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The Crystal Structure of Cupric Tetrammine Sulfate Monohydrate, $Cu(NH_3)_4SO_4.H_2O$

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$Cu(NH_3)_4SO_4.H_2O$ is orthorhombic, *Pmcn*–D_{2h}^{16}, with four molecules in the unit cell. The determination of the structure was carried out by means of Patterson and Fourier projections on (001) and (100). The structure consists in layers parallel to (010) formed by $Cu(NH_3)_4$ squares and SO_4 tetrahedra held together by H_2O molecules. Copper atoms, which lie on symmetry planes, have four nearest NH_3 neighbours (Cu–N = 2·04–2·06 Å) and two more H_2O neighbours (Cu–O = 2·59–3·37 Å), which complete the distorted octahedral co-ordination group. Each SO_4 tetrahedron (S–O = 1·40–1·43–1·46 Å) has two oxygen atoms linked with hydrogen bonds to adjacent H_2O molecules (OH...O = 2·67 Å).

Introduction

The crystallographic study of cupric tetrammine sulfate monohydrate was originally made by Marignac (1856), and later supplemented by Johnsen (1903), who also determined the density and some optical properties. The results as summarized by Groth (1906–19) are:

orthorhombic bipyramidal;
$a:b:c = 0·5903:1:0·8892$;
$d = 1·81$ g.cm.$^{-3}$.

The deep blue crystals are prismatic [100], and often twinned on {021}, perfect cleavage on {010}. [001] is the acute bisectrix; the crystals are strongly pleochroic (blue–violet).

Zemann (1948) determined the cell constants as follows:

$$a = 7·07,\ b = 12·12,\ c = 10·66\ \text{kX.}(\pm 1\%);$$

$Z = 4$; probable space-group: D_{2h}^{16} or D_{2h}^{13}.

Experimental

The crystals for this study were prepared in the usual way, namely by adding an excess of NH_3 to an aqueous solution of $CuSO_4$ followed by slow precipitation with ethyl alcohol. As several small crystals proved to be not single, a chip of a large one was used for the final X-ray work.

Zero-layer Weissenberg pictures of the [100] zone were taken with Cu $K\alpha$ radiation as well as zero- and first-layer precession photographs ($\mu = 30°$) around the [010] and [001] axes with Mo $K\alpha$ radiation. The lattice constants of Zemann are confirmed within the limits of accuracy. The observed extinctions gave *Pmcn*–D_{2h}^{16} or $P2_1cn$–C_{2v}^{9} as the most probable space groups; as a reasonable structure could be found in *Pmcn*, this is apparently the true space group.

Quantitative intensities of the *hk*0 and 0*kl* reflexions were obtained by the multiple-exposure method (0*kl* reflexions: zero-layer Weissenberg photographs; Cu $K\alpha$ radiation; exposure times: $\frac{1}{2}$, 1, 2, 4, 8, and 16 hr.; *hk*0 reflexions: zero-layer precession photographs; $\mu = 30°$; Mo $K\alpha$ radiation; exposure times: 9, 18, 36, and 72 hr.). The X-ray source was kept constant, and the sets of photographs were developed together to make comparison possible. The intensities were estimated visually and transformed into relative F^2's by multiplication with the Lorentz polarisation factor. No absorption factor was applied as the specimen was considered to be sufficiently small.

Patterson projections

From Patterson projections upon (100) and (001) the copper and sulfur atoms could be approximately located.

In *Pmcn* there are three sets of fourfold positions: (4*a*) and (4*b*) with point symmetry $\bar{1}$, and (4*c*) with point symmetry *m*; as well there are eightfold general positions (8*d*) with point symmetry 1.

The positions (4*a*) and (4*b*) can easily be ruled out for Cu—as already suggested by Zemann—and as it would be against all experience in crystal chemistry to put the sulfur atoms of sulfate groups in a centre of symmetry, we have to expect both 4 Cu and 4 S in (4*c*), $\frac{1}{4}, y, z$, etc.

From the strongest Patterson peaks (*D*, *E*, *F* in Fig. 1(*a*), *B* in Fig. 1(*b*)), it is possible to derive three pairs of approximate *y* and *z* parameters for Cu:

(1) $y = 0·25,\ z = 0·00$.
(2) $y = 0·00,\ z = 0·25$.
(3) $y = 0·25,\ z = 0·25$.

Assuming that the peaks *G* and *H* arise from Cu–S vectors, and making use of both Patterson projections,

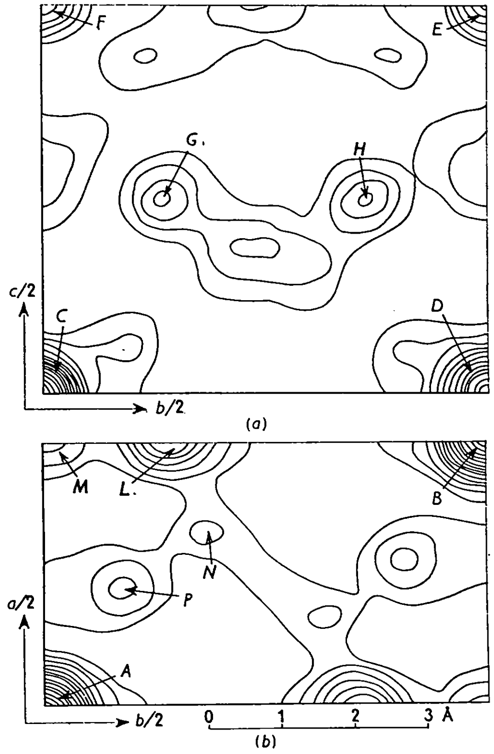

Fig. 1. Patterson projection (*a*) on (100), (*b*) on (001).

one can reduce the possibilities for the Cu and S positions to:

Cu: $\frac{1}{4}$, 0·25, 0·00; $\frac{3}{4}$, 0·75, 0·00; $\frac{3}{4}$, 0·75, 0·50;
$\frac{1}{4}$, 0·25, 0·50;
S: x, 0·12, 0·25; $\bar{x}$, 0·88, 0·75; $\bar{x}$, 0·62, 0·25;
x, 0·38, 0·75; with $x = \frac{1}{4}$ or $\frac{3}{4}$.

With $x_S = \frac{1}{4}$ a Cu–S peak should show up on the (001) projection at (0, 0·13); with $x_S = \frac{3}{4}$ on the same projection at ($\frac{1}{2}$, 0·13). As we find the corresponding peak at ($\frac{1}{2}$, 0·13) and not at (0, 0·13) (*L* in Fig. 1(*b*)), the value for x_S is $\frac{3}{4}$.

On the projection on (001) two Cu atoms are superposed: they act in this projection like only one atom with double the atomic number, so that all the peaks could easily be assigned to interatomic vectors:

B: Cu–Cu; *L*: Cu–S; *M* and *N*: Cu–O; *P*: Cu–N.

The Patterson projection on (001) is approximately a Fourier projection with copper fixed at the origin.

This allowed us to derive approximate parameters of the nitrogen and oxygen atoms, so that it was possible to determine the signs of the *hk*0 structure factors necessary for the computation of the Fourier projection on (001). As was expected, on account of the superposition of two copper atoms, all the signs of the structure factors (except one) are the same as those determined with the contributions of the copper atoms alone.

Fourier projections

From the Fourier projection on (001) (Fig. 2(*a*)) a first idea of the structure was obtained. It was seen that each copper atom is squarely co-ordinated by four NH_3 molecules, but its normal pseudo-octahedral co-ordination could not be completed by oxygen atoms of the SO_4 groups (as in cupric sulfate pentahydrate) because of the too large distances between the SO_4 groups and the copper atoms. It was found that in cupric tetrammine sulfate monohydrate the H_2O molecules, lying in the same symmetry planes as the copper atoms, complete the distorted octahedral group around copper.

Of the four $Cu(NH_3)_4SO_4.H_2O$ present in the unit cell, all copper atoms, sulfur atoms, H_2O-oxygen atoms, and two of the oxygens of each SO_4 group occupy the fourfold special positions (4*c*), that is they

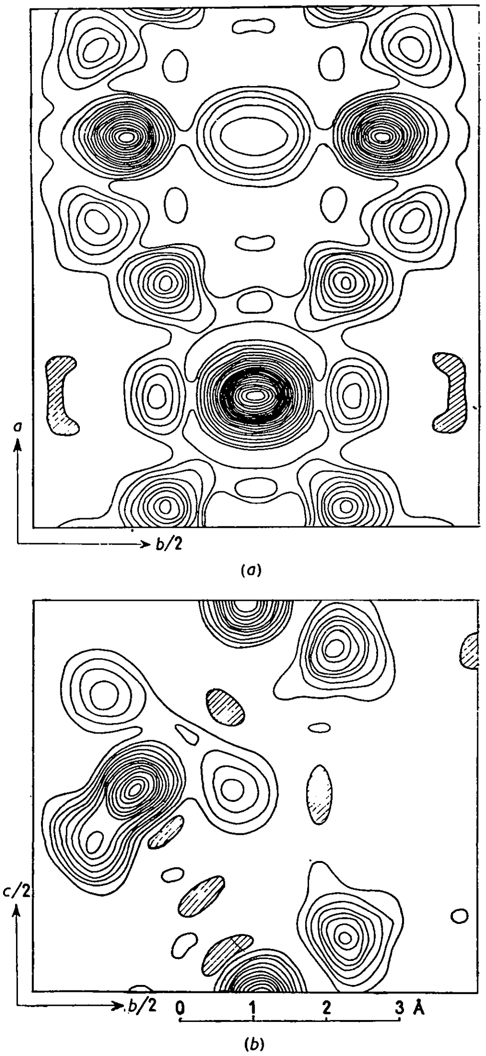

Fig. 2. Electron-density projected (*a*) on (001), (*b*) on (100). The contours are at intervals of 2 e.Å^{-2} (4 e.Å^{-2} in the Cu peaks), starting at 3 e.Å^{-2}. Regions of negative electron density are shaded.

lie on symmetry planes parallel to (100), while one and two sets of general positions (8*d*) are occupied by the remaining eight oxygen atoms of the SO_4 groups and the sixteen nitrogen atoms of the NH_3 groups respectively.

These considerations were useful for the computation of the Fourier projection on (100). If one pays regard only to those F_{0kl}'s, the signs of which are given by the approximate parameters of Cu and S, one gets only $0kl$ structure factors with k even. But, as the x and y parameters of a great part of the atoms were pretty accurately known from the Fourier projection on (001), it was possible to find approximate z parameters from the empirical bond lengths. The right signs for most of the F_{0kl}'s could thus be found and a preliminary Fourier synthesis was computed which allowed refinement to start. From the final projection (Fig. 2(*b*)) the y and z parameters of almost all the atoms can be derived with good accuracy. Sulfur and H_2O-oxygen are superposed in this projection; their parameters are therefore less accurate.

At this stage, a comparison between observed and calculated $0kl$ structure factors gave a 'residual' $R_{0kl} = 0{\cdot}22$ when all the vanishingly small reflexions are taken as having structure amplitudes equal to half the minimum value that it was found possible to observe at the corresponding angle. For this calculation, absolute values of the observed structure factors were obtained (Wilson, 1942); simultaneously the B constant ($B = 2{\cdot}65$ Å^2) was derived and introduced in the expression of the thermal factor, which was applied to the calculated structure factors.

For a better agreement of the observed and calculated structure factors, the least-squares method was applied six times: after each application the R value got smaller and finally reached 0·15. The y and z parameters of Table 1 were deduced in this way.

As most of the atoms (copper, sulfur, H_2O-oxygen, half of the SO_4-oxygen atoms) lie on symmetry planes, their x-parameters ($x = \frac{1}{4}$ or $\frac{3}{4}$) follow from the symmetry of the space group. As to the remaining atoms, it was possible to deduce with good approximation the x parameter for the set of general positions of the SO_4-oxygen atoms from the Fourier projection on (001), but less accurately the x parameters for the two sets of general positions of the NH_3-nitrogen atoms, which are superposed in this projection. The same values of the x parameters were assigned to both sets of nitrogen atoms.

Table 1. *Atomic parameters*

	x/a	y/b	z/c
Cu	0·250	0·258	−0·006
S	0·750	0·112	0·252
$O(H_2O)$	0·250	0·141	0·280
O	0·58	0·068	0·191
O′	0·750	0·230	0·253
O″	0·750	0·081	0·378
N′	0·04	0·355	0·070
N″	0·04	0·346	0·439

As the values of the structure factors are determined in this projection predominantly by copper atoms, it was not considered profitable to apply here the least-squares method. However, the minor accuracy in the determination of these parameters is counterbalanced by the minor length of the a period relative to b and c. The residual for the $hk0$ structure factors is $R_{hk0} = 0{\cdot}10$.

The parameters of one asymmetrical unit are reported in Table 1 and the observed and calculated structure factors are compared in Table 3. It is to be noted that for some reflexions (especially 040, 200, and to some extent also for 002, 008) the agreement between observed and calculated structure factors is remarkably improved if one takes account of the possible situations of the hydrogen atoms, approximately calculated by assuming hydrogen bridges between H_2O and NH_3 groups and the oxygen atoms of the SO_4 groups respectively.

Bond lengths and angles are given in Table 2.

Table 2. *Bond lengths and angles*

Cu–N′	2·06 Å	N′–Cu–N″	87°
Cu–N″	2·04	N_1'–Cu–N_2'	94
		N_1''–Cu–N_2''	92
S–O	1·46	O_1–S–O_2	110
S–O′	1·43	O–S–O′	112
S–O″	1·40	O–S–O″	109
		O′–S–O″	105
Cu–H_2O	3·37	H_2O–Cu–N′	83
Cu–H_2O'	2·59	H_2O'–Cu–N′	95
		H_2O–Cu–N″	90
		H_2O'–Cu–N″	90
$H_2O\ldots O$	2·67	$O_1\ldots H_2O\ldots O_2$	122

Discussion of results

Fundamental elements of the structure are the $Cu(NH_3)_4$ and SO_4 groups. Copper atoms have the normal square co-ordination in $Cu(NH_3)_4$ groups: the measured N–Cu–N angles are 90° within the limits of accuracy (±4°); the Cu–N distances (mean 2·05 Å) are slightly greater than those normally found (2·00 Å: Mathieson & Welsh, 1952; Mazzi, 1953), but values even greater (2·12 Å) have been noticed in cupric tetramethylamine bromide (Lazzarini & Mazzi, 1954). It is interesting to remark that both cupric tetrammine sulfate monohydrate and cupric tetramethylamine bromide, in which the Cu–N distances exceed the value 2·00 Å, easily decompose in the open air, releasing respectively ammonia or methylamine.

The SO_4 groups have the usual tetrahedral structure: the O–S–O angles can be considered normal as well as the S–O distances, which in several compounds are found from 1·35 Å to 1·48 Å (mean 1·43–1·46 Å) (Allen & Sutton, 1950; Jeffrey, 1951).

These two sorts of groups are connected together by means of H_2O molecules. Each H_2O molecule is in contact with two copper atoms and two oxygen atoms belonging to different SO_4 groups. With respect to the copper atoms, the H_2O molecules saturate the two additional bonds which complete the pseudo-octahedral co-ordination; as each H_2O molecule is in contact with two copper atoms, a chain

$$\cdots H_2O \cdots Cu(NH_3)_4 \cdots H_2O \cdots Cu(NH_3)_4 \cdots$$

is formed in the *c* direction, with the oxygen and copper atoms lying in the same plane of symmetry parallel to (100) and the four nitrogen atoms of NH_3 groups around each copper atom, two-by-two on opposite sides of the plane (Fig. 3(*a*)). The distances between each H_2O-oxygen atom and two adjacent copper atoms are not equal: one (2·59 Å) has the same order of magnitude as that found in other compounds (Wells, 1949; Mazzi, 1953), the other, on the contrary, is remarkably greater (3·37 Å); it is also larger than the greatest distance of the two additional bonds given by copper atoms hitherto known, i.e. Cu–Br = 3·17 Å (Helmholz, 1947).

Furthermore, each H_2O molecule is linked with strong hydrogen bonds to two oxygen atoms of SO_4 groups: in this way another chain

$$\cdots HOH \cdots O\text{–}SO_2\text{–}O \cdots HOH \cdots O\text{–}SO_2\text{–}O \cdots$$

is formed in the *a* direction, perpendicularly to the symmetry planes. The OH ··· O distance (2·67 Å) is normal (Beevers & Lipson, 1934) (Fig. 3(*b*)).

The structure consists of layers, parallel to (010), formed by $Cu(NH_3)_4$ squares and SO_4 tetrahedra held together by H_2O molecules. These layers are united by means of NH ··· O hydrogen bridges between NH_3 groups and SO_4 oxygen atoms. These last contacts have also the same order of magnitude (3·00–

Table 3. *Observed and calculated structure factors*

hkl	$\|F_o\|$	F_c
0*k*0		
2	76	−104
4	47	−27 (−45)*
6	78	−85
8	70	63
10	51	−53
12	24	25
14	15	−7
0*k*1		
1	13	−10
2	81	−106
3	20	21
4	57	−61
5	8	−9
6		2
7	19	16
8	35	39
9	28	−29
10	13	−7
11	22	19
12		0
13	16	−14
0*k*2		
0	26	18 (28)*
1	16	14
2	100	−113
3	12	−15
4	64	83
5	8	−8
6		−3
7	< 6	−8
8	36	34
9		1
10	51	−47
11		0
12	35	31
13	< 7	8
0*k*3		
1	10	−17
2	125	124
3	15	−13
4	30	−26
5	12	−7
6	45	−44
7	39	39
8	12	15
9	17	−10
10	20	19
11	17	17
12	< 8	−9
13	17	−14
0*k*4		
0	114	131
1	20	18
2	86	−97
3	8	12
4	50	46
5	43	40
6	67	−59
7		3
8	77	65
9	11	−12
10	22	−23
11	13	−16
12	< 7	8
0*k*5		
1	28	29
2	< 6	7
3	26	24
4	< 6	−2
5	30	−37
6		3
7	7	−10
8	34	31
9	22	−25
10	25	−26
11	15	16
12	19	−13
0*k*6		
0	8	−5
1	18	16
2	36	−30
3	37	−38
4	91	87
5	12	−19
6	48	−50
7	< 8	−6
8		−1
9	17	24
10	21	−23
11		0
12	21	22
0*k*7		
1	6	−8
2	30	28
3	< 7	−6
4	< 7	−8
5	< 8	−4
6	26	−26
7	27	29
8	< 8	−7
9	< 8	−5
10	15	12
0*k*8		
0	46	38 (42)*
1	9	10
2	40	−44
3	15	−13
4	36	40
5	13	13
6	52	−52
7	< 8	−6
8	46	40
9	9	6
10	< 7	4
0*k*9		
1	13	−16
2	25	−23
3	13	14
4	11	13
5	< 8	−5
6	22	16
7	8	9
8	< 7	8
9	< 7	−6
0,*k*,10		
0	11	11
1	22	25

Table 3 (*cont.*)

hkl	$\|F_o\|$	F_c
2	17	−16
3		4
4	46	38
5	11	10
6	23	−24
7	13	−12
8		0
0,*k*,11		
1	< 7	7
2	< 7	− 8
3	< 7	6
4	< 7	5
5	8	− 9
0,*k*,12		
0	31	29
1	< 7	3
2	17	−22
3	12	−15
*h*00		
2	88	−119 (−97)*
4	142	131
6	92	−88
8	31	30
*h*10		
1	56	−57
3	14	20
5	42	−42
7		3
*h*20		
0	109	−104
2	84	89
4	80	−71
6	31	28
*h*30		
1	141	134
3	73	−70
5	66	56
7	50	−43
*h*40		
0	34	−27
2	72	−69
4	<20	10
6	<18	−10
*h*50		
1	18	−13
3	84	85
5		0
7	33	28
*h*60		
0	74	−85
2	99	100
4	42	−43
6	46	45
*h*70		
1	16	13
3	16	−14
5		5
*h*80		
0	60	63
2	70	−64
4	63	56
6	20	−26
*h*90		
1	50	−61
3	<18	18
5	38	−42
h,10,0		
0	46	−53
2		5
4	19	−22
h,11,0		
1	36	38
3	33	−35
5	27	32
h,12,0		
0	27	25

* With the contributions of the hydrogen atoms.

3.20 Å) as those found in other compounds (Brown, 1951). The perfect cleavage (010) is easily intelligible.

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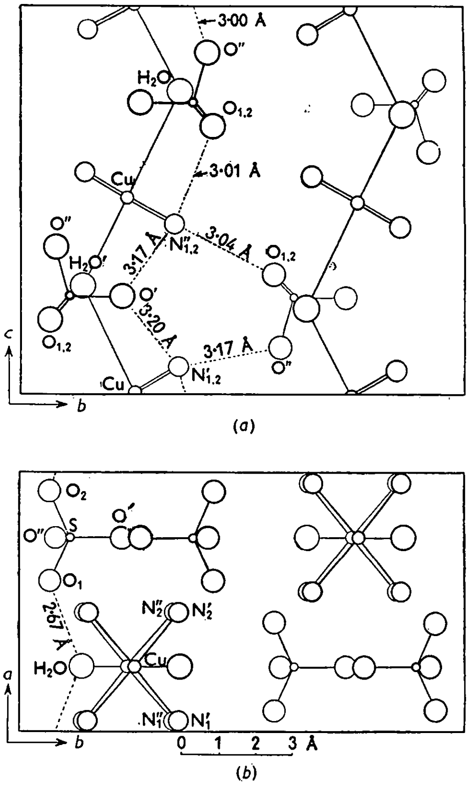

Fig. 3. Projection of the unit cell (*a*) on (100), (*b*) on (001).

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