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$Cu_2O(SO_4)$, Dolerophanite: Refinement of the Crystal Structure, with a Comparison of [O Cu(II)$_4$] Tetrahedra in Inorganic Compounds

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The refinement of the crystal structure of $Cu_2O(SO_4)$, dolerophanite, [$a = 9.370(1)$ Å, $b = 6.319(1)$ Å, $c = 7.639(1)$ Å, $\beta = 122.34(1)°$; space group C 2/m; $Z = 4$; $R = 0.035$] confirmed the trigonal dipyramidal coordination of one Cu(II) atom (mean distance Cu—O = 2.025 Å). One O atom is tetrahedrally surrounded by four Cu(II) atoms; the mean Cu(II)—O distance of 1.918 Å compares well to [O Cu(II)$_4$] tetrahedra found in inorganic crystal structures.

[Keywords: $Cu_2O(SO_4)$; *Dolerophanite; Crystal structure refinement;* [O Cu(II)$_4$] *Tetrahedron]*

$Cu_2O(SO_4)$, *Dolerophanit: Verfeinerung der Kristallstruktur mit einem Vergleich von* [O Cu(II)$_4$]*-Tetraedern in anorganischen Verbindungen*

Die Verfeinerung der Kristallstruktur von $Cu_2O(SO_4)$, Dolerophanit, [$a = 9.370(1)$ Å, $b = 6.319(1)$ Å, $c = 7.639(1)$ Å, $\beta = 122.34(1)°$; Raumgruppe C 2/m; $Z = 4$; $R = 0.035$] bestätigte die trigonal dipyramidale Koordination des einen Cu(II)-Atoms (mittlerer Cu—O-Abstand = 2.025 Å). Ein O-Atom ist tetraedrisch von vier Cu(II)-Atomen umgeben; der mittlere Cu(II)—O-Abstand von 1.918 Å entspricht den in ähnlichen [O Cu(II)$_4$]-Tetraedern von anorganischen Kristallstrukturen gefundenen Werten.

Introduction

Flügel-Kahler[1] determined the crystal structure of $Cu_2O(SO_4)$, dolerophanite, on natural material and gave a detailed description of the structure type. In connection with studies of the coordination chemistry of Cu(II) atoms a refinement of dolerophanite was performed (a) to confirm the trigonal dipyramidal coordination of one Cu(II) atom, and (b) for a

comparison with [O Cu(II)$_4$] tetrahedra in inorganic crystal structures. Because of lack of natural crystals synthetic material was used.

Results

Synthesis

Crystals of $Cu_2O(SO_4)$ were synthesized under following conditions: a mixture of $CuSO_4 \cdot 5\,H_2O$, $KHSO_4$, and $CuCl_2 \cdot 2\,H_2O$ (molecular ratio 1 : 1 : 10) was first heated for 2 hours at 150 (5) °C and afterwards for 5 hours at 600 (10) °C in a china crucible at atmospheric pressure. After a cooling-off period of ~ 12 hours the compounds $Cu_2O(SO_4)$ and $K_4[Cu_2O(SO_4)_2]_2 \cdot KCl$ (cf. caratiite[2]) were obtained. The needle-like crystals of the title compound are yellowish brown in colour (elongated parallel to [010]).

Refinement of the Crystal Structure

For the crystal data as well as for the parameters of the data collection cf. Table 1. The X-ray intensities were corrected for absorption (emperical ψ scans) as well as for *Lorentz-* and polarization effects. The atomic coordinates given in [1] were used in the starting set of a full-matrix least-squares refinement. Complex scattering functions[3] were used, and a secondary isotropic extinction correction was applied[4]. The obtained R values are included into Table 1; the structure parameters are given in Table 2; finally the largest difference of an atomic position given in [1] and in this refinement is 0.06 Å [atom O(2)], the mean value is 0.02 Å.

Table 1. *Summary of crystal data, X-ray intensity measurements, and crystal structure refinement for dolerophanite*

$a = 9.370\,(1)$ Å	STOE four-circle diffractometer and	
$b = 6.319\,(1)$ Å	program system STRUCSI on an ECLIPSE S/140	
$c = 7.639\,(1)$ Å	graphite monochromatized MoKα radiation	
$\beta = 122.34\,(1)°$	crystal dimensions:	$0.025 \times 0.09 \times 0.04$ mm^3
$V = 382.1$ Å^3	scan speed ratio:	$2\theta : \omega = 1 : 1$
Temperature: 295 K	step width:	0.03°
space group: C 2/m	steps/reflection:	$35 + (\alpha_1, \alpha_2)$ splitting
$Z = 4\{Cu_2O(SO_4)\}$	time/step:	0.5 to 1.5 s
μ(MoKα) = 113 cm^{-1}	3 standard reflections measured each 60 min	
	range of data: $3° < 2\theta < 60°$	
no. of variables: 47	measured reflections:	1 040 ($\pm h - k \pm l$)
$R = 0.035$	unique reflections:	598
$R_w = 0.032$	unique reflections with $F_o > 3\sigma(F_o)$: 558	
$w = 1.251/[\sigma(F_o)]^2$	(used for the crystal structure refinement)	

Table 2. *Atomic coordinates and anisotropic temperature parameters for dolerophanite with e.s.d.'s in parentheses.*

$$\mathrm{ATF} = \exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j]$$

Atom	*Wyckoff* notation	Site symmetry	*x/a*	*y/b*	*z/c*	U_{equiv}
Cu(1)	4e	1	1/4	1/4	0	0.009
Cu(2)	4i	m	0.0721 (1)	0	0.2182 (1)	0.010
S	4i	m	0.1024 (2)	1/2	0.3157 (3)	0.008
O(1)	4i	m	0.2038 (7)	1/2	0.2232 (9)	0.019
O(2)	4i	m	0.2947 (6)	0	0.4593 (8)	0.014
O(3)	4i	m	0.1514 (5)	0	0.0217 (7)	0.008
O(4)	8j	1	0.4916 (4)	0.1906 (6)	0.2498 (5)	0.012

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.0055 (4)	0.0106 (4)	0.0138 (4)	−0.0009 (3)	0.0025 (3)	0.0023 (3)
Cu(2)	0.0050 (4)	0.0175 (5)	0.0088 (4)	0	0.0002 (3)	0
S	0.0060 (6)	0.0101 (7)	0.0099 (7)	0	0.0016 (5)	0
O(1)	0.022 (3)	0.028 (3)	0.025 (3)	0	0.017 (3)	0
O(2)	0.008 (2)	0.024 (3)	0.009 (2)	0	−0.003 (2)	0
O(3)	0.004 (2)	0.009 (2)	0.010 (2)	0	0.001 (2)	0
O(4)	0.008 (1)	0.010 (2)	0.018 (2)	0.001 (1)	0.000 (1)	0.002 (1)

Discussion

The Cu(1) atom is "square planar" coordinated by O atoms with Cu(1)—O = 1.882(2) Å and 2.070(3) Å ("[CuO_4] square"). The coordination figure is completed to a distorted octahedron by two distant O atoms [2.526(5) Å]. Contrary the Cu(2) atom is trigonal dipyramidal coordinated with only slightly varying Cu(2)—O bond lengths. The mean Cu(2)—O of 2.025 Å is 2.5% longer than the mean value within the [$Cu(1)O_4$] square. The Cu(2) atom is shifted out of the plane defined by the three equatorial O atoms into the direction of one apex by 0.283 Å. Nevertheless, the bond lengths to both the apexes are equal to each other within one e.s.d. [Cu—O = 1.906(6) Å; 1.907(5) Å], and they are the shortest bonds within the coordination polyhedron of the Cu(2) atom [for the equatorial O atoms Cu—O = 2.000(5) Å; 2.155(3) Å, 2 ×]. Further O atoms have Cu(2)—O $\geqslant$ 3.3 Å. Similar coordinations of Cu(II) atoms have been found only in a few inorganic crystal structures (cf.[5—7]).

The S—O bond lengths of the [SO_4] group can be correlated with the coordination of the O atoms: S—O(1) = 1.456(6) Å and S—O(2) = 1.453(6) Å are equal to each other within one e.s.d.; the O(1) atom builds two long, the O(2) atom one short Cu—O bond. The O(4) atom builds two short Cu—O bonds [S—O(4) = 1.491(3) Å].

Table 3. *Comparison of O atoms coordinated by four Cu(II) atoms in inorganic crystal structures*

Chemical formula (mineral name)	O—Cu (in Å) from–to	mean	Cu—O—Cu (in °) from–to
CuO (tenorite)[8]	1.951–1.961	1.956	95.7–145.8
$Cu_2O(SO_4)$ (dolerophanite)	1.882–2.000	1.918	93.6–117.6
$K_4[Cu_2O(SO_4)_2]_2 \cdot MeCl$ (caratiite)[2]	1.902–1.948	1.925	97.8–114.7
$Cu_4O(PO_4)_2$[9,10]	1.895–1.924	1.911	96.9–142.5
$Cu_5O_2(PO_4)_2$[11]	1.909–1.943	1.932	95.1–125.0
$Cu_3Mo_2O_9$[12]	1.860–1.962	1.899	102.6–135.1

The atom O(3) is tetrahedrally coordinated by two Cu(1) and two Cu(2) atoms. Table 3 gives a survey of inorganic compounds with an O atom coordinated only by Cu(II) atoms. All the coordination polyhedra are more or less distorted tetrahedra. It is to be mentioned that they were only found in compounds without any H_2O molecules or OH groups.

The Cu—O bonds in the different [O $Cu(II)_4$] tetrahedra summarized in Table 3 represent in most cases (short) bonds within "[CuO_4] squares";

two exceptions are known: in $Cu_2O(SO_4)$ and in $Cu_5O_2(PO_4)_4$ trigonal dipyramidal coordinated Cu(II) atoms were found which are involved at the building of [O Cu(II)$_4$] tetrahedra. From the formula given by *Brown* and *Wu*[13] for calculating bond valences one can calculate a formal $O^{[4\,Cu]}$—Cu(II) distance of 1.93 Å, which compares well to the mean values given in Table 3. The maximum difference of the O—Cu bonds within one [O Cu(II)] tetrahedron was found to be 0.118 Å [in $Cu_2O(SO_4)$], in total they vary for 0.140 Å [the shortest was found in $Cu_3Mo_2O_9$, and the longest one in $Cu_2O(SO_4)$ for the $Cu(2)^{[5]}$ atom]. The Cu—O—Cu bond angles are varying within these coordination polyhedra from 93.6° in $Cu_2O(SO_4)$ to 145.8° in CuO.

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