and monochromatization was not sufficient. Recalculation based on only the low-order reflections with $\sin\theta/\lambda \le 0{\cdot}6$ Å^{-1} gave $R(F)$ 0·028 for 110 unique reflections and $wR(F) = 0{\cdot}035$.* Equivalent isotropic thermal parameters, B_{eq}, for Pt, Cl and K decreased from 2·22 (10), 2·89 (6) and 3·33 (24) Å^2 to 1·83 (10), 2·49 (6) and 2·92 (21) Å^2, respectively and approached the X-ray values, 1·69 (1), 2·47 (2) and 2·85 (3) Å^2.

The authors would like to express their thanks to Professor Shinya Wakoh of the University of Library and Information Science, Ibaraki, for providing the program *FORM*. They are indebted to the Institute for Solid State Physics, University of Tokyo, for the use of a FACOM M-160F computer.

References

Archibald, E. H. (1910). *Z. Anorg. Chem.* **66**, 191.
Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. J. & Yang, Y. W. (1979). *Acta Cryst.* A**35**, 63–72.
Coppens, P. & Hall, M. B. (1982). Editors. *Electron Distributions and the Chemical Bond.* New York: Plenum.
Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754–756.
Ewing, F. J. & Pauling, L. (1928). *Z. Kristallogr.* **68**, 223–230.
Fukamachi, T. (1969). *Jpn. J. Appl. Phys.* **8**, 851–854.
Fukamachi, T. (1971). Tech. Rep. B12. Institute for Solid State Physics, Univ. of Tokyo.
Harada, J. (1983). Private communications.
International Tables for X-ray Crystallography (1959). Vol. II, 2nd ed., p. 300. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Iwata, M. & Saito, Y. (1973). *Acta Cryst.* B**29**, 822–832.
Kobayashi, A., Marumo, F. & Saito, Y. (1972). *Acta Cryst.* B**28**, 2709–2715.
Mann, J. B. (1967). *Atomic Structure Calculations* I. Report LA-3690. Los Alamos Scientific Laboratory, Univ. of California.
Ohba, S., Saito, Y. & Noda, Y. (1982). *Acta Cryst.* A**38**, 725–729.
Ohba, S., Sato, S. & Saito, Y. (1981). *Acta Cryst.* A**37**, 697–701.
Ohba, S., Sato, S., Saito, Y., Ohshima, K. & Harada, J. (1983). *Acta Cryst.* B**39**, 49–53.
Ohba, S., Toriumi, K., Sato, S. & Saito, Y. (1978). *Acta Cryst.* B**34**, 3535–3542.
Pauling, L. (1960). *The Nature of the Chemical Bond,* 3rd ed. Ithaca: Cornell Univ. Press.
Stevens, E. D. & Coppens, P. (1976). *Acta Cryst.* A**32**, 915–917.
Stevens, E. D., De Lucia, M. L. & Coppens, P. (1980). *Inorg. Chem.* **19**, 813–820.
Toriumi, K. & Saito, Y. (1978). *Acta Cryst.* B**34**, 3149–3156.
Toriumi, K. & Saito, Y. (1983). *Advances in Inorganic Chemistry and Radiochemistry,* pp. 27–81. New York: Academic Press.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

---

* See deposition footnote.

Acta Cryst. (1984). C**40**, 1641–1643

Preparation and Structure of the Aluminium Ammonium Phosphate Dihydrate $Al_2[NH_4](OH)(PO_4)_2.2H_2O$:* A Tunnel Structure with Ammonium Ions in the Channels

By John B. Parise

The Research School of Chemistry, Australian National University, GPO Box 4, Canberra, ACT 2601, Australia

(*Received* 6 *February* 1984; *accepted* 30 *May* 1984)

Abstract. $M_r = 315{\cdot}0$, monoclinic, $P2_1/n$, $a = 9{\cdot}553$ (1), $b = 9{\cdot}577$ (1), $c = 9{\cdot}614$ (1) Å, $\beta = 103{\cdot}56$ (1)°, $V = 855{\cdot}1$ Å^3, $Z = 4$, $D_x = 2{\cdot}45$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 6{\cdot}4$ cm^{-1}, $F(000) = 640$, $T = 293$ K. Final $R = 0{\cdot}025$ for 2449 observed data. The structure is isomorphous with $GaPO_4.2H_2O$ with columns of Al-centred corner- and edge-shared octahedra linked *via* PO_4 tetrahedra to outline channels approximately parallel to the *b* axis. Ammonium groups occupy these channels and are hydrogen-bonded to framework O atoms and water molecules.

Introduction. Aluminium phosphate hydrates with Al/P = 1·0 have been reported as the minerals variscite (Kniep, Mootz & Vegas, 1977) and metavariscite (Kniep & Mootz, 1973). In these structures P and Al are in tetrahedral and octahedral coordination respectively. Recently a new class of molecular sieves constructed by a network of corner-shared AlO_4 and PO_4 tetrahedra has been described and one of these phases has had its structure determined from single-crystal X-ray data (Wilson, Lok & Flanigen, 1982; Wilson, Lok, Messina, Cannan & Flanigen, 1982). It was during the attempted synthesis of the aluminium phosphate molecular sieve, $AlPO_4$-14 (Wilson, Lok & Flanigen, 1982), that a new structure type for $AlPO_4$ was synthesized. In this structure Al is in an octahedrally coordinated site thereby relating it to variscite and metavariscite.

Subsequent to the determination of the structure of the compound reported here it was found to be isomorphous with $GaPO_4.2H_2O$ (Mooney-Slater,

---

* Dialuminium ammonium hydroxide bis(orthophosphate).

0108-2701/84/101641-03$01.50

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*/U(Å^2)
P(1)	1985 (1)	5319 (1)	3482 (1)	50 (1)
P(2)	2947 (1)	1921 (1)	6368 (1)	50 (1)
Al(1)	1138 (1)	4629 (1)	6280 (1)	57 (1)
Al(2)	1074 (1)	2291 (1)	3150 (1)	55 (1)
O(1)	2099 (1)	3859 (1)	2847 (1)	80 (2)
O(2)	2369 (1)	5200 (1)	5132 (1)	77 (2)
O(3)	2083 (1)	3017 (1)	6966 (1)	93 (2)
O(4)	432 (1)	5859 (1)	2966 (1)	74 (2)
O(5)	2205 (1)	5516 (1)	7899 (1)	74 (2)
O(6)	2392 (1)	1758 (1)	4762 (1)	87 (2)
O(7)	3068 (1)	6274 (1)	3052 (1)	91 (2)
O(8)	−462 (1)	2678 (1)	1658 (1)	89 (2)
O*W*(1)	−34 (1)	6352 (1)	5542 (1)	78 (2)
O*W*(2)	1 (2)	9327 (2)	6466 (2)	139 (3)
O*W*(3)	1828 (2)	8565 (2)	4623 (2)	207 (4)
N	−135 (2)	−1904 (2)	1040 (2)	163 (3)
H(1)	44 (3)	687 (3)	526 (3)	21 (7)
H(2)	−40 (3)	1002 (3)	604 (3)	32 (6)
H(3)	73 (4)	958 (3)	675 (3)	36 (9)
H(4)	224 (4)	854 (4)	393 (5)	66 (12)
H(5)	234 (5)	914 (4)	537 (5)	53 (8)
H(6)	−90 (4)	−140 (4)	95 (4)	44 (7)
H(7)	−8 (4)	−261 (4)	155 (4)	39 (7)
H(8)	58 (4)	−144 (3)	143 (3)	37 (7)
H(9)	−4 (4)	−213 (4)	21 (4)	84 (12)

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ for all non-H atoms; e.s.d.'s according to Schomaker & Marsh (1983).

1966). The study was used as an opportunity to understand the details of the hydrogen-bonding scheme and, by inference, of that in $GaPO_4.2H_2O$ in which H atoms were not located.

Experimental. The starting mixture for an $AlPO_4$-14 preparation (Wilson, Lok & Flanigen, 1982) was sealed in a thick-walled Pyrex-glass capsule and heated at 423 K for 24 h. Clear crystal, 0·15 × 0·08 × 0·08 mm. Weissenberg and precession photographs indicated monoclinic ($2/m$) symmetry, space group $P2_1/n$ (No. 14) with absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$. Cell parameters determined from 12 high-angle ($56 < 2\theta < 60°$) centred reflections. Picker FACS-I diffractometer, pyrolytic-graphite monochromator; intensities measured to $\theta = 30°$ with 20 s fixed background counting times; range of hkl: h $-13\rightarrow13$, k $0\rightarrow13$, l $0\rightarrow13$; three standard reflections monitored periodically showed no significant variation; 64 of 2513 reflections measured had $I \leq 0{\cdot}0$ and were excluded from structure solution or refinement; 2449 intensities corrected for Lorentz and polarization effects, no absorption correction applied ($\mu R \simeq 0{\cdot}1$); structure solved using automatic centrosymmetric direct-methods routine of *SHELX*76 (Sheldrick, 1976) to find $AlPO_4$ framework; difference Fourier techniques to find O*W*, N and H positions; atomic parameters refined using full-matrix least squares; function minimized $\sum w(F_o - F_c)^2$, weights given as $\sigma^{-2}(F)$; σ is based on the σ_2 weights described by Busing & Levy (1957), $\sigma_2 = [(\sigma_1/\mathrm{Lp})^2 + (\mathrm{PSQ})F_o^4/2 - F_o]^{1/2}$ where σ_1 is based on counting statistics, Lp is the Lorentz–polarization factor and PSQ is the instrumental uncertainty factor (= 0·002). The σ_2 scheme tends to down-weight the very intense reflections in the data set. Three 'water' positions [numbered O*W*(1) through O*W*(3)] located. Final refinement employed fixed occupancies, anisotropic non-H atoms, isotropic H; max. peak in final difference map 0·5 e Å^{-3}, 0·9 Å from P-atom sites. There were smaller peaks (0·3 e Å^{-3}) within 1·2 Å of N perhaps indicating a greater degree of disorder for the $[NH_4]^+$ species. Inclusion of these positions (0·02, −0·23, 0·19 and 0·0, −0·26, 0·03) in the least-squares refinement did not improve the R value; a common isotropic thermal parameter refined for the five sites converged to a negative value. A model of four H atoms was accepted as being most consistent with the observed diffraction data.

Analytical expressions for the scattering factors those of Sheldrick (1976) excepting that for Al which was taken from *International Tables for X-ray Crystallography* (1974); anomalous-dispersion correction included; final discrepancy factors (Sheldrick, 1976) $R = 0{\cdot}025$ and $R_w = 0{\cdot}030$ for all data with $I > 0$; $(\Delta/\sigma)_{max} = 0{\cdot}2$. All calculations carried out on ANU Univac 1100 computer; major programs used: *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Discussion. Final atomic parameters are given in Table 1.*

The structure of the $AlPO_4$ framework is essentially as described by Mooney-Slater (1966) for $GaPO_4.2H_2O$. However, H positions, located in the analysis of this structure, give a more complete picture of the hydrogen bonding between water molecules and hydroxyl species attached to Al and the ammonium group, $[NH_4]^+$, which occupies the channels formed by the $[Al_2(OH)(PO_4)_2(H_2O)_2]$ framework (Fig. 1).

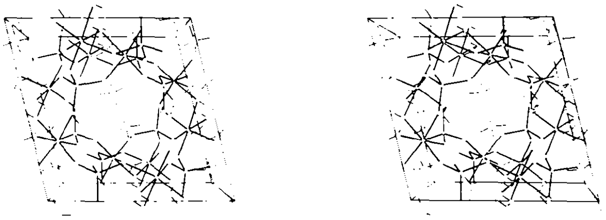

Fig. 1. Stereoscopic drawing (Johnson, 1965) of the structure viewed down the b-axial direction. H atoms have been given arbitrary radii. The $[NH_4]^+$ groups occupy the channel formed by Al-centred octahedra and P-centred tetrahedra.

---

* Lists of structure factors, anisotropic thermal parameters and geometry for the hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39518 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Selected interatomic distances and angles are given in Table 2 and drawings of the individual environments for 'water' are given in Fig. 2.

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

P(1)—O(1)	1·540 (1)	P(2)—O(3)	1·528 (1)
—O(2)	1·546 (1)	—O(5)	1·542 (1)
—O(4)	1·540 (1)	—O(6)	1·518 (1)
—O(7)	1·509 (1)	—O(8)	1·529 (1)
O(1)—P(1)—O(2)	108·6 (1)	O(3)—P(2)—O(5)	108·1 (1)
—O(4)	109·2 (1)	—O(6)	111·2 (1)
—O(7)	108·9 (1)	—O(8)	111·1 (1)
O(2)—P(1)—O(4)	109·6 (1)	O(5)—P(2)—O(6)	109·1 (1)
—O(7)	108·2 (1)	—O(8)	109·4 (1)
O(4)—P(1)—O(7)	112·2 (1)	O(6)—P(2)—O(8)	107·9 (1)
Al(1)—O(2)	1·873 (1)	Al(2)—O(1)	1·853 (1)
—O(3)	1·831 (1)	—O(6)	1·826 (1)
—O(4)	1·872 (1)	—O(8)	1·833 (1)
—O(5)	1·855 (1)	—O(7)	1·845 (1)
—O*W*(1)	2·027 (1)	—O*W*(2)	1·942 (1)
—O*W*(1)	2·048 (1)	—O*W*(1)	2·201 (1)
O(2)—Al(1)—O(3)	97·7 (1)	O(1)—Al(2)—O(6)	94·3 (1)
—O(4)	166·4 (1)	—O(8)	94·0 (1)
—O(5)	93·6 (1)	—O(7)	90·0 (1)
—O*W*(1)	85·9 (1)	—O*W*(2)	178·0 (2)
—O*W*(1)	84·2 (1)	—O*W*(1)	86·4 (1)
O(3)—Al(1)—O(4)	91·3 (1)	O(6)—Al(2)—O(8)	170·7 (1)
—O(5)	87·5 (1)	—O(7)	93·7 (1)
—O*W*(1)	176·1 (1)	—O*W*(2)	84·6 (2)
—O*W*(1)	91·9 (1)	—O*W*(1)	89·7 (2)
O(4)—Al(1)—O(5)	97·0 (1)	O(8)—Al(2)—O(7)	90·5 (1)
—O*W*(1)	84·9 (1)	—O*W*(2)	87·0 (2)
—O*W*(1)	85·3 (1)	—O*W*(1)	86·7 (1)
O(5)—Al(1)—O*W*(1)	94·1 (1)	O(7)—Al(2)—O*W*(2)	91·7 (2)
—O*W*(1)	177·6 (1)	—O*W*(1)	175·3 (1)
O*W*(1)—Al(1)—O*W*(1)	86·7 (1)	O*W*(2)—Al(2)—O*W*(1)	91·9 (2)

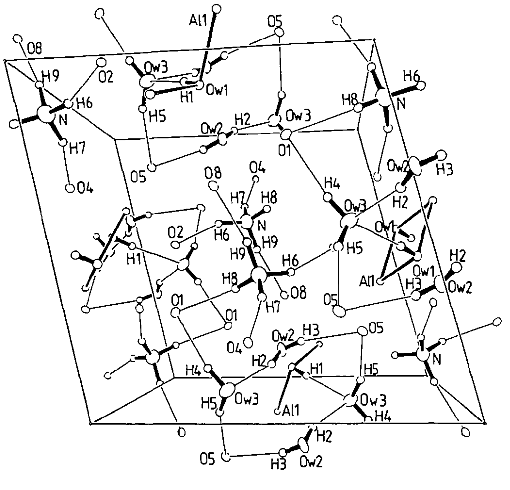

Fig. 2. The unit cell viewed down the *b*-axial direction emphasizing the relationship between water and ammonium species. Hydrogen bonds are depicted as thin lines (see text).

The phosphate tetrahedra are only slightly distorted and the average P—O distances [1·53 (2) and 1·53 (1) Å for P(1) and P(2) tetrahedra respectively] and angles [109 (1)°] are similar for those reported for the other $AlPO_4.2H_2O$ structures, variscite [1·53 (1) Å and 109 (2)°] and metavariscite [1·53 (1) Å and 109 (1)°] (Kniep & Mootz, 1973; Kniep *et al.,* 1977). The Al-centred octahedra are significantly distorted. Average bond lengths between Al and 'non-water' O atoms [1·86 (2) and 1·84 (1) Å for Al(1) and Al(2) octahedra respectively] are shorter than in variscite, 1·88 (2) Å, and metavariscite, 1·88 (1) Å, while the distance between Al atoms and 'water' O atoms is considerably longer (Table 2). The longest of these distances involves O*W*(1) which is 2·201 (1) Å from Al(2). This has the effect of distorting the $[AlO_3(H_2O)OH]$ octahedron towards a square-based pyramid. Angles are also distorted from the ideal with O(2)—Al(1)—O(4) = 166·4 (1)° being the largest deviation. These distortions are more pronounced than those previously described in $GaPO_4.2H_2O$ (Mooney-Slater, 1966).

Fig. 2 illustrates the relationship between OH and H_2O bound to the framework. O*W*(2) and O*W*(3) are hydrogen-bonded to one another [O*W*(3)···H(2)—O*W*(2)] and to framework O atoms (Fig. 2). The ordered $[NH_4]^+$ group is hydrogen-bonded to four framework O atoms; those sites closest to O atoms are H(6) and H(7). There are two O atoms [O*W*(3) and O(4)] at distances of 2·28 and 2·40 Å respectively from H(1) suggesting that only weak hydrogen bonds exist between H(1) and these atoms. The accepted hydrogen bonds have O(or N)—H 0·73 (4)–0·94 (5), H···O 1·93 (3)–2·2 (3), O(or N)···O 2·713 (3)–2·998 (3) Å, and O(or N)—H···O 152 (5)–172 (4)°.

Thanks are due to Dr G. B. Robertson for help in the collecting of the single-crystal X-ray data and to Jane Sutton for typing the manuscript.

References

Busing, W. R. & Levy, H. A. (1957). *J. Chem. Phys.* **26**, 563–568.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

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.

Mooney-Slater, R. C. L. (1966). *Acta Cryst.* **20**, 526–534.

Schomaker, V. & Marsh, R. E. (1983). *Acta Cryst.* A**39**, 819–820.

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

Wilson, T., Lok, B. M. & Flanigen, E. M. (1982). US Patent 4 310 440.

Wilson, T., Lok, B. M., Messina, C. A., Cannan, T. R. & Flanigen, E. M. (1982). *J. Am. Chem. Soc.* **104**, 1146–1147.