The Crystal Structure of $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$

PEDER KIERKEGAARD and BIRGIT NYBERG

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The structure of copper(I,II) sulphite, $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$, has been derived on the basis of three-dimensional X-ray data and refined using least-squares methods. The unit cell, which contains two formula units, has the dimensions

$$a = 5.5671 \pm 0.0014 \text{ Å}$$
$$b = 7.7875 \pm 0.0010 \text{ Å}$$
$$c = 8.3635 \pm 0.0012 \text{ Å}$$
$$\beta = 91.279° \pm 0.013°$$

The coordination figure around the copper(I) atoms is a somewhat distorted tetrahedron formed by three oxygen atoms and one sulphur, with $Cu(I)-O(S)$ distances of $2.11-2.14$ Å. The arrangement around the copper(II) atoms is the distorted $(4 + 2)$ octahedral one, formed by two "water" oxygen atoms with $Cu(II)-O(H_2O) = 1.92$ Å and four oxygens at distances 2.03 ($2 \times$) and 2.47 Å ($2 \times$). The sulphite ions in the structure are trigonal pyramids with the mean distance $S-O = 1.51$ Å, and the average interbond angle $O-S-O = 106.9°$. The tetrahedra, octahedra and pyramids in the structure are coupled together to give a threedimensional network. A discussion of the structure is given.

For some time studies have been conducted at this Institute on the crystal structures of various binary and ternary oxides of copper and also on the structural chemistry of the sulphite ion. The work reported in this article may be said to have its origin in the intersection of these two lines of research.

The existence of a crystalline, red compound of the composition $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$ was first reported by Chevreul[1] in 1812. Several investigators have later on studied this material[2] but no crystallographic data seem to have been reported.

This article will describe the result of an investigation of the crystal structure of $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$.

EXPERIMENTAL

Preparation of crystals. When a stream of sulphur dioxide was passed through an aqueous solution (0.4 M) of copper(II) sulphate at about 70°C for 2 h a red, crystalline precipitate was obtained. (The method according to Pessin and Shabashowa[3]). After

washing with water the air dried sample was investigated under the microscope and found to consist of rectangular or in some cases triangular prisms.

Analysis. A sample was dissolved in a hot ammoniacal solution of hydrogen peroxide. After boiling away the excess of peroxide, one part of the solution was acidified with nitric acid and the amount of *copper* was determined electrolytically according to Vogel.[4] From the second part of the solution, slightly acidified with hydrochloric acid, the amount of *sulphate* was determined gravimetrically as $BaSO_4$.

The *water* was determined by the Hartwig-Bendig[5] modification of Brush[6] and Penfield's[7] method.

	Calculated for $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$	Found
% Cu	49.28	48.9 ± 0.3
% S	16.58	16.0 ± 0.4
% H_2O	9.32	9.3 ± 0.3

Table 1. X-Ray powder data of $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$. $CuK\alpha_1$ radiation. $(\lambda CuK\alpha_1) = 1.54050$ Å

$h\ k\ l$	$10^5 \sin^2 \Theta$ obs	$10^5 \sin^2 \Theta$ calc	$10^5(\sin^2 \Theta_{obs} - \sin^2 \Theta_{calc})$	I obs
0 1 1	1840	1827	+ 13	w
1 0 $\bar{1}$	2704	2706	− 2	vvst
1 0 1	2802	2820	− 18	vvw
1 1 0	2892	2893	− 1	w
0 0 2	3398	3394	+ 4	vst
1 1 $\bar{1}$	3697	3685	+ 12	vw
1 1 1	3797	3799	− 2	vw
0 2 0	—	3913	—	—
0 1 2	4371	4372	− 1	vw
0 2 1	4766	4761	+ 5	vw
1 2 0	5818	5828	− 10	vvw
1 1 $\bar{2}$	6178	6174	+ 4	w
1 1 2	6412	6407	+ 5	vst
1 2 $\bar{1}$	—	6618	—	—
1 2 1	6732	6734	− 2	w
0 2 2	—	7308	—	—
2 0 0	7676	7661	+ 15	stdiff
0 1 3	—	8626	—	—
2 1 0	—	8639	—	—
1 2 $\bar{2}$	9130	9111	+ 19	w
1 2 2	9340	9337	+ 3	w
2 1 $\bar{1}$	—	9374	—	—
1 0 $\bar{3}$	—	9382	—	—
2 1 1	9593	9602	− 9	vw
0 3 1	9645	9653	− 8	vst
1 0 3	—	9733	—	—
1 1 $\bar{3}$	—	10369	—	—
1 1 3	{ 10708	10701	+ 7	
1 3 0		10720	− 12	vw
2 0 $\bar{2}$	—	10828	—	—
2 0 2	—	11283	—	—
1 3 $\bar{1}$	11513	11512	+ 1	m

The powder photograph was measured and interpreted to $\sin^2\Theta = 0.45$. Reflections systematically absent in space group $P2_1/n$ have been omitted.

X-Ray diffraction data and computing methods. The powder pattern could be interpreted by assuming a monoclinic unit cell. Values for the cell dimensions were calculated from a photograph taken with strictly monochromatized $CuK\alpha_1$ radiation in a Guinier-type focusing camera. Potassium chloride ($a = 6.29228$ Å)[8] was used as an internal standard (see Table 1). The unit-cell dimensions (25°C) are:

$$a = 5.5671 \pm 0.0014 \text{ Å}$$
$$b = 7.7875 \pm 0.0010 \text{ Å}$$
$$c = 8.3635 \pm 0.0012 \text{ Å}$$
$$\beta = 91.279° \pm 0.013°$$
$$V = 362.5 \text{ Å}^3$$

The value of 3.57 for the density, found from the apparent loss of weight in benzene, gives 2 formula units in the unit cell.

From rotation and Weissenberg photographs taken of a large number of crystals it was found, that twinning was generally present and in such a way that the photographs showed a false orthorhombic symmetry. However, it was eventually possible to find a crystal which showed a fairly low disturbance by twinning. Extensive X-ray data were collected with rotation around [100] and [001], *viz.* Weissenberg photographs of the layer lines $0kl - 3kl$ and $hk0 - hk4$.This crystal formed a triangular prism with the dimensions 0.109 mm (mean distance in the direction of the a axis) × 0.039 mm (b) × 0.012 mm (c), the latter distances representing the base and height of the triangle. From these photographs, which were taken with CuK radiation, the monoclinic symmetry was confirmed. The reflections systematically absent are $h0l$ with $h + l = $ odd and $0k0$ with $k = $ odd, which is characteristic of the space group $P2_1/n$.

The reflections were recorded photographically with the multiple-film technique. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times.
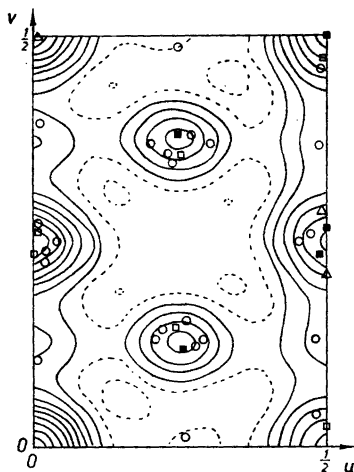
Fig. 1. The Patterson projection $P(uvp)$ for Cu₂SO₃·CuSO₃·2H₂O. The Cu−Cu (■), Cu−S (□), Cu−O (○), and S−S (△) vectors have been indicated for the final structure. Dashed lines indicate negative values.
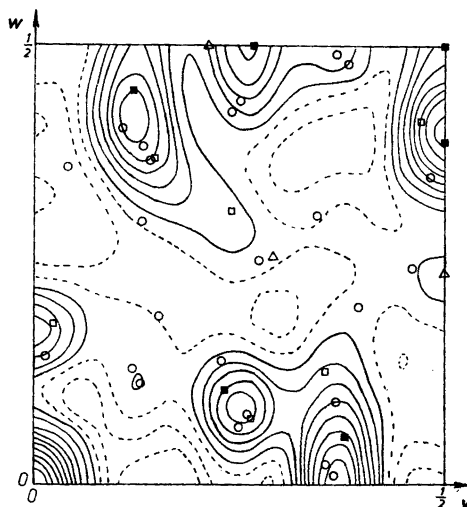
Fig. 2. The Patterson projection $P(pvw)$ for Cu₂SO₃·CuSO₃·2H₂O. The vectors for the final structure have been indicated as in Fig. 1. For the origin maximum only every second contour has been marked. Dashed lines indicate negative values.

Practically all the computational work involved in this study, including refinement of the lattice constants (Program No. 6018), absorption correction (No. 6019), Lorentz-polarization correction (No. 6024), Fourier summations (No. 6015), least-squares refinement (No. 6023) and calculation of interatomic distances (No. 6016), were performed on the electronic computer FACIT EDB. The numbers refer to the list of crystallographic computer programs.[9]

When determining the F^2 values, the linear absorption coefficient, $\mu = 159.4$ cm^{-1}, derived from the atomic absorption coefficients given in the International Tables,[10] was used for the calculation of the absorption factors.

THE STRUCTURE DETERMINATION

In the space group $P2_1/n$ the following point positions exist:

$2(a)$: 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $2(b)$: $\frac{1}{2}00$, $0\frac{1}{2}\frac{1}{2}$; $2(c)$: $00\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$
$2(d)$: $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}0$; $4(e)$: $\pm(xyz)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$

The six copper atoms present in the unit cell could be situated either in three of the twofold positions $2(a) - 2(d)$, or in a general fourfold position $4(e)$ and one of the twofold positions. From the occurrence of high peaks at values of u and $v \neq \frac{1}{2}$ in the Patterson projection $P(uvp)$ (Fig. 1) it was concluded that four of the six copper atoms are situated in $4(e)$. The interatomic vectors corresponding to these four atoms require maxima to occur at

$$\pm [\quad 2x \quad\quad \pm 2y \quad\quad 2z \quad\quad] \text{ weight } 1$$
$$\pm [\quad \tfrac{1}{2} \quad\quad \tfrac{1}{2} + 2y \quad\quad \tfrac{1}{2} \quad\quad] \text{ weight } 2$$
$$\pm [\tfrac{1}{2} + 2x \quad\quad\quad \tfrac{1}{2} \quad\quad \tfrac{1}{2} + 2z \ ] \text{ weight } 2$$

By comparing this table as well as other possible interatomic vectors with the positions of the high peaks present in the Patterson syntheses $P(uvp)$, $P(pvw)$, and $P(u\frac{1}{2}w)$ (Figs. 1—3) and also in other appropriate regions of the Patterson function the following copper positions were obtained:

4 Cu$_1$ in $4(e)$: $x = 0.25$, $y = 0.12$, $z = 0.45$
2 Cu$_2$ in $2(a)$: 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
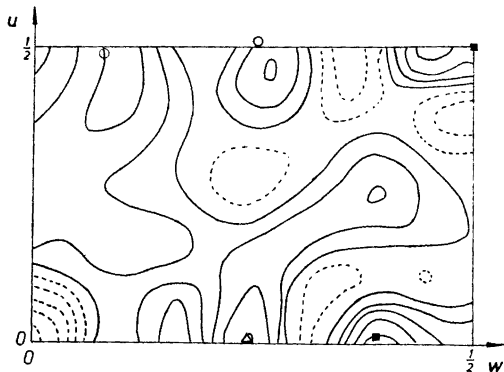
Fig. 3. The Patterson section $P(u\frac{1}{2}w)$ for Cu$_2$SO$_3$·CuSO$_3$·2H$_2$O. The vectors have been indicated as in Fig. 1. Dashed lines indicate negative values.

The electron density function was then studied using the signs of F_{hk0} and F_{0kl} obtained from the copper contributions only. In the preliminary calculations the atomic scattering curves [10] for un-ionized atoms were used. In the concluding stages the curves [11] for ionized atoms were applied. The real part of the anomalous dispersion correction according to Dauben and Templeton [12] was also applied.
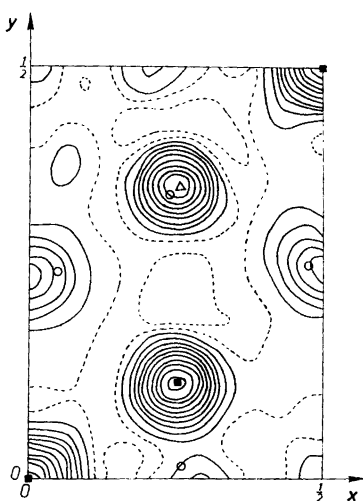

Fig. 4. The electron density projection $\varrho(xyp)$ for $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$. The final positions of the copper (■), sulphur (△), and oxygen (○) atoms have been marked. Dashed lines indicate negative values.
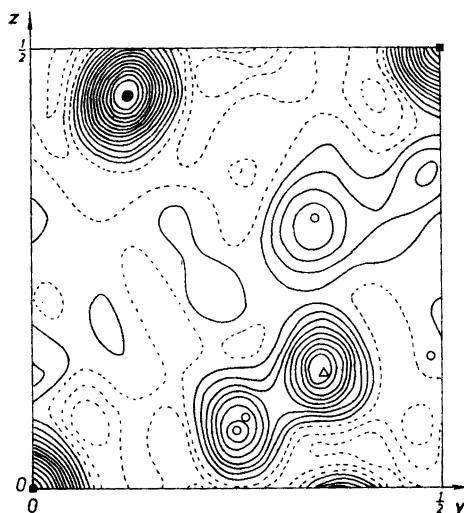
Fig. 5. The electron density projection $\varrho(pyz)$ for $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$. The final positions of the atoms have been marked as in Fig. 4.

The electron density projections $\varrho(xyp)$ (Fig. 4) and $\varrho(pyz)$ (Fig. 5) thus obtained, clearly showed the sulphur atoms which were found to occupy a position $4(e)$. In addition to the maxima corresponding to the copper and sulphur positions there were also peaks which could be interpreted as due to oxygen atoms. By three-dimensional calculations of the Patterson and the electron density functions using all the observed reflections, the positions of the sixteen oxygen atoms in the unit cell — found to be situated in four sets of $4(e)$ — could be determined with a moderate accuracy.

A refinement of the coordinates so obtained was then performed by means of the method of least squares, applying the program mentioned above. The starting values of the individual isotropic temperature factors used in this program, were zero for all the atoms. Initially all 428 of the independent reflections measured were included in the calculations, but after some cycles seven strong, low-angle reflections were omitted as suffering from extinction. The refinement was considered as complete when the parameter shifts were less

Table 2. Weight analysis obtained in the final cycle of the least-squares refinement of $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$. w = weighting factor, $\Delta = ||F_{obs}| - |F_{calc}||$

Interval $\sin \Theta$	Number of independent reflections	$\overline{w\Delta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w\Delta^2}$
0.00—0.46	63	0.92	0—7	10	1.12
0.46—0.58	73	0.88	7—14	51	0.82
0.58—0.67	56	0.99	14—21	104	1.08
0.67—0.74	45	1.20	21—28	65	0.73
0.74—0.79	50	1.34	28—35	66	0.76
0.79—0.84	47	1.07	35—42	52	1.34
0.84—0.89	24	0.62	42—49	20	1.70
0.89—0.93	27	0.44	49—56	20	1.25
0.93—0.97	24	1.16	56—63	9	1.22
0.97—1.00	12	1.44	63—70	24	0.79

than 5 % of the standard deviations, at which stage the discrepancy factor was down to 12.7 %. Cruickshank's weighting function [13]

$$w = (A + |F_{obs}| + C |F_{obs}|^2)^{-1}$$

was used in the refinement with the following final values for the parameters: $A = 9.2$, $C = 0.015$. A weight analysis obtained in the last cycle is given in Table 2. The values of $\overline{w\Delta^2}$ deviate as much from unity as could be expected for the intensity material, which was photographically registered and also suffered from the presence of some twinning in the crystal.

Table 3. The structure of $Cu_2SO_4 \cdot CuSO_3 \cdot 2H_2O$.

Space group: $P2_1/n$
Unit-cell dimensions: $a = 5.5671 \pm 0.0014$ Å
                      $b = 7.7875 \pm 0.0010$ Å
                      $c = 8.3635 \pm 0.0012$ Å
                      $\beta = 91.279° \pm 0.013°$

Cell content: $2[Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O]$
    $2Cu_2$ in $2(a)$: (000); $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$
    $4Cu_1$, $4S$, $4O_1$ $-4O_4$ in 6×4 (e): $\pm (x,y,z,)$; $\pm (\frac{1}{2} + x,\frac{1}{2} - y,\frac{1}{2} + z)$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
Cu_1	0.25425 ± 0.00068	0.11755 ± 0.00044	0.44653 ± 0.00046	1.919 ± 0.059
Cu_2	0	0	0	2.065 ± 0.092
S	0.2536 ± 0.0011	0.3549 ± 0.0007	0.1287 ± 0.0008	1.45 ± 0.08
O_1	0.2373 ± 0.0029	0.3444 ± 0.0017	0.3078 ± 0.0017	1.27 ± 0.23
O_2	0.0452 ± 0.0028	0.2502 ± 0.0021	0.0640 ± 0.0019	1.99 ± 0.29
O_3	0.4770 ± 0.0029	0.2606 ± 0.0020	0.0771 ± 0.0019	1.80 ± 0.26
$O_4(H_2O)$	0.2600 ± 0.0033	0.0137 ± 0.0021	0.8529 ± 0.0022	2.27 ± 0.30

*Table 4.* Interatomic distances and standard deviations (in Å) in $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$.

Cu(I)-tetrahedron:

$Cu_1 - S = 2.140 \pm 0.006$	$S - O_2 = 3.834 \pm 0.017$
$Cu_1 - O_1 = 2.114 \pm 0.014$	$S - O_3 = 3.781 \pm 0.017$
$Cu_1 - O_2 = 2.140 \pm 0.016$	$O_1 - O_2 = 2.812 \pm 0.022$
$Cu_1 - O_3 = 2.133 \pm 0.016$	$O_1 - O_3 = 2.827 \pm 0.022$
$S \quad - O_1 = 3.849 \pm 0.015$	$O_2 - O_3 = 3.130 \pm 0.023$

Cu(II)-octahedron:

$$Cu_2 - 2\,O_1 = 2.467 \pm 0.015$$
$$Cu_2 - 2\,O_2 = 2.034 \pm 0.016$$
$$Cu_2 - 2\,O_4 = 1.924 \pm 0.018$$
$$O_1 - 2\,O_2\,(O_2 - 2\,O_1) = 2.812 \pm 0.022;\ 3.542 \pm 0.021$$
$$O_1 - 2\,O_4\,(O_4 - 2\,O_1) = 3.127 \pm 0.024;\ 3.130 \pm 0.023$$
$$O_2 - 2\,O_4\,(O_4 - 2\,O_2) = 2.779 \pm 0.024;\ 2.840 \pm 0.024$$

SO_3-pyramid:

$S - O_1 = 1.504 \pm 0.016$	$O_1 - O_2 = 2.396 \pm 0.022$
$S - O_2 = 1.509 \pm 0.017$	$O_1 - O_3 = 2.458 \pm 0.022$
$S - O_3 = 1.515 \pm 0.017$	$O_2 - O_3 = 2.405 \pm 0.022$

$O-O < 3.5$ Å *outside the polyhedra*

$$O_1 - O_4\,(O_4 - O_1) = 2.911 \pm 0.024$$
$$O_2 - O_4\,(O_4 - O_2) = 3.452 \pm 0.024$$
$$O_3 - 3\,O_4\,(O_4 - 3\,O_3) = 2.648 \pm 0.023;\ 2.928 \pm 0.023;\ 3.275 \pm 0.024$$

A list of the observed and calculated structure factors is included in a document [14] which may be obtained on request from the secretary of this Institute.

The atomic parameters, the isotropic temperature factors of all the atoms and the standard deviations are listed in Table 3. The calculated interatomic distances and their standard deviations are given in Table 4. All distances were found to be within the normal range and thus supporting the correctness of the coordinates arrived at in the last cycle.

The result obtained from the refinement was further checked by making three-dimensional electron density syntheses based on observed and calculated values of F. Sections were calculated at values of x corresponding to the different sites of the atoms. All atoms stand out clearly in the F_o syntheses and subsequent difference syntheses show very small residual maxima or minima. The largest maximum in these calculations has a magnitude of about 25 % of the heights of the oxygen peaks in the F_o syntheses.

In the unit cell there are also eight hydrogen atoms which should be associated with some of the oxygen atoms. Now, the oxygen atoms differ considerably from a structural point of view. Thus the oxygen atoms O_{1-3} are in contact with sulphur and also with copper atoms, while the oxygen atom O_4 is in contact only with one copper atom. It therefore seems rather probable that the hydrogen atoms are associated with the O_4 atoms to form H_2O molecules. The hydrogen atoms may also be engaged in hydrogen bridges with neighbouring oxygen atoms. However, in this investigation it has not been possible to determine the parameters of the hydrogen atoms.
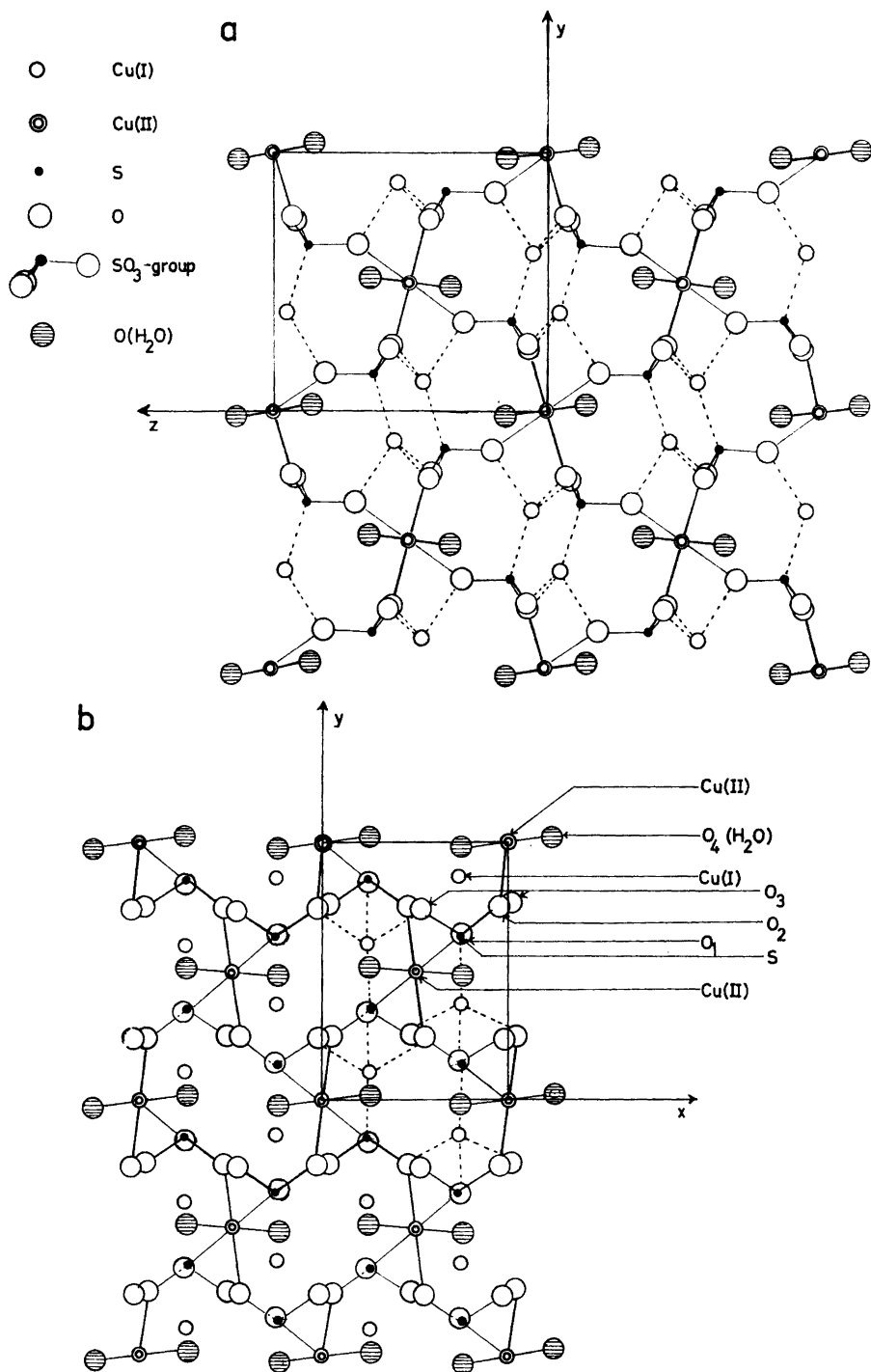
Fig. 6. Schematic drawings showing the structure of $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$. The structure viewed along [100] (a) and [001] (b) showing the contacts between SO_3 pyramids, $Cu(I)O_3S$ tetrahedra, and $Cu(II)O_4(H_2O)_2$ octahedra.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure thus arrived at may be described in terms of coordination polyhedra, *viz.* SO_3 trigonal pyramids, CuO_3S tetrahedra and $CuO_4(H_2O)_2$ octahedra. The polyhedra are linked together giving a three-dimensional network as shown in the schematic drawings Figs. 6 a—b.

The linking is such that the SO_3 pyramids are joined with two $CuO_4(H_2O)_2$ octahedra and with one CuO_3S tetrahedron by corner sharing through oxygen atoms and with one further CuO_3S tetrahedron by having the sulphur atom in common. The tetrahedral coordination polyhedron of CuO_3S is provided by three oxygen and one sulphur atom of four SO_3 groups. Four of the oxygen atoms of the $CuO_4(H_2O)_2$ octahedra are engaged in corner sharing with four SO_3

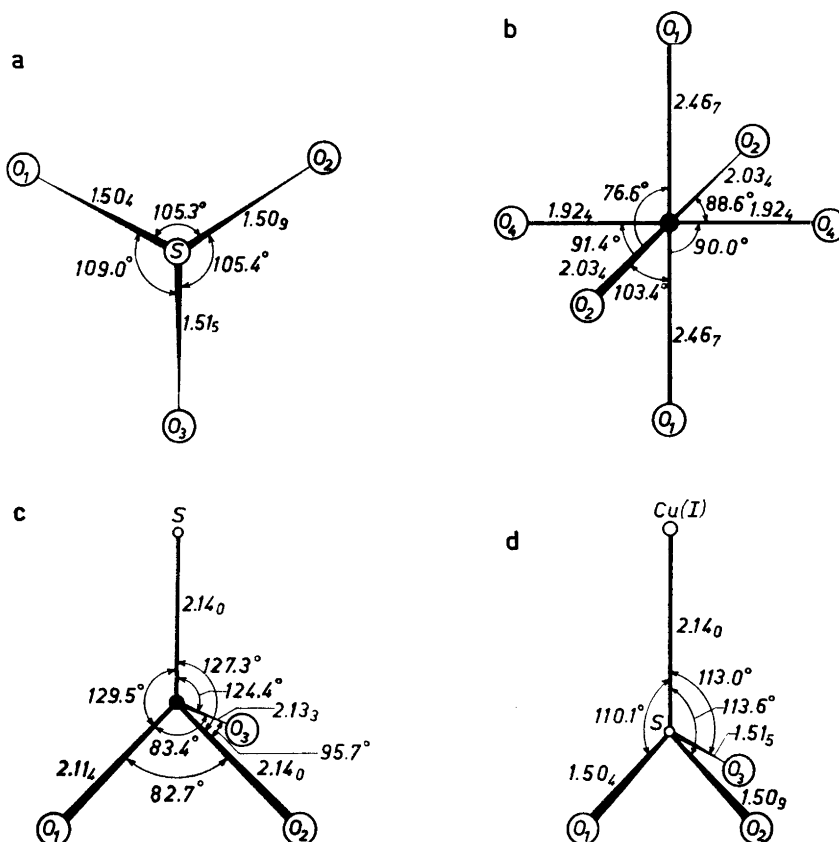*Fig. 7.* The coordination polyhedra in the structure of $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$. The SO_3 trigonal pyramid (a), the $CuO_4(H_2O)_2$ octahedron (b), the CuO_3S tetrahedron (c). Angles related to the others by symmetry have not been indicated. Fig. 7d shows the angular distribution around the sulphur atom when the copper (I) atom is included in the environment of the former atom.

groups while the two hydrate oxygens are linked to other polyhedra only by hydrogen bonding. Edge sharing is present in the structure through pairs of oxygen atoms of the octahedra which in this way are linked with two tetrahedra. The interatomic distances are, however, such (cf. below) that the trinuclear copper complex thus imaginable should be only a rather formal structural element.

The interatomic distances and standard deviations (σ) in $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$ are given in Table 4. A complete list of bond angles is given in the document.[14]

The dimensions of the SO_3 group (Fig. 7a), with S—O distances of 1.51 Å and O—S—O angles of 106.9°, differ somewhat from those reported in 1931 for the sulphite ion in Na_2SO_3 by Zachariasen and Buckley,[15] viz. 1.39 Å and 106.7°. The latter data are likely to be of moderate accuracy and it may be that the large deviation observed for interatomic distances is not a real one. On the other hand the close approach between the sulphur atom and one copper atom (cf. below) may strongly influence the distances within the SO_3 pyramid. Accurate knowledge of the dimensions of the latter in normal sulphites seems desirable and structural studies on such compounds are in progress.

The indication given by the structural symmetry is that the copper atoms are arranged in such a way that the monovalent ones occupy a general fourfold position 4(e) while the divalent atoms are situated in a twofold position 2(a) of the symmetry $\bar{1}$. This distribution of the copper atoms is strongly supported by the complete structure determination. Thus, the interatomic distances within the octahedral arrangement of atoms surrounding the position 2(a) are perfectly compatible with the assumption of the copper atom being in the divalent state. The octahedron is distorted towards a square with two Cu—$O_{(H_2O)}$ distances of 1.92 Å, and two Cu—O distances of 2.03 Å. The two oxygen atoms completing the octahedron (Fig. 7b) are quite remote ones at a distance of 2.47 Å. These dimensions are throughout very similar to those reported for a large number of Cu^{2+} compounds (cf. the surveys by Wells [16] and Orgel [17]).

The tetrahedral arrangement (Fig. 7c) around the copper atoms in 4(e) is a quite plausible one for the monovalent state. The dimensions of this polyhedron are, however, rather remarkable ones. Thus the Cu—S distance (2.14 Å) is very nearly the same as the Cu—O distances (2.11—2.14 Å). The close copper-sulphur contact which is drastically below the one (2.32 Å) present in, e.g., Cu(I)Fe(III)S_2 should be the cause of the decrease of the O—Cu—O angles (83—96°) from the tetrahedral angle. It may also have an influence on the sulphite group. It is worth noting that including the copper atom in the environment of the sulphur atom leads to a rather regular angular distribution around the latter (O—S—O angles of 105—109° and O—S—Cu(I) angles of 110—114°) (cf. Fig. 7d).

Studies on further copper sulphites are in progress in order to make available structural and physico-chemical data needed for a thorough discussion of the bonding conditions and properties of this group of compounds. Studies on the structural chemistry of sulphites of several transition metals are also on the program.

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