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The crystal structure of synthetic $Cu_5(PO_4)_2(OH)_4$, a polymorph of pseudomalachite

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Abstract

A synthetic phase formed in the $Cu_3(PO_4)_2$–phosphoric acid system at 55,000 psi and 400°C has been found to be an interesting polymorph of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$. This new phase crystallizes in the space group $P2_1/a$ with $a = 9.186(2)$, $b = 10.684(2)$, $c = 4.461(1)$ Å, and $\beta = 92.31(1)°$. The structure was solved by direct methods. Full-matrix least-squares refinement of the automatic diffractometer data converged to a residual $R = 0.056$ ($R_w = 0.067$). The unit cell has a volume essentially identical to that of pseudomalachite and one essentially equal axial length which, in both structures, represents the stacking distance between two-dimensional copper-containing sheets. The coordination polyhedra about the copper ions are similar in the two structures; the copper ions occupy two six-coordinated sites in the synthetic structure characterized by four short and two long bonds; the third copper ion is in a distorted square pyramidal coordination (four short and one long bond) with a sixth oxygen atom just outside the coordination sphere. The difference between the two structures is in the polyhedral linkages within these sheets; pseudomalachite is based on a three-connected two-dimensional net, while the synthetic phase is based on a four-connected net.

Introduction

Copper in its divalent oxidation state has the distinction of having a most varied role in oxide crystal chemistry. It has been found to occupy many types of coordination polyhedra ranging from square planar to distorted trigonal bipyramidal, square pyramidal, and octahedral. Superposed on these polyhedral types is the general distortion of four short plus one or two longer bonds characteristic of the divalent copper ion (Wells, 1975).

There are three well-characterized basic copper phosphates known, each with a different Cu:PO_4 ratio. Libethenite, $Cu_2(PO_4)(OH)$, the structure of which has been refined (Walitzi, 1963), is isostructural with andalusite, Al_2SiO_5, with copper ions in five- and six-coordination. Cornetite, $Cu_3(PO_4)(OH)_3$, has a three-dimensional network of polyhedra containing copper ions (Fehlmann *et al.*, 1964) with two copper ions in tetragonal pyramidal coordination and a third in the characteristically distorted (4 + 2) six-coordination. Pseudomalachite, $Cu_5(PO_4)_2(OH)_4$, has a sheet structure (Ghose, 1963) with copper ions reported to be in three crystallographically unique sites, each of distorted six-coordination.

A short description of the structure of pseudomalachite (Ghose, 1963) is in order at this point. The unit cell ($P2_1/c$; $a = 4.47$, $b = 5.75$, $c = 17.08$ Å, $\beta = 91.12°$) contains two types of parallel chains composed of edge-sharing copper-containing polyhedra which join to form sheets in the *bc* plane. These sheets are linked by phosphate groups to give the short *a* dimension. Three crystallographically unique copper ions occupy six-coordinated sites: Cu(1) (on a center of symmetry) has two oxygens and two hydroxyl ions at an average distance of 1.98 Å and two further oxygens at 2.69 Å. Cu(2) has one oxygen and three hydroxyl groups at an average distance of 1.98 Å, a fifth oxygen at 2.39 Å, and a sixth at 2.70 Å. Cu(3) has two oxygens and two hydroxyl ions at an average distance of 1.96 Å and two more oxygens at an average distance of 2.42 Å. Cu(3) octahedra form edge-sharing chains parallel to *b* which are crosslinked by pairs of edge-sharing (across a center of symmetry) Cu(2) polyhedra. Cu(1) octahedra in turn share edges with Cu(2) polyhedra only.

During an investigation of the hydrothermal preparation of crystals of complex phosphates of metals of the first transition series, a phase was isolated which proved to have essentially the same unit cell volume as pseudomalachite (PM)—439 Å^3. A complete X-ray structural analysis of this new phase—as a convenience, hereinafter referred to as PPM—proved its polymorphism with PM. This paper describes this new structure and provides a discussion of the polyhedral linkages within the copper-containing sheets.

Experimental

Dana (Palache *et al.*, 1951) reports that libethenite can be prepared by heating copper(II) phosphate and aqueous phosphoric acid in a closed tube at temperatures up to 200°C. We have found (Ruszala and Kostiner, 1974) that in order to keep divalent copper from being reduced to the metallic state in hydrothermal systems it is necessary to keep the system acidic. In a successful attempt to crystallize $Cu_2(PO_4)(OH)$ out of a $Cu_3(PO_4)_2$–0.1*M* H_3PO_4 mixture, a second phase (~1 weight percent of the product) was isolated. Crystals of this secondary phase, PPM, were emerald-green in color and easily distinguished from the olive-drab crystals of libethenite. After two weeks at 55,000 psi hydrostatic pressure at 400°C in sealed gold capsules (contained in cold-seal hydrothermal vessels), plate-like crystals of PPM attained a maximum dimension of 0.2 mm. Under these conditions needle crystals of libethenite up to 0.05 mm long and 0.01 in cross-section were also formed.

A well-formed PPM crystal of dimensions 0.05 × 0.19 × 0.15 mm was selected for data collection; precession photographs revealed monoclinic symmetry with systematic absences corresponding to the space group $P2_1/a$ in accordance with the Donnay convention.

The lattice parameters were determined in a PICK-II least-squares refinement program, using 44 reflections within the angular range $31° < 2\theta < 49°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using Mo$K\alpha_1$ radiation. At 22°C the lattice parameters are a = 9.186(2), b = 10.684(2), c = 4.461(2) Å, and β = 92.31(1)°, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density, with $Z = 2$, is 4.370 g cm^{-3}.

Diffraction intensities were measured using Zr-filtered Mo$K\alpha$ radiation at a take-off angle of 3.0° with the diffractometer operating in the θ–2θ scan mode. Scans were made at 1° per minute over 1.5° with allowance for dispersion and with 20-second background counts taken at both ends of the scan. Of the 1406 independent data investigated in the angular range $2\theta < 62°$, 1275 were considered observable according to the criterion $|F_o| > 1.58\sigma_F$, where σ_F is defined as $0.02\,|F_o| + [C + k^2B]^{1/2}/2|F_o|\,Lp$; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored, and no variations in intensity greater than 6 percent were observed over the data collection period; the mean variation was much smaller.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections for the crystal with μ = 128.5 cm^{-1} (Mo$K\alpha$) were made using a computer program written by H. W. Alcock and modified by B. Lee for a crystal of general shape. Input for the program included the indices of the plane faces of the crystal, which were determined with the aid of precession photographs, and the orientation angles of the crystal coordinate system with respect to the diffractometer coordinate system, which were obtained from the program PICK-II. The maximum relative absorption correction applied was 65 percent of $|F_o|$.

As the unit cell volume of this new phase was essentially identical to PM, the multisolution symbolic addition program MULTAN (Germain *et al.*, 1971) was used for the unit cell contents $Cu_{10}(PO_4)_4(OH)_8$; this choice of stoichiometry was confirmed by the final refinement. Phases with a probability of being greater than 97 percent correct were used in the starting set. The three strongest peaks in the best electron density map generated by MULTAN from these reflections proved to be copper atoms, one located at the origin and the other two on general positions, and the next two peaks were phosphorus atoms. Difference Fourier maps revealed the positions of the six oxygen atoms.

Full-matrix least-squares refinement (Busing *et al.* 1962a) using a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Cu, P, and O (Cromer and Mann, 1968), isotropic temperature factors, and corrections for anomalous dispersion, yielded a residual $R = 0.096$ and a weighted residual $R_w = 0.111$. The anisotropic refinement, based on a data to parameter ratio of 15 with 87 independently varied parameters, yielded a final $R = 0.056$ and $R_w = 0.067$ for the observed data. The reflections $00l$, for which F_o was very much less than F_c, were discarded in the final refinement as the absorption correction for this class of reflections proved unsatisfactory. The significantly larger values of B_{33} in the anisotropic refinement are undoubtedly due to the approximate nature of the absorption correction. The final atomic coordinates and anisotropic thermal parameters are given in Table 1; the structure factor data are presented in

Table 2.[1] The hydroxyl oxygen atoms are O(5) and O(6).

Results

The cooper ions lie in sheets of edge-sharing coordination polyhedra in the *ab* plane; the sheets are linked together in the *c* direction by rather distorted phosphate tetrahedra. The average P–O distance is 1.540 Å (−0.025, +0.030 Å), and the average O–P–O angle is 109.4° (−4.4, +3.8°). Table 3 presents the tetrahedral bond angles and distances. The standard deviations for all bond lengths and angles were computed by the function and error program ORFFE (Busing *et al.*, 1962b).

Table 3. Bond distances, angles, and polyhedral edge lengths for the phosphorus tetrahedron

Bond Distance (A)		Bond Angles (°)		Edge Length (A)	
P-O(3)	1.515(5)	O(3)-P-O(1)	113.2(3)	O(3)-O(1)	2.541(7)
P-O(1)	1.530(5)	O(3)-P-O(4)	111.8(3)	O(3)-O(4)	2.533(7)
P-O(4)	1.545(5)	O(3)-P-O(2)	110.1(3)	O(3)-O(2)	2.528(7)
P-O(2)	1.570(4)	O(1)-P-O(4)	108.0(3)	O(1)-O(4)	2.487(6)
		O(1)-P-O(2)	108.4(3)	O(1)-O(2)	2.515(6)
		O(4)-P-O(2)	105.0(3)	O(4)-O(2)	2.471(6)

Numbers in parentheses are e.s.d.'s in the last significant figure.

The copper ion polyhedra each exhibit the characteristic distortion of four short and one or two longer bonds found for divalent copper. Table 4 summarizes the bond angles and distances for the three copper polyhedra. Cu(1), at a special position, has two oxygens and two hydroxyl oxygens at an average distance of 1.949 Å and two more hydroxyl oxygens at 2.723 Å. Cu(3) has two oxygens and two hydroxyl oxygens at an average distance of 1.972 Å and two oxygen atoms at an average distance of 2.296 Å. Cu(2) is surrounded by one oxygen atom and three hydroxyl oxygens at an average distance of 1.962 Å and a fifth oxygen at 2.296 Å. A sixth oxygen atom, O(3), lies at 2.909 Å; we consider this outside of the primary coordination sphere of Cu(2) for several reasons. Using the formula given by Brown and Shannon (1973): $s = s_0(R/R_0)^{-N}$, where s is the strength (in valence units) of a bond of length R, s_0 is the ideal strength of the bond of length R_0, and N a characteristic constant, we have calculated the individual bond strengths (in valence units) for each of the copper polyhedra. Values for s_0, R_0, and N for divalent copper were taken as the empirically fit values (Brown and Shannon, 1973) of 0.333, 2.084, and 5.3, respectively. Bond strength sum of 2.07 and 2.09 v.u. were calculated for six-coordinated Cu(1) and Cu(3), respectively. Five-coordinated Cu(2) gave a calculated bond strength sum of 2.04 v.u. (the addition of the sixth oxygen would only contribute 0.05 v.u. to the bond strength sum). As the sum of the bond strengths should level off near the valence of the cation, five-coordination about Cu(2) is indicated. Furthermore, if a bond existed between Cu(2) and O(3), the coordination about O(3) would consist of three copper atoms and one phosphorus atom, whilst O(1), O(2), and O(4) are each bonded to two copper atoms and one phosphorus atom. O(5) and O(6), the hydroxyl

Table 1. Fractional atomic coordinates and anisotropic thermal parameters

Atom	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0	0	0	0.55(4)	0.42(2)	1.37(4)	0	0.40(3)	0
Cu(2)	3647.5(8)	758.2(7)	204(2)	0.26(3)	0.37(3)	1.40(3)	0.09(2)	-0.02(2)	-0.20(2)
Cu(3)	1354.8(8)	2639.3(7)	345(2)	0.38(3)	0.35(3)	1.21(3)	0.15(2)	-0.17(2)	-0.14(2)
P	3874(2)	2989(2)	4793(3)	0.24(5)	0.33(5)	0.89(5)	-0.07(4)	0.02(4)	-0.03(4)
O(1)	-23(5)	1282(4)	2997(10)	0.51(15)	0.72(17)	1.34(17)	0.09(13)	0.00(13)	-0.31(14)
O(2)	2932(4)	2155(4)	2560(10)	0.31(14)	0.44(15)	1.10(16)	-0.02(12)	-0.18(11)	-0.17(13)
O(3)	2896(5)	3826(5)	6570(11)	1.04(17)	0.65(17)	1.64(19)	0.21(14)	0.48(14)	-0.33(15)
O(4)	4725(5)	2051(4)	6834(10)	0.48(15)	0.59(16)	1.11(16)	-0.19(12)	-0.21(12)	0.18(14)
O(5)	724(5)	4202(4)	1625(10)	0.42(14)	0.29(15)	1.28(17)	-0.08(11)	0.16(12)	-0.01(13)
O(6)	1687(5)	890(4)	-1646(10)	0.35(14)	0.06(14)	1.31(17)	-0.18(11)	0.15(12)	-0.22(13)

* *Numbers in parentheses are e.s.d.'s in the last significant figure. The B's are defined by the general temperature factor* $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

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[1] To receive a copy of Table 2, order document number AM-76-022 from the Business Office, Mineralogical Society of America, Suite 1000 lower level, 1909 K Street NW, Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

oxygens, are bonded to three copper atoms and a hydrogen atom. Lastly, close investigation (*vide infra*) of the polyhedral linkages within the sheets indicates the lack of bonding between Cu(2) and O(3).

Difference Fourier maps failed to reveal the exact position of the hydrogen atoms. No evidence for water molecules was found in PPM; this supports Ghose's conclusion (1963) that water is not a part of the structure of PM. The copper-containing polyhedra are edge-linked to form the *ab* sheets. Figure 1 is a projection of these sheets onto the *ab* plane (centered about 1/2, 1/2, 0). The phosphate tetrahedra join the sheets in the *c* direction; the same linkage is found in PM.

Table 4. Bond distances, angles, and polyhedral edge lengths for the copper polyhedra*

	Bond Distance (A)	Bond Angle (°)	Edge Length (A)
Cu(1) Polyhedron			
Cu(1)-O(1)	2x 1.915(5)		
Cu(1)-O(6)	2x 1.984(4)		
Cu(1)-O(3)	2x 2.723(5)		
O(1)-Cu(1)-O(6)*b*		86.9(2)	2.683(6)
O(1)-Cu(1)-O(6)*a*		93.1(2)	2.830(6)
O(1)-Cu(1)-O(3)*c*		92.0(2)	3.383(7)
O(1)-Cu(1)-O(3)*a*		88.0(2)	3.273(7)
O(3)-Cu(1)-O(6)*c*		96.8(2)	3.554(7)
O(3)-Cu(1)-O(6)		83.2(2)	3.173(7)
Cu(2) Polyhedron			
Cu(2)-O(5)*c*	1.950(5)		
Cu(2)-O(2)	1.954(5)		
Cu(2)-O(6)	1.956(4)		
Cu(2)-O(5)*a*	1.986(4)		
Cu(2)-O(4)	2.296(5)		
O(5)*c*-Cu(2)-O(2)		171.1(2)	3.892(6)
O(5)*c*-Cu(2)-O(6)		99.7(2)	2.984(6)
O(5)*c*-Cu(2)-O(5)*a*		81.7(2)	2.574(9)
O(5)*a*-Cu(2)-O(4)		95.5(2)	3.152(6)
O(2) -Cu(2)-O(6)		81.3(2)	2.546(6)
O(2) -Cu(2)-O(5)*a*		98.7(2)	2.990(6)
O(2) -Cu(2)-O(4)		93.2(2)	3.097(7)
O(6) -Cu(2)-O(5)*a*		171.6(2)	3.931(7)
O(6) -Cu(2)-O(4)		95.4(2)	3.153(6)
O(5)*a*-Cu(2)-O(4)		76.2(2)	2.655(6)
Cu(3) Polyhedron			
Cu(3)-O(4)	1.945(4)		
Cu(3)-O(2)	1.974(4)		
Cu(3)-O(5)	1.984(5)		
Cu(3)-O(6)	1.984(4)		
Cu(3)-O(3)	2.379(5)		
Cu(3)-O(1)	2.466(5)		
O(4)-Cu(3)-O(5)		85.0(2)	2.655(7)
O(4)-Cu(3)-O(6)		95.4(2)	2.906(6)
O(4)-Cu(3)-O(3)		89.7(2)	3.066(7)
O(4)-Cu(3)-O(1)		95.2(2)	3.276(7)
O(2)-Cu(3)-O(5)		98.6(2)	3.001(6)
O(2)-Cu(3)-O(6)		80.1(2)	2.546(6)
O(2)-Cu(3)-O(3)		94.7(2)	3.213(7)
O(2)-Cu(3)-O(1)		80.2(2)	2.884(6)
O(5)-Cu(3)-O(3)		90.0(2)	3.097(6)
O(5)-Cu(3)-O(1)		93.5(2)	3.258(7)
O(6)-Cu(3)-O(3)		103.3(2)	3.431(7)
O(6)-Cu(3)-O(1)		73.3(2)	2.683(6)
O(4)-Cu(3)-O(2)		174.3(2)	
O(5)-Cu(3)-O(6)		166.7(2)	
O(3)-Cu(3)-O(1)		174.2(3)	

* *Numbers in parentheses are e.s.d.'s in the last significant figure.*
a) 1/2+x, 1/2-y,z; b) $\bar{x}$ $\bar{y}$ $\bar{z}$; *c) 1/2-x, 1/2+y,*$\bar{z}$

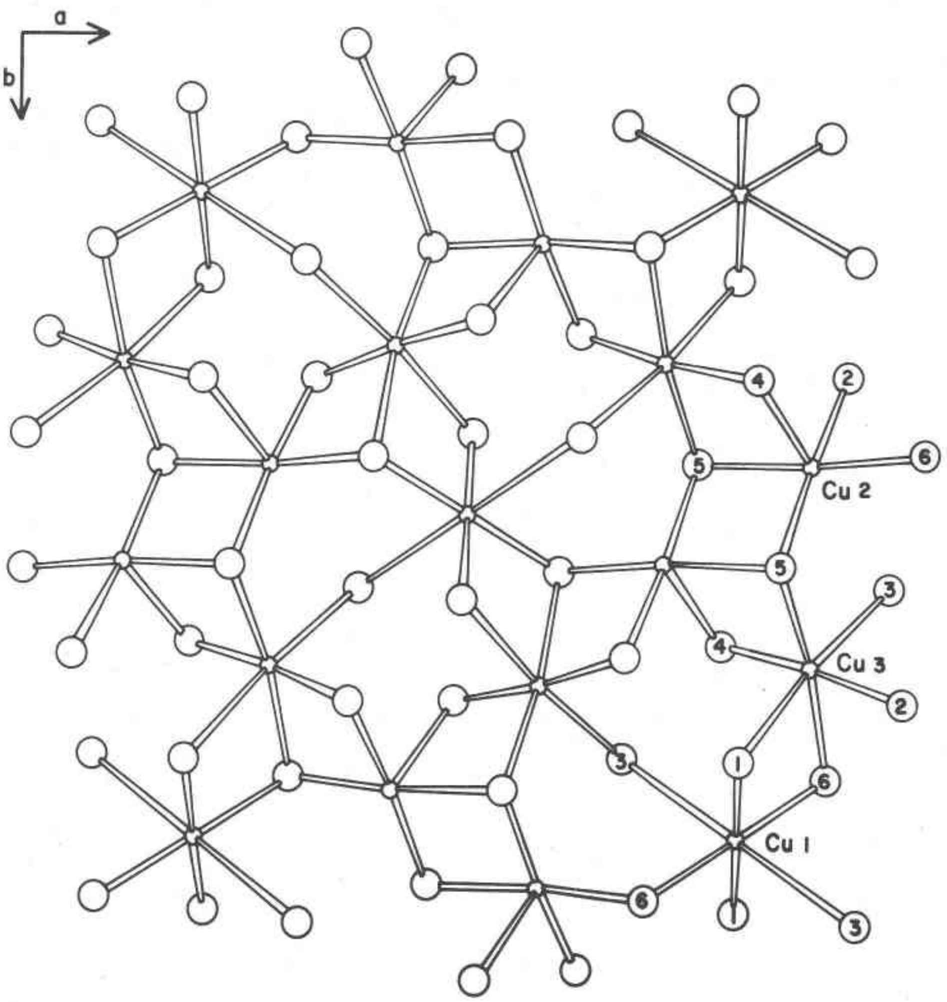

Fig. 1. A view of the copper-containing layer (the *ab* plane) of PPM centered about 1/2, 1/2, 0. Copper atoms are represented by the smaller circles, oxygen atoms by the larger.

Discussion

The structures of PPM and PM are so closely related that a descriptive comparison is in order. In each structure, copper atoms are contained in two-dimensional polyhedral networks which are then linked by phosphate tetrahedra to form the three-dimensional structure. Because the choice of unit cell in the compounds is different, we are comparing the (001) projection of PPM and the (100) projection of PM. The copper-containing polyhedra are essentially the same. The difference between these two structures lies solely in the arrangements of these polyhedra in the two-dimensional planes.

A useful comparison of the two structures can be made if idealized octahedra are used to build the edge-sharing network of Cu(2) and Cu(3) sites while momentarily ignoring the Cu(1) sites. This leads in each case to a two-dimensional layer of edge-sharing octahedra—brucite [$Mg(OH)_2$] or CdI_2 type—from which one third of the octahedra have been removed as edge-sharing pairs. Figures 2a and 2b show the networks of Cu(2) and Cu(3) atoms in PPM and PM, respectively, constructed in this manner. The idealized unit cells are outlined. Close analysis reveals that PPM is based on a four-connected two-dimensional net whereas PM is based on a three-connected net; herein lies the basic difference between the two structures. The topological repeat units which define the four- and three-connected nets, respectively, are emphasized in Figure 2.

In reality the centers of the holes in these idealized nets are filled by the Cu(1) octahedra. The Cu(1) sites have become highly distorted in this idealized construction. The transition from the idealized network

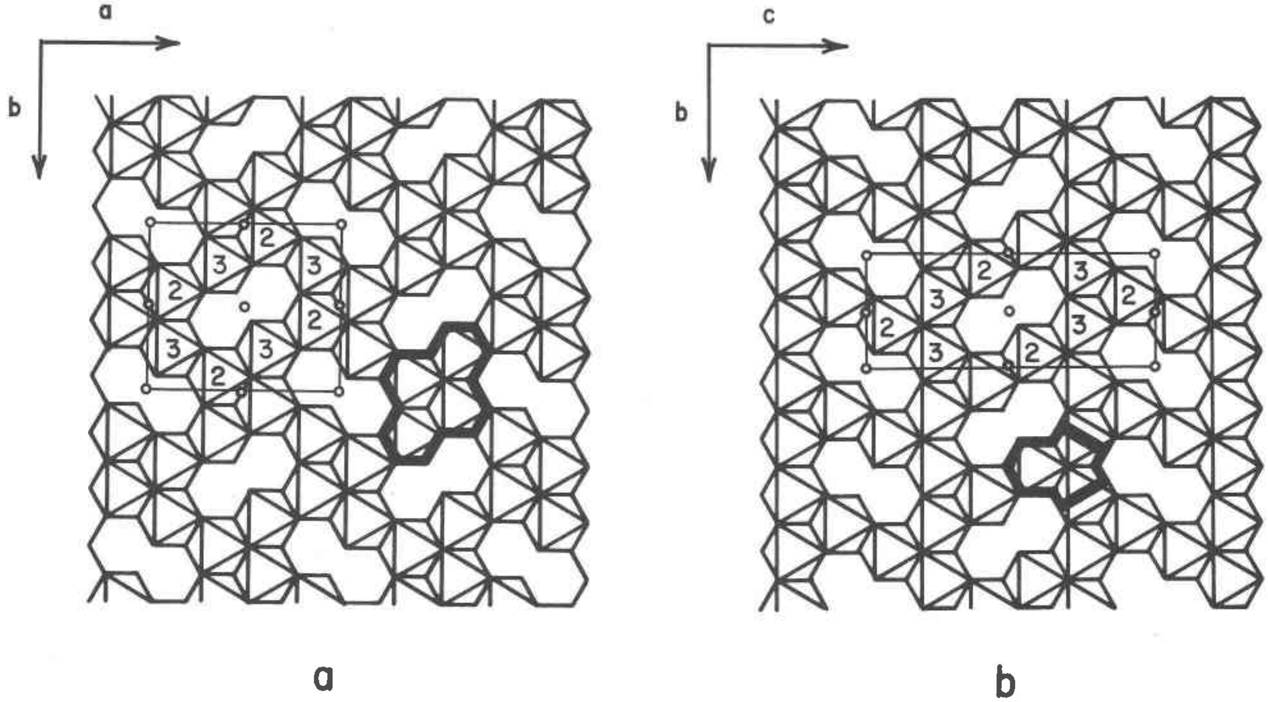

Fig. 2. The idealized networks of edge-sharing Cu(2) and Cu(3) octahedra found in the layers of the two polymorphs of $Cu_5(PO_4)_2(OH)_4$: (a) PPM, slice parallel to (001), (b) PM, slice parallel to (100). The unit cell is outlined, and the locations of the inversion centers are indicated by small circles. The Cu(1) polyhedra are omitted (see text). The heavily outlined areas show the topological repeat units for the two networks: (a) four-connected in PPM, (b) three-connected in PM.

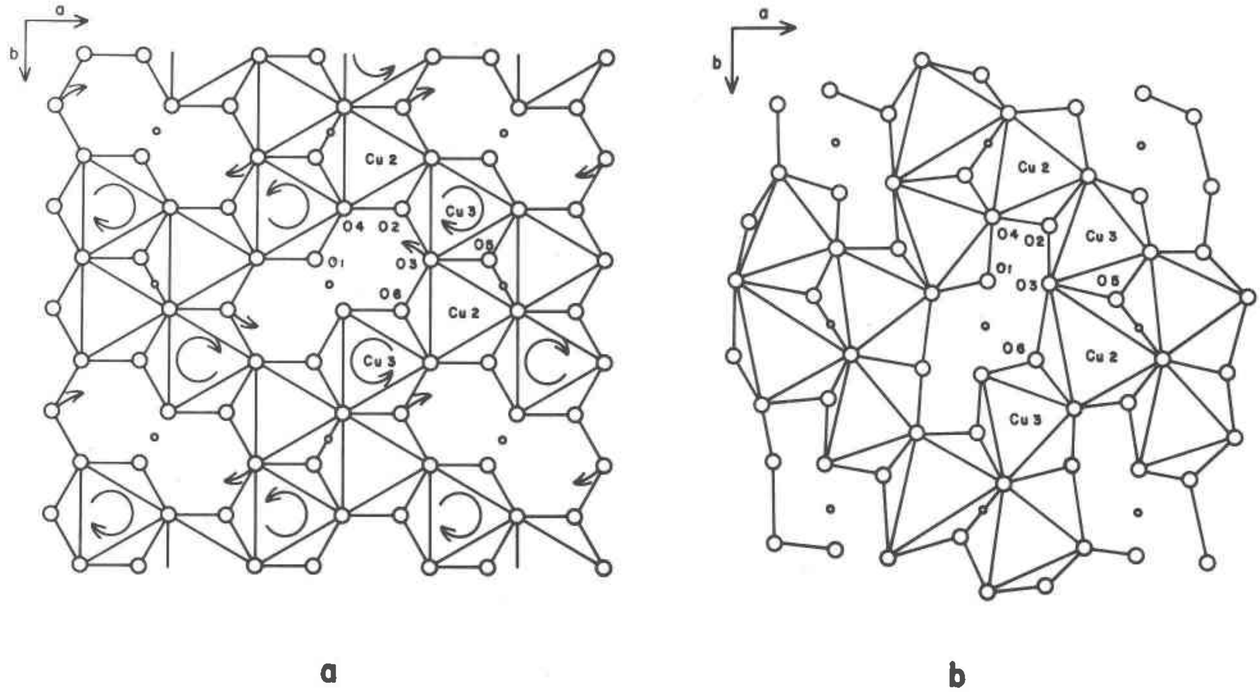

Fig. 3. (a) the idealized net of Cu(2) and Cu(3) polyhedra in PPM; (b) the actual view of the PPM layer. The arrows in (a) depict the relative rotations of Cu(3) octahedra and the motion of O(3) atoms which lead to (b). Cu(1) atoms lie at the centers of the large holes. Phosphate tetrahedra lie above and below the O(2)–O(4)–O(1)–O(3) quadrangle and joining successive layers. The smallest circles indicate the positions of inversion centers.

of PPM to the actual structure is shown in Figures 3a and 3b. In Figure 3a the arrows depict the relative motion of O(3) and the rotations of Cu(3) octahedra which lead to the arrangement shown in Figure 3b. Figure 3b is the projection of the PPM *ab* layer as shown in Figure 1 but with the oxygen–oxygen contacts outlined to show the polyhedral edges. It can be seen that this analysis leads to the correct distortions of the copper polyhedra in PPM. A similar analysis can be made for PM.

The distortions from the idealized network of Figure 2a have the following effects: (1) the Cu(1) octahedral sites become less distorted, (2) the O(1) and O(3) atoms draw together allowing bridging of O(1)–O(2) and O(3)–O(4) by the phosphate tetrahedron, (3) the Cu(2)–O(3) distance lengthens to the point where bonding is no longer possible, and (4) the whole structure shears in the *a* direction. These distortions do not destroy the inversion center or glide planes which are observed in the idealized network.

In view of the great similarities between the two structures it becomes a matter of speculation as to what factors cause the stabilization of one network over the other. In addition, since there are other ways to remove one-third of the octahedral sites as edge-sharing pairs from a CdI_2-type layer than the two shown in Figures 2a and 2b, it seems that other two-dimensional polymorphs of $Cu_5(PO_4)(OH)_4$ might be found. We expect to carry out a refinement of the structure of PM since it would seem, in analogy to the above analysis, that the sixth oxygen in the 4 + 1 + 1 coordination of Cu(2) (Ghose, 1963) should not be bonded to that atom.

Acknowledgments

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