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Brochantite

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Abstract

A new refinement of a single monoclinic crystal of brochantite, $Cu_4SO_4(OH)_6$, from Socorro, New Mexico, USA, yielded new, accurate positions for Cu, S and O. Five of the six H atoms were located from $F_o - F_c$ syntheses.

Comment

As part of the research program of the Geo/Soil/Enviro Sector of the Consortium of the Advanced Photon Source, Argonne National Laboratory, we are selecting various minerals for testing the advances in crystallographic techniques. One of these is brochantite, the crystal structure of which was determined from a twinned crystal by Cocco & Mazzi (1959), using Cu *Kα* radiation from a sealed-tube source. Particularly interesting are the positions of the H atoms, which were not located by Cocco & Mazzi. By carrying out a new structure determination on a single crystal, using X-rays from an Mo *Kα* rotating-anode source, it was possible to improve on the old determination as well as to locate five of the six H atoms. A reference aliquot of the sample, from the University of Chicago Mineral Collection (No. 51 of unlabelled micromount collection) has been deposited in the American Museum of Natural History in New York.

Sabelli & Trosti-Ferroni (1985) classified brochantite in division 14 of the sheet type of sulfate minerals: 'In brochantite, there are two kinds of Cu-polyhedral chains, corner-linked and edge-linked, which are connected together to form sheets. The SO_4 tetrahedra bond these undulating sheets directly to one another, through weak apical Cu—O bonds'.

The cell dimensions of the monoclinic unit cell match within experimental uncertainty those of Cocco & Mazzi (1959). The atomic coordinates of the Cocco & Mazzi determination were obtained for a twinned crystal in a pseudo-orthorhombic cell. The present coordinates for a single crystal are inherently more accurate and were refined directly in the true monoclinic cell.
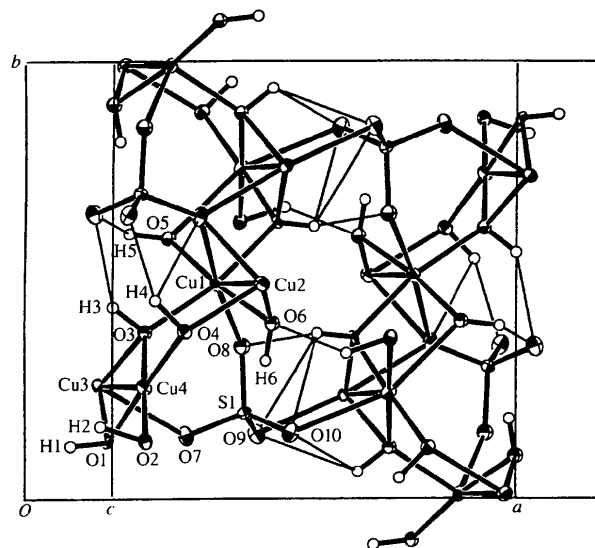

Fig. 1. An *ORTEP*II (Johnson, 1976) plot of the title compound showing the layers linked by Cu—O bonding and hydrogen bonding; displacement ellipsoids are drawn at the 50% probability level.

The first three Cu atoms have two sulfate O atoms at 2.299 (6)–2.415 (6) Å, which together with the four hydroxyl O atoms at a distance of approximately 2 Å in a square, generate a distorted octahedron. Cu4 is bonded to four hydroxyl O atoms at about 2 Å, an additional hydroxyl O atom at 2.342 (6) Å and a sulfate O atom at 2.461 (7) Å (Table 1). The overall structure consists of pairs of Cu atoms, Cu1—Cu2 and Cu3—Cu4, at distances of approximately 3 Å, forming infinite, almost linear chains, bridged by pairs of O atoms (Fig. 1). The two layers described by Cocco & Mazzi (1959) are linked to one another by further Cu—O bonding as well as by hydrogen bonding.

The positions of five of the H atoms were obtained by difference Fourier techniques but the precision of their positions is low, since it was not possible to refine them. H1, H2, H3, H5 and H6 generate hydroxyl groups with atoms O1–O6. The remaining H4 is presumed to be bonded to O4 and was included in a calculated position. We hope to locate all the H atoms with high-energy synchrotron radiation ($\sim$100 keV) and compare the OH geometries with those inferred from single-crystal IR and neutron diffraction techniques. We also hope to map out the bonding of the Cu atoms using single-crystal absorption fine structure.

Experimental

The mineral sample of brochantite came from Socorro County, New Mexico. Most crystals are twinned, leading to pseudo-octahedral symmetry (Palache, 1939). However, a single crystal of only 10 μm thickness was found in a crushed sample.

Crystal data

Cu₄SO₄(OH)₆
$M_r = 452.29$
Monoclinic
$P2_1/a$
$a = 13.087\,(1)$ Å
$b = 9.835\,(1)$ Å
$c = 6.015\,(2)$ Å
$\beta = 103.33\,(1)°$
$V = 753.3\,(3)$ Å³
$Z = 4$
$D_x = 3.988$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10.1$–$19.6°$
$\mu = 11.460$ mm⁻¹
$T = 296.2$ K
Plate
$0.15 \times 0.05 \times 0.01$ mm
Blue

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
$T_{min} = 0.718$, $T_{max} = 0.892$
2301 measured reflections
2219 independent reflections

1163 reflections with $I > 3\sigma(I)$
$R_{int} = 0.112$
$\theta_{max} = 30.06°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -7 \rightarrow 7$
3 standard reflections every 150 reflections intensity decay: 0.46%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.039$
$S = 1.619$
1163 reflections
117 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.0003$
$\Delta\rho_{max} = 0.87$ e Å⁻³
$\Delta\rho_{min} = -0.84$ e Å⁻³
Extinction correction: Zachariasen (1967)
Extinction coefficient: $6\,(3) \times 10^{-8}$
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—Cu2	3.019 (2)	Cu2—O7ⁱⁱ	2.338 (7)
Cu1—Cu2ⁱ	2.997 (2)	Cu2—O8ⁱᵛ	2.299 (6)
Cu3—Cu4	3.020 (2)	Cu3—O1	1.990 (6)
Cu3—Cu4ⁱ	2.996 (2)	Cu3—O2ⁱ	1.992 (6)
Cu1—O1ⁱⁱ	1.992 (6)	Cu3—O3	2.021 (6)
Cu1—O3	2.008 (6)	Cu3—O4ⁱ	1.988 (6)
Cu1—O5	1.926 (6)	Cu3—O7	2.339 (6)
Cu1—O6	1.928 (6)	Cu3—O9ᵛ	2.415 (6)
Cu1—O7ⁱⁱ	2.352 (7)	Cu4—O1	1.987 (6)
Cu1—O8	2.353 (6)	Cu4—O2	1.998 (6)
Cu2—O2ⁱⁱⁱ	2.078 (6)	Cu4—O3	1.984 (6)
Cu2—O4	2.107 (6)	Cu4—O4	1.979 (6)
Cu2—O5ⁱᵛ	1.929 (6)	Cu4—O5ᵛⁱ	2.342 (6)
Cu2—O6	1.912 (6)	Cu4—O10ᵛ	2.461 (7)
Cu2—Cu1—Cu2ⁱ	178.06 (7)	Cu4—Cu3—Cu4ⁱ	178.14 (7)

Symmetry codes: (i) $x, y, z - 1$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$; (iv) $x, y, 1 + z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (vi) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O8ⁱ	0.85	1.91	2.694 (9)	154.5
O2—H2···O6ⁱ	1.07	1.97	2.869 (8)	139.3
O4—H4···O9ⁱⁱ	0.98	2.03	2.919 (9)	150.4
O5—H5···O9ⁱⁱⁱ	0.87	2.20	3.021 (9)	155.6
O1—H1···O9ⁱ	0.85	2.69	3.131 (9)	113.7
O3—H3···O9ⁱ	0.92	2.48	3.059 (9)	121.3

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

Since there were no reflections suitable for a ψ scan, an empirical absorption correction using the program DIFABS (Walker & Stuart, 1983) was applied to the data. O3, O5, O6 and O8 were refined isotropically, while other non-H atoms were refined anisotropically. All but one of the H atoms were fixed in their difference-map positions. The remaining H atom, H4, was included in a calculated position. Each H atom was assigned a displacement parameter of 1.2 times the U_{eq} of the atom to which it is bonded.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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atomic coordinates and interatomic distances are about one order of magnitude smaller, thus making detailed discussions of the crystal structure possible.

The atoms Cu2 and Cu3 are surrounded by five O atoms, forming a distorted square pyramid. In the case of Cu3, a sixth O atom is situated at a distance of 2.566 (4) Å; thus, the coordination around Cu3 may also be regarded as distorted octahedral. For Cu1, compressed octahedral coordination is observed. Each Mo atom is surrounded by four O atoms forming an almost regular tetrahedron. The $Cu1O_6$ octahedra are connected by corners to form strings running in the [010] direction. The $Cu2O_5$ and $Cu3O_6$ polyhedra are linked to the octahedra of a string by edge sharing, while the MoO_4 tetrahedra are linked to them by corner sharing (Figs. 1 and 2).
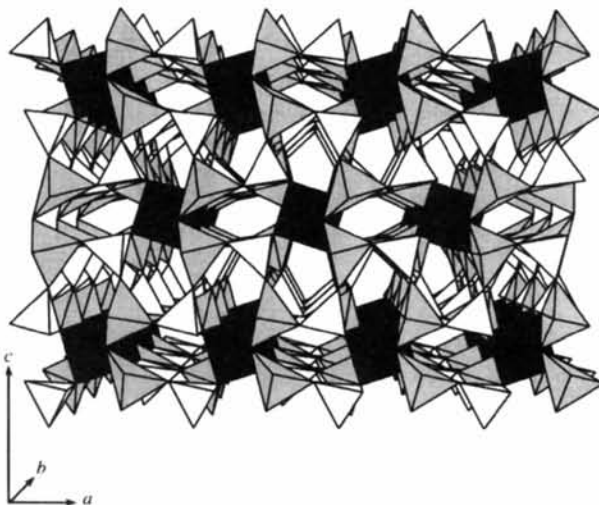
A Reinvestigation of $Cu_3Mo_2O_9$, a Compound Containing Copper(II) in Compressed Octahedral Coordination

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Abstract

The crystal structure of the title copper molybdate consists of strings of corner-sharing CuO_6 octahedra linked to CuO_5 square pyramids and MoO_4 tetrahedra by edges and corners, respectively. The structure contains the Jahn–Teller active ion Cu^{2+} in unusual compressed octahedral coordination.

Comment

The crystal structure of the title compound was first determined by Kihlborg, Norrestam & Olivecrona (1971) in the non-centrosymmetric space group $Pna2_1$ and later in the centrosymmetric space group *Pnam* (Kihlborg & Norrestam, 1972). An interesting feature of this crystal structure is the unusual compressed octahedral environment around the Jahn–Teller active ion Cu^{2+}. Because of the isotropic refinement of the atomic positions, the relatively high *R* value ($R_1 = 0.077$) and standard uncertainties of the atomic coordinates in the solution by Kihlborg & Norrestam (1972), a reinvestigation of this crystal structure seemed to be worthwhile. Our results are in accordance with the data presented by Kihlborg & Norrestam (1972), but the standard uncertainties of the

Fig. 1. A view along [010] of the crystal structure of $Cu_3Mo_2O_9$. $Cu1O_6$ octahedra are dark grey, $Cu2/3O_5$ square pyramids are light grey and MoO_4 tetrahedra are white.
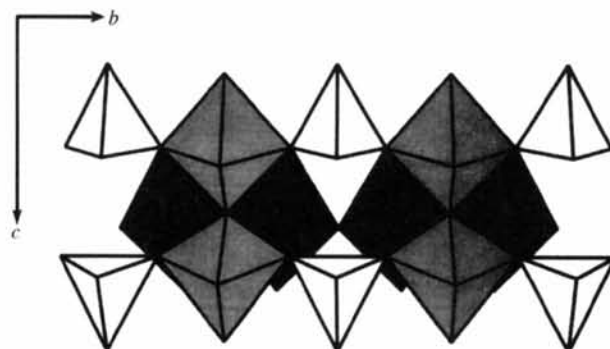

Fig. 2. A string of $Cu1O_6$ octahedra (dark grey) along [010] shared by corners and linked to $Cu2/3O_5$ pyramids (light grey) and MoO_4 tetrahedra (white) by edges and corners, respectively.