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Formation of a New Layered Aluminophosphate $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$

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A new layered aluminophosphate $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$ (**1**) has been crystallized in a gel system with molar ratio of $Al(PrO^i)_3$:3.6 H_3PO_4:5.9 1,2-dimethylimidazole:12 TEG:3.4 H_2O at 180 °C. Its structure is solved by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ (no. 14), with $a = 10.402(1)$, $b = 14.545(1)$, $c = 16.361(1)$ Å, $\beta = 96.397(6)°$, and $Z = 4$. The inorganic layers, which are constructed from alternating tetrahedral AlO_4 and $PO_3(=O)$ units, contain 4.6 nets and are featured by a series of $\Diamond_3(\mathrm{Tp})_5$ chains. The layers are further held together through strong H-bonds between the terminal oxygen groups and ammonium cations NH_4^+ as well as protonated 1,2-dimethylimidazole molecules located in the interlayer. Formation of the 4.6 nets of **1** can be thought as the condensation of $\Diamond_3(\mathrm{Tp})_5$ chains.

Introduction

Microporous aluminophosphates (AlPOs) with an Al/P ratio of 1, whose structures are constructed from alternating AlO_4 and PO_4 units, are conventionally synthesized from aqueous system.[1−3] These materials, like aluminosilicate zeolites, have great potential in applications of adsorption and catalysis. Using a nonaqueous synthesis technique, a large number of novel aluminophosphates with an Al/P ratio lower than unity have been continuously synthesized.[4] Notable examples are 3-dimensional (3-D) microporous aluminophosphates $Al_5P_6O_{24}H^{2-}$ (JDF-20),[5] $Al_4P_5O_{20}H^{2-}$ (AlPO−HDA),[6] and a variety of low-dimensional materials. The low-dimensional materials exclusively contain tetrahedral phosphates with terminal P−OH and/or P═O groups, which renders them potentially useful in the self-assembly process to build up higher dimensional frameworks. In addition, their structural features provide important structural relationship among the 3-D, 2-D, and 1-D aluminophosphate compounds.[7]

Among the low-dimensional compounds, 2-D layered compounds constitute an important area with rich structural and compositional diversity. So far, over 20 organically templated AlPO layer compounds have been reported. Their stoichiometries are found to be $Al_4P_5O_{20}$,[8] $Al_3P_4O_{16}$,[9−19] $Al_2P_3O_{12}$,[20−22] and $AlP_2O_8^{3-}$.[18,23] The $Al_3P_4O_{16}^{3-}$ layer compounds, especially, exhibit rich

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Table 1. Crystal Data and Structure Refinement for $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$

empirical formula	$C_{10}H_{22}Al_3N_5O_{16}P_4$
formula weight	1346.29
temp (K)	298(2)
wavelength (Å)	0.71069
crystal system	monoclinic
space group	$P2_1/c$
unit cell dimensions	$a = 10.402(1)$ Å, $\alpha = 90°$ $b = 14.545(1)$ Å, $\beta = 96.397(6)°$ $c = 16.361(1)$ Å, $\gamma = 90°$
vol (Å^3)	2460.0(4)
Z	4
ρ_{cal} (Mg/m^3)	1.818
absorption coeff (mm^{-1})	0.500
F(000)	1376
crystal size (mm)	0.20 × 0.11 × 0.08
θ range for data collection	2.51−30.00 °
index ranges	$0 \le h \le 14$, $0 \le k \le 20$, $-22 \le l \le 22$
reflections collected	7523
independent reflections	7168
absorption correction	Ψ scan
max/min. transmission	0.9610/0.9131
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	7168/0/274
goodness-of-fit on F^2	1.039
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.1077$
R indices (all data)	$R_1 = 0.0769$, $wR_2 = 0.1190$
extinction coeff	0.0003(2)
largest diff. peak and hole	0.904 and −0.978 e Å^{-3}

structural varieties. The 2-D nets of $Al_3P_4O_{16}{}^{3-}$ layers are exclusively built up from alternating AlO_4 and $PO_3(=O)$ units, with the exception of $Al_3P_4O_{16}H{\cdot}2N_2C_3H_5$, which contains five coordinate Al atoms.[18] Each tetrahedral phosphate shares three oxygens with adjacent Al atoms, leaving one oxygen terminal. The inorganic layers of $Al_3P_4O_{16}{}^{3-}$ compounds contain 4.6 (a),[13] 4.6 (b),[15] 4.6.8,[10] and 4.6.12[9] nets. Many of these layer compounds have the same inorganic sheet but are distinct from each other by either occluded template species or the manner in which the sheets stack.

Herein we report a layered aluminophosphate containing a new type of 4.6 net, which is featured by a series of $\Diamond_3(Tp)_5$ chains, and discuss their structural formation.

Experimental Section

Synthesis and Characterization. Large single crystals of **1** were prepared in a gel system $Al(PrO^i)_3-H_3PO_4-$1,2-dimethylimidazole−TEG. Typically, 2.0 g of finely ground aluminum triisopropoxide was first dispersed into 16 mL of triethylene glycol with stirring, followed by the addition of 5.54 g of 1,2-dimethylimidazole. Phosphoric acid (85 wt % in water, 2.4 mL) was added slowly to the above reaction mixture under continuous stirring. A homogeneous gel was formed and transferred into a 23-mL Parr digestion bomb and heated at 180 °C for 6 days under autogenous pressure. The crystalline phases containing large platelike single crystals and some aggregates were separated from an amorphous phase by sonification and dried at 70 °C. The powder X-ray diffraction (XRD) pattern of the product indicated that **1** was the major phase as compared with the simulated XRD pattern based on single-crystal X-ray diffraction analysis, and $AlPO_4$-5 existed as a minor phase. Upon calcination above 300 °C, **1** transformed into $AlPO_4$-trydimite, as indicated by XRD analysis. Powder X-ray diffraction patterns were recorded on a Philips PW3050 X-ray diffractometer by using CuKα radiation ($\lambda = 1.5418$ Å) with a graphite monochromator in the diffracted beam path.

Energy-dispersive X-ray analysis, which was performed on a JEOL 3010 electron microscope, indicated that the examined single crystals of **1** had an Al/P ratio of ca. 3:4.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$

	x	y	z	U(eq)^a
P(1)	1473(1)	532(1)	4332(1)	15(1)
P(2)	7699(1)	616(1)	2560(1)	12(1)
P(3)	1141(1)	2306(1)	1866(1)	15(1)
P(4)	1191(1)	6043(1)	5816(1)	13(1)
Al(1)	9666(1)	2072(1)	3413(1)	14(1)
Al(2)	607(1)	5656(1)	3921(1)	13(1)
Al(3)	828(1)	730(1)	6147(1)	14(1)
O(1)	2799(2)	578(2)	4060(1)	28(1)
O(2)	756(2)	9677(2)	3970(1)	26(1)
O(3)	1567(2)	482(2)	5274(1)	24(1)
O(4)	639(2)	1370(2)	4072(2)	35(1)
O(5)	6268(2)	655(2)	2510(1)	25(1)
O(6)	8315(2)	1469(1)	3001(1)	26(1)
O(7)	1735(2)	242(1)	6985(1)	25(1)
O(8)	8139(2)	583(1)	1690(1)	21(1)
O(9)	2571(2)	2214(2)	2018(2)	32(1)
O(10)	549(2)	1422(1)	1483(1)	30(1)
O(11)	740(2)	3093(1)	1269(1)	26(1)
O(12)	527(2)	2501(2)	2653(1)	34(1)
O(13)	2458(2)	5772(2)	6279(1)	32(1)
O(14)	69(2)	5420(1)	6003(1)	23(1)
O(15)	1302(2)	6012(2)	4885(1)	25(1)
O(16)	809(2)	7029(1)	6006(1)	26(1)
C(11)	4292(4)	3641(3)	5586(3)	43(1)
C(12)	5486(4)	3932(3)	5483(2)	38(1)
N(13)	5607(3)	3900(2)	4663(2)	35(1)
C(14)	4517(3)	3599(2)	4268(2)	33(1)
N(15)	3684(3)	3445(2)	4804(2)	35(1)
C(16)	4299(5)	3459(4)	3376(3)	62(1)
C(17)	2375(5)	3107(4)	4639(4)	74(2)
C(21)	2949(4)	8260(2)	5003(2)	35(1)
C(22)	3864(4)	8558(3)	5588(2)	37(1)
N(23)	4920(3)	8799(2)	5189(2)	29(1)
C(24)	4653(3)	8649(2)	4388(2)	26(1)
N(25)	3451(3)	8315(2)	4260(2)	27(1)
C(26)	5533(4)	8821(3)	3762(2)	39(1)
C(27)	2775(4)	8049(3)	3467(2)	45(1)
N(3)	6471(3)	5537(2)	2534(2)	28(1)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Single-Crystal Structure Determination. Crystal data for $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$: $M = 336.57$, space group $P2_1/c$, $a = 10.402(1)$ Å, $b = 14.545(1)$ Å, $c = 16.361(1)$ Å, $\beta = 96.397(6)$, $V = 2460.0(4)$ Å^3, $Z = 4$, $D_c = 1.818$ g cm^{-3}, and $F(000) = 1376$. A colorless platelike crystal of 0.2 × 0.11 × 0.08 mm was selected, and intensity data were collected on a Rigaku AFC7R diffractometer using monochromatic MoKα radiation generated by a rotating anode X-ray tube. It should be noted that the Laue symmetry of the present crystal was determined by the intensity distribution measured by an AXIS-IV equipped with an imaging plate. The lattice constants were determined by the least-squares procedure applied to 25 2θ values between 32° and 33°. Intensity data of 7523 reflections ($0 \le h \le 14$, $0 \le k \le 20$, $-22 \le l \le 22$), among which 5511 reflections met the condition of $I > 2\sigma(I_{obs})$, were collected in the ω-2θ scan mode up to $(\sin\theta/\lambda)_{max} = 0.704$. Measured data were corrected for Lorentz and polarization effects together with an absorption correction by an ordinary Ψ-scan algorithm.[24] The structure was solved by direct methods, SIR92,[25] and refined by the least-squares program, SHELXL-97.[26] During the isotropic refinement for framework positions, non-hydrogen atoms of a 1,2-dimethylimidazole template molecule and nitrogen atoms of ammonium cations were clearly observed in the interlayer

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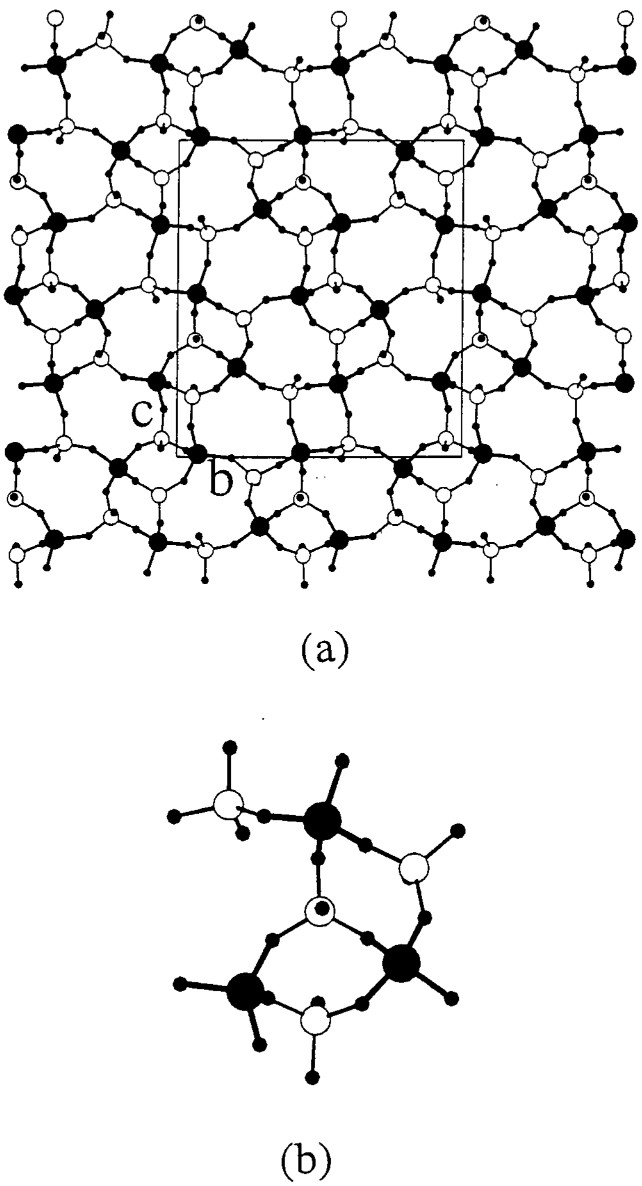

(a)

(b)

Figure 1. (a) Sheet structure of **1** viewed along the [100] direction and (b) secondary building unit (SBU) of **1**: a branched double edge-sharing 4MRs (Al, black circle; P, white circle; O, small circle between Al and P).

region between the sheets. These 1,2-dimethylimidazole and ammonium species were suggested to be protonated so as to make the charge balance of the present compound. After introducing anisotropic temperature factors for framework positions of Al, P, and O atoms, hydrogen atoms, i.e., H131 and H231 (N13−H131 = 0.993(3) Å; N23−H231 = 0.926(3) Å), and four hydrogens of an ammonium cation H31, H32, H33, and H34 (N3−H = 0.74−0.93 Å) were confirmed by difference Fourier maps (no further refinement was carried out for these hydrogens). These hydrogens form strong hydrogen bonds to terminal oxygens of O1, O5, O9, and O13 attached to the inorganic layers. Finally, the remaining H atoms of protonated 1,2-dimethylimidazole were positioned geometrically. The isotropic temperature factors for all H atoms are constrained to be identical. A summary of selected crystallographic data is given in Table 1.

Results and Discussion

Using an aromatic organic amine, 1,2-dimethylimidazole, as a template, **1** has been crystallized in a TEG system with a gel molar composition of $Al(PrO^i)_3$:3.6 H_3PO_4:5.9 1,2-dimethylimidazole:12 TEG:3.4 H_2O at 180 °C for 6 days. A minor phase $AlPO_4$-5 is found to coexist with compound **1**.

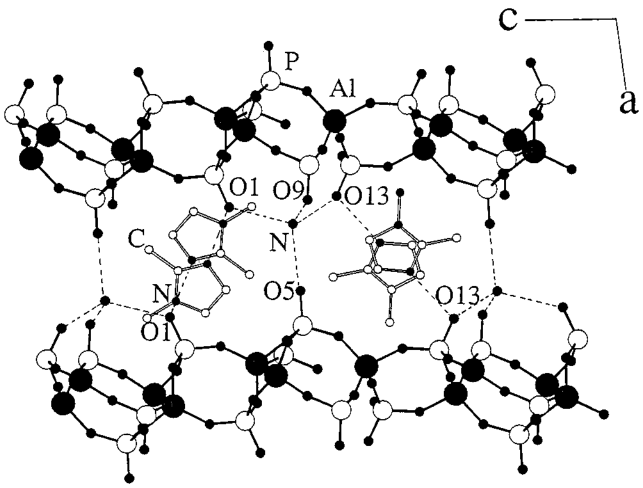

Figure 2. Structure of **1** viewed along the [010] direction (the dashed lines indicate H-bonds).

The type of solvent is an important factor influencing the crystallization. When water or 2-butanol is used as the solvent, keeping other conditions unchanged, no crystalline product is produced, whereas when ethylene glycol is used as the solvent, the product is $AlPO_4$-5.

The P/Al ratio of the gel also affects the synthesis. Crystallization from the gel with composition of $Al(PrO^i)_3$:4.1 H_3PO_4:5.9 1,2-dimethylimidazole:12 TEG:3.9 H_2O at 180 °C for 8 days produces large single crystals of $AlPO_4$-17 ($a = 13.334$ Å, $b = 13.334$ Å, $c = 14.602$ Å, $\gamma = 120°$) and a 2-D layered compound with a 4.6.8 net $Al_3P_4O_{16}^{3-}$ macroanionic sheet ($a = 8.867$ Å, $b = 14.834$ Å, $c = 10.494$ Å, $\beta = 108.92°$) as well as **1**. This is confirmed by single-crystal X-ray diffraction analysis.

Structural analysis indicates that **1** crystallizes in the monoclinic space group $P2_1/c$ and that it has an empirical formula of $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$. The NH_4^+ cation may come from fragmentation of a 1,2-dimethylimidazole template molecule during the solvothermal synthesis. The fragmentation of the organic amine has been reported previously in the synthesis of some AlPO compounds, such as 3-D microporous $AlPO_4$-15 ($NH_4Al_2(OH)(H_2O)(PO_4)_2H_2O$)[27] and 1-D chain $[AlP_2O_8][H_3NCH_2CH_2NH_3][NH_4]$.[28] Table 2 lists the final atomic coordinates and isotropic temperature factors of **1**. Selected bond lengths and angles are given in Table 3.

The structure of **1** contains anionic sheets $Al_3P_4O_{16}^{3-}$ that are charge-balanced by the protonated 1,2-dimethylimidazole molecules and ammonium cations located in the interlayer region. Like other 2-D $Al_3P_4O_{16}^{3-}$ compounds (except for $Al_3P_4O_{16}H\cdot 2C_3H_5N_2$[17]), the 2-D network of **1** is constructed from alternating AlO_4 and $PO_3(=O)$ units. The asymmetric unit contains three crystallographically distinct tetrahedral AlO_4 units. All the oxygens attached to the Al atoms are vertex shared by adjacent P atoms. The Al−O bond lengths are in the range of 1.717(2)−1.741(2) Å, and the O−Al−O angles

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$[a]

Bond Lengths (Å)							
P(1)−O(1)	1.498(2)	P(4)−O(13)	1.498(2)	Al(3)−O(11)#8	1.728(2)	C(21)−C(22)	1.344(5)
P(1)−O(4)	1.529(2)	P(4)−O(16)	1.530(2)	Al(3)−O(7)	1.728(2)	C(21)−N(25)	1.377(4)
P(1)−O(2)#1	1.534(2)	P(4)−O(14)	1.535(2)	Al(3)−O(3)	1.734(2)	C(22)−N(23)	1.385(4)
P(1)−O(3)	1.535(2)	P(4)−O(15)	1.540(2)	Al(3)−O(2)#6	1.741(2)	N(23)−C(24)	1.327(4)
P(2)−O(5)	1.483(2)	Al(1)−O(16)#3	1.721(2)	C(11)−C(12)	1.340(5)	N(23)−H(231)	0.926(3)
P(2)−O(7)#2	1.537(2)	Al(1)−O(4)#4	1.728(2)	C(11)−N(15)	1.392(5)	C(24)−N(25)	1.336(4)
P(2)−O(6)	1.539(2)	Al(1)−O(12)#4	1.727(2)	C(12)−N(13)	1.362(5)	C(24)−C(26)	1.470(5)
P(2)−O(8)	1.545(2)	Al(1)−O(6)	1.728(2)	N(13)−C(14)	1.315(4)	N(25)−C(27)	1.458(5)
P(3)−O(9)	1.487(2)	Al(2)−O(10)#5	1.717(2)	N(13)−H(131)	0.993(3)	N(3)−H(31)	0.746(3)
P(3)−O(12)	1.527(2)	Al(2)−O(14)#6	1.726(2)	C(14)−N(15)	1.318(4)	N(3)−H(32)	0.925(3)
P(3)−O(10)	1.530(2)	Al(2)−O(8)#7	1.732(2)	C(14)−C(16)	1.466(6)	N(3)−H(33)	0.872(3)
P(3)−O(11)	1.531(2)	Al(2)−O(15)	1.739(2)	N(15)−C(17)	1.445(6)	N(3)−H(34)	0.743(3)
Bond Angles (deg)							
O(1)−P(1)−O(4)	113.2(1)	O(10)−P(3)−O(11)	107.3(1)	O(10)#5−Al(2)−O(15)	111.0(1)	C(14)−N(15)−C(17)	127.5(4)
O(1)−P(1)−O(2)#1	110.3(1)	O(13)−P(4)−O(16)	112.2(1)	O(14)#6−Al(2)−O(15)	109.6(1)	C(11)−N(15)−C(17)	124.3(4)
O(4)−P(1)−O(2)#1	107.6(1)	O(13)−P(4)−O(14)	112.9(1)	O(8)#7−Al(2)−O(15)	106.2(1)	C(22)−C(21)−N(25)	107.5(3)
O(1)−P(1)−O(3)	110.1(1)	O(16)−P(4)−O(14)	107.0(1)	O(11)#8−Al(3)−O(7)	110.2(1)	C(21)−C(22)−N(23)	106.4(3)
O(4)−P(1)−O(3)	106.7(1)	O(13)−P(4)−O(15)	109.5(1)	O(11)#8−Al(3)−O(3)	109.6(1)	C(24)−N(23)−C(22)	109.5(3)
O(2)#1−P(1)−O(3)	108.9(1)	O(16)−P(4)−O(15)	106.1(1)	O(7)−Al(3)−O(3)	108.4(1)	N(23)−C(24)−N(25)	107.7(3)
O(5)−P(2)−O(7)#2	112.7(1)	O(14)−P(4)−O(15)	108.8(1)	O(11)#8−Al(3)−O(2)#6	106.8(1)	N(23)−C(24)−C(26)	125.6(3)
O(5)−P(2)−O(6)	111.0(1)	O(16)#3−Al(1)−O(4)#4	106.8(1)	O(7)−Al(3)−O(2)#6	112.0(1)	N(25)−C(24)−C(26)	126.7(3)
O(7)#2−P(2)−O(6)	108.1(1)	O(16)#3−Al(1)−O(12)#4	109.1(1)	O(3)−Al(3)−O(2)#6	109.9(1)	C(24)−N(25)−C(21)	108.9(3)
O(5)−P(2)−O(8)	110.4(1)	O(4)#4−Al(1)−O(12)#4	110.4(1)	C(12)−C(11)−N(15)	106.4(3)	C(24)−N(25)−C(27)	125.9(3)
O(7)#2−P(2)−O(8)	106.5(1)	O(16)#3−Al(1)−O(6)	109.2(1)	C(11)−C(12)−N(13)	107.6(3)	C(21)−N(25)−C(27)	125.2(3)
O(6)−P(2)−O(8)	107.9(1)	O(4)#4−Al(1)−O(6)	109.8(1)	C(14)−N(13)−C(12)	109.0(3)	H(31)−N(3)−H(32)	104.2(3)
O(9)−P(3)−O(12)	112.4(1)	O(12)#4−Al(1)−O(6)	111.5(1)	N(13)−C(14)−N(15)	108.9(3)	H(31)−N(3)−H(33)	96.8(3)
O(9)−P(3)−O(10)	110.1(1)	O(10)#5−Al(2)−O(14)#6	110.0(1)	N(13)−C(14)−C(16)	124.3(4)	H(32)−N(3)−H(33)	112.9(3)
O(12)−P(3)−O(10)	108.3(1)	O(10)#5−Al(2)−O(8)#7	111.0(1)	N(15)−C(14)−C(16)	126.8(4)	H(31)−N(3)−H(34)	116.1(3)
O(9)−P(3)−O(11)	111.8(1)	O(14)#6−Al(2)−O(8)#7	109.0(1)	C(14)−N(15)−C(11)	108.1(3)	H(H(33)−N(3)−H(34)	123.8(3)
O(12)−P(3)−O(11)	106.9(1)						

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, y - 1, z$; #2 $-x + 1, -y, -z + 1$; #3 $-x + 1, -y + 1, -z + 1$; #4 $x + 1, y, z$; #5 $-x, y + 1/2, -z + 1/2$; #6 $-x, -y + 1, -z + 1$; #7 $-x + 1, y + 1/2, -z + 1/2$; #8 $x, -y + 1/2, z + 1/2$; #9 $-x - 1, -y - 1, -z - 1$; #10 $-x + 1, y + 3/2, -z + 1/2$.

Table 4. Hydrogen-Bonding Distances (Å) and Angles (deg) Present in $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$

distances (Å)		angles (deg)	
N(13)−O(13)#9	2.710(4)	N(13)−H(131)−O(13)#9	167.9(2)
N(23)−O(1)#9	2.703(4)	N(23)−H(231)−O(1)#9	167.9(2)
N(3)−O(1)#7	2.797(3)	N(3)−H(32)−O(1)#7	162.6(2)
N(3)−O(5)#7	2.847(3)	N(3)−H(33)−O(5)#7	175.2(2)
N(3)−O(9)#7	2.705(4)	N(3)−H(31)−O(9)#7	164.5(2)
N(3)−O(13)#9	2.856(3)	N(3)−H(34)−O(13)#9	161.0(2)

are in the range of 106.2(1)−112.0(1)°, which are normal for AlPO materials.[9−19] Four crystallographically distinct tetrahedral P atoms share three oxygens with adjacent Al atoms, leaving one oxygen terminal. The P−O bond lengths range between 1.483(2) and 1.545(2) Å, and O−P−O bond angles vary from 106.1(1) to 113.2(2)°. The shorter P−O bond lengths, P(1)−O(1) = 1.498(2), P(2)−O(5) = 1.483(2), P(3)−O(9) = 1.487(2), and P(4)−O(13) = 1.498(2) Å, indicate the P═O bondings. [9−19]

Figure 1a shows the inorganic layer of **1** viewed along the [100] direction. The 2-D net of **1** exhibits a new type of 4.6 net. The branched double edge-sharing four-membered rings (4MRs) can be considered as a secondary building unit (Figure 1b)

Figure 2 shows the packing of the inorganic layers viewed along the [010] direction. The layers stack in a same way along the *a* axis. The protonated 1,2-dimethylimidazole and ammonium cations located in the interlayer region not only play a charge balance role but also act as H-bonding donors to terminal oxygens attached to the phosphate groups. Each NH_4^+ cation is hydrogen-bonded to four terminal oxygens O(1), O(5), O(9), and O(13) (the N···O distances ranging from 2.705 to 2.856 Å and the N−H···O angles varying from 161.0 to 175.2°). Each protonated 1,2-dimethylimidazole forms an H-bond to the terminal O(1) or O(13) atom. The H-bonding information is summarized in Table 4.

It is found that the 2-D network of **1** is featured by a series of $\Diamond_3(\mathrm{Tp})_5$ chains, where $\Diamond_3$ means three corner-sharing four rings and $(\mathrm{Tp})_5$ mean five edge-sharing four rings in a trans conformation.[7] The two types of Al2P2 four-membered ring (4MR) chains, i.e., the corner-sharing and edge-sharing, have been found in the 1-D chains $AlP_2O_8H{\cdot}2Et_3NH$[29] and $AlP_2O_8H{\cdot}NH_3(CH_2)_2NH_3$,[30] respectively. The structure of **1** suggests that these two types of 1-D chains might be the important units for the formation of the 2-D network. Recently, we have developed a procedure to build up hypothetical $Al_3P_4O_{16}{}^{3-}$ 2-D networks by computer. Calculations using the Cerius Package[31] with Burchart 1.01 force field[32,33] shows that a large number of hypothetical 2-D nets are energetically comparable with those known 2-D nets.[34] Some of the hypothetical 2-D nets can possibly be constructed from the further condensation of some intact 1-D chains. For example, the hypothetical 2-D net in Figure 3a can be constructed from alternation of the two types of intact 1-D chains, i.e., corner-sharing and edge-sharing 4MR chains. Figure 3b−d also show that these 2-D net structures can be constructed from

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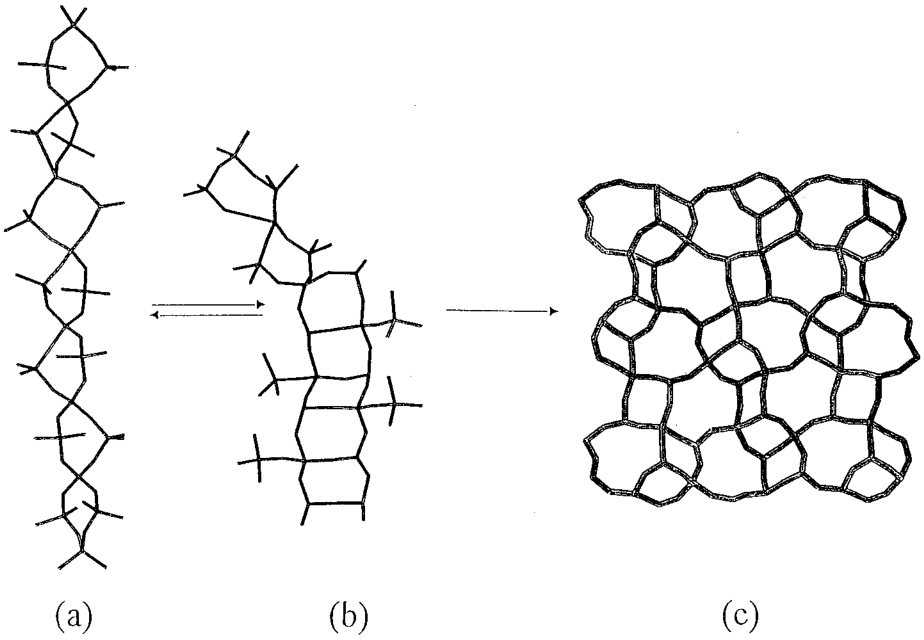

Figure 3. Some hypothetical 2-D $Al_3P_4O_{16}^{3-}$ nets (a) composed of edge-sharing and corner-sharing 4MR chains, (b) composed of $\Diamond_2(\mathrm{Tp})_3$ and zigzag edge-sharing 4MR chains, (c) composed of $\Diamond_2(\mathrm{Tp})_2$ chains and zigzag edge-sharing 4MR chains, and (d) composed of $\Diamond_5(\mathrm{Tp})_2$ and edge-sharing 4MR chains.

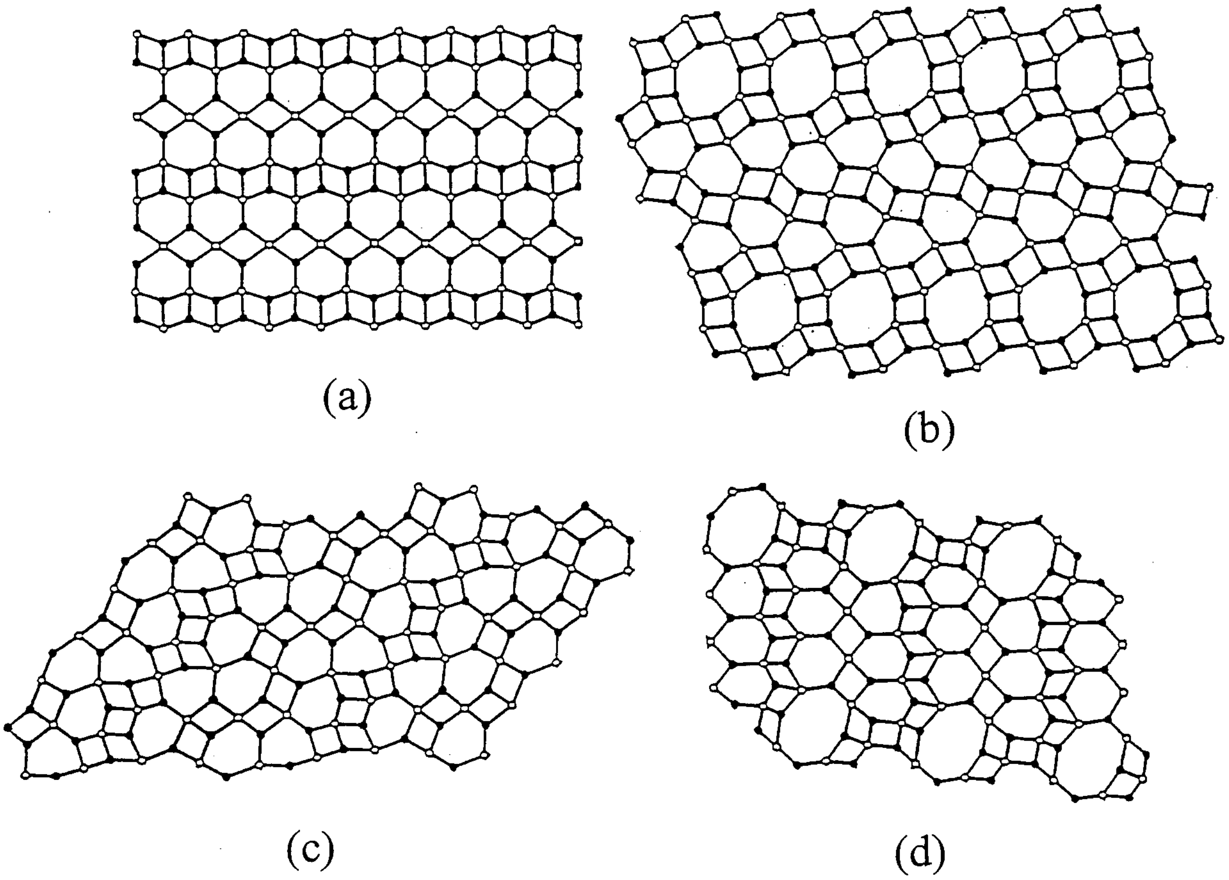

Figure 4. Formation scheme of **1**: (a) linear corner-sharing 4MR chain; (b) $\Diamond_3(\mathrm{Tp})_5$ chain that can be transformed from the linear chain followed by rotation and condensation; and (c) 4.6 net condensed from $\Diamond_3(\mathrm{Tp})_5$ chains.

alternating 1-D chains composed of corner-sharing and edge-sharing 4MR chains.

Ozin et al. proposed that a linear corner-sharing Al_2P_2 4MR chain is the building block for a family of 1-D chain, 2-D layered, and 3-D open-framework aluminophosphate materials. Under certain conditions, the formation of other chain types could occur through hydrolysis−condensation self-assembly pathway. These chains can condense further to more complex porous layered or open-framework AlPO structures.[7] Based on this model, the $\Diamond_3(\mathrm{Tp})_5$ chain of **1** can be derived from the linear corner-sharing 4MR chain through hydrolysis followed by rotation and condensation (Figure 4a,b). Energy calculation shows that the energies of these two chains have not much difference. This suggests that the $\Diamond_3(\mathrm{Tp})_5$ chains possibly can be transformed from the linear corner-sharing 4MR chains under certain solvothermal conditions. The $\Diamond_3(\mathrm{Tp})_5$ chains are then further condensed so as to form the 4.6 net of **1**. The proposed formation scheme of **1** is shown in Figure 4; however, we still need further experimental evidence to elucidate the formation mechanism.

Conclusion

The solvothermal synthesis of a new 2-D layer $[Al_3P_4O_{16}][C_5N_2H_9]_2[NH_4]$ and its crystal structure have been described in this work. The compound is a new member of the $Al_3P_4O_{16}{}^{3-}$ family, and its structure contains 4.6 nets, which are featured by a series of $\Diamond_3(\mathrm{Tp})_5$ chains. We have proposed some hypothetical 2-D nets that are constructed from some 1-D chains composed of corner-sharing and edge-sharing 4MR chains. If we take the linear corner-sharing 4MR chain as a parent chain, the $\Diamond_3(\mathrm{Tp})_5$ chains in **1** can possibly be transformed from it through rotation and condensation under certain solvothermal conditions and may further condense to form the 2-D network. The continuous synthesis of new 2-D layered materials will further assist in the understanding of the formation mechanism of aluminophosphate and related materials as well as realizing the rational synthesis of specific materials.

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Supporting Information Available: Tables listing anisotropic displacement parameters for non-hydrogen atoms and coordinates and isotropic displacement parameters of hydrogen atoms (2 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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