Acta Cryst. (1963). **16**, 124

The Crystal Structure of Pseudomalachite, $Cu_5(PO_4)_2(OH)_4$

BY SUBRATA GHOSE*

Crystallography Laboratory, University of Pittsburgh, Pittsburgh, Pennsylvania, U.S.A.

(*Received* 28 *February* 1962)

Pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ is monoclinic, space group $P2_1/c$, with

$$a_0 = 4{\cdot}47,\ b_0 = 5{\cdot}75,\ c_0 = 17{\cdot}08\ \text{Å};\ \beta = 91°\ 07'.$$

The structure has been determined from sharpened Patterson projections on (100) and (010) and refined by Fourier and difference Fourier syntheses. In the structure there are two types of parallel infinite octahedral chains, the first composed of one $Cu(OH)_2O_4$ and two $Cu(OH)_3O_3$ octahedra, sharing four and three edges respectively and the second of $Cu(OH)_2O_4$ octahedra sharing opposite square edges. These chains alternate, sharing edges, to form a set of infinite parallel sheets, held together by tetrahedral PO_4 groups.

Introduction

From studies of basic copper compounds it is known that the building block of such structures is usually the distorted copper co-ordination octahedron. In these structures the copper octahedra either occur as discrete units, or more commonly share corners or edges to form different types of chains, sheets or three-dimensional networks. The structure of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ has been determined, in order to gain some knowledge about the structural principles of the basic copper phosphates and arsenates, several of which are known as minerals.

Pseudomalachite is a fairly common secondary mineral, found in the oxidized zone of copper deposits. Berry (1950) determined the space group and cell dimensions; he also summarized and added to the optical, X-ray and chemical data on this mineral from various localities. Guillemin (1956) synthesized this mineral by the action of phosphoric acid on malachite, $Cu_2(OH)_2CO_3$. The specimen used for the present structure determination came from Virneberg, Linz, Germany (U.S.N.M. Cat. no. R5381).

Experimental

Pseudomalachite is monoclinic, crystal class $2/m$. The cell dimensions, determined by Berry (1950) for this specimen from precession photographs about a and b with Mo $K\alpha$ and Cu $K\alpha$ radiation, are:

$a_0 = 4{\cdot}47,\ b_0 = 5{\cdot}75,\ c_0 = 17{\cdot}08$ Å; $\beta = 91°\ 07'$.
Space group $P2_1/c$.
$D_{meas.} \sim 4{\cdot}3$ g.cm^{-3} and $D_{calc.} = 4{\cdot}34$ g.cm^{-3}.
Two formula units per cell.

The intensities of $0kl$, $h0l$ and $h1l$ reflections have been visually estimated from multiple-film Weissenberg photographs, taken with Cu $K\alpha$ radiation. The intensities have been corrected for Lorentz and polarization factors, but no absorption corrections have been made. The observed structure factors have been put on an absolute basis in the course of the structure determination. All the calculations have been carried out on the IBM 650 computer, using Shiono's programs (1957, 1959).

Determination of the structure

The structure determination was started with the sharpened Patterson projection on (100), since a is the shortest axis. The unit cell contains 10 Cu, 4 P, 16 O and 8 (OH) ions. Two of the ten copper atoms must be on a two-fold special position. They were arbitrarily placed at $2(a)$; 0, 0, 0 and 0, $\frac{1}{2}$, $\frac{1}{2}$. The Patterson map, therefore, should contain peaks at locations of atoms in the structure. However, the Patterson map contained many strong peaks of about equal height and the structure was not immediately obvious. From the consideration of the Patterson peaks occuring on $v = \frac{1}{2}$ and $w = \frac{1}{2}$, the other two copper atoms were located at $y = \frac{1}{2}$, $z = 0{\cdot}09$ and $y = 0{\cdot}34$, $z = \frac{1}{4}$. The $0kl$ structure factors, calculated with the contribution from the copper atoms only, yielded an R factor of 0·45. Successive Fourier and difference Fourier syntheses brought out the phosphorus and

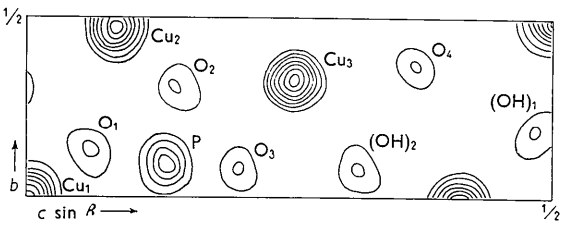

Fig. 1. Electron density projection of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ on (100). Contour intervals 4 e.Å^{-2}.

* Present address: Mineralogical Institute, University of Bern, Sahlistrasse 6, Bern, Switzerland.

Table 1. *Atomic parameters of pseudomalachite,* $Cu_5(PO_4)_2(OH)_4$.

	x	y	z
Cu_1	0	0	0
Cu_2	0·048	0·472	0·0853
Cu_3	−0·014	0·329	0·2570
P	0·518	0·094	0·135
$(OH)_1$	0·182	0·318	−0·014
$(OH)_2$	0·152	0·069	0·317
O_1	0·710	0·155	0·064
O_2	0·320	0·307	0·153
O_3	0·753	0·076	0·204
O_4	0·335	−0·132	0·125

the oxygen atoms. The (100) projection was refined by difference Fourier syntheses till the R factor decreased to 0·12. The final electron-density projection of the structure on (100) is shown in Fig. 1.

A model of the structure was set up next on the basis of the atomic parameters obtained from the (100) projection. The x parameters were estimated from this model, assuming square planar Cu–O (or OH) distances to be 2·00 Å, non-square planar Cu–O distances to be 2·4–2·6 Å and P–O distances to be 1·54 Å. The x parameters of the copper and the phosphorus atoms were confirmed from a sharpened Patterson projection on (010). The R factor for the $h0l$ structure factors, calculated on the basis of these x parameters, was 0.35. The (010) projection was refined also with difference Fourier syntheses. The R factor for $h0l$ reflexions after correcting four strong low-angle reflexions for extinction (Pinnock, Taylor & Lipson, 1956) is 0·15. The R factor for the hll reflexions, calculated with the final parameters, is 0·19. For the structure-factor calculations, the following scattering curves were used: Cu and P, Viervoll & Øgrim (1949) and O, Berghuis *et al.* (1955). The scattering curves were modified by the following isotropic temperature factors: 0·50 Å^2 for Cu and O and 0·15 Å^2 for P. The observed and calculated $0kl$ and $h0l$ structure factors are listed in Table 2. Table 1 lists the final atomic parameters.

Description of the structure

The structure of pseudomalachite is composed of linked distorted co-ordination octahedra around Cu_1, Cu_2 and Cu_3 and discrete tetrahedral phosphate groups. Projections of the structure on (100) and (010) are shown in Figs. 2 and 3 respectively. The interatomic distances and angles are listed in Table 3. The estimated standard errors of bond distances are: Cu–O and P–O ±0·05 Å and O–O ±0.07 Å.

The phosphate group is quite regular, with an average P–O distance of 1·54$_5$ Å. This distance is comparable to the average P–O distance of 1·54 Å in $LiMnPO_4$ (Geller & Durand, 1960). The average O–P–O angle is 109·2° and the average O–O distance is 2.52 Å.

The co-ordination around Cu_1 is 4+(2). Two oxygen and two (OH) ions form a square plane around Cu_1 (Cu_1–$(OH)_1$ 2·02 Å (×2) and Cu_1–O_1 1·94 Å (×2)) with two further oxygens (Cu_1–O_4 2.69 Å (×2)) completing a distorted octahedron. This is comparable to the dimensions of the Cu_1 octahedron in malachite, $Cu_2(OH)_2CO_3$ (Wells, 1951), and the Cu octahedron in salesite, $CuIO_3(OH)$ (Ghose, 1962).

The co-ordination around Cu_2 is 4+1+(1). One oxygen and three (OH) ions form a square array around Cu_2 (Cu_2–$(OH)_1$ 2·02 Å, Cu_2–$(OH)_1'$ 1·98 Å,

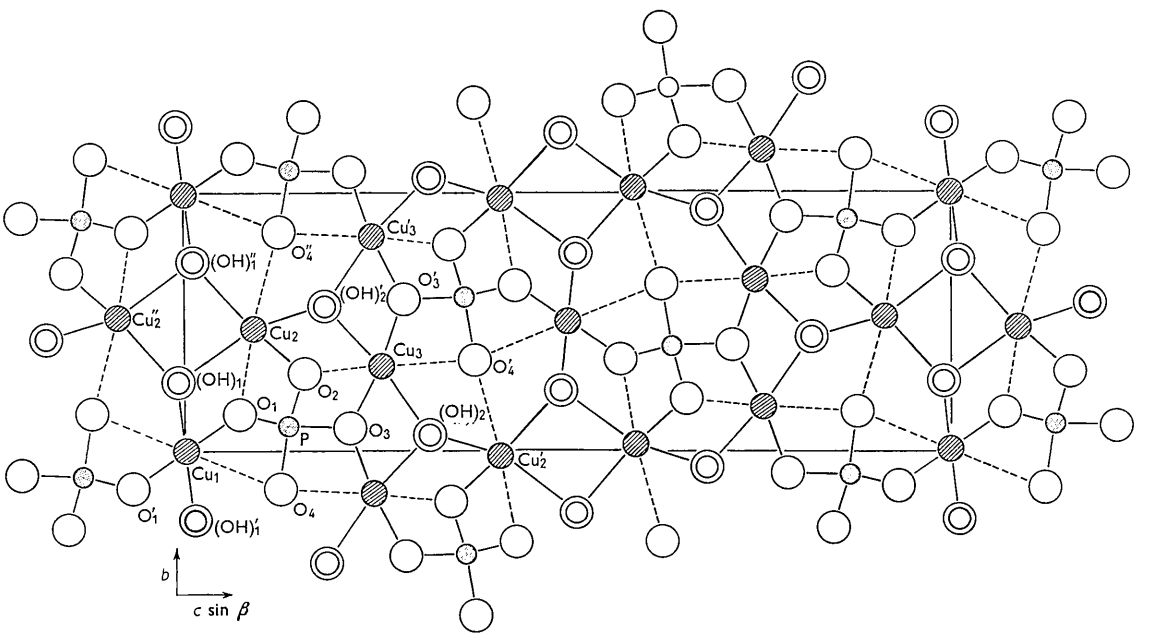

Fig. 2. Projection of the structure of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ on (100).

Table 2. *Observed and calculated structure factors of pseudomalachite,* $Cu_5(PO_4)_2(OH)_2$

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
0 0 2	0	13·4	0 4 1	91·6	−85·7	2 0 8	171·2	178·0
0 0 4	26·6	27·4	0 4 2	82·7	80·6	2 0 10	7·7	15·2
0 0 6	65·8	−72·2	0 4 3	77·3	105·0	2 0 12	121·1	140·7
0 0 8	100·3	106·6	0 4 4	12·0	13·9	2 0 14	28·4	−23·2
0 0 10	0	7·8	0 4 5	15·9	10·0	2 0 16	25·1	26·7
0 0 12	128·9	129·3	0 4 6	7·9	3·1	2 0 18	74·9	−54·0
0 0 14	51·0	47·4	0 4 7	28·5	23·3	2 0 20	53·7	59·6
0 0 16	60·1	61·1	0 4 8	27·5	−28·9	3 0 2	70·2	−58·0
0 0 18	78·7	−75·6	0 4 9	83·0	−87·6	3 0 4	26·1	25·3
0 0 20	17·3	23·5	0 4 10	82·5	77·6	3 0 6	132·2	−112·2
0 1 1	5·1	1·8	0 4 11	30·1	27·4	3 0 8	114·7	117·7
0 1 2	54·6	−52·5	0 4 12	65·6	60·3	3 0 10	21·8	26·0
0 1 3	8·8	10·4	0 4 13	11·3	5·4	3 0 12	97·4	115·5
0 1 4	23·5	−20·6	0 4 14	25·3	24·1	3 0 14	70·9	−50·9
0 1 5	80·8	103·4	0 4 15	46·3	55·0	4 0 2	110·1	−78·2
0 1 6	33·8	29·7	0 4 16	32·3	−34·5	4 0 4	40·8	42·2
0 1 7	91·9	102·6	0 4 17	22·5	−25·1	4 0 6	29·1	−19·4
0 1 8	17·8	−15·7	0 4 18	8·5	15·0	4 0 8	101·9	112·2
0 1 9	69·6	63·2	0 5 1	37·2	−35·2	4 0 10	15·6	−4·1
0 1 10	44·7	49·3	0 5 2	38·4	−42·2	4 0 12	54·6	57·4
0 1 11	106·8	−88·9	0 5 3	46·9	51·0	4 0 14	33·2	−21·3
0 1 12	26·4	15·2	0 5 4	15·0	−20·0	5 0 2	17·7	−18·8
0 1 13	5·6	−9·3	0 5 5	61·4	62·4	5 0 4	56·7	55·8
0 1 14	42·1	29·7	0 5 6	0	4·7	5 0 6	58·2	−37·7
0 1 15	68·4	65·2	0 5 7	0	10·0	5 0 8	112·2	105·4
0 1 16	52·3	−47·5	0 5 8	43·0	45·8	5 0 10	61·5	54·5
0 1 17	74·1	64·9	0 5 9	11·4	13·2	−1 0 2	17·2	13·6
0 1 18	49·1	39·9	0 5 10	14·1	−13·9	−1 0 4*	191·6	188·7
0 2 0	84·4	86·0	0 5 11	16·7	14·5	−1 0 6*	200·5	−213·7
0 2 1	47·3	51·9	0 5 12	9·3	3·0	−1 0 8	33·2	36·8
0 2 2	86·1	101·4	0 5 13	6·5	5·5	−1 0 10	62·9	55·9
0 2 3	52·9	−55·1	0 5 14	34·3	−33·9	−1 0 12	149·9	169·5
0 2 4	59·1	−60·4	0 5 15	17·3	−19·4	−1 0 14	0	0·2
0 2 5	63·3	74·0	0 5 16	8·7	15·0	−1 0 16	12·4	20·6
0 2 6	6·4	9·1	0 6 0	55·7	64·4	−1 0 18	57·6	−45·2
0 2 7	103·1	−110·2	0 6 1	25·4	27·4	−2 0 2	4·5	−8·6
0 2 8	42·1	−41·6	0 6 2	16·1	11·3	−2 0 4	112·9	124·4
0 2 9	35·7	36·6	0 6 3	30·5	36·6	−2 0 6	100·5	−92·2
0 2 10	111·4	115·7	0 6 4	65·3	69·0	−2 0 8	73·6	58·9
0 2 11	71·4	−61·0	0 6 5	11·8	14·1	−2 0 10	44·6	−44·2
0 2 12	36·6	38·1	0 6 6	42·5	−49·0	−2 0 12	92·1	108·7
0 2 13	78·7	69·6	0 6 7	21·6	−27·2	−2 0 14	39·0	37·8
0 2 14	65·8	57·5	0 6 8	35·1	37·7	−2 0 16	64·5	57·6
0 2 15	20·0	−20·3	0 6 9	11·4	−17·1	−2 0 18	92·3	−65·8
0 2 16	19·5	−15·0	0 6 10	5·8	−3·9	−3 0 2	46·0	50·1
0 2 17	3·9	−3·8	0 7 1	11·1	12·6	−3 0 4	142·7	130·2
0 2 18	17·9	−13·1	0 7 2	10·9	−14·5	−3 0 6	70·6	−62·2
0 2 19	30·6	−27·8	0 7 3	14·0	17·9	−3 0 8	15·2	2·8
0 3 1	31·8	−28·8	1 0 0*	201·4	202·4	−3 0 10	40·3	−35·3
0 3 2	54·6	−52·9	2 0 0*	178·6	170·7	−3 0 12	97·9	118·0
0 3 3	71·6	64·7	3 0 0	134·3	140·1	−3 0 14	53·2	43·1
0 3 4	35·9	−33·5	4 0 0	125·2	129·2	−3 0 16	31·1	56·9
0 3 5	112·6	111·3	5 0 0	42·4	43·4	−3 0 18	5·9	−8·8
0 3 6	11·3	7·7	1 0 2	3·8	−14·4	−4 0 2	78·8	67·5
0 3 7	121·6	119·9	1 0 4	129·2	148·2	−4 0 4	75·6	93·2
0 3 8	36·2	34·1	1 0 6	41·9	−51·4	−4 0 6	85·4	−59·3
0 3 9	10·8	7·4	1 0 8	48·2	56·5	−4 0 8	54·7	50·3
0 3 10	16·4	−7·0	1 0 10	59·7	58·3	−4 0 10	13·6	−11·4
0 3 11	24·1	21·0	1 0 12	172·0	205·5	−4 0 12	56·5	60·5
0 3 12	24·3	14·5	1 0 14	74·5	−56·2	−4 0 14	77·6	70·8
0 3 13	24·8	−22·1	1 0 16	21·6	37·7	−4 0 16	63·5	82·5
0 3 14	5·9	−4·7	1 0 18	20·1	−17·6	−5 0 2	0	8·9
0 3 15	45·2	37·8	1 0 20	75·9	68·1	−5 0 4	152·6	136·6
0 3 16	49·9	−47·1	2 0 2	24·3	−25·1	−5 0 6	15·2	3·2
0 3 17	11·6	9·2	2 0 4	30·0	−20·6	−5 0 8	0	4·3
0 3 18	5·3	2·7	2 0 6	111·8	−100·9	−5 0 10	27·3	−32·5
0 4 0	0	3·2						

* Corrected for extinction.

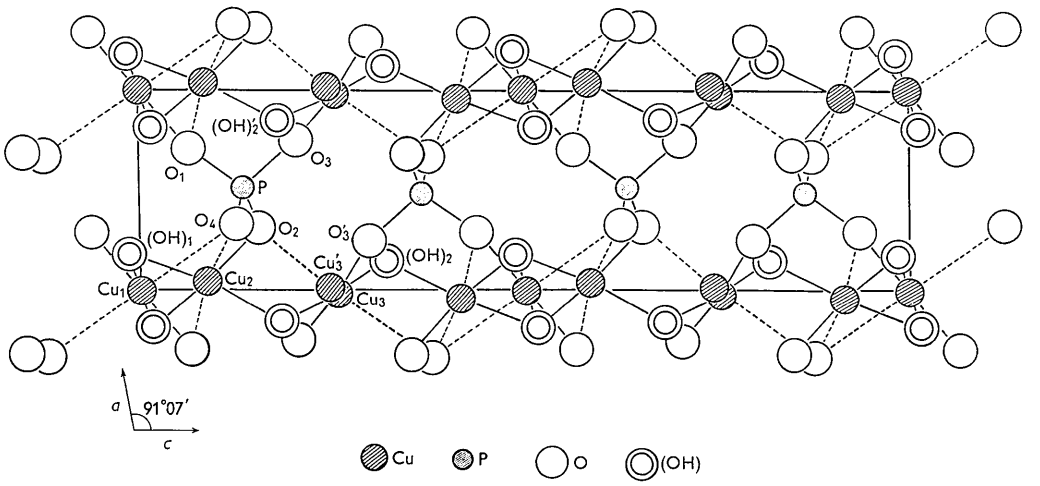

Fig. 3. Projection of the structure of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ on (010). Coordination of Cu_3' not shown.

Table 3. *Interatomic distances and angles in pseudomalachite,* $Cu_5(PO_4)_2(OH)_4$

Within the phosphate group

$P-O_1$	1·54 Å	O_1-P-O_2	108°
$P-O_2$	1·54	O_1-P-O_3	103
$P-O_3$	1·56	O_1-P-O_4	114
$P-O_4$	1·54	O_2-P-O_3	107
O_1-O_2	2·49	O_2-P-O_4	113
O_1-O_3	2·43	O_3-P-O_4	112
O_1-O_4	2·59		
O_2-O_3	2·49		
O_2-O_4	2·57		
O_3-O_4	2·57		

Within the Cu_1 octahedron

$Cu_1-(OH)_1$	2·02	(×2)	$O_1-Cu_1-(OH)_1$	86° (×2)
Cu_1-O_1	1·94	(×2)	$O_1-Cu_1-(OH)_1'$	94 (×2)
Cu_1-O_4	2·69	(×2)	$O_4-Cu_1-O_1$	87 (×2)
$O_1-(OH)_1$	2·70*	(×2)	$O_4-Cu_1-O_1'$	93 (×2)
$O_1-(OH)_1'$	2·90	(×2)	$O_4-Cu_1-(OH)_1$	98 (×2)
$O_4-(OH)_1$	3·58	(×2)	$O_4-Cu_1-(OH)_1'$	82 (×2)
$O_4-(OH)_1'$	3·14*	(×2)		
O_4-O_1	3·39	(×2)		
O_4-O_1'	3·38	(×2)		

Within the Cu_2 octahedron

Cu_2-O_2	1·91 Å	$O_2-Cu_2-(OH)_1$	95°
$Cu_2-(OH)_1$	2·02	$(OH)_1-Cu_2-(OH)_1''$	85
$Cu_2-(OH)_1''$	1·98	$(OH)_1''-Cu_2-(OH)_2'$	96
$Cu_2-(OH)_2'$	1·99	$(OH)_2'-Cu_2-O_2$	86
Cu_2-O_1	2·39	$O_1-Cu_2-O_2$	96
Cu_2-O_4''	2·70	$O_1-Cu_2-(OH)_1$	75
$O_2-(OH)_1$	2·91	$O_1-Cu_2-(OH)_1''$	93
$(OH)_1-(OH)_1''$	2·70*	$O_1-Cu_2-(OH)_2'$	93
$(OH)_1''-(OH)_2'$	2·95	$O_4''-Cu_2-O_2$	87
$(OH)_2'-O_2$	2·66*	$O_4''-Cu_2-(OH)_1$	116
O_1-O_2	3·21	$O_4''-Cu_2-(OH)_1''$	83
$O_1-(OH)_1$	2·70*	$O_4''-Cu_2-(OH)_2'$	77
$O_1-(OH)_1''$	3·19		
$O_1-(OH)_2'$	3·18		
$O_4''-O_2$	3·26		
$O_4''-(OH)_1$	4·01		
$O_4''-(OH)_1''$	3·14*		
$O_4''-(OH)_2'$	2·96*		

Table 3 (*cont.*)

Within the Cu_3 octahedron

Cu_3-O_3	2·00 Å	$O_3-Cu_3-(OH)_2'$	94°
Cu_3-O_3'	1·94	$(OH)_2'-Cu_3-O_3'$	83
$Cu_3-(OH)_2$	1·95	$O_3'-Cu_3-(OH)_2$	99
$Cu_3-(OH)_2'$	1·96	$(OH)_2-Cu_3-O_3$	82
Cu_3-O_2	2·36	$O_2-Cu_3-O_3$	87
Cu_3-O_4'	2·51	$O_2-Cu_3-(OH)_2'$	75
$O_3-(OH)_2'$	2·89	$O_2-Cu_3-O_3'$	85
$(OH)_2'-O_3'$	2·60*	$O_2-Cu_3-(OH)_2$	97
$O_3'-(OH)_2$	2·97	$O_4'-Cu_3-O_3$	97
$(OH)_2-O_3$	2·60*	$O_4'-Cu_3-(OH)_2'$	106
O_2-O_3	3·01	$O_4'-Cu_3-O_3'$	91
$O_2-(OH)_2'$	2·66*	$O_4'-Cu_3-(OH)_2$	82
O_2-O_3'	2·92		
$O_2-(OH)_2$	3·22		
$O_4'-O_3$	3·40		
$O_4'-(OH)_2'$	3·58		
$O_4'-O_3'$	3·19		
$O_4'-(OH)_2$	2·96*		

Copper–copper distances

Cu_1-Cu_2	3·09	Cu_2-Cu_3	3·06 Å
Cu_1-Cu_2''	3·37	Cu_2-Cu_3'	3·40
Cu_2-Cu_2''	2·95	Cu_3-Cu_3'	2·89
		Cu_3-Cu_2'	3·39

Copper–phosphorus distances

Cu_1-P	3·24, 3·28 Å
Cu_2-P	3.13, 3·34
Cu_3-P	3·21, 3·47

* Shared edges.

$Cu_2-(OH)_2'$ 1·99 Å and Cu_2-O_2 1·91 Å). The fifth oxygen, O_1 is at a distance of 2·39 Å, while the sixth one O_4'' is at a distance of 2·70 Å. This type of coordination around copper has been found in azurite, $Cu_3(OH)_2(CO_3)_2$ (Gattow & Zemann, 1958), chalcomenite, $CuSeO_3.2H_2O$ (Gattow, 1958) and $Cu(NH_3)_4SO_4.H_2O$ (Simerská, 1954; Mazzi, 1955).

Cu_3 has a 4+2 co-ordination; it is bonded to two oxygen and two (OH) ions in a square plane (Cu_3-O_3

2·00 Å, Cu_3–O_3' 1·94 Å, Cu_3–$(OH)_2$ 1·95 Å and Cu_3–$(OH)_2'$ 1·96 Å). Two more oxygens (Cu_3–O_2 2·36 Å and Cu_3–O_4' 2·51 Å) complete the distorted octahedron. In both Cu_1 and Cu_3 octahedra, the (OH) ions in the square planar co-ordination occur diagonally opposite to each other.

The Cu_1 octahedron shares four edges with four neighboring Cu_2 octahedra, while each Cu_2 octahedron shares two edges with two adjacent Cu_1 octahedra, one edge with an adjacent Cu_2 octahedron and two edges with two adjacent Cu_3 octahedra. Thus, one Cu_1 and two Cu_2 octahedra, each kind sharing four and three edges alternately, form an infinite chain parallel to *b*, which is very similar to the chain found in lindgrenite, $Cu_3(MoO_4)_2(OH)_2$ (Calvert & Barnes, 1957). On the other hand, the Cu_3 octahedron shares opposite square edges with two adjacent Cu_3 octahedra to form a second type of octahedral chain, parallel to *b*. Furthermore, as mentioned earlier, each Cu_3 octahedron shares two edges with two adjacent Cu_2 octahedra. In this way, these two different types of copper octahedral chains are joined alternately to form a sheet parallel to *bc*.

The phosphorus ions in tetrahedral co-ordination bind these adjacent parallel sheets together in a three-dimensional network. Each oxygen ion, in addition to being bonded to phosphorus, is bonded also to two copper atoms, except O_4, which is bonded to three.

The type of sheet structure found in pseudomalachite is quite different from that found in a number of basic copper compounds, namely, $Cu_2(OH)_3Br$ (Aebi, 1948; Oswald *et al.*, 1961), $Cu_2(OH)_3Cl$, botallackite (Embrey, 1957; Voronova & Vainshtein, 1958), $Cu_2(OH)_3I$ (Oswald *et al.*, 1961), $Cu_2(OH)_3NO_3$ (Nowacki & Scheidegger, 1952), and $Cu_4(OH)_6SO_4$, brochantite (Cocco & Mazzi, 1959). In the above-named compounds, the sheet structure is formed by two types of copper octahedral chain sharing corners; the first type of chain is formed by the octahedra sharing the opposite square edges and is similar to the second type of chain found in pseudomalachite and to the copper octahedral chain found in $Cu(OH)_2$ (Jaggi & Oswald, 1961) and linarite, $PbCu(OH)_2SO_4$ (Bachmann & Zemann, 1961); the second type of chain is formed by the octahedra sharing opposite bipyramidal edges and is similar to the chain found in salesite, $CuIO_3(OH)$ (Ghose, 1962). A corrugated sheet structure, similar to that found in lepidocrocite, FeOOH, has been found in $Cu(OH)_2$ (Jaggi & Oswald, 1961) and a slightly wave sheet structure in CuOHCl (Iitaka *et al.*, 1961).

In pseudomalachite, each (OH) ion is bonded to three copper atoms at the corners of a triangle; this triangle forms the base of a trigonal pyramid, in which the (OH) ion occupies the apex. The proton in the (OH) ion must occur away from the plane of the copper atoms and is possibly not involved in any hydrogen bonds.

The extra water reported in chemical analyses of pseudomalachite from various localities varies from none to about four molecules per unit cell. According to Berry (1950), this water is not a part of the structure. In the present structure analysis, no definite indication of the presence of water molecules in the structure has been found. If these water molecules are really a part of the structure, they must be zeolitic in nature and possibly occur in channels parallel to *b*, between rows of phosphate groups.

Prof. L. G. Berry, Queen's University, Canada and Mr Paul E. Desautels, U.S. National Museum, Washington, D.C. kindly provided mineral specimens. The author is indebted to Prof. George A. Jeffrey for laboratory and computation facilities, and to Mrs Pauline K. Persing Ghose for technical assistance and the diagrams. The computations involved in this work were supported from grant no. G 7395 of the National Science Foundation.

References

Aebi, F. (1948). *Helv. Chim. Acta*, **31**, 369.
Bachmann, H. G. & Zemann, J. (1961). *Acta Cryst.* **14**, 747.
Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* **8**, 478.
Berry, L. G. (1950). *Amer. Min.* **35**, 365.
Calvert, L. D. & Barnes, W. H. (1957). *Canad. Min.* **6**, 31.
Cocco, G. & Mazzi, F. (1958). *Period. di Mineral.* **28**, 121.
Embrey, P. G. (1957). *Brit. J. Appl. Phys.* **8**, 433.
Gattow, G. (1958). *Acta Cryst.* **11**, 377.
Gattow, G. & Zemann, J. (1958). *Acta Cryst.* **11**, 866.
Geller, S. & Durand, J. L. (1960). *Acta Cryst.* **13**, 325.
Ghose, S. (1962). *Acta Cryst.* **15**, 1105.
Guillemin, C. (1956). *Bull. Soc. franç. Minér. Crist.* **79**, 219.
Iitaka, Y., Locchi, S. & Oswald, H. R. (1961). *Helv. Chim. Acta*, **44**, 2095.
Jaggi, H. & Oswald, H. R. (1961). *Acta Cryst.* **14**, 1041.
Mazzi, F. (1955). *Acta Cryst.* **8**, 137.
Nowacki, W. & Scheidegger, R. (1952). *Helv. Chim. Acta*, **35**, 375.
Oswald, H. R., Iitaka, Y., Locchi, S. & Ludi, A. (1961). *Helv. Chim. Acta*, **44**, 2103.
Pinnock, P. R., Taylor, C. A. & Lipson, H. (1956). *Acta Cryst.* **9**, 173.
Shiono, R. (1957). Report no. 2. Also IBM 650 Program Library File no. 84001. University of Pittsburgh Computation and Data processing Center.
Shiono, R. (1959). Report no. 9. IBM 650 Program Library File no. 84002. University of Pittsburgh Computation and Data processing Center.
Simerská, M. (1954). *Czech. J. Phys.* **4**, 277.
Viervoll, H. & Øgrim, O. (1949). *Acta Cryst.* **2**, 277.
Voronova, A. A. & Vainshtein, B. K. (1958). *Kristallografiya*, **3**, 444.
Wells, A. F. (1951). *Acta Cryst.* **4**, 200.