The structure of chloroxiphite, $Pb_3CuO_2(OH)_2Cl_2$*

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SUMMARY. Chloroxiphite, $Pb_3CuO_2(OH)_2Cl_2$, is monoclinic, space group $P2_1/m$, with $a = 10.458$, $b = 5.750$, $c = 6.693$ Å, $\beta = 97.79°$, $Z = 2$. The structure has been refined by the method of least squares from three-dimensional Mo-$K\alpha$ intensity data to a conventional R value of 0.115. The structure consists of sheets of composition $[Pb_3 CuO_2(OH)_2]^{2-}$, in themselves made up of the layer sequence Pb–(O, OH, Cu)–Pb, lying parallel to $(\bar{1}01)$. The structure contains eight-fold PbO_4Cl_4 and seven-fold PbO_5Cl_2 polyhedra common in other oxychlorides, Pb_6 clusters and copper atoms in square planar, $Cu(OH)_4$, coordination.

CHLOROXIPHITE was first described by Spencer and Mountain (1923). In this description the perfect and distinct cleavages were assigned the indices (001) and (100), respectively, resulting in a β angle of 62.75°. In Dana's 7th edition (1944) the crystal was reoriented with the perfect cleavage becoming $(\bar{1}01)$ giving a β angle of 97.79°. The crystal structure was determined on the basis of this orientation although Spencer and Mountain's original orientation could have just as well been used. The structure as determined verifies Mountain's original chemical analysis as well as the reformulation in Dana, which was marked with a question mark.

Experimental. The crystals of chloroxiphite used in the present study were from the type locality of Mendip Hills, Somerset, England (U.S. National Museum no. R11789). A fragment measuring approximately $0.16 \times 0.17 \times 0.19$ mm was obtained from crushing a larger blade-like crystal; no attempt was made to grind a sphere because of the perfect $\{\bar{1}01\}$ and distinct $\{100\}$ cleavages. For a mean spherical diameter of 0.175 mm, $\mu R = 5.78$ (Mo-$K\alpha$, $\mu = 660$ cm^{-1}).

Precession and Weissenberg photographs were used to determine preliminary unit-cell dimensions, space-group extinctions, and to inspect the diffraction images for satellites. Systematic absences and the symmetry of the reciprocal lattice indicated the space group to be $P2_1/m$. A least-squares refinement of nine reflections measured with Mo-$K\alpha$ radiation gave the following lattice constants (standard errors are in parenthesis): a 10.458 (4), b 5.759 (3), c 6.693 (3) Å, β 97.79° (4), $Z = 4$. The calculated density of 6.84 gm cm^{-3} is in close agreement with Spencer and Mountain's (1923) value of 6.93 gm cm^{-3}. In comparison Dana (1944) gives a 10.36, b 5.74, c 6.53 Å, β 97.18°, $\rho = 7.07$ gm cm^{-3}.

The θ–2θ technique with a scintillation detector employing pulse-height discrimination was used to measure the Mo-$K\alpha$ intensity data. Reflections within a quarter sphere limited by $2\theta = 60°$ were measured with a β-filter (Zr). Background radiation was measured at each end

of the scan with crystal and counter stationary, and was assumed to be a linear function of 2θ between these points. A unique set of 1275 reflections was measured; the intensities of 83 reflections were less than $3z$ and were considered unobserved [$\sigma = (N_{sc} + K^2 N_b)^{\frac{1}{2}}$, where N_{sc}, N_b, and K are the total scan counts, background counts, and the time ratio of scan to background, respectively]. Intensities were corrected for Lorentz, polarization, and absorption effects to obtain the observed structure amplitudes; no corrections for extinction were applied. Atomic scattering factors for Pb^{1+} and $Cl^{\frac{1}{2}-}$ were obtained from Cromer and Waber (1965), Cu^{1+} from Doyle and Turner (1968) and O^{1-} from Table 3.31A of *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections for Pb and Cu (Cromer, 1965) were applied throughout the refinement. All reflections were equally weighted.

Determination and refinement of the structure. The three-dimensional Patterson synthesis, $P(uvw)$, led to an unambiguous interpretation of the three lead positions. A difference Fourier with these atoms as input resolved the positions of all the unique remaining six non-hydrogen atoms in the structure.

Least-squares refinement was carried out until the shift in all parameters was less than 1 % of their standard deviations. Due to the predominant influence of the lead atoms on the structure factors, the anion positions could not be determined with high accuracy and a final difference synthesis failed to reveal the hydrogen atoms in the structure. With isotropic thermal vibration parameters, and omitting unobserved reflections, the final residual R (where $R = \Sigma| |F_o|-|F_c| |/\Sigma|F_o|$) was 0·115. Changing from isotropic to anisotropic temperature factors and refining all parameters produced no significant changes in either the atom coordinates or anisotropy in thermal parameters but did reduce R to 0·096. The final least-squares parameters for isotropic refinement are given in Table I. All numerical calculations[1] were performed on a CDC–6600 computer using the X-RAY 67 or 71 system of crystallographic programs (Stewart, 1971).

Discussion. Precession photographs indicate the presence of a pseudotetragonal axis perpendicular to the prominent {$\bar{1}$01} cleavage, an observation borne out by the optical properties ($\alpha = 2\cdot16 \perp$ {$\bar{1}$01}; $\beta = 2\cdot24$; $\gamma = 2\cdot25$ || [010].) The dimensions of the pseudotetragonal cell are $c_{tet} \perp$ {$\bar{1}$01} $= 5\cdot97$, $a_{2(tet)} = b_{mono} = 5\cdot74$ Å, $a_{1(tet)} = 5\cdot82$ Å, $c_{tet} \wedge a_1 = 91° 15'$. The pseudotetragonal axis corresponds to the c-axis assigned by Spencer and Mountain (1923).

The projection of two unit cells on ($\bar{1}$01) in fig. 2 clearly shows the pseudotetragonal symmetry along this axis. The structure consists of sheets of composition $[Pb_3CuO_2(OH)_2]^{2-}$, in themselves made up of the layer sequence Pb–(O,OH,Cu)–Pb, lying parallel to ($\bar{1}$01). These sheets are stacked in an offset manner and linked by a layer of chlorine atoms. The weaker bond between lead and chlorine atoms in their layer arrangement accounts for the perfect {$\bar{1}$01} cleavage. The structure viewed along the b-axis is shown in fig. 1.

Cation coordination. Lead atoms occur in both seven- and eight-fold coordination. Pb(2) occurs in a distorted square antiprism with eight-fold coordination. The antiprism has a small face formed by four coplanar, {$\bar{1}$01}, oxygen atoms, and a large face formed by four slightly non-coplanar chlorine atoms. Lead in similar square antiprismatic coordination is observed in tetragonal $PbTiO_3$ (Shirane *et al.*, 1956), nadorite, $PbSbO_2Cl$ (Sillen and Melander, 1941), perite, $PbBiO_2Cl$ (Gillberg, 1961), diaboleïte, $Pb_2Cu(OH)_4Cl_2$ (Rouse, 1971), and hematophanite $Pb_5Fe_4O_{10}(OH,Cl)_2$ (Rouse, 1973). PbO_4Cl_4 groups are apparently a basic structural unit in lead oxychlorides.

Pb(1) and Pb(3) are in seven-fold coordination in a polyhedron similar to Pb(2) but with the small oxygen face modified to a triangular one containing two oxygen atoms and one hydroxyl

[1] A list of the observed and calculated structure factors may be obtained from the authors.

TABLE I. *Atomic parameters for chloroxiphite (standard deviations apply to the right-most digit of the least-square parameter)*

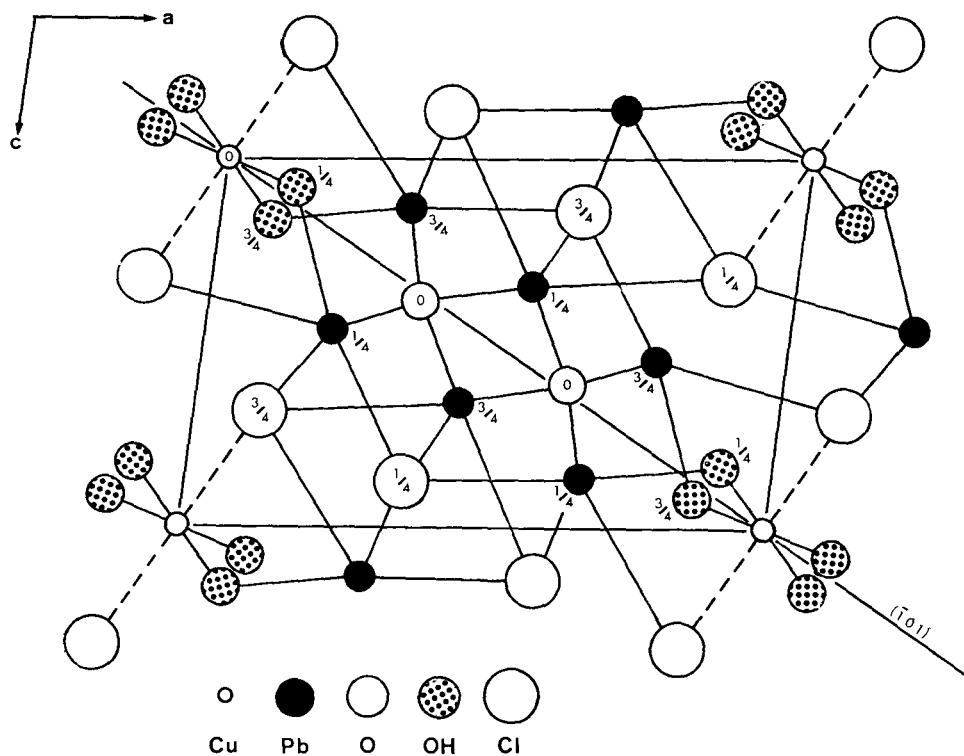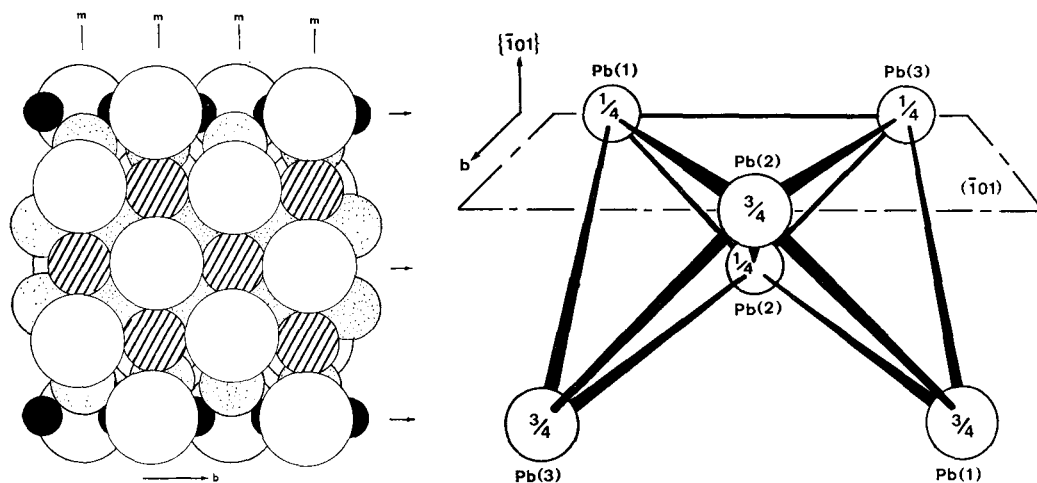| Atom		x	y	z	$B\ (Å^2)$	Atom		x	y	z	$B\ (Å^2)$
Pb (1)	2e	0.2167 (2)	¼	0.4606 (3)	1.43	Cφ (1)	2e	0.378 (1)	¼	0.868 (2)	1.68
Pb (2)	2e	0.5502 (2)	¼	0.3432 (3)	1.34	Cφ (2)	2e	0.886 (2)	¼	0.321 (3)	2.44
Pb (3)	2e	0.6741 (2)	¼	0.8673 (3)	1.35	O (1)	4f	0.366 (3)	0.000 (5)	0.386 (4)	1.32
Cu	2a	0	0	0	1.61	OH (1)	2e	0.907 (4)	¼	0.832 (6)	1.37
						OH (2)	2e	0.126 (4)	¼	0.086 (7)	1.72

FIG. 1. A projection of chloroxiphite on (010).

group. Lead in similar seven-fold coordination is found in mendipite $Pb_3O_2Cl_2$ (Gabrielson, 1957) but with three chlorine and four oxygen atoms.

Ignoring anions, the six lead atoms per unit cell are arranged in units consisting of three distorted face-sharing tetrahedra (illustrated in fig. 3). Similar Pb_6 clusters are found in mendipite and the synthetic compound $Pb_6O(OH)_6(ClO_4)_4·H_2O$ (Shapiro *et al.*, 1969). The Pb–O and Pb–Cl bond lengths (Table II) are consistent with those found in other lead oxychlorides.

Copper atoms occur in a $Cu(OH)_4Cl_2$ tetragonally distorted octahedron. The four hydroxyl groups (assumed to be in the copper coordination) do not lie in ($\bar{1}01$) and it is the skewed orientation of the $Cu(OH)_4Cl_2$ group that destroys the otherwise almost perfect tetragonal

symmetry normal to (101). The Cu–OH bond lengths (Table II) fall within the accepted range 1·9–2·1 Å but the Cu–Cl bond length of 2·966 Å is much longer than expected ($\approx$ 2·5–2·6 Å). Similar Cu–Cl distances (2·946 Å) have been found in diaboleïte, $Pb_2Cu(OH)_4Cl_2$ (Rouse, 1971). Rouse concludes from the unusual length and also from charge distribution that the

FIGS. 2 and 3: FIG. 2 (left). A packing drawing of chloroxiphite on (101). The copper atoms are black and lead atoms line shaded. Oxygen atoms are dotted (O and OH are not differentiated). FIG. 3 (right). An idealized drawing of the three face-sharing tetrahedrons formed by the Pb_6 clusters.

TABLE II. Interatomic distances for chloroxiphite (standard error in parentheses, $n\times$ refers to n number of equivalent distances)

Pb (1)	–O (1)	2x	2.228 (29) Å	Pb (3)	–O (1)	2x	2.219 (28)	Cl (1)	–OH (2)		3.181 (50)
	OH (2)		2.568 (43)		OH (1)		2.479 (42)		O (1)	2x	3.518 (31)
	Cl (1)		3.006 (14)		Cl (1)		3.097 (15)		O (1)	2x	3.655 (32)
	Cl (2)	3x	3.459 (18)		Cl (1)	2x	3.459 (9)		O (1)	2x	3.771 (31)
					Cl (2)		3.508 (17)				
Pb (2)	–O (1)	2x	2.385 (27)					Cl (2)	–OH (2)		3.137 (51)
	O (1)	2x	2.451 (29)	Cu	–OH (2)	2x	1.982 (30) Å		OH (1)		3.310 (46)
	Cl (1)	2x	3.334 (8)		OH (1)	2x	1.995 (27)		OH (1)		3.397 (45)
	Cl (1)		3.436 (14)		Cl (2)	2x	2.966 (17)		O (1)	2x	3.776 (34)
	Cl (2)		3.535 (18)						OH (1)	2x	3.821 (31)
									OH (2)	2x	3.951 (33)

2·946 Å Cu–Cl interaction is very weak. Similarly in chloroxiphite, bond length and charge distributions indicate very little Cu–Cl interaction and on this basis the copper coordination is properly described as square planar $Cu(OH)_4$ groups.

Similar structures. As previously mentioned, chloroxiphite shows similarities to diaboleïte, $Pb_2Cu(OH)_4Cl_2$, which is tetragonal with PbO_4Cl_2 square antiprisms, and mendipite, $Pb_3O_2Cl_2$, which contains Pb in similar seven-fold coordination and Pb_6 clusters. Rouse (1971) has described the diaboleïte structure as a perovskite derivative. In chloroxiphite the skewed

orientation of the Cu(OH)$_4$ group, the higher Pb/Cu ratio, and the offset in stacking normal to (101) make it impossible to identify a perovskite-like pseudo-cell. The structure would be akin to mendipite plus copper if it were not for the arrangement of the Pb$_6$ clusters. In chloroxiphite the long axes of all Pb$_6$ clusters are parallel while in mendipite the clusters are divided into two sets with mutually perpendicular axes.

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Errata: Table I, line 1, *for* Cφ (1) *read* Cl (1)
line 2, *for* Cφ (2) *read* Cl (2)