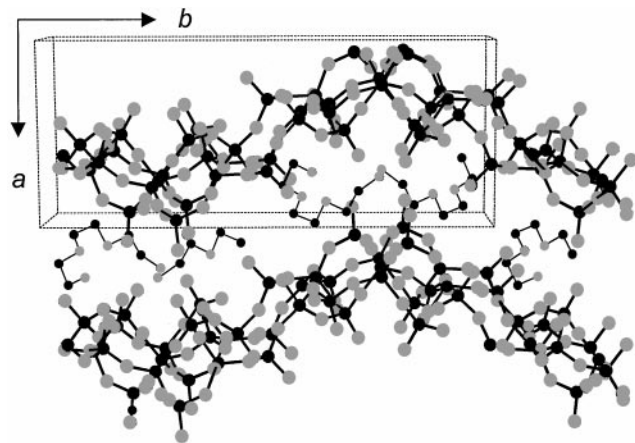


FIG. 2. View of $[\text{C}_6\text{H}_{21}\text{N}_4][\text{Al}_3\text{P}_4\text{O}_{16}]$ structure along the c axis showing the template (*tetam*) molecules between the macroanionic inorganic layers. Large solid circle: Al or P; large shaded circle: O; small solid circle: C; small shaded circle: N. For clarity, H atoms are not shown.

TABLE 3
Selected Bond Distances (Å) for $[\text{C}_6\text{H}_{21}\text{N}_4][\text{Al}_3\text{P}_4\text{O}_{16}]$

Al(1)-O(7)	1.740(5)
Al(1)-O(10)	1.758(5)
Al(1)-O(11)	1.737(5)
Al(1)-O(13)	1.741(5)
Al(2)-O(3)	1.732(5)
Al(2)-O(6)	1.751(5)
Al(2)-O(12)	1.727(5)
Al(2)-O(15)	1.732(5)
Al(3)-O(1)	1.763(5)
Al(3)-O(4)	1.745(5)
Al(3)-O(5)	1.727(6)
Al(3)-O(14)	1.732(5)
P(1)-O(1)	1.547(5)
P(1)-O(2)	1.484(5)
P(1)-O(3)	1.534(5)
P(1)-O(4)	1.527(5)
P(2)-O(5)	1.529(6)
P(2)-O(6)	1.537(5)
P(2)-O(7)	1.540(5)
P(2)-O(8)	1.491(5)
P(3)-O(9)	1.504(5)
P(3)-O(10)	1.552(5)
P(3)-O(11)	1.534(5)
P(3)-O(12)	1.540(5)
P(4)-O(13)	1.545(5)
P(4)-O(14)	1.525(5)
P(4)-O(15)	1.546(5)
P(4)-O(16)	1.480(6)
N(1)-C(1)	1.49(1)
C(1)-C(2)	1.45(1)
C(2)-N(2)	1.48(1)
N(2)-C(3)	1.36(1)
C(3)-C(4)	1.48(2)
C(4)-N(3)	1.50(1)
N(3)-C(5)	1.49(1)
C(5)-C(6)	1.52(1)
C(6)-N(4)	1.48(1)

consists of four-, six-, and eight-membered rings that form a network of alternately linked corner-sharing AlO_4 and PO_4 tetrahedra. If the O atoms are omitted, a two-dimensional network with alternative Al-P linkages is generated. This O-omitting network can be viewed as constructed from two subunits: one being an infinite zigzag double chain (IZDC) containing edge-sharing double-diamonds and the other a finite double chain (FDC) involving three edge sharing four-membered rings. A double-diamond ring unit was also observed previously for a layered aluminophosphate (20) with $\text{P}/\text{Al} = 4/3$ directed by 1,2-diaminopropane. Two adjacent IZDC units are crosslinked together by edge-sharing the FDC units. There is also an Al-P linkage (bridged by an O atom) on each side of the FDC unit, and as a result, six- and eight-membered rings are formed in the 2D network.

Macroanionic layers with a P/Al ratio of 4:3 have been observed previously in a number of aluminophosphate

TABLE 4
Selected Bond Angles (°) for $[\text{C}_6\text{H}_{21}\text{N}_4][\text{Al}_3\text{P}_4\text{O}_{16}]$

O(7)–Al(1)–O(10)	108.0(3)
O(7)–Al(1)–O(11)	111.4(3)
O(10)–Al(1)–O(11)	107.8(3)
O(7)–Al(1)–O(13)	113.8(3)
O(10)–Al(1)–O(13)	107.1(3)
O(11)–Al(1)–O(13)	108.5(3)
O(3)–Al(2)–O(6)	108.1(3)
O(3)–Al(2)–O(12)	108.7(3)
O(6)–Al(2)–O(12)	111.5(3)
O(3)–Al(2)–O(15)	110.3(3)
O(6)–Al(2)–O(15)	111.0(3)
O(12)–Al(2)–O(15)	107.2(3)
O(1)–Al(3)–O(4)	106.8(3)
O(1)–Al(3)–O(5)	109.2(3)
O(4)–Al(3)–O(5)	111.4(3)
O(1)–Al(3)–O(14)	108.8(3)
O(4)–Al(3)–O(14)	107.0(3)
O(5)–Al(3)–O(14)	113.4(3)
O(1)–P(1)–O(2)	110.5(3)
O(1)–P(1)–O(3)	108.0(3)
O(2)–P(1)–O(3)	109.8(3)
O(1)–P(1)–O(4)	106.3(3)
O(2)–P(1)–O(4)	112.4(3)
O(3)–P(1)–O(4)	109.7(3)
O(5)–P(2)–O(6)	108.8(3)
O(5)–P(2)–O(7)	107.2(3)
O(6)–P(2)–O(7)	109.4(3)
O(5)–P(2)–O(8)	111.9(3)
O(6)–P(2)–O(8)	110.1(3)
O(7)–P(2)–O(8)	109.3(3)
O(9)–P(3)–O(10)	111.4(3)
O(9)–P(3)–O(11)	111.7(3)
O(10)–P(3)–O(11)	107.9(3)
O(9)–P(3)–O(12)	110.1(3)
O(10)–P(3)–O(12)	109.8(3)
O(11)–P(3)–O(12)	105.7(3)
O(13)–P(4)–O(14)	106.0(3)
O(13)–P(4)–O(15)	107.4(3)
O(14)–P(4)–O(15)	108.3(3)
O(13)–P(4)–O(16)	111.1(3)
O(14)–P(4)–O(16)	112.4(3)
O(15)–P(4)–O(16)	111.3(3)
Al(3)–O(1)–P(1)	135.0(3)
Al(2)–O(3)–P(1)	137.1(3)
Al(3)–O(4)–P(1)	153.1(3)
Al(3)–O(5)–P(2)	151.8(4)
Al(2)–O(6)–P(2)	143.6(3)
Al(1)–O(7)–P(2)	144.6(4)
Al(1)–O(10)–P(3)	132.4(3)
Al(1)–O(11)–P(3)	147.0(4)
Al(2)–O(12)–P(3)	147.3(4)
Al(1)–O(13)–P(4)	129.6(3)
Al(3)–O(14)–P(4)	145.4(4)
Al(2)–O(15)–P(4)	146.7(4)
N(1)–C(1)–C(2)	114.2(9)
C(1)–C(2)–N(2)	109.2(11)
C(2)–N(2)–C(3)	115.8(10)
N(2)–C(3)–C(4)	112.2(11)
N(3)–C(4)–C(3)	111.0(8)
C(4)–N(3)–C(5)	110.3(7)
N(3)–C(5)–C(6)	114.5(8)
C(5)–C(6)–N(4)	114.1(8)

TABLE 5
Interatomic Distances (Å) between N and O Atoms Linked by Hydrogen Bonds for $[\text{C}_6\text{H}_{21}\text{N}_4][\text{Al}_3\text{P}_4\text{O}_{16}]$

N(1)–H(1)⋯O(16)	2.661
N(1)–H(2)⋯O(9)	2.884
N(1)–H(3)⋯O(2)	2.909
N(4)–H(18)⋯O(8)	2.866
N(4)–H(19)⋯O(8a)	2.824
N(4)–H(20)⋯O(2)	2.720
N(3)–H⋯O(9)	2.668

compounds containing a monoamine or a diamine as templates. Interestingly, the stacking sequence in these compounds may be *ABAB* directed by a diamine, or *AAAA* by

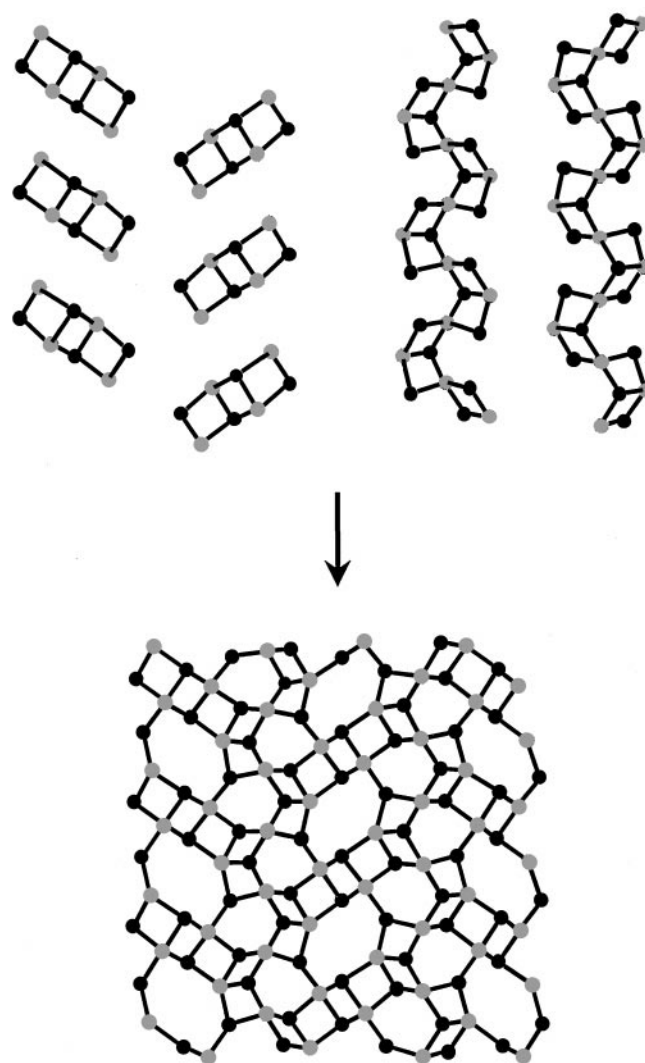


FIG. 3. Schematic representation of the arrangement of the four-, six-, and eight-membered rings in the macroanionic inorganic layer for $[\text{C}_6\text{H}_{21}\text{N}_4][\text{Al}_3\text{P}_4\text{O}_{16}]$ viewed along the *a* axis. The layer can be regarded as the combination of the infinite zigzag double-chain (IZDC) and the finite double-chain (FDC) subunits. For clarity, O atoms are omitted.

monoamine (18). Furthermore, templates with a long alkyl chain such as butyl group leads to the formation of less dense 4.6.12 network (16, 21) instead of the 4.6.8 network directed by short amines. Although the template for the title compound is a chain compound with two terminal -NH_2 groups, similar to a primary diamine, the nitrogen atoms bridging two C atoms inside the chain are also possible proton-acceptors. As a result, the structure-directing effect of the *tetam* molecule is different from that of a primary diamine. In the structure of the title compound, the template chain covers the four-, six-, and eight-membered rings so as to form hydrogen bonds efficiently. It seems that amines with a complex chain structure is promising for the synthesis of aluminophosphates with new structural features.

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