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$Al_{16}P_{20}O_{80}H_4\cdot 4C_6H_{18}N_2$: A New Microporous Aluminophosphate Containing Intersecting 12- and 8-Membered Ring Channels

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Since the first discovery of the aluminophosphate molecular sieves ($AlPO_4$-*n* with *n* representing a particular structure type) in 1982,[1] more than 30 aluminophosphate-based microporous materials composed of 8-, 10-, 12-, 14-, and 18-membered channels have been characterized.[2−6] The Al/P ratio in all of the $AlPO_4$-*n* families normally synthesized hydrothermally is exclusively unity, and their framework is constructed by alternating tetrahedral Al and P connected by bridging oxygens. Recently, a number of aluminophosphates with nonunity Al/P ratios have been synthesized under solvothermal conditions (i.e., replacing water with an organic solvent) by judicious choice of the reaction conditions such as the gel composition, the template agent, and the temperature. These approaches have allowed access to a rich compositional and structural diversity that is not possible by conventional aqueous routes. Notable examples include JDF-20 (an open-framework aluminophosphate $[Al_5P_6O_{24}H]^{2-}$ with 20-membered ring channels that has an Al/P ratio of 5/6),[7] a series of two-dimensional layered aluminophosphate materials having $[Al_3P_4O_{16}]^{3-}$ units with an Al/P ratio of 3/4[8−10] and $[Al_2P_3O_{12}]^{3-}$ anion units with an Al/P ratio of 2/3,[11] and some one-dimensional chain aluminophosphate ($[AlP_2O_8]^{3-}$) materials with an Al/P ratio of 1/2.[12,13] It appears that the decrease of the Al/P ratio from unity lowers the dimensionality of the connectivity for the framework structure, due to the existence of the terminal oxygen groups bounded to the P atoms (with the exception of the three-dimensionally connected JDF-20[7]). However, it is to be noted that aluminophosphate materials with an Al/P ratio of 4/5 have not been observed. It is intriguing to know whether these aluminophosphates would be three-dimensionally or two-dimensionally connected. By using ethylene glycol as the solvent and 1,6-hexanediamine as the template, we have successfully synthesized a novel three-dimensionally connected microporous aluminophosphate $Al_{16}P_{20}O_{80}H_4\cdot 4C_6H_{18}N_2$ (designated AlPO-HDA) with an interconnected 12- and 8-membered ring channel system, which has an Al/P ratio of 4/5.

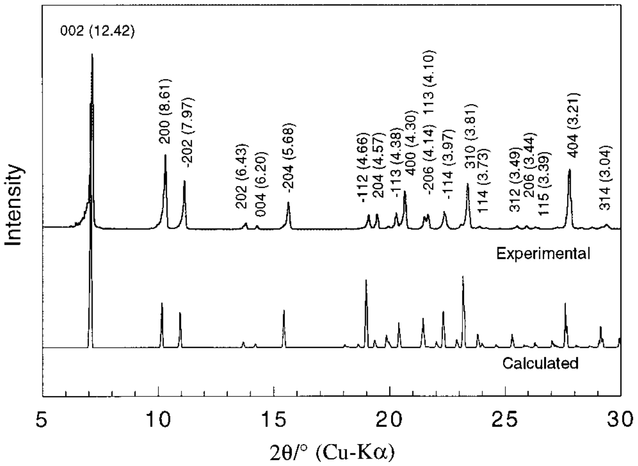

Figure 1. Experimental and simulated powder X-ray diffraction patterns of AlPO-HDA. The indices in the experimental XRD pattern are given for each reflection together with *d*-spacings (Å) in parentheses.

AlPO-HDA was synthesized from an alcoholic system in which ethylene glycol (EG) was used as the solvent and 1,6-hexanediamine (HDA) as the template. Aluminum triisopropoxide and phosphoric acid (85 wt %) were used as the aluminum and phosphorus sources, respectively. Typically, a homogeneous gel reaction mixture with the molar composition 1.0 Al_2O_3:1.8 P_2O_5:2.1 HDA:44 EG was sealed in a Teflon-lined stainless autoclave and heated at 200 °C for 12 days under autogenous pressure. The resulting product, containing colorless long platelike single crystals, was filtered and washed thoroughly with deionized water. Energy-dispersive X-ray analysis, using a JEOL 3010 electron

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Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters *U*(eq) ($Å^2 \times 10^3$) for $Al_{16}P_{20}O_{80}H_4 \cdot 4C_6H_{18}N_2$

atom	*x*	*y*	*z*	*U*(eq)[a]
Al(1)	8489(3)	702(2)	−804(1)	10(1)
Al(2)	8983(1)	−544(2)	1518(1)	10(1)
Al(3)	5144(1)	8914(3)	2929(1)	8(1)
Al(4)	7313(1)	4869(3)	2783(1)	10(1)
P(1)	6930(1)	9809(2)	3364(1)	9(1)
P(2)	5539(1)	3971(2)	2360(1)	8(1)
P(3)	8497(1)	4257(2)	2041(1)	9(1)
P(4)	8969(1)	5536(2)	−1328(1)	9(1)
P(5)	9271(1)	−157(2)	378(1)	15(1)
O(1)	6993(2)	2692(6)	3246(1)	15(1)
O(2)	6116(2)	9233(6)	3445(1)	13(1)
O(3)	7107(2)	8225(6)	2903(1)	14(1)
O(4)	7504(2)	873(6)	−1104(1)	13(1)
O(5)	6346(2)	4540(6)	2279(1)	14(1)
O(6)	9966(2)	−294(6)	1829(1)	14(1)
O(7)	5460(2)	1043(6)	2464(1)	13(1)
O(8)	5355(2)	5525(6)	2831(1)	13(1)
O(9)	7726(2)	4193(6)	2213(1)	16(1)
O(10)	4173(2)	8654(7)	2490(1)	18(1)
O(11)	8555(2)	6972(7)	1804(2)	26(1)
O(12)	8454(2)	2254(7)	1585(1)	20(1)
O(13)	4745(2)	9718(6)	3498(1)	14(1)
O(14)	8994(2)	3601(6)	−865(1)	14(1)
O(15)	8947(2)	8332(6)	−1115(1)	20(1)
O(16)	8287(2)	4891(7)	−1776(1)	20(1)
O(17)	8601(2)	−44(7)	−128(1)	21(1)
O(18)	8889(2)	−1003(7)	835(1)	19(1)
O(19)	9719(2)	2305(8)	481(2)	32(1)
O(20)	9832(2)	−2432(7)	303(2)	28(1)
N(1)	5638(3)	5678(8)	−1035(2)	23(1)
C(1)	6001(4)	5201(13)	−449(2)	37(1)
C(2)	6805(3)	6272(12)	−291(2)	34(1)
C(3)	7234(3)	5502(12)	270(2)	33(1)
C(4)	6825(3)	6053(11)	721(2)	29(1)
C(5)	6675(4)	9062(12)	781(2)	36(1)
C(6)	6191(8)	9630(2)	1242(5)	34(3)
C(6′)	6597(8)	9860(3)	1326(5)	35(3)
N(2)	6754(5)	9358(17)	1765(4)	28(2)
N(2′)	5904(5)	8507(17)	1435(3)	23(2)

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

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

Al(1)−O(17)	1.731(3)	Al(1)−O(4)	1.738(3)
Al(1)−O(15)#1	1.743(3)	Al(1)−O(14)	1.754(3)
Al(2)−O(11)#1	1.721(4)	Al(2)−O(18)	1.728(3)
Al(2)−O(12)	1.738(3)	Al(2)−O(6)	1.743(3)
Al(3)−O(7) #2	1.789(3)	Al(3)−O(8)	1.800(3)
Al(3)−O(13)	1.798(3)	Al(3)−O(10)	1.831(3)
Al(3)−O(2)	1.920(3)	Al(4)−O(3)	1.793(3)
Al(4)−O(9)	1.800(3)	Al(4)−O(1)	1.803(3)
Al(4)−O(16)#3	1.836(3)	Al(4)−O(5)	1.899(3)
P(1)−O(1)#2	1.513(3)	P(1)−O(3)	1.517(3)
P(1)−O(2)	1.529(3)	P(1)−O(4)#3	1.538(3)
P(2)−O(5)	1.516(3)	P(2)−O(7)	1.531(3)
P(2)−O(8)	1.535(3)	P(2)−O(6)#4	1.543(3)
P(3)−O(10) #5	1.489(3)	P(3)−O(9)	1.524(3)
P(3)−O(11)	1.525(4)	P(3)−O(12)	1.538(3)
P(4)−O(16)	1.498(3)	P(4)−O(15)	1.532(3)
P(4)−O(14)	1.532(3)	P(4)−O(13)#6	1.540(3)
P(5)−O(19)	1.477(4)	P(5)−O(18)	1.535(3)
P(5)−O(17)	1.544(3)	P(5)−O(20) #1	1.568(2)
N(1)−C(1)	1.506(7)	C(1)−C(2)	1.491(8)
C(2)−C(3)	1.513(8)	C(3)−C(4)	1.518(8)
C(4)−C(5)	1.573(8)	C(5)−C(6′)	1.483(13)
C(5)−C(6)	1.629(13)	C(6)−N(2)	1.479(15)
C(6′)−N(2′)	1.486(16)	O(20)−H(20)	0.82005(12)

P(1)#1−O(1)−Al(4)	141.2(2)	P(1)−O(2)−Al(3)	130.41(19)
P(1)−O(3)−Al(4)	136.7(2)	P(1)#8−O(4)−Al(1)	140.5(2)
P(2)−O(5)−Al(4)	131.1(2)	P(2)#5−O(6)−Al(2)	140.3(2)
P(2)−O(7)−Al(3)#1	139.8(2)	P(2)−O(8)−Al(3)	133.93(19)
P(3)−O(9)−Al(4)	141.3(2)	P(3)#4−O(10)−Al(3)	159.1(2)
P(3)−O(11)−Al(2)#2	156.0(2)	P(3)−O(12)−Al(2)	133.2(2)
P(4)#9−O(13)−Al(3)	138.6(2)	P(4)−O(14)−Al(1)	133.34(19)
P(4)−O(15)−Al(1)#2	149.4(2)	P(4)−O(16)−Al(4)#8	159.1(3)
P(5)−O(17)−Al(1)	137.2(2)	P(5)−O(18)−Al(2)	140.2(2)
P(5)#2−O(20)−H(20)	109.47(10)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, y - 1, z$; #2 $x, y + 1, z$ #3 $x, -y + 1, z + {}^1/_2$; #4 $x - {}^1/_2, y + {}^1/_2, z$; #5 $x + {}^1/_2, y - {}^1/_2, z$; #6 $x + {}^1/_2, -y + {}^3/_2, z - {}^1/_2$; #7 $x, -y, z + {}^1/_2$; #8 $x, -y + 1, z - {}^1/_2$; #9 $x - {}^1/_2, -y + {}^3/_2, z + {}^1/_2$.

microscope with Link ISIS 300, gave that the crystallites had an Al/P ratio of 4/5. A suitable crystal with dimensions of $0.05 \times 0.04 \times 0.13$ mm^3 was selected for single-crystal X-ray analysis.[14] The experimental and simulated powder X-ray diffraction (XRD) patterns of AlPO-HDA are shown in Figure 1. They are in agreement with each other, proving the phase purity of as-synthesized materials.

AlPO-HDA crystallizes in the monoclinic space group *Cc*.[14] Table 1 shows the final atomic coordinates and temperature factors for AlPO-HDA. The selected bond lengths and bond angles are given in Table 2. The structure of AlPO-HDA consists of an open-framework macroanion $[Al_4P_5O_{20}H]^{2-}$. Charge neutrality is achieved by the incorporation of the template in its diprotonated form ($^+H_3N(CH_2)_6NH_3^+$). Each asymmetric unit contains four crystallographically distinct Al atoms. Al(1) and Al(2) are tetrahedrally coordinated and share four oxygens with adjacent P atoms. The Al−O bond lengths (1.721(4)~1.754(3) Å) are within the typical ranges reported for other AlPO materials. Al(3) and Al(4) are pentacoordinated to five oxygen atoms (Al−O bond lengths: 1.789~1.920(3) Å) that form distorted trigonal bipyramids. Of the five crystallographically distinct PO_4 tetrahedra, four (P(1)−P(4)) have four bridging oxygens to adjacent Al atoms. The P−O bond lengths for P(1)−P(4) are in the range 1.489~1.543(3) Å. However, P(5) shares only two oxygens with adjacent Al atoms, leaving two oxygens, O(19) and O(20), terminal. The shorter bond length of P(5)−O(19) of 1.477 (4) Å implies some double bond character, while the longest bond length of P(5)−O(20) of 1.568(2) Å indicates a P(5)−O(20)H group. The H atom associated with O(20)

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(14) Data were collected on a Rigaku AFC7R diffractometer using monochromatic Mo Kα radiation generated by a rotating anode X-ray tube. The lattice constant was determined by the least-squares procedure applied to the θ values for 25 reflections ($12.1 < \theta < 15.8°$). Intensity data of 6525 independent reflections ($-24 \leq h \leq 24$, $0 \leq k \leq 7$, $-35 \leq l \leq 35$) were collected in the ω-scan mode up to $(\sin \theta/\lambda)_{max} = 0.704$, among which 5457 reflections had the condition $I > 2\sigma(I_{obs})$. Measured intensity data were corrected for Lorentz and polarization effects together with an absorption correction by means of a Ψ-scan algorithm. The structure was solved by direct methods (SIR92; Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M.; *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined using a least-squares program package (SHELXL-97; Sheldrick, G. M.; SHELXL 97, program for the refinement of crystal structures; University of Gottingen, Germany, 1997). During the isotropic refinement for framework positions and non-hydrogen atoms of the 1,6-hexanediamine (HDA) molecule, partial disordering nature of the HDA molecule was detected from difference Fourier maps. After introducing anisotropic temperature factors for framework positions, the possible H atom associated with O(20) was suggested by difference Fourier maps, and this prompted us to include H(20) with a common riding model (O−H = 0.82 Å). It was assumed that, in order for the structure to be charge balanced, the 1,6-hexanediamine is diprotonated. All H atoms on the diprotonated template molecule were also located geometrically AlPO-HDA: $Al_8P_{10}O_{40}C_{12}N_4H_{38}$, Mr = 1404.0, monoclinic space group *Cc* (no. 9), $a = 17.682(1)$ Å, $b = 5.108(1)$ Å, $c = 25.488(1)$ Å, $\beta = 103.07(1)°$, $Z = 2$, $Dc = 2.08$ Mg/m^3 , $F(000) = 1424$. The refinement converged to give a final $R = 0.0459$ for $I > 2\sigma(I_{obs})$ and $wR2 = 0.1126$.

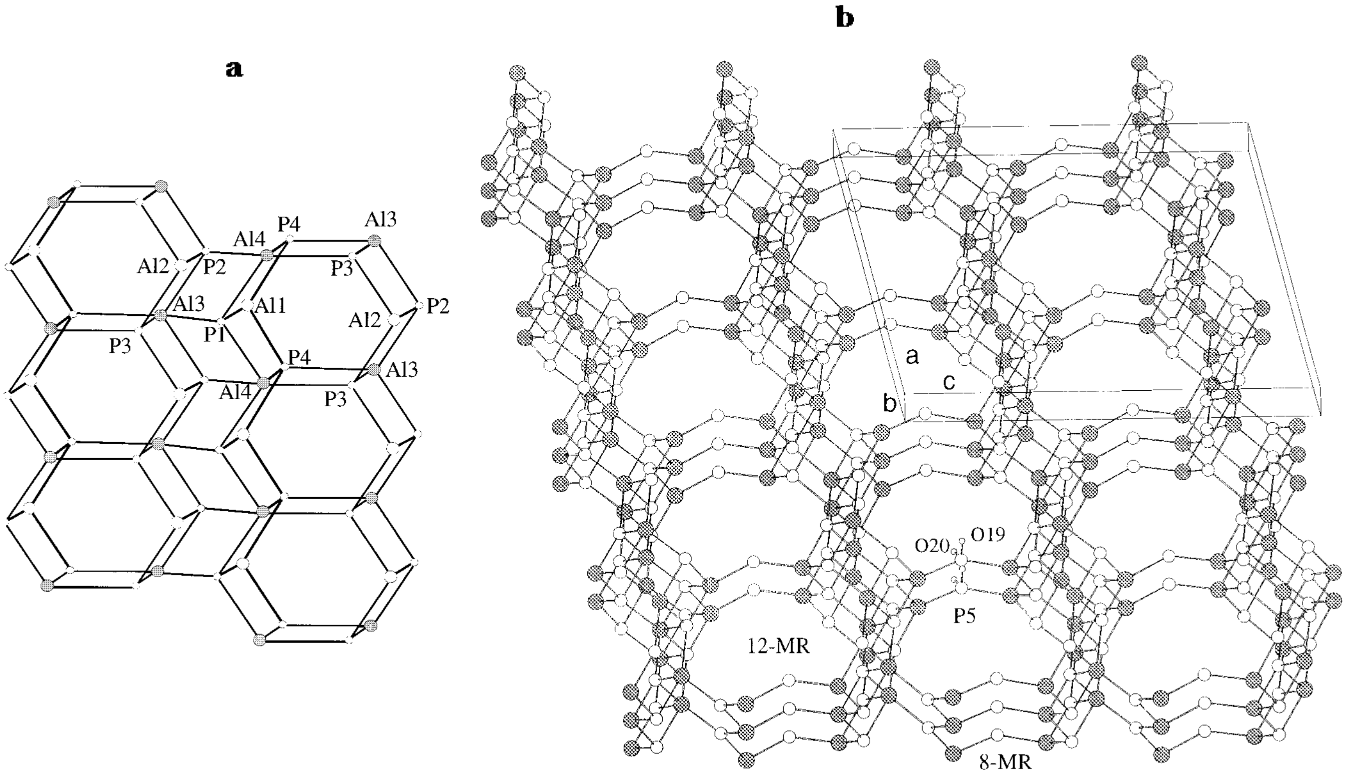

Figure 2. (a) Two columns of D6R connected through 4-MR. (b) Crystal structure of AlPO-HDA showing the 12-MR channels along [010] with intersecting 8-MR channels along [100]. (Al atoms: shaded. Only O(19) and O(20) connected to one P(5) atom are shown. Other bridging oxygens and templates are omitted for clarity.)

is found in the difference Fourier map. P atoms with two terminal oxygen groups, i.e., P=O and P−OH, have been found in the one-dimensional chain $[AlP_2O_8]^{3-}$ anions,[12] in which all the P atoms share only two oxygen atoms with adjacent tetrahedral AlO_4, wherease in the case of the 2-dimensional layer $[Al_3P_4O_{16}]^{3-}$ anions,[8,9] all the tetrahedrally coordinated P atoms share three oxygens with adjacent tetrahedral AlO_4 moieties, leaving one oxygen terminal (P=O/or P−OH). The existence of P atoms with terminal oxygen groups in AlPO-HDA results in the deviation of the Al/P ratio from unity, but the overall framework is three-dimensionally connected, as previously reported for JDF-20.[7]

The structure of AlPO-HDA is based on a network of strictly alternating Al units including tetrahedral AlO_4 and trigonal bipyramid AlO_5 and tetrahedral PO_4 and $PO_2(=O)(OH)$ moieties, in which all the vertices are shared except for the terminal oxygens bonded to P(5) atoms. The framework of AlPO-HDA is composed of a series of intact columns of double six-rings (share four rings possessing two five-coordinated Al atoms each other) stacked in the *b* direction. Figure 2a shows the connectivity of two columns of D6R as an illustration. It can be seen that the 5-coordinated Al atoms are essential for the formation of columns of D6R that are connected through 4-MR to form layers parallel to the (001) plane. It is noted that the two longest Al−O distances (Al(3)−O(2): 1.920(3) Å; Al(4)−O(5): 1.899(3) Å) come from the bonding between the sets of D6R, and these distances also correspond to narrow O−Al−O angles of 83.2 and 84.6° for O(13)−Al(3)−O(2) and O(9)−Al(4)−O(5), respectively. The layers are further connected together through P(5) tetrahedra to build up the three-dimensionally connected network with 12-MR channels along [010] which is intersected with 8-MR channels running along [100] (Figure 2b). It is noted that the entrance to the 12- and 8-membered ring channels has oxygen atoms protruding into it in a manner similar to that for JDF-20[7] and cloverite[15] (a gallophosphate with 20-membered ring openings). It is found that the O···O separation between O(19) and O(20) (bound to the adjacent P(5) atom in the 8-membered ring) is of 2.8 Å and indicates hydrogen bond linking between terminal oxygens along the *b* direction.

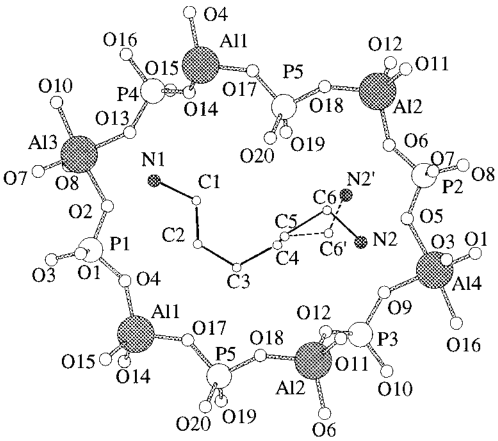

Figure 3. The 1,6-hexanediammonium trapped in the 12-membered ring, one end of the $-CH_2NH_3$ group being partially occupied (ca. 50%).

Compared with the known microporous materials including aluminosilicates and aluminophosphate-based compounds, AlPO-HDA exhibits unique structural fea-

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[15] Estermann, M.; McCusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320.

tures. None of these materials contains columns of D6R in such an arrangement as in AlPO-HDA.

The 1,6-hexanediamine molecules are trapped in the main 12-rings. Figure 3 shows the 1,6-hexanediammonium cation occupying the 12-ring with one end of the $-CH_2NH_3$ group partially disordered (ca. 50% occupancy). It appears that three protons of each $-CH_2NH_3^+$ group preferentially make H-bonds with oxygens coordinated to the pentacoordinated Al atoms, characterized by a [N···O] separation of about 3.0 Å. The partial disorder of the template may arise from N(2)′−H···O(19) bond, as inferred from the short N···O distance of 2.9 Å.

Thermogravimetric analysis shows only one major mass loss of about 17% in the region 400−550 °C, which is correlated to the decomposition of the occluded 1,6-hexanediamine (the theoretical weight loss is 16.5%). Elemental analysis gives C: 11.0; H: 3.2; N: 5.1% in AlPO-HDA (Calc C: 10.3; H: 2.7; N: 4.9%), which further proves the amount of 1,6-hexanediamine according to the formula proposed from the structure analysis. X-ray powder diffraction study indicates that the structure of AlPO-HDA is stable up to 600 °C.

In conclusion, a novel open-framework aluminophosphate with an Al/P ratio of 4/5 has been successfully synthesized in an alcoholic system. The structure is featured by intersecting 12-MR and 8-MR channels. This work further demonstrates the rich compositional and structural diversity in the aluminophosphate families.

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Supporting Information Available: Full details of the structure solution of AlPO-HDA, including the atomic coordinates, anisotropic temperature factors, hydrogen coordinates and isotropic displacement parameters, and bond lengths and bond angles (9 pages). Ordering information is given on any current masthead page.

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