

of some bond lengths found with the structure determinations (*Structure Reports*, 1962). In naphthazarine the C–O distances, 1.30 to 1.33 Å, are longer than in 5CIN, which can be ascribed to the partial loss of the quinonoid double bonding. Similarly, the bonds C(2)–C(3) (1.38 Å) and C(9)–C(10) (1.46 Å) are lengthened in the naphthazarine molecule as compared with 5CIN.

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## The Crystal Structure of Silver Sodium Sulphite Dihydrate $\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$

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The crystal structure of silver sodium sulphite dihydrate,  $\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$ , has been determined from three-dimensional X-ray diffractometer data. The unit cell is triclinic, space group  $P\bar{1}$ , with the following dimensions:  $a = 5.949$  (5),  $b = 9.277$  (9),  $c = 5.465$  (3) Å,  $\alpha = 101.06$  (8),  $\beta = 90.65$  (6),  $\gamma = 117.29$  (6)°. There are two formula units in the cell. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to an  $R$  value of 0.067 for 727 observed reflexions. The silver atom is nearly linearly coordinated by the sulphur atom and one of the sulphite oxygen atoms; thus results a chain-like structure for  $\text{AgSO}_3^-$ . The Ag–S and Ag–O distances are 2.474 (4) and 2.194 (9) Å respectively. Sodium is octahedrally coordinated by three sulphite oxygen atoms and three oxygen atoms belonging to water molecules; the average Na–O distance is 2.418 Å. The average dimensions of the sulphite ion are: S–O distance 1.522 Å and O–S–O angle 106.3°.

#### Introduction

The crystal structures of  $\text{Na}_2\text{SO}_3$  (Larsson & Kierkegaard, 1969) and  $\text{Ag}_2\text{SO}_3$  (Larsson, 1969) have previously been determined at this Institute as a part of a larger program concerning the structural chemistry of

metal sulphites. A recent report (Kierkegaard, Larsson & Nyberg, 1972) gives a general discussion of the structural aspects of sulphites so far studied by X-ray methods.

The present investigation was undertaken to elucidate the crystal structure of the double sulphite of sodium and silver. The existence of such a phase, with formula  $\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$ , has been reported in the early literature (Svensson, 1869) but later doubts have been ex-

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pressed about its being a single compound and not a mixture (Rosenheim & Steinhäuser, 1900).

### Experimental

Silver sulphite,  $\text{Ag}_2\text{SO}_3$ , is insoluble in water ( $\log K_s = -13.8$ ), but dissolves in a sulphite solution. Measurements of the stability constants (Chateau, Duranté & Hervier, 1956*a, b*) for the system  $\text{Ag}^+ - \text{SO}_3^{2-}$  at 25°C indicate the existence of three ionic complexes

- (i)  $\text{Ag}^+ + \text{SO}_3^{2-} \rightleftharpoons \text{AgSO}_3^-$   $\log K = 5.6$   
 (ii)  $\text{Ag}^+ + 2\text{SO}_3^{2-} \rightleftharpoons \text{Ag}(\text{SO}_3)_2^-$   $\log K = 8.7$   
 (iii)  $\text{Ag}(\text{SO}_3)_2^- + \text{SO}_3^{2-} \rightleftharpoons \text{Ag}(\text{SO}_3)_3^{2-}$   $\log K = 0.3$ .

Crystals suitable for X-ray structure analysis of  $\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$  were precipitated from a saturated solution of freshly prepared silver sulphite dissolved in sodium sulphite solution: upon evaporation under a vacuum thin transparent prisms were obtained. All operations were carried out in a nitrogen atmosphere in order to avoid oxidation, and in darkness since the crystals are sensitive to light. Chemical analysis confirmed the formula  $\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$ . Attempts to prepare crystals of  $\text{AgNa}_3(\text{SO}_3)_2$  have not yet been successful.

Weissenberg photographs were used to determine the triclinic symmetry and the approximate unit-cell dimensions. The accurate unit-cell parameters at 25°C were calculated by a least-squares method from a powder photograph obtained with Guinier-Hägg focusing camera using strictly monochromated  $\text{Cu } K\alpha_1$  radiation ( $\lambda = 1.54050 \text{ \AA}$ ). Potassium chloride ( $a = 6.29228 \text{ \AA}$ ) was used as an internal standard. The powder photograph

was interpreted to  $\sin^2 \theta = 0.35$ . The crystal data are summarized in Table 1.

Single-crystal intensity data were obtained on a Philips PW 1100 computer-controlled four-circle diffractometer. Graphite-monochromated  $\text{Cu } K$  radiation and a scintillation counter with pulse-height discrimination were used. The dimensions of the crystal were  $0.15 \times 0.06 \times 0.01 \text{ mm}$ , and it was mounted along the  $a$  axis. The  $\theta - 2\theta$  scan technique was employed with a scan range of  $1^\circ$ . Three test reflexions were used to check for possible decomposition of the crystal in the X-ray beam. The background intensities were calculated as

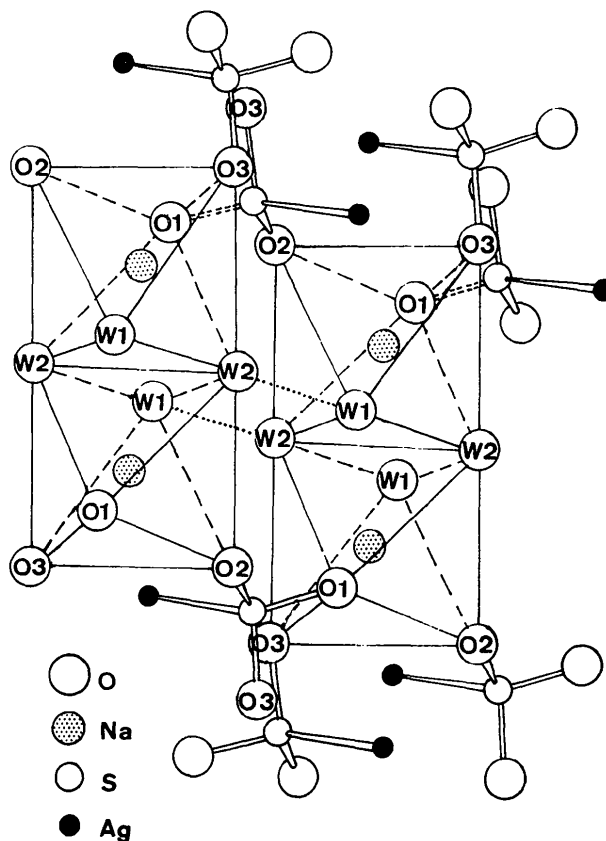


Fig. 1. A view of the structure of  $\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$  showing four  $\text{NaO}_6$  octahedra. Possible hydrogen bonds between the water atoms  $W(1)$  and  $W(2)$  are indicated by dotted lines.

Table 1. Crystal data of silver sodium sulphite dihydrate

Formula	$\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$
Formula weight	262.95
Lattice constants	$a = 5.949 (5) \text{ \AA}$ $b = 9.277 (9)$ $c = 5.465 (3)$ $\alpha = 101.06 (8)^\circ$ $\beta = 90.65 (6)$ $\gamma = 117.29 (6)$
Cell volume	$V = 261.3 \text{ \AA}^3$
Measured density	$D_m = 3.31 \text{ g cm}^{-3}$
Calculated density	$D_x = 3.34 \text{ g cm}^{-3}$
Molecules per unit cell	$Z = 2$
Space group	$P\bar{1}$

Table 2. Final atomic parameters and their estimated standard deviations ( $\times 10^4$ )

The anisotropic temperature factors are of the form:  $\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ag	2709 (2)	252 (1)	1898 (2)	191 (6)	79 (2)	179 (5)	52 (2)	23 (3)	18 (2)
S	6590 (6)	8709 (4)	3495 (6)	64 (13)	34 (5)	163 (13)	23 (6)	-6 (9)	5 (6)
Na	-40 (10)	3009 (6)	4974 (10)	122 (20)	50 (8)	232 (22)	38 (10)	7 (17)	19 (10)
O(1)	3828 (19)	7564 (12)	2474 (21)	90 (37)	66 (15)	269 (42)	-6 (19)	-2 (31)	-7 (20)
O(2)	8131 (19)	7847 (12)	2524 (20)	162 (41)	65 (15)	266 (41)	77 (21)	-17 (32)	-16 (19)
O(3)	7470 (19)	190 (10)	2207 (17)	242 (44)	19 (13)	166 (36)	16 (20)	22 (32)	10 (17)
W(1)	2865 (21)	4065 (12)	2286 (20)	219 (44)	58 (15)	266 (41)	50 (22)	49 (35)	13 (20)
W(2)	7647 (22)	4154 (12)	2621 (21)	238 (47)	62 (15)	279 (44)	40 (22)	-43 (35)	5 (20)

averages of the intensities at each end of the scan interval. All 827 reflexions with  $\theta < 60^\circ$  were recorded, and of these 727 with  $\sigma(I_{\text{net}})/I_{\text{net}} < 0.25$  were accepted for further calculations. The net intensities were corrected for Lorentz and polarization factors and for absorption ( $\mu = 357.3 \text{ cm}^{-1}$ ). All calculations were performed on the IBM 360/75 and IBM 1800 computers (cf. Table 5).

### Structure determination and refinement

The structure was solved by the heavy-atom method. A three-dimensional Patterson function revealed the position of the silver atom in a straightforward way, assuming the centrosymmetric space group  $P\bar{1}$ . The coordinates of the silver atom were used to phase a three-dimensional electron density function in which all non-hydrogen atoms were easily recognized. The atomic positions were refined by a full-matrix least-squares program using anisotropic thermal parameters. In the refinement the weighting scheme of Hughes (1941) with  $|F_{o, \text{min}}| = 5.6$  and  $h = 4.0$  was used. The shifts in the parameters in the last cycle were all less than 0.1 of their estimated standard deviations. The scattering factors for O, Na<sup>+</sup>, S and Ag<sup>+</sup> were those given by McMaster, Kerr Del Grande, Mallet & Hubbell (1969). The refinement gave a final  $R$  value ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ) of 0.067. A difference Fourier synthesis calculated after the full-matrix refinement showed no residual density above  $0.25 \text{ e}\text{\AA}^{-3}$  and no distinct hydrogen positions.

The positional and thermal parameters, with estimated standard deviations, are given in Table 2. The observed and calculated structure factors are listed in Table 3.

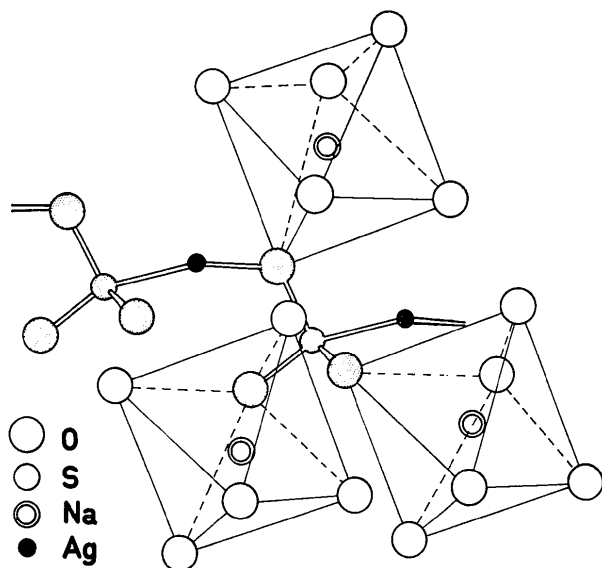


Fig. 2. A view of the structure showing a part of the  $\text{AgSO}_3$  chain (shaded atoms) and the three  $\text{NaO}_6$  octahedra linked together by one sulphite group.

Table 3. Structure factors. Each group of three columns contains  $k$ ,  $10|F_o|$  and  $10|F_c|$ , and is headed by the values of  $h$  and  $l$  common to the group

$h$	$l$	$k$	$10 F_o $	$10 F_c $
0	0	0	100	100
0	0	1	100	100
0	0	2	100	100
0	0	3	100	100
0	0	4	100	100
0	0	5	100	100
0	0	6	100	100
0	0	7	100	100
0	0	8	100	100
0	0	9	100	100
0	0	10	100	100
0	0	11	100	100
0	0	12	100	100
0	0	13	100	100
0	0	14	100	100
0	0	15	100	100
0	0	16	100	100
0	0	17	100	100
0	0	18	100	100
0	0	19	100	100
0	0	20	100	100
0	0	21	100	100
0	0	22	100	100
0	0	23	100	100
0	0	24	100	100
0	0	25	100	100
0	0	26	100	100
0	0	27	100	100
0	0	28	100	100
0	0	29	100	100
0	0	30	100	100
0	0	31	100	100
0	0	32	100	100
0	0	33	100	100
0	0	34	100	100
0	0	35	100	100
0	0	36	100	100
0	0	37	100	100
0	0	38	100	100
0	0	39	100	100
0	0	40	100	100
0	0	41	100	100
0	0	42	100	100
0	0	43	100	100
0	0	44	100	100
0	0	45	100	100
0	0	46	100	100
0	0	47	100	100
0	0	48	100	100
0	0	49	100	100
0	0	50	100	100
0	0	51	100	100
0	0	52	100	100
0	0	53	100	100
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0	0	56	100	100
0	0	57	100	100
0	0	58	100	100
0	0	59	100	100
0	0	60	100	100
0	0	61	100	100
0	0	62	100	100
0	0	63	100	100
0	0	64	100	100
0	0	65	100	100
0	0	66	100	100
0	0	67	100	100
0	0	68	100	100
0	0	69	100	100
0	0	70	100	100
0	0	71	100	100
0	0	72	100	100
0	0	73	100	100
0	0	74	100	100
0	0	75	100	100
0	0	76	100	100
0	0	77	100	100
0	0	78	100	100
0	0	79	100	100
0	0	80	100	100
0	0	81	100	100
0	0	82	100	100
0	0	83	100	100
0	0	84	100	100
0	0	85	100	100
0	0	86	100	100
0	0	87	100	100
0	0	88	100	100
0	0	89	100	100
0	0	90	100	100
0	0	91	100	100
0	0	92	100	100
0	0	93	100	100
0	0	94	100	100
0	0	95	100	100
0	0	96	100	100
0	0	97	100	100
0	0	98	100	100
0	0	99	100	100
0	0	100	100	100

### Description and discussion of the structure

A schematic drawing of the structure of  $\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$  is shown in Fig. 1. The interatomic distances and angles are listed in Table 4.

The silver atom is almost linearly coordinated by the sulphur atom and one of the sulphite oxygen atoms. The S—Ag—O angle is  $169.5^\circ$  and the Ag—S and Ag—O

Table 4. Interatomic distances and angles with their estimated standard deviations (uncorrected for thermal motion)

Ag—O(3)	2.194 (9) Å	O(1)—O(3)	2.441 (14) Å
Ag—S	2.474 (4)	O(1)—O(2)	2.450 (14)
Ag—O(2)	2.694 (10)	O(1)—W(2)	2.832 (16)
Ag—O(3)	2.863 (11)	O(1)—W(1)	3.006 (14)
Ag—O(1)	2.929 (10)		
Ag—O(3)	3.098 (11)	O(2)—O(3)	2.416 (13)
Ag—S	3.246 (4)	O(2)—W(1)	2.760 (15)
S—O(2)	1.510 (10)	W(1)—W(2)	2.811 (16)
S—O(1)	1.514 (11)	W(1)—W(2)	3.047 (15)
S—O(3)	1.542 (9)	W(1)—W(2)	3.150 (16)
Na—O(2)	2.384 (11)	O(1)—S—O(2)	108.2 (6)°
Na—O(1)	2.395 (12)	O(1)—S—O(3)	106.0 (6)
Na—W(1)	2.398 (12)	O(2)—S—O(3)	104.6 (6)
Na—W(1)	2.401 (12)	S—Ag—O(3)	169.5 (2)
Na—W(2)	2.451 (12)		
Na—O(3)	2.476 (10)		

Table 5. *Computer programs used for the crystallographic calculations*

Program name and function	Authors
<i>PIRUM</i> : Indexing of powder photographs and least-squares refinement of unit cell parameters.	Werner, P.-E.
<i>DATAP2</i> : Lp and absorption corrections. Preparative calculations for extinction correction.	Coppens, P., Leiserowitz, L. & Rabinovich, D. Modified by Olofsson, O., Elfström, M., Brandt, B., Åsbrink, S. & Nord, A.
<i>DRF</i> : Fourier summations and structure factor calculations.	Zalkin, A. Modified by Liminga, R., Lundgren, J.-O., Lindgren, O., Brandt, B. & Nord, A.
<i>LALS</i> : Full-matrix least-squares refinement of positional and thermal parameters and of scale factors.	Gantzel, P. K., Sparks, R. A. & Trueblood, K. N. Modified by Zalkin, A., Lundgren, J.-O., Liminga, R., Brändén C.-I., Lindgren, O., Brandt, B. & Nord, A.
<i>DISTAN</i> : Calculation of interatomic distances and bond angles with estimated standard deviations.	Zalkin, A. Modified by Nord, A. & Brandt, B.
<i>ORTEP</i> : Crystal structure illustrations.	Johnson, C. K. Modified by Carlbom, I.

distances are 2.474 and 2.194 Å respectively. The sodium atom is octahedrally coordinated by oxygen atoms, three of them belonging to water molecules and three to sulphite groups. The Na–O distances range from 2.384 to 2.476 Å and agree with the value 2.45 Å for the sum of ionic radii. Two  $\text{NaO}_6$  octahedra are linked together by sharing of one edge [oxygen atom  $W(2)$  at  $(x, y, z)$  and  $(-x, -y, -z)$ ]. The two octahedra are linked to other double octahedra by sulphite groups and, due to short contacts between water molecules and sulphite oxygen atoms, possibly by hydrogen bonds. A possible hydrogen bond scheme for the water molecules is indicated in Fig. 1.

The Ag–S distance of  $2.474 \pm 0.004$  Å found in the structure may be compared with that of 2.465 Å in  $\text{Ag}_2\text{SO}_3$  (Larsson, 1969) and with 2.43 Å, the sum of Pauling's (1960) covalent radii (Ag = 1.39, S = 1.04 Å). The Ag–O distance of  $2.194 \pm 0.009$  Å is closer to the sum of covalent radii, 2.05 Å (O = 0.66 Å), than to 2.66 Å, the sum of ionic radii of  $\text{Ag}^+$  (1.26 Å) and  $\text{O}^{2-}$  (1.40 Å).

According to Pauling, silver may form two covalent bonds of the *sp* type with oxygen atoms.  $\text{AgFeO}_2$  (Okamoto, Okamoto & Ito, 1972) and  $\text{KAgCO}_3$  (Barclay & Hoskins, 1963) represent structures with linear or almost linear O–Ag–O coordination, and the corresponding Ag–O distances are 2.07 and 2.09 Å respectively. The  $\text{AgSO}_3^-$  complex forms infinite chains in the structure (*cf.* Fig. 2), and it may be concluded that the Ag–S and Ag–O interactions in  $\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$  are of predominantly covalent character.

The dimensions of the sulphite group are given in Table 4. The sulphite group is rather regular with an average S–O distance of 1.522 Å and an O–S–O angle of  $106.3^\circ$ . In  $\text{Ag}_2\text{SO}_3$  (Larsson, 1969),  $(\text{NH}_4)_6[\text{Fe}(\text{SO}_3)_6]$  (Larsson & Niinistö, 1972) and  $\text{NH}_4\text{CuSO}_3$  (Nyberg & Kierkegaard, 1968) the corresponding S–O distances are 1.516, 1.517, and 1.514 Å, respectively; and the O–S–O angles are 104.6, 104.5 and  $105.3^\circ$ .

According to Cruickshank (1961) two strong  $\pi$  bonding orbitals are formed with *3d* orbitals of sulphur and *2p* orbitals of oxygen when the lone or 'fourth' electron pair of sulphur is engaged in bonding to a metal or a non-metal anion. The  $\pi$  bonds will make the interatomic distances shorter than in the free anion. In

$\text{AgNaSO}_3 \cdot 2\text{H}_2\text{O}$  as well in  $\text{Ag}_2\text{SO}_3$  the effect is counteracted by the interaction of ligands close to the sulphite oxygen atoms, resulting in slightly longer S–O bond distances than found in  $\text{Na}_2\text{SO}_3$ , in which the S–O distance is 1.504 Å (Larsson & Kierkegaard, 1969).

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