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The Crystal Structure of $Cu_4(PO_4)_2O$

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$Cu_4(PO_4)_2O$ crystallizes in the space group $P\bar{1}$ with $a = 7.5393(8)$ Å, $b = 8.1021(9)$ Å, $c = 6.2764(8)$ Å, $\alpha = 113.65(1)°$, $\beta = 98.42(1)°$ and $\gamma = 74.19(1)°$. The structure was refined by full-matrix least-squares techniques using automatic diffractometer data to $R = 0.046$ ($R_w = 0.056$). Four unique copper atoms are in six-, five-, and four-coordinated polyhedra which are linked together to form a three-dimensional network. The structure is best described in terms of a cubic close-packed array of oxygen atoms with one-tenth of the possible anion sites vacant.

Introduction

In an extension of our preparative and structural studies [see (*1*) for prior references] on the halophosphates of divalent transition metals, we prepared and isolated small single crystals of a material which proved to be a previously unreported compound in the $CuO–P_2O_5$ system (*2*). As we have a continuing interest in the crystal chemistry of complex compounds of divalent copper (*3–5*), we proceeded with a complete determination and full-matrix least-squares refinement of the structure of this compound, $Cu_4(PO_4)_2O$. This paper presents the results of this study as well as a detailed description of this unique structure type.

Experimental

During an attempt to grow single crystals of $Cu_2(PO_4)Cl$, a 60/40 mole ratio mixture of $CuCl_2/Cu_3(PO_4)_2$ contained in a crimped Pt crucible was cooled in air from 950°C to room temperature at 18°C/hr. As a result of the partial oxidation of $CuCl_2$, small green single crystals of a material which proved to have the composition $Cu_4(PO_4)_2O$ were formed.

X-Ray precession photographs revealed triclinic symmetry. Subsequent analysis showed the space group to be $P\bar{1}$, in which the final refinements were carried out.

The lattice parameters were determined in a PICK-II least-squares refinement program, using 48 reflections within the angular range $45° < 2\theta < 58°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using $MoK\alpha_1$ radiation ($\lambda = 0.70930$ Å). At 22°C the lattice parameters for the conventional Donnay unit cell were found to be $a = 7.5393(8)$ Å, $b = 8.1021(9)$ Å, $c = 6.2764(8)$ Å, $\alpha = 113.65(1)°$, $\beta = 98.42(1)$, and $\gamma = 74.19(1)°$, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated volume is 337.6 Å, giving a calculated density, with $Z = 2$, of 4.525 g cm^{-3}.

Attempts to grind a crystal into a spherical shape were foiled by a strong cleavage. Therefore a small euhedral crystal with dimensions $0.20 \times 0.11 \times 0.06$ mm ($V = 1.3 \times 10^{-3}$ cm^3) was chosen for data collection. Precise dimensions of the crystal were determined

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from photomicrographs for use in an absorption correction program written by N. W. Alcock and B. Lee for a crystal of general shape. Input for this program included the three pairs of well-developed faces on the crystal which were found to be normal to major reciprocal lattice rows as judged by precession photographs and the orientation angles of the crystal coordinate system with respect to the diffractometer coordinate system obtained from the program PICK-II.

Diffraction intensities were measured using Zr-filtered Mo$K\alpha$ radiation at a takeoff angle of 1.5° with the diffractometer operating in the ω scan mode. Ten-second background counts were taken at both ends of a 1.4° θ–2θ offset corrected for dispersion. Of the 2022 independent data investigated in the angular range $2\theta < 60°$, 1775 were considered observable according to the criterion $|F_0| > 3.0\sigma_F$, where σ_F is defined as $0.02|F_0| + [C + k^2B]^{1/2}/2|F_0|Lp$; 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; the maximum variation in intensity observed was never greater than ±2% over the data collection period.

Intensity data were corrected for Lorentzian and polarization effects, and absorption corrections ($\mu = 134$ cm^{-1}, Mo$K\alpha$) were made using the program already cited. The maximum absorption correction was 28% of $|F_0|$.

The positions of four unique copper atoms were quickly determined from the best electron density map generated by the program MULTAN (*6*). Phases with a probability of being greater than 65% correct were used in the starting set. Using these four atoms for phasing, a least-squares refinement was run and the refined positions were used to calculate Fourier and difference Fourier maps. The difference Fourier map revealed peaks which were assigned to phosphorus and oxygen atoms.

A full-matrix least-squares refinement (*7*) using the positional parameters for these 15 atoms, a $1/\sigma^2$ weighting scheme, zero-valent scattering factors for Cu, P, and O (*8*), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion yielded a residual $R = 0.060$ and a weighted residual $R_w = 0.074$. The final anisotropic refinement, based on a data:parameter ratio of 13 with 138 independently varied parameters, yielded $R = 0.046$ and $R_w = 0.056$ (figure of merit, 1.331) for the observed data. The maximum extinction correction (*9*) was 2% of $|F_0|$ for the 210 reflection.

Table I presents the positional and anisotropic temperature parameters from the final anisotropic refinement.[1]

Results and Discussion

In the $Cu_4(PO_4)_2O$ structure there are four crystallographically distinct copper sites, two phosphorus sites, and nine oxygen sites. Cu(1) lies in a distorted octahedral environment showing the characteristic 4 + 2 axial lengthening of a divalent copper-containing polyhedron (*10*); four oxygens are at an average distance of 1.969 Å, two more at an average distance of 2.475 Å. Cu(3) and Cu(4) lie in square-pyramidal (4 + 1) sites; the averages of the four short bonds are 1.980 and 1.977 Å, respectively. Cu(2) lies in a distorted square-planar environment with an average Cu–O distance of 1.935 Å. The next-nearest oxygen atoms to Cu(2), Cu(3), and Cu(4) are at 2.978, 2.798, and 2.997 Å, respectively. We have not included these atoms in the primary coordination polyhedra of the copper atoms

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[1] A table of observed and calculated structure factors (10 pages) has been deposited as NAPS document No. 03231 for 10 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance for each NAPS accession number. Institutions and organizations may use purchase order when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the United States and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

TABLE 1

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS FOR $Cu_4(PO_4)_2O^a$

	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	6182(1)	5864(1)	9346(1)	0.92(4)	0.56(3)	1.11(3)	−0.31(2)	0.51(2)	−0.07(2)
Cu(2)	3314(1)	9384(1)	7841(1)	0.96(4)	0.41(3)	0.77(3)	0.00(2)	0.11(2)	0.18(2)
Cu(3)	8940(1)	7568(1)	8716(1)	0.86(4)	1.00(3)	0.89(3)	−0.33(2)	0.34(2)	0.90(2)
Cu(4)	8725(1)	7629(1)	3557(1)	1.40(4)	0.64(3)	1.20(4)	−0.29(2)	−0.50(2)	0.45(2)
P(1)	7363(2)	1498(2)	7790(2)	0.55(5)	0.40(5)	0.70(5)	0.05(4)	0.10(4)	0.18(4)
P(2)	7845(2)	4195(2)	4193(2)	0.46(5)	0.34(5)	0.75(5)	−0.02(4)	0.11(4)	0.14(4)
O(1)	9274(7)	1912(7)	8476(8)	0.61(20)	1.52(15)	1.18(17)	−0.04(14)	−0.01(15)	0.22(13)
O(2)	7013(7)	257(6)	8957(8)	1.83(20)	0.57(15)	1.18(17)	0.18(14)	0.46(15)	0.47(13)
O(3)	5845(6)	3330(6)	8467(8)	0.55(15)	0.42(14)	1.30(17)	0.11(12)	0.26(9)	0.24(12)
O(4)	2739(6)	9621(6)	4845(7)	1.25(18)	0.66(15)	0.67(15)	−0.08(13)	0.16(13)	0.04(12)
O(5)	7806(6)	5342(6)	6831(8)	0.95(17)	0.84(15)	0.90(16)	−0.17(13)	0.48(13)	−0.09(12)
O(6)	3768(6)	6730(6)	6703(8)	0.44(15)	0.44(14)	1.30(17)	0.07(12)	0.10(13)	0.16(12)
O(7)	7953(7)	5349(6)	2841(8)	1.22(18)	0.86(16)	1.33(18)	−0.42(14)	−0.11(13)	0.62(13)
O(8)	9677(6)	2612(6)	3778(7)	0.66(16)	0.69(17)	0.68(15)	0.08(12)	0.17(12)	0.16(12)
O(9)	2735(6)	2050(5)	9061(7)	0.62(15)	0.43(14)	0.89(15)	−0.12(12)	0.10(12)	0.18(12)

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

because (1) bond strength–bond length calculations (*11*) indicate that the valence requirements of the copper atoms are fully satisfied by the above polyhedra, (2) the geometry of the copper sites is supported by the polyhedral linkages in the structural model (see below), and (3) these longer Cu–O distances are greater than or approximately equal to the shortest Cu–Cu distances between these polyhedra: Cu(2)–Cu(3), 2.857 Å; and Cu(2)–Cu(4), 2.876 Å. Table II lists the bond angles and distances for these copper polyhedra. Standard deviations for all bond lengths and angles were computed by the function and error program ORFEE (*12*). The nature of these sites will be discussed more fully.

P(1) and particularly P(2) lie in rather distorted tetrahedral sites with average P–O distances of 1.542 (−0.013, +0.010) and 1.539 Å (−0.023, +0.040 Å), respectively. Table III presents the pertinent angles and distances for the phosphorus tetrahedra.

With the exception of O(9), which is bonded to four copper atoms in a distorted tetrahedral environment, each oxygen atom is considered bonded to two copper atoms and one phosphorus atom. Table IV gives the polyhedral environment about the oxygen atoms.

It is most convenient to discuss the structure of $Cu_4(PO_4)_2O$ in relation to planes of copper atoms which lie parallel to the $(1\bar{1}0)$ plane of the unit cell. The structure is derived from a cubic-close-packed (ccp) arrangement of oxygen atoms with one-tenth of the oxygen atoms missing. When viewed normal to $(1\bar{1}0)$, all oxygen layers are identical, each being crystallographically related by inversion centers which lie between the layers. Figure 1 shows an idealized plan of one layer of copper-containing polyhedra enclosed between two layers of close-packed oxygen atoms. The oxygen atoms necessary to complete an ideal ccp array are indicated by (o) and (+) for the lower and upper layers, respectively. Figure 1 also reveals how the Cu(3) and Cu(4) square-pyramidal polyhedra are derived from idealized octahedral sites by the removal of oxygen atoms. Figures 2a and b show the actual plans of the layers as taken from undistorted projections onto $(1\bar{1}0)$.

It can be seen from Figs. 1 and 2 that although each oxygen layer is identical, there

TABLE II

BOND DISTANCES, ANGLES, AND POLYHEDRAL EDGE LENGTHS FOR THE COPPER POLYHEDRA[a]

	Bond distance (Å)	Bond angle (°)	Edge length (Å)
(i) Cu(1) polyhedron			
Cu(1)–O(9)	1.191(4)		
Cu(1)–O(3)	1.979(4)		
Cu(1)–O(5)	1.980(4)		
Cu(1)–O(3′)	1.999(4)		
Cu(1)–O(6)	2.431(5)		
Cu(1)–O(7)	2.519(5)		
O(9)–Cu(1)–O(5)		83.5(2)	2.597(6)
O(9)–Cu(1)–O(3′)		97.0(2)	2.934(6)
O(9)–Cu(1)–O(6)		106.6(2)	3.501(6)
O(9)–Cu(1)–O(7)		74.1(2)	2.718(6)
O(3)–Cu(1)–O(5)		98.5(2)	3.009(6)
O(3)–Cu(1)–O(3′)		85.6(2)	2.703(8)
O(3)–Cu(1)–O(6)		96.1(2)	3.295(6)
O(3)–Cu(1)–O(7)		84.3(2)	3.045(6)
O(5)–Cu(1)–O(6)		83.1(2)	2.945(7)
O(5)–Cu(1)–O(7)		112.7(2)	3.756(6)
O(3′)–Cu(1)–O(6)		85.4(2)	3.022(6)
O(3′)–Cu(1)–O(7)		78.7(2)	2.892(7)
O(9)–Cu(1)–O(3)		157.3(2)	
O(5)–Cu(1)–O(3′)		168.1(2)	
O(6)–Cu(1)–O(7)		164.0(2)	
(ii) Cu(2) polyhedron			
Cu(2)–O(6)	1.920(4)		
Cu(2)–O(9)	1.924(4)		
Cu(2)–O(4)	1.941(4)		
Cu(2)–O(2)	1.955(5)		
O(6)–Cu(2)–O(9)		176.7(2)	3.842(6)
O(6)–Cu(2)–O(4)		97.2(2)	2.896(6)
O(6)–Cu(2)–O(2)		94.3(2)	2.842(6)
O(9)–Cu(2)–O(4)		84.1(2)	2.588(6)
O(9)–Cu(2)–O(2)		83.6(2)	2.585(6)
O(4)–Cu(2)–O(2)		158.9(2)	3.830(7)
(iii) Cu(3) polyhedron			
Cu(3)–O(9)	1.895(4)		
Cu(3)–O(8)	1.942(4)		
Cu(3)–O(1)	2.029(5)		
Cu(3)–O(5)	2.053(5)		
Cu(3)–O(2)	2.226(5)		
O(9)–Cu(3)–O(8)		170.9(2)	3.825(6)
O(9)–Cu(3)–O(1)		83.3(2)	2.609(6)
O(9)–Cu(3)–O(5)		82.2(2)	2.597(6)
O(9)–Cu(3)–O(2)		77.2(2)	2.585(6)
O(8)–Cu(3)–O(1)		103.8(2)	3.126(6)
O(8)–Cu(3)–O(5)		96.8(2)	2.988(6)
O(8)–Cu(3)–O(2)		94.9(2)	3.078(7)
O(1)–Cu(3)–O(5)		132.8(2)	3.740(7)
O(1)–Cu(3)–O(2)		107.5(2)	3.435(7)
O(5)–Cu(3)–O(2)		112.5(2)	3.559(6)

TABLE II—*continued*

	Bond distance (Å)	Bond angle (°)	Edge length (Å)
(iv) Cu(4) polyhedron			
Cu(4)–O(9)	1.907(4)		
Cu(4)–O(7)	1.949(4)		
Cu(4)–O(8)	1.957(4)		
Cu(4)–O(4)	2.093(4)		
Cu(4)–O(1)	2.302(5)		
O(9)–Cu(4)–O(7)		89.6(2)	2.717(6)
O(9)–Cu(4)–O(8)		176.4(2)	3.862(6)
O(9)–Cu(4)–O(4)		80.5(2)	2.588(6)
O(9)–Cu(4)–O(1)		76.0(2)	2.609(6)
O(7)–Cu(4)–O(8)		93.6(2)	2.848(6)
O(7)–Cu(4)–O(4)		129.0(2)	3.648(6)
O(7)–Cu(4)–O(1)		127.0(2)	3.807(7)
O(8)–Cu(4)–O(4)		98.7(2)	3.074(6)
O(8)–Cu(4)–O(1)		100.8(2)	3.288(7)
O(4)–Cu(4)–O(1)		99.0(2)	3.343(7)

[a] Numbers in parentheses are ESD's in the last significant figure.

TABLE III

BOND DISTANCES, BOND ANGLES, AND EDGE LENGTHS FOR THE PHOSPHATE TETRAHEDRA[a]

(i) Interatomic distances (Å)			
P(1)–O(1)	1.529(5)	P(2)–O(7)	1.516(5)
P(1)–O(4)	1.536(5)	P(2)–O(6)	1.523(5)
P(1)–O(3)	1.551(5)	P(2)–O(5)	1.540(5)
P(1)–O(2)	1.552(5)	P(2)–O(8)	1.578(5)
P(1) tetrahedron		P(2) tetrahedron	
O(1)–O(4)	2.492(7)	O(7)–O(5)	2.508(6)
O(1)–O(3)	2.526(7)	O(7)–O(5)	2.525(6)
O(1)–O(2)	2.551(7)	O(7)–O(8)	2.491(6)
O(4)–O(3)	2.542(6)	O(6)–O(5)	2.545(6)
O(4)–O(2)	2.463(6)	O(6)–O(8)	2.503(6)
O(3)–O(2)	2.532(6)	O(5)–O(8)	2.499(6)
(ii) Angles (°)			
O(1)–P(1)–O(4)	108.8(3)	O(7)–P(2)–O(6)	111.3(3)
O(1)–P(1)–O(3)	110.3(3)	O(7)–P(2)–O(5)	111.4(3)
O(1)–P(1)–O(2)	111.8(3)	O(7)–P(2)–O(8)	107.2(3)
O(4)–P(1)–O(3)	110.7(3)	O(6)–P(2)–O(5)	112.4(3)
O(4)–P(1)–O(2)	105.8(3)	O(6)–P(2)–O(8)	107.1(2)
O(4)–P(1)–O(2)	109.4(3)	O(5)–P(2)–O(8)	106.5(2)

[a] Numbers in parentheses are ESD's in the last significant figure.

TABLE IV

BOND DISTANCES AND BOND ANGLES FOR THE ANION POLYHEDRA[a]

Bond distance (Å)		Bond angle (°)	
(i) O(1) polyhedron			
O(1)–P(1)	1.529(5)	P(1)–O(1)–Cu(3)	139.6(3)
O(1)–Cu(3)	2.029(5)	P(1)–O(1)–Cu(4)	131.1(3)
O(1)–Cu(4)	2.302(5)	Cu(3)–O(1)–Cu(4)	89.1(2)
(ii) O(2) polyhedron			
O(2)–P(1)	1.552(5)	P(1)–O(2)–Cu(2)	134.3(3)
O(2)–Cu(2)	1.955(5)	P(1)–O(2)–Cu(3)	122.8(3)
O(2)–Cu(3)	2.226(5)	Cu(2)–O(2)–Cu(3)	86.0(2)
(iii) O(3) polyhedron			
O(3)–P(1)	1.551(5)	P(1)–O(3)–Cu(1)	127.1(3)
O(3)–Cu(1)	1.979(4)	P(1)–O(3)–Cu(1′)	127.2(3)
O(3)–Cu(1′)	1.999(4)	Cu(1)–O(3)–Cu(1′)	94.4(2)
(iv) O(4) polyhedron			
O(4)–P(1)	1.536(5)	P(1)–O(4)–CU(2)	143.2(3)
O(4)–Cu(2)	1.941(4)	P(1)–O(4)–Cu(4)	123.7(3)
O(4)–Cu(4)	2.093(4)	Cu(2)–O(4)–Cu(4)	90.9(2)
(v) O(5) polyhedron			
O(5)–P(2)	1.540(5)	P(2)–O(5)–Cu(1)	135.2(3)
O(5)–Cu(1)	1.981(4)	P(2)–O(5)–Cu(3)	128.6(3)
O(5)–Cu(3)	2.053(4)	Cu(1)–O(5)–CU(3)	93.5(2)
(vi) O(6) polyhedron			
O(6)–P(2)	1.523(5)	P(2)–O(6)–Cu(2)	119.5(3)
O(6)–Cu(2)	1.920(4)	P(2)–O(6)–Cu(1)	122.2(2)
O(6)–Cu(1)	2.431(5)	Cu(2)–O(6)–Cu(1)	104.3(2)
(vii) O(7) polyhedron			
O(7)–P(2)	1.516(5)	P(2)–O(7)–Cu(4)	135.6(3)
O(7)–Cu(4)	1.949(4)	P(2)–O(7)–Cu(1)	133.7(3)
O(7)–Cu(1)	2.518(5)	Cu(4)–O(7)–Cu(1)	87.3(2)
(viii) O(8) polyhedron			
O(8)–P(2)	1.578(3)	P(2)–O(8)–Cu(3)	112.1(2)
O(8)–Cu(3)	1.942(4)	P(2)–O(8)–Cu(4)	119.7(2)
O(8)–Cu(4)	1.957(4)	Cu(3)–O(8)–Cu(4)	112.3(2)
(ix) O(9) polyhedron			
O(9)–Cu(3)	1.895(4)	Cu(3)–O(9)–Cu(4)	106.5(2)
O(9)–Cu(4)	1.907(4)	Cu(3)–O(9)–Cu(1)	100.8(2)
O(9)–Cu(1)	1.919(4)	Cu(3)–O(9)–Cu(2)	96.9(2)
O(9)–Cu(2)	1.924(4)	Cu(4)–O(9)–Cu(1)	108.9(2)
		Cu(4)–O(9)–Cu(2)	97.3(2)
		Cu(1)–O(9)–Cu(2)	142.5(2)

[a] Numbers in parentheses are ESD's in the last significant figure.

are two distinct types of interstitial cation-containing layers. The layer shown in Figs. 1 and 2a (Type A) contains three of the four copper ions: Cu(1) in an octahedral site and Cu(3) and Cu(4) in square-pyramidal sites. These polyhedra are joined to form distorted ladder-like ribbons parallel to the *c*-axis, in which pairs of edge-sharing Cu(1) octahedra

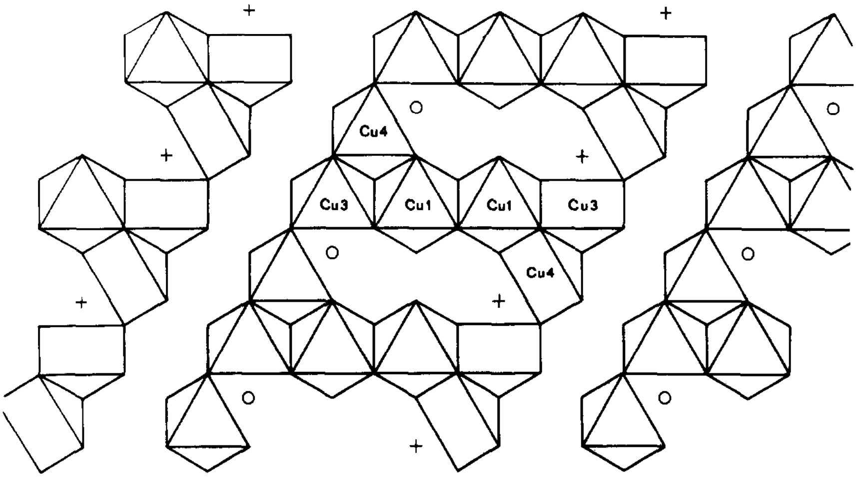

FIG. 1. Plan of the idealized Type A layer (see text). Two layers of close-packed oxygen atoms are shown. "Missing" oxygen atoms are indicated by O and + for the lower and upper layers, respectively. The origin of the square-pyramidal Cu(3) and Cu(4) sites from idealized octahedral sites is evident.

form the rungs, and chains of edge- and vertex-sharing Cu(3) and Cu(4) square pyramids form the sides, of the "ladders." There is a string of unfilled octahedral sites which runs between adjacent ribbons within this (Type A) layer. When viewed normal to $(1\bar{1}0)$, it can be seen that successive Type A layers are staggered and stacked like "English Bond" brickwork so that the ribbons of one layer fall over the gaps of the layers below (see Fig. 3).

The other layer (Type B), shown in Fig. 2b, contains the phosphorus atoms as well as the Cu(2) atom. P(1) tetrahedra serve to bridge the channels between adjacent ribbons while P(2) tetrahedra only serve as pillars joining successive Type A layers.

The Cu(2) site, which bridges successive Type A layers, is derived from four vertices of an octahedral site of the idealized ccp oxygen array in the following manner: Two adjacent corners of the possible Cu(2) octahedron are unavailable for its bonding needs; one vertex would be the anion which is missing from the ideal ccp array and the other would be an O(9) site which is already bonded to four other Cu atoms. The Cu(2) atom has moved out of the center of the idealized octahedral site, away from the "missing" octahedral edge into the center of the remaining four vertices which pull around it in a distorted square-planar arrangement. These Cu(2) sites form pairs of parallel rows in the C-direction separated by only one octahedral edge length, as can be seen in Fig. 3. Along these rows there are alternatively pairs of adjacent O(9) atoms and pairs of adjacent "holes" which lie between neighboring Cu(2) square-planar sites.

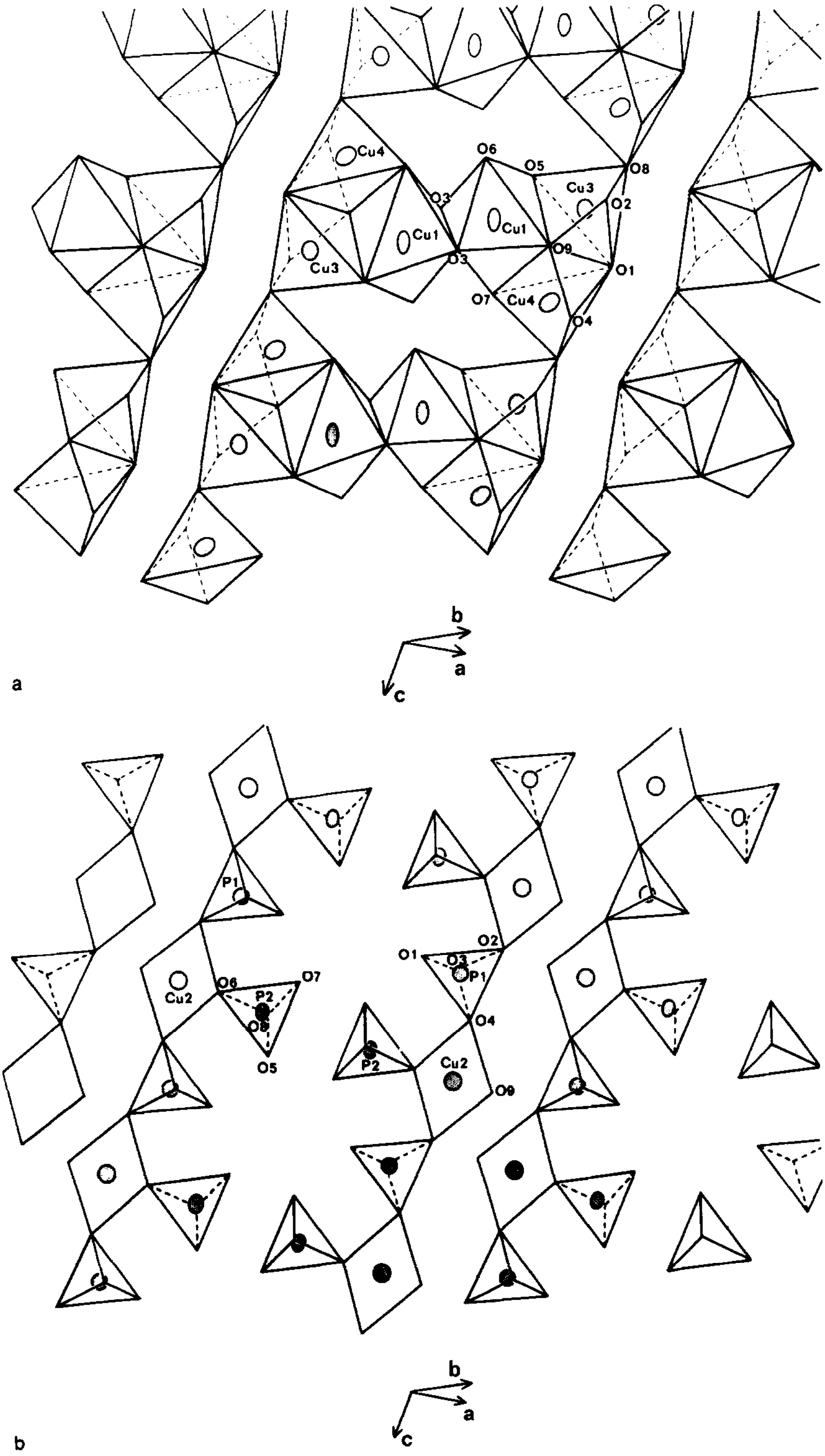

FIG. 2. A projection of the actual Type A and Type B layers, respectively, on (1$\bar{1}$0) (see text). The figures are drawn so that one (b) layer may be directly superimposed onto the other (a) to give the correct structural relationship.

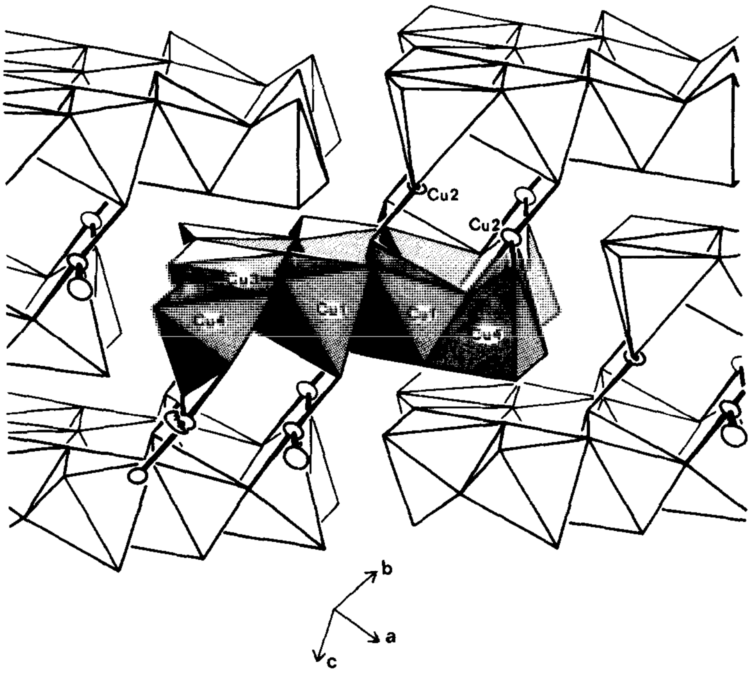

FIG. 3. View of the copper-containing polyhedral framework approximately parallel to *c*. Square-planar Cu(2) atoms which link the chains formed by Cu(1)-, Cu(3)-, and Cu(4)-containing polyhedra are drawn.

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