

The crystal structure of szenicsite, $\text{Cu}_3\text{MoO}_4(\text{OH})_4$

PETER C. BURNS

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana 46556-0767, USA

ABSTRACT

The crystal structure of szenicsite, $\text{Cu}_3\text{MoO}_4(\text{OH})_4$, orthorhombic, $a = 8.5201(8)$, $b = 12.545(1)$, $c = 6.0794(6)$ Å, $V = 649.8(2)$ Å³, space group $Pnmm$, $Z = 4$, has been solved by direct methods and refined by least-squares techniques to an agreement index (R) of 3.34% and a goodness-of-fit (S) of 1.11 for 686 unique observed [$|F| \geq 4\sigma_F$] reflections collected using graphite-monochromated Mo- $K\alpha$ X-radiation and a CCD area detector. The structure contains three unique Cu^{2+} positions that are each coordinated by six anions in distorted octahedral arrangements; the distortions of the octahedra are due to the Jahn-Teller effect associated with a d^9 metal in an octahedral ligand-field. The single unique Mo^{6+} position is tetrahedrally coordinated by four O^{2-} anions. The $\text{Cu}^{2+}\phi_6$ (ϕ : unspecified ligand) octahedra share *trans* edges to form rutile-like chains, three of which join by the sharing of octahedral edges to form triple chains that are parallel to [001]. The MoO_4 tetrahedra are linked to either side of the triple chain of $\text{Cu}^{2+}\phi_6$ octahedra by the sharing of two vertices per tetrahedron, and the resulting chains are cross-linked through tetrahedral-octahedral vertex sharing to form a framework structure. The structure of szenicsite is closely related to that of antlerite, $\text{Cu}_3\text{SO}_4(\text{OH})_4$, which contains similar triple chains of edge-sharing $\text{Cu}^{2+}\phi_6$ octahedra.

KEYWORDS: szenicsite, copper oxysalt, crystal structure, molybdate, Chile.

Introduction

SZENICSITE, $\text{Cu}_3\text{MoO}_4(\text{OH})_4$, was recently described by Francis *et al.* (1997). Large crystals of szenicsite occur at the only known locality, the Jardinería No. 1 mine in Chile's Atacama province, where it is associated with powellite as fracture fillings and as crystals in vugs in a hydrothermally altered granitic matrix (Francis *et al.*, 1997). The large (1 cm diameter) crystals of szenicsite facilitate X-ray diffraction studies; the results of a crystal-structure determination are presented herein.

Experimental

A sample containing several large (~1 cm diameter) crystals of szenicsite, originating from the Atacama province of Chile, was obtained from the Geological Survey of Canada (number 67409). A crystal fragment with dimensions $0.30 \times 0.10 \times 0.04$ mm was selected for study. The crystal was mounted on a Siemens

PLATFORM goniometer equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of five cm. The 1K SMART CCD detector is a two-dimensional area detector with a nine cm diameter active-imaging area. The CCD detector provides improved resolution, sensitivity to weak reflections, and shorter data collection times as compared to a scintillation detector mounted on a serial diffractometer.

The data were collected using monochromatic Mo- $K\alpha$ X-radiation and ω scans (frame widths) of 0.3° , with 10 s used to acquire each frame. More than a hemisphere of three-dimensional data was collected and the data were analysed to locate peaks for the determination of the unit-cell dimensions. The unit-cell dimensions (Table 1) were refined with 2230 reflections using least-squares techniques. Data were collected for $3^\circ \leq 2\theta \leq 58.5^\circ$ and covered the index ranges $10 \leq h \leq 10$, $-15 \leq k \leq 13$, $-7 \leq l \leq 6$. The data were collected in approximately six hours and the intensities of the standard reflections showed no

TABLE 1. Miscellaneous information for szenicsite

a (Å)	8.5201(8)	Crystal size (mm)	0.30×0.10
b (Å)	12.545(1)		$\times 0.04$
c (Å)	6.0794(6)	Total Ref.	3380
V (Å ³)	649.8(2)	Unique Ref.	743
Space group	$Pnmm$	R_{int}	4.41
$F(000)$	788	Unique $ F_o \geq 4\sigma_F$	686
D_{calc}	4.279 g/cm ³	Final R	3.34
μ	11.57 mm ⁻¹	Final S	1.11
Unit-cell contents: $4\{Cu_3MoO_4(OH)_4\}$			

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}$$

$$S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}, \text{ for } m \text{ observations and } n \text{ parameters}$$

significant change during the data collection. The data were corrected for Lorentz, polarization, and background effects. An empirical absorption-correction was done based upon 1528 intense reflections. The crystal was modeled as an ellipse, lowering $R_{azimuthal}$ of the 1528 intense reflections from 5.35 to 3.94%. A total of 3380 reflections was collected, of which there were 743 unique reflections with 686 classed as observed [$|F| \geq 4\sigma_F$].

Structure solution and refinement

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers and Hamilton, 1974). The Siemens SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure.

Reflection statistics indicated the space groups $Pnmm$ or $Pnn2$, and assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.946, indicating the space group $Pnmm$. The space group $Pnmm$ was verified by the successful solution of the structure by direct methods. Refinement of all atomic-positional parameters, and allowing for isotropic atomic-displacement, gave a model with an agreement index (R) of 6.08%. Conversion of the displacement parameters to anisotropic, together with the inclusion of a refinable weighting-scheme of the structure factors, provided a model with an R of 3.44%. At this stage of the refinement the locations of three H atoms were obtained from difference-Fourier maps, and their positional parameters were added to the refinement. The final model gave an R of 3.34% for 686 observed

reflections [$|F| \geq 4\sigma_F$] and a goodness-of-fit (S) of 1.11. The maximum peak and trough in the difference-Fourier maps were 1.3 and -0.85 e/Å^3 , respectively. The final atomic-positional parameters and anisotropic-displacement parameters are given in Table 2, selected interatomic distances and angles are given in Table 3, and a bond-valence analysis is given in Table 4. A list of calculated and observed structure factors has been deposited with the editor of *Mineralogical Magazine* and is available on request.

Discussion

Cation coordination

There are three symmetrically distinct Cu^{2+} positions in the structure; each is coordinated by six anions in a distorted-octahedral arrangement. All three $Cu^{2+}\phi_6$ (ϕ : unspecified anion) octahedra are elongated, such that there are four short ($\sim 1.95 \text{ Å}$) equatorial bonds and two longer ($\sim 2.3 \text{ Å}$) apical bonds, a (4+2) distortion. Virtually all $Cu^{2+}\phi_6$ octahedra in mineral structures are similarly distorted (Burns and Hawthorne, 1996), owing to the well-known Jahn-Teller effect (Jahn and Teller, 1937) that is associated with the electronic energy-degeneracy of a d^9 cation in an octahedral ligand-field.

The $Cu_3\phi_6$ octahedron contains only $(OH)^-$ anions, and the $\langle Cu^{2+}-OH \rangle$ bond-length is 2.092 Å , with a calculated bond-valence sum at the Cu^{2+} site of 1.98 vu (Table 4). The remaining two $Cu^{2+}\phi_6$ octahedra contain both O^{2-} and $(OH)^-$ anions, with the apical positions of the (4+2)-distorted octahedra occupied by O^{2-} anions. The $Cu_1O_3(OH)_3$ and $Cu_2O_2(OH)_4$ octahedra have $\langle Cu^{2+}-\phi \rangle$ bond-lengths of 2.099 and 2.115 Å , respectively, and the bond-

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TABLE 2. Final atomic parameters for szenicsite

	<i>x</i>	<i>y</i>	<i>z</i>	* <i>U</i> _{eq}	** <i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu1	0.26870(9)	0.13257(5)	-0.2495(1)	142(2)	203(4)	128(4)	94(4)	-15(2)	3(3)	3(2)
Cu2	0	0	-½	144(3)	217(7)	129(6)	85(6)	-31(5)	0	0
Cu3	0	0	0	151(3)	229(7)	149(6)	76(6)	-25(5)	0	0
Mo	0.12421(9)	0.36909(5)	0	142(2)	198(4)	125(4)	103(3)	6(2)	0	0
O1	0.2673(7)	0.2687(4)	0	177(11)	240(30)	121(26)	170(26)	5(20)	0	0
O2	0.0086(6)	0.3575(4)	0.2380(6)	214(10)	223(22)	265(23)	154(20)	30(17)	-10(18)	2(15)
O3	0.2223(7)	0.4925(4)	0	195(13)	251(32)	184(28)	151(27)	-5(23)	0	0
OH4	0.2737(8)	0.0375(4)	0	179(12)	272(34)	165(28)	100(25)	24(24)	0	0
OH5	0.0288(5)	0.1008(3)	-0.2509(6)	159(8)	220(22)	113(18)	146(19)	24(16)	-20(16)	-6(15)
OH6	0.2583(7)	0.2256(4)	-½	157(12)	252(29)	118(26)	103(23)	18(23)	0	0
H1	0.34(1)	0.001(8)	0	+200						
H2	-0.025(9)	0.149(6)	-0.25(1)	+200						
H3	0.18(1)	0.230(8)	-½	+200						

* $U_{eq} = U_{eq} \text{ \AA}^2 \times 10^4$ ** $U_{ij} = U_{ij} \text{ \AA}^2 \times 10^4$

+ fixed during refinement

valence sums at the Cu1 and Cu2 sites are 2.10 and 2.04 *vu*, respectively. Inspection of the octahedral bond-angles (Table 3) reveals that all three of the Cu²⁺φ₆ octahedra are significantly distorted, presumably owing to steric constraints.

The structure contains one symmetrically distinct Mo⁶⁺ position. The Mo⁶⁺ cation is coordinated by four O²⁻ anions in a slightly distorted tetrahedral arrangement, with a <Mo⁶⁺-O> bond-length of 1.757 Å. Both the <Mo⁶⁺-O> bond-length and the sum of bond valences incident at the site (6.01 *vu*) indicate that the site is occupied only by Mo⁶⁺.

Structure connectivity

The (4+2)-distorted Cu2φ₆ and Cu3φ₆ octahedra share *trans* equatorial edges to form rutile-like chains of alternating Cu2φ₆ and Cu3φ₆ octahedra that extend along [001] (Fig. 1). The Cu1φ₆ octahedra share *trans* apical-equatorial edges, also forming rutile-like chains that extend along [001] (Fig. 1). The chains of Cu2φ₆ and Cu3φ₆ octahedra are linked on two sides to chains of Cu1φ₆ octahedra by the sharing of octahedral edges, resulting in triple chains that extend along [001] (Fig. 1). The *c* unit-cell length is controlled by the repeat distance of the triple chain of octahedra. The MoO₄ tetrahedra are linked to either side of the triple chain of Cu²⁺φ₆ octahedra

by incorporating equatorial corners of alternate pairs of Cu1φ₆ octahedra, and the MoO₄ tetrahedra on either side of the triple chain are coincident (Fig. 1).

Projection of the structure along [001] shows the nature of the linkages between adjacent triple chains of edge-sharing Cu²⁺φ₆ octahedra (Fig. 2). Each triple chain is two-connected to MoO₄ tetrahedra on either side, as illustrated in Fig. 1. Each MoO₄ tetrahedron also shares one of its two remaining ligands with octahedra of each of two adjacent triple chains, resulting in a mixed tetrahedral-octahedral framework structure. According to the structural hierarchy proposed for Cu²⁺ oxysalt minerals by Eby and Hawthorne (1993), the structure of szenicsite can be classed as a *M = M-T* framework.

Relationship to other species

Lindgrenite, Cu₃(MoO₄)₂(OH)₂, is chemically similar to szenicsite, with a Cu:Mo ratio of 3:2, as opposed to a Cu:Mo ratio of 3:1 in szenicsite. The structure of lindgrenite contains strips of edge-sharing Cu²⁺φ₆ octahedra that are parallel to [001] and are two octahedra wide (Hawthorne and Eby, 1985). The strips of octahedra are cross-linked by sharing octahedral corners with MoO₄ tetrahedra, resulting in a tetrahedral-octahedral framework that is similar to that of szenicsite (Fig. 3a).

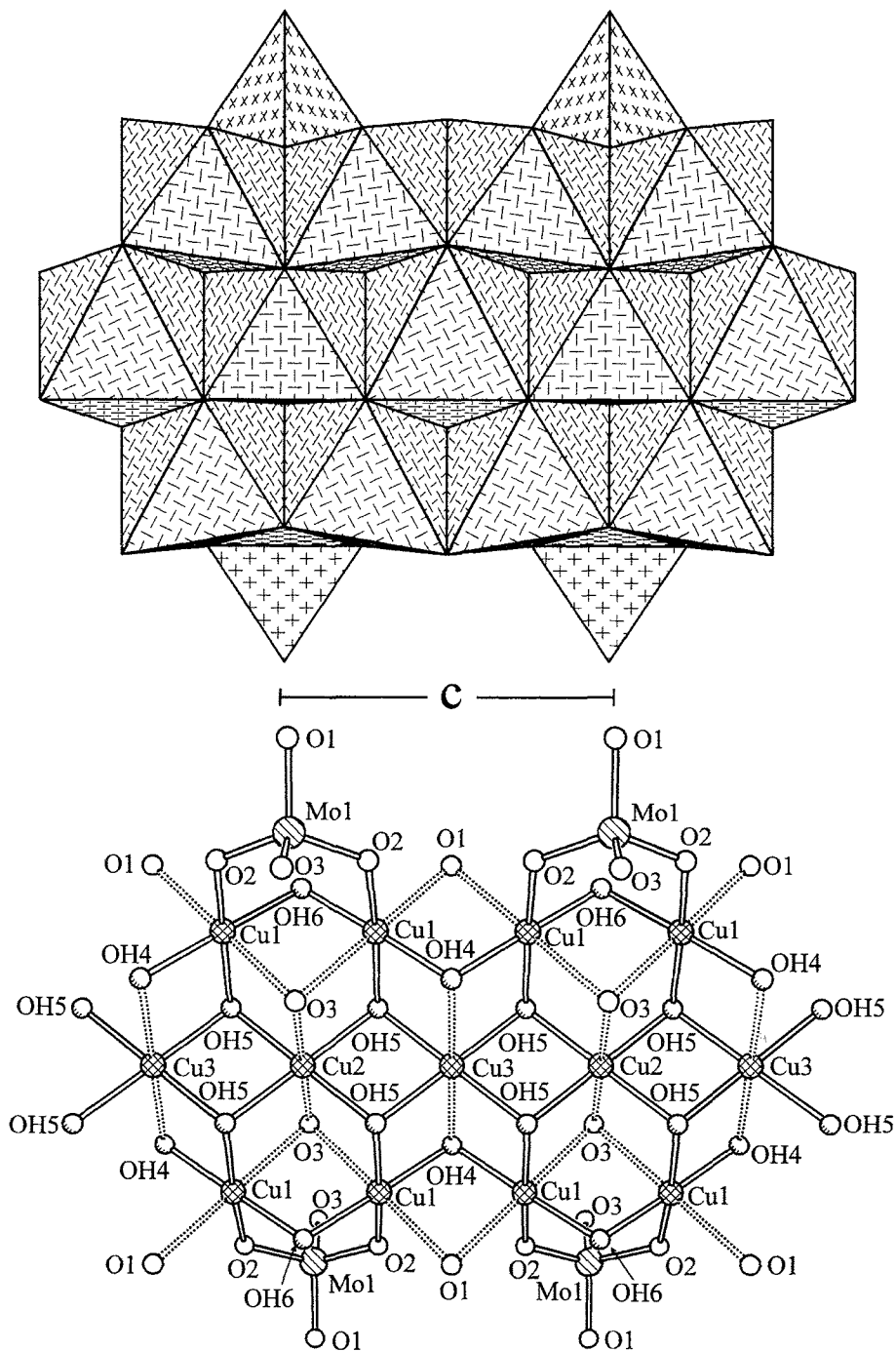


FIG. 1. The triple chain of edge-sharing $\text{Cu}^{2+}\phi_6$ octahedra in the structure of szenicsite projected along $[110]$. The $\text{Cu}^{2+}\phi_6$ octahedra are shaded with a herring-bone pattern and the MoO_4 tetrahedra are shaded with crosses. Equatorial and apical Cu^{2+} - ϕ bonds are illustrated with solid and broken lines, respectively.

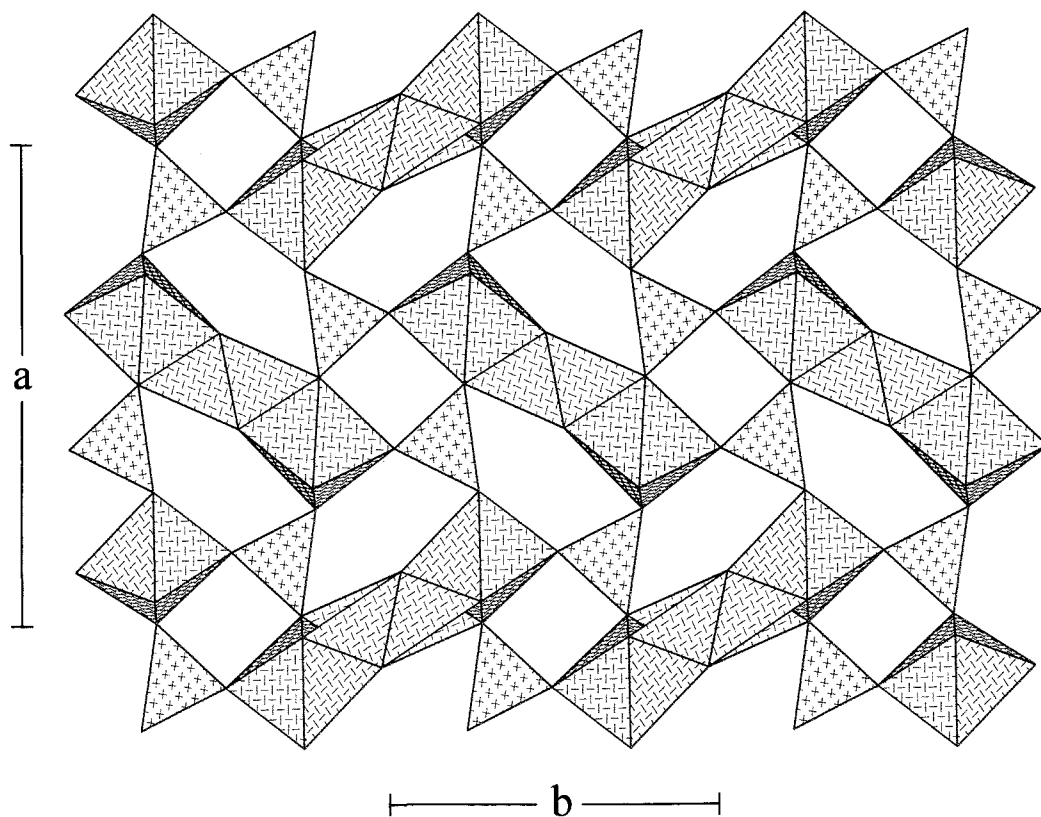


FIG. 2. The structure of szenicsite projected along [001]. Legend as in Fig. 1.

Antlerite, $\text{Cu}_3\text{SO}_4(\text{OH})_4$, is the sulphate chemical analogue of szenicsite, and has similar unit-cell dimensions: $a = 8.244(2)$, $b = 6.043(1)$, $c = 11.987(3)$ Å, but the space group $Pnma$ (Hawthorne *et al.*, 1989). The structure of antlerite is shown projected along [010] in Fig. 3*b*. The structure contains triple chains of edge-sharing $\text{Cu}^{2+}\phi_6$ octahedra that are cross-linked by tetrahedral-octahedral vertex sharing to form a framework structure (Hawthorne *et al.*, 1989) which is very similar to that of szenicsite, as can be seen by comparing Fig. 2 and 3*b*.

The triple chains of $\text{Cu}^{2+}\phi_6$ octahedra that occur in the structures of szenicsite and antlerite are compared in Fig. 4. The triple chains of $\text{Cu}^{2+}\phi_6$ octahedra are identical in each structure, but the mode of attachment of the $(\text{Mo,S})\text{O}_4$ tetrahedra results in different structures. In the szenicsite chain, the MoO_4 tetrahedra that are attached to either side of the triple chain are

coincident (Fig. 4*a*); whereas, in the antlerite chain, the SO_4 tetrahedra attached to either side of the triple chain are staggered (Fig. 4*b*), resulting in the space group $Pnma$ for the antlerite structure, as opposed to $Pnmm$ for the szenicsite structure. Hawthorne *et al.* (1989) noted that the attachment of SO_4 tetrahedra to the triple chain requires substantial distortion of the $\text{Cu}^{2+}\phi_6$ octahedra, and attributed the observed configuration of SO_4 tetrahedra to a cooperative distortion such that the shortening of alternating vertex separations on one side of the chain spontaneously produces an offset distortion of the other side of the chain, as can be seen in Fig. 4*b*. However, in the case of the szenicsite chain, the larger MoO_4 tetrahedra are attached to the triple chains without significant distortion of the $\text{Cu}^{2+}\phi_6$ octahedra, thus a staggered arrangement of MoO_4 tetrahedra on either side of the triple chain is not necessary.

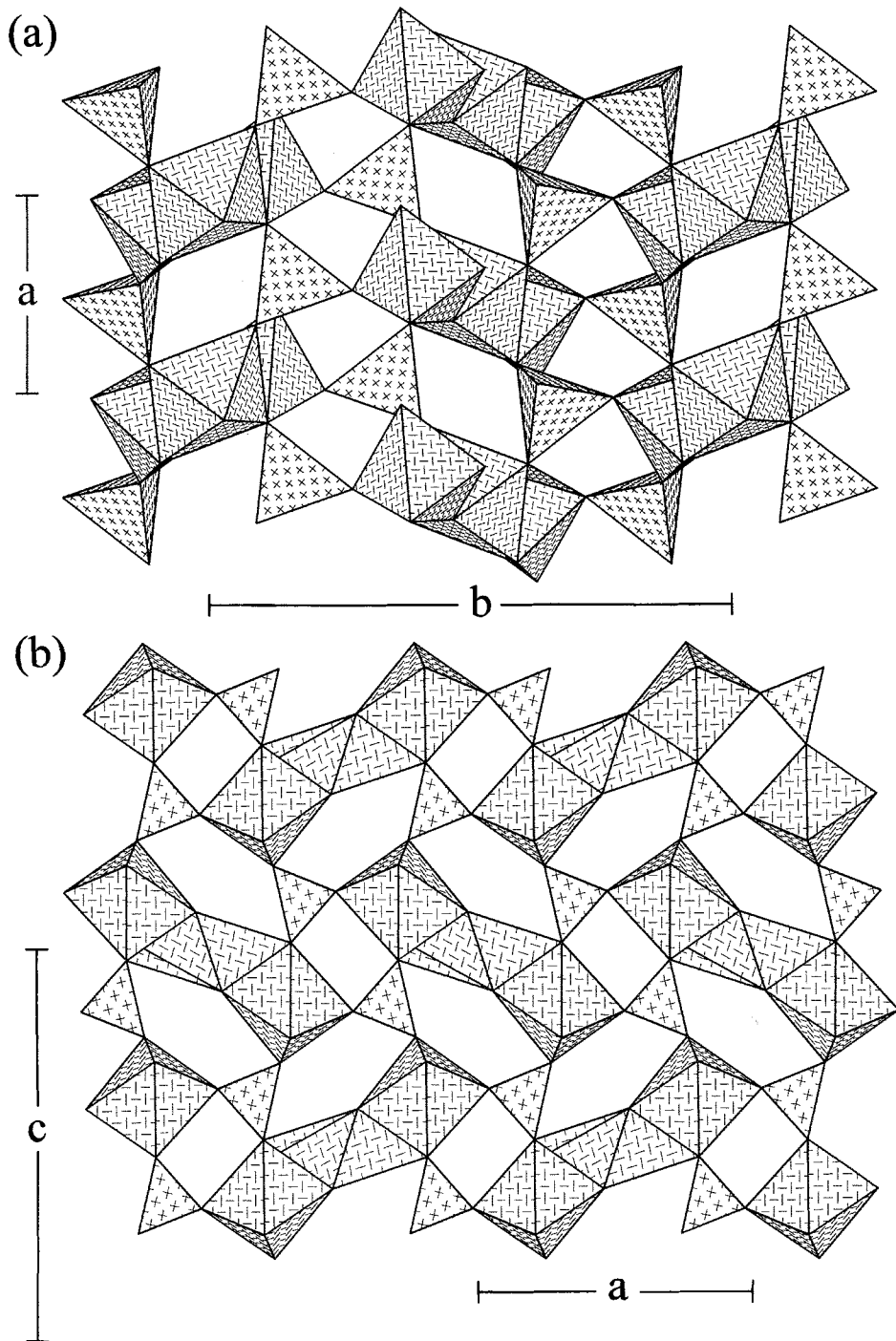


FIG. 3. The structures of Cu^{2+} oxysalts that are related to szenicsite. (a) the structure of lindgrenite projected along $[001]$, (b) the structure of antlerite projected along $[010]$. SO_4 tetrahedra are shaded with crosses in (b), otherwise legend as in Fig. 1.

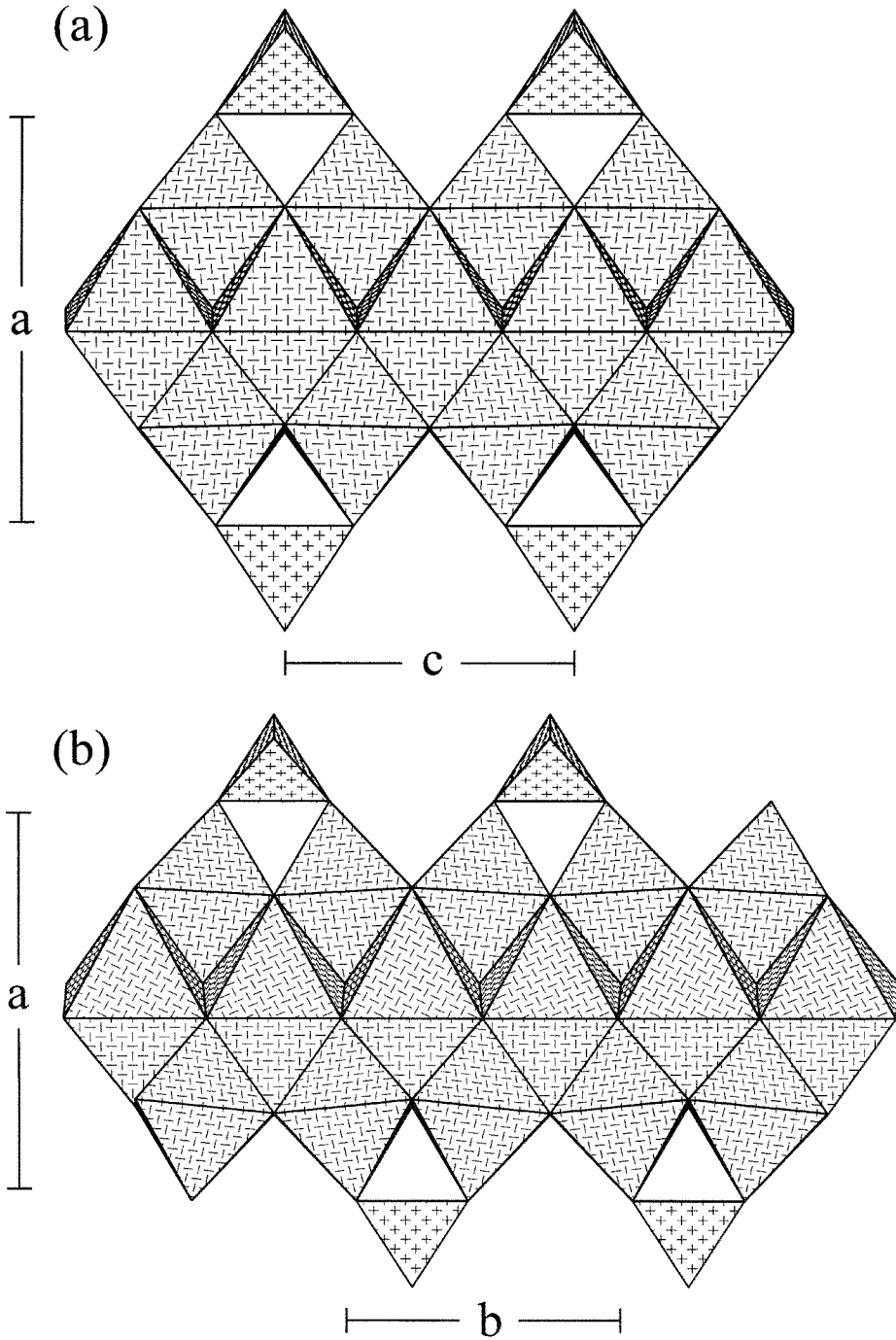


FIG. 4. Comparison of the triple chains of edge-sharing $\text{Cu}^{2+}\phi_6$ octahedra that occur in (a) szenicsite, and (b) antlerite. Legend as in Fig. 3.

TABLE 3. Selected interatomic distances (Å) and angles (°) for szenicsite

Cu1-OH6	1.921(3)	Cu3-OH5,e,g,h	1.996(4) × 4
Cu1-OH4	1.930(4)	Cu3-OH4,h	2.284(4) × 2
Cu1-O2a	2.049(5)	<Cu3-φ>	2.092
Cu1-OH5	2.082(4)		
Cu1-O1	2.284(4)	Mo-O1	1.753(5)
Cu1-O3b	2.326(4)	Mo-O2,g	1.757(4) × 2
<Cu1-φ>	2.099	Mo-O3	1.760(6)
		<Mo-O>	1.757
Cu2-OH5,c,d,e	1.988(4) × 4		
Cu2-O3b,f	2.368(6) × 2	OH5,d-Cu2-OH5c,e	180 × 2
<Cu2-φ>	2.115	OH5,c-Cu2-OH5e,d	80.8(2) × 2
		OH5,c-Cu2-OH5d,e	99.2(2) × 2
OH6-Cu1-OH4	178.4(3)	OH5,c,d,e-Cu2-O3b,f	84.3(2) × 4
OH6-Cu1-O2a	88.8(2)	OH5,c,d,e-Cu2-O3b,f	95.6(2) × 4
OH6-Cu1-OH5	93.9(2)	O3b-Cu2-O3f	180
OH6-Cu1-O1	94.1(2)		
OH6-Cu1-O3b	86.6(2)	OH5,g-Cu3-OH5e,h	180 × 2
OH4-Cu1-O2a	92.5(2)	OH5,e-Cu3-OH5g,h	99.6(2) × 2
OH4-Cu1-OH5	84.6(2)	OH5,g-Cu3-OH5e,h	80.4(2) × 2
OH4-Cu1-O1	86.5(2)	OH5,e,g,h-Cu3-OH4,h	75.7(2) × 4
OH4-Cu1-O3b	92.7(2)	OH5,e,g,h-Cu3-OH4,h	104.2(2) × 4
O2a-Cu1-OH5	172.1(2)	OH4-Cu3-OH4h	180
O2a-Cu1-O1	89.1(2)		
O2a-Cu1-O3b	89.3(2)	O1-Mo-O2,g	109.3(2) × 2
OH5-Cu1-O1	98.1(2)	O1-Mo-O3	107.6(3)
OH5-Cu1-O3b	83.4(2)	O2g-Mo-O2	110.9(3)
O1-Cu1-O3b	178.3(2)	O2,g-Mo-O3	109.8(2) × 2
		<O-Mo-O>	109.4
Possible H bonds			
OH4-H1	0.8(1)		
H1...O2i	2.7(1)	OH4-H1-O2i	140(5)
H1...O2j	2.7(1)	OH4-H1-O2j	140(5)
OH5-H2	0.76(8)		
H2...O1f	2.5(1)	OH5-H2...O1f	139(5)
H2...O2g	2.6(1)	OH5-H2...O2g	137(5)
OH6-H3	0.6(1)		
H3...OH5	2.6(1)	OH6-H3...OH5	117(5)
H3...OH5d	2.6(1)	OH6-H3...OH5d	117(5)

a = $x+1/2, -y+1/2, z-1/2$; b = $-x+1/2, y-1/2, -z-1/2$; c = $-x, -y, -z-1$; d = $x, y, -z-1$; e = $-x, -y, z$; f = $x-1/2, -y+1/2, z-1/2$; g = $x, y, -z$; h = $-x, -y, -z$; i = $1/2-x, y-1/2, 1/2-z$; j = $1/2-x, y-1/2, z-1/2$.

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TABLE 4. Bond-valence* analysis (*vu*) for szenicsite

	Cu1	Cu2	Cu3	Mo	Σ
O1	0.19 ^{×2→}			1.52	1.90
O2	0.37			1.50 ^{×2↓}	1.87
O3	0.17 ^{×2→}	0.16 ^{×2↓}		1.49	1.99
OH4	0.51 ^{×2→}		0.15 ^{×2↓}		1.17
OH5	0.34	0.43 ^{×4↓}	0.42 ^{×4↓}		1.19
OH6	0.52 ^{×2→}				1.04
Σ	2.10	2.04	1.98	6.01	

* bond-valence parameters from Brese and O'Keeffe (1991)

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