Table 4. *Selected geometric parameters* (Å, °) *for* (II)

Cu—Cl(1)	2.292 (3)	Cr—N(1)	2.096 (9)
Cu—Cl(2)	2.554 (4)	Cr—N(2)	2.066 (7)
Cu—Cl(3)	2.319 (3)	Cr—N(3)	2.083 (9)
Cl(1)—Cu—Cl(1^{vi})	179.3 (1)	Cl(3)—Cu—Cl(3^{vi})	143.6 (1)
Cl(1)—Cu—Cl(2)	89.6 (1)	N(1)—Cr—N(2)	90.7 (3)
Cl(1)—Cu—Cl(3)	89.5 (1)	N(1)—Cr—N(3)	91.0 (3)
Cl(2)—Cu—Cl(3)	108.2 (1)	N(2)—Cr—N(3)	91.3 (3)

Symmetry code: (vi) $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$.

For (I), X-ray intensities were measured at room temperature and the structure was refined to check the crystal specimen before the low-temperature measurement. Secondary extinction correction was applied. The smallest (F_o^2/F_c^2) value is 0.20 for 400. $R = 0.041$ and $wR = 0.047$ for 1437 observed reflections. After averaging symmetry-related reflections corrected for extinction, $R = 0.030$ and $wR = 0.031$ for 345 unique reflections.

For (II), the typical peak half-width became 0.18 from 0.12° on lowering the temperature. The X-ray intensity was measured by ω scans as a superposition of the reflections from the three twin components since the lattice constants are almost cubic:

$$I_{\rm total}(hkl) = (1 - P_x - P_y)I(hkl) + P_xI(lhk) + P_yI(klh) \quad (1)$$

where P_x and P_y are the populations of the twin components which have their tetragonal unique axes parallel to x and y, respectively. For $2\theta({\rm Mo}\,K\alpha) \leq 25°$, $+h$ $\pm k$ $\pm l$ reflections were measured. For $25 < 2\theta \leq 55°$, $+h$ $+k$ $\pm l$ reflections were measured. The space group was assumed to be the same as that of $[Co(NH_3)_6][CuCl_5]$ in the low-temperature phase. Coordinates of the equivalent positions of $F4_1/adc$ were listed in Table 2 of the previous paper (Aoyama *et al.*, 1992). Atomic coordinates of $[Co(NH_3)_6][CuCl_5]$ at 120 K were utilized as initial parameters and the structure was refined at first in single-domain approximation; $R(F) = 0.21$. Then the function $\sum[I_{\rm obs}(hkl) - KI_{\rm total}(hkl)]^2$ was minimized, taking account of the scale factor K. $F_c^2(hkl)$ values of the preceding refinement were used for $I(hkl)$ in equation (1). With the refined P_x, P_y and K values, the X-ray intensities were corrected for twinning:

$$I_{\rm corr}(hkl) = [I_{\rm obs}(hkl)/K - P_xF_c^2(lhk) - P_yF_c^2(klh)]/(1 - P_x - P_y). \quad (2)$$

The structure was further refined based on the corrected structure factors. After two cycles of the correction for twinning and refinement, $R(I) = \sum|I_{\rm corr}(hkl) - I_c(hkl)|^2/\sum[I_{\rm corr}(hkl)]^2 = 0.014$, $P_x = 0.208\,(1)$, $P_y = 0.210\,(1)$ and $K = 0.901\,(1)$. The smallest $(F_o{}^2/F_c^2)$ value in the extinction correction is 0.58 for 400. Final $R(F) = 0.100$, which is larger than that of the low-temperature study of $[Co(NH_3)_6][CuCl_5]$ with $P_x = 0.143\,(2)$, $P_y = 0$, $R(F) = 0.071$. The larger R value of the present study may be due to the larger population of twin components, P_x and P_y.

Refinement was performed by the full-matrix least-squares program *RADIEL* (Coppens *et al.*, 1979) on a FACOM M-780/10 computer at Keio University. The DSC measurements of $[Cr(NH_3)_6][CuCl_5]$ were carried out with a calibrated General V4.1C DuPont 2100 DSC instrument.

This work was supported by a Grant-in-Aid for Scientific Research (No. 04303010) from the Japanese Ministry of Education, Science and Culture.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: OH1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthetic Copper Monophosphate

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(*Received* 24 September 1994; *accepted* 27 *March* 1995)

Abstract

$Cu_9O_2(PO_4)_4(OH)_2$ belongs to the monophosphate group and contains five kinds of copper coordination polyhedron. One Cu atom is at the center of symmetry and has square-planar coordination, the others occupy distorted square-pyramidal sites. Three kinds of copper–oxygen polyhedra are connected to each other by edge sharing to form zigzag double chains along [110] and these chains are connected by PO_4 tetrahedra to form sheets parallel to $(1\bar{1}0)$. H atoms are connected to O atoms, which are shared by three copper polyhedra, to form hydroxyl ions. H atoms are also connected to O atoms shared by both Cu and P polyhedra to form hydrogen bonds.

Comment

This study has been carried out for the purposes of synthesizing new phases of phosphates and contributing to the crystal chemistry of copper monophosphates. The chemical composition was determined by electron microprobe analysis. A stereographic diagram, drawn using *ORTEP*II (Johnson, 1971), is shown in Fig. 1. The configuration around the hydrogen bond is illustrated in Fig. 2. The distance O(1)···O(10) is 2.68 (1) Å and corresponds to a hydrogen bond. The O(10) atoms are shared by Cu(5) and P(1) polyhedra *via* corner sharing. The interatomic distances and angles are compatible with those of related compounds: $Cu_2PO_4(OH)$ (Walitzi, 1963), $Cu_3PO_4(OH)_3$ (Fehlmann & Ghose, 1964), $Cu_5(PO_4)_2(OH)_4$ (Anderson, Shoemaker, Kostiner & Ruszala, 1977), $Cu_5(PO_4)_2(OH)_4$ (Shoemaker, Anderson & Kostiner, 1981) and those in a *General Review of the Structure of Phosphates* (Corbridge, 1971).

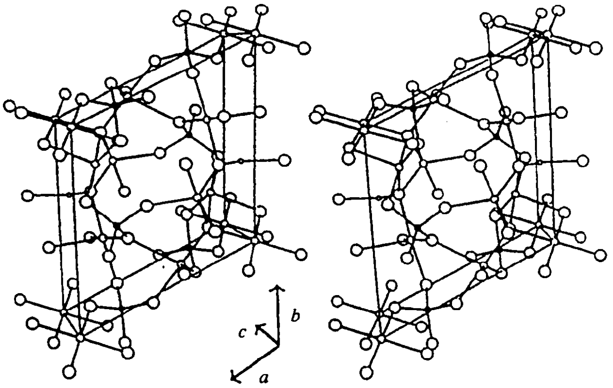

Fig. 1. Stereographic view of $Cu_9O_2(PO_4)_4(OH)_2$ along [001]. The small filled, small open, medium open and large open circles represent P, H, Cu and O atoms, respectively.

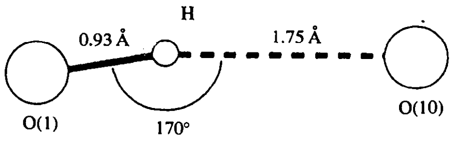

Fig. 2. The configuration around the H atom. The O(1)—H and O(10)···H distances and the O(1)—H···O(10) angle constitute a hydrogen-bonding interaction.

Experimental

The crystals were obtained after heating a reagent mixture of $CuSO_4.5H_2O$, Rb_2CO_3 and 4 mol H_3PO_4 solution at 873 K and 1000 kg cm^{-2}. The mixtures were sealed in silver tubes and heated for 72 h in an electric furnace. They were cooled at a rate of 1 K per 20 min. The crystals obtained were emerald green with apparent euhedral forms.

Crystal data

$Cu_9O_2(PO_4)_4(OH)_2$
$M_r = 1017.85$
Triclinic
$P\bar{1}$
$a = 8.166$ (2) Å
$b = 8.845$ (2) Å
$c = 5.934$ (1) Å
$\alpha = 102.54$ (2)°
$\beta = 94.37$ (2)°
$\gamma = 113.57$ (2)°
$V = 377.0$ (2) Å^3
$Z = 1$
$D_x = 4.48$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12.5$–27.5°
$\mu = 13.44$ mm^{-1}
$T = 297$ K
Granular
0.18 × 0.18 × 0.19 mm
Emerald green

Data collection

Rigaku AFC-5*R* diffractometer
Absorption correction: spherical
$T_{min} = 0.125$, $T_{max} = 0.148$
1657 measured reflections
1657 independent reflections
1652 observed reflections $[F > 3\sigma(F)]$

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 10$
$l = -7 \rightarrow 7$
3 standard reflections monitored every 300 reflections
intensity decay: none

Refinement

Refinement on *F*
$R = 0.042$
$wR = 0.057$
$S = 1.77$
1652 reflections
154 parameters
Only coordinates of H atoms refined

Unit weights applied
$(\Delta/\sigma)_{max} = 0.11$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -1.79$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu(1)	0	0	0	1.03 (4)
Cu(2)	0.3984 (2)	0.0544 (2)	0.1797 (2)	1.11 (3)
Cu(3)	0.3242 (2)	0.3580 (2)	0.0283 (2)	1.18 (3)
Cu(4)	0.1780 (2)	0.2874 (1)	0.4349 (2)	1.01 (3)
Cu(5)	0.2167 (2)	0.6792 (1)	0.3184 (2)	1.06 (3)
P(1)	0.7529 (3)	0.4065 (3)	0.1992 (4)	1.02 (6)
P(2)	0.7280 (3)	0.9706 (3)	0.3377 (4)	0.97 (6)
O(1)	0.1691 (10)	0.4338 (8)	0.2202 (11)	1.27 (19)
O(2)	0.2416 (9)	0.1666 (8)	0.1643 (11)	1.10 (18)
O(3)	0.5672 (9)	0.9451 (8)	0.1543 (11)	1.19 (19)
O(4)	0.6726 (10)	0.2956 (8)	0.3674 (11)	1.25 (19)
O(5)	0.9112 (9)	0.0789 (9)	0.2745 (11)	1.38 (20)
O(6)	0.7128 (10)	0.7918 (8)	0.3341 (11)	1.34 (19)
O(7)	0.9059 (9)	0.5813 (8)	0.3317 (11)	1.15 (18)
O(8)	0.2827 (9)	0.9343 (8)	0.4146 (11)	1.21 (19)
O(9)	0.5974 (9)	0.4391 (8)	0.0864 (12)	1.42 (19)
O(10)	0.8231 (10)	0.3130 (9)	0.0090 (11)	1.31 (20)
H	0.05 (2)	0.40 (2)	0.15 (3)	

Table 2. *Selected geometric parameters* (Å, °)

Cu(1)—O(2)	1.942 (6)	Cu(4)—O(7^{vi})	1.954 (8)
Cu(1)—O(2^{i})	1.942 (6)	Cu(5)—O(1)	1.986 (7)
Cu(1)—O(5^{ii})	1.938 (7)	Cu(5)—O(4^{vi})	1.935 (7)
Cu(1)—O(5^{iii})	1.938 (7)	Cu(5)—O(7^{ii})	2.345 (7)
Cu(2)—O(2)	1.916 (9)	Cu(5)—O(8)	2.032 (7)
Cu(2)—O(3^{iv})	1.973 (9)	Cu(5)—O(10^{v})	1.966 (7)

Cu(2)—O(3$^{\rm v}$)	2.024 (7)	P(1)—O(4)	1.549 (8)
Cu(2)—O(4)	2.361 (6)	P(1)—O(7)	1.532 (5)
Cu(2)—O(8$^{\rm iv}$)	2.001 (7)	P(1)—O(9)	1.546 (9)
Cu(3)—O(1)	1.979 (8)	P(1)—O(10)	1.536 (8)
Cu(3)—O(2)	1.933 (7)	P(2)—O(3)	1.549 (8)
Cu(3)—O(6$^{\rm v}$)	2.194 (6)	P(2)—O(5$^{\rm vii}$)	1.547 (7)
Cu(3)—O(9)	2.026 (7)	P(2)—O(6)	1.531 (8)
Cu(3)—O(9$^{\rm v}$)	1.942 (8)	P(2)—O(8$^{\rm viii}$)	1.555 (7)
Cu(4)—O(1)	2.021 (8)	H—O(1)	0.93 (16)
Cu(4)—O(2)	1.953 (7)	H···O(10$^{\rm ii}$)	1.75 (15)
Cu(4)—O(5$^{\rm ii}$)	2.182 (6)	O(1)···O(10$^{\rm ii}$)	2.68 (1)
Cu(4)—O(6$^{\rm vi}$)	1.974 (8)		
O(2)—Cu(1)—O(5$^{\rm ii}$)	86.9 (3)	O(5$^{\rm ii}$)—Cu(4)—O(6$^{\rm vi}$)	106.3 (3)
O(2)—Cu(1)—O(5$^{\rm iii}$)	93.1 (3)	O(5$^{\rm ii}$)—Cu(4)—O(7$^{\rm vi}$)	96.5 (3)
O(2$^{\rm i}$)—Cu(1)—O(5$^{\rm ii}$)	93.1 (3)	O(6$^{\rm vi}$)—Cu(4)—O(7$^{\rm vi}$)	94.3 (3)
O(2$^{\rm i}$)—Cu(1)—O(5$^{\rm iii}$)	86.9 (3)	O(1)—Cu(5)—O(4$^{\rm vi}$)	91.5 (3)
O(2)—Cu(2)—O(3$^{\rm v}$)	90.7 (3)	O(1)—Cu(5)—O(7$^{\rm ii}$)	86.3 (3)
O(2)—Cu(2)—O(4)	99.2 (3)	O(1)—Cu(5)—O(10$^{\rm v}$)	92.1 (3)
O(2)—Cu(2)—O(8$^{\rm iv}$)	95.0 (3)	O(4$^{\rm vi}$)—Cu(5)—O(7$^{\rm ii}$)	104.0 (3)
O(3$^{\rm iv}$)—Cu(2)—O(3$^{\rm v}$)	81.6 (3)	O(4$^{\rm vi}$)—Cu(5)—O(8)	88.0 (3)
O(3$^{\rm iv}$)—Cu(2)—O(4)	80.6 (3)	O(7$^{\rm ii}$)—Cu(5)—O(8)	97.5 (3)
O(3$^{\rm iv}$)—Cu(2)—O(8$^{\rm iv}$)	92.4 (3)	O(7$^{\rm ii}$)—Cu(5)—O(10$^{\rm v}$)	92.1 (3)
O(3$^{\rm v}$)—Cu(2)—O(4)	97.0 (2)	O(8)—Cu(5)—O(10$^{\rm v}$)	87.3 (3)
O(4)—Cu(2)—O(8$^{\rm iv}$)	110.0 (2)	O(4)—P(1)—O(7)	111.7 (4)
O(1)—Cu(3)—O(2)	84.0 (3)	O(4)—P(1)—O(9)	106.6 (4)
O(1)—Cu(3)—O(6$^{\rm v}$)	135.3 (3)	O(4)—P(1)—O(10)	110.8 (4)
O(1)—Cu(3)—O(9$^{\rm v}$)	91.7 (3)	O(7)—P(1)—O(9)	107.5 (4)
O(2)—Cu(3)—O(6$^{\rm v}$)	96.8 (3)	O(7)—P(1)—O(10)	109.8 (4)
O(2)—Cu(3)—O(9)	102.6 (3)	O(9)—P(1)—O(10)	110.4 (4)
O(6$^{\rm v}$)—Cu(3)—O(9)	93.7 (3)	O(3)—P(2)—O(5$^{\rm vii}$)	110.5 (4)
O(6$^{\rm v}$)—Cu(3)—O(9$^{\rm v}$)	87.6 (3)	O(3)—P(2)—O(6)	106.8 (4)
O(9)—Cu(3)—O(9$^{\rm v}$)	78.8 (3)	O(3)—P(2)—O(8$^{\rm viii}$)	110.2 (5)
O(1)—Cu(4)—O(2)	82.4 (3)	O(5$^{\rm vii}$)—P(2)—O(6)	110.4 (5)
O(1)—Cu(4)—O(5$^{\rm ii}$)	95.2 (3)	O(5$^{\rm vii}$)—P(2)—O(8$^{\rm viii}$)	108.3 (3)
O(1)—Cu(4)—O(7$^{\rm vi}$)	89.3 (3)	O(6)—P(2)—O(8$^{\rm viii}$)	110.7 (4)
O(2)—Cu(4)—O(5$^{\rm ii}$)	80.2 (3)	O(1)—H···O(10$^{\rm ii}$)	170.4 (3)
O(2)—Cu(4)—O(6$^{\rm vi}$)	95.0 (3)		

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

The positions of the H atoms were determined from difference syntheses and confirmed by the calculation of the sum of electrostatic charges around connected O atoms (Brown & Wu, 1976). B(H) was fixed at 1.0 Å^2.

Intensity collection: *AFC/MSC Diffractometer Control Program* (Rigaku Corporation, 1991). Refinement of cell dimensions: *AFC/MSC Diffractometer Control Program*. Data reduction: *AFC/MSC Diffractometer Control Program*. Patterson and Fourier syntheses: *UNICS RSSFR*-5 (Sakurai, 1971). Refinement by full-matrix least squares: *UNICS RSFLS*-4. Interatomic distances and angles: *CCPC* (Kawamura & Kawahara, 1980). Stereographic figures: *ORTEP*II (Johnson, 1971). F_o and σF_o printing: *LISTHKL* (Yamakawa & Kawahara, 1992).

The intensity measurements were carried out an a Rigaku AFC-5R at the X-ray laboratory at Okayama University, Japan.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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