

## Structure of $N^1, N^1, N^3, N^3$ -Tetramethyl- $\alpha, \alpha^1$ -diselenobisformamidinium Bromide

BY H. M. K. K. PATHIRANA, J. H. REIBENSPIES, E. A. MEYERS\* AND R. A. ZINGARO  
 Department of Chemistry, Texas A & M University, College Station, TX 77843, USA

(Received 14 May 1990; accepted 31 August 1990)

**Abstract.**  $C_6H_{16}N_4Se_2^{2+} \cdot 2Br^-$ ,  $M_r = 461.94$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.081$  (1),  $b = 12.970$  (4),  $c = 17.716$  (6) Å,  $V = 1397.3$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.196$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 10.41$  mm<sup>-1</sup>,  $F(000) = 872$ ,  $T = 186$  K,  $R = 0.065$  for 1451 reflections and 127 parameters. The structure consists of ions,  $Br^-$  and  $[(CH_3)_2NC(NH_2)Se]_2^{2+}$ . The latter ion is produced from  $N,N$ -dimethylselenourea (DMSeU) by coupling planar DMSeU moieties through a single Se—Se bond, 2.384 (3) Å. The average bond distances within the DMSeU units are Se—C = 1.91 (2), H<sub>2</sub>N—C = 1.34 (3), (CH<sub>3</sub>)<sub>2</sub>N—C = 1.31 (2) and H<sub>3</sub>C—N = 1.47 (1) Å. The angle between DMSeU planes is 31.5°. There are close contacts between Br and H atoms of the NH<sub>2</sub> groups which range from 2.50 to 2.56 Å, with N—H...Br angles which range from 153 to 173°. In addition, there is a short contact, Br(1)...Se(2) = 3.057 (3) Å with Br(1)...Se(2)—Se(1) = 168.8 (1)°, indicative of a nearly linear unsymmetrical three-center bond.

**Experimental.** A solution of 1 mmol TeBr<sub>4</sub> in 3 ml anhydrous ethanol was placed in a small vial which was then carefully placed in a larger vial containing a solution of 1 mmol  $N,N$ -dimethylselenourea in 6 ml anhydrous acetonitrile. Acetonitrile was added to the outer vial until the solutions in the two vials came into contact. The larger vial was sealed and protected from light. Red crystals of  $2(DMSeU)_2TeBr_2 \cdot TeBr_4 \cdot C_2H_5OH \cdot 3CH_3CN$ , orange crystals of  $(DMSeU)_4TeBr_2$  and yellow crystals of the title compound  $(DMSeU)_2Br_2$ , grew and were harvested after three days. The crystals were washed with acetonitrile and ethanol and dried *in vacuo* over CaSO<sub>4</sub>. A yellow crystal of dimensions 0.10 × 0.15 × 0.22 mm was attached with Dow stopcock grease to a glass fiber, mounted on a Nicolet (now Siemens) R3m/V diffractometer and cooled to  $T = 186$  K with a stream of N<sub>2</sub> gas. Unit-cell dimensions were obtained from measurements of  $2\theta$  for 25 reflections ( $16.30 \leq 2\theta \leq 27.92^\circ$ ), using graphite-monochromatized Mo  $K\alpha$  radiation. Intensities were measured for reflections in the range  $4.0 \leq 2\theta \leq 40^\circ$ ,  $-7 \leq h \leq 1$ ,  $-2 \leq k \leq 15$ ,  $-21 \leq l \leq 2$ , with  $\theta-2\theta$  scans, variable

scan speed, 1.50 to 15.0° min<sup>-1</sup> in  $\theta$ , a scan range of  $\Delta\theta = 1.20^\circ$  plus  $K\alpha$  separation and with backgrounds obtained with a stationary crystal, stationary counter at the beginning and end of the scan, each for 25% of the total scan time. Since the crystal quality was only fair, a learnt profile was applied to the intensity data. The intensities of three standard reflections which were measured every 97 reflections remained nearly unchanged throughout the data collection.

Intensities of 1757 reflections were measured, of which 1565 were independent, 1451 had  $I > 0.5\sigma(I)$  and  $R_{int} = 0.047$ . Lorentz and polarization corrections were applied and a face-indexed numerical absorption correction was made:  $T_{max} = 0.8992$ ,  $T_{min} = 0.8542$ . The structure was solved by direct methods. Least-squares refinements were carried out on the coordinates and anisotropic temperature factors of all non-H atoms with the H atoms of the NH<sub>2</sub> groups placed in idealized positions. The atom C(1), attached to Se(1), behaved badly. Its temperature factor was large and highly anisotropic. Examination of  $F_o$  and  $F_c$  indicated that the difficulty was probably due to some problems with the data at low values of  $\sin\theta$ . Attempts were made to improve the the absorption correction, the Patterson function was examined in detail, a number of difference syntheses were calculated, and parameters for both enantiomers were refined, all to no avail. Finally, improvement was made when the weights were changed to reduce the importance of reflections at low values of  $\sin\theta$ . Difference electron density maps were calculated and eight of 12 H atoms in CH<sub>3</sub> groups were identified and used to obtain idealized positions for all methyl H atoms which were then held fixed in further refinements. Final refinements (carried out until the change in any parameter was less than 0.01 of its  $\sigma$ ) of the scale factor, coordinates and temperature factors of all non-H atoms gave  $R = 0.065$ ,  $wR = 0.066$ , 1451 reflections with  $I > 0.5\sigma(I)$ , 127 parameters, goodness-of-fit = 1.18, quantity minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $w = [1 - \exp(-5)(\sin\theta/\lambda)^2] / [\sigma^2(F) + 0.0005F^2]$  with  $\sigma^2(F)$  estimated from  $\sigma(I)$ . For all 1565 independent data,  $R = 0.070$ ,  $wR = 0.066$ , and the residuals on the final difference map varied from 1.36 to  $-1.20 e \text{ \AA}^{-3}$ . Calculations were

\* To whom inquiries should be directed.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Se(1)	-647 (3)	1501 (2)	1286 (1)	47 (1)
Se(2)	1925 (3)	2056 (1)	2218 (1)	44 (1)
Br(1)	5289 (3)	2319 (1)	3485 (1)	49 (1)
Br(2)	7611 (3)	1017 (1)	9353 (1)	47 (1)
C(1)	1471 (29)	775 (15)	720 (12)	49 (6)
N(1)	3053 (23)	1358 (12)	369 (10)	52 (5)
N(2)	1386 (23)	-215 (11)	571 (10)	48 (5)
C(2)	-409 (35)	-871 (15)	871 (15)	63 (7)
C(3)	2830 (39)	-741 (14)	21 (12)	57 (6)
C(4)	1475 (24)	808 (14)	2790 (11)	42 (5)
N(3)	-236 (23)	811 (11)	3238 (9)	47 (5)
N(4)	2783 (23)	8 (10)	2703 (10)	46 (5)
C(5)	2389 (28)	-939 (13)	3135 (10)	45 (5)
C(6)	4830 (31)	83 (17)	2278 (12)	59 (6)

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

Se(1)—Se(2)	2.384 (03)	Se(1)—C(1)	1.885 (19)
Se(2)—C(4)	1.929 (18)	C(1)—N(1)	1.373 (24)
C(1)—N(2)	1.311 (24)	N(2)—C(2)	1.482 (26)
N(2)—C(3)	1.479 (27)	C(4)—N(3)	1.309 (22)
C(4)—N(4)	1.316 (22)	N(4)—C(5)	1.467 (23)
N(4)—C(6)	1.458 (24)		
Se(2)—Se(1)—C(1)	94.1 (06)	Se(1)—Se(2)—C(4)	91.0 (05)
Se(1)—C(1)—N(1)	116.4 (13)	Se(1)—C(1)—N(2)	124.7 (14)
N(1)—C(1)—N(2)	118.5 (17)	C(1)—N(2)—C(2)	121.3 (16)
C(1)—N(2)—C(3)	124.1 (16)	C(2)—N(2)—C(3)	114.1 (15)
Se(2)—C(4)—N(3)	115.4 (13)	Se(2)—C(4)—N(4)	120.9 (13)
N(3)—C(4)—N(4)	123.6 (17)	C(4)—N(4)—C(5)	120.0 (15)
C(4)—N(4)—C(6)	121.6 (15)	C(5)—N(4)—C(6)	117.7 (14)

made with *SHELXTL-Plus* (Sheldrick, 1987). Scattering factors,  $f$  and  $f'$  were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).\* The refined coordinates and equivalent isotropic temperature factors for the structure are listed in Table 1, bond distances and bond angles are pre-

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53535 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

*Acta Cryst.* (1991). **C47**, 904–906

## Structure of (*E,E*)-Bis(2-acetoxy-1-iodo-2-phenylvinyl) Disulfide

BY ANETTE FROST JENSEN AND RITA GRØNBÆK HAZELL

Department of Inorganic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

(Received 5 June 1990; accepted 19 September 1990)

**Abstract.**  $C_{20}H_{16}I_2O_4S_2$ ,  $M_r = 638.3$ , triclinic,  $P\bar{1}$ ,  $a = 14.3123$  (11),  $b = 7.5965$  (6),  $c = 11.5344$  (9) Å,  $\alpha = 109.289$  (5),  $\beta = 97.592$  (5),  $\gamma = 92.150$  (5)°,  $V =$

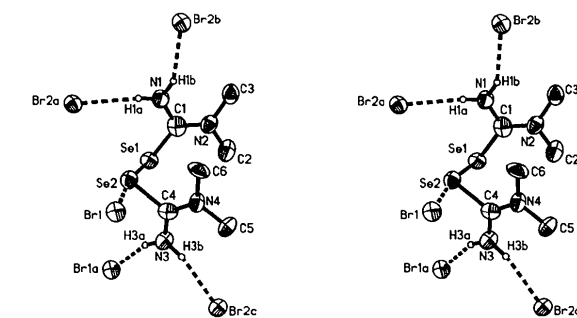


Fig. 1. Stereoview of  $(DMSeU)_2$  with Br atoms which make close contacts with H or Se atoms included (methyl H atoms deleted; thermal ellipsoids at 0.50 probability).

sented in Table 2 and Fig. 1 presents a stereoview of the ions present in the structure.

**Related literature.** Husebye (1983, 1988) has thoroughly reviewed the structures of many selenium-containing complexes, and in particular has discussed the variation of bond distances with ligand configuration including possible three-center bond formation. The structure of a closely related compound,  $(SU)_2Cl_2$  with SU = selenourea (Villa, Nardelli & Tani, 1970), has been reported in which short halogen to selenium contacts have been observed in a nearly linear  $Cl \cdots Se—Se$  configuration.

The authors wish to express their appreciation to the Robert A. Welch Foundation of Houston, Texas, USA, for its financial assistance in support of this investigation.

### References

- HUSEBYE, S. (1983). *Proc. Fourth Int. Conf. Selenium and Tellurium*, edited by F. J. BERRY & W. R. MCWHINNIE, pp. 298–378. Univ. of Aston, Birmingham, England.
- HUSEBYE, S. (1988). *Phosphorus Sulfur*, **38**, 271–280.
- SHELDRICK, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
- VILLA, A. C., NARDELLI, M. & TANI, M. E. V. (1970). *Acta Cryst.* **B26**, 1504–1510.