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ANTLERITE, $Cu_3SO_4(OH)_4$, A HETEROPOLYHEDRAL WALLPAPER STRUCTURE

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ABSTRACT

The crystal structure of antlerite, $Cu_3SO_4(OH)_4$, orthorhombic, *a* 8.244(2), *b* 6.043(1), *c* 11.987(3) Å, *V* 597.1(2) Å^3, $Z = 4$, space group *Pnma*, has been refined by a full-matrix least-squares procedure to an *R* index of 3.1 % for 754 observed ($I \geq 2.5\sigma I$) reflections using graphite-monochromated, Mo*K*α X radiation. The two unique Cu atoms are in octahedral coordination with reasonably strong Jahn–Teller distortion, <Cu–O> (equatorial) = 1.98 Å, <Cu–O> (apical) = 2.54 Å. The hydrogen atoms were located, and a sensible hydrogen-bonding scheme was assigned. The structure consists of triple chains of edge-sharing $Cu\phi_6$ octahedra (ϕ: unspecified anion) extending along the *Y* axis, with further along-chain linkage supplied by staggered flanking (SO_4) groups. Viewed down [010], the structure consists of triple chains viewed end-on, cross-linked by sulfate tetrahedra; in this projection, the structure can be idealized as monomeric and dimeric colorings of the triangular tesselation (3^6).

Keywords: antlerite, crystal structure, copper, Jahn–Teller effect, sulfate, chains of octahedra.

SOMMAIRE

La structure cristalline de l'antlerite, $Cu_3SO_4(OH)_4$, orthorhombique, *a* 8.244(2), *b* 6.043(1), *c* 11.987(3) Å, *V* 597.1(2) Å^3, $Z = 4$, groupe spatial *Pnma*, a été affinée par moindres carrés sur matrice entière jusqu'à un résidu *R* de 3.1 % pour 754 réflexions observées ($I \geq 2.5\sigma I$) (rayonnement Mo*K*α, monochromatisation au graphite). Les deux atomes distincts de Cu possèdent une coordinence octaédrique et font preuve d'une distortion de Jahn–Teller relativement importante: la longueur <Cu–O> équatoriale est de 1.98 Å, tandis que la longueur apicale est de 2.45 Å. Nous avons réussi à localiser les atomes d'hydrogène, et à déterminer un schéma raisonnable de liaisons impliquant l'hydrogène. La structure contient des chaînes triples de polyèdres $Cu\phi_6$ à arêtes partagées (ϕ: anion non spécifié), alongées selon l'axe *Y*; les groupes (SO_4) sont disposés en marge des chaînes, en alternance. Vue le long de [010], la structure montre l'aboutissement des chaînes triples, et leur articulation par les tétraèdres de sulfate. Dans cette orientation, la structure idéalisée serait un agencement de coloris monomères et de dimères définissant une tesselation triangulaire (3^6).

(Traduit par la Rédaction)

Mots-clés: antlerite, structure cristalline, cuivre, effet de Jahn–Teller, sulfate, chaînes d'octaèdres.

INTRODUCTION

Antlerite, $Cu_3(SO_4)(OH)_4$, forms mainly by oxidation of copper-bearing sulfides. It commonly occurs as crusts on chalcocite, associated with brochantite $Cu_4(SO_4)(OH)_6$, and as vein infillings, where it has been deposited by low-temperature solutions. Although uncommon elsewhere, antlerite is the principal ore mineral at Chuquicamata, Chile (Bandy 1938), where the aridity of the environment has allowed antlerite to accumulate. It is also found in a somewhat similar mineralogical association but very different environment as one of the components of the weathering patina developing on the Statue of Liberty. Apparently the copper skin of the statue altered initially to cuprite, then to brochantite (Matyi & Baboian 1986). More recent samples from weathered parts of the statue show that the brochantite has altered to antlerite, perhaps as a result of exposure to acid rain.

The crystal structure of antlerite is further refined here to elucidate the details of its hydrogen-bonding arrangement, and to analyze the polyhedral connectivity in terms of recent ideas on structural hierarchy (Hawthorne 1985a, 1986).

EXPERIMENTAL METHODS

The crystals used in this work are from Torre Capdulla, Lerida, Italy; they are now in the collection of the Department of Mineralogy, Royal Ontario Museum, catalogue number M43756.

The intensity data were collected and reduced according to the method of Hawthorne (1985b): pertinent data are given in Table 1. Ten strong reflections, uniformly distributed with regard to 2θ, were measured at 10° intervals of psi (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 350°. The crystal shape was modeled as an ellipsoid, reducing *R* (azimuthal) from 3.4 to 1.9%. Application of the correction to all the intensity data resulted in minimum and maximum transmissions of 0.10 and 0.14, respectively.

Systematic absences are compatible with the space group *Pnma* assigned by Finney & Araki (1963). Scattering curves for neutral atoms, together with anomalous dispersion coefficients, were taken from the International Tables for X-ray Crystallography (1974). *R* indices are of the form given in Table 1,

TABLE 1. MISCELLANEOUS INFORMATION FOR ANTLERITE

a	8.244(2) Å	Crystal size (mm)	0.14x0.16x0.18
b	6.043(1) Å	Rad/Mono	Mo/Gr
c	11.987(3) Å	Total |Fo|	954
V	597.1(2)$Å^3$	|Fo|, I>2.5σI	754
Space Group	Pnma	Final R (obs)	3.3%
Cell content:	$4[Cu_3SO_4(OH)_4]$	Final wR (obs)	3.1%

$R = \Sigma(/Fo|-|Fc|)/\Sigma|Fo|$

$wR = [\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2]^{\frac{1}{2}}$, $w = 1/(\sigma^2F+0.0032(2)F^2)$

and are expressed as percentages. Using the results of Finney & Araki (1963) as input, the refinement converged rapidly to an *R* index of 3.2% using an anisotropic thermal model. At this stage, recognizable H positions were taken from difference-Fourier maps; however, refinement of these positions caused the O–H distances to shorten significantly (a feature typical of X-ray structure refinements), making the interpretation of the hydrogen-bonding scheme rather difficult. Consequently, the hydrogen positions were taken from the difference-Fourier map and kept fixed during the final cycle of refinement. Final convergence occurred at an *R* index of 3.2% and a *wR* index of 3.1%. Final parameters are given in Table 2; the observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Selected interatomic distances and angles are given in Table 3, a suggested hydrogen-bonding scheme in Table 4, and a bond-valence analysis in Table 5.

DISCUSSION

There is one unique S position in the antlerite structure, surrounded by four oxygen atoms in a slightly distorted tetrahedral arrangement; the minor bond-length variations are compatible with the local bond-valence requirements of the anions in the structure (Table 5). There are two unique Cu positions, both surrounded by six anions in distorted octahedral arrangements. In both cases, there are four short equatorial distances and two longer apical distances, indicative of Jahn–Teller distortion, as is usual for most octahedrally coordinated Cu^{2+} in minerals. Inspection of the bond-length distortion ($\Delta = \Sigma[(l_i-l_o)/l_o]^2$) and bond-angle distortion ($\sigma^2 = \Sigma(90-\theta)^2/12$) parameters (Δ: Cu(1) = 0.064, Cu(2) = 0.053; σ^2: Cu(1) = 133.9, Cu(2) = 21.6) shows that whereas the two distinct $Cu\phi_6$ octahedra have similar bond-length distortions, the Cu(1) octahedron has far more angular distortion than the Cu(2) octahedron. This angular distortion is such that the Cu–Cu distances are significantly increased over that for the same arrangement with regular octahedra. Such a distortion is not directly related to the Jahn–Teller effect, as the latter could occur in a triple chain of edge-sharing octahedra without any angular distortion. However, such Jahn–Teller type bond-length distortion will bring the Cu atoms in each of the linear chains closer together, and the angular relaxation seen here will offset this effect. This effect is more extreme for the $Cu(1)\phi_6$ (ϕ = unspecified ligand) octahedron, as it is equatorially surrounded by six $Cu\phi_6$ octahedra, whereas the $Cu(2)\phi_6$ octahedron is only linked to four $Cu\phi_6$ octahedra.

Bond-valence analysis (Table 5) shows the hydroxyl ions to have a slight excess of bond valence, which suggests the presence of significant hydrogen bonding between them and the oxygen atoms, which show slight bond-valence deficiencies if the contributions from hydrogen bonding are not considered. A hydrogen bonding scheme is suggested in Table 4, with the corresponding bond-valence distribution shown in Table 5. The OH(3)–H(3)...O(1) angle of 118° is smaller than that usually observed, but does

TABLE 2. FINAL ATOMIC PARAMETERS FOR ANTLERITE

Atom	x	y	z	*U equiv.	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.0049(1)	1/4	0.00135(7)	121(2)	145(3)	81(3)	137(3)	0	-33(2)	0
Cu(2)	0.28982(5)	0.00278(9)	0.12585(4)	123(1)	126(2)	97(2)	146(2)	-1(2)	-20(2)	12(2)
S	0.1304(2)	1/4	0.3642(1)	106(3)	109(6)	100(6)	108(6)	0	3(5)	0
O(1)	0.2618(5)	1/4	0.2829(4)	170(12)	145(20)	154(21)	209(23)	0	22(17)	0
O(2)	0.1979(5)	1/4	0.4778(4)	168(12)	216(22)	144(20)	143(21)	0	-60(18)	0
O(3)	0.0312(3)	0.0481(5)	0.3477(3)	158(8)	137(12)	120(14)	218(14)	-15(10)	15(11)	-24(11)
OH(1)	0.2809(5)	1/4	0.0250(4)	133(11)	150(20)	111(19)	137(21)	0	4(17)	0
OH(2)	0.7010(5)	1/4	0.7792(3)	129(11)	130(19)	114(20)	142(21)	0	-6(16)	0
OH(3)	0.0469(3)	0.5060(5)	0.1016(2)	127(7)	141(12)	129(12)	110(11)	18(13)	10(10)	-12(13)
**H(1)	0.373	1/4	0.971	100						
**H(2)	0.220	3/4	0.261	100						
**H(3)	0.497	0.025	0.660	100						

$^*U_{ij} = U_{ij} \times 10^4$; **fixed during refinement

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN ANTLERITE

S-O(1)	1.457(5)		
S-O(2)	1.471(5)	Cu(2)-OH(1)	1.923(3)
S-O(3)	1.482(3) x2	Cu(2)-O(3)e	2.033(3)
<S-O>	1.473	Cu(2)-OH(2)f	1.906(3)
		Cu(2)-OH(3)a	2.024(3)
Cu(1)-OH(3),a	1.989(3) x2	Cu(2)-O(2)g	2.344(4)
Cu(1)-OH(3)b,c	1.970(3) x2	Cu(2)-O(1)	2.414(4)
Cu(1)-OH(1)	2.293(4)	<Cu(2)-O>	2.107
Cu(1)-O(2)d	2.543(5)		
<Cu(1)-O>	2.126		
Possible hydrogen...bond contacts			
OH(1)...O(3)	3.188(5) x2	OH(3)...O(1)	3.136(5)
		OH(3)...O(3)	2.971(5)
OH(2)...O(3)	3.230(5) x2	OH(3)...OH(2)	3.299(5)
O(1)-O(2)	2.396(7)	O(1)-S-O(2)	109.8(3)
O(1)-O(3)	2.389(5) x2	O(1)-S-O(3)	108.7(2) x2
O(2)-O(3)	2.410(5) x2	O(2)-S-O(3)	109.4(2) x2
O(3)-O(3)a	2.440(6)	O(3)-S-O(3)a	110.8(2)
<O-O>S	2.406	<O-S-O>	109.5
OH(1)-OH(3)	2.637(5)	OH(1)-Cu(1)-OH(3)	75.7(1) x2
OH(1)-OH(3)c	3.432(6)	OH(1)-Cu(1)-OH(3)c	107.0(1) x2
OH(3)-O(2)d	3.404(6)	OH(3)-Cu(1)-O(2)d	96.6(1) x2
OH(3)-OH(3)b	2.557(6)	OH(3)-Cu(1)-OH(3)b	80.5(1) x2
OH(3)-OH(3)a	3.094(6)	OH(3)-Cu(1)-OH(3)a	102.1(2)
O(2)d-OH(3)c	2.967(5)	O(2)d-Cu(1)-OH(3)c	81.1(1) x2
OH(3)b-OH(3)c	2.949(6)	OH(3)b-Cu(1)-OH(3)c	96.9(2)
<O-O>Cu(1)	3.003	<O-Cu(1)-O>	90.1
O(1)-OH(1)	3.095(7)	O(1)-Cu(2)-OH(1)	90.3(1)
O(1)-O(3)e	2.978(5)	O(1)-Cu(2)-O(3)e	83.6(1)
O(1)-OH(2)f	3.127(3)	O(1)-Cu(2)-OH(2)f	91.9(1)
O(1)-OH(3)a	3.202(5)	O(1)-Cu(2)-OH(3)a	91.9(1)
OH(1)-O(2)g	3.079(2)	OH(1)-Cu(2)-O(2)g	91.8(1)
OH(1)-O(3)e	2.841(5)	OH(1)-Cu(2)-O(3)e	91.8(2)
OH(1)-OH(3)a	2.637(5)	OH(1)-Cu(2)-OH(3)a	83.8(2)
O(2)g-O(3)e	3.344(6)	O(2)g-Cu(2)-O(3)e	99.4(1)
O(2)g-OH(2)f	2.913(6)	O(2)g-Cu(2)-OH(2)f	85.9(1)
O(2)g-OH(3)a	2.967(5)	O(2)g-Cu(2)-OH(3)a	85.2(1)
O(3)e-OH(2)f	2.754(5)	O(3)e-Cu(2)-OH(2)f	88.6(2)
OH(2)f-OH(3)a	2.921(5)	OH(2)f-Cu(2)-OH(3)a	96.0(2)
<O-O>Cu(2)	2.988	<O-Cu(2)-O>	90.0

Equivalent positions: a:x, 1/2-y,z; b:$\bar{x}$, 1-y, $\bar{z}$; c:$\bar{x}$,1/2+y-1,$\bar{z}$; d:1/2+x-1, y, 1/2-z; e:1/2+x, y, 1/2-z; f:1-x, $\bar{y}$, 1-z; g:1/2-x, $\bar{y}$, 1/2+z-1

TABLE 4. SUGGESTED HYDROGEN-BONDING SCHEME IN ANTLERITE

OH(1)....O(3)	3.188(5)Å		
OH(1)-H(1)	1.00	OH(1)-H(1)....O(3)	168°
H(1).....O(3)	2.46 x2		
OH(2)....O(3)	3.230(5) x2		
OH(2)-H(2)	0.81	OH(2)-H(2)....O(3)	136
H(2).....O(3)	2.60 x2		
OH(3)....O(3)	2.971(5)		
OH(3)....O(1)	3.136(5)	OH(3)-H(3)....O(1)	118
OH(3)-H(3)	0.80	OH(3)-H(3)....O(3)	142
H(3).....O(3)	2.30		
H(3).....O(1)	2.68		

TABLE 5. BOND-VALENCE* TABLE FOR ANTLERITE

	Cu(1)	Cu(2)	S	Σ	H(1)	H(2)	H(3)	Σ
O(1)		0.130$^{\times2}_{\rightarrow}$	1.584	1.844			0.114	1.958
O(2)	0.095	0.155$^{\times2}_{\rightarrow}$	1.521	1.926				1.926
O(3)		0.364	1.443$^{\times2}_{\downarrow}$	1.807	0.097$^{\times2}_{\downarrow}$	0.036$^{\times2}_{\downarrow}$	0.115	2.025
OH(1)	0.177	0.508$^{\times2}_{\rightarrow}$		1.193	0.807			2.0
OH(2)		0.536$^{\times2}_{\rightarrow}$		1.072		0.928		2.0
Oh(3)	0.415$^{\times2}_{\downarrow}$ 0.440$^{\times2}_{\downarrow}$	0.374		1.229			0.771	2.0
Σ	1.982	2.067	5.991		1.0	1.0	1.0	

*calculated from the curves of Brown (1981).

not exceed the observed range for hydrogen bonds from neutron-diffraction data (Baur 1972).

Each Cu(1)ϕ_6 octahedron links by *trans* edge-sharing to two other Cu(1)ϕ_6 octahedra to form a rutile-like chain; similarly, each Cu(2)ϕ_6 octahedron links by *trans* edge-sharing to form a rutile-like chain. Three of these chains then merge by edge-sharing to form a triple chain, a central Cu(1)ϕ_4 chain flanked by two Cu(2)ϕ_4 chains. One of these units is shown in Figure 1. Alternate pairs of Cu(2)ϕ_6 octahedra are linked through one set of their axial ligands by (SO$_4$) groups; this forces the Cu(2)ϕ_4 to be modulated such that the axial vertex separation along the chain is alternately long and short, the short separation corresponding to the position of the linking (SO$_4$) group. These (SO$_4$) groups adopt a staggered configuration either side of the triple chain; note that this is a cooperative distortion such that the shortening of alternate vertex separations on one side of the chain spontaneously produces an offset distortion on the other side of the chain (see Fig. 1), explaining why the sulfate groups usually assume a staggered configuration in these edge-sharing chain structures (Hawthorne, in prep.). Also, note that this cooperative series of displacements produces large angular distortions of the polyhedra in the central chain [the Cu(1)ϕ_6 octahedra], distortions that correspond to the values actually observed in antlerite. Thus, although one can make the normal argument (see above) that the Cu(1) octahedron shows strong angular distortion to decrease cation–cation repul-

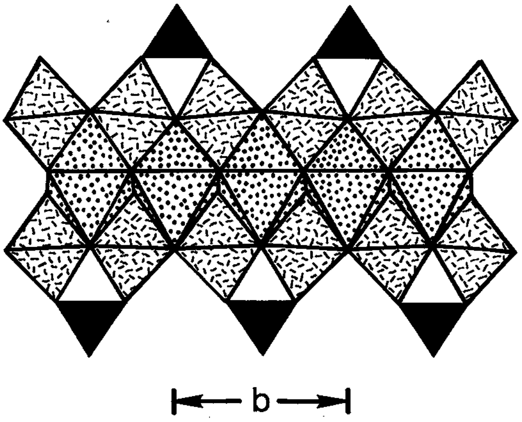

FIG. 1. The edge-sharing octahedral triple chain that extends along the *Y* axis in antlerite; the triple chain is made of three "rutile-like" edge-sharing chains that fuse by edge-sharing, giving a repeat of ≈ 3 Å along *Y*. Further along-chain linkage is provided by the (SO$_4$) tetrahedra (shown in black), which repeat in a staggered fashion on either side of the chain; this staggering doubles the *Y*-axis repeat to ≈ 6 Å. The Cu(1) octahedra are shown dotted, and the Cu(2) tetrahedra are shown dashed.

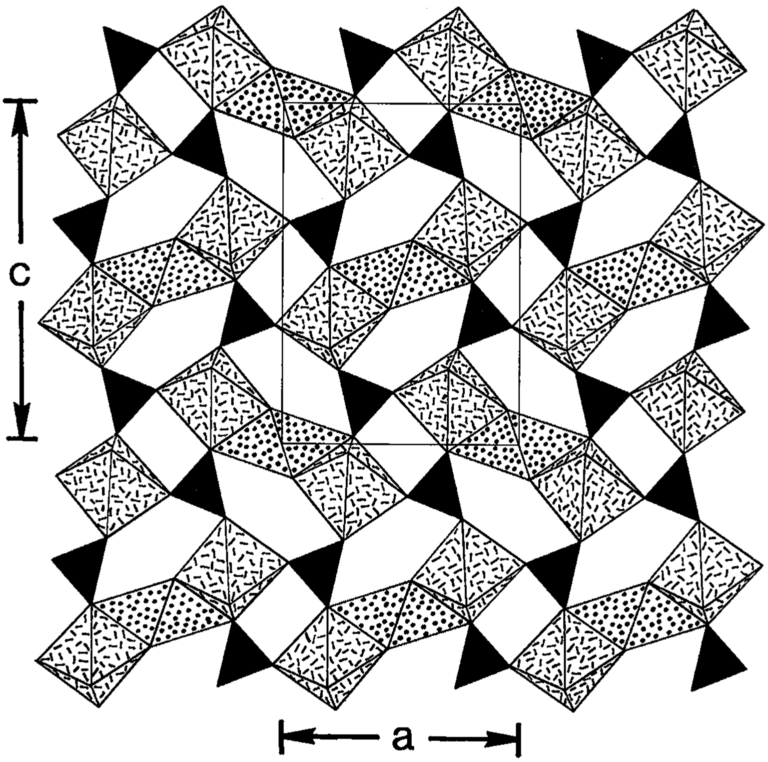

FIG. 2. Projection of the antlerite structure onto (010); shading as in Figure 1. The edge-sharing triple chains (shown in Fig. 1) are seen "end-on", and are cross-linked into a heteropolyhedral framework by corner-sharing between octahedra and tetrahedra.

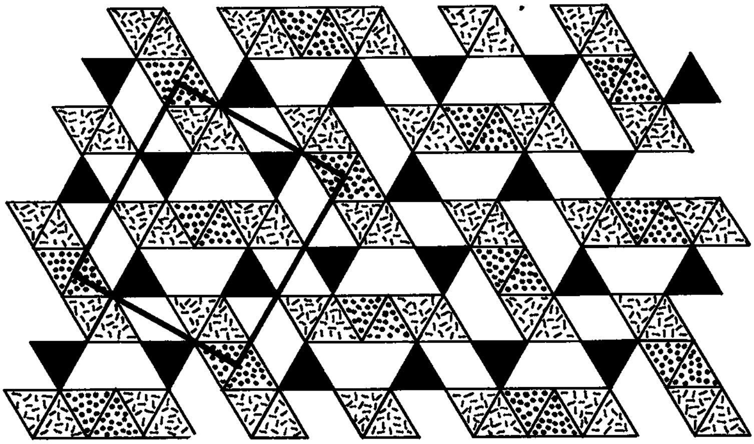

FIG. 3. Geometrical idealization of Figure 2. The [010] projection of antlerite expressed as a mixed monomeric–dimeric coloring of the triangular tesselation 3^6.

sion, we suggest that the distortions result from the linkage requirements of disparate-sized polyhedra with this (graphical) arrangement.

In Figure 1, it can be seen that the *Y*-axis repeat is controlled by the repeat distance along the triple chain (+ linking tetrahedra), that is, b = 6.04 Å. A projection of the structure down *Y* (Fig. 2) shows that the edge-sharing octahedral chains are three octahedra wide, and are also cross-linked by octahedral–tetrahedral vertex sharing; the structure is thus a mixed tetrahedral–octahedral framework structure (Hawthorne 1983, 1985a, 1987). This structure may be geometrically idealized while retaining its graphical (in the mathematical sense) characteristics. This idealized structure (Fig. 3) is a tetrahedral analog of what Moore & Araki (1974) called the complex 3 Å wallpaper structures. The 3 Å comes from the repeat distance along a rutile-like chain; the actual repeat is often a multiple of 3 Å, caused by ordering of cations either within the chain or flanking the chain (as for antlerite itself, in which $b = 6.04 \approx 2 \times 3$ Å). Hawthorne (1986) showed that there are polyborate representatives of the triangular–octahedral family, and there are also polymerized tetrahedral representatives (Eby & Hawthorne, unpublished). This family of structures is extremely large, and may be viewed as monomeric and dimeric colorings of the triangular tesselation (3^6); the combinatorial aspects of this family are currently under investigation.

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