

SHORT STRUCTURAL PAPERS

Papers intended for publication under this heading must be in the format prescribed in Notes for Authors, *Acta Cryst.* (1973). B29, 154.

Acta Cryst. (1975). B31, 893

The Crystal Structure of $[(\text{CH}_3)_2\text{S}]_2\text{N}^+\text{Br}^- \cdot \text{H}_2\text{O}$

BY ALISON M. GRIFFIN AND GEORGE M. SHELDRIK

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(Received 26 August 1974; accepted 11 September 1974)

Abstract. $[(\text{CH}_3)_2\text{S}]_2\text{N}^+\text{Br}^- \cdot \text{H}_2\text{O}$, monoclinic, $P2_1/n$, $a=8.12$ (2), $b=8.27$ (3), $c=15.31$ (4) Å, $\beta=102.7$ (1)°, $U=1004$ Å³, $Z=4$, $D_x=1.56$ g cm⁻³ at -70°C . The cation possesses a bent S–N–S unit and approximately tetrahedral angles at sulphur, with average bond lengths and angles: S–N, 1.64 (4), S–C, 1.80 (5) Å, S–N–S, 110.8 (20), N–S–C, 102.9 (21), C–S–C, 99.1 (30)°. The structure was refined to R 0.085 for 349 unique observed reflexions measured at about -70°C with an automated two-circle diffractometer.

Introduction. This structure has been determined by single-crystal X-ray diffraction as part of a study of multiple bonding in sulphur–nitrogen compounds. The salt is formed in an unusual reaction between one molecule of cyanogen bromide and two molecules of dimethyl sulphoxide, one molecule of carbon dioxide being eliminated (Blanc, 1965). We experienced considerable difficulty in growing single crystals; it appears that solvent molecules are readily incorporated in the lattice, and when these solvent molecules are eliminated the external appearance of the crystal is retained, but the diffraction pattern corresponds to that of a powder. Eventually we were successful in growing suitable thin needle-shaped plates from nitrobenzene (which may have been slightly damp); the crystal structure determination revealed the presence of a water molecule, which may have stabilized the lattice by hydrogen bonding. The analysis figures for C, H and Br were also consistent with the monohydrate formula. The data were collected at low temperature because we believed the crystals to be unstable.

Intensities were determined with a computer-controlled two-circle Stoe Stadi-2 diffractometer and Stoe low-temperature attachment at $-70 \pm 5^\circ\text{C}$. The data were of relatively poor quality because the crystal was extremely thin, and because of practical difficulties in low-temperature operation. 1027 reflexions with intensities greater than 3σ (based on counting statistics) were measured for layers $h0l$ to $h8l$ from a crystal mounted about the y (needle) axis in a Lindemann glass capillary tube, with Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) and a graphite crystal monochromator. Averaging of equivalent reflexions led to 349 unique observed reflexions; no corrections for absorption were applied.

The cell dimensions were obtained from diffractometer measurements at -70°C ; a slightly larger cell was obtained by a least-squares analysis of $\sin^2 \theta$ values from a room-temperature Guinier powder photograph [$a=8.16$ (1), $b=8.30$ (1), $c=15.45$ (2) Å, $\beta=102.7^\circ$].

The bromine and sulphur coordinates were found from a Patterson synthesis, and the remaining atoms located by difference syntheses; hydrogen atoms were not located. Interlayer scale factors were refined, but no significant improvement was obtained by introducing an isotropic secondary extinction parameter, so it was omitted in the final refinement. Complex neutral-atom scattering factors were employed (Cromer, 1965; Cromer & Waber, 1965). The weighting scheme was $w = \sum [\sigma^2(N) + 0.001N^2]^{-1} / [36.78 + |F_o| + 0.00935 F_o^2]$, where N is the net peak count, and the summation is over equivalent reflexions. Final atomic coordinates, interatomic distances and angles are presented in Tables 1–3.* The final weighted residual $R' = \sum w^{1/2} \Delta / \sum w^{1/2} F_o$ was 0.084, with a corresponding unweighted R of 0.085.

Discussion. The structure is quite loosely packed, with the cations arranged in chains along x . The water

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30657 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates ($\times 10^4$) and isotropic temperature factors (Å² $\times 10^3$)

	x/a	y/b	z/c	U
Br	601 (6)	4641 (7)	2868 (3)	†
S(1)	6243 (12)	5286 (17)	1637 (6)	13 (3)
S(2)	8110 (13)	7750 (15)	1235 (7)	13 (3)
N(1)	6747 (37)	6326 (44)	832 (19)	16 (10)
C(1)	3950 (54)	5271 (71)	1334 (30)	38 (13)
C(2)	6510 (47)	3270 (54)	1282 (25)	10 (10)
C(3)	9997 (51)	7197 (58)	797 (27)	25 (12)
C(4)	7366 (56)	9472 (66)	600 (29)	32 (12)
O	834 (37)	1686 (40)	1419 (19)	35 (8)

† Anisotropic, with U_{11} 26 (3), U_{22} 20 (fixed), U_{33} 15 (2), U_{23} 10 (3), U_{13} 6 (2), and U_{12} 6 (4) Å² $\times 10^3$, where the exponential term takes the form: $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)$.

Table 2. Bond lengths (Å) and angles (°)

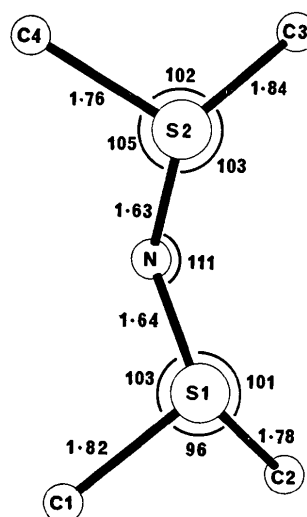
S(1)-N	1.63 (4)	N—S(1)-C(1)	103.0 (2.2)
S(2)-N	1.64 (4)	N—S(1)-C(2)	101.3 (2.0)
Mean	1.64	N—S(2)-C(3)	103.0 (2.0)
S(1)-C(1)	1.82 (5)	N—S(2)-C(4)	104.6 (2.1)
S(1)-C(2)	1.78 (5)	Mean	102.9
S(2)-C(3)	1.84 (5)	C(1)-S(1)-C(2)	95.9 (2.4)
S(2)-C(4)	1.76 (6)	C(3)-S(2)-C(4)	102.2 (2.3)
Mean	1.80	Mean	99.1
S(1)-N-S(2)	110.8 (2.0)		

Table 3. Non-bonded distances (Å) less than 3.9 Å

Symmetry code superscript: None x, y, z ; (i) $1+x, y, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $1+x, 1+y, z$; (v) $1-x, 1-y, -z$; (vi) $x, 1+y, z$; (vii) $1\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $1\frac{1}{2}-x, y-\frac{1}{2}, -z$.

Br ⁱ ...S(1)	3.67	O ^{iv} ...C(4)	3.36
Br ⁱ ...S(2)	3.84	O ^v ...C(3)	3.44
Br...O	3.34	O ⁱ ...C(2)	3.71
Br ⁱⁱ ...C(1)	3.81	O ^{iv} ...C(3)	3.86
Br ⁱ ...C(2)	3.83	O ^v ...C(4)	3.82
Br ⁱⁱⁱ ...C(2)	3.83	O ⁱⁱ ...C(1)	3.60
Br ⁱ ...C(3)	3.75		
Br ⁱⁱⁱ ...C(4)	3.72		
Within cation			
S(1)...S(2)	2.69	N...C(4)	2.69
N...C(1)	2.70	C(1)...C(2)	2.67
N...C(2)	2.64	C(3)...S(1)	3.88
N...C(3)	2.73	C(3)...C(4)	2.80
Between cations			
C(2 ^{vi})...C(4)	3.43	N ^v ...C(1)	3.50
S(1 ⁱⁱⁱ)...S(2)	3.81	N ^v ...C(2)	3.72
S(2 ^{viii})...C(2)	3.77	C(1 ⁱ)...C(3)	3.54

molecules lie in holes in the structure; they may be hydrogen bonded to the bromide ions (O...Br 3.34 Å) but not to the cations. The cation possesses a bent S-N-S unit (mean S-N, 1.64 Å; S-N-S, 110.8°) with approximately tetrahedral angles at sulphur (Fig. 1). The S-N bond length and small S-N-S angle indicate an S-N bond order not much greater than unity; compare [Cl-S-N-S-Cl]⁺, S-N 1.535 Å, S-N-S 149.2° (Glemser, Krebs, Wegener & Kindler, 1969); Me₂S=N-SO₂Me, 'S=N', 1.63 'S-N', 1.58 Å, S-N-S, 116° (Kálmán, 1967); S₄N₄, S-N, 1.616 Å, S-N-S, 112.8° (Sharma & Donohue, 1963); and S₄N₄H₄, S-N, 1.65 Å, S-N-S, 129.2° (Sabine & Cox, 1967). However even in S₄N₄H₄ the S₂NH units are planar, suggesting some delocalization of the nitrogen lone pair into the N-S bonds. The structure of the cation may be represented: Me₂S=N-S⁺Me₂ ↔ Me₂S⁺-N⁻-S⁺Me₂ ↔ Me₂S⁺-N=SMe₂ ↔ Me₂S=N⁺=SMe₂ with the major contribution from the second structure, which has two

Fig. 1. The [Me₂SNSMe₂]⁺ cation, showing bond lengths and angles.

lone pairs on nitrogen and one on each sulphur atom. The S-C bonds are significantly longer than in Me₂S=N-SO₂Me [S(IV)-C 1.74 Å], probably because the considerable thermal motion of the two S(IV) methyl groups in the latter compound causes a librational shortening of the apparent S-C bond length. One advantage of the use of low-temperature data for [Me₂SNSMe₂]⁺Br⁻·H₂O is that atomic thermal motion has been reduced.

We are grateful to the Science Research Council for providing the diffractometer, and for a maintenance grant to A.M.G. The calculations were carried out on the Cambridge University IBM 370/165 computer with programs written by G.M.S.

References

- BLANC, P. Y. (1965). *Experimentia*, **21**, 308-310.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17-23.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104-109.
 GLEMSER, O., KREBS, B., WEGENER, J. & KINDLER, E. (1969). *Angew. Chem. Int. Ed.* **8**, 598.
 KÁLMÁN, A. (1967). *Acta Cryst.* **22**, 501-507.
 SABINE, T. M. & COX, G. W. (1967). *Acta Cryst.* **23**, 574-577.
 SHARMA, B. D. & DONOHUE, J. (1963). *Acta Cryst.* **16**, 891-897.