Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* $(NH_4)_6P_6O_{18}.H_2O$

E.s.d.'s are given in parentheses.

The PO_4 tetrahedron

P	O(1)	O(2)	O(*L*)	O(*L*)
O(1)	1·483 (1)	2·561 (2)	2·544 (1)	2·469 (1)
O(2)	119·30 (6)	1·484 (1)	2·476 (2)	2·542 (1)
O(*L*)	110·65 (6)	106·32 (6)	1·609 (1)	2·482 (1)
O(*L*)	106·54 (5)	111·14 (5)	101·48 (4)	1·597 (1)
	P—P	2·9544 (5)	P—O(*L*)—P	134·35 (6)
			P—P—P	108·51 (1)

The ammonium coordination

N—O(1)	2·796 (2)	N—O(2)	3·101 (2)
N—O(1)	2·841 (2)	N—O(2)	3·074 (2)
N—O(2)	2·854 (2)	N—O(*L*)	3·209 (2)
N—O(1)	3·264 (2)	N—O(2)	3·256 (2)

The hydrogen bonds

	N—H	H···O	N···O	N—H···O
N—H(1)···O(2)	0·88 (2)	1·99 (2)	2·854 (2)	167 (2)
N—H(2)···O(2)	0·88 (2)	2·33 (2)	3·101 (2)	147 (2)
N—H(3)···O(1)	0·84 (2)	2·02 (2)	2·841 (2)	165 (2)
N—H(4)···O(1)	0·84 (2)	1·95 (2)	2·796 (2)	176 (2)

and so is constructed by only one crystallographically independent tetrahedron. Its geometrical features are quite similar to those observed in previously investigated P_6O_{18} rings with the same internal symmetry (Table 2). The NH_4 groups also form $(NH_4)_6$ rings around the $\bar{3}$ axis with an N—N distance of 3·975 (2) Å and an N—N—N angle of 108·56 (3)°. P_6O_{18} and $(NH_4)_6$ rings alternatate along the $\bar{3}$ axis separated by a distance of $c/2$.

Within a range of 3·5 Å the ammonium group is eight-coordinated with N—O distances ranging from 2·796 to 3·264 Å (Table 2). A three-dimensional network of hydrogen bonds connects the NH_4 groups to the external O atoms of the phosphoric ring. Numerical details of this network are reported in Table 2.

In addition it is worth noticing the existence on the $\bar{3}$ axis of a water molecule not belonging to the cation coordination. Located at 0, 0, $\frac{1}{2}$ this water molecule is exactly at the center of gravity of the $(NH_4)_6$ ring at a distance of 3·658 (9) Å from the N atoms.

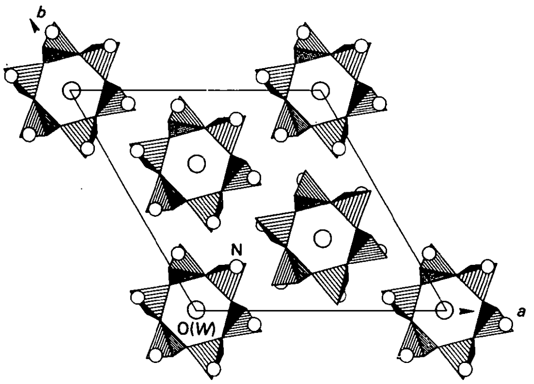

Fig. 1. Projection along the *c* axis of the atomic arrangement of $(NH_4)_6P_6O_{18}.H_2O$.

Fig. 1 shows a projection of this atomic arrangement along the *c* axis.

References

Averbuch-Pouchot, M. T. (1988*a*). *Z. Kristallogr.* To be published.

Averbuch-Pouchot, M. T. (1988*b*). *Z. Anorg. Allg. Chem.* To be published.

Averbuch-Pouchot, M. T. (1989). *Acta Cryst.* To be published.

Enraf–Nonius (1977). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

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

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Schülke, U. & Kayser, R. (1985). *Z. Anorg. Allg. Chem.* **531**, 167–176.

Stout, G. H. & Jensen, L. M. (1968). In *X-ray Structure Determination.* New York: Macmillan.

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Redetermination of the Crystal Structure of Mo_4P_3

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Abstract. Mo_4P_3, $M_r = 476·68$, orthorhombic, *Pnma*, $a = 12·4316$ (11), $b = 3·1581$ (6), $c = 20·4468$ (30) Å, $V = 802·7$ (3) Å^3, $Z = 8$, D_m not measured, $D_x = 7·89$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu_{\text{Mo }K\alpha} = 12·9$ mm^{-1}, $F(000) = 1704$, $T = 293$ K, 1476 reflections, $R = 0·032$, $wR = 0·039$. Lattice built up from MoP_6 and MoP_5 polyhedra. Mo—P distances range from 2·375 to 3·002 Å.

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Table 1. *Atomic parameters*

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Mo(1)	0·37920 (8)	0·25	0·18898 (5)	0·16 (1)
Mo(2)	0·49116 (8)	0·25	0·32727 (5)	0·21 (1)
Mo(3)	0·59992 (8)	0·25	0·47274 (5)	0·22 (1)
Mo(4)	0·70185 (8)	0·25	0·61348 (5)	0·19 (1)
Mo(5)	0·80564 (8)	0·25	0·77323 (5)	0·21 (1)
Mo(6)	0·29763 (8)	0·75	0·08400 (5)	0·19 (1)
Mo(7)	0·11583 (8)	0·25	0·35191 (5)	0·26 (1)
Mo(8)	0·09510 (8)	0·75	0·46660 (5)	0·27 (1)
P(1)	0·17938 (24)	0·25	0·13687 (15)	0·23 (4)
P(2)	0·25424 (24)	0·25	0·47219 (15)	0·25 (4)
P(3)	0·48229 (25)	0·75	0·41870 (15)	0·20 (4)
P(4)	0·45909 (26)	0·25	0·08070 (16)	0·28 (4)
P(5)	0·30046 (25)	0·25	0·29489 (14)	0·26 (4)
P(6)	0·01556 (24)	0·75	0·27448 (15)	0·24 (4)

Table 2. Mo—P *distances* (Å)

Mo(1)—P(1)	2·703 (3)
—P(4)	2·426 (3)
—P(5)	2·376 (3)
—P(6^{i})	2·434 (2)
—P(6^{ii})	2·434 (2)
Mo(2)—P(1^{ii})	2·452 (3)
—P(3^{iii})	2·450 (2)
—P(3)	2·450 (2)
—P(5)	2·461 (3)
—P(6^{i})	2·629 (3)
—P(6^{ii})	2·629 (3)
Mo(3)—P(1^{ii})	2·449 (3)
—P(2^{iv})	2·655 (3)
—P(2^{v})	2·655 (3)
—P(3^{iii})	2·419 (3)
—P(3)	2·419 (3)
—P(3^{iv})	2·444 (3)
Mo(4)—P(2^{iv})	2·421 (2)
—P(2^{v})	2·421 (2)
—P(3^{iv})	2·382 (3)
—P(5^{iv})	2·450 (2)
—P(5^{v})	2·450 (2)
Mo(5)—P(1^{iv})	2·430 (3)
—P(1^{v})	2·430 (3)
—P(5^{iv})	2·485 (2)
—P(5^{v})	2·485 (2)
—P(6^{iv})	2·427 (3)
Mo(6)—P(1)	2·413 (2)
—P(1^{vi})	2·413 (2)
—P(2^{vii})	2·375 (3)
—P(4)	2·555 (3)
—P(4^{vi})	2·555 (3)
Mo(7)—P(4^{viii})	2·386 (3)
—P(5)	2·574 (3)
—P(6^{iii})	2·560 (3)
—P(6)	2·560 (3)
—P(2)	3·002 (3)
Mo(8)—P(2)	2·534 (2)
—P(2^{vi})	2·534 (2)
—P(4^{ix})	2·428 (2)
—P(4^{viii})	2·507 (3)
—P(4^{x})	2·507 (3)

Symmetry codes: (i) $\frac{1}{2}+x, y-1, \frac{1}{2}-z$; (ii) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (iii) $x, y-1, z$; (iv) $1-x, y-\frac{1}{2}, 1-z$; (v) $1-x, \frac{1}{2}+y, 1-z$; (vi) $x, 1+y, z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (viii) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (ix) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (x) $x-\frac{1}{2}, 1+y, \frac{1}{2}-z$.

Introduction. During the study of the Na—Mo—P—O system, single crystals of molybdenum phosphide Mo_4P_3 were isolated. The crystal structure of the compound had already been determined by Rundqvist (1965), using multiple-film techniques. However, the R factor remained rather high, 0·12, and many atoms had negative thermal factors, in spite of the careful study carried out by the author, owing to the quality of the data. Thus the present work deals with the refinement of the crystal structure from a new data collection performed on an automatic diffractometer, in order to obtain better accuracy in the atomic positions.

Experimental. Crystal: 0·024 × 0·020 × 0·012 mm, mounted along the needle axis, **b**. Precession and Weissenberg films: *mmm* symmetry with systematic absences $0kl$ for $k + l$ odd and $hk0$ for h odd. Enraf–Nonius CAD-4 diffractometer. Unit cell: least squares on 25 reflections $\pm 2\theta$, $18 \le \theta \le 22°$. Intensity measurement up to $\theta = 45°$ with an ω–$4/3\theta$ scan of $(1{\cdot}22 + 0{\cdot}35\tan\theta)°$ width and a counter slit aperture of $(1{\cdot}2 + \tan\theta)$ mm, values determined by a study of some reflections in the ω–θ plane. Scanning speed adjusted to obtain $\sigma(I)/I < 0{\cdot}018$ or to approach it in a time limited to 60 s. Three standards for count every 2000 s and orientation every 600 reflections: no appreciable trends. 1476 reflections with $I > 3\sigma(I)$ used to solve and refine the structure. No correction made for extinction or absorption. All subsequent calculations on an IBM 3090 by local adaptations of the classical programs. Structure solved by Patterson function and heavy-atom method, and refined on F by a full-matrix least-squares method with anisotropic thermal motion.* The usual f's from *International Tables for X-ray Crystallography* (1974). $(\Delta/\sigma)_{max} = 0{\cdot}001$, $\Delta\rho < 1{\cdot}5$ e Å^{-3}, $R = 0{\cdot}032$, $wR = 0{\cdot}039$, $w = f[(\sin\theta)/\lambda]$, $S = 1{\cdot}5$. Atomic parameters in Table 1.

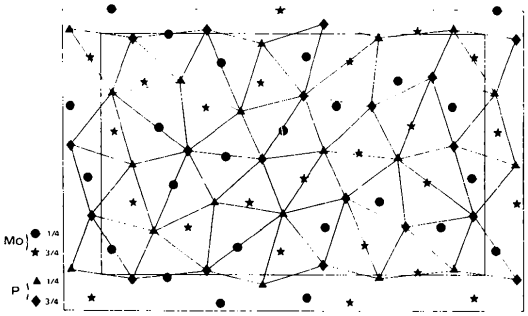

Fig. 1. Projection of the structure along [010] showing the MoP_5 and MoP_6 polyhedra.

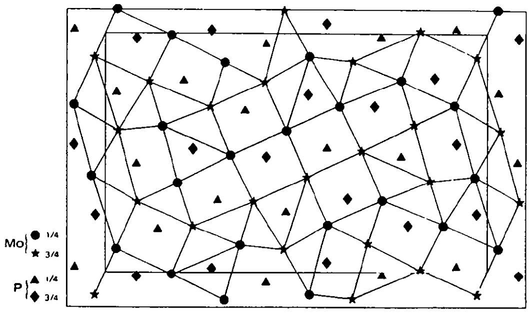

Fig. 2. Projection of the structure along [010] showing the PMo_6 and PMo_7 polyhedra.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51527 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The general features of the structure (Fig. 1) are the same as those determined by Rundqvist (1965). The interatomic distances (Table 2) are almost the same as those previously established by Rundqvist but the thermal motion factors are positive definite. The Mo—P distances range from 2·375 to 3·002 Å. All the atoms are located in the mirror planes of the unit cell. One observes three types of P polyhedra around the Mo atoms: two MoP_6 octahedra around Mo(2) and M(3), two MoP_5 triangular bipyramids around Mo(1) and Mo(7), and four MoP_5 square pyramids around Mo(4), Mo(5), Mo(6) and Mo(8). The structure can be described as layers of corner-, edge- and face-sharing MoP_6 and MoP_5 polyhedra parallel to the (010) plane (Fig. 1). Two successive layers share the edges of their polyhedra. Around the P atoms one observes two types of Mo polyhedra: one triangular prism around P(3) and five mono-capped triangular prisms around the others (Fig. 2). This ratio explains the fact that the asymmetric unit formula is Mo_8P_6 instead of Mo_4P_3.

References

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

RUNDQVIST, S. (1965). *Acta Chem. Scand.* **19**, 393–400.

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Structure of Intermediate Albite, $NaAlSi_3O_8$

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Abstract. $M_r = 262{\cdot}22$, triclinic, $C\bar{1}$, $a = 8{\cdot}149\ (1)$, $b = 12{\cdot}840\ (1)$, $c = 7{\cdot}120\ (1)$ Å, $\alpha = 93{\cdot}83\ (1)$, $\beta = 116{\cdot}47\ (1)$, $\gamma = 89{\cdot}51\ (1)°$, $V = 665{\cdot}2\ (3)$ Å^3, $Z = 4$, $D_x = 2{\cdot}62$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 9{\cdot}0$ cm^{-1}, $F(000) = 520$, $T = 294\ (1)$ K, $R = 0{\cdot}030$ for 2055 unique reflections with $I > 3\sigma(I)$ of 2303 total unique data. Mean tetrahedral bond lengths (Å) and estimated average Al/(Al + Si) occupancies are: T_10 1·677, 0·51 Al; T_1m 1·631, 0·15 Al; T_20 1·632, 0·16 Al, T_2m 1·633, 0·17 Al.

Introduction. The K feldspar ($KAlSi_3O_8$) and Na feldspar ($NaAlSi_3O_8$) minerals are isostructural (space group $C\bar{1}$) in their completely ordered ('low') modifications: the Al atom is ordered into a particular tetrahedral (T) site (designated T_10), with Si in the other three nonequivalent T sites (*i.e.* T_1m, T_20, T_2m). Both K and Na end members may have completely disordered 'high' (= high temperature) modifications, with $t \equiv \text{Al}/(\text{Al} + \text{Si}) = 0{\cdot}25$ in all four T sites, but at room temperature the K feldspar is monoclinic ($C2/m$) and the Na feldspar is triclinic ($C\bar{1}$). [The unconventional space group preserves a common unit-cell orientation for all alkali feldspars.]

In nature, series of both monoclinic (with $t_10 = t_1m$ and $t_20 = t_2m$) and triclinic (with $t_10 > t_1m \geq t_20 \sim t_2m$) K-rich feldspars are well documented (Kroll & Ribbe, 1983, 1987), but K-free Na feldspar ('albite') has only been reported in its ordered form, as though a first-order transformation occurred during cooling (see discussions by Ribbe, 1983; Smith, 1983). This is not the case, however, as Goldsmith & Jenkins (1985) demonstrated in their studies at high pressures of the equilibrium Al,Si order–disorder relations in albite. They found that the 'low ↔ high' albite conversion takes place continuously, without change in symmetry, over the range ~925–1125 K. Salje (1985) and Salje, Kuscholke, Wruck & Kroll (1985) predicted the thermodynamic properties of albite with a two-parameter Landau-type free-energy expression, confirming the conclusions of Goldsmith & Jenkins (1985).

Su, Ribbe, Bloss & Goldsmith (1986) investigated a suite of albite single crystals with degrees of Al,Si order ranging from low (ordered) to high (~90% dis-

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