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*Acta Cryst.* (1986). C42, 1118–1120

## Hydrated Aluminophosphate ( $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$ ) with $\text{PO}_4$ , $\text{AlO}_4$ and $\text{AlO}_4(\text{H}_2\text{O})_2$ Groups and Encapsulated Water

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(Received 23 December 1985; accepted 17 April 1986)

**Abstract.** Aluminium phosphate hydrate,  $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$ ,  $M_r = 148.98$ , orthorhombic, *Pbca*,  $a = 19.3525$  (13),  $b = 9.7272$  (7),  $c = 9.7621$  (8) Å,  $V = 1837.7$  (2) Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 2.15$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 68.2$  cm<sup>-1</sup>,  $F(000) = 1200$ ,  $T \sim 295$  K,  $R = 0.033$  for 1530 diffractions. A 4-connected framework contains  $\text{PO}_4$  tetrahedra interposed between  $\text{AlO}_4$  tetrahedra and  $\text{AlO}_4(\text{H}_2\text{O})_2$  octahedra at the nodes of cross-linked alternate  $6^3$  and  $4.8^2$  nets. A two-dimensional channel system, limited by 8-rings, lies between adjacent  $6^3$  nets. One  $\text{H}_2\text{O}$  of each octahedron lies in a 6-ring, and the other forms a continuous chain with a third  $\text{H}_2\text{O}$  which is held in place only by hydrogen bonds.

**Introduction.** Variscite, metavariscite, and new hydrates of  $\text{AlPO}_4$  (including  $H_1$ – $H_4$ ) were synthesized by d'Yvoire (1961). We have determined the crystal structure of a hydrated aluminophosphate,  $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$ , whose new type of framework topology is described by Pluth & Smith (1985) and which resembles the species  $H_3$  of d'Yvoire.

**Experimental.** Crystals of  $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$  were isolated from a synthetic mixture exhibiting X-ray powder diffraction lines similar to those of the  $H_3$  reported by d'Yvoire. Square prismatic needle elongated on **b** ( $0.04 \times 0.04 \times 0.22$  mm) after Weissenberg photographic examination for space group and preliminary cell-parameter determination coated with oil to control humidity, mounted on automated Picker–Krisel 4-circle

diffractometer with **b** offset  $7^\circ$  from  $\phi$  axis. Refinement using 20 diffractions ( $41 < 2\theta < 77^\circ$ ), each the average of automatic centering of the 8 possible settings, gave cell parameters. 19 551 measured intensities averaged to produce 1530 merged intensities ( $R_{\text{int}} = 0.027$ ), all with  $I > 0$ , max.  $\sin \theta/\lambda = 0.58$  Å<sup>-1</sup>; data collection range  $h \pm 22$ ,  $k \pm 11$ ,  $l \pm 11$ ; max. intensity variation of 3 standard reflections 1.7%. Absorption correction using analytical method gave transmission factors 0.62–0.78. Initial phase determination from *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) followed by Fourier refinement. Positions for four H atoms attached to O(9) and O(10) from difference Fourier synthesis, but least-squares refinement unsatisfactory. In final model, isotropic H atoms constrained at 0.85 Å from neighboring O atom. In contrast to these two water molecules, which are bonded to Al(2), the last oxygen O(11), is not within bonding distance of any Al. It is presumed to be part of a water molecule, held only by hydrogen bonds, whose H atoms are too disordered to be located from the Fourier synthesis. Final least-squares refinement\* minimized all  $F$ 's with  $\sigma_F$  computed from  $\sigma$ , the square root of [total counts + (2% of total counts)<sup>2</sup>],  $w = \sigma_F^{-2}$ ,  $R = 0.033$ ,  $wR = 0.039$ ,  $S = 4.8$ ;

\* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42992 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positions and mean-square displacements ( $\text{\AA}^2$ ) of  $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$ 

For non-H atoms  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i, \mathbf{a}_j)$ ; for H atoms  $U_{\text{iso}}$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
P(1)	0.44769 (4)	0.34071 (8)	0.13498 (9)	0.0084 (2)
P(2)	0.29050 (4)	0.06565 (8)	0.33879 (9)	0.0078 (2)
Al(1)	0.44808 (4)	0.08470 (9)	0.32419 (10)	0.0089 (3)
Al(2)	0.28207 (5)	0.33224 (9)	0.14654 (10)	0.0079 (3)
O(1)	0.37433 (10)	0.3765 (2)	0.1701 (2)	0.0146 (7)
O(2)	0.46047 (12)	0.1662 (2)	0.4804 (2)	0.0174 (7)
O(3)	0.49520 (10)	0.4497 (2)	0.1971 (2)	0.0163 (7)
O(4)	0.46889 (11)	0.2004 (2)	0.1942 (2)	0.0134 (7)
O(5)	0.27397 (10)	0.0582 (2)	0.4913 (2)	0.0114 (7)
O(6)	0.36522 (10)	0.0190 (2)	0.3136 (2)	0.0160 (7)
O(7)	0.28329 (11)	0.2158 (2)	0.2953 (2)	0.0133 (7)
O(8)	0.25855 (10)	0.4758 (2)	0.2592 (2)	0.0112 (7)
O(9)	0.18446 (12)	0.2831 (3)	0.1193 (3)	0.0220 (8)
O(10)	0.30512 (12)	0.1730 (2)	0.0340 (3)	0.0155 (8)
O(11)	0.11929 (14)	0.1440 (3)	0.3627 (4)	0.0568 (13)
H(1)	0.15752 (12)	0.2988 (3)	0.0523 (3)	0.20 (4)
H(2)	0.16096 (12)	0.2574 (3)	0.1883 (3)	0.15 (3)
H(3)	0.28123 (12)	0.1025 (2)	0.0541 (3)	0.066 (16)
H(4)	0.30108 (12)	0.1902 (2)	0.9490 (3)	0.054 (17)

max. shift/e.s.d. = 0.4; max. and min. heights on final difference-Fourier map 0.8 and  $-0.7 \text{ e \AA}^{-3}$  near O(11); neutral scattering factors (*International Tables for X-ray Crystallography*, 1974); computer programs: *SHELX76* (Sheldrick, 1976), *ORFFE* (Busing, Martin & Levy, 1964), *ORTEP* (Johnson, 1965), *AGNOST* (Ibers, personal communication) plus local data reduction. Final atomic coordinates and displacement factors are given in Table 1 and interatomic distances and angles in Table 2.

**Discussion.** A stereoview down the *c* axis (Fig. 1) supplements the stereoview down the *a* axis (Pluth & Smith, 1985, Fig. 1). Each P atom is tetrahedrally coordinated *via* a shared O atom with four adjacent Al atoms. Each Al(1) atom shares an O atom with one P(2) and three P(1) atoms. Each Al(2) atom is bonded to two water molecules in addition to four framework O atoms shared with one P(1) and three P(2) atoms. The resulting octahedral complex,  $\text{AlO}_4(\text{H}_2\text{O})_2$ , is also found in metavariscite (Kneip & Mootz, 1973). The water-free portion of the structure can be regarded as a hypothetical tetrahedral framework, whose topological properties are depicted by Pluth & Smith (1985, Fig. 2).

One of the two water molecules [O(10), H(3), H(4)] projects into a 6-ring (Figs. 1 and 2), whereas the second one [O(9), H(1), H(2)] projects into a channel parallel to *c* (Fig. 1) which is limited by 8-rings. The third water molecule, represented by a large circle [O(11)] lacking H positions, alternates with the second water to form a zigzag chain parallel to *c*. These three water molecules collectively fill the void space inside the framework. The resulting formula of  $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$  is less hydrous than the  $\text{AlPO}_4 \cdot 1.67\text{H}_2\text{O}$  determined by d'Yvoire (1961) for  $H_3$  by bulk analysis although the powder pattern listed for  $H_3$  by d'Yvoire can be indexed completely from the present structural data.

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$ 

P(1)—O(1)	1.501 (2)	P(2)—O(5)	1.524 (2)
P(1)—O(2)	1.531 (2)	P(2)—O(6)	1.536 (2)
P(1)—O(3)	1.529 (2)	P(2)—O(7)	1.528 (2)
P(1)—O(4)	1.538 (2)	P(2)—O(8)	1.506 (2)
Mean	1.525	Mean	1.524
Al(1)—O(2)	1.735 (2)	Al(2)—O(1)	1.851 (2)
Al(1)—O(3)	1.724 (2)	Al(2)—O(5)	1.860 (2)
Al(1)—O(4)	1.744 (2)	Al(2)—O(7)	1.842 (2)
Al(1)—O(6)	1.730 (2)	Al(2)—O(8)	1.835 (2)
Mean	1.734	Al(2)—O(9)	1.967 (2)
		Al(2)—O(10)	1.951 (2)
		Mean	1.884
O(1)—P(1)—O(2)	112.8 (1)	O(1)—Al(2)—O(9)	179.1 (1)
O(1)—P(1)—O(3)	108.5 (1)	O(1)—Al(2)—O(10)	92.0 (1)
O(1)—P(1)—O(4)	111.9 (1)	O(5)—Al(2)—O(7)	175.0 (1)
O(2)—P(1)—O(3)	108.9 (1)	O(5)—Al(2)—O(8)	91.8 (1)
O(2)—P(1)—O(4)	106.8 (1)	O(5)—Al(2)—O(9)	87.0 (1)
O(3)—P(1)—O(4)	107.8 (1)	O(5)—Al(2)—O(10)	90.9 (1)
O(5)—P(2)—O(6)	109.9 (1)	O(7)—Al(2)—O(8)	89.9 (1)
O(5)—P(2)—O(7)	107.3 (1)	O(7)—Al(2)—O(9)	88.3 (1)
O(5)—P(2)—O(8)	110.1 (1)	O(7)—Al(2)—O(10)	87.3 (1)
O(6)—P(2)—O(7)	108.9 (1)	O(8)—Al(2)—O(9)	91.6 (1)
O(6)—P(2)—O(8)	109.8 (1)	O(8)—Al(2)—O(10)	177.0 (1)
O(7)—P(2)—O(8)	110.7 (1)	O(9)—Al(2)—O(10)	87.2 (1)
O(2)—Al(1)—O(3)	111.5 (1)	P(1)—O(1)—Al(2)	146.1 (2)
O(2)—Al(1)—O(4)	108.2 (1)	P(1)—O(2)—Al(1)	145.5 (2)
O(2)—Al(1)—O(6)	110.5 (1)	P(1)—O(3)—Al(1)	149.7 (2)
O(3)—Al(1)—O(4)	104.9 (1)	P(1)—O(4)—Al(1)	141.7 (2)
O(3)—Al(1)—O(6)	107.5 (1)	P(2)—O(5)—Al(2)	138.7 (2)
O(4)—Al(1)—O(6)	114.1 (1)	P(2)—O(6)—Al(1)	138.9 (2)
O(1)—Al(2)—O(5)	92.8 (1)	P(2)—O(7)—Al(2)	143.9 (2)
O(1)—Al(2)—O(7)	91.9 (1)	P(2)—O(8)—Al(2)	155.1 (2)
O(1)—Al(2)—O(8)	89.3 (1)		
Water molecules			
Al(2)—O(9)—H(1)	130.5 (3)	Al(2)—O(10)—H(3)	112.7 (3)
Al(2)—O(9)—H(2)	118.6 (3)	Al(2)—O(10)—H(4)	111.9 (2)
Hydrogen bonds			
H(1)...O(11)	2.070 (5)	O(9)—H(1)...O(11)	162.8 (3)
H(2)...O(11)	2.183 (4)	O(9)—H(2)...O(11)	164.5 (3)
H(3)...O(5)	1.990 (3)	O(10)—H(3)...O(5)	148.7 (3)
H(4)...O(7)	1.790 (3)	O(10)—H(4)...O(7)	159.4 (3)
		O(9)...O(11)	2.893 (5)
		O(9)...O(11)	3.011 (4)
		O(10)...O(5)	2.716 (3)
		O(10)...O(7)	2.603 (3)
		O(11)...O(4)	3.013 (4)
		O(11)...O(8)	3.047 (4)

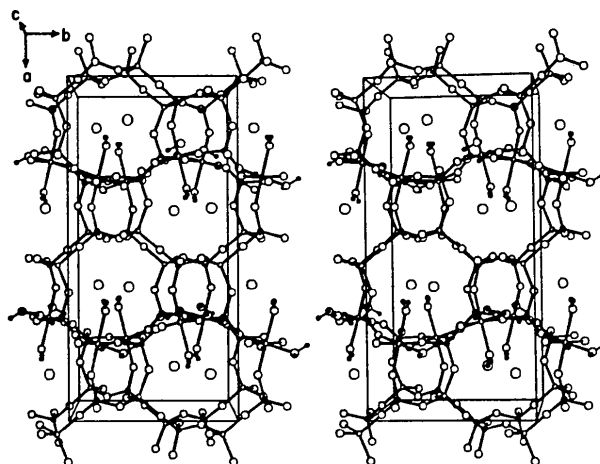


Fig. 1. Stereoview of  $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$  structure. Small open and filled circles at line intersections represent Al and P atoms respectively. Larger open circles are O atoms. Pairs of H atoms (small dots) are shown for each water molecule attached to Al(2), but not for the loosely bonded water molecule (largest circle). The positions of  $6^2$  and  $4.8^2$  nets are shown perpendicular to *a* at  $x = \frac{1}{4}, \frac{3}{4}$  and  $x = 0, \frac{1}{2}, 1$  respectively.

The framework topology is new (Pluth & Smith, 1985). In stereoview, Fig. 1 shows a layer of vertex-shared Al and P polyhedra overlying another layer, both with the connectivity of a  $4.8^2$  two-dimensional net. Each 4-ring contains one tetrahedral and one octahedral Al alternating with tetrahedral P atoms, and each 8-ring has the sequence  $-Al^{IV}-P^{IV}-Al^{IV}-P^{IV}-Al^{VI}-P^{IV}-Al^{VI}-P^{IV}-$ . The 8-rings are crinkled, and the 4-rings are tilted out of the  $ab$  plane. Each pair of superimposed 4-rings is connected by 4-rings parallel to the  $ac$  plane to generate a double-crankshaft chain (Smith, 1978).

Less visible in the stereoview (Fig. 1) of the resulting 4-connected 3D net are alternating  $4.8^2$  and  $6^3$  2D nets parallel to the  $bc$  plane. Each net is crinkled, and is joined to the adjacent nets by 4-rings of the double-crankshaft chains. The  $4.8^2$  nets, which are quite distinct from those parallel to the  $ab$  plane, contain only tetrahedral Al and P atoms, while the  $6^3$  nets contain octahedral Al atoms alternating with tetrahedral P atoms. Between each pair of  $6^3$  nets is a two-dimensional channel system bounded by distorted 8-rings. An  $a$ -axis projection (Fig. 2) shows the geometrical relationships of the tetrahedra and octahedra in a  $6^3$  layer. One water molecule lies nearly at the center of a 6-ring, while the other projects out into a channel (Fig. 1).

The bond distances and angles of the polyhedra (Table 2) are generally consistent with those in other aluminophosphates with similar bonding features. O atoms of water molecules are more distant (1.95–1.97 Å) from Al(2) than those bonded to P (1.84–1.86 Å). The weakening of the octahedral Al(2)–O...P bonds with respect to the tetrahedral Al(1)–O...P

bonds (1.72–1.74 Å) is mainly responsible for the P–O...Al(2) distances (1.501, 1.524, 1.528, 1.506 Å) being shorter than the P–O...Al(1) distances (1.531, 1.529, 1.538, 1.536 Å). The two longer distances are caused by O(5) and O(7) being hydrogen bonded to O(10) *via* H(3) and H(4).

Water oxygens O(9) and O(11) alternate at 2.9 and 3.0 Å in a channel parallel to  $c$ , and are linked by weak hydrogen bonds (2.1, 2.2 Å) through H(1) and H(2). The protons attached to O(11) were not located. The closest framework O atoms O(4) and O(8) ( $\sim 3.0$  Å) along with two O(9) atoms do not provide the usual tetrahedral geometry of a hydrogen-bonded water-oxygen complex. Hence the protons attached to O(11) are probably disordered in response to the several possible positions weakly hydrogen bonded to framework oxygens. Water O(10), near the center of a 6-ring, has the strongest hydrogen bonds from H(3) to O(5) and H(4) to O(7) at  $\sim 1.9$  Å. As expected for minimum electrostatic potential, the protons are angled away from the nearest Al atom.

To conclude, the  $AlPO_4 \cdot 1.5H_2O$  structure extends the fascinating variety of structure types displayed by the other known aluminophosphates (references listed in Pluth, Smith & Bennett, 1986). In spite of the complexity of the  $AlPO_4 \cdot 1.5H_2O$  structure, the different units fit together neatly, and encapsulated water plays an important structural role.

We thank S. T. Wilson and E. M. Flanigen for supplying the crystals, J. M. Bennett, E. M. Flanigen, R. L. Patton and S. T. Wilson for reviewing the manuscript, NSF for grants CHE 84-05167 and DMR 82-16892, and Union Carbide Corporation (Linde Molecular Sieves) for financial support.

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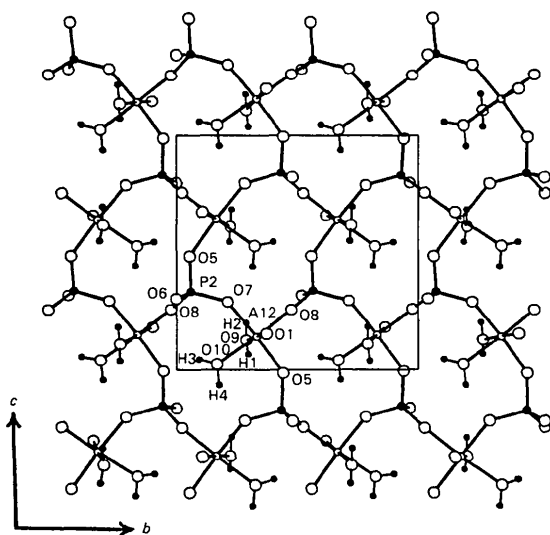


Fig. 2. Plan of a  $6^3$  net. Symbols as in Fig. 1.