

The unit-cell volumes of the $RAI\text{Ge}$ phases decrease with increasing atomic number of the rare-earth elements as expected from the lanthanide contraction. In Fig. 2 are plotted the cube roots of the unit-cell volumes of the $RAI\text{Ge}$ phases versus the trivalent ionic rare-earth radii r^{3+} (Templeton & Dauben, 1954). The cube roots of the unit-cell volumes for the phases with $\alpha\text{-ThSi}_2$ type diffraction pattern and for the phases with the $YAI\text{Ge}$ type follow the same linear function of r^{3+} . The only deviation from the linearity is observed with EuAlGe .

We wish to acknowledge the help of Mrs Birgitta Künzler with the preparation of the drawings. We also thank Mr T. Graf in the group of DPMC of Geneva University for the differential thermal analysis. This study was supported by the Swiss National Science Foundation under contract 20-28490.90.

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Acta Cryst. (1990). **C46**, 2279–2284

Structure of Copper(II) Hydroxide, $\text{Cu}(\text{OH})_2$

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(Received 19 March 1990; accepted 29 May 1990)

Abstract. $\text{Cu}(\text{OH})_2$, mineral name spertiniite, $M_r = 97.578$, orthorhombic, $Cmc2_1$, $a = 2.9471$ (5), $b = 10.593$ (1), $c = 5.2564$ (7) Å, $V = 164.1$ (1) Å³, $Z = 4$, $D_x = 3.949$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 124.62$ cm⁻¹, $F(000) = 188$, $T = 295$ K, R is 0.042 for 417 unique observed reflections. The general features of the structure determined in the centrosymmetric space group $Cmcm$ from X-ray powder data [Jaggi & Oswald (1961). *Acta Cryst.* **14**, 1041–1045] could be confirmed. An analysis of the thermal displacement parameters of the O atoms, however, shows that the correct space group is non-centrosymmetric, $Cmc2_1$. Therefore, the resulting Cu—O coordination polyhedron is square pyramidal or strongly (4 + 1 + 1) distorted octahedral, but not (4 + 2) octahedral. In addition, the H-atom positions could be localized from difference Fourier syntheses. Cu—O distances are 1.948 (3) and 1.972 (3) Å within the equatorial

plane of the square pyramid, the apical distance is 2.356 (5) Å and the Cu atom is displaced by 0.134 Å from the equatorial plane. Assuming octahedral coordination the next vertex distance is 2.915 (5) Å resulting in a (4 + 1 + 1) configuration. Chains of octahedra are formed by sharing equatorial edges along [100]. These chains build up corrugated layers perpendicular to the b axis by sharing edges of apical and equatorial OH⁻ ions. The layers are connected via hydrogen bonds of the type O(1)—H(1)⋯O(1') with distances O(1)⋯O(1') = 2.904 (4), H(1)⋯O(1') = 1.92 (2) Å and the angle around H(1) is 167 (2)°.

Introduction. The structure of $\text{Cu}(\text{OH})_2$ was first solved with powder diffraction X-ray data by Jaggi & Oswald (1961) in the space group $Cmcm$, and it was described as a layered structure type related to lepidocrocite, $\gamma\text{-FeOOH}$. The decomposition of

$\text{Cu}(\text{OH})_2$ on electron irradiation and thermal treatment has been investigated by X-ray diffraction, thermoanalytical and electron microscopic methods, and the topotactic relation between $\text{Cu}(\text{OH})_2$, CuO and Cu_2O has been established (Günter & Oswald, 1970). Polymorphism of $\text{Cu}(\text{OH})_2$ was found by Schönenberger, Günter & Oswald (1971), and a reversible phase transition at 333 K with a slight hysteresis effect could be observed. The phase transition might be related to some change in the hydrogen-bonding system between the corrugated layers of the distorted $\text{Cu}(\text{OH})_6$ octahedra. Together with the knowledge of the thermochemical reactivity of this material, conclusive interpretations may be derived for the conditions under which $\text{Cu}(\text{OH})_2$ could grow as the quite recently discovered mineral spertiniite (Grice & Gasparrini, 1981). Thus it was highly desirable to produce single crystals of sufficient size to determine the hydrogen atomic positions by X-ray analysis. On the other hand it is interesting to compare the title compound with different cupric hydroxide salts in order to examine Jahn–Teller distortions of CuO_6 octahedra within this class of compounds.

Experimental. The crystal structure of copper hydroxide, $\text{Cu}(\text{OH})_2$, was determined by X-ray diffraction using a CAD-4 diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Single crystals were synthesized by the following procedure: a ribbon of high-purity copper metal was brought into a 1:1 solution of ammonia (12.5%) and acetone. This mixture was kept at 277 K for three weeks in the absence of carbon dioxide (in order to avoid the possible formation of basic copper carbonates such as azurite or malachite). After this period, the mother liquor was poured off and the $\text{Cu}(\text{OH})_2$ single crystals grown on the copper ribbon as well as on the walls of the beaker were washed with diluted ammonia solution and with acetone. Subsequently, the crystals were dried in a desiccator at room temperature. Another method of synthesis of $\text{Cu}(\text{OH})_2$ has been described using $\text{Na}_2\text{Cu}(\text{OH})_4$ as an intermediate material (Cudennec, Lecerf, Riou & Gerault, 1988); however, single crystals of X-ray diffraction quality could not be obtained.

All light-blue crystals of the sample showed tiny hollows or cavities and similar dimensions (see Figs. 1*a,b*). Some of the crystals were twinned. The plate-shaped crystal used for the measurement had dimensions of approximately $0.05 \times 0.016 \times 0.06 \text{ mm}$. The unit-cell parameters were determined by least-squares refinement of the setting angles of 25 automatically centered reflections in the range $11.5 < \theta < 22.5^\circ$. Intensities of 2005 reflections (excluding standards) in the interval $-5 < h < 5$, $-19 < k < 19$, $-9 < l < 9$ with θ between 1.0 and 40.0° were collected

using the ω - 2θ scan technique. The scan rate varied from 0.37 to $8.24^\circ \text{ min}^{-1}$, the maximum measuring time was 240 s. Two standard reflections were monitored every three hours of measuring time, no loss of intensities was noted. Orientation was controlled every 200 reflections using three standard reflections. 376 reflections had negative intensities and were excluded from the data set. A numerical absorption correction ($\mu = 124.6 \text{ cm}^{-1}$) based on ten indexed crystal faces and carefully measured distances between faces was applied with *SHELX76* (Sheldrick, 1976). The transmission factors range from 0.766 to 0.525. Data reduction led to 553 unique reflections (1629 reflections averaged, $R_{\text{int}} = 0.047$). The data were corrected for Lorentz and polarization effects. 417 reflections were considered observed with $I \geq 3\sigma(I)$, 136 reflections were unobserved.

The atomic parameters from Jaggi & Oswald (1961) were used as starting values for the refinement in the space group *Cmcm*. The missing H atoms could be located in difference Fourier maps. At a first glance the refinement seemed to be successful, confirming the model of Jaggi & Oswald (1961) with conventional R/wR values of 4.09/3.14% for 241 unique observed data. Two aspects led to the conclusion that the centrosymmetric structure represents a statistical average of the non-centrosymmetric configurations. Firstly, the oxygen O(2) exhibits an unusually high displacement parameter U_{33} of 0.13 \AA^2 in the *c* direction of the unit cell, indicating

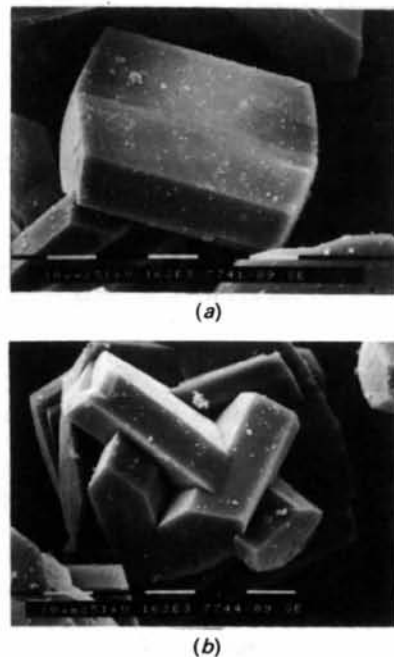


Fig. 1. Scanning electron micrographs of single crystals of copper(II) hydroxide (*a*) and twinned aggregates (*b*) crystallized from the same batch.

positional disorder along *c* (Fig. 2*a*); secondly, the H atom H(1) located by difference Fourier syntheses, which is involved in a relatively strong hydrogen bond of the type O(1)—H(1)⋯O(1'), appeared to have split positions with distances H(1)⋯H(1') = 0.90 Å, O(1)⋯H(1') = 1.26 Å [coordinates H(1): 0.0, 0.4817, 0.433] as a result of a center of symmetry. The average position of H(1) is lying at this centre of symmetry at $0, \frac{1}{2}, \frac{1}{2}$, the refined displacement parameter of H(1) is $U_{\text{iso}} = 0.15(8) \text{ \AA}^2$ and the average O—H distance is 1.448(3) Å. At this stage the structure determination was repeated in the space group *Cmc*2₁, using the Patterson interpretation routine of the program *SHELXS*86 (Sheldrick, 1985). The structure was refined by full-matrix least-squares calculations with *SHELX*76 (Sheldrick, 1976), minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma^2(F_o) + 0.001F_o^2]$ with anisotropic thermal parameters for the non-H atoms (Table 2). The H atoms were localized by

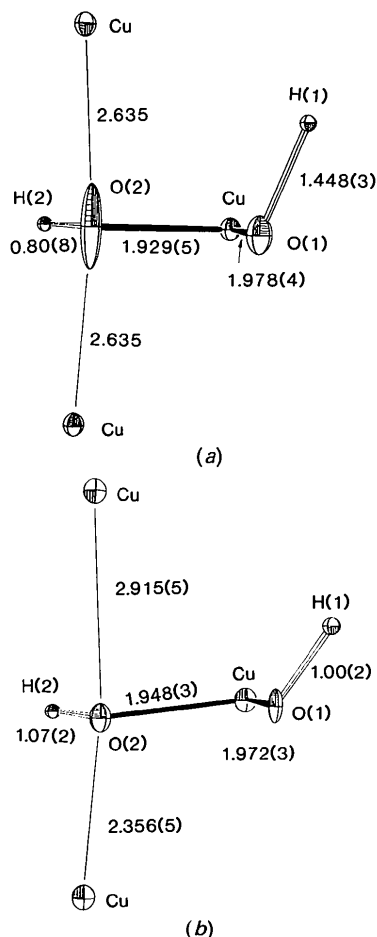


Fig. 2. Anisotropic displacement parameters of Cu, O(1) and O(2) at the 60% probability level and bond distances and angles based on the refinement in (a) the centrosymmetric space group *Cmc*, (b) the non-centrosymmetric space group *Cmc*2₁. H atoms are shown as spheres of arbitrary size.

Table 1. Positional coordinates and equivalent isotropic displacement parameters U_{eq} (e.s.d.'s in parentheses) for the atoms of $\text{Cu}(\text{OH})_2$

$\sigma(U_{\text{eq}})$ calculated after Schomaker & Marsh (1983).				
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{\AA}^2)$
Cu	0.5	0.6820 (1)	0.2500	0.0086 (1)
O(1)	0.0	0.5583 (4)	0.2534 (20)	0.0125 (9)
O(2)	0.0	0.7994 (4)	0.1967 (9)	0.0101 (10)
H(1)	0.0	0.5058 (23)	0.4118 (24)	0.027 (2)
H(2)	0.0	0.9001 (23)	0.1914 (24)	0.032 (2)

In order to refine Cu, O(1), O(2) and the located H atoms in the same asymmetric unit, the position of the Cu atom has been shifted from its original coordinates (0.0, *y*, *z*), determined by Jaggi & Oswald (1961) to $(\frac{1}{2}, \frac{1}{2} + y, z)$.

Table 2. Anisotropic displacement parameters (e.s.d.'s in parentheses) for the atoms of $\text{Cu}(\text{OH})_2$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0.0083 (2)	0.0076 (2)	0.0098 (2)	-0.0009 (11)	0.0	0.0
O(1)	0.0125 (12)	0.0083 (12)	0.0168 (12)	0.0047 (22)	0.0	0.0
O(2)	0.0099 (13)	0.0064 (14)	0.0039 (17)	0.0008 (11)	0.0	0.0

difference Fourier syntheses. Compared to the *Cmcm* refinement the displacement parameters for O(2) now appear to have normal values (Fig. 2*b* and Table 2). Unequivocal hydrogen positions were obtained in the difference Fourier map, and the final refinement converged at $R/wR = 4.15/4.70\%$, with 24 variable parameters. The maximum shift/e.s.d. ratio was 0.18 for an H-atom parameter and 0.005 for U_{11} of O(1). Maximum and minimum electron densities in the final difference Fourier synthesis were 4.88 e \AA^{-3} (0.62 \AA from Cu) and $-3.204 \text{ e \AA}^{-3}$ (located 0.79 \AA from Cu). The present X-ray measurement was not affected by extinction errors. Owing to the importance of the weak reflections in resolving the centrosymmetric–non-centrosymmetric ambiguity (Marsh, 1981), *E* statistics (Karle, Dragonette & Brenner, 1965) and *N*(*Z*) tests (Howells, Phillips & Rogers, 1950) were carried out with all 2005 (including unobserved) measured reflections. The theoretical values for $\langle |E^2 - 1| \rangle$ are 0.968 for centrosymmetric and 0.736 for non-centrosymmetric structures, the value for this structure is 0.610. Furthermore, the non-centrosymmetric structure and its inversion were refined using the complete data set consisting of all observed reflections and their Friedel opposites [1128 data with $I > 3\sigma(I)$]. The final R/wR values for the structure presented here were 5.02/5.81%, those for its inversion were 5.09/5.88%. As ΔR is only 0.07%, enantiomorphic twinning cannot be excluded with certainty. On the other hand, application of the significance test on wR values (Hamilton, 1965) favours the presented configuration with a probability $> 99.5\%$ ($R = 5.88/5.81 = 1.012$; $\mathcal{A}_{1,1104,0.005} = 1.0037$). A refinement of the structure in the space

Table 3. Selected distances (Å) and angles (°) between atoms for Cu(OH)₂

Cu—O(1)	1.972 (3) (2 ×)	Cu—O(2 ⁱⁱ)	2.356 (5)
Cu—O(2)	1.948 (3) (2 ×)	Cu—O(2 ⁱⁱⁱ)	2.915 (5)
O(1)—Cu—O(1 ⁱ)	96.7 (2)	O(2 ⁱ)—Cu—O(1 ⁱ)	82.0 (1)
O(1 ⁱ)—Cu—O(2 ⁱ)	92.7 (3)	O(2 ⁱ)—Cu—O(2)	98.3 (2)
O(1 ⁱ)—Cu—O(2 ⁱⁱⁱ)	93.1 (3)	O(2 ⁱ)—Cu—O(2 ⁱⁱ)	95.2 (1)
O(1)—Cu—O(2 ⁱⁱ)	92.7 (3)	O(2)—Cu—O(1 ⁱ)	172.1 (3)
O(1)—Cu—O(2 ⁱⁱⁱ)	93.1 (3)	O(2)—Cu—O(1)	82.0 (1)
O(2 ⁱⁱ)—Cu—O(2 ⁱⁱⁱ)	171.3 (2)	O(2)—Cu—O(2 ⁱⁱ)	95.2 (1)
O(2 ⁱ)—Cu—O(2 ⁱⁱⁱ)	79.2 (1)	O(2)—Cu—O(2 ⁱⁱⁱ)	79.2 (1)
O(2 ⁱ)—Cu—O(1)	172.1 (3)		

The shortest Cu—Cu distance corresponds to the unit-cell parameter *a* of 2.9471 (5) Å. The next four Cu—Cu distances are 3.340 (1) Å. (i) = 1 + *x*, *y*, *z*; (ii) = 0.5 - *x*, 1.5 - *y*, 0.5 + *z*; (iii) = 0.5 - *x*, 1.5 - *y*, -0.5 + *z*.

Table 4. Hydrogen-bonding contacts (Å, °) in Cu(OH)₂

X—H...Y	X—H	H...Y	X...Y	X—H...Y	Sym. op.
O(1)—H(1)···O(1 ⁱ)	1.00 (2)	1.92 (2)	2.904 (4)	167 (2)	- <i>x</i> , 1 - <i>y</i> , $\frac{1}{2}$ + <i>z</i>
O(2)—H(2)···O(1 ⁱⁱⁱ)	1.07 (2)	2.26 (2)	3.128 (5)	137.7 (5)	$\frac{1}{2}$ + <i>x</i> , $\frac{1}{2}$ + <i>y</i> , <i>z</i>
O(2)—H(2)···O(1 ⁱⁱ)	1.07 (2)	2.26 (2)	3.128 (5)	137.7 (5)	$-\frac{1}{2}$ + <i>x</i> , $\frac{1}{2}$ + <i>y</i> , <i>z</i>

group *Cmcm* with all 1128 significant data resulted in *R/wR* values of 5.44/6.36%.

The *N(Z)*-test results, the *E*-statistics calculations and the Hamilton test (Hamilton, 1965) as well as the successful refinement unambiguously favour the non-centrosymmetric structure of the space group *Cmc*₂. For comparison, stereo plots of the centrosymmetric and the non-centrosymmetric structure including the H atoms are given in Figs. 6*a,b*. Neutral atomic scattering factors and dispersion corrections for Cu were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 55–147), for O and H atoms from *SHELX76* (Sheldrick, 1976). Positional parameters are shown in Table 1.

Discussion. The general features of the structure of Cu(OH)₂ as determined by Jaggi & Oswald (1961) from X-ray powder data could be confirmed by the single-crystal structure analysis presented here. The correct space group, however, is *Cmc*₂ and not *Cmcm*. The copper coordination is square pyramidal with Cu—O distances of 1.948 (3) and 1.972 (3) Å in the equatorial plane and an apical distance of 2.356 (5) Å. The distance between copper and the second vertex O atom is rather long at 2.915 (5) Å. The mean value of these two vertex distances equals exactly the distance of 2.63 Å found in the centro-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bonding parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53258 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

symmetric refinement of the structure. Thus, the correct non-centrosymmetric structure exhibits a (4 + 1 + 1) strongly distorted octahedron in which the copper ion juts out by 0.134 Å from the equatorial plane in the direction of the vertex O atom with the shorter bonding distance. Coordination distances are shown in Fig. 3, and the corresponding angles and symmetry operators are given in Table 3. Corrugated layers of distorted Cu(OH)₆ octahedra are formed by edge sharing of the octahedra (Figs. 4, 5). These layers are held together by hydrogen bonds of the type O(1)—H(1)···O(1^v). Hydrogen-bonding parameters are given in Table 4. The O(1)···O(1^v) distance of 2.904 (4) Å corresponds to a medium hydrogen-bond strength which is in accordance with the IR absorption band at 3304 cm⁻¹ measured at room temperature. The O(2)···O(1), O(2)···O(1ⁱ) distances of 3.128 (5) Å indicate very weak bifurcated O(2)—H(2)···O(1) interactions, if any, in close correspondence with the data derived from IR measurements (IR absorption band ν = 3580, 3574 and 3560 cm⁻¹) (Jaggi & Oswald, 1961; Schönenberger, Günter & Oswald, 1971; Cudennec, Lecerf, Riou & Gerault, 1988).

Detailed reviews on the stereochemistry of copper(II) complexes have been given by Gazo, Bersuker, Garaj, Kabesova, Kohout, Langfelderova, Melnik, Serator & Valach (1976) and by Hathaway (1984). To our knowledge there are only two further examples of structures containing a Cu(OH)₆ polyhedron: Ba₂Cu(OH)₆, where isolated, extremely (4 + 2)-distorted [Cu(OH)₆]⁴⁻ anions are observed (Dubler, Korber & Oswald, 1973) and the mineral posnjakite, Cu₄(SO₄)(OH)₆·H₂O (Mellini & Merlino, 1979). In both complexes the equatorial Cu—OH distances of 1.958 (4) and 1.972 (4) Å and of 1.98 (2) to 2.02 (2) Å respectively agree well with those found in Cu(OH)₂. The vertex distance of 2.805 (4) Å in Ba₂Cu(OH)₆ is comparable with the long vertex distance in Cu(OH)₂, whereas the corresponding distances of 2.35 (2) and 2.38 (2) Å in Cu₄(SO₄)(OH)₆·H₂O are identical with the short

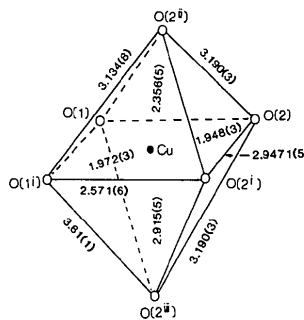


Fig. 3. Coordination and O···O distances in the distorted CuO₆ octahedron.

vertex distance in $\text{Cu}(\text{OH})_2 \cdot \text{Na}_2\text{Cu}(\text{OH})_4$, which obviously also represents an example of a structure containing $\text{Cu}(\text{OH})_6$ polyhedra, but its crystal structure has not yet been determined in detail (Cudennec, Lecerf, Riou & Gerault, 1988).

Copper coordination polyhedra of the type $\text{Cu}(\text{OH})_4(\text{X})_2$ which are closely related to that in $\text{Cu}(\text{OH})_2$ are also observed in different hydroxide salts of copper as for instance in the three polymorphic forms of $\text{Cu}_2(\text{OH})_3\text{Cl}$, atacamite, paratacamite and botallackite (Oswald & Feitknecht, 1964) and in $\text{Cu}(\text{NH}_3)_2\text{Sn}(\text{OH})_6$ (Dubler, Hess & Oswald, 1976). In atacamite (Parise & Hyde, 1986), paratacamite (Fleet, 1975) and in botallackite (Voronova & Vainshtein, 1958), the chloride anions occupy the apical positions of the (4+2)- or (4+1+1)-distorted octahedra, whereas in $\text{Cu}(\text{NH}_3)_2\text{Sn}(\text{OH})_6$ a (4+2)-distorted $\text{Cu}(\text{OH})_4(\text{NH}_3)_2$ octahedron with

two of the four OH groups in the apical position is observed.

The physical and chemical properties of bivalent Mg, Ca and 3d-metal hydroxides have been reviewed, and the exceptional behaviour of $\text{Cu}(\text{OH})_2$ compared to the other metal hydroxides has been worked out extensively by Oswald & Asper (1977). The electron-induced and thermal decomposition as well as the polymorphism of $\text{Cu}(\text{OH})_2$ have been investigated by Günter & Oswald (1970) and Schönenberger, Günter & Oswald (1971). A reversible structural phase transition, connected with an elongation of the *c* axis by 1% and a shortening of the *b* axis by 0.2%, has been established in these investigations. In view of the hydrogen-bonding parameters resulting from the structure determination presented here, it seems unlikely that this transition is caused by an order-disorder transition

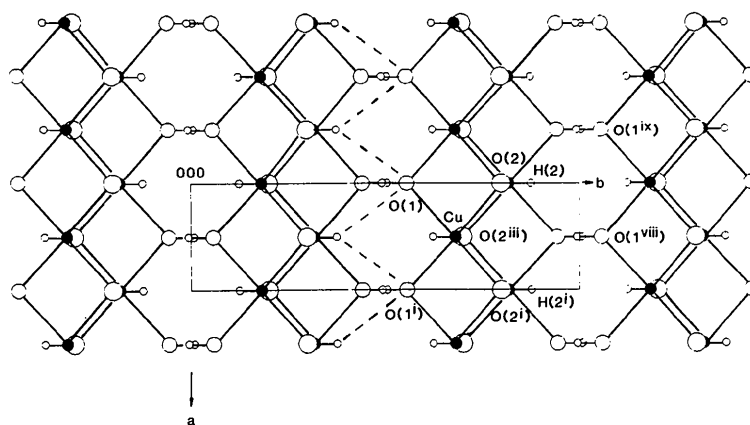


Fig. 4. The *ab* projection of the unit cell. Blackened circles indicate Cu atoms, O(1) and O(2) are shown as circles of different arbitrary sizes, H atoms are shown as small spheres. Weak O(2)—H(2)···O(1) bifurcated interactions are given in broken lines. (i) = $\frac{1}{2} + x, y, z$; (iii) = $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$; (viii) = $\frac{1}{2} + x, \frac{1}{2} + y, z$; (ix) = $-\frac{1}{2} + x, \frac{1}{2} + y, z$.

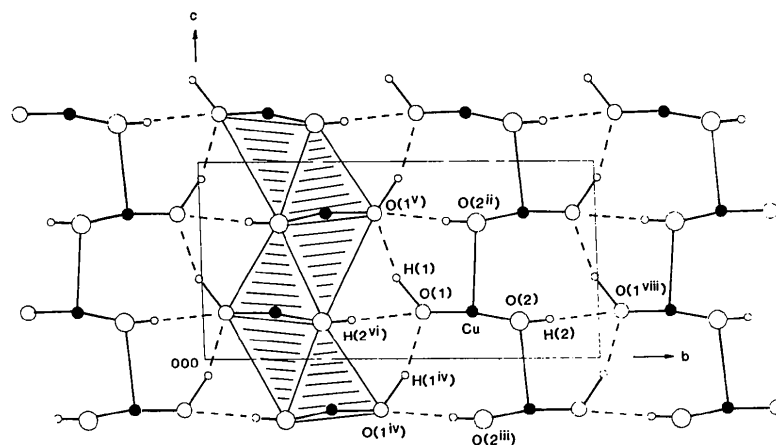


Fig. 5. The *bc* projection of the unit cell with the atom-numbering scheme. One half of the cell is drawn in octahedron representation. The hydrogen bonds O(1)—H(1)···O(1) and O(2)—H(2)···O(1) interactions are indicated by broken lines. (ii) = $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) = $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iv) = $-x, 1 - y, -\frac{1}{2} + z$; (v) = $-x, 1 - y, \frac{1}{2} + z$; (vi) = $\frac{1}{2} + x, -\frac{1}{2} + y, z$; (viii) = $\frac{1}{2} + x, \frac{1}{2} + y, z$.

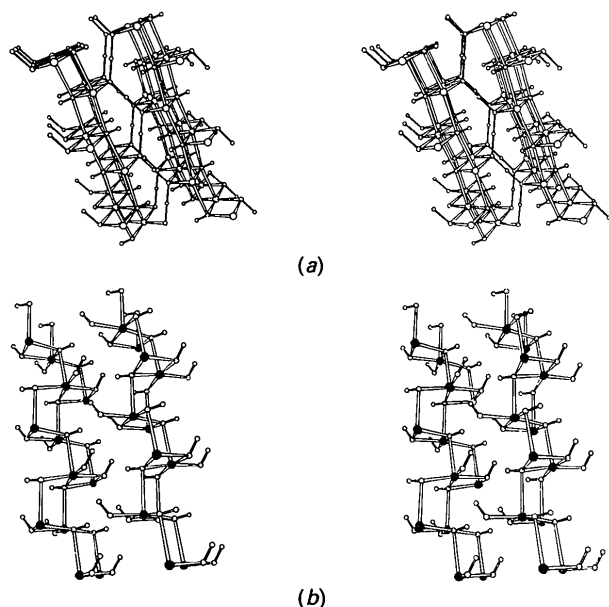


Fig. 6. SCHAKAL (Keller, 1986) stereo plots of the structure of $\text{Cu}(\text{OH})_2$ based on atomic parameters of (a) the centrosymmetric refinement of single-crystal data, corresponding to the structure reported from X-ray powder data (Jaggi & Oswald, 1961), (b) non-centrosymmetric refinement.

involving H atoms, since the hydrogen bonds observed are much too weak to suggest such a transition mechanism.

Gratitude is expressed to the Swiss National Science Foundation for financial support under No. 2000-5.422.

Acta Cryst. (1990). C46, 2284–2287

Structure of $\text{Cs}_5\text{Mo}_{21}\text{Se}_{23}$ Containing Mo_{21} Clusters

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(Received 3 November 1989; accepted 11 May 1990)

Abstract. Pentacaesium hencosamolybdenum tricosaselenium, $\text{Cs}_5\text{Mo}_{21}\text{Se}_{23}$, $M_r = 4495.35$, hexagonal, $P6_3/m$, $a = 9.6513(7)$, $c = 29.939(6)$ Å, $V = 2415.1(5)$ Å³, $Z = 2$, $D_x = 6.181$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 259.9$ cm⁻¹, $F(000) = 3878$, $T = 295$ K, $R = 0.034$ for 1290 observed. The main building block of the title compound is the new cluster unit $\text{Mo}_{21}\text{Se}_{23}$ whose Mo core consists of six

0108-2701/90/122284-04\$03.00

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face-linked Mo_6 octahedra. These cluster units are linked to each other through Mo–Se interunit bonds and delimit large voids and channels where the Cs ions reside in a tri- or tetra-capped trigonal prismatic Se environment.

Introduction. In a recent systematic survey of the lower ternary chalcogenides of molybdenum with the