Preparation, Characterisation, and Crystal and Molecular Structure of a Novel Tetrameric Aluminium Phosphate Complex: [{$Al(PO_4)(HCl)(C_2H_5OH)_4$}$_4$]

By **John E. Cassidy, John A. J. Jarvis,** and **Roger N. Rothon,*** Imperial Chemical Industries Ltd., Mond Division, Research and Development Department, P.O. Box 8, The Heath, Runcorn, Cheshire WA7 9QD

A tetrameric complex of aluminium phosphate has been prepared by reaction of aluminium trichloride with phosphoric acid in ethanol. It is a crystalline solid, soluble in water and most simple alcohols, readily decomposes to $AlPO_4$ on heating, and has empirical formula corresponding to $Al(PO_4)(HCl)(EtOH)_4$. The crystal structure has been determined from three-dimensional *X*-ray diffractometer data, and refined by block-diagonal least-squares to *R* 0.090 for 1607 independent reflections. Crystals are tetragonal, with unit-cell dimensions $a = b = 15.45$, $c = 14.44$ Å, space group $I\bar{4}$, $Z = 2$ tetramers. The structure consists of aluminium phosphate tetramers of approximately cubic shape. Each aluminium atom is octahedrally co-ordinated, carrying oxygens from three ethanol ligands, in addition to three phosphate oxygens. There are four further ethanol molecules hydrogen bonded to each tetramer unit. The fourth oxygen of each phosphate tetrahedron is hydrogen bonded to a chlorine atom. These chlorine atoms are also hydrogen bonded to other, adjacent, tetramer units and serve to hold the structure together. Because of its ready conversion to aluminium phosphate, the complex can be used to form thin, glassy, films of $AlPO_4$. Various related solid complexes have also been prepared.

WE have prepared a crystalline complex of aluminium phosphate, which is soluble in water and most simple alcohols, and decomposes to aluminium phosphate at $\geqslant 50$ °C. The complex and its derivatives have considerable promise as refractory binders, or surface coatings.[1] We now describe the characterisation of this complex, and determination of its molecular structure.

EXPERIMENTAL

Preparation.—When anhydrous aluminium trichloride and phosphoric acid are allowed to react in ethanol, crystals of the complex separate out. The best yields are obtained if the reaction is carried out at, or below, 0 °C, and if equimolar quantities of aluminium trichloride and phosphoric acid are used. It is also advantageous to exclude water from the system.

Characterisation.—The elemental analysis, i.r. spectrum, and *X*-ray powder data for the complex have been determined.† As the complex is readily hydrolysed it was stored and handled under dry-box conditions.

Elemental Analysis.—This was carried out by standard procedures, and fairly closely corresponds to the empirical formula, $AlPClH_{25}C_8O_8$ or $Al(PO_4)(HCl)(EtOH)_4$. Part of the difference between experimental and calculated values is due to water (*ca.* 0.6% by weight) present in the sample, probably resulting from the phosphoric acid which contained *ca.* 12% w/w of water [Found: C, 27.0; H, 6.7; Al, 7.8; Cl, 10.3; P, 8.6. $Al(PO_4)(HCl)(C_2H_5OH)_4$ requires C, 28.0; H, 7.3; Al, 7.9; Cl, 10.3; P, 9.0%].

Determination of Crystal and Molecular Structure.—Suitable single crystals were obtained by setting aside the filtrate from a preparation for several months in a sealed vessel in a refrigerator. Crystals so obtained had an identical *X*-ray powder pattern to that of the bulk solid obtained from the preparation. A crystal was cemented, using the mother liquor as adhesive, to the inside of a thin walled, 1-mm diameter, Lindemann glass-capillary tube, which was sealed under dry nitrogen. Intensity data and cell dimensions were then obtained by use of a Picker automatic four-circle goniometer and niobium-filtered molybdenum radiation. A total of 4 200 reflections with $2\theta < 55°$ in the octants hkl and $hk\bar{l}$ were measured and corrected for Lorentz polarisation factors. These gave, after averaging of symmetry-related reflections, a total of 2 069 independent structure factor amplitudes, of which 462 with $I < 35\ \sigma(I)$ were counted as unobserved. The structure was solved by three-dimensional Patterson and Fourier synthesis, and refined by block-diagonal least-squares to *R* 0.090, by use of computer programmes written by Dr. R. H. B. Mais. A difference synthesis at this stage showed maximum excursions of just $< \pm 2$ e close to the chlorine atom, in the typical pattern associated with uncorrected anisotropic vibration. Similar excursions of ± 1 e were found next to the aluminium and phosphorus atoms. There were also peaks of up to $1\frac{1}{2}$ e adjacent to the presumed positions of the carbon atoms of the ethanol molecules, which indicated that these might be disordered. It was decided at this point that the most important features of the structure had been adequately established and that the extra information which might result from pursuing the disordered carbon atoms would not justify the effort involved.

RESULTS

Crystal Data.—$(AlPClH_{25}C_8O_8)_4$, $M = 1\,370.8$, Tetragonal, $a = b = 15.45 \pm 0.01$, $c = 14.44 \pm 0.01$ Å, $U = 3\,447$ Å^3, $Z = 2$, $D_c = 1.32$, $F(000) = 1\,456$. Space group $I\bar{4}$ (S_4^2 No. 82). Niobium-filtered, Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) $= 3.22$ cm^{-1}.

Atomic parameters are given in Table 1, and bond lengths and angles in Table 2. The angles between hydrogen-bonded atoms are given in Table 3. Atoms are specified as follows: bridging phosphate oxygens are O(1)—(3), and the non-bridging oxygen is O(7); oxygen atoms associated with the ethanol molecules are O(4)—(6), and O(8); primary carbon atoms in the ethanol molecules are C(1)—(4), and the secondary carbons C(5)—(8). Temperature factors were large for all carbon atoms, and a difference synthesis indicated that six out of the eight in each asymmetric unit are disordered; no attempt was made to discover the nature of this disorder. Although the exact locations of the carbon atoms are therefore not known, the positions of their associated oxygen atoms have been accurately identified and this has proved sufficient to define the main features

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† Results are listed together with final observed and calculated structure factors in Supplementary Publication No. SUP 21281 (12 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[1] B.P. 1,322,722.

TABLE 1

Atom co-ordinates and thermal parameters

Atom	*x*	*y*	*z*	*U*	Atom	*x*	*y*	*z*	*U*
Al	0.0600	0.1452	−0.1188	0.030	C(1)	0.245	0.198	−0.076	0.099
P	0.0496	0.1284	0.1003	0.026	C(2)	0.299	0.269	−0.069	0.173
Cl	0.2792	0.1878	0.1515	0.056	C(3)	0.022	0.341	−0.092	0.087
O(1)	0.0693	0.1624	0.0057	0.041	C(4)	0.046	0.389	−0.142	0.219
O(2)	0.0979	0.0462	0.1206	0.043	C(5)	0.001	0.161	−0.322	0.118
O(3)	0.1239	0.0455	−0.1200	0.040	C(6)	0.018	0.155	−0.411	0.332
O(4)	0.1678	0.2115	−0.1326	0.042	C(7)	0.273	0.079	−0.339	0.143
O(5)	0.0019	0.2574	−0.1340	0.046	C(8)	0.339	0.029	−0.350	0.256
O(6)	0.0668	0.1408	−0.2547	0.046					
O(7)	0.0838	0.1999	0.1725	0.041					
O(8)	0.1977	0.0407	−0.3224	0.092					

of the structure. No attempt was made to determine hydrogen atom positions.

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances (±0.01Å)	
(i) In cage unit	
Al–O(1)	1.82
Al–O(2)	1.80
Al–O(3)	1.83
P–O(1)	1.50
P–O(2)	1.50
P–O(3)	1.50
(ii) To ethanol ligands	
Al–O(4)	1.97
Al–O(5)	1.97
Al–O(6)	1.97
Cl · · · O(4′)	3.09
Cl · · · O(5)	3.07
(iii) Other distances	
P–O(7)	1.61
Cl · · · O(7)	3.04
O(8) · · · O(7)	2.90
O(8) · · · O(6)	2.73
(*b*) Bond angles (±0.5°)	
(i) In cage unit	
O(1)–Al–O(2)	98.4
O(2)–Al–O(3)	98.6
O(3)–Al–O(1)	95.2
Al–O(1)–P	146.4
Al–O(2)–P	166.3
Al–O(3)–P	148.1
O(1)–P–O(2)	112.1
O(2)–P–O(3)	114.2
O(3)–P–O(1)	112.9
(ii) Between oxygen ligands	
O(4)–Al–O(5)	85.2
O(5)–Al–O(6)	86.8
O(6)–Al–O(4)	82.6
(iii) Ligand oxygens to cage oxygens	
O(1)–Al–O(4)	87.6
O(1)–Al–O(5)	90.9
O(1)–Al–O(6)	170.1
O(2)–Al–O(5)	86.5
O(2)–Al–O(6)	91.2
O(2)–Al–O(4)	169.9
O(3)–Al–O(6)	86.1
O(3)–Al–O(4)	88.9
O(3)–Al–O(5)	171.3
(iv) Terminal O to cage O	
O(7)–P–O(1)	106.4
O(7)–P–O(2)	106.9
O(7)–P–O(3)	103.4

TABLE 3

Angles (°) between hydrogen-bonded atoms

O(8) · · · O(7)–P	105
Cl · · · O(7)–P	110
O(7) · · · Cl · · · O(5)	86
O(7) · · · Cl · · · O(4′)	108
O(5) · · · Cl · · · O(4′)	137
O(8) · · · O(6) –Al	115

Primes denote atoms in tetramers at ($\pm\frac{1}{2}$, $\pm\frac{1}{2}$, $\pm\frac{1}{2}$) relative to the reference tetramer centred at (0,0,0).

Description of Structure.—The structure consists of tetrameric $Al(PO_4)(HCl)(EtOH)_4$ molecules, possessing $\bar{4}$ symmetry, one of which is depicted in Figure 1. The nucleus of the molecule approximates to a cubic cage, with aluminium and phosphorus atoms at the vertices, linked by bridging oxygens along the edges of the cube. Bond lengths involving these bridging oxygens are Al–O 1.82 and P–O 1.50 Å. Each aluminium is octahedrally co-ordinated, the remaining sites being occupied by ethanol ligands with Al–O 1.97 Å. The phosphorus atoms are surrounded by four oxygen atoms in a tetrahedral configuration, the fourth oxygen being outside the cage, with P–O 1.61 Å.

Each chlorine is sufficiently close to three oxygen atoms to suggest the existence of O–H · · · Cl hydrogen bonds. These are to O(5) and O(7) in the same tetramer, and to O(4) in an adjacent one. Figure 1 shows how the four chlorine atoms associated with each molecule are linked across alternate edges of the cage, and Figure 2 how each molecule is hydrogen bonded to its eight nearest neighbours.

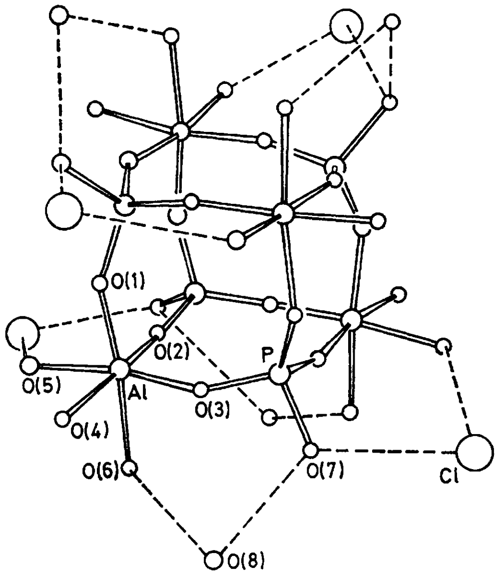

FIGURE 1 Perspective drawing of one tetrameric unit of the complex

In addition to the ethanol ligands associated with each aluminium atom, there are four more ethanol molecules associated with each cage unit. These do not act as ligands, but each does enter into hydrogen bonding, both to oxygen in one of the co-ordinated ethanol ligands, and to the terminal oxygen of a PO_4 group. In Figure 1, O(8), the oxygen of one of these ethanols, is hydrogen bonded to O(6) at 2.73, and more weakly to O(7) at 2.90 Å.

The extensive hydrogen bonding observed, which involves all the non-bridging oxygen atoms, implies that the ligands are, in fact, ethanol molecules, rather than ethoxide groups. This view is reinforced by valency considerations, and by the fact that all the Al–O-(ligand) bond lengths are identical (1.97 Å). It also implies that O(7) (the terminal oxygen of the PO_4 groups) has a hydrogen attached, and this is further reinforced by the long bond length of 1.61 Å, which is similar to that of P–OH bonds in crystalline H_3PO_4.[2]

It is interesting to compare some of the interatomic distances in the complex with those observed in other aluminium compounds. The structure of metavariscite [3] ($AlPO_4,2H_2O$) is an infinite three-dimensional assembly of PO_4 tetrahedra sharing their four corners with four $AlO_4(H_2O)_2$ octahedra, in which the water molecules are on the same edge. All oxygen bridges are Al–O–P, with Al–O 1.81—1.90, and P–O 1.50—1.55 Å. The water molecules have Al–O distances of 1.91 and 1.94 Å. There is thus a less definite difference between bridging and terminal oxygen bonds than in the finite $[\{Al(PO_4)(EtOH)_3\}_4]$ complex. A similar sharp distinction is observed, however, in aluminium tris[μ-carbonyl-(dicarbonyl)cyclopentadienyltungstate]–tris(tetrahydrofuran),[4] where the aluminium is bonded to tetrahydrofuran groups and three $-OC-W(CO)_2(\pi-C_5H_5)$ groups. Al–O Distances are 1.94 Å to tetrahydrofuran ligands and 1.83 Å to the carbonyl groups on tungsten.

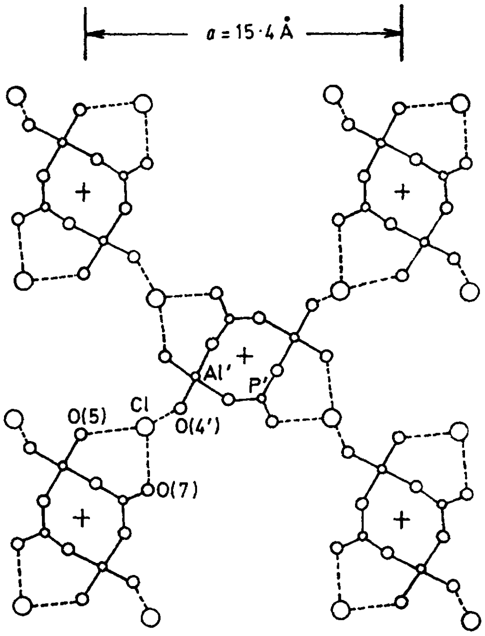

FIGURE 2 Partial projection of the structure down the $\bar{4}$ axis. The four outer groups of atoms belong to the upper faces of tetrameric units with centres at $z = 0$. The central group is the lower face of a unit centred at $z = \frac{1}{2}$

DISCUSSION

The complex has an unusual structure, essentially consisting of isolated $AlPO_4$ tetramers, which are prevented from linking together by the ethanol ligands on the aluminium atoms and by protonation of the non-bridging oxygen atoms. The solubility of the complex arises from the presence of these small units, and the ready conversion to insoluble aluminium phosphate which occurs on heating arises from the removal of the protective groups, allowing the tetramers to link together into a long-range structure.

Our interest in this complex is mainly due to this solubility, and ready conversion into aluminium phosphate. This latter material has good thermal stability, and hence solutions of the complex are useful in the refractories field. Solutions of the complex are also of interest for surface-coatings applications, where they can be used to form thin, glassy, films of $AlPO_4$ on a wide range of substrates, including organic polymers. The $AlPO_4$ glass produced in this way is of additional interest as it is impossible to form a glass of the $AlPO_4$ composition by conventional melt processes.

We have produced several related solid complexes, in which the nature of the stabilising groups has been varied.[1] For example, the ethanol has been replaced by propan-2-ol, and by water, and the chlorine by bromine.

[4/800 *Received, 22nd April,* 1974]

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