

Crystal structure, H positions, and the Se lone pair of synthetic chalcomenite, $\text{Cu}(\text{H}_2\text{O})_2[\text{SeO}_3]$

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ABSTRACT

Synthetic chalcomenite, $\text{Cu}(\text{H}_2\text{O})_2[\text{SeO}_3]$, is orthorhombic, $P2_12_12_1$, with $a = 6.674(2)$, $b = 9.161(1)$, $c = 7.398(3)$, and $Z = 4$. Its structure has been refined to an unweighted residual of 0.019 using all 459 observed reflections. The overall structure can be described as cross-linked chains of Cu and Se coordination polyhedra. Linked by O2 and O3, SeO_3 groups alternate with Cu in square pyramidal coordination to form chains parallel to **b**. These chains are connected to one another through O1 shared by a SeO_3 group in one chain and a Cu square pyramid in an adjacent chain.

The O atoms at the apex and one of the basal vertices of the Cu square pyramid are each bonded to two H atoms, forming structural H_2O molecules. At least three of the H atoms form H bonds with O atoms. These weak bonds serve to connect adjacent chains further.

Se is situated 0.968 Å from a plane of three O atoms. A significant cavity occurs in the structure on the opposite side of Se from the three O atoms, and this cavity reveals the position of the Se lone pair of electrons. When the Se lone pair of electrons is considered as a member of the anionic framework, it is found that a closest-packed arrangement is approached in the structure of synthetic chalcomenite.

INTRODUCTION

Mindful of the complex stereochemistry of Cu^{2+} , we synthesized compounds that contain Cu and Se as part of a study of phases that contain cations with lone pairs of electrons. Some blue-green crystals that were produced were determined to be the synthetic equivalent of the rare mineral chalcomenite.

The structure of chalcomenite was initially determined by Gattow (1958) and later refined by Asai and Kiriyama (1973). In neither study were H atom positions determined nor the Se lone pair discussed. We present a detailed description of the structure, the H positions, the role of the Se lone pair of electrons in the structure, and comparisons to related phases.

EXPERIMENTAL PROCEDURES

A U-tube type of vessel (Nassau et al., 1973) was charged with silica gel. To one side of the U tube was added 75 mL of an aqueous solution of copper nitrate (0.40 M). To the other side was added 75 mL of a solution of potassium selenate (0.40 M), prepared from selenous acid and potassium hydroxide. The two tubes were

stopped and the vessel left undisturbed for 1 yr. Crystals that formed in the gel at the contact point of the two solutions were washed from the tube with H_2O , manually separated from the gel, and air dried.

A crystal was chosen and unit-cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 24 centered reflections in the range $45.93 < 2\theta < 49.41^\circ$. On the basis of systematic absences of the type $h00/h \neq 2n$, $0k0/k \neq 2n$, and $00l/l \neq 2n$, the space group was determined to be $P2_12_12_1$.

Data were obtained at 23 °C. Weak reflections [$I < 10.0\sigma(I)$] were rescanned (a maximum of two rescans), and the counts accumulated. Stationary background counts were recorded on both sides of each reflection. The ratio of peak counting time to background counting time was 2/1, and the diameter of the incident beam collimator was 1.0 mm.

The intensities were corrected for Lorentz, polarization, and absorption (ψ scans) factors. Three standard reflections measured after every 100 reflections exhibited an average intensity change of less than 1% without systematic trend; hence an exposure-dependent correction was not applied. Experimental details are given in Table 1.

TABLE 1. Experimental data for synthetic chalcocite

Crystal cell data	
Formula	Cu(H ₂ O) ₂ [SeO ₃]
Z	4
D _{calc} (g·cm ⁻³)	3.326
μ _r (MoKα) (cm ⁻¹)	127.19
a (Å)	6.674(2)
b (Å)	9.161(1)
c (Å)	7.398(3)
V (Å ³)	452.3(4)
F ₀₀₀	428
Intensity measurements	
Diffractometer	Rigaku AFC5S
Monochromator	graphite
Scan type	ω-2θ
Scan rate	3.0°/min (in ω)
Scan width (°)	(1.50 + 0.30 tan θ)
2θ max (°)	50
Radiation	MoKα (λ = 0.71069 Å)
Crystal size (mm)	0.15 × 0.10 × 0.12
No. of reflections measured	486
No. of reflect. with I _{net} > 3.00σ(I _{net})	459
Transm. fact. (max., min.)	1.0, 0.70

STRUCTURE REFINEMENT

The crystal structure was redetermined using direct methods. Full-matrix least-squares refinement was performed to minimize $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$ (S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz-polarization factor, and p = 0.05). Neutral atom scattering factors and real and imaginary dispersion corrections were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). All computer programs were from the Texsan crystal-structure analysis package (available from the Molecular Structure Corporation, The Woodlands, Texas).

The positional and anisotropic thermal parameters of non-H atoms were refined to convergence, and H positions were obtained from a different-Fourier synthesis. Attempts were made to refine the H positional and isotropic thermal parameters together and separately, with all data and partial data ($\leq \sin \theta/\lambda = 0.36 \text{ \AA}^{-1}$). In all cases the H bond geometry deviated considerably from accepted values. All positions and thermal parameters of non-H atoms were then fixed, and the positional parameters of the H atoms were varied using the full data set (isotropic temperature factors of H atoms were fixed at $1.2 \times B_{eq}$ of O atoms of associated H₂O). The resultant H bond geometry was satisfactory; the H atomic coordinates were therefore accepted.

The final cycles of refinement were performed with 65 variables, including positional and anisotropic thermal parameters for the non-H atoms, one scale factor, and a secondary extinction parameter. H atoms were included at the positions obtained in the previously described least squares cycle but were not varied. Convergence yielded an R factor of 0.019 for all 459 observed reflections. The largest peaks in the final difference map were +0.27 and -0.24 e/Å³.

TABLE 2A. Positional coordinates and thermal parameters (Å²) in synthetic chalcocite

Atom	x	y	z	B (Å ²)
Se	0.73173(9)	0.89063(5)	0.45720(8)	0.79(3)
Cu	0.0282(1)	0.85137(8)	0.7860(1)	1.19(3)
O1	0.9735(7)	0.8882(4)	0.5279(6)	1.3(2)
O2	0.7488(7)	0.7804(4)	0.2718(6)	1.4(2)
O3	0.7294(7)	0.0586(4)	0.3580(6)	1.4(2)
O4(w)	0.0578(7)	0.7872(5)	0.0440(7)	1.7(2)
O5(w)	0.2090(7)	0.0597(5)	0.8106(7)	2.1(2)
H1	0.9286	0.7825	0.0938	0.0258
H2	0.0964	0.7009	0.0269	0.0258
H3	0.2502	0.1002	0.6735	0.0319
H4	0.3268	0.0519	0.9096	0.0319

Note: B_{iso} of the non-H atoms is the mean of the principal axes of the thermal ellipsoid. For H, B_{iso} is the isotropic Debye-Waller thermal parameter. Estimated standard errors (in parentheses) refer to the last digit.

Final atomic coordinates and equivalent isotropic temperature factors for the non-H atoms and the H positional and isotropic thermal parameters are listed in Table 2a. Anisotropic thermal parameters are given in Table 2b.¹ The observed and calculated structure factors are given in Table 3.

DESCRIPTION OF THE STRUCTURE

The structure of synthetic chalcocite is formed of cross-linked chains extending parallel to the **b** axis, each chain consisting of Cu in square pyramidal coordination alternating with SeO₃ groups. Within a chain, each Cu square pyramid is arranged such that its apex is opposed by the base of the next square pyramid (Fig. 1). Each chain, with all its Cu square pyramids pointing in the same general direction (along **b** or -**b**), is surrounded by four chains with Cu square pyramid apices oriented in the opposite direction (Fig. 1). A vector passed through the Cu and apical O atom of each square pyramid is at an acute angle to the trend of a chain, and apices of succeeding Cu polyhedra alternate in orientation on either side of the main trend of the chain. Within a chain, each SeO₃ group shares O2 with the following Cu polyhedron and O3 with the preceding Cu polyhedron. As O2 and O3 are diagonally opposed basal vertices of the Cu square pyramid, the SeO₃ groups alternate from one side to the other of the main trend of the chain.

Adjacent chains are linked through O1, which is a basal vertex of the Cu polyhedron and the remaining ligand of SeO₃ groups. Viewed parallel to the **b** axis (Fig. 1), this cross linkage, combined with the diagonal disposition of the basal O planes of the two SeO₃ groups linked to each Cu polyhedron within chains, imparts a pinwheel-like appearance to the chains. The remaining vertices of the Cu polyhedron, a basal vertex and the apex (O4 and O5, respectively), are structural H₂O positions.

¹ Copies of Tables 2b and 3 may be ordered as Document AM-92-498 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

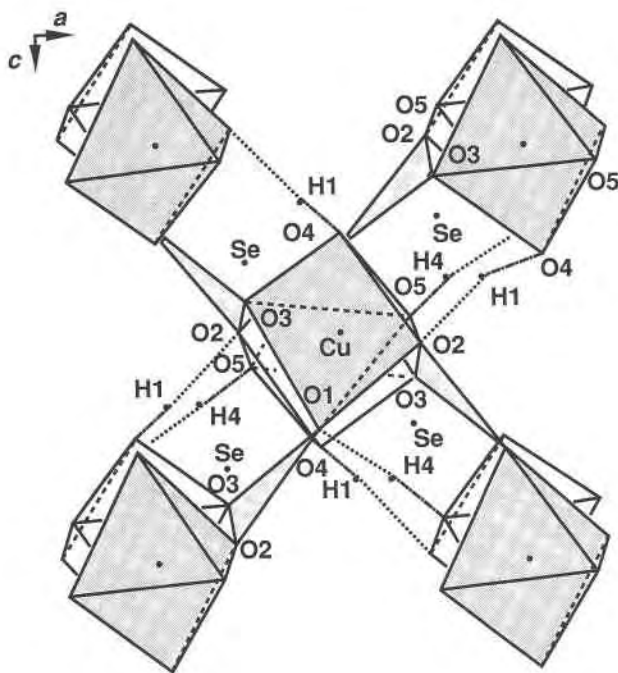


Fig. 1. Synthetic chalcocite viewed down the Cu-Se chains (parallel to *b*). Shading indicates Cu square pyramids closer to the viewer and the planes of three O atoms bonded to Se atoms. Some O-H and H...O bonds are shown. The *a* and *c* axis directions are indicated (but their intersection is not placed at the cell origin).

THE COORDINATION POLYHEDRA

Bond and edge lengths and bond angles for the Cu square pyramid are shown in Table 4. They are not significantly different from those of Asai and Kiriyama (1973). The O coordination about Cu has been described in various ways (Gattow, 1958; Asai and Kiriyama, 1973; Effenberger, 1977). We conclude that the Cu coordination polyhedron in synthetic chalcocite is best described as a slightly distorted square pyramid. Distorted octahedral coordination, as described by Gattow (1958), is ruled out as a possibility for Cu in synthetic chalcocite. As noted by Asai and Kiriyama (1973), Cu is not located on the least-squares plane through O1-O2-O3-O4, and the Cu-O5' distance is much longer than Cu-O5. The results of the present study indicate that Cu is located within the square pyramid volume, 0.187 Å away from the least-squares plane in the direction of the apex (O5), and that Cu-O5 is 2.265 Å, compared with Cu-O5' at 3.187 Å. The latter separation yields a very small bond valence (0.018 vu).

The Cu square pyramid shows very little distortion (Fig. 2). The basal edges range from 2.733 to 2.835 Å in length, and the basal O-O-O angles range from 87.3 to 91.2°. The edges rising to the apex are slightly longer than the basal edges, at 3.052 to 3.199 Å. The Cu bond lengths to the basal O atoms range from 1.951 to 2.007 Å, whereas the apical bond is longer, as noted above. As observed

TABLE 4. Bond distances (Å) and angles (°) of synthetic chalcocite

		Se group		
Se-O1	1.696(5)	O1-O2	2.610(6)	100.2(2)
-O2	1.707(4)	O1-O3	2.583(6)	98.8(2)
-O3	1.705(4)	O2-O3	2.630(5)	100.9(2)
Mean	1.703		2.608	99.97
		Cu square pyramid		
Cu-O1	1.973(5)	O1-O2d	2.821(6)	91.9(2)
-O2d	1.951(4)	O1-O3b	2.835(6)	91.6(2)
-O3b	1.980(5)			
-O4	2.007(5)	O1-O5	3.052(7)	91.9(2)
-O5	2.265(5)	O2-O4a	2.733(7)	87.3(2)
		O2-O5a	3.186(6)	97.9(2)
		O3-O4c	2.750(6)	87.2(2)
		O3-O5c	3.140(7)	95.2(2)
		O4-O5	3.199(7)	96.8(2)
Mean	2.035		2.965	92.5

Note: Standard deviations of the last digit are in parentheses. Symmetry codes: $a = -0.5 + x, 1.5 - y, 1.0 - z$; $b = 1.5 - x, 2.0 - y, 0.5 + z$; $c = 1.5 - x, 2.0 - y, -0.5 + z$; $d = 0.5 + x, 1.5 - y, 1.0 - z$.

by Asai and Kiriyama (1973), the basal O atoms are nearly coplanar. Distances from a least-squares plane passed through O1, O2, O4, and O3 are 0.032, -0.033, 0.042, and -0.033 Å, respectively. Consequently, the Cu polyhedron is a slightly distorted square pyramid that has a height nearly equal to the basal edge length.

The SeO₃ group in synthetic chalcocite may be compared to the SeO₃ group in other phases (Gladkova and Kondrashev, 1964; Weiss et al., 1966; Larsen et al., 1971; Lehmann and Larsen, 1971; Effenberger, 1985, 1986). The Se-O and O-O lengths and the O-Se-O angles of synthetic chalcocite (Table 4) do not deviate significantly from those of related compounds. In synthetic chalcocite, Se is situated nearly equidistant from three O atoms, O1, O2, and O3, and is located 0.968 Å from a plane containing them.

STRUCTURAL INTERPRETATION OF THE ROLE OF THE Se LONE PAIR

X-ray diffraction yields no direct evidence (electron density distribution) of the location of the Se lone pair. Therefore, the interpretation that follows is based solely on the nuclear distribution inferred from our refinement. The electronic configuration of Se⁴⁺, [Ar]3d¹⁰4s², yields a lone pair of electrons in the outer shell. In synthetic chalcocite, a cavity occurs on the side of Se opposite from its three O ligands (Fig. 1), and it is here that localization of the lone pair charge is expected. Se is thus implied to have tetrahedral coordination, i.e., SeO₃ψ (where ψ symbolizes the lone pair of electrons).

This type of ligand and lone pair coordination polyhedron has been discussed by many authors (cf. Hyde and Andersson, 1989). The essential features of such a polyhedron, as compared with a normal coordination tetrahedron, are (1) decreased angles between the bond pairs because of lone pair-bond pair interaction (Andersson and Åström, 1972) and (2) a shorter distance between the cation and the vertex occupied by the lone pair centroid than the distances between the cation and ligands (Hyde

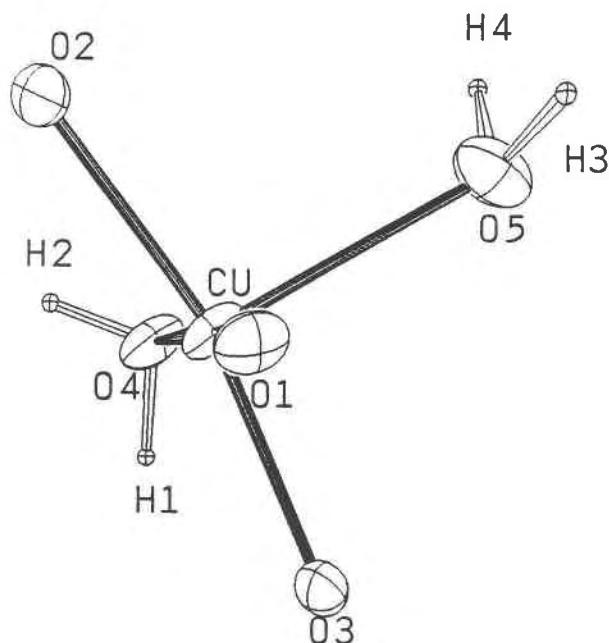


Fig. 2. Spoke diagram showing bonds to Cu and the locations of the structural H₂O molecules.

and Andersson, 1989). In an undistorted tetrahedron the angle between bond pairs is $109^{\circ}28'$, but in synthetic chalcocite the O-Se-O angles are smaller, ranging from 98.8 to 100.9° . The second characteristic is also met in synthetic chalcocite because the Se-O distances range from 1.696 to 1.707 Å, but the average $\text{Se}^{4+}-\psi$ distance in various structures has been estimated to be approximately 1.22 Å (Hyde and Andersson, 1989). Using Gattow's (1958) structural data, Galy et al. (1975) calculated an effective Se lone pair radius of 1.36 Å for chalcocite. Performing the same calculation for synthetic chalcocite, we find that $\text{Se}-\psi$ is 1.16 Å, which is in better agreement with the other Se-bearing structures cited in the above source.

Asai and Kiriyama (1973) suggested that O forms a σ and a π bond with Se. If, on the other hand, Se is sp^3 hybridized, as the previously discussed features indicate, there are no p-p π bonds with the coordinating O atoms. In contrast to the scheme of Asai and Kiriyama (1973), we suggest that each of these O atoms forms σ bonds with Se and Cu, has one lone pair oriented toward a H atom, and has the other lone pair residing in the remaining p orbital.

Another effect of the presence of the Se lone pair can be illustrated with the anion packing efficiency, V_E (Andersson and Åström, 1972; Moore and Shen, 1984). V_E is the cell volume divided by the number of included anions. V_E for synthetic chalcocite is 22.6 Å³. If the Se lone pair is considered as a member of the anionic framework in synthetic chalcocite, a packing efficiency of 18.8 Å³ is calculated. For a hexagonal closest packed array of O atoms, V_E is approximately 16 Å³ (Andersson and Åström, 1972).

If ψ is included in the anion tally, the above observations suggest that the structure of synthetic chalcocite may approach closest packing. Indeed, visual examination of the structure (Fig. 1) initially led the authors to suspect the structural importance of the lone pair in this phase. It was apparent that, perpendicular to the (101) and (101) planes, (1) anion-rich layers are interspersed with cation-rich layers and (2) a significant proportion of the faces of coordination polyhedra are subparallel. Because the stacking vectors are approximately perpendicular to the pyramidal faces of the Cu polyhedra, the packing may approach hexagonal closest packing. Deviation from perfect closest packing is probably, in part, due to the presence of structural H₂O molecules.

The lone pair and packing considerations discussed above are germane to the phase teinite, which is isostructural with chalcocite (Effenberger, 1977), and to the closely related phase $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$ (Gladkova and Kondrashev, 1964).

STRUCTURAL H₂O AND H BONDS

Structural H₂O molecules are located at the apex and at one of the basal vertices of the Cu square pyramid (O5 and O4, respectively). H1 and H2 form a structural H₂O molecule with O4, and H3 and H4 with O5 (Figs. 1, 2). H1, H2, H4, and possibly H3 form H bonds with the closest O2, O3, O1, and O4, respectively, in adjacent chains.

O-H, O-H...O, and H...O distances and angles are given in Table 5. Bond valences (Table 6) indicate that O4 is oversaturated (2.19 vu) and O5 is undersaturated (1.83 vu). The large departure of the O5-H3...O4 angle from 180° (143.6°) and the distortion of the O5 structural H₂O molecule bond angle (117.5°) suggest that the weak H3 attraction neither resides solely, nor perhaps even predominantly, with O4. In addition, the direct distance from proton-donor atom to proton-acceptor atom (O5-O4) in the case of H3 is significantly longer than analogous distances associated with the other H atoms. A lack

TABLE 5. H bond distances, H-O...H (Å) and angles ($^{\circ}$) of synthetic chalcocite

H1-O4w	0.939(5)	O4w-H1...O2	2.664(7)	155.4(3)	H1...O2 = 1.782(5)
H2-O4w	0.841(5)	O4w-H2...O3	2.632(7)	138.4(4)	H2...O3 = 1.943(4)
H3-O5w	1.114(5)	O5w-H3...O4w	2.877(7)	143.6(3)	H1-O4w-H2 = 107.3(5)
H4-O5w	1.077(5)	O5w-H4...O1	2.702(7)	155.3(4)	H3...O4 = 1.904(5)
					H4...O1 = 1.686(4)
					H3-O5w-H4 = 117.5(4)

Note: Standard deviations of the last digit are in parentheses.

TABLE 6. Bond valences for synthetic chalcogenite

	O1	O2	O3	O4	O5	Σ
Se	1.36	1.32	1.33			4.01
Cu	0.45	0.48	0.44	0.41	0.21	1.99
H1		0.20		0.80		1.00
H2			0.17	0.83		1.00
H3				0.15	0.85	1.00
H4	0.23				0.77	1.00
Σ	2.04	2.00	1.94	2.19	1.83	

Note: H bond valences are calculated by the method described in Sen Gupta et al. (1991) and Brown and Altermatt (1985). H bond valence sums are assumed to be 1.00.

of H bonding for H3 may also be indicated by the bond-valence results. If there is no H bond between H3 and O4, the O4 and O5 bond-valence sums are 2.04 and 1.98, respectively. Finally, Asai and Kiriyaama (1973) were only able to find three ν_{OH} bands in the IR spectrum of chalcogenite.

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