

O(1) shifted significantly when O(1A) was included in the model. The two largest shifts were  $12\sigma$  in the  $z$  coordinate and  $14\sigma$  in  $\beta_{33}$ . The final  $\Delta\rho$  map contained no peaks larger than  $0.07 \text{ e } \text{\AA}^{-3}$  in the vicinity of O(1) and O(1A). This type of disorder, where the coordination pyramid around  $\text{H}_3\text{O}^+$  is turned inside out, has been described earlier (Lundgren, 1979; Gustafsson, 1985).

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## Structure of Tetrapotassium Copper *cyclo*-Triphosphate Tetrahydrate

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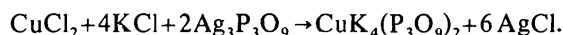
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**Abstract.**  $\text{CuK}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ ,  $M_r = 765.84$ , monoclinic,  $P2_1/a$ ,  $a = 8.510(5)$ ,  $b = 14.303(8)$ ;  $c = 8.487(5) \text{ \AA}$ ,  $\beta = 96.51(2)^\circ$ ,  $V = 1026(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 2.478 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Ag K}\alpha) = 0.5608 \text{ \AA}$ ,  $\mu = 1.272 \text{ mm}^{-1}$ ,  $F(000) = 758$ ,  $T = 293 \text{ K}$ , final  $R = 0.028$  for 2336 independent reflexions. The crystal structure is built up by double layers of  $\text{KO}_n$  polyhedra alternating with layers of  $\text{CuO}_6$  octahedra, both perpendicular to the  $c$  axis. The phosphoric anion  $\text{P}_3\text{O}_9$  is a trimeric ring.

**Introduction.** Copper-alkali (or monovalent cation) cyclophosphates are not very common. In order of increasing condensation one can only mention:  $\text{Na}_4\text{Cu}(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  (Durif & Averbuch-Pouchot, 1984),  $\text{Li}_2\text{Cu}_2\text{P}_6\text{O}_{18}$  (Läügt & Durif, 1974),  $\text{Cu}_3\text{M}'_2\text{P}_8\text{O}_{24}$  ( $M' = \text{NH}_4, \text{Cs, Tl, Rb}$ ) (Läügt & Guitel, 1975). The present study describes the chemical preparation and crystal structure of a new copper-potassium *cyclo*-triphosphate.

**Experimental.**  $\text{CuK}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  was prepared by the metathesis reaction of Boullé (1941) using silver trimetaphosphate monohydrate as starting material. An aqueous solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{KCl}$  in stoichiometric proportions is added with the corresponding amount of  $\text{Ag}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$ . The reaction scheme is:



After filtration, to eliminate the insoluble silver chloride,

the resulting solution is kept at room temperature until the formation of  $\text{CuK}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  crystals; they appear as thick monoclinic platelets; density not measured. Cubic fragment  $0.22 \times 0.22 \times 0.22 \text{ mm}$ . Philips PW 1100 diffractometer; graphite monochromator; systematic absences:  $0k0$  ( $k = 2n$ ),  $h0l$  ( $h = 2n$ ); 21 reflexions ( $9.5 < \theta < 11.5^\circ$ ) for refining the unit-cell dimensions,  $\omega$  scan; 3078 reflexions measured ( $3 < \theta < 30^\circ$ ), 2916 unique,  $R_{\text{int}} = 0.000$ ,  $\pm h, k, l$ ,  $h_{\text{max}} = 15$ ,  $k_{\text{max}} = 25$ ,  $l_{\text{max}} = 10$ ; scan width  $1.20^\circ$ ; scan speed  $= 0.02^\circ \text{ s}^{-1}$ ; total background measuring time 20 s. Two orientation and intensity control reflexions ( $\bar{1}\bar{1}\bar{2}$  and  $1\bar{1}\bar{2}$ ) every 2 h, no variation. Lorentz-polarization corrections, no absorption correction. Direct methods (MULTAN77, Main, Lessinger, Woolfson, Germain & Declercq, 1977) used to solve the structure. Anisotropic full-matrix least-squares refinement (on  $F$ ); unit weights; hydrogen atoms located on difference Fourier maps and refined isotropically; final refinements with 2336 reflexions corresponding to  $I > 5\sigma(I)$ ; final  $R = 0.028$  ( $wR = 0.032$ ). For the complete set of unique reflexions  $R = 0.032$ . Extinction coefficient refined:  $0.69 \times 10^{-7}$  (Stout & Jensen, 1968),  $S = 1.182$ , max.  $A/\sigma = 0.02$  (extinction coefficient). Maximum peak height in final difference Fourier map  $0.63 \text{ e } \text{\AA}^{-3}$ . 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: PDP 11–70.

**Discussion.** Table 1 reports the final atomic coordinates and  $B_{eq}$ \* Fig. 1 is a projection of the atomic arrangement along the  $b$  axis. If one considers the stacking of the associated-cation polyhedra, the atomic arrangement can be described as layers of distorted  $\text{CuO}_6$  octahedra alternating along the  $b$  axis with double layers of potassium polyhedra. The centro-

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43687 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates for  $\text{CuK}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  and  $B_{eq}$  for non-hydrogen atoms,  $B_{iso}$  for hydrogen atoms with *e.s.d.*'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j a_i a_j \beta_{ij}$$

General-position coordinates  $\pm(x, y, z) \pm(\frac{1}{2} + x, \frac{1}{2} - y, z)$ .

	$x$	$y$	$z$	$B_{eq}/B_{iso}(\text{\AA}^2)$
Cu	0	0	$\frac{1}{2}$	1.19 (1)
K(1)	0.67548 (8)	0.40312 (5)	0.94663 (9)	1.81 (1)
K(2)	0.50340 (9)	0.21887 (6)	0.33325 (9)	2.42 (2)
P(1)	0.75728 (9)	0.16541 (5)	0.00048 (9)	1.19 (1)
P(2)	0.80958 (8)	0.17353 (5)	0.67164 (8)	1.10 (1)
P(3)	0.56549 (8)	0.05025 (5)	0.76721 (9)	1.32 (1)
O(E11)	0.7063 (3)	0.2359 (2)	0.1106 (3)	1.99 (5)
O(E12)	0.8880 (3)	0.1012 (2)	0.0587 (3)	2.08 (5)
O(L12)	0.7962 (2)	0.2197 (1)	0.8435 (2)	1.39 (4)
O(E21)	0.9439 (3)	0.1072 (2)	0.6879 (3)	1.77 (5)
O(E22)	0.7986 (3)	0.2485 (2)	0.5520 (3)	1.76 (5)
O(E31)	0.3924 (3)	0.0555 (2)	0.7295 (3)	2.39 (6)
O(E32)	0.6438 (4)	0.9576 (2)	0.7734 (3)	2.14 (5)
O(L23)	0.6442 (2)	0.1171 (2)	0.6459 (2)	1.50 (5)
O(L13)	0.6068 (3)	0.1040 (2)	0.9326 (3)	1.97 (5)
O(W1)	0.6489 (3)	0.4053 (2)	0.4243 (3)	1.69 (5)
O(W2)	0.8339 (3)	0.0575 (2)	0.3557 (3)	1.64 (5)
H(W11)	0.702 (5)	0.426 (3)	0.361 (5)	3.3 (10)
H(W12)	0.691 (5)	0.371 (3)	0.486 (5)	3.1 (10)
H(W21)	0.856 (5)	0.074 (3)	0.279 (5)	2.1 (8)
H(W22)	0.753 (5)	0.022 (3)	0.332 (5)	3.3 (10)

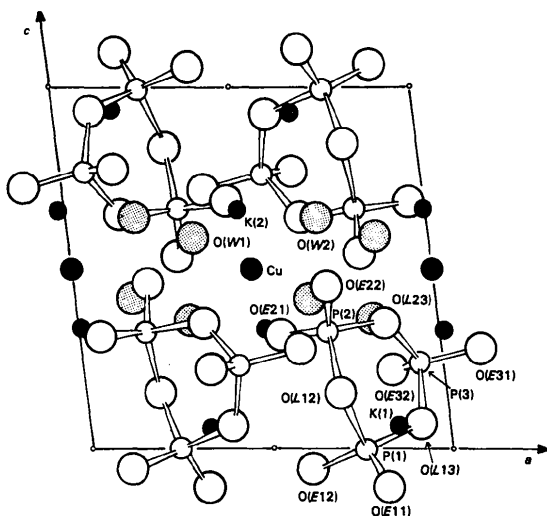


Fig. 1. Projection along the  $b$  axis of the atomic arrangement of  $\text{CuK}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ . H atoms have been omitted.

Table 2. Main interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) in the atomic arrangement of  $\text{CuK}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$

$\text{P}_3\text{O}_9$ ring anion				
P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	1.473 (2)	2.539 (3)	2.484 (3)	2.503 (3)
O(E12)	1.184 (1)	1.483 (2)	2.549 (3)	2.508 (3)
O(L12)	107.3 (1)	111.0 (1)	1.609 (2)	2.487 (3)
O(L13)	108.8 (1)	108.6 (1)	101.4 (1)	1.605 (2)
$\text{P}_3\text{O}_9$ ring anion				
P(2)	O(E21)	O(E22)	O(L12)	O(L23)
O(E21)	1.480 (2)	2.573 (3)	2.508 (3)	2.539 (3)
O(E22)	1.213 (1)	1.472 (2)	2.510 (3)	2.476 (3)
O(L12)	108.1 (1)	108.6 (1)	1.617 (2)	2.480 (3)
O(L23)	110.1 (1)	106.5 (1)	100.2 (1)	1.616 (2)
$\text{P}_3\text{O}_9$ ring anion				
P(3)	O(E31)	O(E32)	O(L13)	O(L13)
O(E31)	1.473 (2)	2.548 (3)	2.493 (3)	2.463 (3)
O(E32)	1.192 (1)	1.481 (2)	2.525 (3)	2.531 (3)
O(L13)	108.1 (12)	109.7 (1)	1.606 (2)	2.496 (3)
O(L13)	106.3 (1)	110.2 (1)	102.1 (1)	1.604 (2)
$\text{CuO}_6$ octahedron				
2x Cu—O(E21)	2.300 (2)			
2x Cu—O(W1)	2.010 (2)			
2x Cu—O(W2)	1.945 (2)			
O(E21)—Cu—O(W1)	92.26 (9) and 87.74 (9)			
O(E21)—Cu—O(W2)	92.21 (8) and 87.79 (8)			
O(W1)—Cu—O(W2)	92.7 (1) and 87.3 (1)			
O(E21)—O(W1)	3.114 (3) and 2.994 (3)			
O(E21)—O(W2)	3.069 (3) and 2.954 (3)			
O(W1)—O(W2)	2.861 (3) and 2.730 (3)			
$\text{K}O_n$ polyhedra				
K(1)—O(E11)	2.765 (2)	K(1)—O(E21)	2.784 (2)	
K(1)—O(E12)	2.883 (2)	K(1)—O(E31)	2.815 (2)	
K(1)—O(E12)	2.724 (2)	K(1)—O(E32)	2.791 (2)	
K(1)—O(L12)	2.984 (2)	K(1)—O(W2)	3.379 (2)	
K(2)—O(E11)	2.711 (2)	K(2)—O(E32)	2.916 (2)	
K(2)—O(E11)	3.050 (2)	K(2)—O(L23)	3.142 (2)	
K(2)—O(E22)	2.979 (2)	K(2)—O(W1)	3.004 (2)	
K(2)—O(E22)	2.727 (2)			
O(W)—H—O—				
O(W)—H(W11)...	O(E32)	0.80 (5)	1.89 (5)	2.675 (3)
O(W)—H(W12)...	O(E22)	0.78 (5)	2.02 (5)	2.741 (3)
O(W)—H(W21)...	O(E12)	0.74 (4)	1.96 (4)	2.686 (3)
O(W)—H(W22)...	O(E31)	0.86 (5)	1.70 (5)	2.555 (3)

symmetrical  $\text{CuO}_6$  octahedron is built up by two oxygen atoms and four water molecules. Potassium atoms K(1) and K(2) have respectively eight and seven neighbours within a range of 3.5  $\text{\AA}$ . Details of the various associated-cation polyhedra are reported in Table 2. Bond lengths and angles for the ring anion,  $\text{P}_3\text{O}_9$ , also reported in Table 2, correspond to a geometry not significantly different from that commonly observed in this type of anion when no internal symmetry is present.

The ammonium salt  $(\text{NH}_4)_4\text{Cu}(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  is isotypic with the title compound. Its unit-cell dimensions are:  $a = 8.79$  (1),  $b = 14.65$  (2),  $c = 8.60$  (1)  $\text{\AA}$ ,  $\beta = 96.66$  (8) $^\circ$ . The chemical preparation is identical to that of the potassium salt.

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## Phosphate Hydrogénophosphate de Manganèse

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**Abstract.**  $\text{Mn}_7[\text{PO}_3(\text{OH})]_4(\text{PO}_4)_2$ ,  $M_r = 958.43$ , triclinic,  $P\bar{1}$ ,  $a = 6.608$  (9),  $b = 8.078$  (6),  $c = 9.792$  (15) Å,  $\alpha = 67.76$  (12),  $\beta = 69.80$  (11),  $\gamma = 78.59$  (10)°,  $V = 453$  (1) Å<sup>3</sup>,  $D_m = 3.50$  (1),  $D_x = 3.515$  Mg m<sup>-3</sup>,  $Z = 1$ ,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 5.192$  mm<sup>-1</sup>,  $F(000) = 461$ , room temperature,  $R = 0.043$  for 1350 reflections. The new phase  $\text{Mn}_7[\text{PO}_3(\text{OH})]_4(\text{PO}_4)_2$  has been studied by single-crystal X-ray structure analysis with an automatic diffractometer. The structure contains  $[\text{MnO}_6]$ ,  $[\text{MnO}_4(\text{OH})_2]$  and  $[\text{MnO}_5]$  polyhedra linked together by  $[\text{PO}_3(\text{OH})]$  or  $[\text{PO}_4]$  tetrahedra to build a three-dimensional structure. One of the essential features of this structure is that it contains hydroxyl groups shared between Mn and P atoms.

**Introduction.** De nombreux travaux ont été consacrés à l'étude chimique et structurale des phosphates de manganèse(II). Dans un mémoire récent consacré au système ternaire  $\text{MnO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$  (Cudennec, Riou & Gerault, 1986), nous avons rappelé les différents travaux antérieurs et décrit une méthode de préparation d'un hydrogénophosphate-phosphate de manganèse(II) de formule  $\text{Mn}_5[\text{PO}_3(\text{OH})]_2(\text{PO}_4)_2(\text{H}_2\text{O})_4$  qui était précédemment connu comme un minéral naturel: la hureaulite. Dans le même mémoire, nous avons également décrit la préparation par synthèse hydrothermale d'une autre hydrogénophosphate-phosphate de formule  $\text{Mn}_7[\text{PO}_3(\text{OH})]_4(\text{PO}_4)_2$  qui, à notre connaissance, n'avait jamais été signalé dans la littérature chimique. Ce composé de stoechiométrie originale ne possède aucun équivalent connu dans le cas d'autres éléments divalents; il nous a donc paru intéressant de déterminer la structure complète de ce composé. Ce travail fait l'objet du présent mémoire.

**Partie expérimentale.** Cristaux de  $\text{Mn}_7[\text{PO}_3(\text{OH})]_4(\text{PO}_4)_2$  obtenus à partir d'un mélange de carbonate de manganèse commercial, d'acide phosphorique et d'eau selon le rapport pondéral 1/2/3,5. Après mélange dioxyde de carbone éliminé à 353 K pendant 12 h. Mélange obtenu placé en tube scellé à 433 K pendant 30 jours. Les cristaux se présentent sous forme de plaquettes parallélépipédiques roses. Etudes préliminaires menées sur chambres photographiques de Weissenberg et de précession. Paramètres de la maille cristalline affinés par moindres carrés à partir de 25 réflexions, correspondant à des valeurs de  $\theta$  comprises entre 5 et 15°, et optimisés sur diffractomètre automatique. Masse volumique expérimentale mesurée grâce à la méthode de la poussée d'Archimède. Enregistrement des intensités diffractées sur un diffractomètre automatique (Enraf–Nonius); monochromateur: lame de graphite; distance cristal–détecteur: 173 mm;  $1 < \theta < 25^\circ$ ; balayage  $\omega - 2\theta$ ; amplitude de balayage:  $(1,00 + 0,35 \text{ tg } \theta)^\circ$ ; ouverture:  $(2,00 + 0,45 \text{ tg } \theta)^\circ$ . 2304 réflexions indépendantes mesurées, corrigées du facteur de Lorentz–polarisation mais pas de correction d'absorption; dimensions du cristal:  $275 \times 150 \times 75$  µm; pas de variations significatives des trois réflexions standards:  $23\bar{1}$ ,  $12\bar{2}$  et  $23\bar{2}$ .  $h$ :  $-7$  à  $7$ ;  $k$ :  $-9$  à  $9$ ;  $l$ :  $0$  à  $11$ . 1350 réflexions avec  $I > \sigma(I)$  conservées pour la résolution de la structure. Structure résolue par la méthode de l'atome lourd: positions des atomes de manganèse déterminées par déconvolution de la fonction de Patterson tridimensionnelle. Positionnement des atomes de phosphore puis d'oxygène appartenant aux groupements phosphates ou hydrogénophosphates à l'aide des cartes de densité électroniques tridimensionnelles. Affinement de la structure par une méthode de moindres carrés à matrice totale en minimisant la