

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: HA1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Ethylamino-3-*p*-tolyl-1 λ^4 ,2,4-thia-selenazol-1-ylum Bromide: a New Heteroaromatic System

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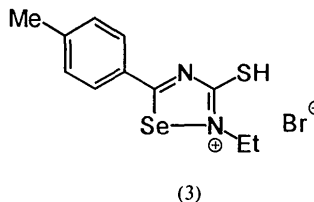
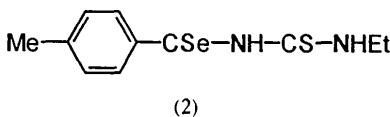
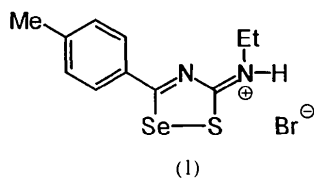
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Abstract

In the title compound, C₁₁H₁₃N₂SSe⁺.Br⁻, the Se—S bond length is 2.189 (2) Å and the C(2)—Se and C(1)—S bond lengths are 1.890 (3) and 1.765 (3) Å, respectively. The C(2)—Se—S and C(1)—S—Se bond angles are 89.36 (10) and 93.36 (11)°, respectively. In the planar heterocyclic ring, π -electron delocalization extends over the exocyclic N(2) atom.

Comment

The structure determination of the title compound, (1), obtained by intramolecular oxidative coupling of compound (2) with bromine (Lai, 1992), was undertaken in order to confirm that Se—S coupling had indeed occurred in (2), rather than Se—N coupling which would lead to the isomeric salt (3).



The cation in (1) is a derivative of the 1 λ^4 ,2,4-thiaselenazol-1-ylum cation, a new heteroaromatic system whose derivatives we are employing in a new synthesis of hypervalent heterocyclic compounds, in particular 1,6,6a λ^4 -triheterapentalenes (Lai, 1992). A feature of these hypervalent interactions is a correlation between the bond lengths within the three-heteroatom system. The length of the Se—S bond [2.189 (2) Å] is almost the same as the accepted covalent Se—S bond length [2.195 (15) Å; Allen *et al.*, 1987]. This indicates the absence of any significant three-centre bonding involving Se, S and Br. This is also confirmed by the long S···Br distance (3.558 Å), despite the near linearity of the system, with an angle of 178.7° at S. The C(2)—Se and

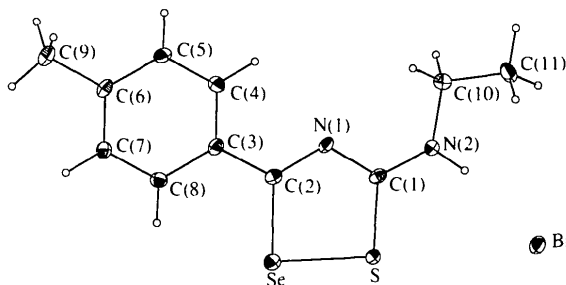


Fig. 1. ORTEP (Johnson, 1976) diagram of the title compound with the atomic labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

C(1)—S bonds are essentially C_{sp^2} —S single bonds. The cation in (1) is planar and the bond lengths of the heterocyclic ring indicate that there is π -electron delocalization extending over the C(2), N(1), C(1), N(2) sequence, with the C(2)—N(1) and C(1)—N(2) bonds being shorter than the C(1)—N(1) bond. Fig. 1 shows a labelled ORTEPII (Johnson, 1976) diagram of the final structure.

Experimental

The title compound was obtained as yellow needle-shaped crystals from the reaction mixture after washing with acetonitrile (m.p. 511–513 K).

Crystal data

$C_{11}H_{13}N_2SSe^+Br^-$

$M_r = 364.16$

Monoclinic

$P2_1/n$

$a = 7.237(2) \text{ \AA}$

$b = 10.434(1) \text{ \AA}$

$c = 17.450(2) \text{ \AA}$

$\beta = 99.42(1)^\circ$

$V = 1299.9(4) \text{ \AA}^3$

$Z = 4$

$D_x = 1.861 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction: analytical

$T_{\min} = 0.370$, $T_{\max} = 0.530$

3911 measured reflections

3776 independent reflections

Refinement

Refinement on F^2

$R(F) = 0.0355$

$wR(F^2) = 0.0969$

$S = 0.983$

3776 reflections

148 parameters

H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0617P^2)]$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 8-15^\circ$

$\mu = 6.033 \text{ mm}^{-1}$

$T = 123 \text{ K}$

Needle

$0.34 \times 0.15 \times 0.14 \text{ mm}$

Yellow

2840 observed reflections
 $[F > 4\sigma(F)]$

$R_{\text{int}} = 0.03$

$\theta_{\text{max}} = 30^\circ$

$h = -10 \rightarrow 10$

$k = 0 \rightarrow 14$

$l = 0 \rightarrow 24$

3 standard reflections

frequency: 60 min
intensity decay: random

$(\Delta/\sigma)_{\text{max}} = -0.001$

$\Delta\rho_{\text{max}} = 1.07 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.99 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors
from *International Tables for Crystallography* (1992, Vol. C)

| | | | | |
|-------|-------------|------------|------------|-----------|
| N(1) | 0.3164 (4) | 0.9039 (3) | 0.5614 (2) | 0.011 (1) |
| N(2) | 0.4128 (4) | 0.7498 (3) | 0.6538 (2) | 0.013 (1) |
| C(2) | 0.2821 (4) | 0.9320 (3) | 0.4869 (2) | 0.011 (1) |
| C(1) | 0.3786 (4) | 0.7845 (3) | 0.5811 (2) | 0.012 (1) |
| C(3) | 0.2093 (4) | 1.0567 (3) | 0.4604 (2) | 0.012 (1) |
| C(4) | 0.1695 (5) | 1.1477 (3) | 0.5141 (2) | 0.014 (1) |
| C(5) | 0.1010 (4) | 1.2668 (3) | 0.4899 (2) | 0.014 (1) |
| C(6) | 0.0690 (4) | 1.3000 (3) | 0.4107 (2) | 0.013 (1) |
| C(7) | 0.1080 (4) | 1.2097 (3) | 0.3573 (2) | 0.013 (1) |
| C(8) | 0.1756 (4) | 1.0883 (3) | 0.3809 (2) | 0.013 (1) |
| C(9) | -0.0028 (5) | 1.4307 (3) | 0.3855 (2) | 0.018 (1) |
| C(10) | 0.3917 (5) | 0.8318 (3) | 0.7200 (2) | 0.019 (1) |
| C(11) | 0.3486 (5) | 0.7515 (4) | 0.7865 (2) | 0.018 (1) |

Table 2. Geometric parameters (\AA , $^\circ$)

| | | | |
|-----------------|------------|------------------|-----------|
| Se—C(2) | 1.890 (3) | C(3)—C(4) | 1.396 (4) |
| Se—S | 2.189 (2) | C(3)—C(8) | 1.408 (4) |
| S—C(1) | 1.765 (3) | C(4)—C(5) | 1.379 (4) |
| N(1)—C(2) | 1.315 (4) | C(5)—C(6) | 1.407 (4) |
| N(1)—C(1) | 1.350 (4) | C(6)—C(7) | 1.386 (4) |
| N(2)—C(1) | 1.304 (4) | C(6)—C(9) | 1.500 (4) |
| N(2)—C(10) | 1.465 (4) | C(7)—C(8) | 1.396 (4) |
| C(2)—C(3) | 1.451 (4) | C(10)—C(11) | 1.505 (4) |
| C(2)—Se—S | 89.36 (10) | C(4)—C(3)—C(2) | 120.0 (3) |
| C(1)—S—Se | 93.36 (11) | C(8)—C(3)—C(2) | 121.3 (3) |
| C(2)—N(1)—C(1) | 117.3 (3) | C(5)—C(4)—C(3) | 120.7 (3) |
| C(1)—N(2)—C(10) | 125.2 (3) | C(4)—C(5)—C(6) | 121.0 (3) |
| N(2)—C(1)—N(1) | 120.4 (3) | C(7)—C(6)—C(5) | 118.3 (3) |
| N(2)—C(1)—S | 118.8 (2) | C(7)—C(6)—C(9) | 121.3 (3) |
| N(1)—C(1)—S | 120.7 (2) | C(5)—C(6)—C(9) | 120.3 (3) |
| N(1)—C(2)—C(3) | 121.0 (3) | C(6)—C(7)—C(8) | 121.2 (3) |
| N(1)—C(2)—Se | 119.2 (2) | C(7)—C(8)—C(3) | 119.9 (3) |
| C(3)—C(2)—Se | 119.8 (2) | N(2)—C(10)—C(11) | 110.1 (3) |
| C(4)—C(3)—C(8) | 118.7 (3) | | |

As the crystals proved to be unstable in the X-ray beam at ambient temperature, data were collected at 123 K. This was performed using a liquid-nitrogen gas-flow cryostat mounted on a CAD-4 diffractometer equipped with standard Enraf-Nonius data-collection routines.

Data reduction, including the analytical absorption correction, was performed using the PC version of the NRCVAX set of programs (Gabe, Lee & Le Page, 1985). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined by full-matrix least-squares methods based on F^2 using *SHELXL93* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KA1156). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

| | $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ | | | |
|----|---|------------|------------|-----------------|
| | x | y | z | U_{eq} |
| Br | 0.5532 (1) | 0.4582 (1) | 0.6666 (1) | 0.016 (1) |
| Se | 0.3300 (1) | 0.8077 (1) | 0.4139 (1) | 0.014 (1) |
| S | 0.4137 (1) | 0.6724 (1) | 0.5091 (1) | 0.011 (1) |