Chloroxiphite Pb$_3$CuO$_2$(OH)$_2$Cl$_2$: structure refinement and description in terms of oxocentred OPb$_4$ tetrahedra

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ABSTRACT

The crystal structure of chloroxiphite, Pb$_3$CuO$_2$(OH)$_2$Cl$_2$, from Merehead Quarry (monoclinic, $P2_1/m$, a = 6.6972(8), b = 5.7538(5), c = 10.4686(14) Å, β = 97.747(10)º, V = 399.72(8) Å^3) has been refined to R_1 = 0.041. The structure contains three symmetrically unique Pb sites and one Cu site. The strong distortion of the Pb^{2+} coordination polyhedra is due to the stereoactivity of the s^2 lone electron pairs on the Pb^{2+} cations. The Cu-site is coordinated by four OH$^-$ groups to form an almost planar Cu(OH)$_4$ square that is complemented by two apical Cl$^-$ anions, forming an elongated [Cu(OH)$_4$Cl$_2$] octahedron. Because of the large size and variability of coordination polyhedra around Pb^{2+} cations and the strength of the $Me-$O bonds in comparison to the $Me-$Cl bonds (Me = metal), it is convenient to describe the structure of chloroxiphite in terms of oxocentred OPb$_4$ tetrahedra. The O1 atom is tetrahedrally coordinated by four Pb^{2+} cations forming relatively short and strong O$-$Pb bonds. The OPb$_4$ tetrahedra link together via common edges to form [O$_2$Pb$_3$]$^{2+}$ double chains. The difference between chloroxiphite and other natural oxyhalides is the presence of Cu^{2+} cations which form an independent structural unit that links to units formed by OPb$_4$ tetrahedra. In this sense, chloroxiphite can be considered as a modular structure consisting of both strong cation- and anion-centred units.

Introduction

Lead oxy- and hydroxyhalides are common minerals in alteration zones of Pb-containing sulphide deposits, where they form as a result of hydrolysis of Pb^{2+} ions by aqueous chloride during oxidation of Pb sulphide minerals. Chloroxiphite, Pb$_3$CuO$_2$(OH)$_2$Cl$_2$, was first described by Spencer and Mountain (1923) from the Mendip Hills, Somerset, England. It occurs here as olive-green bladed crystals embedded entirely in mendipite (Turner, 2006). Later, chloroxiphite was identified by Vergasova and Filatov (1993) in the products of fumarolic activity of the great Tolbachik fissure eruption (1975−1976, Kamchatka Peninsula, Russia). The crystal structure of chloroxiphite was solved by Finney *et al.* (1977) and refined to 11.5% without anisotropic refinement of the displacement parameters of atoms. The structure was described as Pb$_6$ clusters of face-sharing Pb tetrahedra and Cu-centred hydroxide chloride polyhedra.

Here, we report results of the structure refinement of chloroxiphite and describe its structure in terms of oxocentred tetrahedra, thus considering this structure type within the framework of the structural chemistry of anion-centred tetrahedra (Krivovichev *et al.*, 1998*a*; Krivovichev and Filatov, 2001; Siidra *et al.* 2008*a,b*).

Experiment

The sample used in this study was from the Natural History Museum, London, and was collected *in situ* at the Merehead Quarry, Somerset, England, in the late 1970s by Dr Bob Symes and the late Dr Alan Criddle. The specimen appears to originate from the #1 vein and is typical, consisting of small bladed crystals of chloroxiphite embedded entirely in mendipite which in turn fills a calcite-lined cavity in a manganese-oxide matrix. This paragenesis was described previously (Symes and Embrey, 1977; Turner, 2006).

The crystal of chloroxiphite selected for data collection was mounted on a Stoe IPDS II Image-Plate-based X-ray diffractometer operated at 50 kV and 40 mA. More than a hemisphere of three-dimensional data was collected using monochromatic Mo-$K\alpha$ X-radiation, with frame widths of 2° in ω, and a counting time of 180 s for each frame. The unit-cell parameters (Table 1) were refined using least-squares techniques. The unit-cell parameters are in good agreement with those reported by Finney *et al.* (1977). The intensity data were integrated and corrected for Lorentz polarization and background effects using the Stoe program *X-area*. Systematic absences of reflections indicate space group $P2_1/m$, also in agreement with the results obtained by Finney *et al.* The atomic coordinates provided by these authors were successfully refined on the basis of F^2 for all unique data in this space group. The *SHELXL* program package was used for all structural calculations (Sheldrick, 1997). The final model included all atomic positional parameters, anisotropic-displacement parameters for Pb, Cl, O and a refinable weighting scheme of

the structure factors. The final refinement converged to an agreement index (R_1) of 0.041, calculated for the 1021 unique reflections with $|F_o| = 4\sigma_F$. The final atom coordinates and anisotropic-displacement parameters are given in Table 2, selected interatomic distances are shown in Table 3. The list of observed and calculated structure factors can be provided by the authors upon request.

TABLE 1. Crystallographic data and refinement parameters for chloroxiphite.

a (Å)	6.6972 (8)
b (Å)	5.7538 (5)
c (Å)	10.4686 (14)
β (°)	97.747 (10)
V (Å^3)	399.72 (8)
Radiation	Mo-$K\alpha$
Total reflections	3803
Unique reflections	1174
Unique $[F_o] \geqslant 4\sigma_F$	1021
GooF	1.212
Space group	$P2_1/m$
F_{ooo}	682
Z	2
Crystal size (mm)	$0.05 \times 0.07 \times 0.10$
μ, cm^{-1}	66.230
Maximum 2θ(°)	58.5
R_1	0.0412
wR_2	0.0502
S	1.212

Note: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$;
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P $= (F_o^2 + 2F_c^2)/3$;
$S = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

TABLE 3. Selected bond lengths (Å) in the structure of chloroxiphite.

Pb(1)−O(1)	2.378(6) × 2	Pb(3)−O(1)	2.242(7) × 2
Pb(1)−O(1)	2.427(6) × 2	Pb(3)−OH(2)	2.598(10)
Pb(1)−Cl(1)	3.3346(19) × 2	Pb(3)−Cl(1)	3.023(3)
Pb(1)−Cl(1)	3.426(3)	Pb(3)−Cl(2)	3.474(4)
		Pb(3)−Cl(2)	3.475(3) × 2
Pb(2)−O(1)	2.237(7) × 2		
Pb(2)−OH(3)	2.516(9)		
Pb(2)−Cl(1)	3.085(3)	Cu(1)−OH(3)	1.983(6) × 2
Pb(2)−Cl(1)	3.460(2) × 2	Cu(1)−OH(2)	1.994(6) × 2
Pb(2)−Cl(2)	3.486(4)	Cu(1)−Cl(2)	2.948(4) × 2

TABLE 2. Coordinates and displacement parameters (Å) of atoms in chloroxiphite.

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	0.65691(7)	¼	0.94966(4)	0.01154(15)	0.0089(3)	0.0097(2)	0.0160(2)	0	0.00163(18)	0
Pb2	1.13269(8)	¼	0.82594(4)	0.01198(16)	0.0102(3)	0.0114(2)	0.0138(2)	0	−0.00052(17)	0
Pb3	0.53955(8)	¼	1.28320(4)	0.01272(16)	0.0132(3)	0.0120(2)	0.0128(2)	0	0.00098(17)	0
Cu1	1	0	½	0.0151(4)	0.0185(9)	0.0107(7)	0.0141(7)	0.0017(6)	−0.0051(6)	−0.0034(6)
Cl1	0.1308(5)	¼	1.1205(3)	0.0170(7)	0.0156(16)	0.0162(15)	0.0180(14)	0	−0.0017(12)	0
Cl2	0.6834(7)	¼	0.6147(4)	0.0274(8)	0.0197(18)	0.038(2)	0.0238(17)	0	0.0012(14)	0
O1	0.6125(10)	0.0016(11)	1.1311(6)	0.0123(14)	0.012(3)	0.007(3)	0.018(3)	0.002(2)	0.001(3)	−0.001(2)
OH2	0.9213(15)	¼	0.3710(8)	0.0134(19)	0.012(5)	0.013(5)	0.014(4)	0	0.001(4)	0
OH3	1.1680(15)	¼	0.5897(8)	0.0112(18)	0.013(5)	0.004(4)	0.015(4)	0	−0.003(3)	0

Results

Cation coordination

The structure of chloroxiphite contains three symmetrically unique Pb sites and one Cu site. The Pb1 cation is coordinated by four O1 atoms and three Cl1 atoms (Fig. 1*a*). The Pb2 cation is coordinated by the two O1 atoms, one O2 atom, three Cl1 and one Cl2 atoms. The Pb3 cation is coordinated by the one O2 atom, two O1 atoms, three Cl2 and one Cl1 atoms. In accord with previous results on Pb oxyhalides, the general feature of the Pb^{2+} coordination in chloroxiphite is the presence of several short Pb−O and Pb−OH bonds (2.24−2.60 Å) located in one coordination hemisphere of the Pb^{2+} cations. In the opposite hemisphere, the Pb^{2+} cations form from three or four long Pb−Cl bonds. The strong distortion of the Pb^{2+} coordination polyhedra is due to the stereoactivity of s^2 lone electron pairs on the Pb^{2+} cations, and is in good agreement with general observations for structures containing cations with lone electron pairs (Brown, 1974). Bond valences were calculated using the parameters of Krivovichev and Brown (2001) for the Pb^{2+}−O bonds and Brese and O'Keeffe (1991) for the other bonds. Bond-valence sums for the Pb atoms range from 1.90 to 1.94 valence units (v.u.), whereas the bond-valence sum at the Cu site is 1.84 v.u. The bond-valence sums at the O1, O2, O3, Cl1 and Cll2 sites are 1.95, 1.11, 1.18, 0.96 and 0.47 v.u., in agreement with the assignment of these sites to $O^{2−}$, $OH^−$ and $Cl^−$ anions. The bond-valence sum at the Cl2 site is notably smaller than the expected value of 1 v.u.

The Cu site is coordinated by four $OH^−$ groups to form an almost planar $Cu(OH)_4$ square that is complemented by two apical $Cl^−$ anions. As a result, an elongated $[Cu(OH)_4Cl_2]$ octahedron is formed (Fig. 1*b*). This type of coordination is typical of mixed-ligand Cu^{2+} coordination polyhedra (Burns and Hawthorne, 1995*a*) and has been observed, for example, in allochalcoselite (Krivovichev *et al*., 2006), georgbokiite (Krivovichev *et al*., 1999) and chloromenite (Krivovichev *et al*., 1998*b*). The $[Cu(OH)_4Cl_2]$ octahedra are distorted owing to the Jahn-Teller effect (Jahn and Teller, 1937; Burns and Hawthorne, 1995*a,b*).

Description of the structure

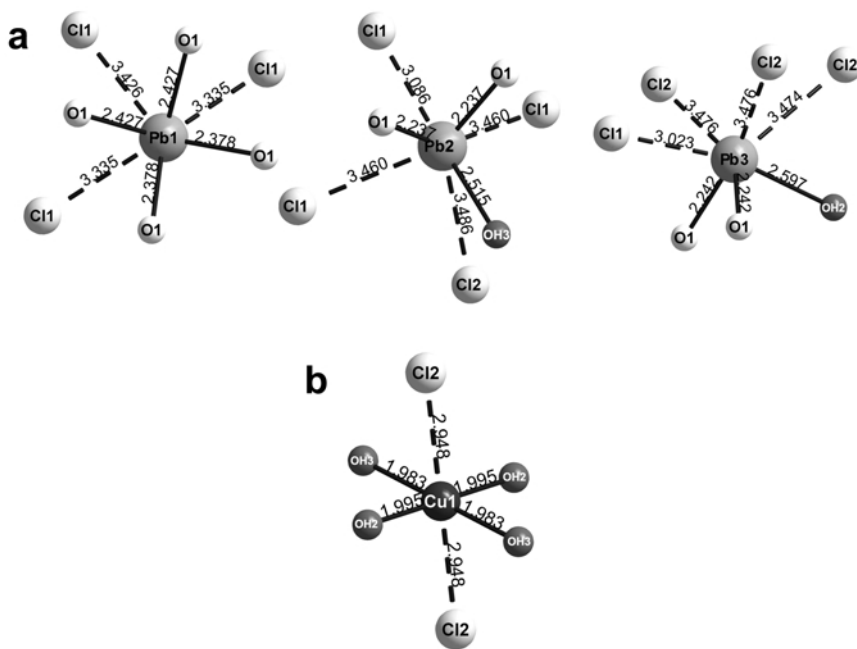Because of the large size and variability of coordination polyhedra around Pb^{2+} cations and

FIG. 1. Coordination of (*a*) Pb^{2+}; and (*b*) Cu^{2+} cations in the structure of chloroxiphite.

the strength of the *Me*−O bonds in comparison to the *Me*−Cl bonds, it is convenient to describe the structure of chloroxiphite (Fig. 2) in terms of oxocentred OPb$_4$ tetrahedra. The structure contains three O^{2-} anions. The O2 and O3 anions are OH groups and their bond-valence requirements are strongly-influenced by the formation of the hydrogen (O···H) bonds. The O1 atom is tetrahedrally coordinated by four Pb^{2+} cations, forming relatively short and strong O−Pb

bonds. From the viewpoint of bond-valence theory, these bonds are the strongest in the structure and thus it makes absolute sense to consider the O^{2-} anions as centres of oxocentred OPb$_4$ tetrahedra. The mean O−Pb length in the O1Pb$_4$ tetrahedron is 2.32 Å which is typical for such units (Krivovichev *et al.*, 1998*a*), whereas the individual values vary in the range 2.23−2.42 Å. The mean Pb···Pb distance for OPb$_4$ tetrahedra in chloroxiphite is 3.78 Å, close
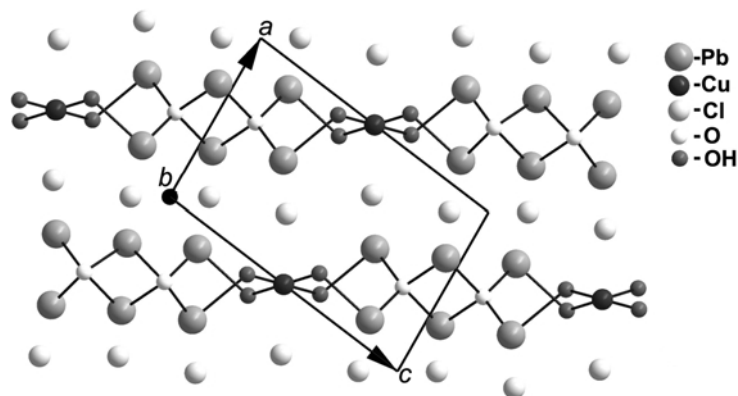

FIG. 2. The crystal structure of chloroxiphite projected along the *b* axis. Only the Pb−O, Pb−OH and Cu−OH bonds are shown.
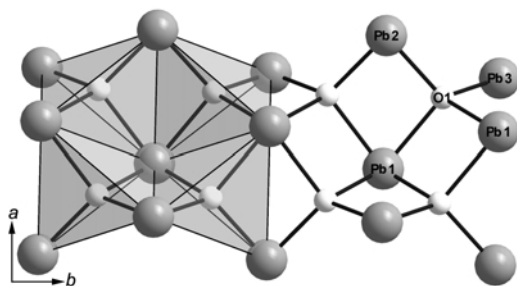
FIG. 3. Structure of $[O_2Pb_3]^{2+}$ chains in the crystal structure of chloroxiphite.

to the typical value of 3.74 Å given by Krivovichev and Filatov (1999).

The OPb$_4$ tetrahedra link together via common edges to form $[O_2Pb_3]^{2+}$ double chains (Fig. 3). In this unit, each tetrahedron shares three of six edges with adjacent tetrahedra. The $[O_2Pb_3]^{2+}$ double chains extend along the b axis. The Pb-Pb shared edges are shorter than the non-shared ones. Parallel to the chains of oxocentred tetrahedra are $[Cu(OH)_2Cl_2]^{2-}$ single chains (Fig. 4) formed by face-sharing $Cu(OH)_2Cl_2$ octahedra. The $[Cu(OH)_2Cl_2]^{2-}$ and $[O_2Pb_3]^{2+}$ chains are connected via Pb−OH bonds to form layers parallel to ($\bar{1}01$) which are connected through Pb−Cl bonds only.

Discussion

The structure of chloroxiphite is an example of a Pb oxyhalide based on $[O_2Pb_3]^{2+}$ chains (Siidra and Krivovichev, 2008) built from the OPb$_4$ oxocentred tetrahedra. These chains have been observed previously in crystal structures of natural and synthetic lead oxyhalide compounds (Siidra et al., 2008a). In mendipite (Krivovichev and Burns, 2001; Siidra et al., 2008b), the chains extend along the b axis. They have two mutually
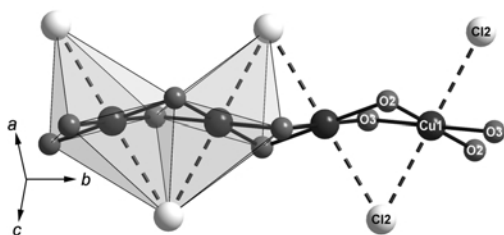

FIG. 4. Structure of $[Cu(OH)_2Cl_2]^{2-}$ chains in the crystal structure of chloroxiphite.

perpendicular orientations and are linked through weak Pb−Cl bonds only. In contrast, in damaraite, the $[O_2Pb_3]^{2+}$ chains are linked through OH groups to form $[Pb_3O_2](OH)$ sheets. As is common in structures containing Pb−O/OH clusters, OH groups in damaraite form two short (OH)−Pb bonds that result in $(OH)Pb_2$ dimers. In the structures of $Pb_7O_4(OH)_4X_2$ (X = Cl, Br) (Krivovichev and Burns, 2002; Siidra et al., 2007), the $[O_2Pb_3]^{2+}$ chains are linked by the $(OH)Pb_2$ dimers into a 3-dimensional framework, that hosts Cl$^-$ anions.

Chloroxiphite differs from other natural oxyhalides in the presence of Cu^{2+} cations that form an independent structural unit. In this sense, chloroxiphite can be considered as a modular structure consisting of both strongly bonded cation- and anion-centred units. Another such structure is philolithite, $[Pb_2O]_6[Mn(Mg,Mn)_2(Mn,Mg)_4(OH)_{12}(SO_4)(CO_3)_4]Cl_4$ (Moore et al., 2000), that consists of a complex framework of Mn- and Mg-centred octahedra, SO$_4$ and CO$_3$ groups that host chains of trans-edge-sharing OPb$_4$ tetrahedra. According to Kampf et al. (1998), philolithite occurs as crust-like overgrowths and simple tetragonal tablets in a matrix of calcite-rich Mn oxide from the Långban Fe-Mn mineral deposit. The Långban mine has many geochemical and mineralogical similarities to the Mendip manganese deposits that explain structural and chemical relations between chloroxiphite, philolithite and other Pb oxyhalide species (e.g. Turner, 2006).

The combination of Pb-oxyhalide and transition-metal chemistries (Cu, Zn, Mn, Fe, etc.) may be a productive pathway to the synthesis of new compounds that combine properties and characterisics of both. It is also possible that chloroxiphite and philolithite are not the only mineral species with such architecture and that other minerals of this kind will be discovered.

Acknowledgements

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