The Crystal Structure of a Mixed-Valence Complex of Selenium: Bis(tetraethylammonium) Di-μ-bromo-{tetrabromoselenate(IV) dibromoselenate(II)}, $[(C_2H_5)_4N]_2Se(IV)Se(II)Br_8$

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The compound $[(C_2H_5)_4N]_2Se_2Br_8$ forms monoclinic crystals, space group $P2_1/c$ (No. 14) with $Z = 4$, and $a = 17.825(2)$, $b = 10.364(2)$, $c = 17.393(2)$ Å and $\beta = 93.38(1)°$. The structure has been determined by X-ray methods and refined to $R = 0.074$ for 2908 observed reflections. The anion is a mixed-valence complex, $[Se(IV)Se(II)Br_8]^{2-}$. Se(IV) is octahedrally coordinated to six bromine atoms, two of which form bridges to Se(II), and a distorted square-planar $Se(II)Br_4$ group is formed. The bridging Se(IV)–Br bond lengths are 2.748(2) and 2.720(2) Å, and the bridging Se(II)–Br bond lengths are 2.993(2) and 3.010(2) Å. The terminal Se(II)–Br bond lengths are 2.461(2) and 2.427(2) Å. The lengths of the Se(IV)–Br bonds co-planar with the bridging bonds (equatorial) are 2.459(2) and 2.442(2) Å, and those of the axial Se(IV)–Br bonds are 2.522(2) and 2.600(2) Å. The least-squares plane of the $Se(II)Br_4$ group is tilted 56.8° with respect to the equatorial plane of Se(IV). The total lengths of the linear three-centre systems are 5.122(2), 5.179(2) and 5.190(2) Å for Br–Se(IV)–Br, and 5.420(2) and 5.471(2) Å for Br–Se(II)–Br.

Dedicated to Professor Olav Foss on his 70th birthday

In an attempt to make $[(C_2H_5)_4N]_2Se_2Br_6$ by allowing selenium diselenocyanate to react with bromine and bromide:

$$2\,Se(SeCN)_2 + 8\,Br_2 + 6\,Br^- \rightarrow 3\,Se_2Br_6^{2-} + 4\,BrCN$$

brown-orange plates deposited. The plates are shown from analyses and from the crystal structure presented here to be $[(C_2H_5)_4N]_2Se_2Br_8$. The reaction can be written summarily as:

$$2\,Se(SeCN)_2 + 11\,Br_2 + 6\,Br^- \rightarrow 3\,Se_2Br_8^{2-} + 4\,BrCN$$

Experimental

Preparation. A solution of $(C_2H_5)_4NBr$ (1.26 g, 6 mmol) and Br_2 (1.28 g, 8 mmol) in CH_3CN (15 cm^3) was added, with stirring, to a solution of $Se(SeCN)_2$ (0.58 g, 2 mmol) in CH_2Cl_2 (30 cm^3). The reaction mixture eventually turned dark brown, and orange-brown six-edged plates crystallized slowly after cooling to −20 °C. Found: C 18.06; H 3.68; N 2.76; Br 58.97; Se 16.73. Calc. for $C_{16}H_{40}N_2Br_8Se_2$: C 18.17; H 3.81, N 2.65; Br 60.44; Se 14.93.

X-Ray structure analysis. The crystal used for X-ray measurements was kept in a sealed capillary tube to prevent decomposition. Data for unit cell dimensions and intensities were recorded on a CAD4 diffractometer using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). Unit cell dimensions were determined from the diffractometer angles for 25 automatically centred reflections. Intensities out to $\theta = 28°$ were recorded using the ω-scan mode with scan width of $1.00 + 0.35\tan\theta$, plus 25 % on each side for background. The scan rate was 5.03 − 0.75°

Table 1. Atomic coordinates for $[(C_2H_5)_4N]_2Se_2Br_8$ with e.s.d.'s in parentheses.

Atom	p	x	y	z	$B_{eq}/Å^2$
Se(1)	1.0	0.84203(13)	−0.02494(23)	0.32235(11)	2.89(5)
Se(2)	1.0	0.62445(14)	0.01261(24)	0.28629(12)	2.34(5)
Br(1)	1.0	0.91985(15)	0.01394(32)	0.44155(13)	5.14(7)
Br(2)	1.0	0.92390(16)	−0.20073(28)	0.28576(15)	5.15(7)
Br(3)	1.0	0.91970(15)	0.13425(26)	0.25143(13)	4.24(6)
Br(4)	1.0	0.75669(17)	−0.18538(29)	0.39187(14)	5.41(7)
Br(5)	1.0	0.74846(15)	0.17317(26)	0.35987(13)	4.23(6)
Br(6)	1.0	0.75333(15)	−0.06442(27)	0.19179(12)	4.48(6)
Br(7)	1.0	0.54892(17)	0.05514(29)	0.39749(15)	5.43(7)
Br(8)	1.0	0.55154(16)	−0.17477(28)	0.24393(14)	5.13(7)
N(1)	1.0	0.2591(10)	−0.0302(17)	0.3519(8)	3.2(4)
C(11)	1.0	0.2508(21)	−0.182(4)	0.3433(18)	9.5(10)
C(12)	1.0	0.2260(16)	−0.243(3)	0.4224(14)	6.1(7)
C(13)	1.0	0.2826(20)	0.019(3)	0.2753(17)	8.7(9)
C(14)	1.0	0.3560(17)	−0.021(3)	0.2488(15)	6.8(7)
C(15)	1.0	0.3182(21)	0.005(4)	0.4182(18)	9.2(10)
C(16)	1.0	0.3354(15)	0.148(3)	0.4204(13)	5.0(6)
C(17)	1.0	0.1887(23)	0.047(4)	0.3757(19)	11.2(12)
C(18)	1.0	0.1158(17)	−0.016(3)	0.3292(14)	6.4(7)
N(2)	0.5	0	0	0	3.4(5)
C(21)	0.5	0.0196(29)	0.140(5)	0.0050(25)	4.7(11)
C(21′)	0.5	0.0509(39)	0.024(7)	−0.0668(31)	8.0(17)
C(22)	1.0	0.0760(22)	0.179(4)	−0.0596(18)	10.3(11)
C(23)	0.5	0.0405(36)	0.033(6)	0.0807(30)	7.3(16)
C(23′)	0.5	0.0781(42)	−0.095(7)	0.0054(36)	10.0(21)
C(24)	1.0	0.1178(23)	−0.058(4)	0.0870(20)	11.0(12)
N(3)	0.5	$^1/_2$	0	0	4.1(6)
C(31)	0.5	0.5099(30)	0.070(5)	0.0764(25)	5.0(12)
C(31′)	0.5	0.4988(29)	0.142(5)	−0.0134(23)	3.9(10)
C(32)	1.0	0.5158(17)	0.226(3)	0.0614(15)	6.9(8)
C(33)	0.5	0.5564(29)	0.035(5)	−0.0578(24)	4.7(11)
C(33′)	0.5	0.5742(34)	−0.051(6)	0.0389(29)	6.7(15)
C(34)	1.0	0.6464(20)	−0.014(4)	−0.0241(17)	9.1(10)

min^{-1}. The intensities were corrected for Lorentz and polarization effects, and for decay and absorption. Maximum decay correction, based on three reference reflections measured every 90 min of exposure time, was 8 %, and transmission factors were 0.074–0.407. Of 7721 reflections, 2908 had $I > 2\sigma(I)$ and were used in the calculations. Scattering factors, refinement procedures and programs for calculations were as in Ref. 1.

The structure was solved by direct (MULTAN) and Fourier methods. The E-map and first electron density map revealed the positions of the bromine and selenium atoms, as well as the nitrogen and carbon atoms of one of the two tetraethylammonium ions of the asymmetric unit. The positional and thermal parameters for these atoms were then refined and the remaining non-hydrogen atoms were located from the resulting difference electron density map. Two half tetraethylammonium ions are located with nitrogen atoms in symmetry centres. This is not consistent with ordered ethyl groups, but from absences of the $0k0$ reflections with k odd, centric intensity distributions, and similarity in agreement indexes for the two absolute configurations when refined in the acentric space group Pc, we conclude that the space group is $P2_1/c$. The H atoms were not found from difference maps, and were omitted in the refinement.

With anisotropic thermal parameters for Se

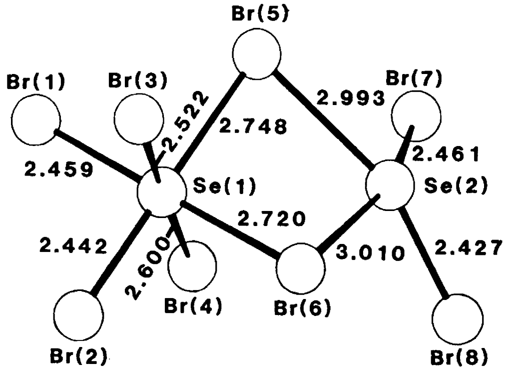

Fig. 1. A view of the Se(IV)Se(II)Br_8^{2-} ion in the tetraethylammonium salt.

and Br, and isotropic parameters for C and N (177 variables) the refinement converged at R = 0.074, R_w = 0.079, S = 2.349. The shifts in the last cycle were less than one per cent of the associated standard deviations. Atomic coordinates and equivalent thermal parameters are listed in Table 1. Complete lists of anisotropic thermal parameters, and of bond lengths and angles are available from the authors upon request.

Crystal data. $[(C_2H_5)_4N]_2Se_2Br_8$, M = 1057.7, monoclinic, space group $P2_1/c$ (No. 14); a = 17.825(2), b = 10.364(2), c = 17.393(2) Å, β = 93.38(1)°, V = 3207.5(1.2) Å^3, Z = 4, D_x = 2.190 g cm^{-3}; $F(000)$ = 1992, $\mu(\mathrm{Mo}K\alpha)$ = 130.5 cm^{-1}.

Discussion

In the present structure the anion is a dinuclear complex with selenium as central atoms (Fig. 1). One selenium has octahedral coordination and the other a square-planar environment. The two coordination groups are linked together by two bromine atoms situated in equatorial positions of the octahedral configuration. The angle between the least-squares planes of the atoms of the equatorial plane and the square-planar configuration is 56.8°.

If a charge of −1 is assigned to the bromine

Table 2. Distances (Å) and angles (°) in the anionic selenium-bromine species, with e.s.d.'s in parentheses.

Bond lengths			
Se(1)–Br(1)	2.459(2)	Se(2)–Br(5)	2.993(2)
Se(1)–Br(2)	2.442(2)	Se(2)–Br(6)	3.010(2)
Se(1)–Br(3)	2.522(2)	Se(2)–Br(7)	2.461(2)
Se(1)–Br(4)	2.600(2)	Se(2)–Br(8)	2.427(2)
Se(1)–Br(5)	2.748(2)		
Se(1)–Br(6)	2.720(2)		
Bond angles			
Br(1)–Se(1)–Br(2)	91.49(8)	Br(4)–Se(1)–Br(6)	87.98(7)
Br(1)–Se(1)–Br(3)	90.38(8)	Br(5)–Se(1)–Br(6)	88.83(7)
Br(1)–Se(1)–Br(4)	91.67(8)		
Br(1)–Se(1)–Br(5)	89.85(7)	Br(5)–Se(2)–Br(6)	79.21(6)
Br(1)–Se(1)–Br(6)	178.64(9)	Br(5)–Se(2)–Br(7)	89.36(7)
Br(2)–Se(1)–Br(3)	90.40(8)	Br(5)–Se(2)–Br(8)	160.63(9)
Br(2)–Se(1)–Br(4)	91.09(8)	Br(6)–Se(2)–Br(7)	161.30(8)
Br(2)–Se(1)–Br(5)	178.60(8)	Br(6)–Se(2)–Br(8)	91.97(7)
Br(2)–Se(1)–Br(6)	89.83(7)	Br(7)–Se(2)–Br(8)	94.24(8)
Br(3)–Se(1)–Br(4)	177.44(9)		
Br(3)–Se(1)–Br(5)	89.19(7)	Se(1)–Br(5)–Se(2)	85.77(6)
Br(3)–Se(1)–Br(6)	89.93(7)	Se(1)–Br(6)–Se(2)	85.93(6)
Br(4)–Se(1)–Br(5)	89.28(7)		
Angles between planes			
Se(1)Br(1)Br(2)Br(5)Br(6)/Se(2)Br(5)Br(6)Br(7)Br(8)	56.8		

atoms, the two selenium atoms together must have a charge of +6. Since a charge of +3 is unknown for selenium and the environments are typical for Se(IV) and Se(II) compounds, the valence of the octahedrally coordinated selenium is four and that of the square-planar coordinated selenium is two.

The octahedral coordination. In the equatorial plane, Se(IV) is bonded with long bonds to two bridging bromine atoms and with rather short bonds to two terminal bromine atoms. The environment of the Se(IV) in the plane is very much the same as found for divalent selenium in the dinuclear complex ion $Se_2Br_6^{2-}$ in the tetraphenylphosphonium salt[2] and in the anion in $[C_6H_5(CH_3)_3N]_2Se_4Br_{14}$.[1] The *3c–4e* model has been used to explain the bonding in the compounds. In the following, the mean values of bond lengths and angles are given with the corresponding figures for $[C_6H_5(CH_3)_3N]_2Se_4Br_{14}$ in parentheses. The angle of the Br–Se–Br sequence: 178.62° (174.36°); short Se–Br bonds: 2.451 Å (2.413 Å); long Se–Br bonds: 2.734 Å (2.778 Å); total length of Br–Se–Br: 5.185 Å (5.191 Å).

The axial Br–Se–Br sequence is nearly symmetric, with an angle of 177.44(9)° and bond lengths of 2.522(2) and 2.600(2) Å; these bond lengths are nearly the same as found for Se–Br bonds, i.e. 2.553(2)–2.579(2) Å, in the crystal structure of H_2SeBr_6,[3] and they do not differ greatly from bond lengths found in symmetric Br–Se–Br sequences of divalent selenium. In dibromo(tetramethylthiourea)selenium(II)[4] the distances are 2.569(3) and 2.620(3) Å, and in tetramethylammonium dibromocyanoselenate(II)[5] the distance is 2.575(1) Å. The bonds in Se(IV) complexes are generally expected to be a little shorter than in corresponding Se(II) compounds, owing to greater electrostatic attraction.

The square-planar coordination at Se(II) is distorted. The Se(II) atom is 0.321 Å out of a least-squares coordination plane. The lengths of the selenium–terminal bromine bonds are 2.427(2) and 2.461(2) Å (Table 2), and thus equal to those of the corresponding bonds at Se(IV). They are also about equal to the bond lengths found in dinuclear complexes of divalent selenium.[1,2] The bridging bonds are very long, viz. 2.993(2) and 3.010(2) Å, which is ca. 0.27 Å longer than at Se(IV) or 0.22 Å longer than corresponding bonds in complexes referred to above. The angles of the Br–Se–Br sequences are 160.63(9) and 161.30(8)°. The rather large deviations from linearity are in accordance with the lengthening of the bridging bonds.

The coordination at Se(II) can also be looked upon as a $SeBr_2$ molecule being approached at 180° to the Se–Br bonds by two equatorial bromine atoms of a $SeBr_6^{2-}$ ion. The $SeBr_2$ molecule retains its shape approximately. Table 3 gives the dimensions in this structure, in other bromine

Table 3. Se–Se and Se–Br bonds, and X–Se–X bond angles in $Se(SeCN)_2$ and $Se(II)X_2$ parts of dinuclear selenium complexes, with e.s.d.'s in parentheses.

	Se–Se	Se–Se	ΣSe–Se	Se–Se–Se
$Se(SeCN)_2$[a]	2.334(1)	2.334(1)	4.668	102.97(6)
$RbSe(SeCN)_3 \cdot \frac{1}{2} H_2O$[b]	2.393(2)	2.391(2)	4.784	99.32(7)
$KSe(SeCN)_3 \cdot \frac{1}{2} H_2O$[c]	2.411(2)	2.395(2)	4.806	98.41(5)
	2.403(2)	2.419(2)	4.822	97.60(5)
$RbSe(SeCN)_3 \cdot \frac{1}{2} H_2O$[b]	2.406(2)	2.409(2)	4.815	97.55(7)
	Se–Br	Se–Br	ΣSe–Br	Br–Se–Br
$[C_6H_5(CH_3)_3N]_2Se_4Br_{14}$[d]	2.416(2)	2.411(2)	4.827	95.18(6)
	2.407(2)	2.416(2)	4.823	93.78(6)
$[P(C_6H_5)_4]_2Se_2Br_6$[e]	2.399(1)	2.485(1)	4.884	95.24(2)
$[(C_2H_5)_4N]_2Se(IV)Se(II)Br_8$	2.461(2)	2.427(2)	4.888	94.24(8)

[a]Ref. 11. [b]Ref. 12. [c]Ref. 13. [d]Ref. 1. [e]Ref. 2.

compounds and in related selenocyanate compounds, when the selenium atom of SeX_2 is being approached. The average bond angle at dibonded selenium listed by Abrahams[6] is about 104°, the same value as found in the selenopentathionate ion.[7–9] The angle between two 3*c*–4*e* bonds based on two *p*-orbitals at the central atom is expected to be 90°. Taking into account the larger bonding radius of selenium and the greater electronegativity of bromine, the observations in Table 3 indicate an approximately linear relation between the sum of the Se–Se or Se–Br bond lengths and the bond angle. An increase of 0.02 Å in the sum corresponds to a decrease of about one degree in the angle.

A classification of mixed-valence compounds has been made by Robin and Day.[10] The present compound fits best into their Class I, which requires the ions of differing valence to be in sites of very different symmetry. In the present structure, Se(II) and Se(IV) are present in the same ion, making it quite unique in this respect.

The tetraethylammonium ions. The atoms of one cation are in general positions and the dimensions are: N–C = 1.51(2)–1.58(3) Å, C–C = 1.47 (3)–1.63(3) Å, C–N–C = 106.4(14)–117.4(16)° and N–C–C = 110.0(16)–118.7(18)°.

The nitrogen atoms of the two disordered half-ions lie in symmetry centres. The arrangements around the nitrogen atoms are two centrosymmetrically related tetrahedrons of carbon atoms and four terminal carbon atoms, each of which is shared between two carbon atoms of different tetrahedrons. The dimensions of these ions are: N–C = 1.49(3)–1.70(5) Å, C–C = 1.58(3)–1.78 (4) Å, C–N–C = 111.7(21)–115.0(17)° and N–C–C = 103.3(20)–114.3(20)°.

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