Four- and Six-coordinated Al and an Encapsulated Isopropylamine Species in $7AlPO_4.2(C_3H_7NH_2).2H_2O$

By Joseph J. Pluth and Joseph V. Smith

Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, USA

Abstract. Aluminium phosphate–isopropylamine hydrate, $M_r = 1007.9$, monoclinic, $C2/c$, $a = 24.085$ (1), $b = 14.393$ (1), $c = 8.7122$ (4) Å, $\beta = 94.260$ (4)°, $V = 3012$ Å^3, $Z = 4$, $D_x = 2.22$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 71$ cm^{-1}, $F(000) = 2032$, $T \simeq 295$ K, $R = 0.039$ for 2517 reflections. The framework structure contains tetrahedral P and both tetrahedral and octahedral Al. Two octahedral Al are connected by three tetrahedral species (two P and one Al) to form a five-atom cluster which consists of three 4-rings. Two clusters are linked by two tetrahedral P to form a lozenge-shaped cage. Sharing of each cluster by adjacent cages produces a zigzag chain. Crosslinking of zigzag chains by twisting chains of 4-rings produces a (100) sheet which is linked to adjacent sheets by several types of 4-rings, most of which belong to an interrupted sheet. Two octahedral Al share an OH and the encapsulated organic species is probably isopropylammonium ion; thus the chemical formula can be written as $\{Al_7P_7O_{28}(OH)_2.2C_3H_7NH_3\}$.

Introduction. A new class of microporous materials was synthesized from aluminophosphate gels containing at least one of a variety of organic amine and quaternary ammonium cations (Wilson, Lok, Messina, Cannan & Flanigen, 1982, 1983). Many of the new materials are microporous after calcination to remove encapsulated organic material, and the tetrahedral frameworks with alternating Al and P include structural analogs of the aluminosilicate zeolites erionite (AlPO$_4$-17) and sodalite (AlPO$_4$-20). The novel framework of the synthesized AlPO$_4$-5 (Wilson, Lok & Flanigen, 1982) contains tetrapropylammonium hydroxide in a tripod configuration in non-connecting channels bounded by 12 rings (Bennett, Cohen, Flanigen, Pluth & Smith, 1983).

Five of the aluminophosphates synthesized in the presence of amine have been found by structure refinement to contain Al atoms coordinated to four, five or six oxygens. In two, the amine apparently fragmented. Diaminobutane allowed synthesis of AlPO$_4$-15, NH$_4$Al$_2$(OH)(H$_2$O)(PO$_4$).2H$_2$O, which has a tetramer of edge-sharing AlO$_4$(OH)$_2$ and vertex-sharing AlO$_4$(OH)(H$_2$O) octahedra sharing vertices with PO$_4$ tetrahedra to give a framework three-connected at (OH) and

two-connected at O (Pluth, Smith, Bennett & Cohen, 1984; Parise, 1984*b*). Three types of tetrahedral P, one type of tetrahedral Al and two types of trigonal-bipyramidal Al occur in AlPO$_4$-21 (Bennett, Cohen, Artioli, Pluth & Smith, 1985; Parise & Day 1985), and the 1,3-propanediamine molecule used in the synthesis of crystals studied by Bennett *et al.* (1985) split into three triatomic species encapsulated by the framework. The other aluminophosphates encapsulated intact organic species: AlPO$_4$-12 (Parise, 1984*a*), AlPO$_4$-EN3 (Parise, 1985), AlPO$_4$-17 (Pluth, Smith & Bennett, 1986). Among the other aluminophosphate structures reviewed by Bennett, Dytrych, Pluth, Richardson & Smith (1986), those of particular interest here are variscite (Kniep, Mootz & Vegas, 1977), metavariscite (Kniep & Mootz, 1973) and a synthetic material AlPO$_4$.1.5H$_2$O (Pluth & Smith, 1985, 1986) with an X-ray powder pattern resembling that of H_3 (d'Yvoire, 1961).

In all the AlPO$_4$-n structures, except AlPO$_4$-12, each Al atom shares each of the four adjacent O atoms with an adjacent P atom of the 4-connected AlPO$_4$ framework. Some Al atoms are also bonded to one or two oxygen species at a longer distance. The five- and six-coordinated Al atoms are in distorted trigonal-bipyramidal or octahedral coordination with non-equivalency of the oxygen species.

We now describe the crystal structure of a new phase which occurred as a few large crystals in the overwhelmingly dominant preparation of AlPO$_4$-14 from a reaction mixture containing isopropylamine (Wilson, Lok & Flanigen 1982). A few large crystals of AlPO$_4$-15 were also found in the synthesized product.

Experimental. An aluminophosphate gel, produced from hydrated alumina and phosphoric acid, was mixed with isopropylamine (C$_3$H$_7$NH$_2$) and held at 423 K for 4 d. From the dominant fine-grained product of AlPO$_4$-14, a few crystals of an impurity, designated here as AlPO$_4$-14*A*, were selected. A needle composed of {100}, {010} and {001} pinacoids was selected and mounted with c offset 4° from the spindle axis; lengths along *a*, *b* and *c* are 0.030, 0.040 and 0.46 mm. An automatic Picker four-circle diffractometer with Krisel automation was used. Refinement of 20 reflections

$(64 < 2\theta < 80°)$, each the average of the automatic centering of eight possible settings, gave the cell parameters. 5397 measured intensities were averaged to produce 2517 merged allowed intensities $[R_{int}(F) = 0\cdot0142]$, maximum $(\sin\theta)/\lambda = 0\cdot58$ Å^{-1}, data collection range $h \pm 28$, $k \pm 16$, $l + 10$, and maximum intensity variation of three standard reflections 2·6%. An absorption correction gave transmission factors 0·59–0·82. The structure was solved by centrosymmetric direct methods (SHELX76, Sheldrick, 1976), followed by difference Fourier calculations which revealed the C and N atoms of the organic species and a hydrogen attached to a framework oxygen. The remaining H atoms were not located, though irregular peaks occur in the final difference Fourier map. The final least-squares refinement minimized all F's with σ_F computed from σ_I the square root of [total counts + (2% of total counts)^2] and with $w = \sigma_F^{-2}$: $R = 0\cdot039$, $wR = 0\cdot051$, $S = 2\cdot9$; maximum $\Delta/\sigma = 0\cdot03$: maximum and minimum height on final difference Fourier synthesis 1·0 and $-0\cdot4$ e Å^{-3}; isotropic extinction correction; 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 positional and equivalent displacement parameters are given in Table 1 and interatomic distances and angles in Table 2.*

Discussion. The structure (Fig. 1) consists of a framework of linked PO_4 and AlO_4 tetrahedra and $AlO_5(OH)$ octahedra which encapsulates an isopropylamine species. To obtain charge balance, it is proposed that each isopropylamine species is electrostatically coupled with a water molecule to produce an encapsulated isopropylammonium ion $[C_3H_7NH_3]^+$ plus an OH$^-$ ion which crosslinks two Al atoms in the framework. Hence the chemical formula can be written as $Al_7P_7O_{28}(OH)_2\cdot2C_3H_7NH_3$. Although there are equal numbers of Al and P atoms, it is not possible to select a moiety $7(AlPO_4)$ in which the Al and P atoms alternate at the nodes of a four-connected net with each oxygen lying between one Al and one P atom. In this respect, $AlPO_4$-14A differs from all but one of the structures listed in the Introduction, which do fit with this simple topological concept. The other exception, $AlPO_4$-12, can be matched with a four-connected net only by breakage of one Al—O—P linkage and creation of a new one.

---

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43656 (17 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 displacements of* $AlPO_4$-14A

$$U_{eq} = \frac{1}{3} \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* (\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
P(1)	0·33817 (3)	0·73198 (6)	0·42986 (11)	0·0082 (3)
P(2)	0·17397 (4)	0·53087 (6)	0·06070 (11)	0·0078 (3)
P(3)	0·5	0·49464 (9)	0·75	0·0104 (4)
P(4)	0·00842 (4)	0·32112 (6)	0·47374 (11)	0·0093 (3)
Al(1)	0·0	0·55471 (10)	0·25	0·0107 (4)
Al(2)	0·22189 (4)	0·62359 (7)	0·37596 (12)	0·0088 (3)
Al(3)	0·45019 (4)	0·62979 (7)	0·50032 (13)	0·0112 (3)
Al(4)	0·09788 (4)	0·38885 (7)	0·25913 (12)	0·0082 (3)
O(1)	0·17511 (10)	0·7082 (2)	0·4315 (3)	0·0154 (8)
O(2)	0·14182 (10)	0·2882 (2)	0·1995 (3)	0·0137 (8)
O(3)	0·38148 (10)	0·6611 (2)	0·4929 (3)	0·0175 (8)
O(4)	0·28631 (10)	0·6761 (2)	0·3749 (3)	0·0170 (8)
O(5)	0·15011 (10)	0·5921 (2)	−0·0688 (3)	0·0134 (8)
O(6)	0·13047 (10)	0·4706 (2)	0·1253 (3)	0·0148 (8)
O(7)	0·22085 (10)	0·4696 (2)	0·0019 (3)	0·0139 (8)
O(8)	0·20189 (10)	0·5950 (2)	0·1865 (3)	0·0137 (8)
O(9)	0·46013 (12)	0·5554 (2)	0·6546 (4)	0·0374 (11)
O(10)	0·46549 (13)	0·4347 (3)	0·8443 (4)	0·0505 (13)
O(11)	0·05565 (11)	0·4905 (2)	0·3356 (3)	0·0116 (8)
O(12)	0·03037 (10)	0·3742 (2)	0·6178 (3)	0·0135 (8)
O(13)	0·00697 (11)	0·77674 (15)	0·4709 (3)	0·0193 (8)
O(14)	0·05694 (9)	0·3061 (2)	0·3740 (3)	0·0114 (7)
O(15)	0·04188 (10)	0·3716 (2)	0·0979 (3)	0·0151 (8)
N	0·3680 (2)	0·2717 (3)	0·3968 (7)	0·062 (2)
C(1)	0·3305 (4)	0·3466 (6)	0·4384 (10)	0·140 (5)
C(2)	0·2887 (3)	0·3702 (6)	0·3146 (9)	0·107 (4)
C(3)	0·1455 (3)	0·0844 (5)	0·4596 (10)	0·085 (3)
H	0·066 (2)	0·501 (3)	0·398 (5)	0·005 (13)

Framework topology. In detail, a unique feature of the structure is an $Al_3P_2O_{18}H_2$ cluster (Fig. 2) containing two tetrahedral P(4), one tetrahedral Al(1) and two octahedral Al(4) species. The five cations of the cluster generate three 4-rings (Fig. 3: *pqrs, pqst, qrst*). Each pair of adjacent Al atoms [Al(1) and Al(4)] shares an O(11) of an hydroxyl, and the hydrogen is weakly bonded to O(6) which is shared between Al(4) and P(2).

A chain parallel to **c** is generated by linking each Al_3P_2 cluster (*e.g. pqrst*) to the next cluster (*uvwxy*) by two P(2) labeled k and l, and by links between Al(1) and P(4) labeled *ry* and *tw*. The combined group of six Al and six P atoms forms a lozenge-shaped cage bounded by four 4-rings and four 5-rings; it can be idealized to *mmm* symmetry. Each cage shares each of the two Al_3P_2 clusters with another cage to generate a zigzag chain (*e.g. u–y* is shared between cages *p–t, k, l*, *u–y* and *u–y, m, n, p'–t'*). The repeat unit contains four P atoms and three Al atoms.

The lozenge-cage chains are crosslinked by chains (*defgh*) of twisted 4-rings to form a sheet in the *bc* plane (Fig. 3). Tetrahedral Al(3) and P(3) alternate along the nodes of each twisted chain. The 4-rings of five chains appear in Fig. 1; the chains lie at four edges of the unit cell and at $x = y = \frac{1}{2}$. Linkages *ew* and *gu* between a twisted 4-ring chain and a lozenge-cage chain produce a row of 6-rings (Fig. 3). The sheets of linked chains at

$x = 0$, $\frac{1}{2}$ and 1 are joined by 4-rings. Most obvious in Fig. 1 is a single 4-ring at $x = y \simeq \frac{1}{4}$ and $\frac{3}{4}$. Other 4-rings are present; five located at the lower left of Fig. 1 are recognizable as part of a double-crankshaft chain.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $AlPO_4$-14A

P(1)—O(1)	1·536 (3)	P(2)—O(5)	1·511 (3)
P(1)—O(2)	1·496 (3)	P(2)—O(6)	1·502 (3)
P(1)—O(3)	1·531 (3)	P(2)—O(7)	1·550 (3)
P(1)—O(4)	1·532 (3)	P(2)—O(8)	1·548 (3)
Mean	1·524	Mean	1·528
Al(1)—2O(11)	1·749 (3)	Al(2)—O(1)	1·752 (3)
Al(1)—2O(12)	1·742 (3)	Al(2)—O(4)	1·727 (3)
Mean	1·746	Al(2)—O(7)	1·734 (3)
		Al(2)—O(8)	1·734 (3)
		Mean	1·737
P(3)—2O(9)	1·503 (3)	P(4)—O(12)	1·530 (3)
P(3)—2O(10)	1·487 (3)	P(4)—O(13)	1·543 (3)
Mean	1·495	P(4)—O(14)	1·522 (3)
		P(4)—O(15)	1·508 (3)
		Mean	1·526
Al(3)—O(3)	1·712 (3)	Al(4)—O(2)	1·890 (3)
Al(3)—O(9)	1·721 (4)	Al(4)—O(5)	1·904 (3)
Al(3)—O(10)	1·709 (4)	Al(4)—O(6)	1·869 (3)
Al(3)—O(13)	1·703 (3)	Al(4)—O(11)	1·929 (3)
Mean	1·711	Al(4)—O(14)	1·881 (3)
		Al(4)—O(15)	1·890 (3)
		Mean	1·894

O(1)—P(1)—O(2)	112·8 (2)	O(3)—Al(3)—O(13)	111·8 (2)
O(1)—P(1)—O(3)	105·5 (2)	O(9)—Al(3)—O(10)	104·9 (2)
O(1)—P(1)—O(4)	109·1 (2)	O(9)—Al(3)—O(13)	109·2 (2)
O(2)—P(1)—O(3)	112·4 (2)	O(10)—Al(3)—O(13)	112·5 (2)
O(2)—P(1)—O(4)	110·4 (2)	O(2)—Al(4)—O(5)	88·6 (2)
O(3)—P(1)—O(4)	106·3 (2)	O(2)—Al(4)—O(6)	92·4 (2)
O(5)—P(2)—O(6)	112·3 (2)	O(2)—Al(4)—O(11)	175·6 (2)
O(5)—P(2)—O(7)	109·3 (2)	O(2)—Al(4)—O(14)	89·3 (2)
O(5)—P(2)—O(8)	107·6 (2)	O(2)—Al(4)—O(15)	94·5 (2)
O(6)—P(2)—O(7)	109·9 (2)	O(5)—Al(4)—O(6)	96·7 (2)
O(6)—P(2)—O(8)	111·0 (2)	O(5)—Al(4)—O(11)	87·3 (2)
O(7)—P(2)—O(8)	106·5 (2)	O(5)—Al(4)—O(14)	90·8 (2)
O(9)—P(3)—O(9)	108·9 (3)	O(5)—Al(4)—O(15)	175·8 (2)
2O(9)—P(3)—O(10)	106·4 (2)	O(6)—Al(4)—O(11)	89·7 (2)
2O(9)—P(3)—O(10)	113·1 (2)	O(6)—Al(4)—O(14)	172·3 (2)
O(10)—P(3)—O(10)	109·1 (3)	O(6)—Al(4)—O(15)	85·9 (2)
O(12)—P(4)—O(13)	106·0 (2)	O(11)—Al(4)—O(14)	89·2 (2)
O(12)—P(4)—O(14)	107·8 (2)	O(11)—Al(4)—O(15)	89·5 (2)
O(12)—P(4)—O(15)	108·5 (2)	O(14)—Al(4)—O(15)	86·5 (2)
O(13)—P(4)—O(14)	105·1 (2)	P(1)—O(1)—Al(2)	141·5 (2)
O(13)—P(4)—O(15)	111·4 (2)	P(1)—O(2)—Al(4)	147·1 (2)
O(14)—P(4)—O(15)	117·3 (2)	P(1)—O(3)—Al(3)	145·1 (2)
O(11)—Al(1)—O(11)	116·2 (2)	P(1)—O(4)—Al(2)	160·1 (2)
2O(11)—Al(1)—O(12)	112·0 (2)	P(2)—O(5)—Al(4)	149·8 (2)
2O(11)—Al(1)—O(12)	104·2 (2)	P(2)—O(6)—Al(4)	159·1 (2)
O(12)—Al(1)—O(12)	108·1 (2)	P(2)—O(7)—Al(2)	134·0 (2)
O(1)—Al(2)—O(4)	107·1 (2)	P(2)—O(8)—Al(2)	153·0 (2)
O(1)—Al(2)—O(7)	108·9 (2)	P(3)—O(9)—Al(3)	147·1 (2)
O(1)—Al(2)—O(8)	106·8 (2)	P(3)—O(10)—Al(3)	156·5 (2)
O(4)—Al(2)—O(7)	113·4 (2)	Al(1)—O(11)—Al(4)	131·3 (2)
O(4)—Al(2)—O(8)	106·6 (2)	P(4)—O(12)—Al(1)	134·4 (2)
O(7)—Al(2)—O(8)	113·7 (2)	P(4)—O(13)—Al(3)	146·3 (2)
O(3)—Al(3)—O(9)	105·8 (2)	P(4)—O(14)—Al(4)	132·0 (2)
O(3)—Al(3)—O(10)	112·2 (2)	P(4)—O(15)—Al(4)	151·4 (2)

Hydroxyl			
O(11)—H	0·60 (4)	Al(1)—O(11)—H	121 (4)
O(6)—H	2·46 (4)	Al(4)—O(11)—H	107 (4)
O(6)—O(11)	2·679 (4)	O(11)—H—O(6)	166 (5)

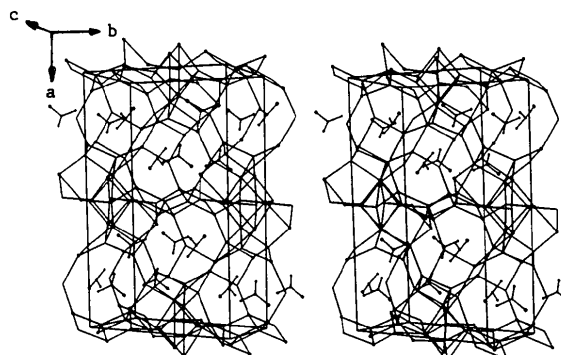| Template molecule			
C(1)—N	1·47 (1)	N—C(1)—C(2)	112·9 (7)
C(1)—C(2)	1·46 (1)	N—C(1)—C(3)	115·8 (7)
C(1)—C(3)	1·43 (1)	C(2)—C(1)—C(3)	121·6 (7)
N—O(14)	2·824 (6)	C(1)—N—O(14)	119·3 (5)
N—O(5)	3·036 (5)	C(1)—N—O(5)	112·9 (4)
N—O(8)	3·106 (5)	C(1)—N—O(8)	109·0 (4)
N—O(1)	3·107 (5)	C(1)—N—O(1)	105·9 (4)

Fig. 1. Stereoplot of $AlPO_4$-14A. Each isopropylammonium ion is represented by three C (small dot) and one N (large dot). The framework is shown by lines connecting Al (dot) and P (unmarked node). Twisted chains of 4-rings are parallel to **c** at $x = 0,1$, $y = 0,1$ and $x = y = \frac{1}{2}$. Parts of the chains of lozenge-shape units are shown at $x = 0,1$, $y = \frac{1}{2}$ and $x = \frac{1}{2}, y = 0,1$ but the lozenges are difficult to recognize end-on. The sheets of linked chains at $x = 0$, $\frac{1}{2}$ and 1 are joined by several types of 4-rings and incomplete fragments of double-crankshaft chains of 4-rings.
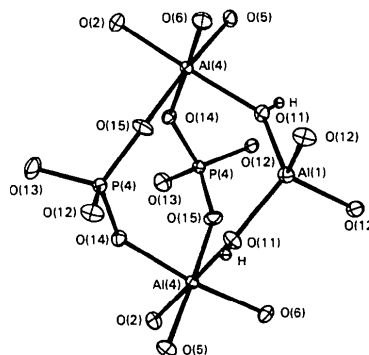

Fig. 2. The triple 4-ring unit which forms each end of a lozenge-shaped unit (Fig. 3). Ellipsoids at 50% probability level.
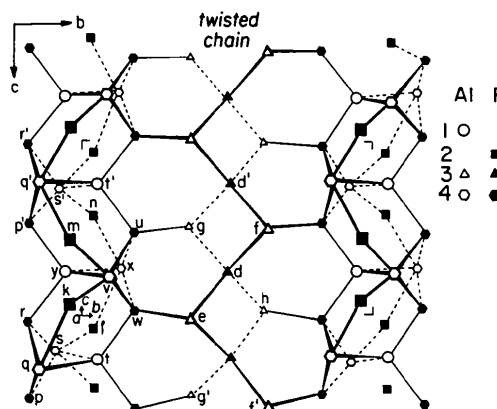

Fig. 3. Projection of two chains of lozenge-shaped units and one twisted chain of 4-rings. A triple 4-ring unit ($u–y$) is connected by k and l to form one lozenge with $p–t$ and by m and n to form the next lozenge with $p'–t'$. Each atomic position is coded by shape and absence or presence of filling (upper right).

It must now be stated quite frankly that we have not been able to invent a simple stereoscopic drawing which shows clearly the relation between the linking 4-rings and the sheets. Detailed study of a model revealed a remarkable pattern of linked 4-rings (Fig. 4). The distorted arrangement in $AlPO_4$-14A can be idealized so that each 4-ring lies at one of a sequence of levels. 20 tetrahedra at heights 3 and 4 form a fragment of a double-crankshaft chain (pq: Fig. 4, top). Each 4-ring is also part of another fragment (e.g. a ring at height 3 also belongs to rs). In the horizontal direction there is a jump of three units between the end of one fragment and the beginning of the next (e.g. at t between rings at 2 and 5).
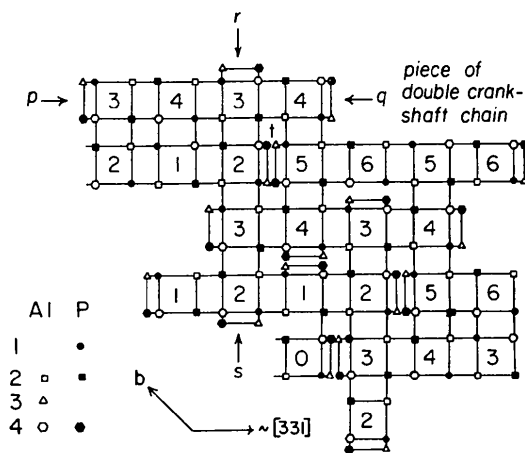

Fig. 4. The *idealized* interrupted sheet of 4-rings which is composed of fragments of double-crankshaft chains at different levels shown by an integer at the center of each 4-ring. A square represents a horizontal 4-ring and a rectangle a tilted one. Chain fragments intersect: e.g. pq and rs intersect at height 3. Each node is coded for the labeling of Al and P.
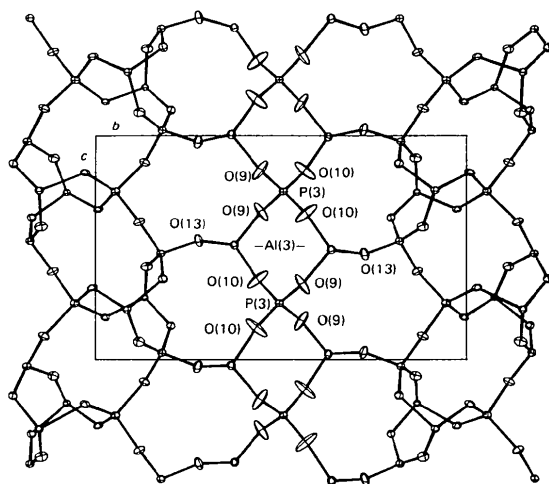

Fig. 5. Displacement ellipsoids for the atoms of the sheets of vertex-sharing chains. Ellipsoids at 50% probability level.

To conclude this section, the framework of $AlPO_4$-14A is complex, and it can be decomposed mathematically into cages, chains and sheets. 4-rings are more abundant than 5-, 6- and 8-rings. The framework contains a complex channel system linked in two dimensions by 8-rings and separated from adjacent pore systems by sheets of linked chains parallel to (100).

Framework geometry. The Al—O and P—O distances (Table 2) are unexceptional except for those involving Al(3) and P(3) which are consistently smaller than average values by 0·03 Å. Fig. 5 shows that the displacement ellipsoids of O(9) and O(10), which link Al(3) and P(3) of the twisted 4-ring chains, are much larger than for the other oxygens, and the shorter distances to these oxygens can be explained by the swinging-arm effect. Refinement of the structure in the lower space group Cc resulted in smaller but statistically insignificant values of the thermal parameters together with greater dispersion of bond lengths. It is presumed that there is positional disorder related to the angular orientation of the PO_4 tetrahedron. The short distances from Al(3) to O(3) and O(13) cannot be explained in this way because U_{eq} are not large enough. It appears that there is a genuine range of at least 0·03 Å in the individual distances in Table 2. Because there is no simple explanation of the detailed variations it is necessary to suggest that complex stereochemical calculations will be needed when simpler structures have been explained.

The tetrahedral angles range from 104·2 to 117·3° and the octahedral ones from 85·9 to 96·7 and 172·3 to 175·8°. The P—O—Al angles run from 132·0 to 160·1° and the Al(1)—O(11)—Al(4) angle is 131·4°.

Hydrogen bonding. The H atom (Fig. 2) lies between O(11) and O(6), which are respectively connected to Al(1) and Al(4) and to P(2) and Al(4). The listed distances (Table 2) of O(11)—H = 0·60 (4) and O(6)—H = 2·46 (4) Å must be systematically biased from values near 0·9–1·0 and 2·0–2·1 Å that would be expected for neutron diffraction.

Encapsulated isopropylamine. Although the U_{eq} values are large for the extra-framework atoms, the atomic coordinates are consistent with encapsulation of isopropylamine during synthesis. Because H atoms were not located, it was not possible to check the presumption (see earlier) that protonation to isopropylammonium ion had occurred during synthesis. Each isopropyl species occupies a wide part of the channel system, and the N atom points towards one side of an 8-ring of framework oxygens as expected for weak hydrogen bonding. For an ammonium ion, there should be three H atoms, each of which might be hydrogen-bonded to a framework oxygen at about 3 Å from the N atom. Actually there are four framework oxygens at 2·8–3·1 Å from the N atom, with C(1)—N—O angles of 119–106° (Table 2). It is possible that

three H atoms are disordered over the four possible positions, and that this disorder precluded recognition on the final difference Fourier synthesis.

Concluding remarks. The complexity of the AlPO$_4$-14A structure testifies to the remarkable stereochemical properties of the aluminophosphates synthesized in the presence of organic species. Particularly important is the presence of three adjacent Al atoms (Figs. 2 and 3) which makes it impossible to convert the structure into a 4-connected framework by removal of the hydroxyl and encapsulated organic species. It is quite certain that the occurrence of Al in four-, five- and six-coordination, and the change of charge balance when hydroxyl bridges between two Al atoms, results in a new range of geometrical possibilities for viable structures additional to those for the zeolites which are restricted to four-coordinated Al. Whereas all tetrahedrally coordinated aluminophosphates have alternating Al and P with consequent even-numbered rings, the occurrence of adjacent Al atoms in AlPO$_4$-14A allows the presence of 5-rings.

We thank S. T. Wilson and E. M. Flanigen (Union Carbide Corporation) for synthesis and supply of the specimen, N. Weber for technical help, NSF for grant CHE 84-05167 and for general support from the Materials Research Laboratory supported by NSFDMR-8519460.

References

BENNETT, J. M., COHEN, J. P., ARTIOLI, G., PLUTH, J. J. & SMITH, J. V. (1985). *Inorg. Chem.* **24**, 188–193.

BENNETT, J. M., COHEN, J. P., FLANIGEN, E. M., PLUTH, J. J. & SMITH, J. V. (1983). *Intrazeolite Chemistry.* Am. Chem. Soc. Symp. Ser. Vol. 218, pp. 109–118. Washington, DC: American Chemical Society.

BENNETT, J. M., DYTRYCH, W. J., PLUTH, J. J., RICHARDSON, J. W. JR & SMITH, J. V. (1986). *Zeolites.* In the press.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE.* Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KNIEP, R. & MOOTZ, D. (1973). *Acta Cryst.* B**29**, 2292–2294.

KNIEP, R., MOOTZ, D. & VEGAS, A. (1977). *Acta Cryst.* B**33**, 263–265.

PARISE, J. B. (1984*a*). *J. Chem. Soc. Chem. Commun.* pp. 1449–1450.

PARISE, J. B. (1984*b*). *Acta Cryst.* C**40**, 1641–1643.

PARISE, J. B. (1985). *Zeolites,* edited by B. DRZAJ, S. HOCEVAR & S. PEJOVNIK, pp. 271–278. Amsterdam: Elsevier.

PARISE, J. B. & DAY, C. S. (1985). *Acta Cryst.* C**41**, 515–520.

PLUTH, J. J. & SMITH, J. V. (1985). *Nature (London),* **318**, 165–166.

PLUTH, J. V. & SMITH, J. V. (1986). *Acta Cryst.* C**42**, 1118–1120.

PLUTH, J. J., SMITH, J. V. & BENNETT, J. M. (1986). *Acta Cryst.* C**42**, 283–286.

PLUTH, J. J., SMITH, J. V., BENNETT, J. M. & COHEN, J. P. (1984). *Acta Cryst.* C**40**, 2008–2011.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

WILSON, S. T., LOK, B. M. & FLANIGEN, E. M. (1982). US patent No. 4,310,440.

WILSON, S. T., LOK, B. M., MESSINA, C. A., CANNAN, T. R. & FLANIGEN, E. M. (1982). *J. Am. Chem. Soc.* **104**, 1146–1147.

WILSON, S. T., LOK, B. M., MESSINA, C. A., CANNAN, T. R. & FLANIGEN, E. M. (1983). *Intrazeolite Chemistry.* Am. Chem. Soc. Symp. Ser. Vol. 218, pp. 79–106. Washington, DC: American Chemical Society.

YVOIRE, F. D' (1961). *Bull. Soc. Chem. Fr.* pp. 1762–1776.

Structure of Di-μ-bromo-bis-μ-{1-[2-(dimethylamino)phenyl]-2-(4-methylphenyl)-1-propenyl-*N,C*}-tetracopper(I)

BY W. J. J. SMEETS AND A. L. SPEK*

Vakgroep Algemene Chemie, Afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands

Abstract. [Cu$_4$Br$_2$(C$_{18}$H$_{20}$N)$_2$], $M_r = 914.72$, tetragonal, $I\bar{4}c2$, $a = 20.430$ (8), $c = 17.52$ (1) Å, $V = 7313$ (6) Å^3, $Z = 8$, $D_x = 1.662$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 44.9$ cm^{-1}, $F(000) = 3648$, $T = 295$ K, $R = 0.0572$ for 860 observed reflections with $I > \sigma(I)$. The molecule has twofold crystallographic axial symmetry and consists of a central rhombus-type core of Cu atoms to which the propenyl and Br groups are bound in a bridging fashion. The two propenyl and the two Br groups each occupy adjoining edges of the Cu$_4$ core. The Br-bridged edges are 2.507 (3) Å and significantly longer than the propenyl-bridged edges

* Author to whom correspondence should be addressed.