The Crystal Structure of Silver Sulphite

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The crystal structure of Ag_2SO_3 has been determined and refined to a final R value of 0.095 from three-dimensional X-ray single crystal data. The space group is $P2_1/c$ (No. 14) and the unit cell dimensions at 25°C are

$$a = 4.6507 \pm 0.004 \text{ Å}$$
$$b = 7.8910 \pm 0.008 \text{ Å}$$
$$c = 11.173 \pm 0.002 \text{ Å}$$
$$\beta = 120.7 \pm 2°$$

The structure consists of pyramidal SO_3 groups each of which is bonded to one silver atom. The coordination around one of the two nonequivalent silver atoms consists of three oxygen atoms from different SO_3 groups and one sulphur atom, forming a tetrahedron. The other silver atom is surrounded by a very distorted tetrahedron comprising four oxygen atoms, each from a different sulphite group. Within the sulphite ions, all of which are crystallographically equivalent, the average value of the distances are $S-O = 1.516 \pm 0.024$ Å $O-O = 2.399 \pm 0.033$ Å and the angle (average value) $O-S-O$ is $104.6 \pm 1.3°$.

D uring the course of crystal structure studies at this Institute on sulphite compounds, reports have been published on the structures of the phases $Cu_2SO_3 \cdot CuSO_3 \cdot 2 \, H_2O$ [1] and NH_4CuSO_3.[2,3] Subsequent investigations of further sulphite structures include Ag_2SO_3, Na_2SO_3, *etc.* A report on a structural refinement of the sodium compound is now being prepared.[4] This article describes the determination and refinement of the structure of Ag_2SO_3.

EXPERIMENTAL

Preparation of the crystals. The sample of Ag_2SO_3 used in this work was synthesized by bubbling of SO_2 through a solution of $AgNO_3$. A white crystal mass was obtained. The crystals were washed in water and dried in a nitrogen atmosphere. Needle-like transparent prisms were obtained. The crystals are somewhat unstable when exposed to light or X-rays.

Analysis. A sample of Ag_2SO_3 was dissolved in HNO_3 (1 M) and hydrogen peroxide was added to the solution. After boiling away of the excess of peroxide, part of the solution was used for electrolytical determination of the amount of silver according to Cohen.[5]

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The other part was used for the analysis of sulphur which was determined gravimetrically as $BaSO_4$. (Found: Ag 71.5; S 10.3. Calc. for Ag_2SO_3; Ag 72.9; S 10.8).

Collecting of X-ray diffraction data and computing methods. Values for the lattice parameters were calculated from a powder photograph obtained from a Guinier Hägg focusing camera of 80 mm diameter with strictly monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å). Potassium chloride ($a = 6.29228$ Å) [6] was used as an internal standard. A powder photograph without internal standard showed that no reaction had occurred between Ag_2SO_3 and KCl. The unit cell dimensions (see Table 1) at 25°C are:

Table 1. X-Ray powder data of Ag_2SO_3. $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å).

h	k	l	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	I_{obs}
0	1	1	1603	1595	v st
1	0	2	3144	3129	m
0	1	2	3538	3522	v w
1	1	1	3737	3728	v st
0	2	0	3813	3811	m
1	1	2	4092	4082	st
1	1	0	4665	4659	m
1	1	3	5719	5719	m
0	2	2	6375	6380	v st
1	2	1	6591	6587	v st
0	1	3	6747	6732	v v st
1	1	−1	6880	6875	st
1	2	2	6943	6940	m
1	2	0	7524	7518	st
1	0	4	7686	7689	st
0	3	0 ⎱	8576	8575	v w
1	2	3 ⎰		8578	
0	3	1	9221	9217	m
1	0	−2	9428	9422	m
0	2	3	9582	9591	v v st
1	2	−1	9738	9733	st
1	1	−2	10370	10374	m
2	0	2 ⎱	11122	11102	st (d)
0	3	2 ⎰		11144	
0	1	4	11225	11228	st
1	3	1	11347	11351	w
1	2	4	11503	11500	m
1	3	2	11703	11704	m
2	1	3	12117	12119	v st
1	3	0	12285	12282	m
1	2	−2 ⎱	13267	13233	m
2	1	1 ⎰		13275	
2	1	4	13467	13468	w

The powder photograph was measured and interpreted to $\sin^2\theta = 0.38$. Reflections systematically absent in space group $P2_1/c$ have been omitted.

$a = 4.6507 \pm 0.004$ Å, $b = 7.8910 \pm 0.008$ Å, $c = 11.1730 \pm 0.015$ Å, $\beta = 120.7 \pm 0.2°$, $V = 355.7$ Å³.

The value of 5.4 ± 0.1 for the density determined from the loss of weight in benzene corresponds to four formula units in the unit cell (calculated density = 5.52).

The reflections ($0kl - 2kl$, $h0l - h4l$) of two single crystals, taken with Ni-filtered $CuK\alpha$ radiation, were recorded photographically with a Weissenberg camera using multiple film technique. The relative intensities were estimated visually by comparison with an

intensity scale obtained from one reflection photographed with different exposure times. The dimensions of the two crystals investigated were 0.044 mm and 0.080 mm in the direction of the a-axis, 0.008 mm and 0.016 mm (b-axis), 0.012 mm and 0.024 mm (c-axis).

Different crystals had to be used for the collection of two sets of data due to the slow decomposition of Ag_2SO_3 in X-ray light. A total of 625 reflections were recorded and of these 448 were independent. The space group of the structure, $P2_1/c$, could be uniquely determined from the reflections systematically absent, viz. $h0l$ with $l=$odd and $0k0$ with $k=$odd.

In the determination of the $|F|^2$ values, the linear absorption coefficient $\mu=941.0$ cm^{-1}, derived from the values given in the *International Tables*,[7] was used for the calculation of the absorption factors.

The computational work, including refinement of lattice parameters, absorption and Lorentz-polarization correction, Fourier summations, least-square refinement and calculation of interatomic distances and angles was performed on the electronic computer CD 3600.

THE STRUCTURE DETERMINATION

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

$$
\begin{array}{lll}
2(a) & 0,0,0; & 0,\tfrac{1}{2},\tfrac{1}{2} \\
2(b) & \tfrac{1}{2},0,0; & \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2} \\
2(c) & 0,0,\tfrac{1}{2}; & 0,\tfrac{1}{2},0 \\
2(d) & \tfrac{1}{2},0,\tfrac{1}{2}; & \tfrac{1}{2},\tfrac{1}{2},0 \\
4(e) & \pm(x,y,z); & \pm(\bar{x},\tfrac{1}{2}+y,\tfrac{1}{2}-z)
\end{array}
$$

From the absence of any maximum in the Patterson syntheses $P(0,v,w)$ at $v=w=\tfrac{1}{2}$ it was concluded that position $4(e)$ was the only one possible for silver. The interatomic vectors corresponding to $4(e)$ are

$$
\begin{array}{ll}
\pm(2x,2y,2z) & \text{weight 2} \\
\pm(2x,\tfrac{1}{2},\tfrac{1}{2}+2z) & \text{weight 2} \\
\pm(0,\tfrac{1}{2}+2y,\tfrac{1}{2}) & \text{weight 2}
\end{array}
$$

By the use of the symmetry minimum function of the asymmetric part of the Patterson function according to Simpson *et al.*[8] the following parameters were obtained

$$
\begin{array}{lll}
x_{Ag(1)} = 0.13 & y_{Ag(1)} = 0.50 & z_{Ag(1)} = 0.31 \\
x_{Ag(2)} = 0.23 & y_{Ag(2)} = 0.63 & z_{Ag(2)} = 0.07
\end{array}
$$

The electron density $\varrho(x,y,z)$ over the asymmetric part of the unit cell was then calculated, using the signs of F_{hkl} obtained from the silver contribution. Atomic scattering curves for the neutral atoms were used. From the electron density synthesis the positions of the 4 sulphur and the 12 oxygen atoms in position $4(e)$ could be obtained.

A refinement of the coordinates so obtained was then performed by means of the least-squares program mentioned above. The starting values for the individual isotropic temperature factors used in this program were equal 1.0 for all the atoms. At the end of the refinement, 14 strong reflections with low $\sin\theta/\lambda$ values were omitted as suffering from extinction. Anisotropic temperature factors were used for the silver and the sulphur atoms. The refinement was considered to be complete when the shifts were well below 5 % of the standard deviations at which point the discrepancy index

$R = \sum |F_o(hkl) - F_c(hkl)| / \sum |F_o(hkl)|$ was down to 0.095. No non-observed reflections were introduced in the refinement. A three-dimensional difference synthesis with all atoms, at points spaced 0.25 Å apart, showed no peak heights above 25 % of the average oxygen peak height. Finally, a structure factor calculation showed that none of the nonobserved reflections with $\sin\theta/\lambda$ less than 0.64 had structure factor values exceeding twice the figures of the faintest observed reflections.

Hughes' weighting function $w = 1/h^2 |F_{obs}, \min|^2$ for $|F_{obs}| \leq h|F_{obs}, \min|$ and $w = 1/|F_{obs}|^2$ for $|F_{obs}| > |F_{obs}, \min|$ was used in the refinement, with the parameters $h = 4.0$ and $F_{obs}, \min = 10.0$. A weight analysis obtained in the last cycle is given in Table 2. For the positional parameters and temperature factors of all the atoms and their standard deviations, see Table 3. The calculated interatomic distances and angles with their standard deviations are listed in Table 4. The structure factors are given in Table 5.

Table 2. Weight analysis obtained in the final cycle of the least-squares refinement of Ag_2SO_3.

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

Interval $\sin\theta$	Number of independent reflections	$w\Delta^2$	Interval F_{obs}	Number of independent reflections	$w\Delta^2$
0.00 − 0.46	56	1.18	0.0 − 18.3	43	0.76
0.46 − 0.58	70	1.10	18.3 − 24.1	43	1.12
0.58 − 0.67	60	1.29	24.1 − 29.6	43	1.22
0.67 − 0.74	71	0.75	29.6 − 32.9	44	1.16
0.74 − 0.79	52	0.87	32.9 − 39.5	43	1.41
0.79 − 0.84	38	1.11	39.5 − 47.9	44	1.10
0.84 − 0.89	37	1.14	47.9 − 56.9	43	0.95
0.89 − 0.93	27	1.09	56.9 − 71.3	44	0.77
0.93 − 0.97	17	0.56	71.3 − 86.6	43	0.53
0.97 − 1.00	6	0.90	86.6 − 162.4	44	0.99
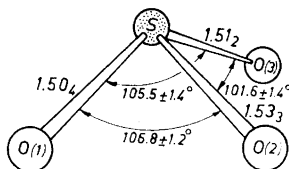
Fig. 1. The sulphite pyramid in Ag_2SO_3.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals of Ag_2SO_3 contain pyramidal sulphite groups (cf. Fig. 1) linked together by the silver atoms. The distances and angles within the sulphite group of Ag_2SO_3, viz. $S-O = 1.51_6$ (average value) and $O-S-O = 104.6°$ (average value), are in close agreement with the values found for NH_4CuSO_3

Table 3. The structure of Ag_2SO_3.

Space group: $P2_1/c$

Unit cell dimensions:
$$a = 4.6507 \pm 0.0004 \text{ Å}$$
$$b = 7.8910 \pm 0.0008 \text{ Å}$$
$$c = 11.173 \pm 0.002 \text{ Å}$$
$$\beta = 120.7 \pm 0.2°$$

Cell content: 4 $[Ag_2SO_3]$

Arrangement of atoms: 8 Ag, 4 S, and 12 O in $4(e)$: $\pm(x,y,z)$; $\pm(\bar{x},\tfrac{1}{2}+y,\tfrac{1}{2}-z)$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å²
Ag(1)	0.1524 ± 0.0006	0.4800 ± 0.0003	0.3038 ± 0.0003	Anisotropic (*v.infra*)
Ag(2)	0.2733 ± 0.0006	0.6230 ± 0.0004	0.0599 ± 0.0002	Anisotropic »
S	0.4324 ± 0.0016	0.2100 ± 0.0010	0.1218 ± 0.0007	Anisotropic »
O(1)	0.2778 ± 0.0052	0.2266 ± 0.0033	0.2112 ± 0.0022	2.83 ± 0.39
O(2)	0.1440 ± 0.0055	0.2920 ± 0.0035	0.4703 ± 0.0023	3.06 ± 0.42
O(3)	0.5917 ± 0.0061	0.3800 ± 0.0034	0.1301 ± 0.0025	3.13 ± 0.45

The temperature factor for the silver and sulphur atoms is of the form:

$$T = \exp[B_{11}h^2 + B_{22}k^2 + B_{33}l^{22} + B_{12}hk + B_{13}hl + B_{23}kl]$$

Atom	$B_{11} \pm \sigma(B_{11})$	$B_{22} \pm \sigma(B_{22})$	$B_{33} \pm \sigma(B_{33})$
Ag(1)	0.0434 ± 0.0017	0.0049 ± 0.0009	0.0091 ± 0.0003
Ag(2)	0.0378 ± 0.0015	0.0100 ± 0.0009	0.0073 ± 0.0003
S	0.0298 ± 0.0036	0.0040 ± 0.0014	0.0063 ± 0.0007

Atom	$B_{12} \pm \sigma(B_{12})$	$B_{13} \pm \sigma(B_{13})$	$B_{23} \pm \sigma(B_{23})$
Ag(1)	-0.0105 ± 0.0012	0.0178 ± 0.0014	0.0003 ± 0.0006
Ag(2)	0.0113 ± 0.0014	0.0133 ± 0.0010	0.0003 ± 0.0006
S	0.0119 ± 0.0039	0.0145 ± 0.0027	0.0011 ± 0.0016

Table 4. Interatomic distances and angles with their standard deviations in Ag_2SO_3.

Ag(1)—O(2)	$= 2.395 \pm 0.025$	Ag(2)—O(2)	$= 2.234 \pm 0.024$
—O(1)	$= 2.454 \pm 0.025$	—O(3)	$= 2.302 \pm 0.026$
—O(3)	$= 2.455 \pm 0.025$	—O(1)	$= 2.475 \pm 0.022$
—S	$= 2.465 \pm 0.008$	—O(3)	$= 2.502 \pm 0.025$
—O(1)	$= 2.734 \pm 0.024$	—Ag(2)	$= 2.924 \pm 0.005$
—Ag(2)	$= 3.252 \pm 0.003$	—O(1)	$= 3.039 \pm 0.022$
		—S	$= 3.136 \pm 0.007$

S —O(1)	$= 1.504 \pm 0.022$	O(1) —S	$= 1.504 \pm 0.022$
—O(3)	$= 1.512 \pm 0.027$	—O(3)	$= 2.400 \pm 0.034$
—O(2)	$= 1.533 \pm 0.023$	—O(2)	$= 2.438 \pm 0.030$
—Ag(1)	$= 2.465 \pm 0.008$	—2Ag(1)	$= 2.454 \pm 0.025;$
			2.734 ± 0.024
—Ag(2)	$= 3.136 \pm 0.007$	—2Ag(2)	$= 2.475 \pm 0.022;$
			3.039 ± 0.022
		—O(2)	$= 3.297 \pm 0.031$
		—2O(3)	$= 3.086 \pm 0.033$

O(2) —S	$= 1.533 \pm 0.023$	O(3) —S	$= 1.512 \pm 0.027$
—Ag(2)	$= 2.234 \pm 0.024$	—Ag(2)	$= 2.302 \pm 0.026$
—O(3)	$= 2.360 \pm 0.035$	—O(2)	$= 2.360 \pm 0.035$
—Ag(1)	$= 2.395 \pm 0.025$	—O(1)	$= 2.400 \pm 0.034$
—O(1)	$= 2.438 \pm 0.030$	—Ag(1)	$= 2.455 \pm 0.025$
		—Ag(2)	$= 2.502 \pm 0.025$

$$O(1)-S-O(2) = 106.8 \pm 1.2°$$
$$O(1)-S-O(3) = 105.5 \pm 1.4°$$
$$O(2)-S-O(3) = 101.6 \pm 1.4°$$

Table 5. Observed and calculated structure factors of Ag₂SO₃. The reflections marked with an asterisk (*) were rejected in the least-squares refinement.

	h	k	l	$|F_{obs}|$	$|F_{calc}|$
	0	0	-10	-	4
	0	0	-8	94	-97
	0	0	-6	21	-18
	0	0	-4	-	2
	0	0	-2	-	-5
	1	0	-12	55	-49
	1	0	-10	18	12
	1	0	-8	39	-37
	1	0	-6	56	47
*	1	0	-4	209	304
	1	0	-2	31	-31
	1	0	0	16	10
	1	0	2	86	-94
	1	0	4	108	-112
	1	0	6	33	24
	1	0	8	44	-47
	1	0	10	33	29
	2	0	-12	16	-11
	2	0	-10	32	30
	2	0	-8	129	147
	2	0	-6	64	-65
	2	0	-4	-	2
*	2	0	-2	137	-168
	2	0	0	127	-142
	2	0	2	63	57
	2	0	4	70	-71
	2	0	6	70	77
	2	0	8	46	45
	3	0	-12	50	50
	3	0	-10	21	-22
	3	0	-8	23	17
	3	0	-6	162	-168
	3	0	-4	57	-64
	3	0	-2	25	21
	3	0	0	59	-50
	3	0	2	94	102
	3	0	4	30	26
	3	0	6	21	23
	4	0	-12	-	5
	4	0	-10	83	-84
	4	0	-8	30	-23
	4	0	-6	34	28
	4	0	-4	-	-7
	4	0	-2	96	96
	4	0	0	-	1
	4	0	2	23	24
	5	0	-10	-	13
	5	0	-8	31	23
	5	0	-6	67	71
	5	0	-4	20	-19
	5	0	-2	33	36
	5	0	0	16	-13
	0	1	-12	14	17
	0	1	-11	34	30
	0	1	-10	29	36
	0	1	-9	44	46
	0	1	-8	16	-17
	0	1	-7	-	-3
	0	1	-6	91	-95
	0	1	-5	119	135
	0	1	-4	90	-100
*	0	1	-3	142	-158
	0	1	-2	21	-16
	0	1	-1	50	-53
	1	1	-12	-	-2
	1	1	-11	13	11
	1	1	-10	74	-64
	1	1	-9	63	55
	1	1	-8	50	-47
	1	1	-7	124	-127
	1	1	-6	27	-21
	1	1	-5	-	-1
	1	1	-4	-	5
	1	1	-3	77	-93
	1	1	-2	38	32
*	1	1	-1	74	-99
	1	1	0	34	36
*	1	1	1	117	183
*	1	1	2	107	129
	1	1	3	33	-27
	1	1	4	17	-17
	1	1	5	97	106
	1	1	6	59	-58
	1	1	7	31	32
	1	1	8	33	-36
	1	1	9	42	-40
	1	1	10	-	-9
	2	1	-13	10	15
	2	1	-12	28	-22
	2	1	-11	80	-68
	2	1	-10	-	1
	2	1	-9	-	0
	2	1	-8	50	48
	2	1	-7	80	-75

	h	k	l	$|F_{obs}|$	$|F_{calc}|$
	2	1	-6	20	22
	2	1	-5	22	-21
	2	1	-4	52	59
*	2	1	-3	117	140
	2	1	-2	53	58
	2	1	-1	48	-49
	2	1	0	35	-30
*	2	1	1	138	156
	2	1	2	87	-85
	2	1	3	-	2
	2	1	4	74	-72
	2	1	5	63	-57
	2	1	6	14	-13
	2	1	7	-	1
	2	1	8	23	13
	2	1	9	37	-38
	3	1	-10	-	3
	3	1	-12	29	29
	3	1	-11	38	-41
	3	1	-10	45	36
	3	1	-9	20	23
	3	1	-8	22	21
	3	1	-7	67	66
	3	1	-6	47	43
	3	1	-5	31	-27
	3	1	-4	26	-20
*	3	1	-3	117	140
	3	1	-2	74	-68
	3	1	-1	54	-44
	3	1	0	68	-64
	3	1	1	63	-51
	3	1	2	25	-26
	3	1	3	-	-12
	3	1	4	30	33
	3	1	5	52	-55
	3	1	6	12	14
	4	1	-13	23	23
	4	1	-12	-	6
	4	1	-11	25	24
	4	1	-10	-	7
	4	1	-9	-	-2
	4	1	-8	-	-14
	4	1	-7	82	82
	4	1	-6	27	-21
	4	1	-5	58	-54
	4	1	-4	58	-55
	4	1	-3	28	-26
	4	1	-2	-	-1
	4	1	-1	31	-27
	4	1	0	40	42
	4	1	1	50	-54
	4	1	2	33	30
	4	1	3	33	37
	4	1	4	14	12
	5	1	-11	31	33
	5	1	-10	-	15
	5	1	-9	42	39
	5	1	-8	39	-27
	5	1	-7	-	-3
	5	1	-6	-	-6
	5	1	-5	27	-32
	5	1	-4	38	42
	5	1	-3	33	-30
	5	1	-2	32	34
	5	1	-1	35	41
	0	2	-10	28	30
	0	2	-9	-	-3
	0	2	-8	65	-68
	0	2	-7	23	16
	0	2	-6	38	36
	0	2	-5	92	100
	0	2	-4	43	38
	0	2	-3	111	133
	0	2	-2	96	-110
	0	2	-1	19	24
	0	2	0	61	70
	1	2	-12	37	-35
	1	2	-11	17	19
	1	2	-10	32	30
	1	2	-9	56	58
	1	2	-8	30	19
	1	2	-7	72	69
	1	2	-6	51	-42
	1	2	-5	19	-5
	1	2	-4	91	102
	1	2	-3	40	-35
*	1	2	-2	128	-167
*	1	2	-1	120	-200
	1	2	0	94	113
	1	2	1	113	-131
	1	2	2	15	14
	1	2	3	-	-5
	1	2	4	90	-105
	1	2	5	24	24

	h	k	l	$|F_{obs}|$	$|F_{calc}|$
	1	2	6	58	52
	1	2	7	64	64
	1	2	8	35	-33
	1	2	9	33	31
	1	2	10	18	16
	2	2	-13	27	30
	2	2	-12	16	-8
	2	2	-11	28	25
	2	2	-10	19	16
	2	2	-9	-	2
	2	2	-8	40	36
	2	2	-7	38	-31
	2	2	-6	86	-90
*	2	2	-5	133	-150
*	2	2	-4	120	134
	2	2	-3	87	-92
	2	2	-2	20	-16
	2	2	-1	-	7
	2	2	0	41	-42
	2	2	1	61	56
	2	2	2	46	38
	2	2	3	71	80
	2	2	4	48	-52
	2	2	5	33	31
	2	2	6	35	39
	2	2	7	25	20
	2	2	8	13	-9
	3	2	-13	-	-1
	3	2	-12	-	7
	3	2	-11	23	-18
	3	2	-10	51	-48
	3	2	-9	77	-78
	3	2	-8	61	71
	3	2	-7	48	-38
	3	2	-6	30	-15
	3	2	-5	33	32
	3	2	-4	16	-10
	3	2	-3	67	68
	3	2	-2	40	34
	3	2	-1	78	85
	3	2	0	69	-63
	3	2	1	23	19
	3	2	2	72	75
	3	2	3	20	16
	3	2	4	21	-18
	3	2	5	24	-22
	3	2	6	20	-14
	4	2	-13	32	-35
	4	2	-12	32	30
	4	2	-11	-	-10
	4	2	-10	32	-26
	4	2	-9	20	21
	4	2	-8	18	19
	4	2	-7	53	60
	4	2	-6	15	-15
	4	2	-5	57	61
	4	2	-4	48	-44
	4	2	-3	-	8
	4	2	-2	77	78
	4	2	-1	17	11
	4	2	0	36	-31
	4	2	1	35	-33
	4	2	2	-	5
	4	2	3	42	-43
	5	2	-10	36	-21
	5	2	-9	20	30
	5	2	-8	29	-23
	5	2	-7	-	-1
	5	2	-6	41	43
	5	2	-5	-	-1
	5	2	-4	23	-23
	5	2	-3	39	-31
	5	2	-2	-	9
	5	2	-1	35	-34
	0	3	-11	-	6
	0	3	-10	15	12
	0	3	-9	40	-37
	0	3	-8	19	15
	0	3	-7	89	-69
	0	3	-6	66	-64
	0	3	-5	71	71
	0	3	-4	32	-24
	0	3	-3	62	-58
	0	3	-2	101	-115
	0	3	-1	113	101
	1	3	-12	12	-9
	1	3	-11	37	-36
	1	3	-10	29	-28
	1	3	-9	51	49
	1	3	-8	25	-17
	1	3	-7	27	-21
	1	3	-6	72	-68
	1	3	-5	118	135
	1	3	-4	32	31

	h	k	l	$|F_{obs}|$	$|F_{calc}|$
	1	3	-3	40	41
	1	3	-2	88	108
	1	3	-1	77	-69
	1	3	0	91	96
	1	3	1	85	89
	1	3	2	80	73
*	1	3	3	144	-164
	1	3	4	35	-31
	1	3	5	38	-32
	1	3	6	32	-24
	1	3	7	-	-7
	1	3	8	20	-19
	1	3	9	10	-4
	1	3	10	32	-31
	2	3	-13	16	16
	2	3	-12	-	-5
	2	3	-11	-	1
	2	3	-10	39	-38
	2	3	-9	93	96
	2	3	-8	13	12
	2	3	-7	18	-14
	2	3	-6	82	82
	2	3	-5	18	-15
	2	3	-4	65	63
	2	3	-3	52	54
	2	3	-2	86	83
*	2	3	-1	135	-153
	2	3	0	73	-70
	2	3	1	-	0
	2	3	2	28	-22
	2	3	3	37	-30
	2	3	4	19	-18
	2	3	5	22	. 17
	2	3	6	41	-43
	2	3	7	56	60
	3	3	-13	41	42
	3	3	-12	11	12
	3	3	-11	19	-24
	3	3	-10	26	27
	3	3	-9	23	-24
	3	3	-8	49	49
	3	3	-7	-	12
	3	3	-6	33	27
	3	3	-5	91	-99
	3	3	-4	80	-80
	3	3	-3	33	28
	3	3	-2	31	-20
	3	3	-1	44	-38
	3	3	0	37	-32
	3	3	1	48	51
	3	3	2	30	-31
	3	3	3	64	79
	3	3	4	-	10
	3	3	5	28	-23
	3	3	6	17	17
	4	3	-12	26	25
	4	3	-11	-	-13
	4	3	-10	-	9
	4	3	-9	41	-44
	4	3	-8	49	-55
	4	3	-7	24	25
	4	3	-6	23	-24
	4	3	-5	46	-43
	4	3	-4	23	-23
	4	3	-3	64	69
	4	3	-2	29	-26
	4	3	-1	56	59
	4	3	0	18	17
	4	3	1	23	-21
	4	3	2	16	14
	4	3	3	17	16
	5	3	-10	-	-7
	5	3	-9	23	-24
	5	3	-8	26	-18
	5	3	-7	43	49
	5	3	-6	-	1
	5	3	-5	26	27
	5	3	-4	-	12
	5	3	-3	-	-15
	5	3	-2	-	9
	0	4	-11	16	-19
	0	4	-10	54	62
	0	4	-9	20	17
	0	4	-8	18	16
	0	4	-7	-	1
	0	4	-6	68	74
	0	4	-5	30	29
	0	4	-4	18	16
	0	4	-3	28	22
	0	4	-2	146	-165
	0	4	-1	76	-84
	1	4	-11	-	7
	1	4	-10	43	45
	1	4	-9	27	30

Table 5. Continued.

h	k	l	$\|F_{obs}\|$	$\|F_{calc}\|$	h	k	l	$\|F_{obs}\|$	$\|F_{calc}\|$	h	k	l	$\|F_{obs}\|$	$\|F_{calc}\|$	h	k	l	$\|F_{obs}\|$	$\|F_{calc}\|$
1	4	-8	42	-38	3	4	2	28	-20	2	5	-10	-	-14	0	7	5	57	59
1	4	-7	-	4	3	4	3	-	12	2	5	-9	59	70	0	7	6	-	-13
1	4	-6	94	-102	3	4	4	59	-54	2	5	-8	-	10	0	7	7	-	-6
1	4	-5	46	-40	4	4	-12	30	36	2	5	-7	27	26	0	7	8	-	-14
1	4	-4	24	-15	4	4	-11	-	14	2	5	-6	49	-49	1	7	-7	51	-32
1	4	-3	72	74	4	4	-10	-	1	2	5	-5	23	-20	1	7	-6	-	-17
1	4	-2	121	-139	4	4	-9	26	-23	2	5	-4	83	-86	1	7	-5	-	14
1	4	-1	-	-4	4	4	-8	45	54	2	5	-3	-	-7	1	7	-4	-	15
1	4	0	80	73	4	4	-7	28	-23	2	5	-2	39	34	1	7	-3	50	-56
1	4	1	-	2	4	4	-6	32	27	2	5	-1	133	-130	1	7	-2	25	-19
1	4	2	65	69	4	4	-5	32	32	2	5	0	-	-18	1	7	-1	25	-25
1	4	3	18	-8	4	4	-4	61	-76	2	5	1	36	28	1	7	0	109	-102
1	4	4	48	48	4	4	-3	-	-6	2	5	2	37	51	1	7	1	95	91
1	4	5	27	-23	4	4	-2	26	-20	2	5	3	31	-22	1	7	2	-	21
1	4	6	103	96	4	4	-1	-	16	2	5	4	31	35	2	7	-5	-	6
1	4	7	44	35	4	4	0	65	-62	2	5	5	-	-11	2	7	-4	89	-82
1	4	8	42	-31	4	4	1	-	-12	2	5	6	-	0	2	7	-3	68	78
1	4	9	-	-8	5	4	-7	-	1	0	6	0	67	56	2	7	-2	26	29
2	4	-12	32	-30	5	4	-6	-	-13	0	6	1	66	60	2	7	-1	-	-5
2	4	-11	-	0	5	4	-5	19	21	0	6	2	55	-50	2	7	0	31	-31
2	4	-10	55	-56	5	4	-4	55	-53	0	6	3	-	18	2	7	1	44	36
2	4	-9	30	-30	5	4	-3	19	-22	0	6	4	-	12	2	7	2	51	47
2	4	-8	14	-11	5	4	-2	26	28	0	6	5	72	74	2	7	3	-	-14
2	4	-7	44	39	0	5	1	147	-139	0	6	6	23	21	2	7	4	28	31
2	4	-6	83	-88	0	5	2	19	-9	0	6	7	64	67	0	8	0	89	84
2	4	-5	22	-16	0	5	3	58	-59	1	6	-5	42	-37	0	8	1	72	75
2	4	-4	81	90	0	5	4	100	-97	1	6	-4	45	49	0	8	2	-	3
2	4	-3	24	19	0	5	5	32	34	1	6	-3	75	80	0	8	3	-	16
2	4	-2	36	34	0	5	6	-	4	1	6	-2	71	-73	1	8	-7	-	-2
2	4	-1	18	-12	0	5	7	52	-55	1	6	-1	22	-11	1	8	-6	32	29
2	4	0	65	59	0	5	8	-	-10	1	6	0	49	41	1	8	-5	46	-49
2	4	1	39	-33	0	5	9	-	-10	1	6	1	85	86	1	8	-4	67	66
2	4	2	108	117	0	5	10	-	6	1	6	2	-	1	1	8	-3	56	63
2	4	3	66	64	1	5	-11	-	-14	1	6	3	64	64	1	8	-2	-	-14
2	4	4	72	-74	1	5	-10	-	10	1	6	4	34	-30	1	8	-1	-	-19
2	4	5	-	-10	1	5	-9	-	10	1	6	5	68	-69	1	8	0	-	20
2	4	6	21	-16	1	5	-8	55	64	1	6	6	44	44	1	8	1	-	14
2	4	7	-	0	1	5	-7	45	-48	2	6	-6	52	-51	1	8	2	31	-31
3	4	-13	19	-10	1	5	-6	17	-13	2	6	-5	-	-10	1	8	3	-	9
3	4	-12	10	-12	1	5	-5	114	120	2	6	-4	51	49	1	8	4	56	-57
3	4	-11	10	-8	1	5	-4	-	2	2	6	-3	87	79	2	8	-6	-	-19
3	4	-10	24	-26	1	5	-3	77	75	2	6	-2	28	-29	2	8	-5	-	-20
3	4	-9	17	-17	1	5	-2	40	-30	2	6	-1	32	25	2	8	-4	-	19
3	4	-8	72	74	1	5	-1	37	-34	2	6	0	-	-5	2	8	-3	33	35
3	4	-7	22	21	1	5	0	122	-127	2	6	1	76	-75	2	8	-2	47	-44
3	4	-6	-	-4	1	5	1	25	18	2	6	2	47	44	2	8	-1	-	1
3	4	-5	40	-38	1	5	2	31	33	2	6	3	36	-34	2	8	0	45	-44
3	4	-4	82	80	1	5	3	90	-91	2	6	4	18	-25	2	8	1	30	-29
3	4	-3	32	-27	1	5	4	24	-22	2	6	5	54	-56	2	8	2	-	-7
3	4	-2	79	66	1	5	5	-	8	0	7	1	50	-47	0	9	-1	-	-8
3	4	-1	57	52	1	5	6	30	28	0	7	2	-	-7	0	9	1	-	20
3	4	0	84	-89	1	5	7	-	-10	0	7	3	37	-39	0	9	2	63	59
3	4	1	18	-7	2	5	-11	-	-22	0	7	4	96	-95	0	9	3	41	-39

(1.50$_6$ Å and 105.8°, Nyberg and Kierkegaard [2]) and $(NH_4)_2(SO_3 \cdot H_2O$ (1.53 Å and 105.4°, Batelle and Trueblood [9]). Evidently there are no indications of any substantial influence of the presence of the silver or copper atoms on the geometry of the sulphite group.

The coordination around the silver atoms may be described in terms of SO_3Ag- and AgO_4-tetrahedra, which are linked together by sharing of corners so that a three-dimensional network is formed. A schematic drawing showing the structure of Ag_2SO_3 is given in Fig. 2.

The configuration around Ag(1) is a relatively regular oxygen-sulphur (O_3S) tetrahedron. The three oxygens belong to three different sulphite groups, *cf.* Fig. 3. The Ag—S distance is 2.47 Å and the mean Ag—O distance is 2.43 Å which is in good agreement with the values reported for $KAgCO_3$ (Ag—O = 2.42 Å, Donohue *et al.*[10]) which also is colourless. The configuration around Ag(2) is more irregular. The AgO_4 tetrahedron is very distorted, *cf.* Fig. 4, and can alternatively be described as a distorted planar square group. The Ag—O distances vary from 2.23 ± 0.02 Å to 2.50 ± 0.03 Å and the mean Ag—O distance is 2.38 Å.
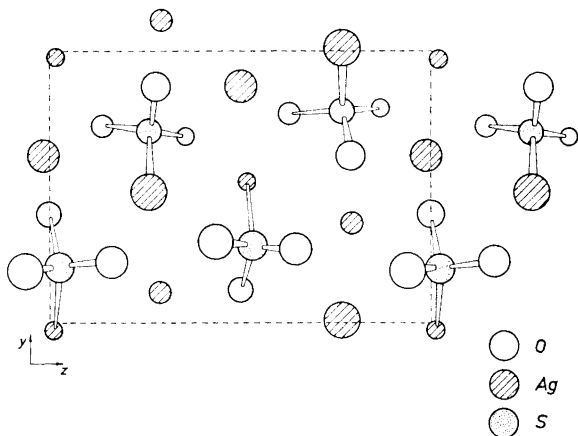
Fig. 2. The structure of Ag_2SO_3. Schematic drawing showing the SO_3Ag tetrahedra, which are linked together by AgO_4 tetrahedra. The AgO_4 tetrahedra are not indicated in the figure.

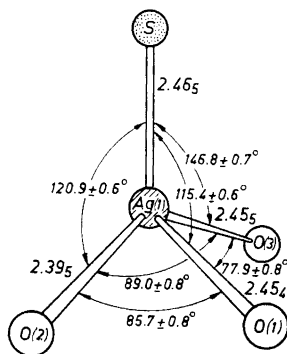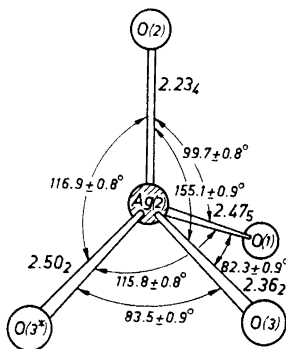Fig. 3. The distorted AgO_3S tetrahedron in Ag_2SO_3.

Fig. 4. The distorted AgO_4 tetrahedron in Ag_2SO_3.

The distance $Ag-S = 2.465 \pm 0.008$ Å shows that a π-bonding between silver and sulphur may exist as the bond length $Ag-S$ is 0.10 Å shorter than the sum of Pauling's covalent radii (2.57 Å).

A further discussion on the configuration of the sulphite group and the structural chemistry of metal sulphites will be given in a forthcoming paper.

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