

The Crystal Structure of Ammonium Copper(I) Sulphite

BIRGIT NYBERG and PEDER KIERKEGAARD

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

The crystal structure of NH_4CuSO_3 has been determined from single-crystal X-ray data and refined using least squares methods. The hexagonal unit cell, which contains six formula units has the dimensions

$$\begin{aligned} a &= 5.4289 \pm 0.0004 \text{ \AA} \\ c &= 23.166 \pm 0.004 \text{ \AA} \end{aligned}$$

The structure (space group $R\bar{3}m$) may be described in terms of trigonal SO_3 pyramids and CuO_3S tetrahedra. The somewhat distorted tetrahedral coordination around copper is provided by three oxygen atoms and one sulphur atom of four SO_3 groups with $\text{Cu}-\text{O}(\text{S})$ distances of 2.12–2.15 Å. The sulphite ions have the $\text{S}-\text{O}$ distance 1.51 Å and the angle $\text{O}-\text{S}-\text{O} = 105.3^\circ$. The CuO_3S tetrahedra and SO_3 pyramids are linked to form double-layers extending parallel to the ab plane. These are held together by the ammonium ions.

In recent years the dimensions of the sulphite group has been discussed by several authors. Theoretical calculations by Cruickshank¹ based on IR-spectra and bond-order discussions predict an $\text{S}-\text{O}$ distance in normal sulphite of about 1.54 Å, which differs considerably from the value 1.39 Å reported in 1931 for Na_2SO_3 by Zachariassen and Buckley.²

X-Ray investigations of a series of different sulphites have been undertaken at this Institute in order to widen the knowledge of the detailed structural chemistry and of the bonding conditions in the sulphites. The crystal structure of $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ is described in a recent article in this journal.³ The compound NH_4CuSO_3 , the structure of which is the subject of the present article, was first synthesized in 1851 by Rogojski.⁴

EXPERIMENTAL

Preparation of crystals. The sample of NH_4CuSO_3 used in this work was synthesized according to Ramberg.⁵ 20 g copper(II) sulphate was dissolved in 60 ml hot water. 60 ml ammonia (density 0.91) was added and a vivid stream of sulphur dioxide was passed through the solution until the entire solution and the crystalline precipitate were colourless. After washing with cold water, alcohol and ether, the colourless and dried substance was investigated under the microscope and found to consist of hexagonal plates.

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.⁶ From the second part of the solution, slightly acidified with hydrochloric acid, the amount of sulphate was determined gravimetrically as BaSO₄. The amount of NH₄⁺ was determined as ammonia by boiling of a sample with a known excess of sodium hydroxide and titrating of the excess with hydrochloric acid.

	Calculated for NH ₄ CuSO ₃	Found
% Cu	39.36	39.3 ± 0.1
% S	19.84	19.4 ± 0.3
% NH ₄ ⁺	11.13	11.0 ± 0.1

X-Ray diffraction data and computing methods. Single-crystal photographs, (rotation, precession, and Weissenberg photographs) showed the Laue symmetry of NH₄CuSO₃ to be 3*m*. The unit cell dimensions were calculated from a powder photograph taken with strictly monochromatized CuKα₁ radiation in a Guinier-type focusing camera. Potassium chloride (*a* = 6.2923 Å) was used as an internal standard (see Table 1). The unit cell dimensions (25°C) are:

$$a = 5.4289 \pm 0.0004 \text{ \AA}$$

$$c = 23.166 \pm 0.004 \text{ \AA}$$

$$V = 591.2 \text{ \AA}^3$$

Table 1. X-Ray powder data of NH₄CuSO₃. CuKα radiation = 1.54050 Å.

<i>h k l</i>	10 ⁵ sin ² θ _{obs}	10 ⁵ sin ² θ _{calc}	10 ⁵ ·(sin ² θ _{obs} - sin ² θ _{calc})	<i>I</i> _{obs}
0 0 3	992	995	- 3	v st
1 0 1	2796	2795	+ 1	v v st
0 1 2	3123	3126	- 3	v v st
0 0 6	3983	3980	+ 3	w
1 0 4	4451	4453	- 2	w
0 1 5	5440	5448	- 8	v v w
1 1 0	8060	8052	+ 8	v v st
1 0 7	8095	8101	- 6	st
0 0 9	—	8954	—	—
1 1 3	9040	9047	- 7	st
0 1 8	9738	9759	-21	v v w
0 2 1	—	10847	—	—
2 0 2	11185	11178	+ 7	w
1 1 6	—	12032	—	—
0 2 4	12516	12505	+11	w
2 0 5	13492	13500	- 8	m
1 0 10	13737	13739	- 2	w
0 0 12	—	15919	—	—
0 1 11	16072	16060	+12	w
0 2 7	—	16151	—	—
1 1 9	17016	17006	+10	w
2 0 8	17794	17811	-17	v v w
2 1 1	18904	18898	+ 6	m
1 2 2	19223	19230	- 7	st
1 0 13	21363	21367	- 4	v v w
0 2 10	21785	21791	- 6	w

The powder photograph was measured and interpreted to sin²θ = 0.49. Reflections systematically absent in space group *R*3*m* have been omitted.

The value of 2.73 for the density found from the apparent loss of weight in absolute alcohol gives six formula units in the unit cell. (Calculated density = 2.72.)

All reflections with $-h+k+l \neq 3n$ were found to be absent. This is characteristic of the two space groups No. 160 $R3m$ and No. 166 $R\bar{3}m$. The higher symmetry was taken as the starting point of the structure investigation. The result thus obtained was found to be consistent throughout. It was not significantly improved by lowering the symmetry. The reflections ($0kl-3kl$) of a single crystal — a hexagonal plate 0.013 mm thick and the edge 0.027 mm — taken with $\text{CuK}\alpha$ radiation were recorded photographically with an integrating Weissenberg camera using multiple film technique. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with carefully timed exposures.

In the computational work the absorption correction (No. 6019) and the Lorentz polarization correction (No. 6024) were performed on the electronic computer TRASK. (The numbers refer to the list of crystallographic computer programs ⁷). In the determination of the $|F|^2$ values the linear absorption coefficient $\mu = 116.3 \text{ cm}^{-1}$, derived from the atomic absorption coefficient given in the *International Tables*, was used for the calculation of absorption factors. Further computational work including the refinement of the lattice constants, Fourier summations, least-squares refinement and calculation of interatomic distances was performed on the electronic computer CD 3600.

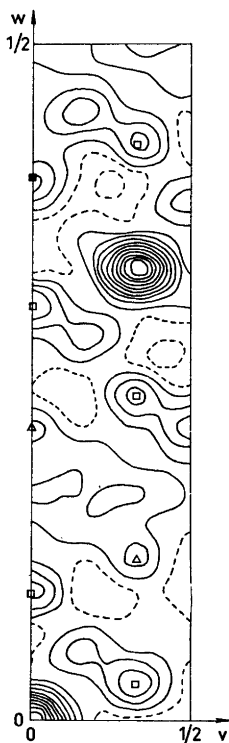


Fig. 1. The Patterson projection $P(pvw)$ for NH_4CuSO_5 . The Cu—Cu (■), Cu—S (□) and S—S (▲) vectors have been indicated for the final structure. Dashed lines indicate negative values.

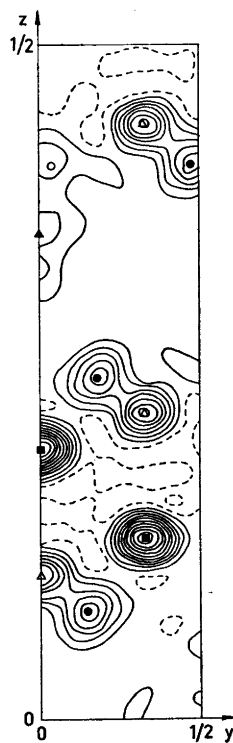


Fig. 2. The electron density projection $\rho(py z)$ for NH_4CuSO_5 . The final positions of the copper (■), sulphur (△), oxygen (●) and nitrogen (○) atoms have been marked. Dashed lines indicate negative values.

In No. 166 $R\bar{3}m$ (hexagonal axes) and six formula units in the cell the only available positions for copper, sulphur, and nitrogen are $(0,0,0; \frac{1}{3}, \frac{2}{3}, \frac{1}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}) + :$

$$\begin{aligned} 6(c): & \pm (0,0,z) \\ 3(b): & 0,0,\frac{1}{2} \\ 3(c): & 0,0,0 \end{aligned}$$

From the absence of any maximum at $(0, \frac{1}{3})$ in the Patterson projection $P(pvw)$ (Fig. 1) it was concluded that sixfold positions were the only ones available for the heavier atoms, *i.e.* copper and sulphur. The interatomic vectors corresponding to 6(c) are

$$\begin{aligned} \pm [0 \ 0 \ 2z] & \quad \text{weight 3} \\ \pm [\frac{2}{3} \ \frac{1}{3} \ \frac{1}{3}] & \quad \text{weight 6} \\ \pm [\frac{1}{3} \ \frac{2}{3} \ \frac{1}{3} \pm 2z] & \quad \text{weight 3} \end{aligned}$$

The interatomic vectors between unlike atoms in 6-fold positions c_1 and c_2 are

$$\begin{aligned} \pm [0 \ 0 \ z_1 + z_2] \\ \pm [0 \ 0 \ z_1 - z_2] \\ \pm [\frac{2}{3} \ \frac{1}{3} \ \frac{1}{3} \pm (z_1 + z_2)] \\ \pm [\frac{1}{3} \ \frac{2}{3} \ \frac{1}{3} \pm (z_1 - z_2)] \end{aligned}$$

all with the weight 6. By comparing these vectors with the Patterson projection $P(pvw)$ and assuming all the interatomic distances to fall within normal ranges the following parameters were obtained:

$$\begin{aligned} z_{\text{Cu}} &= 0.19, \\ z_{\text{S}} &= 0.10. \end{aligned}$$

The electron density projection $\rho(pyz)$ (Fig. 2) was then calculated, using the signs of F_{0kl} obtained from the copper and sulphur contributions. In the preliminary calculations the atomic scattering curves for neutral atoms were applied.⁸ In the final stages the curves for ionized atoms were applied.⁹ The real part of the anomalous dispersion correction according to Dauben and Templeton¹⁰ was also applied. From the electron density projection the positions of the eighteen oxygen atoms in 18(h) and of the six nitrogens in 6(c) could easily be obtained.

A refinement of the coordinates so obtained was then performed by means of the least-squares program mentioned above. The starting value of the individual isotropic temperature factors used in this program were zero for all the atoms. The refinement was considered to be complete when the parameter shifts were less than 5 % of the standard deviations. At this stage the discrepancy factor was 9.0 %.

Table 2. Weight analysis obtained in the final cycle of the least-squares refinement of NH_4CuSO_3 .

$$w = \text{weighting factor, } \Delta = ||F_{\text{obs}}| - |F_{\text{calc}}||$$

Interval F_{obs}	Number of independent reflections	$\overline{w\Delta^2}$	Interval $\sin \theta$	Number of independent reflections	$\overline{w\Delta^2}$
0.0—29.9	14	1.20	0.00—0.46	23	0.60
29.9—44.3	14	1.39	0.46—0.59	20	0.84
44.3—54.5	14	0.70	0.59—0.67	20	0.86
54.5—66.4	14	0.88	0.67—0.74	14	0.61
66.4—80.0	14	1.20	0.74—0.79	13	1.00
80.0—98.8	14	0.28	0.79—0.84	10	0.59
98.8—114.1	14	1.00	0.84—0.89	14	1.10
114.1—157.1	14	0.97	0.89—0.93	10	1.67
157.1—181.7	14	1.12	0.93—0.97	9	0.82
181.7—379.6	15	1.26	0.97—1.00	8	1.93

Cruikshank's weighting function

$$w = (A + |F_{\text{obs}}| + C|F_{\text{obs}}|^2 + D|F_{\text{obs}}|^3)^{-1}$$

was used in the refinement with the following final values for the parameters:

$$A = 24.2625 \quad C = -0.00254 \quad D = 0$$

Table 3. The structure of NH_4CuSO_3 .

Space group: $R\bar{3}m$

Unit-cell dimensions: $a = 5.4289 \pm 0.0004 \text{ \AA}$

$c = 23.166 \pm 0.004 \text{ \AA}$

Cell content: $6[\text{NH}_4/\text{CuSO}_3]$

Arrangement of atoms: $(000; \frac{1}{2} \frac{1}{2} \frac{1}{2}; \frac{1}{2} \frac{1}{2} \frac{1}{2}) +$

6 Cu, 6 S and 6 N in $6(c): \pm (00z)$

18 O in $18(h): \pm (x\bar{x}z); \pm (x2xz); \pm (2\bar{x}\bar{x}z)$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B) \text{ \AA}^2$
Cu	0	0	0.2000 ± 0.0002	2.20 ± 0.12
S	0	0	0.1073 ± 0.0003	1.56 ± 0.13
O	0.1478 ± 0.0013	0.2956 ± 0.0013	0.9186 ± 0.0005	2.03 ± 0.22
N	0	0	0.3629 ± 0.0011	1.97 ± 0.45

A weight analysis obtained in the last cycle is given in Table 2. The positional parameters and the isotropic temperature factors of all the atoms and their standard deviations are given in Table 3.

A three-dimensional difference synthesis calculated at values of z corresponding to the sites of the various atoms showed very small residual maxima or minima. The highest maximum was about 1/8 of the height of the oxygen peaks in the F_o synthesis.

The calculated interatomic distances and their standard deviations are given in Table 4. All distances lie within normal ranges, thus supporting the correctness of the coordinates arrived at in the last cycle.

In the unit cell there are also twentyfour hydrogen atoms. It was not possible to determine their parameters from the present set of experimental data.

Table 4. Interatomic distances and standard deviations in NH_4CuSO_3 .

Cu	— 3 O	= 2.120 ± 0.012	O	— S	= 1.514 ± 0.012
	— S	= 2.147 ± 0.008		— Cu	= 2.120 ± 0.012
	— 3 O	= 3.079 ± 0.012		— 2 O	= 2.408 ± 0.016
	— 3 S	= 3.192 ± 0.002		— 2 N	= 2.973 ± 0.011
	— 3 Cu	= 3.493 ± 0.004		— 2 O	= 3.021 ± 0.016
	— N	= 3.775 ± 0.026		— Cu	= 3.079 ± 0.012
	— 3 N	= 3.950 ± 0.016		— N	= 3.106 ± 0.024
				— S	= 3.779 ± 0.013
				— O	= 3.968 ± 0.022
S	— 3 O	= 1.514 ± 0.012	N	— 6 O	= 2.973 ± 0.011
	— Cu	= 2.147 ± 0.008		— 3 O	= 3.106 ± 0.024
	— 3 Cu	= 3.192 ± 0.002		— 3 N	= 3.421 ± 0.020
	— 3 N	= 3.614 ± 0.013		— 3 S	= 3.614 ± 0.013
	— 3 O	= 3.779 ± 0.013		— Cu	= 3.775 ± 0.026
				— 3 Cu	= 3.950 ± 0.016

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals of NH_4CuSO_3 are built up of double layers formed by CuO_3S tetrahedra and SO_3 trigonal pyramids linked together by corner sharing. Schematic drawings of the structure viewed along $[100]$ and $[001]$ show the linking (Fig. 3a–b). The layers are parallel to the ab plane and are held together by ammonium ions.

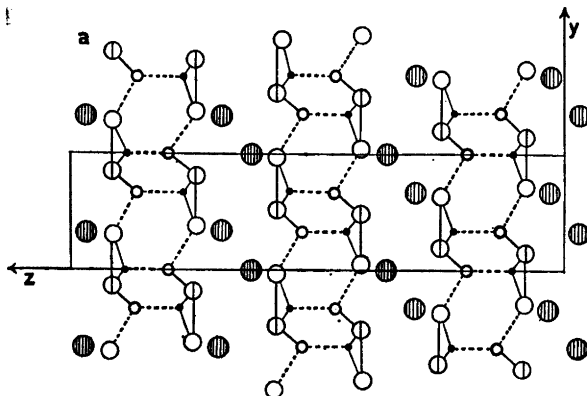
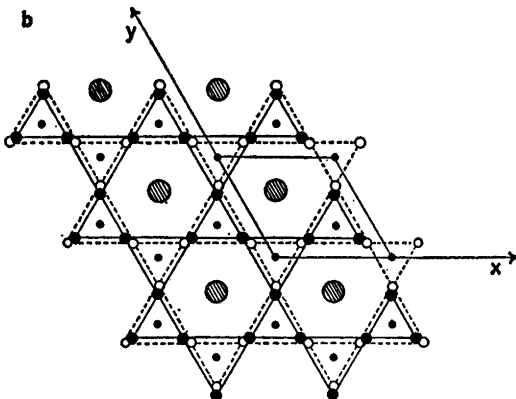


Fig. 3. Schematic drawings showing the structure of NH_4CuSO_3 . a) The structure viewed along $[100]$ showing the double layers formed by CuO_3S tetrahedra and SO_3 groups linked together by sharing corners and also showing the stacking of the double layers and the ammonium ions. Open large circles denote oxygen atoms linked to the sulphur atoms (small filled circles) and the copper atoms (heavy contour circles). Lined open circles denote two overlapping oxygen atoms and hatched large circles denote ammonium ions. The hydrogen atoms are not indicated.



b) The double layers formed by CuO_3S tetrahedra and SO_3 pyramids. Only one double layer is indicated (*i.e.* atoms with z parameters within the limits $0 < z < 0.26$). Open and full circles denote oxygen atoms situated in two planes $c(1/3 + 2z_0) = 3.96 \text{ \AA}$ apart. The small crossmarked circles denote overlapping sulphur and copper atoms 2.14 \AA apart. The large hatched circles denote ammonium ions situated between and linking together the double layers as indicated in Fig. 3a.

Table 5. Comparison between calculated and observed structure factors from Weissenberg photographs of NH_4CuSO_3 . CuK radiation.

$h k l$	F_{calc}	F_{obs}	$h k l$	F_{calc}	F_{obs}
0 1 2	-207	203	0 0 24	15	-
0 1 5	58	75	0 0 27	9	-
0 1 8	-68	72			
0 1 11	204	220	0 1 $\bar{1}$	267	236
0 1 14	-15	-	0 1 $\bar{4}$	-108	115
0 1 17	-91	109	0 1 $\bar{7}$	-323	331
0 1 20	139	169	0 1 $\bar{10}$	274	266
0 1 23	-110	151	0 1 $\bar{13}$	-181	163
0 1 26	23	35	0 1 $\bar{16}$	45	48
0 1 29	25	23	0 1 $\bar{19}$	93	111
			0 1 $\bar{22}$	-100	113
0 2 1	-9	-	0 1 $\bar{25}$	68	105
0 2 4	-172	173	0 1 $\bar{28}$	15	-
0 2 7	-82	78			
0 2 10	312	295	0 2 $\bar{2}$	-81	78
0 2 13	-265	268	0 2 $\bar{5}$	254	231
0 2 16	-22	-	0 2 $\bar{8}$	-113	106
0 2 19	149	167	0 2 $\bar{11}$	19	12
0 2 22	-49	69	0 2 $\bar{14}$	10	-
0 2 25	21	41	0 2 $\bar{17}$	19	-
			0 2 $\bar{20}$	109	128
0 3 0	245	235	0 2 $\bar{23}$	-155	175
0 3 3	-198	182	0 2 $\bar{26}$	25	-
0 3 6	39	40			
0 3 9	164	166	0 3 $\bar{3}$	-96	80
0 3 12	-147	146	0 3 $\bar{6}$	46	40
0 3 15	-4	-	0 3 $\bar{9}$	82	98
0 3 18	-10	-	0 3 $\bar{12}$	-158	146
			0 3 $\bar{15}$	53	76
0 3 $\bar{24}$	-35	32	0 3 $\bar{18}$	-	-
0 3 $\bar{21}$	33	44	0 3 $\bar{21}$	-4	-
			0 3 $\bar{24}$	-44	-
0 4 2	-50	45			
0 4 5	93	99	0 4 $\bar{1}$	27	45
0 4 8	-40	46	0 4 $\bar{4}$	-77	79
0 4 11	26	-	0 4 $\bar{7}$	-53	-
0 4 14	-11	-	0 4 $\bar{10}$	161	175
0 4 17	10	-	0 4 $\bar{13}$	-143	147
0 4 20	70	64	0 4 $\bar{16}$	-8	-
			0 4 $\bar{19}$	91	96
0 5 1	57	-	0 4 $\bar{22}$	-35	29
0 5 4	-4	-			
0 5 7	-61	-	0 5 $\bar{2}$	-83	83
0 5 10	63	62	0 5 $\bar{5}$	16	-
0 5 13	-82	70	0 5 $\bar{8}$	25	-
0 6 0	108	73	0 5 $\bar{11}$	54	59
			0 5 $\bar{14}$	-47	45
0 0 3	-248	-	0 5 $\bar{17}$	-17	-
0 0 6	-222	224			
0 0 9	177	163	0 6 $\bar{3}$	-46	27
0 0 12	-62	68			
0 0 15	83	95	1 $\bar{2}$ 0	379	380
0 0 18	-137	160	1 $\bar{2}$ $\bar{3}$	-209	198
0 0 21	1	-	1 $\bar{2}$ $\bar{6}$	63	72

$h k l$	F_{calc}	F_{obs}	$h k l$	F_{calc}	F_{obs}
$1 \bar{2} \bar{9}$	166	158	$1 4 \bar{12}$	- 78	80
$1 \bar{2} \bar{12}$	-207	211	$1 4 \bar{15}$	- 8	-
$1 \bar{2} \bar{15}$	44	51	$1 4 \bar{18}$	- 4	-
$1 \bar{2} \bar{18}$	- 21	21			
$1 \bar{2} \bar{21}$	19	21	$1 5 \bar{1}$	42	39
$1 \bar{2} \bar{24}$	- 42	36	$1 5 \bar{4}$	- 28	20
$1 \bar{2} \bar{27}$	- 4	-	$1 5 \bar{7}$	- 44	43
			$1 5 \bar{10}$	69	60
$1 \bar{3} \bar{2}$	-187	188			
$1 \bar{3} \bar{5}$	73	67	$1 5 2$	- 41	-
$1 \bar{3} \bar{8}$	- 2	-	$1 5 5$	13	-
$1 \bar{3} \bar{11}$	119	110	$1 5 8$	4	-
$1 \bar{3} \bar{14}$	- 52	50	$1 5 11$	37	-
$1 \bar{3} \bar{17}$	- 51	55			
$1 \bar{3} \bar{20}$	128	145	$2 \bar{4} 0$	324	358
$1 \bar{3} \bar{23}$	- 93	95	$2 \bar{4} \bar{3}$	-122	119
$1 \bar{3} \bar{26}$	5	-	$2 \bar{4} \bar{6}$	- 72	49
			$2 \bar{4} \bar{9}$	98	99
$1 \bar{4} \bar{1}$	108	114	$2 \bar{4} \bar{12}$	- 52	42
$1 \bar{4} \bar{4}$	- 55	49	$2 \bar{4} \bar{15}$	30	22
$1 \bar{4} \bar{7}$	-130	129	$2 \bar{4} \bar{18}$	- 56	55
$1 \bar{4} \bar{10}$	154	155	$2 \bar{4} \bar{21}$	1	-
$1 \bar{4} \bar{13}$	-113	112	$2 \bar{4} \bar{24}$	- 1	-
$1 \bar{4} \bar{16}$	17	-			
$1 \bar{4} \bar{19}$	68	59	$2 \bar{5} \bar{2}$	- 44	40
$1 \bar{4} \bar{22}$	- 58	59	$2 \bar{5} \bar{8}$	- 36	45
			$2 \bar{5} \bar{11}$	87	83
$1 \bar{5} \bar{3}$	- 60	55	$2 \bar{5} \bar{14}$	- 5	-
$1 \bar{5} \bar{6}$	7	-	$2 \bar{5} \bar{17}$	- 36	30
$1 \bar{5} \bar{9}$	58	55			
$1 \bar{5} \bar{12}$	- 83	80	$2 \bar{5} \bar{20}$	55	48
$1 \bar{5} \bar{15}$	21	27			
$1 \bar{5} \bar{18}$	2	-	$2 \bar{6} \bar{1}$	29	-
			$2 \bar{6} \bar{4}$	- 53	-
$1 2 \bar{1}$	132	121	$2 \bar{6} \bar{7}$	- 36	-
$1 2 \bar{4}$	- 13	-	$2 \bar{6} \bar{13}$	- 85	65
$1 2 \bar{7}$	-171	161	$2 \bar{6} \bar{10}$	98	65
$1 2 \bar{10}$	162	169			
$1 2 \bar{13}$	-161	164	$2 3 \bar{1}$	106	99
$1 2 \bar{16}$	52	51	$2 3 \bar{4}$	- 62	59
$1 2 \bar{19}$	94	95	$2 3 \bar{7}$	-117	110
$1 2 \bar{22}$	- 91	98	$2 3 \bar{10}$	130	139
$1 2 \bar{25}$	39	36	$2 3 \bar{13}$	- 71	77
			$2 3 \bar{16}$	4	-
$1 3 \bar{2}$	- 86	96	$2 3 \bar{19}$	42	44
$1 3 \bar{5}$	37	20			
$1 3 \bar{8}$	- 33	29	$2 4 \bar{2}$	- 25	19
$1 3 \bar{11}$	91	103	$2 4 \bar{5}$	36	18
$1 3 \bar{14}$	- 19	-	$2 4 \bar{8}$	- 17	-
$1 3 \bar{17}$	- 35	38	$2 4 \bar{11}$	24	-
$1 3 \bar{20}$	82	90	$2 4 \bar{14}$	- 12	-
$1 3 \bar{23}$	- 76	74			
			$3 \bar{6} 0$	128	118
$1 4 0$	149	164	$3 \bar{6} \bar{3}$	- 63	66
$1 4 \bar{3}$	-103	105	$3 \bar{6} \bar{6}$	- 8	-
$1 4 \bar{6}$	4	-	$3 \bar{6} \bar{9}$	62	66
$1 4 \bar{9}$	95	97	$3 \bar{6} \bar{12}$	- 55	53

The distances between neighbouring atoms are given in Table 4. The distances and angles in the coordination polyhedra are very nearly the same as those found in $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ for the $\text{Cu(I)}\text{O}_3\text{S}$ tetrahedra and SO_3 pyramids.³

The S—O distance (1.51 Å) now found in the sulphite group is markedly longer than the value reported by Zachariassen and Buckley² for Na_2SO_3 (1.39 Å) and rather close to the value recently reported by Battelle and Trueblood¹¹ for $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ (1.53 Å) and by Spinnler and Becker¹² for $\text{PdSO}_3(\text{NH}_3)_3$ (1.50 Å).

A further discussion will await the results of the structural investigations of several sulphites now in progress at this Institute.

Acknowledgements. This study has been performed within a research program sponsored by the *Swedish Natural Science Research Council*.

The authors wish to thank Professor Arne Magnéli for his encouraging interest and for all facilities placed at their disposal.

REFERENCES

1. Cruickshank, D. W. J. *J. Chem. Soc.* **1961** 5486.
2. Zachariassen, W. H. and Buckley, H. E. *Phys. Rev.* **37** (1931) 1295.
3. Kierkegaard, P. and Nyberg, B. *Acta Chem. Scand.* **19** (1965) 2189.
4. Rogojski, J. B. *J. prakt. Chem.* **53** (1851) 409.
5. Ramberg, L. *Z. physik. Chem.* **69** (1909) 512.
6. Vogel, I. A. *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed., London 1961, p. 609.
7. *IUCr World List of Crystallographic Computer Programs*, 1st Ed., Sept. 1962.
8. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
9. Hansson, H. P., Herman, F., Lea, J. P. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
10. Dauben, C. H. and Templeton, D. H. *Acta Cryst.* **8** (1955) 841.
11. Battelle, L. and Trueblood, K. N. *Acta Cryst.* **19** (1965) 531.
12. Spinnler, M. A. and Becker, L. N. *Unpublished work*.

Received September 18, 1967.