

## The Structure of Tripotassium Dicopper(II) Hydrogendiprophosphate

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**Abstract.**  $K_3Cu_2[(P_2O_7)H(P_2O_7)]$ ,  $M_r = 593.28$ , triclinic,  $P\bar{1}$ ,  $a = 5.266$  (1),  $b = 5.528$  (1),  $c = 12.789$  (2) Å,  $\alpha = 90.37$  (1),  $\beta = 100.41$  (1),  $\gamma = 117.08$  (1)°,  $V = 324.4$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 3.04$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 4.6$  mm<sup>-1</sup>,  $F(000) = 288$ , room temperature,  $R = 0.024$  for 2517 reflections up to  $(\sin\theta)/\lambda = 0.81$  Å<sup>-1</sup>. The two K atoms are best described as irregular [10] and [9] coordinated to O atoms, the Cu atom is tetragonal pyramidal [4 + 1] coordinated. In the pyrophosphate groups, the P–O distances to the bridging O atoms (1.620 and 1.617 Å) are definitely larger than the others (average 1.520 and 1.514 Å). Each pair of these groups is connected by a symmetric hydrogen bond with the H atom at  $\bar{1}$  and  $O \cdots O = 2.437$  (3) Å; the P–O distance to this O atom is only 1.522 Å.

**Introduction.** Syntheses of potassium copper(II) phosphates (Effenberger, 1984, 1987a) produced the new compound  $K_3Cu_2[(P_2O_7)H(P_2O_7)]$ ; the chemical formula was found by a structure analysis. In connection with studies of short hydrogen bonds (Effenberger, 1985, 1987b; Effenberger & Pertlik, 1986), the structure type of the title compound seemed to be of interest. The aim of the present paper was to give a contribution to the variation of the P–O distances within the pyrophosphate groups if they are combined into dimers by symmetric hydrogen bonds.

**Experimental.** Crystals of the title compound were grown under hydrothermal conditions in a steel vessel lined with Teflon (~6 ml capacity). The insert was 1 g of  $KH_2PO_4$  and 2 g of a Cu<sup>II</sup> phosphate precipitation [obtained from an aqueous Cu nitrate solution precipitated with a solution of  $(NH_4)_2HPO_4$ ; precipitate consists predominantly of  $Cu_3(PO_4)_2 \cdot 3H_2O$  and  $Cu_2(OH)(PO_4)$  as identified by X-ray powder diagrams]. The vessel was filled with H<sub>2</sub>O to about 80 vol.% and was heated to 493 (5) K for 48 h. After cooling to room temperature, crystals of  $K_3Cu_2[(P_2O_7)H(P_2O_7)]$  and  $Cu_2O$  (cuprite) were obtained. The investigated crystals are light blue in colour and have diameters up to 0.5 mm.

Synthetic crystal,  $0.06 \times 0.10 \times 0.36$  mm; four-circle diffractometer AED2 (Stoe & Cie, Darmstadt,

Federal Republic of Germany), graphite-monochromatized Mo  $K\alpha$  radiation; lattice parameters from 75 reflections up to  $2\theta = 42^\circ$ ;  $2\theta/\omega$  scan mode, minimum of 50 steps per reflection increased for  $\alpha_1$ – $\alpha_2$  splitting, step width  $0.03^\circ$ , step time 0.5 to 1.5 s per step, 8 steps each side for background correction; three standard reflections with no significant intensity variation; 3561 reflections measured up to  $2\theta = 70^\circ$  ( $h$ :  $-9 \rightarrow 9$ ,  $k$ :  $-9 \rightarrow 9$ ,  $l$ :  $-21 \rightarrow 3$ ), 2842 reflections in unique data set ( $R_{int} = 0.038$ ), 2517 reflections with  $F_o > 3\sigma(F_o)$  used for refinement; 7  $\psi$  scans for absorption correction (transmission factors: 0.505–0.712); corrections for Lorentz and polarization effects. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974). All calculations were performed with program system STRUCSY (Stoe & Cie, Darmstadt) on an Eclipse S140 (Data General). The atomic coordinates of the Cu, K and P atoms were located by direct methods, the O atoms by a difference Fourier synthesis. Several cycles of least-squares refinement on  $F$  with anisotropic temperature parameters for all atoms gave  $R = 0.025$ ,  $wR = 0.024$ ,  $w = [\sigma(F_o)]^{-2}$  (108 variables), goodness of fit 1.94.

The maximum of the difference Fourier synthesis was obtained at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and was assigned to the H atom. Next largest peaks had heights up to half this maximum but were in close vicinity to other atoms. The consideration of the H atom during refinement reduced  $R$  to 0.024 and  $wR$  to 0.023. Particularly for reflections with  $(\sin\theta)/\lambda < 0.40$  Å<sup>-1</sup>, the agreement between  $F_o$  and  $F_c$  improved in comparison with disregarding the H atom. Max.  $\Delta/\sigma < 10^{-3}$ . Max. and min. heights in final difference Fourier map 0.54 and  $-0.44$  e Å<sup>-3</sup>. The value for the isotropic secondary-extinction coefficient  $g$  (Zachariasen, 1967) is  $5.4$  (7)  $\times 10^{-5}$ . The final atomic coordinates and equivalent isotropic temperature parameters are given in Table 1.\* Table 2 gives some important interatomic distances and bond angles.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43813 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic fractional coordinates and equivalent isotropic temperature parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
K(1)	0	0	$\frac{1}{2}$	0.0288
K(2)	0.20232 (7)	0.84870 (7)	0.06287 (4)	0.0159
Cu	0.97073 (4)	0.22326 (4)	0.22019 (2)	0.0099
P(1)	0.58685 (8)	0.53035 (5)	0.15976 (4)	0.0089
P(2)	0.55859 (9)	0.28881 (8)	0.35154 (4)	0.0106
O(1)	0.6535 (2)	0.5603 (2)	0.2892 (1)	0.0117
O(2)	0.2547 (2)	0.3755 (2)	0.1243 (1)	0.0119
O(3)	0.7306 (2)	0.3636 (2)	0.1273 (1)	0.0119
O(4)	0.7132 (2)	0.8131 (2)	0.1252 (1)	0.0128
O(5)	0.2345 (2)	0.1144 (2)	0.3106 (1)	0.0184
O(6)	0.7405 (3)	0.1553 (2)	0.3302 (1)	0.0155
O(7)	0.6331 (3)	0.3915 (3)	0.4693 (1)	0.0201
H	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.14 (3)

Table 2. Interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

The e.s.d.'s for K—O, Cu—O and P—O are 0.001  $\text{\AA}$ , for O—O 0.002  $\text{\AA}$ , and 0.08 $^\circ$  for the angles.

K(1')—O(6 <sup>v,ix</sup> )	2.709	K(2')—O(4 <sup>v</sup> )	2.755
K(1')—O(5 <sup>i,vii</sup> )	2.861	K(2')—O(4 <sup>v</sup> )	2.760
K(1')—O(7 <sup>vi,xii</sup> )	2.999	K(2')—O(3 <sup>v</sup> )	2.840
K(1')—O(7 <sup>i,vii</sup> )	3.142	K(2')—O(2 <sup>v</sup> )	2.853
K(1')—O(1 <sup>vi,xii</sup> )	3.256	K(2')—O(2 <sup>viii</sup> )	2.867
K(1')—O(7 <sup>v,ix</sup> )	3.481	K(2')—O(2 <sup>ii</sup> )	2.887
		K(2')—O(3 <sup>ii</sup> )	2.907
Cu <sup>1</sup> —O(6 <sup>i</sup> )	1.949	K(2')—O(3 <sup>v</sup> )	2.957
Cu <sup>1</sup> —O(5 <sup>v</sup> )	1.954	K(2')—O(4 <sup>xi</sup> )	3.027
Cu <sup>1</sup> —O(3 <sup>i</sup> )	1.993	K(2')—O(5 <sup>ii</sup> )	3.427
Cu <sup>1</sup> —O(2 <sup>iv</sup> )	1.995		
Cu <sup>1</sup> —O(4 <sup>iii</sup> )	2.242	O(7 <sup>i</sup> )...O(7 <sup>xii</sup> )	2.437
		H <sup>1</sup> —O(7 <sup>i,xii</sup> )	1.218
		P(2')—O(7 <sup>i</sup> )—H <sup>1</sup>	118.57
P(1')—O(4 <sup>i</sup> )	1.500	O(4 <sup>i</sup> )—O(3 <sup>i</sup> )	2.528 113.13
P(1')—O(3 <sup>i</sup> )	1.530	O(4 <sup>i</sup> )—O(2 <sup>i</sup> )	2.520 112.53
P(1')—O(2 <sup>i</sup> )	1.531	O(4 <sup>i</sup> )—O(1 <sup>i</sup> )	2.516 107.41
P(1')—O(1 <sup>i</sup> )	1.620	O(3 <sup>i</sup> )—O(2 <sup>i</sup> )	2.530 111.56
		O(3 <sup>i</sup> )—O(1 <sup>i</sup> )	2.512 105.77
		O(2 <sup>i</sup> )—O(1 <sup>i</sup> )	2.514 105.84
P(2')—O(6 <sup>i</sup> )	1.507	O(6 <sup>i</sup> )—O(5 <sup>i</sup> )	2.534 114.09
P(2')—O(5 <sup>i</sup> )	1.513	O(6 <sup>i</sup> )—O(7 <sup>i</sup> )	2.489 110.49
P(2')—O(7 <sup>i</sup> )	1.522	O(6 <sup>i</sup> )—O(1 <sup>i</sup> )	2.522 107.57
P(2')—O(1 <sup>i</sup> )	1.617	O(5 <sup>i</sup> )—O(7 <sup>i</sup> )	2.523 112.46
		O(5 <sup>i</sup> )—O(1 <sup>i</sup> )	2.509 106.52
		O(7 <sup>i</sup> )—O(1 <sup>i</sup> )	2.492 105.09
P(1')—P(2')	2.795	P(1')—O(1 <sup>i</sup> )—P(2')	119.44

Symmetry code: (i)  $x, y, z$ ; (ii)  $x, 1+y, z$ ; (iii)  $x, -1+y, z$ ; (iv)  $1+x, y, z$ ; (v)  $-1+x, y, z$ ; (vi)  $-1+x, -1+y, z$ ; (vii)  $-x, -y, 1-z$ ; (viii)  $-x, 1-y, -z$ ; (ix)  $1-x, -y, 1-z$ ; (x)  $1-x, 1-y, -z$ ; (xi)  $1-x, 2-y, -z$ ; (xii)  $1-x, 1-y, 1-z$ .

**Discussion.** As is well known for K atoms (*cf.* Cocco, Fanfani & Zanazzi, 1972), the coordination figures of the two crystallographically different K atoms in the title compound are irregular and not clear-cut. If one takes the shortest distance between the K atoms and any P atom [*i.e.* K(2)—P(1) = 3.332  $\text{\AA}$ ] as the limit of the coordination sphere of the K atoms, the K(1) atom is [10] coordinated and the K(2) atom is [9] coordi-

nated with K—O distances varying from 2.709 (1) to 3.256 (1)  $\text{\AA}$ .

The Cu atom shows [4 + 1] coordination with the four nearest O atoms in an only slightly distorted square-planar arrangement. The O—Cu—O angles within the  $\text{CuO}_4$  square vary from 86.70 (5) to 92.46 (6) $^\circ$  for neighbouring O atoms and 167.37 (6) to 175.23 (6) $^\circ$  for opposite O atoms. The Cu atom is shifted out of the best plane defined by the four nearest neighbours towards the fifth O atom: the O—Cu—O angles between the apex and each of the basal O atoms vary from 90.09 (5) to 97.89 (6) $^\circ$ . Such a coordination of formal divalent Cu atoms agrees with the common crystal-chemical experience for inorganic crystal structures (*cf.* Zemann, 1961, 1972; Hathaway, 1984; Wells, 1984). The  $\text{CuO}_5$  coordination polyhedron in  $\text{K}_3\text{Cu}_2[(\text{P}_2\text{O}_7)\text{H}(\text{P}_2\text{O}_7)]$  shares four O—O edges with the coordination polyhedra around the K atoms.

The two longest P—O distances within the pyrophosphate group are observed at the bridging O(1) atom; within the limits of error, the two crystallographically different values are equal (1.62  $\text{\AA}$ ). The other P—O bond lengths vary from 1.50 to 1.53  $\text{\AA}$ . The O(1)—P—O angles (105.09 to 107.57 $^\circ$ ) are definitely smaller than the O—P—O angles which do not involve the bridging O(1) atom (110.49 to 114.09 $^\circ$ ). The angle P(1)—O(1)—P(2) = 119.44 $^\circ$  compares well with those values found for hydrated pyrophosphate groups as compiled by Dumas & Lapasset (1979).

An interesting feature in crystal chemistry is the connection of two pyrophosphate groups by a symmetric hydrogen bond to form a dimer. The distance O(7)...H...O(7) = 2.437  $\text{\AA}$  is very short compared with common hydrogen bonds (Baur, 1972; Brown, 1976; Catti & Ferraris, 1976). Obviously it leads to the short P(2)—O(7) distance of 1.522  $\text{\AA}$ . It should be mentioned that Ferraris & Ivaldi (1984) found for  $(\text{HP}_2\text{O}_7)^{3-}$  groups an average P—OH distance of 1.564  $\text{\AA}$ . Although X-rays were used for the determination of the crystal structure, the assumption of a symmetric hydrogen bond seems to be justified; but a

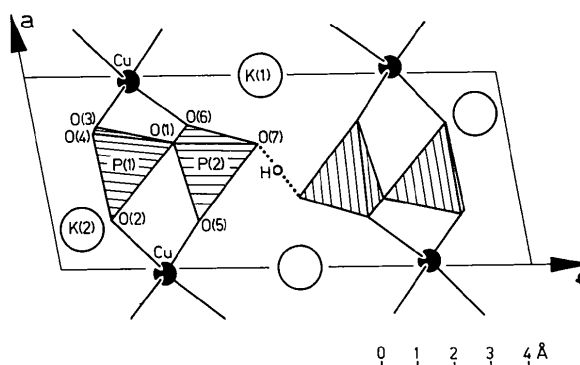


Fig. 1. The crystal structure of  $\text{K}_3\text{Cu}_2[(\text{P}_2\text{O}_7)\text{H}(\text{P}_2\text{O}_7)]$  in a projection onto (010).

slight dislocation of the H atom towards an only apparently symmetric hydrogen bond cannot be excluded with certainty. The O(7)···H···O(7) bond is simultaneously a common O—O edge between two K(1)O<sub>10</sub> coordination polyhedra with K—O bonds of 2.999 and 3.142 Å. Comparable connections of two alkaline-earth polyhedra where the O—O edge represents a very short hydrogen bond were described, for example, in Na<sub>5</sub>Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>[(PO<sub>4</sub>)H(PO<sub>4</sub>)] and in Na<sub>5</sub>-Cu<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>[(AsO<sub>4</sub>)H(AsO<sub>4</sub>)] (Effenberger, 1985, 1987b).

As can be seen from Fig. 1, the pyrophosphate groups and the CuO<sub>4</sub> squares share common O-atom corners forming formal chains running parallel to [100]. Each pair of these chains is connected by the hydrogen bond. A three-dimensional network is built up by the fifth Cu—O bond and the K atoms.

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## Structure du Nitrate de Thorium(IV) Tétrahydraté

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**Abstract.** Th(NO<sub>3</sub>)<sub>4</sub>.4H<sub>2</sub>O,  $M_r = 552.12$ , monoclinic,  $P2_1/n$ ,  $a = 7.438$  (1),  $b = 17.530$  (8),  $c = 9.183$  (1) Å,  $\beta = 99.72$  (1)°,  $V = 1180$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.107$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu(\text{Mo K}\alpha) = 13.18$  mm<sup>-1</sup>,  $F(000) = 1016$ ,  $T = 295$  K,  $R = 0.037$  for 1214 independent reflections [ $I > 3\sigma(I)$ ]. The Th atom is twelve-coordinated by O atoms, eight being from four bidentate nitrate groups. The four water molecules belong to the environment of the metal. Hydrogen bonds are either strong intramolecular water–water [2.72 (2) Å] or weak intermolecular water–nitrate O [2.92 (2) Å].

**Introduction.** De nombreux hydrates de nitrate de thorium(IV) ont été signalés dans la littérature, mais l'accord ne semble fait ni sur leur nombre ni sur leur composition exacte. Cependant Ferraro, Katzin & Gibson (1954), en étudiant à 298 K le système nitrate de thorium–eau–acide nitrique ont bien caractérisé les

hydrates à cinq et quatre molécules d'eau. Seule la structure du pentahydrate a été obtenue, simultanément par diffraction des rayons X (Ueki, Zalkin & Templeton, 1966) et des neutrons (Taylor, Mueller & Hitterman, 1966): le thorium est entouré par onze oxygènes dont huit proviennent de quatre nitrates bidentés et trois de molécules d'eau, les deux molécules d'eau restantes assurant la cohésion de la structure par des liaisons hydrogène. Nous avons entrepris l'étude de la structure du tétrahydrate afin d'établir la coordination de l'atome de thorium et la comparer à celle observée dans le pentahydrate.

**Partie expérimentale.** Cristaux obtenus par évaporation à température ambiante d'une solution aqueuse de Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O (2 mol l<sup>-1</sup>), HNO<sub>3</sub> (1 mol l<sup>-1</sup>) et hexanoïque (1%); cristal incolore de dimensions 250 × 200 × 200 µm; diffractomètre Enraf–Nonius CAD-4 équipé d'un monochromateur de graphite; paramètres