AVERBUCH-POUCHOT, M. T. (1989*c*). *Acta Cryst.* C**45**, 1275–1277.
AVERBUCH-POUCHOT, M. T. (1989*d*). *Z. Anorg. Allg. Chem.* Submitted.
Enraf–Nonius (1977). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
GRIFFITH, E. G. & BUXTON, R. L. (1965). *Inorg. Chem.* **4**, 549–551.
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.

Acta Cryst. (1989). C**45**, 1275–1277

Crystal Chemistry of *cyclo*-Hexaphosphates. II. Structure of Copper *cyclo*-Hexaphosphate Tetradecahydrate

BY M. T. AVERBUCH-POUCHOT

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'Université J. Fourier, 166 *X*, 38042 *Grenoble CEDEX, France*

(*Received* 20 *September* 1988; *accepted* 13 *January* 1989)

Abstract. $Cu_3P_6O_{18}.14H_2O$, $M_r = 916{\cdot}67$, triclinic, $P\bar{1}$, $a = 10{\cdot}944\,(8)$, $b = 7{\cdot}539\,(4)$, $c = 8{\cdot}974\,(4)$ Å, $\alpha = 110{\cdot}49\,(5)$, $\beta = 110{\cdot}14\,(5)$, $\gamma = 77{\cdot}82\,(5)^\circ$, $V = 647\,(1)$ Å^3, $Z = 1$, $D_x = 2{\cdot}350$ Mg m^{-3}, λ(Mo $K\alpha$) = $0{\cdot}7107$ Å, $\mu = 3{\cdot}039$ mm^{-1}, $F(000) = 461$, $T = 293$ K, final R value = $0{\cdot}036$ for 3439 reflections. Alternating corner-sharing P_6O_{18} ring anions and $CuO_4(H_2O)_2$ octahedra form chains spreading along the c axis. These chains are themselves interconnected by a centrosymmetrical cluster of two edge-sharing $CuO(H_2O)_5$ octahedra.

Introduction. The present study is part of a systematic study of the crystal chemistry of *cyclo*-hexaphosphates.

In previous articles we reported chemical preparations and crystal structures of various monovalent *cyclo*-hexaphosphates (Averbuch-Pouchot, 1989*a*,*c*) and of the first example of a bivalent-cation *cyclo*-hexaphosphate: $Cd_3P_6O_{18}.6H_2O$ (Averbuch-Pouchot, 1989*b*). The present work is devoted to the crystal chemistry of another divalent-cation *cyclo*-hexaphosphate: $Cu_3P_6O_{18}.14H_2O$.

The present structural study confirms the hydration state previously observed for this compound during investigations of its thermal behaviour with polycrystalline samples (Lazarevski, Kubasova, Chudinova & Tananaev, 1980, 1982).

Experimental. Crystals of the title compound can be obtained by several processes: adding water solutions of $CuCl_2$ [or $Cu(NO_3)_2$] to an aqueous solution of $Li_6P_6O_{18}.6H_2O$ or adding a water solution of copper nitrate to a solution of guanidinium *cyclo*-hexaphosphate in stoichiometric ratio. After some days of evaporation of the resulting solutions at room temperature, crystals of $Cu_3P_6O_{18}.14H_2O$ appear as turquoise calcite-like pseudo-rhombohedra. Density not measured. $0{\cdot}30 \times 0{\cdot}30 \times 0{\cdot}15$ mm crystal. Philips PW 1100 diffractometer, graphite monochromator. 18 reflections ($14 < \theta < 16^\circ$) for refining unit-cell dimensions. $\omega/2\theta$ scan. Scan width: $1{\cdot}20^\circ$, scan speed: $0{\cdot}02^\circ$ s^{-1}, total background measuring time: 10 s. 4707 reflections measured ($3 < \theta < 35^\circ$), $\pm h$, $\pm k$, l, $h_{max} = 17$, $k_{max} = 12$, $l_{max} = 12$. Two intensity and orientation reflections (051 and $0\bar{5}\bar{1}$) measured every three hours without significant variation. 4273 independent reflections ($R_{int} = 0{\cdot}009$). Lorentz and polarization corrections, no absorption correction. Crystal structure by investigation of the Patterson map and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. H atoms located by difference-Fourier map. Unit weights. Final refinement with 3439 reflections ($I > 9\sigma_I$).

Final $R = 0{\cdot}036$ ($wR = 0{\cdot}041$), $S = 0{\cdot}984$, max. $\Delta/\sigma = 0{\cdot}03$. Max. peak height in final difference-Fourier syntheses $1{\cdot}425$ e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX II.

0108-2701/89/091275-03$03.00

Discussion. Table 1 reports the final atomic coordinates* and Fig. 1 shows a projection of the atomic arrangement along the *b* axis.

The P_6O_{18} *ring anion.* The anion is centrosymmetric, built up by three independent corner-sharing PO_4 tetrahedra. If the local geometry around a PO_4 tetrahedron (P—O distances, O—P—O and P—O—P angles,...) is quite similar to what is normally observed in cyclic or linear condensed phosphoric anions, the P—P—P angles differ very

Table 1. *Final atomic coordinates and* B_{eq} *values for* $Cu_3P_6O_{18}.14H_2O$

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

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
Cu(1)	0·000	0·000	0·000	1·060 (8)
Cu(2)	0·60594 (4)	0·43034 (5)	0·37989 (4)	1·514 (7)
P(1)	0·77830 (7)	0·06270 (9)	0·45385 (8)	1·06 (1)
P(2)	0·80155 (6)	0·86776 (9)	0·11915 (8)	0·96 (1)
P(3)	0·92896 (6)	0·28482 (8)	0·77783 (8)	0·97 (1)
O(*E*11)	0·7702 (2)	0·8773 (3)	0·4714 (3)	2·04 (4)
O(*E*12)	0·6634 (2)	0·2087 (3)	0·4625 (3)	1·55 (4)
O(*L*12)	0·8173 (2)	0·0352 (3)	0·2907 (2)	1·24 (3)
O(*L*13)	0·9065 (2)	0·1529 (3)	0·5887 (3)	1·64 (4)
O(*E*21)	0·1677 (2)	0·0523 (3)	−0·0069 (2)	1·34 (4)
O(*E*22)	0·3218 (2)	0·2181 (3)	0·9381 (3)	1·61 (4)
O(*L*23)	0·9174 (2)	0·7089 (3)	0·1700 (2)	1·17 (3)
O(*E*31)	0·8643 (2)	0·4797 (3)	0·7874 (3)	1·56 (4)
O(*E*32)	0·1031 (2)	0·8180 (3)	0·1264 (2)	1·47 (4)
O(*W*1)	0·8083 (3)	0·4708 (3)	0·3801 (4)	2·86 (6)
O(*W*2)	0·5699 (2)	0·2659 (3)	0·1471 (3)	1·89 (4)
O(*W*3)	0·9762 (2)	0·7524 (3)	0·7442 (3)	2·16 (5)
O(*W*4)	0·3792 (2)	0·4141 (3)	0·3854 (3)	1·88 (5)
O(*W*5)	0·6704 (2)	0·3855 (3)	0·9660 (3)	2·16 (5)
O(*W*6)	0·3778 (3)	0·0405 (4)	0·2838 (4)	3·20 (7)
O(*W*7)	0·4584 (3)	0·3362 (4)	0·6864 (4)	3·38 (7)

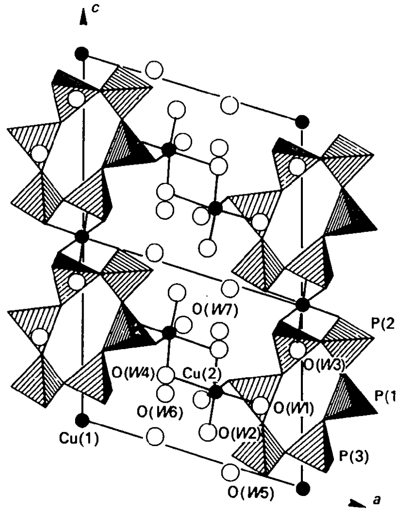

Fig. 1. Projection of the atomic arrangement of $Cu_3P_6O_{18}.14H_2O$ along the *b* axis. H atoms are not represented.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in* $Cu_3P_6O_{18}.14H_2O$

The P_6O_{18} ring

$P(1)O_4$ tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*13)
O(*E*11)	1·484 (3)	2·541 (3)	2·549 (4)	2·520 (3)
O(*E*12)	117·3 (2)	1·491 (2)	2·524 (3)	2·516 (3)
O(*L*12)	111·6 (1)	109·6 (1)	1·596 (2)	2·408 (3)
O(*L*13)	109·6 (1)	109·0 (1)	97·8 (1)	1·598 (2)

$P(2)O_4$ tetrahedron

P(2)	O(*L*12)	O(*E*21)	O(*E*22)	O(*L*23)
O(*L*12)	1·594 (2)	2·453 (3)	2·552 (2)	2·498 (2)
O(*E*21)	105·0 (1)	1·495 (3)	2·558 (4)	2·540 (3)
O(*E*22)	112·6 (1)	119·2 (1)	1·471 (2)	2·473 (3)
O(*L*23)	102·4 (1)	109·7 (1)	106·7 (1)	1·610 (2)

$P(3)O_4$ tetrahedron

P(3)	O(*L*13)	O(*L*23)	O(*E*31)	O(*E*32)
O(*L*13)	1·602 (2)	2·425 (2)	2·544 (3)	2·526 (3)
O(*L*23)	99·0 (1)	1·589 (2)	2·488 (3)	2·537 (3)
O(*E*31)	111·4 (1)	108·5 (1)	1·477 (2)	2·540 (3)
O(*E*32)	109·0 (1)	110·4 (1)	117·1 (1)	1·501 (3)

P(1)—P(2)	2·920 (1)	P(2)—P(1)—P(3)	139·94 (4)
P(1)—P(3)	2·904 (1)	P(1)—P(2)—P(3)	96·30 (3)
P(2)—P(3)	2·883 (1)	P(1)—P(3)—P(2)	114·10 (3)

P(1)—O(*L*12)—P(2)	132·4 (2)
P(1)—O(*L*13)—P(3)	130·3 (2)
P(2)—O(*L*23)—P(3)	128·6 (2)

Least-squares plane involving P(1), P(2), P(3), O(*L*12), O(*L*23) and O(*L*13)

Equation: $10{\cdot}11x - 1{\cdot}322y - 2{\cdot}287z - 7{\cdot}300 = 0$

Deviations

P(1)	−0·550 (1)	O(*L*12)	0·254 (2)
P(2)	−0·614 (1)	O(*L*13)	0·320 (2)
P(3)	−0·061 (1)	O(*L*23)	0·652 (2)

CuO_6 octahedron

$Cu(1)O_6$

Cu(1)—O(*E*21)	1·982 (2) (×2)
Cu(1)—O(*E*32)	1·999 (2) (×2)
Cu(1)—O(*W*3)	2·369 (2) (×2)

$Cu(2)O_6$

Cu(2)—O(*E*12)	1·960 (2)	Cu(2)—O(*W*4)	2·528 (3)
Cu(2)—O(*W*1)	2·297 (3)	Cu(2)—O(*W*4)	1·989 (2)
Cu(2)—O(*W*2)	1·970 (2)	Cu(2)—O(*W*7)	1·967 (3)

Hydrogen bonds

		O(*W*)—H	H···O	O(*W*)—O	O(*W*)—H···O	H—O(*W*)—H
O(*W*1)	H(1*W*1)···O(*W*3)	0·67 (6)	2·26 (7)	2·909 (4)	162 (7)	131 (10)
	H(2*W*1)···O(*E*11)	0·64 (6)	2·25 (7)	2·859 (3)	157 (8)	
O(*W*2)	H(1*W*2)···O(*E*22)	0·85 (6)	1·89 (5)	2·730 (3)	172 (7)	115 (7)
	H(2*W*2)···O(*W*5)	0·65 (8)	2·07 (7)	2·709 (4)	165 (6)	
O(*W*3)	H(1*W*3)···O(*E*31)	0·51 (9)	2·33 (11)	2·798 (4)	155 (13)	98 (10)
	H(2*W*3)···O(*E*11)	1·09 (5)	1·92 (6)	2·981 (3)	164 (6)	
O(*W*4)	H(1*W*4)···O(*E*31)	0·85 (5)	1·86 (6)	2·697 (3)	169 (4)	118 (5)
	H(2*W*4)···O(*W*6)	0·97 (6)	1·69 (6)	2·641 (4)	164 (6)	
O(*W*5)	H(1*W*5)···O(*E*32)	0·82 (6)	2·06 (7)	2·847 (3)	163 (4)	109 (6)
	H(2*W*5)···O(*E*22)	0·92 (7)	1·91 (7)	2·817 (3)	169 (7)	
O(*W*6)	H(1*W*6)···O(*E*21)	1·03 (5)	1·92 (5)	2·836 (3)	146 (5)	133 (7)
	H(2*W*6)···O(*E*12)	0·72 (8)	2·72 (6)	3·278 (4)	137 (5)	
O(*W*7)	H(1*W*7)···O(*E*11)	0·78 (6)	2·15 (6)	2·918 (4)	169 (5)	127 (5)
	H(2*W*7)···O(*W*5)	0·83 (6)	1·96 (8)	3·067 (7)	157 (5)	

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51857 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

significantly to those previously measured in other P_6O_{18} anions. These angles are: 108·5° for $(NH_4)_6P_6O_{18}.H_2O$; 112·2° for $Ag_6P_6O_{18}.H_2O$; 116·4 and 115·8° for $Cd_3P_6O_{18}.6H_2O$.

Here the values of the three P—P—P angles vary from 96·3 to 139·9° (Table 2) with an average of 116·8°.

In spite of this large angular distortion the calculation of the least-squares plane of the P and bonding O atoms (Table 2) shows this group of atoms to be almost planar.

The copper coordination. Two independent distorted copper octahedra are observed in the atomic arrangement. The first is located around the origin and is built up of four O atoms and two water molecules. This octahedron, whose main geometrical features are reported in Table 2, shares four of its O atoms with the P_6O_{18} ring anions, thus building chains: P_6O_{18}—$CuO_4(H_2O)_2$—P_6O_{18}..., spreading along the *c* axis. These chains are themselves interconnected by the centrosymmetric cluster $Cu_2(H_2O)_8O_2$ built up of two edge-sharing $CuO(H_2O)_5$ octahedra. This second kind of copper coordination polyhedron shares only one O atom with the phosphoric ring anion.

In addition it must be noted that two of the water molecules [O(*W*5) and O(*W*6)] are not involved in the copper coordination.

The three-dimensional network of hydrogen bonds is described in Table 2.

References

Averbuch-Pouchot, M. T. (1989*a*). *Z. Kristallogr.* Submitted.

Averbuch-Pouchot, M. T. (1989*b*). *Z. Anorg. Allg. Chem.* Submitted.

Averbuch-Pouchot, M. T. (1989*c*). *Acta Cryst.* C**45**, 539–540.

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.)

Lazarevski, E. V., Kubasova, L. V., Chudinova, N. N. & Tananaev, I. V. (1980). *Izv. Akad. Nauk, SSSR. Neorg. Mater.* **16**, 120–125.

Lazarevski, E. V., Kubasova, L. V., Chudinova, N. N. & Tananaev, I. V. (1982). *Izv. Akad. Nauk, SSSR. Neorg. Mater.* **18**, 1544–1549.

Acta Cryst. (1989). C**45**, 1277–1279

$KMoWP_3O_{12}$, a Tunnel Structure of the $KMo_2P_3O_{12}$-Type

By A. Benmoussa, A. Leclaire, A. Grandin and B. Raveau

Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT, ISMRa,
Bd du Maréchal Juin, 14032 *Caen CEDEX, France*

(*Received* 23 *December* 1988; *accepted* 20 *January* 1989)

Abstract. Potassium molybdotungstotriphosphate(V), $KMoWP_3O_{12}$, $M_r = 603·80$, orthorhombic, *Pbcm*, $a = 8·8180\ (6)$, $b = 9·1574\ (8)$, $c = 12·3836\ (8)$ Å, $V = 1000·0\ (2)$ Å^3, $Z = 4$, $D_x = 4·01$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 13·9$ mm^{-1}, $T = 294$ K, $F(000) = 276$, $R = 0·035$ and $wR = 0·042$ for 2291 observed reflections. The framework is built up from MoO_6 octahedra and PO_4 tetrahedra which delimit tunnels running along **b**, where the K ions are located. The structure leads to the formula $KMoWO(PO_4)(P_2O_7)$.

Introduction. Molybdenum and tungsten exhibit very different behavior in spite of their similar electronic structure. Recent studies of the phosphates of these elements support this point of view, as shown for instance by the existence of phosphate tungsten bronzes (see Raveau, 1986, for review), and the synthesis of original frameworks of phosphates of Mo^{III} (Leclaire, Borel, Grandin & Raveau, 1988, 1989*a*; Riou, Leclaire, Grandin & Raveau, 1989; Lii & Haushalter, 1987*a*) and Mo^V (Leclaire, Monier & Raveau, 1983; Leclaire, Borel, Grandin & Raveau, 1989*b*; Lii & Haushalter, 1987*b*; Chen, Lii & Wang, 1988). On the other hand tetravalent molybdenum and tungsten have features in common: if one considers the MoO_2 and WO_2 oxides which are isostructural with the TiO_2 rutile form.

Since the synthesis of the tungsten phosphate isotypic with $AMo_2P_3O_{12}$ (A = K, Rb, Tl) (Leclaire, Monier & Raveau, 1985; Leclaire & Raveau, 1988) has so far been unsuccessful, the substitution of tungsten for molybdenum in $KMo_2P_3O_{12}$ has thus been investigated. We report here on the crystal structure of $KMoWP_3O_{12}$.

Experimental. The synthesis was performed in two steps. First, $(NH_4)_2HPO_4$, MoO_3, WO_3 and K_2CO_3

0108-2701/89/091277-03$03.00