

the reactor hall. Furthermore, the thermal diffuse scattering from acoustic phonons has been neglected.

Now the diffuse background remains practically the same at low temperatures too. Even a diagram taken at 4 K has the same form and magnitude. Since here a dynamic interpretation is not possible because of the occupation number, some static disorder has to be taken into account. According to the model discussed at the end of the preceding section there are two structural motifs  $AA = BB$  and  $AB = BA$  for the sequence of two adjacent layers perpendicular to the  $c$  axis. Here  $A$  and  $B$  denote a rotation of the octahedra around  $[001]$  to the right and to the left. Assuming a random distribution the corresponding diffuse intensity (see, for example, Jagodzinski, 1949) is for small angles of rotation  $\varphi$  proportional to  $|\Delta F|^2 \sim p_1 p_2 |2\pi y \times (h \sin 2\pi kx - k \sin 2\pi hx)|^2$ . Here  $x = x_0 \cos \varphi$ ,  $y = x_0 \sin \varphi$  and  $p_1$  and  $p_2$  are the probabilities for the occurrence of motifs  $AA$  and  $AB$ . This static diffuse scattering has the same form as the dynamic, thus giving a good hint that the suggested disorder model is indeed present at low temperatures. Because of this disorder the Bragg scattering is also affected, i.e. at low temperatures only an average structure is refined with apparently large temperature factors (depending on the values of  $p_1$  and  $p_2$ ). At high temperatures, however, the large anisotropic temperature factors are due to the librational motion of the Cl octahedra.

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## The Crystal Structure of $(NH_4)_2[Cu(H_2O)_6][CuSO_3]_4$

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$(NH_4)_2[Cu(H_2O)_6][CuSO_3]_4$  is tetragonal, space group  $P4_2/n$ , with  $a = 14.876$  (1),  $c = 17.218$  (3) Å,  $Z = 8$ . Full-matrix least-squares calculations resulted in an  $R$  of 0.043 for 2308 independent reflexions. The structure can be described in terms of distorted  $Cu^I O_3 S$  tetrahedra, the ligands being atoms from four different sulphite groups (mean distances: Cu–O 2.11, Cu–S 2.16 Å),  $Cu(H_2O)_6$  octahedra implying a (4 + 2) coordination (mean distances: Cu–O 1.99 and 2.33 Å) and ammonium ions. The  $Cu^I O_3 S$  tetrahedra form double layers almost parallel to (110). The average dimensions within the sulphite group are: S–O 1.52, O–O 2.42 Å and  $\angle O-S-O$  105.3°.

### Introduction

Crystals of the colourless compound  $\text{NH}_4\text{CuSO}_3$  (Nyberg & Kierkegaard, 1968) turn green in a humid atmosphere indicating that oxidation occurs. Gradually the compound decomposes forming, among others, the red compound  $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$  (Kierkegaard & Nyberg, 1965). To complete the investigation of the ammonium copper sulphites the green compound was synthesized.

### Experimental

The compound was prepared according to the synthesis given by Brauer & Eichner (1956). The crystals are green plates, which decompose slowly, but remain stable long enough for X-ray data collection. The Cu content of the compound was determined by electroanalysis (measured 40.6%, calculated 40.62%). The final structure determination confirms the chemical composition  $(\text{NH}_4)_2\text{Cu}_5(\text{SO}_3)_4(\text{H}_2\text{O})_6$ .

Cell dimensions were determined from a powder pattern recorded on a Hägg–Guinier focusing camera at 25°C with Cu  $K\alpha_1$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) and KCl as an internal standard. Least-squares analysis of 47 reflexions yielded  $a = 14.876 (1)$  and  $c = 17.218 (3) \text{ \AA}$ . The density ( $2.67 \text{ g cm}^{-3}$ ), found from the apparent loss of weight in benzene, gives  $Z = 8$  ( $d_c = 2.72 \text{ g cm}^{-3}$ ).

Weissenberg photographs indicated the lower Laue class  $4/m$ . The lattice was almost C-centred. A preliminary collection of Weissenberg data around [001] was made. The intensities of the reflexions with  $h + k = 2n + 1$  were with few exceptions significantly weaker than the rest; thus these reflexions were

ignored. The photographs were indexed with the reduced cell  $A = 10.519$ ,  $c = 17.218 \text{ \AA}$  and the Laue class was  $4/mmm$ . The systematic extinctions indicated space group  $P4_2bc$  or  $P4_2mbc$ .

For the large unit cell the following conditions limiting possible reflexions were found:  $hk0$ ,  $h + k = 2n$ ;  $00l$ ,  $l = 2n$ . These are consistent with space group  $P4_2/n$ .

When the substructure was solved a crystal was selected for data collection on an Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer. All reflexions, strong as well as weak, were measured. The crystal was a plate, 0.038 mm thick along [001], with an almost rectangular surface ( $0.178 \times 0.143 \text{ mm}$ ) truncated along  $(210)$ . Graphite-monochromatized Mo  $K\alpha$  radiation was used with a take-off angle of  $3^\circ$ . Intensities were collected by an  $\omega$ - $2\theta$  scan with  $\Delta\omega = 0.8^\circ + 0.4^\circ \tan \theta$  and an upper limit of  $\theta = 30^\circ$ .

The intensities of 6102 reflexions were measured. 2308 independent reflexions with  $I > 3\sigma(I)$ , where  $\sigma(I)$  is based on counting statistics, were considered to be significant. The reflexions 602, 534 and 377 were used as standards and were checked after every 50 measurements. Their intensities were constant throughout the experiment. The intensities of the reflexions were corrected for Lp and absorption effects. The range of the transmission factors was  $0.34$ – $0.70$  ( $\mu = 98 \text{ cm}^{-1}$ ).

### Structure determination and refinement

Patterson syntheses based on the Weissenberg data collected for the substructure together with interatomic distances from the structure of  $\text{NH}_4\text{CuSO}_3$  revealed the positions of the Cu, S and sulphite O atoms. For these calculations space group  $P4_2mbc$  was chosen.

Table 1. Final positional and thermal parameters

All values except  $B$  are multiplied by  $10^4$ . Estimated standard deviations are given in parentheses.

	$x$	$y$	$z$	$B (\text{\AA}^2)$		$x$	$y$	$z$	$B (\text{\AA}^2)$
Cu(1)	0	0	$\frac{1}{2}$		O(1A)	7860 (5)	9906 (5)	3620 (5)	2.4 (1)
Cu(2)	0	0	0		O(1B)	7887 (5)	98 (5)	1393 (6)	2.7 (2)
Cu(3)	7711 (1)	8909 (1)	2025 (1)		O(1C)	9909 (5)	2942 (5)	3601 (5)	2.0 (1)
Cu(4)	7692 (1)	1085 (1)	2981 (1)		O(1D)	101 (5)	2987 (5)	1411 (5)	2.3 (1)
Cu(5)	8898 (1)	2767 (1)	2017 (1)		O(2A)	6838 (5)	8659 (5)	3643 (5)	2.2 (1)
Cu(6)	1102 (1)	2756 (1)	2984 (1)		O(2B)	6890 (5)	1382 (5)	1327 (5)	2.4 (1)
S(1)	7711 (2)	8978 (2)	3290 (2)		O(2C)	8770 (5)	1799 (5)	3571 (5)	2.4 (1)
S(2)	7744 (2)	1028 (2)	1721 (2)		O(2D)	1251 (5)	1829 (5)	1402 (6)	3.1 (2)
S(3)	8990 (2)	2717 (2)	3264 (2)		O(3A)	8443 (5)	8397 (5)	3639 (5)	2.6 (1)
S(4)	1019 (2)	2746 (2)	1742 (2)		O(3B)	8505 (5)	1603 (5)	1398 (5)	2.4 (1)
N(1)	2500 (0)	2500 (0)	5038 (10)	3.9 (2)	O(3C)	8356 (5)	3364 (5)	3676 (5)	2.6 (1)
N(2)	2500 (0)	7500 (0)	4997 (17)	3.6 (2)	O(3D)	1667 (5)	3410 (5)	1354 (5)	2.6 (1)
N(3)	5008 (6)	4517 (6)	2502 (8)	3.6 (2)	O(W1)	4784 (4)	1331 (4)	5012 (7)	2.9 (1)
					O(W2)	5661 (5)	26 (5)	3768 (5)	2.9 (1)
					O(W3)	6330 (4)	4786 (4)	4966 (6)	2.9 (1)
					O(W4)	6203 (5)	144 (5)	5455 (5)	2.8 (1)
					O(W5)	4863 (5)	3798 (5)	4520 (5)	3.0 (1)
					O(W6)	4997 (5)	4329 (5)	6222 (5)	2.9 (1)

The coordinates so obtained were transformed to the full structure (space group  $P4_2/n$ ). The origin was set at  $\bar{1}$  (second setting in *International Tables for X-ray Crystallography*, 1952). With the diffractometer data and the transformed coordinates of the above atoms,  $R$  fell to 0.13 for 2156 reflexions [ $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ ].

A difference map revealed the rest of the atoms. Full-matrix least-squares refinement gave  $R = 0.043$ ,  $R_w = 0.052$  and  $S = 1.20$  for 2308 reflexions [ $R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i|F_o|^2]^{1/2}$ ,  $S = [\sum w_i(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ ].

For all atoms except Cu the scattering curves for neutral atoms were applied (Doyle & Turner, 1968). The corresponding values of  $\text{Cu}^{2+}$  were used for Cu(1) and Cu(2) and the values of  $\text{Cu}^+$  for Cu(3) - Cu(6). The weights were calculated from  $w_i^{-1} = \sigma^2(|F_o|^2) / 4|F_o|^2 + 0.0002|F_o|^2 + 10$ . Anisotropic temperature factors were used for the Cu and S atoms. In the last cycle the shifts of all parameters were  $< 0.01\sigma$ . The final atomic parameters are given in Table 1.\* The highest peak in a difference map was now  $1.2 \text{ e } \text{Å}^{-3}$ . No attempts were made to locate the H atoms. The interatomic distances and angles (Table 2) were not corrected for thermal motion.

### Discussion

The structure can be described in terms of linked  $\text{Cu}^{\text{I}}\text{O}_3\text{S}$  tetrahedra, separate  $\text{Cu}^{\text{II}}\text{O}_6$  octahedra and ammonium ions. The double layers of tetrahedra extend almost parallel to the  $ab$  plane around  $z = 0.25$  and  $0.75$  (Fig. 1). In the same drawing half the N atoms [N(3)] are illustrated. The ammonium ions are located in cavities in the structure. In the large tunnels along the  $\text{CuO}_6$  octahedra are situated at  $z = 0$  and  $0.5$ .

The distorted tetrahedral configuration around Cu(3) - Cu(6) confirms that these atoms are monovalent. Each  $\text{Cu}^{\text{I}}$  atom is surrounded by one S and three O atoms from four different sulphite groups. Cu(3) and Cu(6) are bonded to two and Cu(4) and Cu(5) to three independent sulphite groups. The mean distances and angles are almost identical with those in the same group in  $\text{NH}_4\text{CuSO}_3$  (Nyberg & Kierkegaard, 1968). In both compounds the  $\text{CuO}_3\text{S}$  tetrahedra form double layers.

The distorted octahedral coordination around Cu(1) and Cu(2) is provided by six water O atoms; therefore, these two Cu atoms must be divalent and the groups are  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  ions. Waite & Hitchman (1976) have discussed the structure of this ion. Depending on the structural surroundings the ion exhibits a range of

Table 2. Selected interatomic distances (Å) and angles (°)

Standard deviations are given in parentheses. Oxygen atoms belonging to one sulphite group are denoted with the same letter. Water oxygen atoms are indicated O(W).

Sulphite groups*			
S(1)—O(1A)	1.509 (8)	S(2)—O(1B)	1.509 (9)
—O(2A)	1.511 (8)	—O(3B)	1.524 (8)
—O(3A)	1.514 (8)	—O(2B)	1.533 (8)
S(3)—O(2C)	1.501 (8)	S(4)—O(1D)	1.522 (8)
—O(3C)	1.522 (8)	—O(2D)	1.524 (9)
—O(1C)	1.523 (8)	—O(3D)	1.533 (8)
		Angles	O—O distances
O(1A)—S(1)—O(2A)	105.2 (4)	O(1A)—S(1)—O(3A)	2.398 (10)
O(1A)—S(1)—O(3A)	105.5 (4)	O(2A)—S(1)—O(3A)	2.407 (10)
O(2A)—S(1)—O(3A)	106.2 (4)	O(2B)—S(2)—O(3B)	2.420 (10)
O(2B)—S(2)—O(3B)	105.1 (4)	O(1B)—S(2)—O(2B)	2.428 (10)
O(1B)—S(2)—O(2B)	105.5 (5)	O(1B)—S(2)—O(3B)	2.421 (10)
O(1B)—S(2)—O(3B)	105.8 (4)	O(1C)—S(3)—O(3C)	2.420 (10)
O(1C)—S(3)—O(3C)	103.8 (4)	O(1C)—S(3)—O(2C)	2.397 (10)
O(1C)—S(3)—O(2C)	105.1 (4)	O(2C)—S(3)—O(3C)	2.401 (10)
O(2C)—S(3)—O(3C)	105.6 (4)	O(1D)—S(4)—O(3D)	2.414 (10)
O(1D)—S(4)—O(3D)	104.5 (4)	O(2D)—S(4)—O(3D)	2.416 (10)
O(2D)—S(4)—O(3D)	105.5 (5)	O(1D)—S(4)—O(2D)	2.434 (11)
O(1D)—S(4)—O(2D)	105.8 (5)		2.429 (11)
Copper octahedra			
Cu(1)—2O(W4)	1.980 (7)	Cu(2)—2O(W4)	1.965 (7)
—2O(W3)	2.005 (6)	—2O(W1)	2.006 (6)
—2O(W6)	2.329 (8)	—2O(W2)	2.339 (8)
Copper tetrahedra			
Cu(3)—O(1B')	2.093 (8)	Cu(4)—O(1A')	2.086 (8)
—O(3A')	2.122 (8)	—O(3C')	2.130 (8)
—O(2A'')	2.132 (8)	—S(2)	2.172 (4)
—S(1)	2.181 (4)	—O(2C)	2.175 (7)
Cu(5)—O(2B')	2.095 (7)	Cu(6)—O(1C')	2.087 (7)
—O(1D')	2.096 (8)	—O(3D')	2.109 (8)
—O(3B)	2.115 (7)	—O(2D'')	2.113 (9)
—S(3)	2.153 (4)	—S(4)	2.143 (4)
Water molecules [distances O(W)—O < 2.9 Å†]			
O(W1)—O(1B)	2.688 (14)	O(W3)—O(1A)	2.653 (13)
—O(1C)	2.698 (13)	—O(1D)	2.728 (13)
—O(W4)	2.759 (10)	—O(W5)	2.741 (10)
—O(W4)	2.856 (10)	—O(W5)	2.893 (10)
O(W2)—O(2A)	2.692 (10)	O(W5)—O(3D)	2.724 (11)
—O(2D)	2.799 (11)	—O(2C)	2.756 (11)
O(W4)—O(3B)	2.759 (10)	O(W6)—O(3A)	2.706 (10)
—O(2D)	2.799 (11)	—O(2B)	2.753 (10)
N—O distances < 3.5 Å			
N(1)—2O(3A)	2.989 (15)	N(2)—2O(3C)	2.915 (25)
—2O(2A)	3.016 (15)	—2O(2B)	2.964 (24)
—2O(3D)	3.020 (16)	—2O(3B)	3.128 (24)
—2O(2D)	3.256 (16)	—2O(2C)	3.276 (24)
N(3)—O(W2)	2.772 (14)		
—O(W6)	2.786 (14)		
—O(2C)	3.245 (13)		
—O(2D)	3.332 (14)		
—O(3B)	3.359 (13)		

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33283 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

\* Atoms marked with primes and double primes are symmetry-related to those in Table 1. Atoms not marked have coordinates as in Table 1.

† In the rest of Table 2 the shortest distances between independent atoms are given.

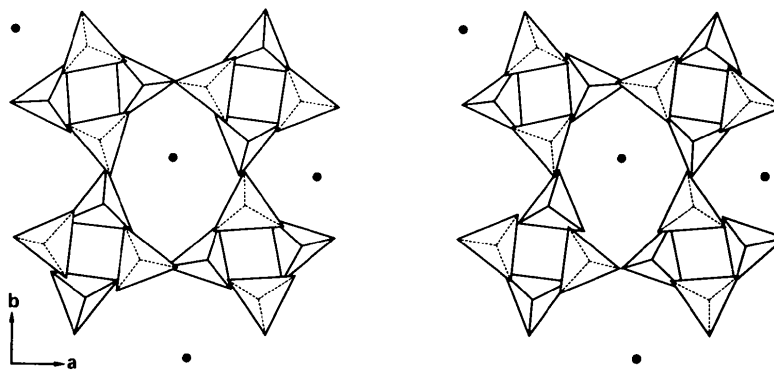


Fig. 1. Stereoscopic view of the  $\text{Cu}_4\text{O}_3\text{S}$  tetrahedra. The tetrahedra with centres within one unit cell with  $0.13 < z < 0.37$  are drawn. They form double layers. Filled circles denote N atoms, N(3), in one unit cell at  $z = 0.25$ .

configurations. In the present compound three different  $\text{Cu}^{\text{II}}-\text{O}$  distances exist, but two of these distances are almost equal. The coordination around Cu(1) and Cu(2) can therefore be described as being of the type (4 + 2) as in a number of other  $\text{Cu}^{\text{II}}$  compounds, e.g. copper hydrogen maleate (Prout, Carruthers & Rossotti, 1971). Average lengths of the short and long bonds are 1.99 and 2.33 Å. These values are normal and agree well with the corresponding distances in the above compound.

Some short  $\text{O}(W)-\text{O}$  distances are listed in Table 2. Each of the sulphite O atoms is probably involved in at least one hydrogen bond to a water molecule and thus a three-dimensional network is formed. O(W2) and O(W6) are bonded differently from the other water O atoms, and show short contacts to N atoms.

The geometry of the sulphite group has been discussed by Kierkegaard, Larsson & Nyberg (1972). The shortening effect on the S—O bond due to the S—metal bond is clearly seen in  $(\text{C}_2\text{H}_{10}\text{N}_2)^{2+}[\text{Au}(\text{SO}_3)_2\text{en}]_2^-$  (Dunand & Gerdil, 1975) with an average S—O distance of 1.47 Å. In the present structure, sulphite O atoms are involved in metal bonding (to  $\text{Cu}^{\text{I}}$ ) and hydrogen bonding. The effect on the S—O bonds due to Cu—S bonds (mean distance 2.16 Å) is therefore counteracted and the result is a geometry not very different from that of the sulphite groups in  $\text{NH}_4\text{CuSO}_3$  and  $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$ .

There are two structurally different ammonium ions. N(1) and N(2) are situated between two different  $\text{CuO}_3\text{S}$  layers and have eight O atoms as neighbours (mean distance 3.07 Å). The average N—O distance for coordination number six found by Khan & Baur (1972) in selected ammonium salts is 2.98 Å. The authors accept only bonds up to 3.2 Å as coordination contacts. With a coordination number of six, N(1) and N(2) have a mean distance of 3.01 Å. For N(3) with two short N—O distances [to O(W2) and O(W6)] and

with an almost tetrahedral O—N—O angle ( $104.1^\circ$ ) it is most probable that two hydrogen bonds exist. The rest of the O atoms are at significantly longer distances and are not in coordination contact with N(3). The average N—O value of 2.78 Å for coordination number two is consistent with the average value 2.86 Å for coordination number four found as a mean value for eight ammonium salts.

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