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Structure of an Unusual Aluminium Phosphate ($[Al_5P_6O_{24}H]^{2-}$ $2[N(C_2H_5)_3H]^+ \cdot 2H_2O$) JDF-20 with Large Elliptical Apertures

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The structure and thermal properties of a new large-pore three-dimensional aluminophosphate are reported. The P/Al ratio of this compound is 6 : 5, the structure consists of Al- centered and P- centered tetrahedra in which all the Al vertices are shared, but not all the P vertices, giving rise to an interrupted structure type. The framework contains 20-membered rings with elliptical apertures having a free diameter of 6.2 by 14.5 Å intersected by smaller 10- and 8-membered rings. In these channels are water molecules and triethylammonium cations which are hydrogen bonded to the framework. The space group of the compound is $C2/c$, with a = 32.035(12), b = 14.308(3), c = 8.852(2) Å, β = 104.65(2)°, and V = 3925.6 Å^3. The crystal structure has been refined to yield residuals of R = 0.126 and R_w = 0.113. © 1993 Academic Press, Inc.

Introduction

Crystalline microporous aluminosilicates (zeolites) and their derivatives have been extensively used as selective adsorbents, sensors, ion exchangers, heterogeneous catalysts (*1*, *2*), and potential hosts for novel low-dimensional electronic quantum wire (*3*) or quantum dot (*4*) conductors. However, the largest pores that occur among naturally occurring and synthetic zeolites are limited to so-called 12-membered rings (*5*). Efforts to synthesize larger-pore zeolites have so far failed, but the successful synthesis of a series of microporous aluminophosphates, possessing properties similar to, and often more selective than, those of zeolites has been achieved since 1982 (*6*, *7*). Much attention has been focused on this new family of microporous materials and

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their framework-substituted transition metal derivatives which *inter alia* exhibit high catalytic selectivity (*8*). VPI-5 (*9*), a new member of this family has nonintersecting one-dimensional circular channels of 18-membered ring apertures, the largest size so far reported for the aluminium phosphate (ALPO) family. Here we describe a novel microporous templated ALPO composed of 20-membered ring apertures very different from a recently reported (*10*) gallium phosphate, which also has 20-membered rings, and from all other microporous aluminophosphates. To our knowledge the nature of the pores in this new material, which we designate JDF-20, is unique.

Synthesis

JDF-20, like many of the other novel chain (*11*) sheet (*12*) and three-dimensionally (*13*) extended aluminium phosphates that we have recently prepared and characterized, was synthesized from a predominantly nonaqueous system in which triethylene glycol (TEG) was used as a solvent and triethylamine (TEA) was the nitrogenous template. The reaction mixture had a starting composition of 4.7 TEA : 1.0 Al_2O_3 : 1.8 P_2O_5 : 18 TEG. This was heated at 180°C for 5 days under autogenous conditions. In due course a crystalline product emerged, was filtered off, washed with water, and dried at ambient temperature.

Characterization and Determination of the Structure

The as-synthesised compound exhibits an X-ray powder diffraction pattern that does not correspond to any known compound (recorded in various data bases). Thermogravimetric and thermal analysis show that JDF-20 loses water during an endothermic change at ca 300°C, at which temperature template decomposition is extensive. From the single crystal X-ray analysis the formula is $Al_5P_6O_{24}H\ 2Et_3NH \cdot 2H_2O$. Thermogravimetric analyses indicated weight losses of between 25 and 29%, in agreement with the X-ray-derived formula. Elemental analysis by energy dispersive X-ray emission using a JEOL 2000 FX electron microscope confirmed that the P : Al ratio was close to 1.2 : 1 and quite uniform in a spatial sense. Upon calcination at 500°C, samples of JDF-20 turn black, and X-ray powder diffraction shows that it is a mixture of the microporous solid ALPO-5 (*14*) and the aluminium phosphate analogue to tridymite, the relative proportions of these two solids being dependent upon the rate of heating of the sample. The manner in which this remarkable structure changes merits further study.

Crystal data for $[Al_5P_6O_{24}H]^{2-}$ $2[N(C_2H_5)_3H]^+ \cdot 2H_2O$, M: 946.17, monoclinic, space group: $C2/c$, with a = 32.035(12), b = 14.308(3), c = 8.852(2) Å, β = 104.65(2)°, V = 3925.6 Å^3, D_c = 1.601 g cm^{-3}, Z = 4 μ(CuKα) = 44.917 cm^{-1} = 44.916 cm^{-1}. Data were collected using an Enraf–Nonius CAD4 – diffractometer using graphite monochromated CuK_α radiation (λ = 1.5418 Å). A total of 9302 reflections were collected ($2\theta < 150°$) which gave 3491 unique reflections of which 1257 were considered to be observed $I > 3\ \sigma(I)$. The structure was solved by direct methods (*15*) and refined by full-matrix least-squares (*16*) to give residuals of R = 0.126, R_w = 0.113. It proved possible to locate the templating triethylammonium cation and a water molecule in the channels of the structure. One of the ethyl chains of the triethylammonium cation was disordered, and restraints were applied to maintain the geometry of the two orientations. The largest peak in the final difference map was 1.48 eÅ^{-3} and was situated 0.948 Å from P(1). Complex neutral scattering factors were taken from "International Tables from Crystallography," Vol. IV (*17*).

Description of the Structure and Discussion

The atomic coordinates and isotropic thermal parameters (U(equiv) and U(iso)),

TABLE I

ATOMIC COORDINATES AND *U*(equiv) OR *U*(iso) WITH e.s.d.'s IN PARENTHESES

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(equiv)/*u*(iso)
P(1)	−0.0430(1)	0.6194(3)	−0.0927(5)	0.0183
P(2)	−0.1887(1)	0.4649(3)	−0.0169(6)	0.0145
P(3)	−0.1808(1)	0.7831(3)	−0.0051(6)	0.0137
Al(1)	0.0000	0.4603(5)	−0.2500	0.0216
Al(2)	−0.2286(2)	0.6278(4)	0.1454(6)	0.0178
Al(3)	−0.1455(2)	0.6189(4)	−0.1767(6)	0.0168
O(1)	−0.0357(4)	0.5292(9)	−0.179(2)	0.035(3)
O(2)	−0.0199(4)	0.7014(8)	−0.147(1)	0.026(3)
O(3)	−0.0904(5)	0.640(1)	−0.132(2)	0.042(4)
O(4)	−0.0287(4)	0.609(1)	0.087(2)	0.041(4)
O(5)	−0.2204(4)	0.5290(9)	0.034(1)	0.030(3)
O(6)	−0.2136(4)	0.4032(9)	−0.151(2)	0.035(3)
O(7)	−0.1550(4)	0.522(1)	−0.070(2)	0.038(3)
O(8)	−0.1659(4)	0.5976(9)	−0.382(2)	0.033(3)
O(9)	−0.2183(4)	0.8462(9)	−0.091(1)	0.029(3)
O(10)	−0.1969(4)	0.7200(9)	0.114(2)	0.034(3)
O(11)	−0.1711(4)	0.720(1)	−0.136(2)	0.037(3)
O(12)	−0.1418(4)	0.835(1)	0.079(2)	0.042(3)
O(100)	0.0754(7)	0.130(2)	0.079(3)	0.099(7)
N(1)	0.6116(6)	0.355(1)	0.099(2)	0.048(5)
C(1)	0.6107(9)	0.259(2)	0.028(3)	0.071(8)
C(2)	0.5881(9)	0.186(2)	0.104(3)	0.063(7)
C(3)	0.635(1)	0.423(2)	0.020(4)	0.079(9)
C(4)	0.681(1)	0.403(3)	0.059(5)	0.13(2)
C(5)	0.5671(8)	0.391(2)	0.095(3)	0.09(1)
C(6)	0.538(1)	0.401(3)	−0.071(4)	0.11(2)
C(61)	0.546(4)	0.34(1)	0.21(2)	0.11(2)

interatomic distances, and angles are listed in Tables I, II, and III, respectively.

Despite the final poor residuals for the structure (which may be the result of crystallographic twinning) the derived metrical parameters (av Al–O 1.758 Å, av P–$O_{bridging}$ 1.537 Å) are comparable with those of related structures, e.g., in α-berlinite the corresponding values are 1.739 and 1.516 Å (*18*). A bond-valence calculation (*19*) shows that the two terminal oxygen O(2) and O(12) atoms have unsatisfied valencies. These two oxygens are satisfied in different ways: O(12) has strong hydrogen-bonding interactions with both the adsorbed water molecule O–O 2.87(3)Å and the template ion, O–N 2.78(2) Å. In O(2) the observed O–O separation of 2.48(2) Å between two symmetry-related oxygen atoms indicates a strong, ostensibly symmetric, hydrogen bond. The residual valency requirements of O(2) seem to be satisfied by the location of a hydrogen atom midway between the symmetry-related atoms, though there may be a weak hydrogen bond to the occluded water molecule O(2)–O(100) 3.14 (3).

The main feature of the structure of JDF-20 is a main 20-membered ring system with elliptical apertures having a free diameter of 6.2 by 7.9 Å (Fig. 1). Intersecting this channel are two others (Fig. 2), the larger of these consisting of irregular 10-rings, the smaller of fairly regular 8-rings. The entrance to the main channel has oxygen atoms projecting into the channel in a manner similar to the situation that obtains in cloverite (*10*), where four hydroxyl groups protrude into the channel. In JDF-20, however, there are

TABLE II

INTERATOMIC CONTACTS IN Å WITH e.s.d.'s IN PARENTHESES

P(1)–O(1)	1.550(14)
P(1)–O(2)	1.526(12)
P(1)–O(3)	1.498(14)
P(1)–O(4)	1.546(15)
P(2)–O(5)	1.519(13)
P(2)–O(6)	1.535(14)
P(2)–O(7)	1.522(14)
P(2)–O(8)	1.524(14)
P(3)–O(9)	1.546(13)
P(3)–O(10)	1.573(13)
P(3)–O(11)	1.558(13)
P(3)–O(12)	1.483(15)
Al(1)–O(1)	1.740(14) × 2
Al(1)–O(4)	1.802(14) × 2
Al(2)–O(5)	1.782(13)
Al(2)–O(6)	1.797(15)
Al(2)–O(9)	1.687(12)
Al(2)–O(10)	1.729(14)
Al(3)–O(3)	1.736(15)
Al(3)–O(7)	1.743(15)
Al(3)–O(8)	1.792(14)
Al(3)–O(11)	1.750(14)
N(1)–C(1)	1.51(3)
N(1)–C(3)	1.51(4)
N(1)–C(5)	1.51*
C(1)–C(2)	1.52(4)
C(3)–C(4)	1.44(5)
C(5)–C(6)	1.54[a]
C(5)–C(61)	1.54[a]

[a] A restraint was applied to the bond.

TABLE III

INTERATOMIC ANGLES IN ° WITH e.s.d.'s IN PARENTHESES

O(2)–P(1)–O(1)	109.7(7)
O(3)–P(1)–O(1)	108.5(8)
O(3)–P(1)–O(2)	108.6(8)
O(4)–P(1)–O(1)	112.7(8)
O(4)–P(1)–O(2)	110.9(7)
O(4)–P(1)–O(3)	106.2(8)
O(6)–P(2)–O(5)	108.6(7)
O(7)–P(2)–O(5)	110.2(8)
O(7)–P(2)–O(6)	110.1(8)
O(8)–P(2)–O(5)	110.2(7)
O(8)–P(2)–O(6)	108.8(7)
O(8)–P(2)–O(7)	108.9(8)
O(10)–P(3)–O(9)	108.7(7)
O(11)–P(3)–O(9)	104.4(7)
O(11)–P(3)–O(10)	109.3(7)
O(12)–P(3)–O(9)	114.1(7)
O(12)–P(3)–O(10)	109.1(8)
O(12)–P(3)–O(11)	111.1(8)
O(1)–Al(1)–O(1)	111.0(10)
O(4)–Al(1)–O(1)	105.8(6)
O(4)–Al(1)–O(1)	110.5(6)
O(4)–Al(1)–O(1)	110.5(6)
O(4)–Al(1)–O(1)	105.8(6)
O(4)–Al(1)–O(4)	113.2(10)
O(6)–Al(2)–O(5)	108.7(6)
O(9)–Al(2)–O(5)	107.2(6)
O(9)–Al(2)–O(6)	109.6(6)
O(10)–Al(2)–O(5)	110.0(6)
O(10)–Al(2)–O(6)	109.2(7)
O(10)–Al(2)–O(9)	112.1(7)
O(7)–Al(3)–O(3)	108.7(7)
O(8)–Al(3)–O(3)	110.3(7)
O(8)–Al(3)–O(7)	110.3(7)
O(11)–Al(3)–O(3)	108.2(7)
O(11)–Al(3)–O(7)	113.1(7)
O(11)–Al(3)–O(8)	106.2(7)
Al(1)–O(1)–P(1)	147.7(10)
Al(3)–O(3)–P(1)	158.7(10)
Al(1)–O(4)–P(1)	146.7(10)
Al(2)–O(5)–P(2)	147.8(9)
Al(2)–O(6)–P(2)	150.9(9)
Al(3)–O(7)–P(2)	146.0(10)
Al(3)–O(8)–P(2)	150.9(9)
Al(2)–O(9)–P(3)	151.0(9)
Al(2)–O(10)–P(3)	148.3(9)
Al(3)–O(11)–P(3)	145.4(9)
C(3)–N(1)–C(1)	110.5(19)
C(5)–N(1)–C(1)	112.6(20)
C(5)–N(1)–C(3)	110.6(22)
C(2)–C(1)–N(1)	113.7(21)
C(4)–C(3)–N(1)	111.1(28)
C(6)–C(5)–N(1)	113.7[a]
C(61)–C(5)–N(1)	114.1[a]

[a] Restraints were applied to atoms involved in this bond.

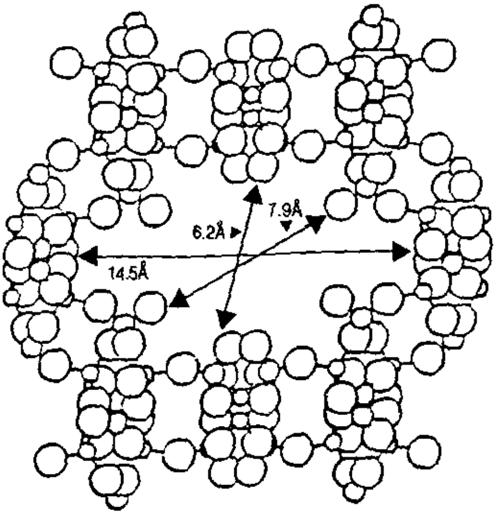

FIG. 1. View along the channel showing the internal dimensions of the channel. The circles in order of dimimshing size represent O, P, and Al.

four P=O groups and two O—H—O units, defining a star shape.

JDF-20 thus falls in the class of three-dimensional open framework solids possessing an interrupted framework structure, comparing cloverite (*10*), the naturally occurring iron mineral cacoxenite (*20*), and two recently reported zinc phosphates (*21*). The role of such features in facilitating the synthesis of new large-pore materials is noteworthy. An additional interesting feature of JDF-20 is the aluminium-to-phosphorous ratio of 5 : 6 which does not fall into the Al/P ratio of 1 : 1 previously seen in three-dimensional phosphates, clearly extending the scope for the synthesis of large-pore aluminophosphate compounds.

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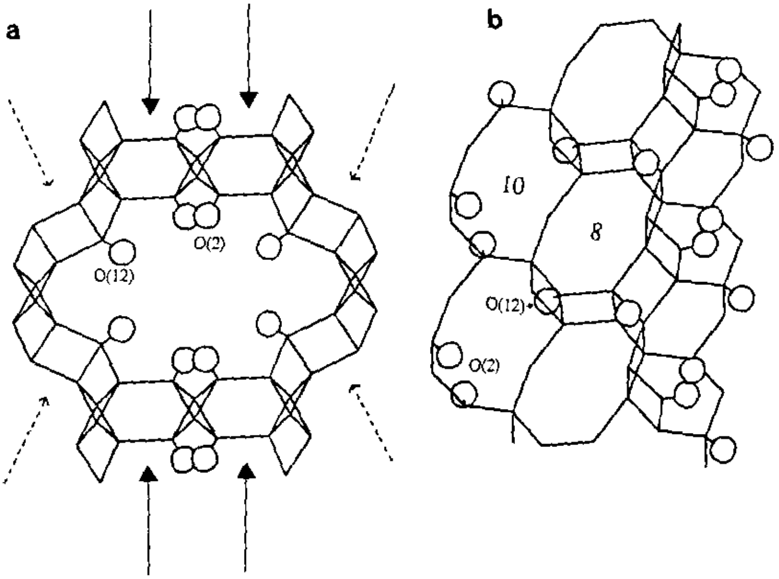

FIG. 2. (a) View of the elliptical 20-ring channel showing the connectivity of the tetrahedral sites, the location of those oxygen atoms protruding into the channel and of the 10- and 8-membered rings; (→) refers to the 10-rings, (---→) refers to 8-rings. (b) View of the 10- and 8-membered window openings.

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