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A Reinvestigation of $\text{Cu}_3\text{Mo}_2\text{O}_9$, a Compound Containing Copper(II) in Compressed Octahedral Coordination

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(Received 6 December 1996; accepted 15 April 1997)

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 Kihlberg, Norrestam & Olivecrona (1971) in the non-centrosymmetric space group $Pna2_1$ and later in the centrosymmetric space group $Pnam$ (Kihlberg & 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 Kihlberg & Norrestam (1972), a reinvestigation of this crystal structure seemed to be worthwhile. Our results are in accordance with the data presented by Kihlberg & Norrestam (1972), but the standard uncertainties of the

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

The atoms Cu_2 and Cu_3 are surrounded by five O atoms, forming a distorted square pyramid. In the case of Cu_3 , a sixth O atom is situated at a distance of 2.566(4) Å; thus, the coordination around Cu_3 may also be regarded as distorted octahedral. For Cu_1 , compressed octahedral coordination is observed. Each Mo atom is surrounded by four O atoms forming an almost regular tetrahedron. The Cu_1O_6 octahedra are connected by corners to form strings running in the [010] direction. The Cu_2O_5 and Cu_3O_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).

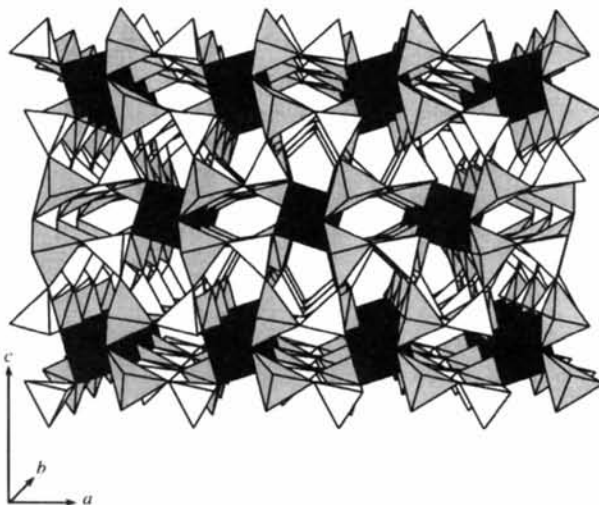


Fig. 1. A view along [010] of the crystal structure of $\text{Cu}_3\text{Mo}_2\text{O}_9$. Cu_1O_6 octahedra are dark grey, $\text{Cu}_2/3\text{O}_5$ square pyramids are light grey and MoO_4 tetrahedra are white.

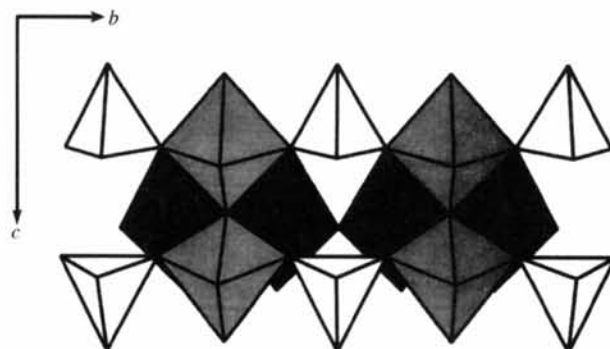


Fig. 2. A string of Cu_1O_6 octahedra (dark grey) along [010] shared by corners and linked to $\text{Cu}_2/3\text{O}_5$ pyramids (light grey) and MoO_4 tetrahedra (white) by edges and corners, respectively.

The crystal structure of monoclinic Zn₃Mo₂O₉ (Söhnle, Reichelt, Oppermann, Mattausch & Simon, 1996) shows a strong resemblance to the structure of the title compound, as it contains compressed ZnO₆ octahedra, ZnO₅ pyramids and MoO₄ tetrahedra linked in the same way. The axial bond lengths, d_{ax} , in the compressed ZnO₆ octahedra are 1.943 (1) Å and the equatorial bond lengths, d_{eq} , are 2.212 (3) and 2.242 (2) Å.

A compressed octahedral environment for a Jahn–Teller active ion such as Cu²⁺ is unusual. Compressed CuF₆ octahedra were observed in the crystal structure of KAlCuF₆ (Atanasov *et al.*, 1993) and compressed CuO₆ octahedra were recently investigated by Grub & Glaum (1997) in the compound Cu₃Cr₄(PO₄)₆. A comparison of several isotopic compounds $M_3M_4(PO_4)_6$ by these authors showed the compression of the octahedra to be enhanced by Jahn–Teller active ions such as Cu²⁺ or Cr²⁺. This fact is confirmed by comparison of the ratio between the axial and equatorial bond lengths, d_{ax}/d_{eq} , of the octahedra in the structures of the copper and zinc molybdates $M_3Mo_2O_9$: 0.840 and 0.872, respectively. The value in Cu₃Mo₂O₉ is almost the same as that of 0.844 observed by Grub & Glaum (1997) for the CuO₆ octahedra in the structure of Cu₃Cr₄(PO₄)₆.

The octahedral compression seems to be directed by lattice strain. This fact can be illustrated by bond length–

bond strength calculations (Brown, 1981) for the title compound. According to expectations, this gives the following sums of bond strength Σs : 5.89 for Mo1, 6.09 for Mo2, 2.11 for Cu1, 2.15 for Cu2, 1.91 for Cu3 ($\Sigma s = 2.00$ if the sixth O atom at a distance of 2.566 Å is taken into consideration). The Σs values of the O atoms are expected to be about 2.0; the calculation gives values between 1.95 (for O5, O6 and O7) and 2.2 for O1. The axial O atoms in the Cu1O₆ octahedra are linked to four Cu atoms with bond strength s from 0.5 to 0.6; the equatorial O atoms are linked to one Mo atom ($s = 1.3$) and two Cu atoms ($s = 0.4$ and 0.25). The short axial bond lengths in the Cu1O₆ octahedra between Cu1 and O1 are a result of the edge sharing of the Cu2 and Cu3 polyhedra. Elongated Cu1O₆ octahedra in this case would lead to improbably small Cu–Cu distances (between Cu1 and Cu2 or Cu3) and Cu–O distances (involving the O4 and O5 atoms) and to bond-strength sums for Cu1, O4 and O5 much greater than 2.0.

Experimental

Crystals of Cu₃Mo₂O₉ grown by chemical transport reactions at the lower temperature of a gradient 973–1023 K with Br₂ as transport agent (Steiner, Reichelt & Oppermann, 1996) proved to be too large and of insufficient quality for X-ray single crystal investigations. Suitable crystals were separated from the material remaining in the source region after the chemical transport experiments.

Crystal data

Cu₃Mo₂O₉
 $M_r = 526.50$
 Orthorhombic
Pnma
 $a = 7.667 (1) \text{ \AA}$
 $b = 6.862 (1) \text{ \AA}$
 $c = 14.608 (2) \text{ \AA}$
 $V = 768.5 (2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 4.550 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 9.75\text{--}14.27^\circ$
 $\mu = 11.363 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Prism
 $0.18 \times 0.15 \times 0.15 \text{ mm}$
 Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – 2θ scans
 Absorption correction: empirical, ΔF (XEMP; Siemens, 1989)
 $T_{\min} = 0.098$, $T_{\max} = 0.182$
 3371 measured reflections
 1799 independent reflections

1762 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 34.95^\circ$
 $h = 0 \rightarrow 12$
 $k = -11 \rightarrow 11$
 $l = -23 \rightarrow 0$
 3 standard reflections
 frequency: 120 min
 intensity decay: 1.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$

$\Delta\rho_{\text{max}} = 2.10 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -3.28 \text{ e \AA}^{-3}$

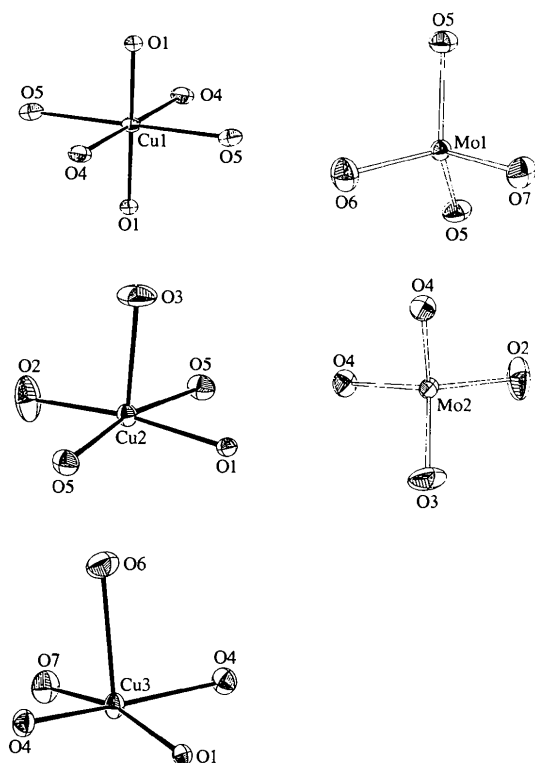


Fig. 3. A ZORTEP plot (Zsolnai, 1994) of the Cu–O and Mo–O polyhedra in the crystal structure of Cu₃Mo₂O₉. Displacement ellipsoids are drawn at the 50% probability level.

$wR(F^2) = 0.073$
 $S = 1.338$
 1799 reflections
 80 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.6979P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

Extinction correction:
SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.0480 (15)
 Scattering factors from
International Tables for Crystallography (Vol. C)

two disordered, actually elongated CuO_6 octahedra, simulating the compressed geometry. The maximum electron density in the final difference Fourier map occurred 0.69 Å from Mol. A refinement in the non-centrosymmetric space group *Pna2₁* produced no noticeable decrease in the *R* values or modification of the bond lengths, indicating that there is no reason for treating the structure as non-centrosymmetric.

Data collection: *CAD-4-PC Software* (Enraf-Nonius, 1994). Cell refinement: *CAD-4-PC Software*. Data reduction: *CAD-4-PC Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1995); *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL93*.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cu1	0	0	0	0.01135 (10)
Cu2	0.16078 (5)	3/4	0.14049 (3)	0.01189 (10)
Cu3	0.20486 (5)	1/4	0.43590 (3)	0.01366 (10)
Mo1	0.26232 (3)	1/4	0.16618 (2)	0.01138 (9)
Mo2	0.15120 (3)	3/4	0.38525 (2)	0.01157 (9)
O1	0.0902 (3)	3/4	0.0139 (2)	0.0109 (3)
O2	0.1973 (7)	3/4	0.2689 (2)	0.0336 (8)
O3	0.4294 (4)	3/4	0.0968 (3)	0.0302 (7)
O4	0.2446 (3)	0.9624 (3)	0.4356 (1)	0.0183 (3)
O5	0.1392 (2)	0.0382 (3)	0.1339 (1)	0.0180 (3)
O6	0.2974 (5)	1/4	0.2820 (2)	0.0259 (6)
O7	0.4663 (4)	1/4	0.1106 (2)	0.0232 (5)

Table 2. Selected geometric parameters (Å)

Cu1—O1 ⁱ	1.861 (1)	Cu3—O4 ^a	1.997 (2)
Cu1—O1 ⁱⁱ	1.861 (1)	Cu3—O4 ⁱⁱⁱ	1.997 (2)
Cu1—O4 ⁱⁱⁱ	2.187 (2)	Cu3—O6	2.358 (3)
Cu1—O4 ^{iv}	2.187 (2)	Cu3—O3 ^{viii}	2.566 (4)
Cu1—O5	2.243 (2)	Mo1—O6	1.713 (3)
Cu1—O5 ^v	2.243 (2)	Mo1—O7	1.762 (3)
Cu2—O2	1.896 (3)	Mo1—O5 ^{vi}	1.796 (2)
Cu2—O1	1.927 (2)	Mo1—O5	1.796 (2)
Cu2—O5 ^{vi}	1.987 (2)	Mo2—O3 ^{ix}	1.721 (3)
Cu2—O5 ^{vii}	1.987 (2)	Mo2—O2	1.737 (3)
Cu2—O3	2.156 (3)	Mo2—O4	1.783 (2)
Cu3—O1 ^{viii}	1.941 (2)	Mo2—O4 ^x	1.783 (2)
Cu3—O7 ^{ix}	1.951 (3)		

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x, y-1, z$; (iii) $x-\frac{1}{2}, y-1, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (v) $-x, -y, -z$; (vi) $x, \frac{1}{2}-y, z$; (vii) $x, 1+y, z$; (viii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (ix) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (x) $x, \frac{3}{2}-y, z$.

Starting positional parameters for Mo and Cu were obtained by direct methods. The O atoms were located during successive difference Fourier syntheses using *SHELXL93* (Sheldrick, 1993). To facilitate comparison with the earlier results, the refinement was repeated using the atomic coordinates determined by Kihlborg & Norrestam (1972), converted to the setting *Pnma*, as a starting set. The anisotropic displacement parameters for the O atoms (Fig. 3) coordinating to Cu1 show no anomalies, giving no hint of a possible superposition of

The authors thank Dr Hj. Mattausch (MPI für Festkörperforschung Stuttgart) and Dr R. Glaum (Justus-Liebig Universität Gießen) for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1185). Services for accessing these data are described at the back of the journal.

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