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Refinement of the crystal structure of pseudomalachite

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Abstract

The crystal structure of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$, (from Rheinbreitenbach, Germany) has been refined by full-matrix least-squares techniques to a residual $R = 0.040$ ($R_w = 0.047$) using automatic diffractometer data. The lattice parameters (space group $P2_1/c$) are $a = 4.4728(4)$, $b = 5.7469(5)$, $c = 17.032(3)$ A, and $\beta = 91.043(7)°$. The copper ions lie in sheets of edge-sharing coordination polyhedra in the *bc* plane; the sheets are linked together in the *a* direction by highly distorted phosphate tetrahedra. This work confirms the essential features of an earlier structural study of pseudomalachite with increased precision. Through an analysis of bond distances, coordination, and bond valence sums, probable locations of hydrogen bonds were determined. Hydrogen bonds appear to be important in stabilizing the pseudomalachite structure.

Introduction

We recently reported (Anderson *et al.*, 1977) the preparation and crystal-structure determination of synthetic $Cu_5(PO_4)_2(OH)_4$, a polymorph of pseudomalachite (PM). The structure of this synthetic phase (called PPM for convenience) differs from that of PM only in the difference in the polyhedral linkages in two-dimensional copper-containing sheets.

In our comparison of the two structures, the only difference in cooper coordination seemed to occur about the Cu(2) ion, which we considered to be five-coordinated (4 + 1) in PPM but which Ghose (1963) reports as six-coordinated (4 + 1 + 1) in PM. As a result, we decided to complete a three-dimensional least-squares refinement of the structure of PM in order to compare the coordination polyhedra at the same level of accuracy. This paper reports the results of that refinement.

Experimental

Samples of pseudomalachite were obtained from the Harvard University Mineralogical Museum and from the Smithsonian Institution. The best crystals for X-ray diffraction were found in a sample from Rheinbreitenbach, Germany (Harvard #110744). According to published analyses, pseudomalachite from Rheinbreitenbach contains traces of iron, but an examination of fragments from our sample by electron microprobe showed none.

A sphere was ground to a radius of 0.0065(5) cm. Precession photographs revealed monoclinic symmetry with systematic absences corresponding to the space group $P2_1/c$. The lattice parameters were determined in a PICK-II least-squares refinement program, using 50 reflections within the angular range $37° < 2\theta < 50°$; 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 $a = 4.4728(4)$ $b = 5.7469(5)$, $c = 17.032(3)$ A, and $\beta = 91.043(7)°$, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density, with $Z = 2$, is 4.367 g cm^{-3}.

Diffraction intensities were measured using Zr filtered Mo$K\alpha$ radiation at a take-off angle of 2.5° with the diffractometer operating in the ω scan mode. 10-second background counts were taken at the ends of a 1.4° θ–2θ scan corrected for dispersion. Of the 1694 independent data investigated in the angular range $2\theta < 65°$, 1411 were considered observable according to the criterion $|F_o| > 3.00\sigma_F$, 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 3

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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	1.25(3)	0.98(3)	1.32(3)	0	0.43(2)	0
Cu(2)	461(1)	4726(1)	856.0(3)	1.18(2)	1.26(2)	0.76(2)	0.33(2)	-0.03(1)	0.04(2)
Cu(3)	-171(1)	3287(1)	2570.5(3)	1.24(2)	0.87(2)	1.07(2)	-0.10(2)	-0.39(1)	0.08(2)
P	5255(2)	942(2)	1348.0(7)	0.75(4)	0.98(4)	0.74(4)	-0.01(3)	-0.03(3)	0.00(3)
O(1)	7109(7)	1561(6)	622(2)	1.16(11)	1.55(13)	1.02(11)	0.10(10)	0.26(9)	0.04(10)
O(2)	3242(7)	3059(6)	1511(2)	1.22(11)	1.26(12)	0.90(10)	0.57(10)	-0.08(8)	-0.09(9)
O(3)	7405(7)	762(6)	2077(2)	1.19(11)	0.86(11)	0.99(11)	0.02(9)	-0.35(9)	0.08(9)
O(4)	3487(8)	8725(7)	1247(2)	1.40(12)	1.50(13)	1.78(14)	-0.30(11)	-0.24(10)	-0.01(11)
O(5)	1722(7)	3201(6)	-142(2)	0.96(10)	1.13(11)	0.92(10)	0.14(9)	0.00(8)	0.05(9)
O(6)	1521(7)	719(5)	3166(2)	0.88(10)	0.82(10)	0.82(10)	-0.09(8)	-0.13(8)	0.11(8)

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

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 were made for the spherical crystal with $\mu R = 0.83$ (Mo$K\alpha$). The maximum relative absorption correction applied was 3.5 percent of $|F_o|$.

Using the positional parameters reported by Ghose (1963) as a trial structure, full-matrix least-squares refinement (Busing *et al.*,1962a) with a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Cu, P, and O (Cromer and Mann, 1968), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual $R = 0.067$ and weighted residual $R_w = 0.078$. The anisotropic refinement, based on a data to parameter ratio of 16 with 87 independently varied parameters, yielded a final $R = 0.040$ and $R_w = 0.047$ for the observed data (figure of merit = 0.959). In the final refinement, the maximum extinction correction (Zachariasen, 1968) was 15 percent of $|F_o|$ for the $\bar{1}04$ reflection. The final atomic coordinates and aniso-

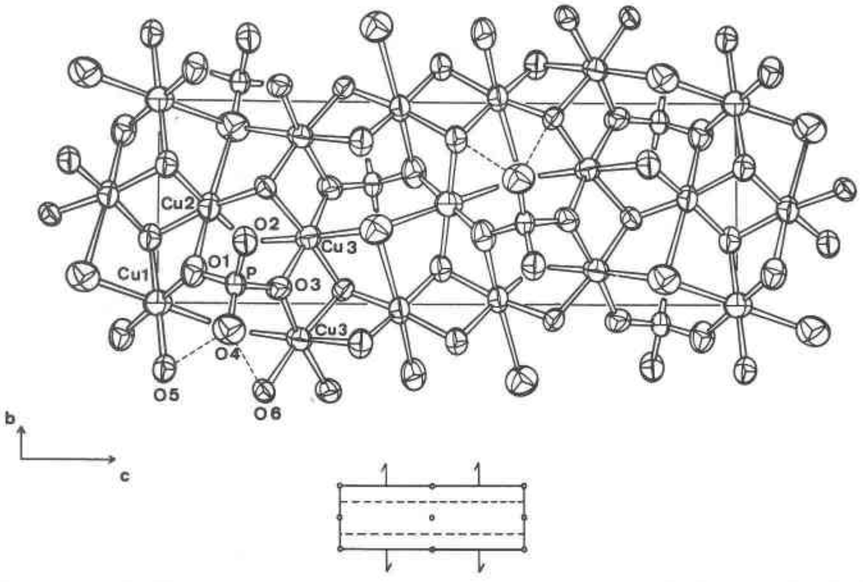

Fig. 1. Section of the pseudomalachite structure projected onto the *bc* plane, illustrating the layer of edge-sharing copper-containing polyhedra and the phosphate tetrahedra which join successive layers. Broken bonds go to hidden atoms. Dotted lines indicate the positions of proposed hydrogen bonds between the layers. Insert shows the symmetry elements for $P2_1/c$. Thermal ellipsoids of vibration (98%) are shown.

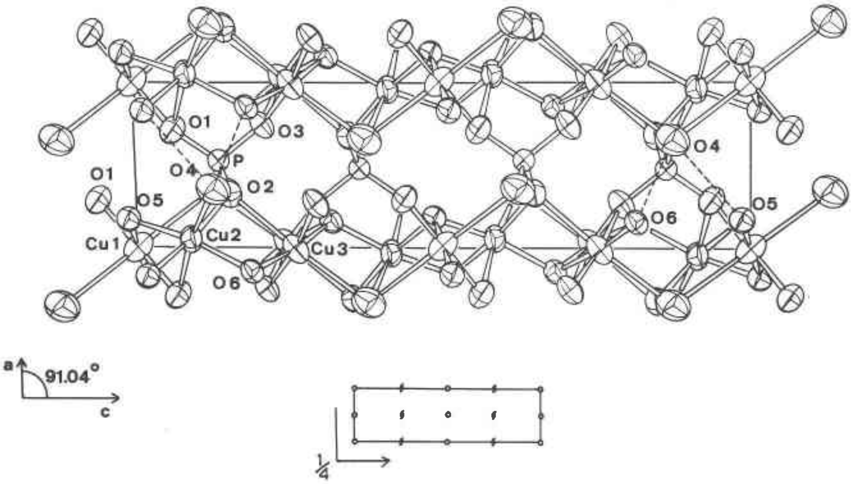

Fig 2. Projection of the pseudomalachite structure onto the *ac* plane illustrating the layers of copper-containing polyhedra joined by phosphate tetrahedra. Broken bonds go to hidden atoms. Dotted lines indicate the positions of proposed hydrogen bonds. Insert shows the symmetry elements for $P2_1/c$. Thermal ellipsoids of vibration (98%) are shown.

tropic 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 crystal structure of PM was described by Ghose (1963). The copper ions lie in sheets of edge-sharing coordination polyhedra (Fig. 1) in the *bc* plane; the sheets are linked together in the *a* direction by highly distorted phosphate tetrahedra (Fig. 2). The average P–O distance is 1.538A (−0.027, +0.049A), and the average O–P–O angle is 109.4° (−3.7, +3.2°). 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.*, 1962*b*).

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

Bond Distance (Å)		Bond Angles (°)		Edge Length (Å)	
P-O(4)	1.511(4)	O(4)-P-O(1)	112.6(2)	O(4)-O(1)	2.520(5)
P-O(1)	1.518(3)	O(4)-P-O(2)	112.5(2)	O(4)-O(2)	2.533(5)
P-O(2)	1.536(3)	O(4)-P-O(2)	111.1(2)	O(4)-O(3)	2.555(5)
P-O(3)	1.587(3)	O(1)-P-O(2)	105.7(2)	O(1)-O(2)	2.485(4)
		O(1)-P-O(3)	108.8(2)	O(1)-O(3)	2.525(5)
		O(2)-P-O(3)	105.8(2)	O(2)-O(3)	2.491(5)

* *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 two longer bonds common for divalent copper (Wells, 1975). Cu(1), on an inversion center, has two oxygens and two hydroxyl oxygens at an average distance of 1.946 A and two more oxygens at 2.757 A. Cu(3) has two oxygens and two hydroxyl oxygens at an average distance of 1.986 A and two oxygen atoms at an average distance of 2.420 A. Cu(2) is surrounded by one oxygen atom and three hydroxyl oxygens at an average distance of 1.964 A, a fifth oxygen at 2.395 A, and a sixth oxygen atom at 2.755 A. Table 4 summarizes the bond angles and distances for the three copper polyhedra, and Table 5 presents the relevant bond angles and distances about each oxygen atom.

To verify the cation coordination, we calculated the bond valences (in v.u.) about each of the *metal* atoms using Brown and Shannon's (1973) empirical correlation of bond length and bond valence: $S = S_0(R/R_0)^{-N}$, where S = bond valence, R = bond length, and S_0, R_0 and N are empirically fit constants for a given atom. The values (Brown and Shannon, 1973) of S_0, R_0, N for Cu^{2+} and P^{5+} are 0.333, 2.084, 5.3 and 1.25, 1.534, 3.2, respectively (see Table 6).

Assignment and location of hydrogen atoms

Bond-valence sums (in valence units) calculated for each *oxygen* atom are given in Table 6. Clearly, O(4), O(5), and O(6) are under-bonded in this model. The chemical formulation of PM, $Cu_5(PO_4)_2(OH)_4$, requires two unique hydrogen atoms per asymmetric unit for charge balance. Since the phosphorus–oxygen bonds of the phosphate tetrahedra are all

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[1] To receive a copy of Table 2, order document number AM-77-049 from the Business Office, Mineralogical Society of America, Suite 1000 lower level, 1909 K Street NW, Washington, D. C. 20006. Please remit $1.00 for the microfiche.

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

	Bond Distance (Å)	Bond Angle (°)	Edge Length (Å)
Cu(1) Polyhedron			
Cu(1)-O(1)	2x 1.884(3)		
Cu(1)-O(5)	2x 2.007(3)		
Cu(1)-O(4)	2x 2.757(4)		
O(1)-Cu(1)-O(5)		83.6(1)	2.596(4)
O(1)-Cu(1)-O(5)*c*		96.4(1)	2.901(5)
O(1)-Cu(1)-O(4)		94.9(1)	3.469(5)
O(1)-Cu(1)-O(4)*c*		85.1(1)	3.203(5)
O(5)-Cu(1)-O(4)		96.6(1)	3.592(5)
O(5)-Cu(1)-O(4)*c*		83.4(1)	3.218(5)
Cu(2) Polyhedron			
Cu(2)-O(2)	1.939(3)		
Cu(2)-O(6)	1.958(3)		
Cu(2)-O(5)*c*	1.974(3)		
Cu(2)-O(5)	1.985(3)		
Cu(2)-O(1)	2.395(4)		
Cu(2)-O(4)	2.755(4)		
O(2)-Cu(2)-O(6)		86.6(1)	2.672(4)
O(2)-Cu(2)-O(5)		95.7(1)	2.909(4)
O(2)-Cu(2)-O(1)		97.5(1)	3.272(5)
O(2)-Cu(2)-O(4)		87.1(1)	3.289(5)
O(6)-Cu(2)-O(5)*c*		97.3(1)	2.952(4)
O(6)-Cu(2)-O(1)		95.0(1)	3.224(5)
O(6)-Cu(2)-O(4)		76.6(1)	2.987(5)
O(5)*c*-Cu(2)-O(5)		82.8(1)	2.618(6)
O(5)*c*-Cu(2)-O(1)		92.2(1)	3.161(5)
O(5)*c*-Cu(2)-O(4)		84.1(1)	3.218(5)
O(5)-Cu(2)-O(1)		72.0(1)	2.596(4)
O(5)-Cu(2)-O(4)		116.2(1)	4.045(5)
O(2)-Cu(2)-O(5)*c*		169.3(1)	
O(6)-Cu(2)-O(5)		167.0(1)	
O(1)-Cu(2)-O(4)		170.2(1)	
Cu(3) Polyhedron			
Cu(3)-O(6)	1.951(3)		
Cu(3)-O(6)*b*	1.979(4)		
Cu(3)-O(3)*b*	1.985(3)		
Cu(3)-O(3)	2.005(3)		
Cu(3)-O(2)	2.346(3)		
Cu(3)-O(4)	2.493(4)		
O(6)-Cu(3)-O(3)*b*		97.8(1)	2.965(5)
O(6)-Cu(3)-O(3)		83.6(1)	2.637(4)
O(6)-Cu(3)-O(2)		96.0(1)	3.204(4)
O(6)-Cu(3)-O(4)		83.5(1)	2.987(5)
O(6)*b*-Cu(3)-O(3)*b*		83.4(1)	2.637(4)
O(6)*b*-Cu(3)-O(3)		94.1(1)	2.917(5)
O(6)*b*-Cu(3)-O(2)		75.8(1)	2.672(4)
O(6)*b*-Cu(3)-O(4)		104.9(1)	3.558(5)
O(3)*b*-Cu(3)-O(2)		82.7(1)	2.874(5)
O(3)*b*-Cu(3)-O(4)		92.8(1)	3.260(5)
O(3)*b*-Cu(3)-O(2)		89.2(1)	3.065(5)
O(3)-Cu(3)-O(4)		95.4(1)	3.342(5)
O(6)-Cu(3)-O(6)*b*		171.5(2)	
O(3)-Cu(3)-O(3)*b*		171.9(1)	
O(2)-Cu(3)-O(4)		175.3(1)	

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

within the limits found for a normal orthophosphate group, we conclude that none of the phosphate oxygens are hydroxyls. This leaves O(5) and O(6) as hydroxyl oxygens, as proposed by Ghose in 1963. Geometrically, this is quite acceptable since the hydrogen atoms will point into the space between the layers of copper atoms, and complete a roughly tetrahedral arrangement of cations around O(5) and O(6).

The distance of O(4) from Cu(1) and Cu(2) indicates that these copper atoms do *not* play a major role in fulfilling its bonding requirements (Table 6). The valence deficiency of O(4) coupled with its large anisotropic thermal parameters suggests that it may be receiving electron contribution from hydrogen bonds. Two of the major thermal-ellipsoid axes of O(4) appear to be pointed in the general direction of O(5) and O(6) in the adjacent Cu layer, as can be seen

Table 5. Bond distances, bond angles, and polyhedral edge lengths for oxygen polyhedra

	Distance (Å)	Angle(°)	Edge Length (Å)
i) O(1) Polyhedron			
O(1)-P	1.518(3)		
O(1)-Cu(1)	1.884(3)		
O(1)-Cu(2)	2.395(4)		
P-O(1)-Cu(1)		134.9(2)	3.145(1)
P-O(1)-Cu(2)		112.2(2)	3.284(1)
Cu(1)-O(1)-Cu(2)		91.7(1)	3.091(1)
ii) O(2) Polyhedron			
O(2)-P	1.536(3)		
O(2)-Cu(2)	1.939(3)		
O(2)-Cu(3)	2.346(3)		
P-O(2)-Cu(2)		131.9(2)	3.177(1)
P-O(2)-Cu(3)		123.7(2)	3.443(1)
Cu(2)-O(2)-Cu(3)		90.0(1)	3.043(1)
iii) O(3) Polyhedron			
O(3)-P	1.587(3)		
O(3)-Cu(3)	1.985(3)		
O(3)-Cu(3)	2.007(3)		
P-O(3)-Cu(3)		132.3(2)	3.272(1)
P-O(3)-Cu(3)		128.4(2)	3.239(1)
Cu(3)-O(3)-Cu(3)		92.7(1)	2.8873(3)
iv) O(4) Polyhedron			
O(4)-P	1.511(4)		
O(4)-Cu(3)	2.493(4)		
O(4)-Cu(2)	2.755(4)		
O(4)-Cu(1)	2.757(4)		
P-O(4)-Cu(3)		107.3(2)	3.277(1)
P-O(4)-Cu(2)		172.5(2)	4.257(1)
P-O(4)-Cu(1)		99.7(2)	3.359(1)
Cu(3)-O(4)-Cu(2)		79.8(1)	3.372(1)
Cu(3)-O(4)-Cu(1)		108.2(1)	4.255(1)
Cu(2)-O(4)-Cu(1)		75.4(1)	3.371(1)
v) O(5) Polyhedron			
O(5)-Cu(2)	1.974(3)		
O(5)-Cu(2)	1.985(3)		
O(5)-Cu(1)	2.007(3)		
Cu(2)-O(5)-Cu(2)		97.2(1)	2.969(2)
Cu(2)-O(5)-Cu(1)		115.7(2)	3.371(1)
Cu(2)-O(5)-Cu(1)		101.5(1)	3.091(1)
vi) O(6) Polyhedron			
O(6)-Cu(3)	1.951(3)		
O(6)-Cu(2)	1.958(3)		
O(6)-Cu(3)	1.979(4)		
Cu(3)-O(6)-Cu(2)		119.2(2)	3.372(1)
Cu(3)-O(6)-Cu(3)		94.6(1)	2.8873(3)
Cu(2)-O(6)-Cu(3)		101.2(1)	3.043(1)

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

Table 6. Individual bond strengths and bond-strength sums about each atom (in v.u.)

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	Σ cation
P	1.29	1.24	1.12	1.31	----	----	4.96
Cu(1)*	.59	----	----	.07	.41	----	1.05
Cu(2)	.16	.49	----	.08	.44 .43	.46	2.06
Cu(3)	----	.18	.43 .41	.13	----	.47 .44	2.06
Σ oxygen	2.02	1.91	1.96	1.59	1.28	1.37	

Cu(1) is located on an inversion center

in Figures 1 and 2. Examination of oxygen–oxygen distances reveals that O(4) lies sufficiently close to both O(5) (3.044A) and O(6) (3.009A) in the next layer to permit weak, interlayer hydrogen bond interactions.

Not surprisingly, difference Fourier maps failed to reveal the hydrogen atom positions. Several trial positions for hydrogen atoms were postulated with O(5) and O(6) as H-bond donors and O(4) and O(2) as the logical H-bond acceptors. The hydrogen atoms were added to the model structure and allowed to vary isotropically during least-squares refinements. No stable position was found around O(6) for a hydrogen atom, but, surprisingly, a hydrogen stabilized between O(5) and O(4) (at 0.68, 0.69, 0.04) at a distance of 0.80A from O(5), 2.30A from O(4), and an O–H ··· O angle of 155°. Further attempts using scattering factors for charged atoms gave essentially the same results except for a slight improvement in the statistical fit.

As Brown (1976) implies from a survey of neutron-diffraction data that the maximum observed valence contribution from long hydrogen-acceptor bonds is about 0.2 v.u. when the O–O distance is 2.73A, the longer O–O distances in PM suggest a smaller contribution. Therefore, the contribution from one long hydrogen bond alone does not appear to be sufficient to satisfy O(4)'s valence requirements. We hypothesize that although the second H atom was not experimentally found, a second hydrogen bond exists between O(6) and O(4). The positions of these hydrogen bonds are indicated in Figures 1 and 2.

Discussion

The structural details of PM are now nearly complete, but the factors affecting its stability relative to the structures of other copper phosphates are not entirely clear. In many of these structures the copper atoms appear to favor a 4 + 2 distorted octahedral environment with vertex and edge-shared connections to neighboring polyhedra. In PM the coordination of the Cu(2) atom to O(4) is strongly dependent on the P–O(4) interaction. Since O(4) atom receives most of its valence requirements from the bond to phosphorus, its close approach lengthens the Cu(2)–O(4) distance to an extent that the valence contribution from the copper is small. O(4) receives a larger valence contribution from each of its two long H-acceptor bonds than it does from either Cu(1) or Cu(2). This suggests that the hydrogen bonds play an important role in the stabilization of this structure.

In study of the structure of PPM (Anderson *et al.*, 1977) we discussed the similarity between the structures of the two polymorphs of $Cu_5(PO_4)_2(OH)_4$, naturally occurring PM and our synthetic phase PPM. These structures differ only in the system of linkages between copper polyhedra in the copper-containing sheets, PM being based on a 3-connected two-dimensional network whereas PPM is based on a 4-connected two-dimensional net. In PPM O(3) is in a position similar to O(4) in PM. O(3) in PPM is primarily bonded to P, but is valence-deficient and is expected to gain the remainder of its valence needs from acceptor H-bonds to O(5) and O(6) in neighboring layers. The factors affecting the relative stability of PM *vs.* PPM are still unknown.

Acknowledgments

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