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Cation Distribution in the $(Mg_{1-x}Cu_x)_3(PO_4)_2$ Solid Solution, $x = 0.46$ and 0.79[1]

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Cation distributions in two related structures, $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$(I) and $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$(II) belonging to the system $Mg_3(PO_4)_2$–$Cu_3(PO_4)_2$ have been determined by single-crystal X-ray diffraction. $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ I is isotypic with $Mg(PO_4)_2$: $a = 7.608(3)$, $b = 8.026(5)$, $c = 5.116(3)$Å, $\beta = 92.73(4)°$, monoclinic, $P2_1/n$, $V = 312.0(3)$Å^3, $Z = 2$, $D_{calc} = 3.374$ g cm^{-3}, $R = 5.8\%$ for 549 observed reflections. $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ II, is isotypic with $Cu_3(PO_4)_2$, $a = 4.845(3)$, $b = 5.265(3)$ $c = 6.246(2)$Å, $\alpha = 71.98(4)$, $\beta = 93.04(4)$, $\gamma = 111.42(4)°$, triclinic, $P1$ bar, $V = 140.7(1)$Å^3, $Z = 1$, $D_{calc} = 4.198$ g cm^{-3}, $R = 8.5\%$ for 645 observed reflections. Both structures show mixed Mg/Cu trigonal bipyramidal sites (31% Mg^{2+}/69%Cu^{2+}). In I, additional positions of octahedral symmetry are occupied uniquely by Mg^{2+} ions. In II, square planar sites contain only Cu^{2+} ions.

INTRODUCTION

The distribution of bivalent cations Me^{2+} (Me^{2+} = Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd) between five-coordinate (trigonal bipyramidal) and six-coordinate (octahedral) sites in orthophosphates has been the focus of recent research (1–4). The apportionment of ions between the two environments in a structure depends generally upon the nature of the element and its ability to adopt a deformed coordination geometry.

The substitution for Mg^{2+} ions of the cations Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} in the orthophosphate $Mg_3(PO_4)_2$, as studied by Nord *et al.*, shows a preference for substitution in the site of five-coordination following the order $Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$ (1, 2, 5, 6). Distribution of the ions Mg^{2+}, Fe^{2+}, Mn^{2+}, and Zn^{2+} in the compounds $(Mg_{0.5}Fe_{0.5})_3(PO_4)_2$, $(Mg_{2/3}Mn_{1/3})_3(PO_4)_2$, and $(Zn_{2/3}Mg_{1/3})_3(PO_4)_2$ has been determined for powder samples using the Rietveld method. The increase in the intensities of certain peaks in the electronic reflectance spectra of the solid solution $(Mg_{1-x}Co_x)_3(PO_4)_2$ has been correlated with the presence of increased amounts of Co^{2+} in the trigonal bipyramidal sites of five-coordination (7).

The maximum molar solubility of Cu^{2+} observed by Nord *et al.* in the structure of $Mg_3(PO_4)_2$ was 15% at 1070 K (2). The probability of finding Cu^{2+} preferably in the more distorted site (five-coordination) has been suggested by these authors; however, no proof of this hypothesis has been shown.

In a previous article (8), we have shown that the solid solution $(Mg_{1-x}Cu_x)_3(PO_4)_2$ is more extended than observed by Nord *et al.* We have studied the solubility of Mg^{2+} in $Cu_3(PO_4)_2$ in the range $0.77 \le x \le 1$ (9). The structure of $Cu_3(PO_4)_2$ (Shoemaker *et al.* (10)) has Cu^{2+} in positions of square planar or trigonal bipyramidal coordination. We report here single crystal structures of $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ **I**, $x = 0.46$, isotypic with $Mg_3(PO_4)_2$, and $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ **II**, $x = 0.79$, isotypic with $Cu_3(PO_4)_2$, which permits determination of the distribution of Mg^{2+} and Cu^{2+} in the metallic sites of the two orthophosphates.

EXPERIMENTAL

Sample Preparation

The preparation of powder samples of the solid solution $(Mg_{1-x}Cu_x)_3(PO_4)_2$ has been previously reported (8). Single crystals of **I** and **II** have been prepared by heating to fusion a powder sample corresponding to $x = 0.5$ in the following manner. The temperature of a mixture of the starting materials (99% purity) MgO, CuO, and $(NH_4)_2HPO_4$ corresponding to $x = 0.5$ was raised slowly

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TABLE 1
Crystal Data

	$(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ **I**	$(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ **II**
Empirical formula	$Mg_{1.62}Cu_{1.38}(PO_4)_2$	$Mg_{0.21}Cu_{0.79})_3(PO_4)_2$
Formula weight	317.01	355.86
Crystal color	pale green	blue
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P1$ bar
Lattice parameters		
a	7.608(3)Å	4.845(3)Å
b	8.026(5)	5.265(3)
c	5.116(3)	6.246(2)
α	90.0°	71.98(4)°
β	92.73(4)	93.04(4)
γ	90.0	111.42(4)
V	312.0(3)Å^3	140.7(1)Å^3
Z	2	1
D_{calc}	3.374 g cm−3	4.198 g cm^{-3}
$F(000)$	306	169
μMo$K\alpha$	54.46 cm^{-1}	95.86 cm^{-1}
Diffractometer	Syntex–Nicolet P3	Syntex–Nicolet P3
Radiation	Mo$K\alpha$(λ = 0.71069Å)	Mo$K\alpha$(λ = 0.71069Å)
Temperature	29° C	29° C
Scan type	θ–2θ	θ–2θ
Octants meas.	$\pm h, k, l$	$\pm h, k, \pm l$
No. independ. reflns. meas.	1717	1731
No. obs. reflns.	549	645
No. variables	62	62
R/R_w	5.8/7.5%	8.5%
G.O.F.	0.64	0.77
Max. peak in final diff. map	3.19 e^-/Å^3	2.87 e^-/Å^3

to 1173 K in a platinum crucible. The mixture was maintained at this temperature for 48 hr. The reaction product was then heated to fusion (1473 K). The resulting liquid was cooled slowly to 873 K (5 K per hr), whereupon heating was discontinued. The crystalline product contained two different crystalline forms recognizable by their color (pale green or blue). A selection of pale green crystals was ground to give a powder spectrum which resembled that of $Mg_3(PO_4)_2$; that of the blue material (alone) was similar to the spectrum of $Cu_3(PO_4)_2$.

Crystallographic Studies

Crystals of **I** and **II** (dimensions 0.12 × 0.10 × 0.10 mm, pale green color, **I**; 0.11 × 0.11 × 0.11 mm, blue color, **II**) were mounted on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least-squares refinement of angular positions for 15 independent reflections ($2\theta > 15°$) (Table 1) during normal alignment procedures. Data (1717, (**I**) and 1731, (**II**) independent points after removal of forbidden space group, **I**, and of redundant data, **I** and **II**) were collected at room temperature using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ to 1.2° above $K\alpha_2$ with a maximum 2θ value of 60°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz and polarization effects. Observed reflections (549 (**I**) and 645 (**II**) points, $I > 3.0\sigma(I)$) were used for solution and refinement. Direct methods (MULTAN (11)) permitted location of the heavy atom positions. A cycle of least-squares refinement followed by a difference Fourier synthesis allowed location of the PO_4^{3-}groups. Distribution of Cu^{2+} and Mg^{2+} in heavy atom positions was determined by placing a Cu^{2+} and a Mg^{2+} atom in each metal site and constraining their positional and thermal parameters to remain identical for the atoms in each site. Population parameters were constrained to total 1 for each site. Refinement (XRAY (12)) of scale factor, positional, and isotropic thermal parameters was carried out to convergence (function minimized, $\Sigma w(|F_o|-|F_c|)^2$) leading to a final agreement factor ($R = (\Sigma w|\,|F_o| - |F_c|\,|/\Sigma w|F_o|) \times 100$). For both structures, scattering factors were taken from Cromer and Mann (13).

TABLE 2
Positional Parameters for $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ I

Atom	X(Sig(X))	Y(Sig(Y))	Z(Sig(Z))
Mg1	0.0000	0.0000	0.0000
Mg2	0.3862	0.1407	0.3870
Cu2	0.3862(2)	0.1407(2)	0.3870(3)
P1	0.3034(3)	0.3032(3)	−0.0360(4)
O1	0.4400(8)	0.3483(8)	0.1865(12)
O2	0.1503(8)	0.4278(8)	−0.0411(12)
O3	0.2394(8)	0.1296(8)	0.0503(12)
O4	0.3846(8)	0.3026(9)	−0.3005(12)

Anomalous dispersion corrections were made for Cu and Mg (*International Tables for X-Ray Crystallography* (14)). In the final stages of refinement a weight of $1/\sigma(F)^2$ was used. R/R_w = 5.8/7.5%, **I**; 8.5/10.7%, **II**.

DISCUSSION

Positional parameters for **I** and **II** are given in Tables 2 and 3 respectively. Bond angles and distances are listed in Tables 4 and 5.

Refinement of occupancy factors for the single crystal structures **I** and **II** has determined their compositions to be $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ **I** and $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ **II**, corresponding to x = 0.46 and x = 0.79 in the solid solution $(Mg_{1-x}Cu_x)_3(PO_4)_2$. These two compositions belong to two different domains, $0 \leq x \leq 0.46$ (isotypic with $Mg_3(PO_4)_2$) and $0.79 \leq x \leq 1$ (isotypic with $Cu_3(PO_4)_2$(9)).

In the structure of $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ **I**, special positions (0 0 0 and 0.5 0.5 0.5, 1 bar symmetry) of the space group $P2_1/n$ are occupied solely by Mg^{2+} ions. A general position is occupied by Mg^{2+} and Cu^{2+} ions in the ratio Mg/Cu: 0.62/1.38 or 31% Mg^{2+} and 69% Cu^{2+}. Thus, copper occupies only mixed sites.

Mg^{2+} ions located on inversion centers show regular octahedral geometry with Mg–O: 2.048(6)–2.103(6)Å. In the mixed sites, Mg/Cu displays distorted trigonal bipyramidal geometry with Mg/Cu–O: 1.908(7)–2.099(6)Å. Thus in the domain $0 \leq x \leq 0.46$ (isotypic with $Mg_3(PO_4)_2$), Cu^{2+} ions substitute preferentially into the sites of deformed trigonal bipyramidal geometry.

TABLE 3
Positional Parameters for $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ II

Atom	X(Sig(X))	Y(Sig(Y))	Z(Sig(Z))
Cu1	0.0000	0.0000	0.0000
Cu2	0.2805(3)	−0.2296(3)	0.6866(2)
Mg2	0.2805	−0.2296	0.6866
P1	0.3592(4)	0.6463(4)	0.2225(3)
O1	0.6707(11)	0.6492(11)	0.1715(9)
O2	0.3846(12)	0.8452(12)	0.3684(9)
O3	0.1527(13)	0.3422(14)	0.3390(10)
O4	0.2312(12)	0.7745(11)	−0.0027(9)

TABLE 4
Bond Angles (°) and Distances (Å) for $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ I

Mg1–O3	2.103(6)	O3–Mg1–O3′	180.0
Mg2–O3′	2.103(6)	O3–Mg1–O4″	87.0(2)
Mg2–O4″	2.099(7)	O3–Mg1–O4^{iii}	93.0(2)
Mg2–O4^{iii}	2.099(7)	O3–Mg1–O1^{iv}	87.8(2)
Mg2–O1^{iv}	2.048(6)	O3–Mg1–O1^{v}	92.2(2)
Mg2–O1^{v}	2.048(6)	O3′–Mg1–O4″	93.0(2)
$Mg_{0.31}Cu_{0.69}$–O1	2.009(7)	O3′–Mg1–O4^{iii}	87.0(2)
$Mg_{0.31}Cu_{0.69}$–O3	2.010(6)	O3′–Mg1–O1^{iv}	92.2(2)
$Mg_{0.31}Cu_{0.69}$–O4^{vi}	2.061(7)	O3′–Mg1–O1^{v}	87.8(2)
$Mg_{0.31}Cu_{0.69}$–O2^{vii}	2.099(6)	O4″–Mg1–O4^{iii}	87.0(2)
$Mg_{0.31}Cu_{0.69}$–O2^{v}	1.908(7)	O4″–Mg1–O1^{iv}	81.3(2)
P1–O1	1.548(6)	O4″–Mg1–O1^{v}	98.7(2)
P1–O2	1.534(7)	O4^{iii}–Mg1–O1^{iv}	98.7(2)
P1–O3	1.548(7)	O4^{iii}–Mg1–O1^{v}	81.3(2)
P1–O4	1.514(6)	O1^{iv}–Mg1–O1^{v}	180.0
		O1–$Mg_{0.31}Cu_{0.69}$–O3	73.6(2)
		O1–$Mg_{0.31}Cu_{0.69}$–O4^{vi}	83.2(3)
		O1–$Mg_{0.31}Cu_{0.69}$–O2^{vii}	95.2(2)
		O1–$Mg_{0.31}Cu_{0.69}$–O2^{v}	172.4(3)
		O3–$Mg_{0.31}Cu_{0.69}$–O4^{vi}	132.0(2)
		O3–$Mg_{0.31}Cu_{0.69}$–O2^{vii}	128.8(2)
		O3–$Mg_{0.31}Cu_{0.69}$–O2^{v}	103.2(2)
		O4^{vi}–$Mg_{0.31}Cu_{0.69}$–O2^{vii}	94.0(2)
		O4^{vi}–$Mg_{0.31}Cu_{0.69}$–O2^{v}	103.8(3)
		O2^{vii}–$Mg_{0.31}Cu_{0.69}$–O2^{v}	81.4(2)
		O1–P1–O2	110.1(4)
		O1–P1–O3	102.1(3)
		O1–P1–O4	111.7(4)
		O2–P1–O3	110.0(3)
		O2–P1–O4	109.2(4)
		O3–P1–O4	113.5(4)

Note. ′ = −x, −y, −z; ″ = −0.5 + x, 0.5 − y, 0.5 + z; iii = 0.5 − x, −0.5 + y, −0.5 − z; iv = −0.5 + x, 0.5 − y, −0.5 + z; v = 0.5 − x, −0.5 + y, 0.5 − z; vi = x, y, 1 + z; vii = 0.5 + x, 0.5 − y, 0.5 + x.

In $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ **II**, sites of square pyramidal geometry (located on a center of symmetry) are occupied only by Cu^{2+} ions (Cu–O: 1.910(7)–1.977(4)Å). Mg^{2+} and Cu^{2+} ions occupy a second position of trigonal bipyramidal geometry with 31% Mg^{2+} and 69% Cu^{2+} occupancy (Mg/Cu: 0.63/1.37; Mg/Cu–O: 1.958(6)–2.207(6)Å).

Mg-O distances in **I** and **II** ($Mg_{octahedral}$–O av. 2.083(6); $Mg_{trigonal\ bipyramidal}$–O av. 2.017(7) **I**; $Mg_{trigonal\ bipyramidal}$–O av. 2.027(6)Å **II**) are similar to the values observed in $Mg_3(PO_4)_2$ ($Mg_{octahedral}$–O av. 2.121(6); $Mg_{trigonal\ bipyramidal}$–O av. 2.029(7)).

Cu–O values in **I**, $Cu_{trigonal\ bipyramidal}$–O, av. 2.017(7), **II** $Cu_{trigonal\ bipyramidal}$–O, av. 2.027(6), and $Cu_{square\ planar}$–O), av. 1.941(6)Å are similar to those observed in $Cu_3(PO_4)_2$ ($Cu_{trigonal\ bipyramidal}$–O, av. 2.025, and $Cu_{square\ planar}$–O, av. 1.953Å).

The ionic radii of Mg^{2+} and Cu^{2+}, when six-coordinate,

TABLE 5
Bond Angles(°) and Distances(Å) for $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ II

Cu1–O4′	1.910(7)	O4′–Cu1–O1″	90.0(2)
Cu1–O1″	1.977(4)	O4′–Cu1–O1^{iii}	90.0(2)
Cu1–O1^{iii}	1.977(4)	O4′–Cu1–O4^{iv}	180.0(6)
Cu1–O4^{iv}	1.910(7)	O1″–Cu1–O1^{iii}	180.0(5)
$Mg_{0.313}Cu_{0.686}$–O4^{v}	1.976(6)	O1″–Cu1–O4^{iv}	90.0(2)
$Mg_{0.313}Cu_{0.686}$–O2′	1.958(6)	O1^{iii}–Cu1–O4^{iv}	90.0(2)
$Mg_{0.313}Cu_{0.686}$–O2^{vi}	2.019(5)	O4^{v}–$Mg_{0.313}Cu_{0.686}$–O2′	168.6(3)
$Mg_{0.313}Cu_{0.686}$–O1^{vii}	2.207(6)	O4^{v}–$Mg_{0.313}Cu_{0.686}$–O2^{vi}	87.2(2)
$Mg_{0.313}Cu_{0.686}$–O3^{viii}	1.974(6)	O4^{v}–$Mg_{0.313}Cu_{0.686}$–O1^{vii}	88.8(2)
P1–O1	1.552(6)	O4^{v}–$Mg_{0.313}Cu_{0.686}$–O3^{viii}	90.0(2)
P1–O2	1.558(7)	O2′–$Mg_{0.313}Cu_{0.686}$–O2^{vi}	81.5(2)
P1–O3	1.510(6)	O2′–$Mg_{0.313}Cu_{0.686}$–O1^{vii}	98.9(3)
P1–O4	1.564(6)	O2′–$Mg_{0.313}Cu_{0.686}$–O3^{viii}	96.5(2)
		O2^{vi}–$Mg_{0.313}Cu_{0.686}$–O1^{vii}	124.8(2)
		O2^{vi}–$Mg_{0.313}Cu_{0.686}$–O3^{viii}	132.8(3)
		O1^{vii}–$Mg_{0.313}Cu_{0.686}$–O3^{viii}	102.2(2)
		O1–P1–O2	110.2(3)
		O1–P1–O3	109.8(4)
		O1–P1–O4	109.7(4)
		O2–P1–O3	111.3(3)
		O2–P1–O4	106.0(3)
		O3–P1–O4	109.8(3)

Note. ′ = $x, -1 + y, z$; ″ = $-1 + x, -1 + y, z$; iii = $1 - x, 1 - y, -z$; iv = $-x, 1 - y, -z$; v = $x, -1 + y, 1 + z$; vi = $1 - x, 1 - y, 1 - z$; vii = $1 - y, -y, 1 - z$; viii = $-x, -y, 1 - z$.

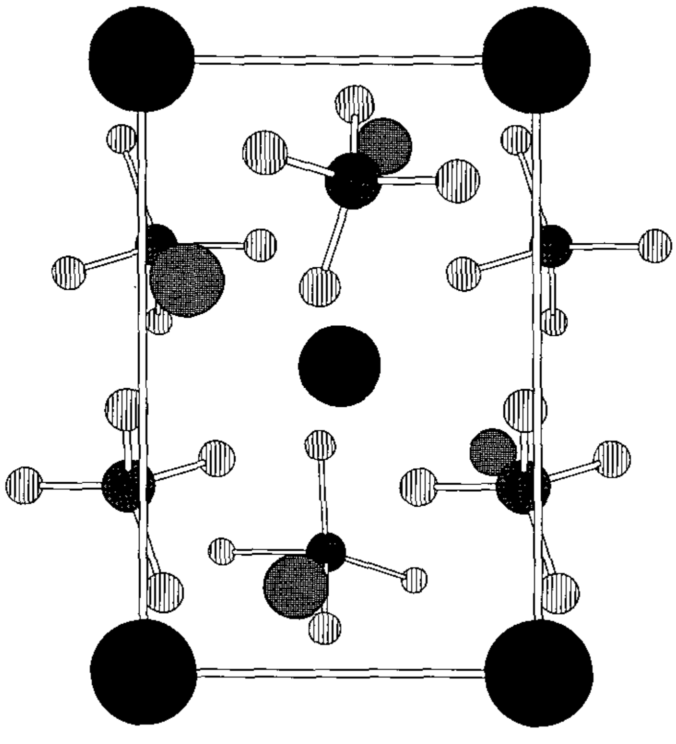

FIG. 1. Projection view of $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ **I** on the 1 0 1 plane.

have been estimated to be 0.72 and 0.73Å, respectively. Values for five-coordinate Mg^{2+} are 0.66: five coordinate copper (geometry unspecified), 0.65Å; and square planar Cu^{2+}, 0.57Å (Shannon (15)). Thus, the two metals are similar in size and their ability to share a site is not remarkable. However, the observation that occupancy of mixed sites Mg/Cu of deformed trigonal bipyramidal geometry is identical in the two structures is unexpected.

The structures of the two compounds are shown in Figs. 1 and 2, respectively.

CONCLUSION

A single crystal study of $(Mg_{0.54}Cu_{0.46})_3(PO_4)_2$ **I** corresponding to $x = 0.46$ in the solid solution $(Mg_{1-x}Cu_x)_3(PO_4)_2$ shows that substitution of Cu for Mg in the solid isotypic with $Mg_3(PO_4)_2$ proceeds preferentially in the site of deformed trigonal bipyramidal geometry. Octahedral sites of $Mg_3(PO_4)_2$ remain occupied only by Mg^{2+} ions.

In $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ **II** corresponding to $x = 0.79$ in the solid solution, $(Mg_{1-x}Cu_x)_3(PO_4)_2$, of the domain $0.79 \leq x \leq 1$ (isotypic with $Cu_3(PO_4)_2$), substitution of Mg^{2+} for Cu^{2+} proceeds in sites of trigonal bipyramidal geometry. Sites of square planar geometry remain occupied by Cu^{2+} ions alone.

The mixed occupancy sites of **I** and **II** show identical Mg^{2+}/Cu^{2+} occupancies: 31%/69%.

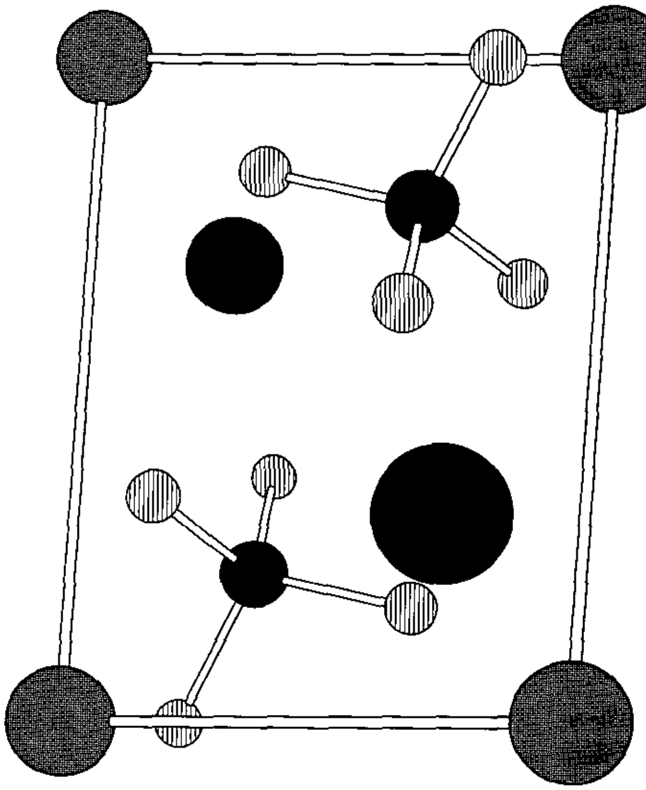

FIG. 2. Projection of $(Mg_{0.21}Cu_{0.79})_3(PO_4)_2$ **II** on the 0 1 1 plane.

Substitution of Cu for Mg in $Mg_3(PO_4)_2$ and of Mg for Cu in $Cu_3(PO_4)_2$, both of which present a choice of substitution site, appears dominated by the preference of Mg for a site of octahedral or near octahedral coordination.

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