JOURNAL OF SOLID STATE CHEMISTRY 89, 392–395 (1990)

Synthesis and Characterization of a Novel Aluminophosphate with Layer Structure

WANG TIELI,* YU LONG†‡, AND PANG WENQIN†

*Institute of Theoretical Chemistry, and †Department of Chemistry, Jilin University, Changchun, People's Republic of China

Communicated by J. M. Honig, September 20, 1990

An aluminophosphate with a layer structure has been synthesized hydrothermally. The ratio P/Al = 2 for the framework; its structure consists of Al-centered tetrahedra and P-centered tetrahedra as basic building units to form a two-dimensional layer structure. The protonated ethylenediamine molecules are located in the interlayer space and sustain the framework. The water molecules are located in the space between two layers. Layers are joined together by van der Waals force to form a three-dimensional structure which crystallizes in the space group *Pbnb*, with $a = 8.052(6)$, $b = 8.760(2)$, $c = 17.037(7)$ Å, and $V = 1201.88$ Å^3. The crystal structure has been refined to yield values of $R = 0.0418$, $R_w = 0.0447$.

Introduction

Since the first series of microporous aluminophosphates, denoted as $AlPO_4$-*n*, was prepared in 1982 (*1*), these materials have been extensively studied (*2–5*). Some of them are isostructural with known zeolites, but a majority has novel structures (*6*). We synthesized a novel aluminophosphate, named $AlPO_4$-CJ, by the hydrothermal method. The framework of the sample has a unique layer structure, for which the ratio P/Al = 2.

Synthesis

The title compound ($AlPO_4$-CJ) was synthesized by a hydrothermal method. An aqueous mixture of aluminum hydroxide, phosphoric acid, and ethylenediamine with the gel composition 1.0 Al_2O_3 : 1.6 P_2O_5 : 1.8 ethylenediamine : 2.0 NH_4F : 60 H_2O was heated at 150°C for 12 days under autogenous pressure. The product was filtered, washed with distilled water, and dried in air at about 80°C. Excellent single crystals suitable for structural analysis by X-ray diffraction could be selected. Comparison with the characteristic X-ray powder diffraction pattern of the $AlPO_4$ framework reported so far indicated that the product synthesized has a novel structure.

Determination of the Structure

A colorless crystal was selected. The crystal data: orthorhombic system; space group: *Pbnb* with $a = 8.052(6)$, $b = 8.760(2)$, $c = 17.037(7)$ Å, and $V = 1201.88$ Å^3; $Z = 8$; $F(000) = 576$; MU = 4.49 cm^{-1}; $\mu(Mo_3K\alpha) = 67$ cm^{-1}; $\lambda = 0.7107$ Å; graphite monochromator; crystal dimensions 0.1 × 0.1 × 0.5 mm; $R = 0.0418$; $R_w = 0.0487$;

‡To whom correspondence should be addressed.

0022-4596/90 $3.00

TABLE I

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS (Å^2 $\times$ 10^3)

Atom	X	Y	Z	U
P	613(0)	8622(0)	6478(0)	15(0)*
O(1)	−1257(2)	8707(1)	6502(1)	31(0)*
O(2)	1297(2)	8492(2)	5657(1)	33(0)*
O(3)	1122(2)	7234(2)	6978(1)	43(0)*
O(4)	1327(3)	10050(2)	6873(1)	51(1)*
O_w	2500(0)	3829(4)	2500(0)	45(1)*
Al	2500(0)	11136(1)	7500(0)	14(0)*
N	2145(3)	5855(2)	4897(1)	23(1)*
C	516(4)	5211(4)	4645(2)	27(1)*
H_1	2049(36)	6673(31)	5200(16)	
H_2	2656(40)	6108(33)	4480(22)	
H_3	2674(44)	5259(39)	5202(17)	
H_4	618(35)	4189(37)	4309(18)	
H_5	36(42)	5967(41)	4254(23)	
H_6	1873(49)	3298(43)	2847(21)	

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor.

for 1312 unique observed reflections with $I \geq 3\ \sigma\ (I_0)$ collected at 20°C on a Nicolet R3 four-circle diffractometer by using the ω-scan technique with variable scan speed from 4.0 to 29.3° min^{-1} in the range of $3° \leq 2\theta \leq 67°$. The structure was solved by direct methods and refined by block-matrix least-squares. All computations were carried out on an Eclipse S/250 computer using the SHELXTL program. All atoms were located from a difference Fourier map.

TABLE II

BOND LENGTHS (Å)

P–O(1)	1.508(2)	P–O(2)	1.510(4)
P–O(3)	1.539(2)	P–O(4)	1.533(2)
Al_a–O(3)	1.717(2)	Al–O(4)	1.714(3)
Al–O(3a)	1.717(2)	Al–O(4a)	1.714(3)
Al–O(3b)	1.717(2)	N(1)–C(1)	1.491(4)
C(1)–C(1a)	1.513(6)	N(1)–H(1)	0.886(28)
N(1)–H(2)	0.852(36)	N(1)–H(3)	0.851(33)
C(1)–H(4)	1.067(33)	C(1)–H(5)	1.015(38)
O_w–H(6)	0.906(38)	O_w–H(6a)	0.906(38)

TABLE III

BOND ANGLES (Degrees)

O(1)–P–O(2)	113.2(1)	O(1)–P–O(3)	106.9(1)
O(2)–P–O(3)	110.9(1)	O(1)–P–O(4)	108.8(1)
O(2)–P–O(4)	109.4(1)	O(3)–P–O(4)	107.6(1)
P–O(3)–Al_a	154.3(2)	P–O(4)–Al	159.0(2)
O(4)–Al–O(3a)	110.1(1)	O(4)–Al–O(3b)	106.1(1)
O(3a)–Al–O(3b)	111.9(2)	O(4)–Al–O(4a)	112.6(2)
O(3a)–Al–O(4a)	106.1(1)	O(3b)–Al–O(4a)	110.1(1)
N–C(1)–C(1a)	110.2(3)	H(1)–N–C(1)	113.4(1.9)
H(2)–N–C(1)	106.4(2.3)	H(3)–N–C(1)	112.6(2.4)
H(1)–N–H(2)	108.5(2.8)	H(1)–N–H(3)	100.7(2.9)
H(2)–N–H(3)	115.3(3.2)	H(4)–C(1)–N	113.9(1.6)
H(3)–C(1)–N	106.1(2.0)	H(4)–C(1)–H(5)	103.0(2.7)
H(4)–C(1)–C(1a)	105.4(1.7)	H(5)–C(1)–C(1a)	118.3(2.0)
H(6)–O_w–H(6a)	118.1(4.8)		

Description of the Structure and Discussion

The atomic coordinates and equivalent thermal parameters (Ueq), interatomic distances, and angles are listed in Tables I, II, and III, respectively.

The structural analysis indicates that the structure consists of Al-centered tetrahedra and P-centered tetrahedra. The composition of the product corresponds to the asymmetric unit content $AlP_2O_8 \cdot H_3^+NCH_2CH_2N^+H_3 \cdot H_2O$. The coordination environment of Al and P atoms in the asymmetric unit is shown in Fig. 1. Each Al atom is tetrahedrally coor-

TABLE IV

ANISOTROPIC TEMPERATURE FACTORS (Å^2 $\times$ 10^3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	16(0)	15(0)	17(0)	−1(0)	−4(0)	0(0)
O_1	17(1)	47(1)	29(1)	6(1)	−2(1)	4(1)
O_2	43(1)	29(1)	26(1)	−3(1)	14(1)	−1(0)
O_3	38(1)	37(1)	52(1)	22(1)	−11(1)	8(1)
O_4	64(2)	36(1)	53(1)	−20(1)	−17(1)	−14(1)
O_w	41(2)	48(2)	46(2)	0(0)	11(2)	0(0)
Al	18(0)	11(0)	14(0)	0(0)	0(0)	0(0)
N	22(1)	24(1)	23(1)	0(0)	3(1)	−1(1)
C	23(1)	36(1)	21(1)	0(0)	2(1)	−8(1)
H_1	23(8)					
H_2	31(9)					
H_3	40(9)					
H_4	29(8)					
H_5	49(10)					
H_6	99(18)					

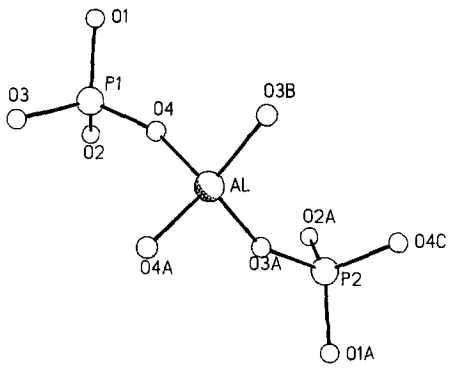

FIG. 1. Asymmetric unit of $AlPO_4$-CJ.

dinated and shares an oxygen atom with an adjacent phosphorus atom. Each P atom is also tetrahedrally coordinated, but it has two terminal oxygens. Two of the four types of oxygen atoms are bonded to one P atom. O_w represents the position of a water molecule.

The structure of $AlPO_4$–CJ consists of infinite two-dimensional layers. In the structure, AlO_4 and PO_4 tetrahedra form four-membered rings, which then form infinite one-dimensional chains by sharing Al atoms. The nonbonded distance H_1–O_2 is

TABLE V

NONBONDED DISTANCE (Å)

H(1)–O(2)	1.873
H(3)–O(2)	1.918
H(2)–O(1)	1.896

1.873 Å, H_3–O_2 is 1.918 Å and H_2–O_1 is 1.896 Å as obtained from Table V. Thus, the hydrogen atoms of the protonated ethylenediamine molecules form hydrogen bonds, with a terminal oxygen belonging to the P atoms. Via these hydrogen bonds, protonated ethylenediamine molecules, connect adjacent chains composed of AlO_4 and PO_4 tetrahedra. This results in two-dimensional layers. Infinite layers are joined together by van der Waals forces to form the three-dimensional structure. The stereoview of the $AlPO_4$-CJ framework along the *a*-axis is shown in Fig. 2. The water molecules are located in the space between one layer and another. We omit the water molecules in Fig. 2 for clarity.

In the synthesis of the product, the ethylenediamine molecules were used as the tem-

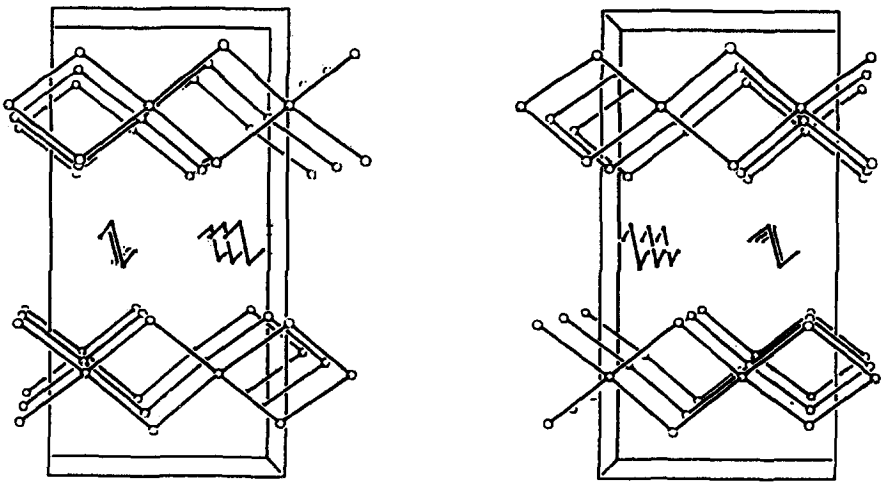

FIG. 2. Stereoview of the framework of $AlPO_4$-CJ along the *a*-axis, showing connections between alternating Al and P atoms, which are represented by circles. There are ethylenediamine molecules protonated between two chains.

plating agent; the X-ray diffraction shows that protonated ethylenediamine molecules are located in the interlayer space and sustain the framework.

In summary, we have synthesized a novel aluminophosphate crystal with a layer structure. One of the unique structural features is that the molar ratio of P/Al of the framework has the value 2. Another feature is that the phosphorus atom has two terminal oxygens. Protonated ethylenediamine molecules sustain the two-dimensional structure by hydrogen bonding, and the three-dimensional framework is formed by infinite layers connected by van der Waals forces.

References

1. S. T. WILSON, B. M. LOK, C. A. MESSINA, T. R. CANNAN, AND E. M. FLANIGEN, *J. Amer. Chem. Soc.* **104,** 1146 (1982).
2. J. M. BENNETT, W. J. DYTRYCH, J. J. PLUTH, J. W. RICHARDSON, JR. AND J. V. SMITH, *Zeolites* **6,** 349 (1986).
3. E. M. FLANIGEN, B. M. LOK, R. L. PATTON, AND S. T. WILSON, "Proceedings of the 7th International Zeolite Conference," p. 103, Kadasha, Elsevier (1986).
4. J. V. SMITH, *Chem. Rev.* **88,** 149 (1988).
5. J. B. PARISE, AND C. S. DAY, *Acta Crystallogr. Sect. C* **41,** 515 (1985).
6. M. E. DAVIS, C. SALDARRIAGA, C. MONTES, J. GARCES, AND C. CROWDER, *Nature (London)* **331,** 698 (1988).