

# Structure of $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ : a Novel Corrosion Product of Copper

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During laboratory studies of the atmospheric corrosion of copper in humid air containing sub-ppm amounts of  $\text{SO}_2$ ,  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  was identified as a corrosion product. The crystal structure was solved in the space group  $P\bar{1}$  (No. 2) with unit-cell dimensions  $a = 6.064(2)$ ,  $b = 11.012(6)$ ,  $c = 5.490(2)$  Å,  $\alpha = 102.68(4)$ ,  $\beta = 92.43(3)$ ,  $\gamma = 92.06(3)^\circ$ . The structure was refined to  $R = 0.052$  for 714 unique observed reflections.  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  contains  $(\text{Cu}_2(\text{OH})_3(\text{SO}_4))_n$  layers parallel to the *ac*-plane. Between these layers there are planar monomeric  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  units that are weakly linked to the layers with two sulfate oxygens.

Sulfur dioxide has long been recognized as an important accelerator for the atmospheric corrosion of several metals as well as for calcareous building stone.<sup>1</sup> In the case of copper and its alloys the importance of  $\text{SO}_2$  in the atmosphere is indicated by the frequent occurrence of copper hydroxysulfates in the corrosion layer. Brochantite  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , and antlerite  $\text{Cu}_3(\text{OH})_4\text{SO}_4$  are the corrosion products mainly responsible for the green colour of the patina that forms on copper and bronze surfaces exposed in an urban environment.<sup>2</sup>

A number of copper hydroxysulfates have been described in the literature. Among these, brochantite<sup>3</sup>  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , posnjakite<sup>4</sup>  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$ , langite<sup>5,6</sup>  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and antlerite<sup>7</sup>  $\text{Cu}_3(\text{OH})_4\text{SO}_4$  have been subjected to full structure determinations. In addition there have been a number of reports of more poorly characterized phases, i.e. wroewolfeite<sup>8</sup>  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$  and the hydroxysulfates<sup>9,10</sup>  $\text{Cu}_3(\text{OH})_2(\text{SO}_4)_2$ ,  $\text{Cu}_3(\text{OH})_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}_3(\text{OH})_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$ .

In the course of a laboratory study of the atmospheric corrosion of copper in humid air containing sub-ppm amounts of  $\text{SO}_2$  we identified a corrosion product with an X-ray powder diffraction pattern that did not belong to any of the known copper hydroxysulfate phases.<sup>11</sup> Together with cuprite,  $\text{Cu}_2\text{O}$ , the new phase was the first crystalline corrosion product to appear during exposure. A similar diffraction pattern, but lacking in detail, was reported by Ericsson and Sydberger in a corrosion study of copper.<sup>12</sup> Moreover, in 1969 Lachenal and

Gauthier<sup>10,13</sup> reported on a salt with the suggested composition  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$  and in 1992 Pollard *et al.*<sup>14</sup> studied a copper hydroxysulfate with the proposed stoichiometry  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ . Both sets of authors reported diffraction patterns resembling that of the present compound, and were probably actually working with  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . In this study we report on the synthesis and crystal structure of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

## Experimental

*Preparation of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .* The compound was prepared by treating tenorite ( $\text{CuO}$ ; Merck, gepulvert, zur analyse) in a saturated solution of  $\text{CuSO}_4(\text{aq})$  at  $20^\circ\text{C}$ . 1.0 g of  $\text{CuO}(\text{s})$  and 10 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$  were mixed in a 50 ml round-bottomed flask, and 5 ml of high-purity water was added slowly to the mixture. The reagents were of analytical grade. After 24 h of agitation of this mixture in the stoppered flask using a magnetic stirrer the reaction was completed, and the greenish white product was collected on a sintered glass crucible no. 3 by applying suction. The product was washed with water and 99.5% ethanol and dried with suction for 10 min. Finally it was dried in a vacuum over silica gel. The product consisted of crystallites about  $10^{-6}$  m in size.

The purity of the product was highly dependent on the reactivity of the tenorite. Thus, different batches of  $\text{CuO}$  from the same supplier gave rise to products with large variations in purity. Finely divided  $\text{CuO}$  (Merck, 1967 and 1971) produced X-ray pure  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ,

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while less active CuO (Merck, 1990) resulted in the formation of a brownish green product with traces of unreacted oxide after 24 h treatment. Using prolonged reaction times resulted in the formation of impurities consisting of other hydroxysulfates, i.e. brochantite, posnjakite and antlerite. Increasing the reaction temperature also resulted in an impure product.

In order to prepare crystals of sufficient size and quality for the single-crystal structure determination an alternative synthetic method was used. A piece of copper sheet which had been oxidized to form tenorite on its surface was covered with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$  and exposed

Table 1. Powder diffraction data for  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . Guinier-Hägg camera technique,  $\text{CuK}\alpha_1$ ,  $\lambda = 1.54056 \text{ \AA}$ , Si internal standard.

$l_{\text{obs}}$	$d_{\text{obs}}/\text{\AA}$	$2\theta_{\text{obs}}/^\circ$	$l_{\text{calc}}$	$d_{\text{calc}}/\text{\AA}$	$h$	$k$	$l$
100	10.812	8.171	100	10.778	0	1	0
47	5.390	16.434	37	5.389	0	2	0
17	5.161	17.167	12	5.160	1	1	0
12	4.420	20.075	9	4.417	0	1	1
11	4.126	21.517	6	4.127	1	0	-1
6	3.938	22.561	3	3.940	1	-1	1
9	3.920	22.667	7	3.920	1	2	0
22	3.591	24.776	16	3.593	0	3	0
12	3.519	25.289	8	3.520	1	-2	1
3	3.431	25.950	3	3.432	0	2	1
13	3.354	26.555	8	3.357	0	3	-1
7	3.167	28.158	5	3.169	1	-3	0
4	2.959	30.181	2	2.960	2	-1	0
5	2.901	30.797	3	2.900	1	2	1
8	2.749	32.541	3	2.751	0	1	-2
28	2.698	33.180	7	2.700	2	0	-1
			6	2.695	0	4	0
23	2.649	33.807	10	2.651	0	2	-2
4	2.601	34.455	2	2.601	2	-1	1
26	2.579	34.763	5	2.581	2	-1	-1
			6	2.578	2	0	1
10	2.477	36.239	4	2.479	2	2	-1
31	2.424	37.055	4	2.427	0	3	-2
20	2.352	38.229	8	2.354	2	-2	-1
2	2.260	39.866	1	2.262	1	3	-2
3	2.226	40.486	1	2.229	2	3	-1
10	2.208	40.844	4	2.209	0	2	2
12	2.196	41.069	5	2.196	2	2	1
16	2.158	41.821	8	2.160	0	4	-2
8	2.093	43.193	4	2.095	2	-3	-1
11	2.026	44.686	4	2.028	2	-4	1
6	1.955	46.404	2	1.955	2	3	1
5	1.900	47.820	2	1.903	0	5	-2
5	1.847	49.293	3	1.849	2	-4	-1
5	1.795	50.838	2	1.796	0	6	0
2	1.739	52.594	1	1.740	2	5	-1
7	1.732	52.797	4	1.733	2	4	1
4	1.716	53.356	2	1.717	0	4	2
4	1.677	54.699	2	1.678	0	6	-2
6	1.598	57.619	2	1.600	2	1	-3
6	1.587	58.072	3	1.588	2	2	-3
4	1.576	58.531	2	1.577	2	0	-3
16	1.539	60.085	3	1.538	2	-2	3
6	1.514	61.147	2	1.515	4	0	0
5	1.512	61.277	1	1.512	4	-1	0
3	1.504	61.601	2	1.504	2	0	3
7	1.479	62.763	2	1.480	4	-2	0

to air at approximately 100% relative humidity at 22–25°C. After several months exposure minute quantities of greenish crystals with maximum dimensions of  $3 \times 10^{-5} \text{ m}$  had formed. One of these crystals was selected for the single-crystal work.

*X-Ray powder diffraction analysis.* The product was examined by X-ray powder diffraction using the Guinier-Hägg camera technique. Silicon was used as internal standard. Film intensities were measured by an optical scanner (LS-20), and the resulting data were processed using the computer program SCANPI 7<sup>15</sup> (Table 1).

*Infrared spectrum.* The spectrum of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  was recorded on a Perkin Elmer F-1800 FTIR spectrometer using the KBr disc technique. A characteristic band in the  $\text{SO}_4^{2-}$  stretching region was registered at  $1092 \text{ cm}^{-1}$  (Fig. 1). Table 2 displays all the observed frequencies.

*Chemical analysis.* The copper and sulfate content in a sample of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  was determined using the following procedure: 2.5 g  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  were dissolved in 7 ml of concentrated  $\text{HNO}_3$  and diluted with 140 ml of water. From this solution three samples were taken. Each sample was first analysed with respect to copper content by electrogravimetry and then with respect to sulfate content using a modified version of the method described by Vogel.<sup>16</sup> Sulfate was determined by precipitation as lead sulfate in a nearly boiling sample solution containing 50% ethanol. The precipitate was re-dissolved in 0.5 M EDTA and back-titrated with 0.05 M  $\text{ZnCl}_2$  solution using Erio T-KCl as an indicator. The analytical results expressed as an average of six determinations were: Cu  $46.72 \pm 0.04\%$ ;  $\text{SO}_4^{2-}$   $27.54 \pm 0.12\%$ . Calculated for  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ : Cu 46.45%;  $\text{SO}_4^{2-}$  28.09%. The small deviation from the calculated results may be due to traces of other copper compounds not detected by XRD [e.g. posnjakite and copper(II) oxide].

Table 2. Infrared frequencies of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (400–4000  $\text{cm}^{-1}$ ). Tentative assignments based on Ref 22 are given.

Frequency/ $\text{cm}^{-1}$	Frequency/ $\text{cm}^{-1}$
3589	668
3549	618
3449	586
3229	544
3054	513
1625	495
1092	458
982	436
937	
783	

OH stretching } Sulfate bending  $\nu_4$   
H-O-H stretching }  
H-O-H bending } Sulfate bending  $\nu_2$   
Sulfate stretching  $\nu_3$   
Sulfate stretching  $\nu_1$   
or Cu-O-H bending  
Cu-O-H bending

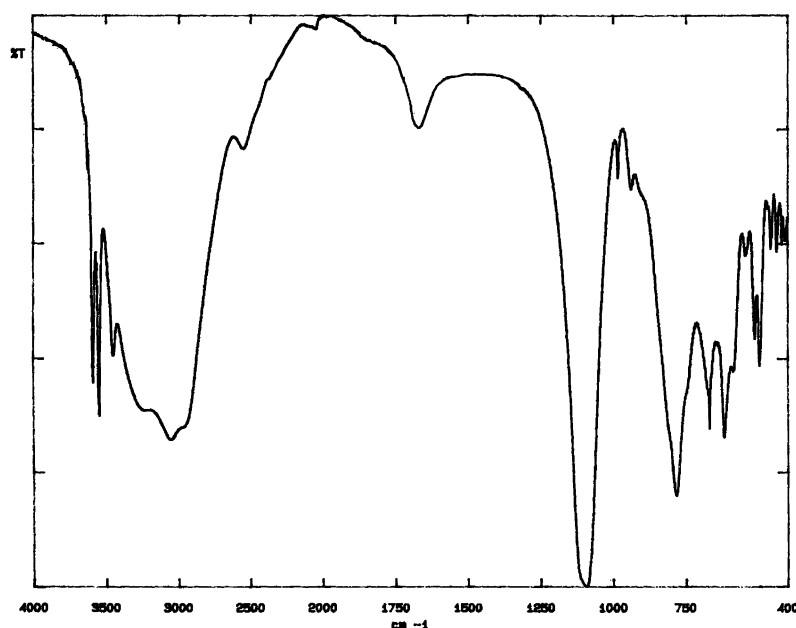


Fig. 1. FTIR spectrum of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

### Structure determination

A green rectangular crystal of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  having approximate dimensions  $0.03 \times 0.02 \times 0.01$  mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo  $K_\alpha$  radiation and a 12 kW rotating-anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 24 carefully centered reflections in the range  $15.15 < 2\theta < 26.80^\circ$  corresponded to a triclinic cell with dimensions:  $a = 6.064(2)$ ,  $b = 11.012(6)$ ,  $c = 5.490(2)$  Å,  $\alpha = 102.68(4)$ ,  $\beta = 92.43(3)$ ,  $\gamma = 92.06(3)^\circ$ ,  $V = 357.0(5)$  Å<sup>3</sup>.

For  $Z = 2$  and formula weight 341.97, the calculated density is  $3.181 \text{ g cm}^{-3}$ . The space group was determined to be  $P\bar{1}$  (No. 2).

The data were collected at a temperature of  $-130 \pm 1^\circ\text{C}$  using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $50.1^\circ$ . Scans of  $(1.15 + 0.30 \tan \theta)^\circ$  were made at a speed of  $1.0^\circ \text{ min}^{-1}$  (in  $\omega$ ). The weak reflections [ $I < 10.0\sigma(I)$ ] were rescanned (maximum of 3 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

Of the 1388 reflections which were collected, 1257 were unique ( $R_{\text{int}} = 0.041$ ). The intensities of three reflections measured after every 150 reflections remained constant and no decay correction was applied. The linear absorption coefficient for Mo  $K_\alpha$  is  $77.3 \text{ cm}^{-1}$ . The data were corrected for Lorentz and polarization effects but not for

absorption. A correction for secondary extinction was applied (coefficient =  $0.21992 \times 10^{-6}$ ).

The structure was solved by combination of Patterson and direct methods.<sup>17</sup> The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 714 observed reflections [ $I > 1.96\sigma(I)$ ] and 119 variable parameters and converged with unweighted and weighted agreement factors of:  $R = \Sigma \|F_o\| - |F_c| / \Sigma |F_o| = 0.052$  and  $R_w = [(\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2} = 0.061$ .

The standard deviation of an observation of unit weight was 1.54. The weighing scheme was based on counting statistics and included a factor ( $p = 0.04$ ) to downweight the intense reflections. The maximum and minimum

Table 3. Positional parameters and  $B(\text{eq})^a$  for  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

Atom	x	y	z	$B(\text{eq})/\text{Å}^2$
Cu(1)	1.0000	0	0	0.8(1)
Cu(2)	0.5000	0	0	0.8(1)
Cu(3)	0.7510(4)	-0.0028(2)	0.5044(4)	0.79(8)
Cu(4)	0.5000	0.5000	0	1.2(1)
S(1)	0.8234(7)	0.2777(4)	0.2869(8)	0.8(2)
O(1)	0.736(2)	-0.093(1)	0.834(2)	1.4(5)
O(2)	0.501(2)	0.084(1)	0.707(2)	0.5(4)
O(3)	1.006(2)	0.081(1)	0.711(2)	1.1(5)
O(4)	0.768(2)	0.145(1)	0.245(2)	0.9(4)
O(5)	0.965(2)	0.296(1)	0.087(2)	1.2(5)
O(6)	0.621(2)	0.345(1)	0.278(2)	1.1(5)
O(7)	0.938(2)	0.321(1)	0.531(2)	1.4(5)
O(8)	0.225(2)	0.492(1)	0.148(2)	1.5(5)
O(9)	0.388(2)	0.361(1)	-0.296(2)	1.6(5)

<sup>a</sup>  $B(\text{eq}) = (8/3)\pi^2 \Sigma_i \Sigma_j u_{ij} a_i^* a_j^* a_j$ .

Table 4. Bond distances (in Å) for  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

Atom	Atom	Distance
Cu(1)	O(1) <sup>i</sup> , O(1) <sup>ii</sup>	1.95(1)
Cu(1)	O(3) <sup>i</sup> , O(3) <sup>ii</sup>	1.99(1)
Cu(1)	O(4), O(4) <sup>iii</sup>	2.39(1)
Cu(2)	O(1) <sup>i</sup> , O(1) <sup>iv</sup>	1.93(1)
Cu(2)	O(2) <sup>i</sup> , O(2) <sup>iv</sup>	2.03(1)
Cu(2)	O(4), O(4) <sup>v</sup>	2.39(1)
Cu(3)	O(2) <sup>iv</sup> , O(3)	1.95(1)
Cu(3)	O(3) <sup>ii</sup>	2.03(1)
Cu(3)	O(2)	2.06(1)
Cu(3)	O(1)	2.25(1)
Cu(3)	O(4)	2.39(1)
Cu(4)	O(8), O(8) <sup>vi</sup>	1.89(1)
Cu(4)	O(9), O(9) <sup>vi</sup>	2.05(1)
Cu(4)	O(6), O(6) <sup>vi</sup>	2.64(1)
S(1)	O(4)	1.45(1)
S(1)	O(6)	1.46(1)
S(1)	O(7)	1.46(1)
S(1)	O(5)	1.47(1)

(i)  $x, y, z - 1$ . (ii)  $2 - x, -y, 1 - z$ . (iii)  $2 - x, -y, -z$ . (iv)  $1 - x, -y, 1 - z$ . (v)  $1 - x, -y, -z$ . (vi)  $1 - x, 1 - y, -z$ .

peaks on the final difference Fourier map corresponded to 1.17 and  $-1.40 \text{ e } \text{Å}^{-3}$ , respectively.

Neutral atom scattering factors were taken from Ref. 18. Anomalous dispersion effects were included in  $F_{\text{calc}}$ ;<sup>19</sup> the values for  $\Delta f'$  and  $\Delta f''$  were chosen from Ref. 18. All calculations were performed using the TEXSAN<sup>20</sup> crystallographic software package.

Tables 3–5 describe positional parameters,  $B(\text{eq})$ , bond distances and bond angles for  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

## Results and discussion

$\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  contains negatively charged corrugated  $(\text{Cu}_2(\text{OH})_3(\text{SO}_4))_n$  sheets parallel to the  $ac$ -plane, the sulfate groups projecting from both sides. Sandwiched between the sheets monomeric  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  units are found that are weakly linked to the layers through two sulfate oxygens (Figs. 2 and 3).

The copper atoms in the layers Cu(1), Cu(2) and Cu(3) are coordinated to six oxygen atoms in distorted octahedral arrangements with Cu–O distances in the equatorial plane involving O(1), O(2) and O(3) ranging from 1.93–2.06 Å, while the axial oxygen atoms are situated 2.39 [(O(4))] and 2.25 [O(1)] Å from the copper ion (Table 4). This coordination is typical of divalent copper.

Cu(4) is coordinated to four equatorial oxygens [O(8) and O(9)] at 1.89 and 2.05 Å distance, respectively, and with two axial oxygens [O(6)] at 2.64 Å. Thus the mean value of the axial/equatorial bond length ratio is 1.34. This may be compared to the corresponding values for Cu(1), Cu(2) and Cu(3), which are 1.21, 1.21 and 1.20, respectively. CuO, which is usually considered to contain square-planar copper,<sup>21</sup> exhibits an even greater axial/equatorial bond length ratio than Cu(4) with the planar oxygens at 1.96 Å, while the distance to the two axial

Table 5. Bond angles (in °) for  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}^a$ .

Atoms	Atoms	Atoms	Angle
O(3) <sup>i</sup> –Cu(1)–O(4) <sup>iii</sup>	O(3) <sup>ii</sup> –Cu(1)–O(4)		83.8(4)
O(1) <sup>i</sup> –Cu(1)–O(3) <sup>i</sup>	O(1) <sup>ii</sup> –Cu(1)–O(3) <sup>ii</sup>		86.4(5)
O(1) <sup>i</sup> –Cu(1)–O(4)	O(1) <sup>ii</sup> –Cu(1)–O(4) <sup>iii</sup>		88.9(4)
O(1) <sup>i</sup> –Cu(1)–O(4) <sup>iii</sup>	O(1) <sup>ii</sup> –Cu(1)–O(4)		91.1(4)
O(1) <sup>i</sup> –Cu(1)–O(3) <sup>ii</sup>	O(1) <sup>ii</sup> –Cu(1)–O(3) <sup>i</sup>		93.6(5)
O(3) <sup>i</sup> –Cu(1)–O(4) <sup>iii</sup>	O(3) <sup>ii</sup> –Cu(1)–O(4)		96.2(4)
O(1) <sup>i</sup> –Cu(1)–O(1) <sup>ii</sup>	O(3) <sup>ii</sup> –Cu(1)–O(3) <sup>i</sup>	O(4)–Cu(1)–O(4) <sup>iii</sup>	180.00
O(1) <sup>i</sup> –Cu(2)–O(2) <sup>i</sup>	O(1) <sup>iv</sup> –Cu(2)–O(2) <sup>iv</sup>		84.2(5)
O(2) <sup>i</sup> –Cu(2)–O(4) <sup>v</sup>	O(2) <sup>iv</sup> –Cu(2)–O(4)		86.2(4)
O(1) <sup>i</sup> –Cu(2)–O(4)	O(1) <sup>iv</sup> –Cu(2)–O(4) <sup>v</sup>		89.5(5)
O(1) <sup>iv</sup> –Cu(2)–O(4)	O(1) <sup>i</sup> –Cu(2)–O(4) <sup>v</sup>		90.5(5)
O(2) <sup>i</sup> –Cu(2)–O(4)	O(2) <sup>iv</sup> –Cu(2)–O(4)		93.9(4)
O(1) <sup>i</sup> –Cu(2)–O(2) <sup>iv</sup>	O(1) <sup>iv</sup> –Cu(2)–O(2) <sup>i</sup>		95.8(5)
O(1) <sup>i</sup> –Cu(2)–O(1) <sup>iv</sup>	O(4)–Cu(2)–O(4) <sup>v</sup>	O(2) <sup>i</sup> –Cu(2)–O(2) <sup>iv</sup>	180.00
O(2)–Cu(3)–O(1)			75.9(4)
O(3)–Cu(3)–O(1)			79.3(5)
O(2) <sup>iv</sup> –Cu(3)–O(2)			81.0(4)
O(3)–Cu(3)–O(3) <sup>ii</sup>			81.3(5)
O(3) <sup>ii</sup> –Cu(3)–O(4)			83.0(5)
O(2) <sup>iv</sup> –Cu(3)–O(4)			87.9(4)
O(3)–Cu(3)–O(4)			90.9(5)
O(2)–Cu(3)–O(4)			93.3(4)
O(2) <sup>iv</sup> –Cu(3)–O(3) <sup>ii</sup>			98.3(5)
O(3)–Cu(3)–O(2)			99.4(5)
O(2) <sup>iv</sup> –Cu(3)–O(1)			102.0(5)
O(3) <sup>ii</sup> –Cu(3)–O(1)			107.8(5)
O(1)–Cu(3)–O(4)			163.8(4)
O(3) <sup>ii</sup> –Cu(3)–O(2)			176.2(5)
O(2) <sup>iv</sup> –Cu(3)–O(3)			178.7(5)
O(8) <sup>vi</sup> –Cu(4)–O(6) <sup>vi</sup>	O(8)–Cu(4)–O(6)		84.5(5)
O(9) <sup>vi</sup> –Cu(4)–O(6) <sup>vi</sup>	O(9) <sup>vi</sup> –Cu(4)–O(6)		86.1(4)
O(8) <sup>vi</sup> –Cu(4)–O(9)	O(8) <sup>vi</sup> –Cu(4)–O(9) <sup>vi</sup>		90.0(5)
O(8)–Cu(4)–O(9)	O(8)–Cu(4)–O(9) <sup>vi</sup>		90.0(5)
O(9)–Cu(4)–O(6)	O(9) <sup>vi</sup> –Cu(4)–O(6) <sup>vi</sup>		93.9(4)
O(8) <sup>vi</sup> –Cu(4)–O(6)	O(8)–Cu(4)–O(6) <sup>vi</sup>		95.5(5)
O(8) <sup>vi</sup> –Cu(4)–O(8)	O(9)–Cu(4)–O(9) <sup>vi</sup>	O(6)–Cu(4)–O(6) <sup>vi</sup>	180.00
O(4)–S(1)–O(5)			107.4(7)
O(4)–S(1)–O(6)			109.2(7)
O(6)–S(1)–O(7)			109.4(7)
O(4)–S(1)–O(7)			109.8(7)
O(6)–S(1)–O(5)			110.3(7)
O(7)–S(1)–O(5)			110.8(7)

<sup>a</sup> For symmetry codes see Table 4.

oxygens is 2.78 Å, the ratio being 1.42. The fact that the symmetry of the  $\text{CuO}_6$  group approaches  $D_{2h}$  may be an argument for the 4 + 2 description for Cu(4). However, we find that the coordination of Cu(4) is best described as being planar, resulting in monomeric  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  units. To our knowledge the planar  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  monomer has not been described previously.

The positions of the hydrogen atoms were not determined in this study, but were interpreted assuming tetrahedral bonding geometry for oxygen. Each oxygen atom in the sheets forms three strong bonds with copper atoms, and thus has only one direction available for hydrogens. Hence the oxygens in the sheets are considered to be hydroxy groups. The remaining hydrogen atoms are then located on Cu(4) between the sheets, creating monomeric  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  units. Both crystallographically unique water molecules in the monomer are within 2.85 Å from two other oxygen atoms [O(8) in contact with O(5)

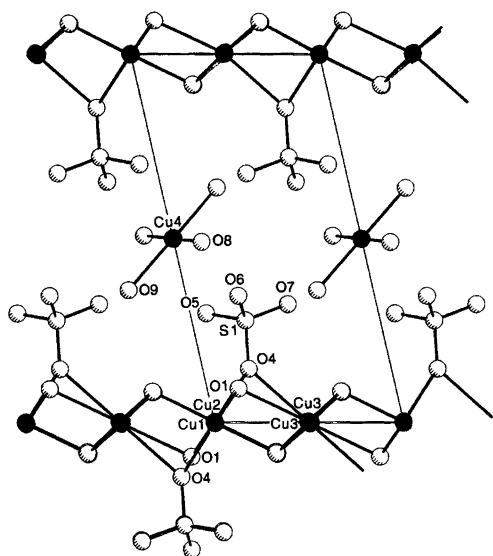


Fig. 2. Structure of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  in the  $bc$ -plane showing  $(\text{Cu}_2(\text{OH})_3(\text{SO}_4))_n$  layers and monomeric  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  units.

and O(7) and O(9) in contact with O(6) and O(7)]. Hence, different hydrogen-bonding surroundings could explain the differences in the bond lengths [1.89(1) and 2.05(1) Å].

The sulfate group is only slightly distorted from tetrahedral symmetry, with bond angles from 107.4 to 109.8°. The S–O distances, ranging from 1.45(1) to 1.47(1) Å, are typical of the sulfate ion. Among the sulfate oxygens only O(4) and O(6) coordinate Cu, and then only in the axial position.

Except for the monomeric  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  units, the structure of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  is similar to the hydroxysulfates brochantite<sup>3</sup>  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , posnjakite<sup>4</sup>  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$ , langite<sup>5,6</sup>  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and antlerite<sup>7</sup>  $\text{Cu}_3(\text{OH})_4\text{SO}_4$ . These compounds all contain corrugated layers of distorted  $\text{CuO}_6$  octahedra with sulfate groups attached, hydrogen bonds and weak (axial)

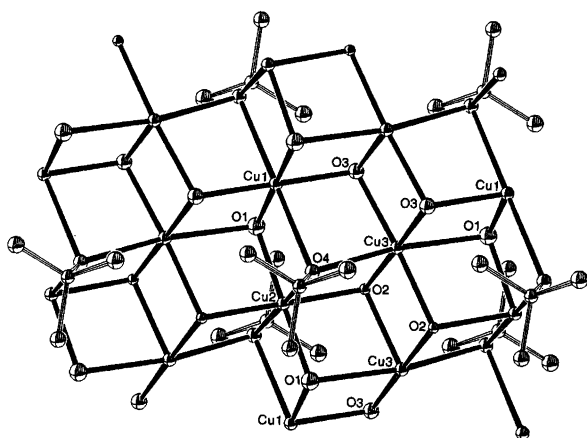


Fig. 3. Structure of  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  in the  $ac$ -plane showing  $(\text{Cu}_2(\text{OH})_2\text{SO}_4 \cdot \text{H}_2\text{O})_n$  layers.

Table 6.  $\text{SO}_4^{2-}/\text{OH}^-$  ratios for the copper hydroxysulfates.

Mineral name	Formula	$\text{SO}_4^{2-}/\text{OH}^-$
	$\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$	1/3
Antlerite	$\text{Cu}_3(\text{OH})_4\text{SO}_4$	1/4
Brochantite	$\text{Cu}_4(\text{OH})_6\text{SO}_4$	1/6
Posnjakite	$\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$	1/6
Wroewolfeite	$\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$	1/6
Langite	$\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 2\text{H}_2\text{O}$	1/6

Cu–O bonds connecting adjacent layers. As in the present compound posnjakite and langite contain corrugated sheets built from Cu(II) atoms and  $\text{OH}^-$  groups, each hydroxide being linked to three copper atoms. All three compounds also contain sulfate groups coordinated to copper through one oxygen and projecting into the space between sheets. In posnjakite the only water molecule is coordinated to copper in sheets, and in langite one water molecule is coordinated to copper while the other is held only by hydrogen bonds.

Secco<sup>22</sup> studied the IR spectra of antlerite and brochantite in some detail. OH bands were reported to occur in the range 3600–3200  $\text{cm}^{-1}$  depending on the degree of hydrogen bonding. According to the same study the peaks at 3589 and 3549  $\text{cm}^{-1}$  fall in the range of non-hydrogen bonded OH, while the peaks at 3449 and 3229  $\text{cm}^{-1}$  would belong to the range for OH groups involved in medium and strong hydrogen bonds, respectively. The 3054  $\text{cm}^{-1}$  peak lies outside this range and may be due to water. The presence of water is confirmed by the 1625  $\text{cm}^{-1}$  peak. The spectrum in the range 1200–400  $\text{cm}^{-1}$  is also reminiscent of the spectra of antlerite and brochantite. Tentative assignments based on Secco's work are given in Table 2.

Among the copper hydroxysulfates that have been subject to structure determination,  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  is the one with the highest  $\text{SO}_4^{2-}/\text{OH}^-$  ratio (Table 6). Thus  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  would be stabilized by low pH and high sulfate activity. However,  $\text{Cu}_{2.5}(\text{OH})_3\text{SO}_4 \cdot 2\text{H}_2\text{O}$  decomposes with time even in concentrated  $\text{CuSO}_4(\text{aq})$ , forming brochantite, posnjakite or antlerite.

As most corrosion products also occur as minerals, it is suggested that the present compound may form a mineral in nature.

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