

# Syntheses and Crystal Structures of Phenyltrimethylammonium Salts of Hexabromoselenate(IV), $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]$ , and *catena*-poly[(Di- $\mu$ -bromobis{tetrabromotellurate(IV)})- $\mu$ -bromine], $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_{2n}[\text{Se}_2\text{Br}_{10}\cdot\text{Br}_2]_n$

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The crystal structures of  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]$  (**1**) and  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_{2n}[\text{Se}_2\text{Br}_{10}\cdot\text{Br}_2]_n$  (**2**) have been determined by X-ray methods and refined to  $R=0.030$  and  $0.060$  for 2834 and 1573 reflections, respectively. Crystals of **1** are monoclinic, space group  $P2_1/c$  with  $Z=2$  and  $a=8.681(2)$ ,  $b=10.533(3)$ ,  $c=14.060(2)$  Å,  $\beta=104.26(2)^\circ$ . Crystals of **2** are triclinic, space group  $P1$  with  $Z=1$  and unit cell dimensions  $a=8.698(1)$ ,  $b=8.931(1)$ ,  $c=11.563(1)$  Å,  $\alpha=94.74(1)$ ,  $\beta=101.87(2)$ ,  $\gamma=90.47(2)^\circ$ . The  $[\text{SeBr}_6]^{2-}$  octahedron of **1** is centrosymmetric with  $\text{Se}-\text{Br}=2.5740(3)$ ,  $2.5706(3)$ ,  $2.5695(3)$  Å and  $\text{Br}-\text{Se}-\text{Br}=90.47(1)$ ,  $90.13(1)$ ,  $91.17(1)^\circ$ . The anion of **2** has a dimeric, centrosymmetric  $\text{Se}_2\text{Br}_{10}$  unit, consisting of two edge-sharing  $\text{SeBr}_6$  octahedra, with one of the axial Br atoms of each octahedron linked to an equivalent Br atom by a  $\text{Br}_2$  bridge, so forming a polymeric  $[\text{Se}_2\text{Br}_{10}\cdot\text{Br}_2]_n^{2n-}$  chain. The  $\text{Se}_2\text{Br}_{10}$  unit has  $\text{Se}-\text{Br}$  dimensions  $2.3840(22)$  and  $2.4228(23)$  Å for equatorial terminal,  $2.7920(22)$  and  $2.9428(21)$  Å for equatorial bridging, and  $2.5617(22)$  and  $2.5727(22)$  Å for axial bonds. The  $\text{Br}-\text{Br}_2-\text{Br}$  bridge has  $\text{Br}-\text{Br}_2=3.0973(23)$  Å,  $\text{Br}-\text{Br}'=2.3385(35)$  Å,  $\text{Br}-\text{Br}-\text{Br}'=173.00(19)^\circ$  and  $\text{Se}-\text{Br}-\text{Br}=114.23(8)^\circ$ .

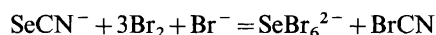
Selenium(IV) forms six-coordinated octahedral complexes with bromide. The known modifications of such complexes are the monomeric  $\text{SeBr}_6^{2-}$  ion,<sup>1–6</sup> the dimeric  $\text{Se}_2\text{Br}_{10}^{2-}$  ion formed by two octahedra sharing one edge,<sup>1,5,7</sup> the dimeric  $\text{Se}_2\text{Br}_9^-$  anion formed by two octahedra sharing one face,<sup>6,7</sup> the trimeric  $\text{Se}_3\text{Br}_{13}^-$  ion formed by three octahedra, each sharing one face with the two others,<sup>8</sup> and the tetrameric  $\text{Se}_4\text{Br}_{16}$  molecule formed by four octahedra, each sharing one edge with each of the three others in a cubane-like structure.<sup>9</sup> In the crystals of  $[(\text{CH}_3)_3\text{NH}]_{2n}[\text{SeBr}_6\cdot\text{Br}_2]_{2n}$ ,<sup>1,6</sup> the  $\text{SeBr}_6$  octahedra are polymerised by  $\text{Br}_2$  molecules connected to two *cis*-positioned Br atoms. We report here the preparation and crystal structure of a new salt of the monomeric anion,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]$  (**1**) and a new structure variant,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_{2n}[\text{Se}_2\text{Br}_{10}\cdot\text{Br}_2]_n$  (**2**).

## Experimental

**Preparations.** In the syntheses elemental selenium or selenocyanate were used as selenium sources. The oxidation was by bromine and solvents employed were acetonitrile and dichloromethane.

$[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]$  (**1**).

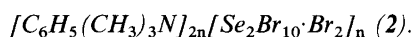
1. To a solution of 6.0 mmol (0.96 g) bromine and 2.0 mmol (0.43 g) phenyltrimethylammonium bromide in 3.5 g acetonitrile was added 2.0 mmol (0.48 g) phenyltrimethylammonium selenocyanate. From the resulting clear solution crystallization of wine red bipyramidal prisms started at room temperature. The solution was eventually placed in a refrigerator. Total yield 1.40 g, 86% of theoretical value calculated from equation



2. To 2.0 mmol (0.158 g) selenium in 3.5 g acetonitrile was added 4.0 mmol (0.64 g) bromine followed by 4.0 mmol (0.86 g) phenyltrimethylammonium bromide. The suspension was diluted with 3.5 g acetonitrile and heated to boiling. The clear solution was set aside at

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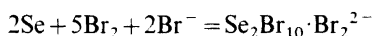
room temperature. Yield 1.45 g, 87% of theoretical value calculated from the equation



1. To a suspension of 0.50 mmol (0.120 g) phenyltrimethylammonium selenocyanate in 3 g of dichloromethane, a solution of 1.75 mmol (0.280 g) bromine in 2 g of dichloromethane was added. The solution was left at room temperature. Short dark irregular prisms or plates with some blue reflection crystallized. Yield 0.30 g, 86% of theoretical value calculated from the equation



2. To 5.25 mmol (0.84 g) bromine in 2 g acetonitrile, 2.0 mmol (0.158 g) selenium was added. The suspension was stirred until all selenium had reacted. 4 g acetonitrile and 2.0 mmol (0.432 g) of phenyltrimethylammonium bromide were added. The solution was heated until all solid was dissolved and then set aside at room temperature. Yield 0.90 g, 65% of theoretical value calculated from the equation



*X-Ray structure analyses.* The determination of unit-cell parameters and the data collections were carried out on

an Enraf-Nonius CAD4 diffractometer, using monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). Crystal data and conditions for data collections are given in Table 1. The cell parameters were based on a least-squares fit of accurate setting angles for 25 reflections. Intensities were corrected for Lorentz and polarization effects, decay and absorption. Reflections with  $I > 2\sigma(I)$  were regarded as observed.

The structure of compound **1** was solved by direct methods (MULTAN) and compound **2** by combination of direct and Patterson methods. The intensity statistics of **2** indicated the centrosymmetric space group  $P\bar{1}$ , but we were not able to solve the structure by direct methods in this space group. A solution was however found in space group  $P1$ , and by combination with Se coordinates from a Patterson map assuming space group  $P\bar{1}$ , the structure was eventually refined in the latter space group. The structures were refined by full-matrix least-squares calculations, using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed geometrically with bond lengths  $\text{C-H} = 0.95 \text{ \AA}$ , and held fixed with thermal parameters equal to  $1.3 B_{\text{eq}}$  for the atom to which they are attached. A secondary extinction coefficient,  $g$ , in  $F_{\text{corr}} = F_c(1 + gI_c)^{-1}$ , was included as a variable and refined to  $2.06 \times 10^{-7}$  for compound **1**, but was found to be negligible for **2**.

Table 1. Crystallographic data.

	1	2
Formula	$\text{C}_{18}\text{H}_{28}\text{N}_2\text{Br}_6\text{Se}$	$\text{C}_{18}\text{H}_{28}\text{N}_2\text{Br}_{12}\text{Se}_2$
$M$	830.9	1389.3
System	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
$a/\text{\AA}$	8.681(2)	8.698(1)
$b/\text{\AA}$	10.533(3)	8.931(1)
$c/\text{\AA}$	14.060(2)	11.563(1)
$\alpha/^\circ$		94.74(1)
$\beta/^\circ$	104.26(2)	101.87(2)
$\gamma/^\circ$		90.47(2)
$V/\text{\AA}^3$	1245.9	875.7
$Z$	2	1
$T/\text{K}$	93	293
$D_x/\text{g cm}^{-3}$	2.215	2.634
$D_0/\text{g cm}^{-3}$	2.13 <sup>a</sup>	2.63
$F(100)$	788	638
$\Theta_{\text{max}}$	30	25
Scan mode	$\omega$	$\omega$
Min scan width/ $^\circ$	1.00	1.00
Loss of intensity (%)	0.9	24.8
$\mu$ (MoK $\alpha$ )/ $\text{cm}^{-1}$	110.3	156.7
Correction for absorption	Empirical <sup>b</sup>	Empirical <sup>b</sup>
Correction factors	0.92–1.12	0.76–1.40
No. of independent measurements	3616	3251
No. with $I > 2\sigma(I)$	2834	1573
No. of parameters refined	125	154
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.030	0.060
$R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$	0.028	0.046
$S = [\sum w(F_o - F_c)^2 / (n - m)]^{1/2}$	1.09	1.40
Max. $\Delta(\rho)/\text{e \AA}^{-3}$	0.90	1.15

<sup>a</sup> Measured at room temperature. <sup>b</sup> Ref. 10.

The programs used were Enraf-Nonius' Structure Determination Package 1987. All refined atomic coordinates are given in Table 2.

## Results and discussion

Bond lengths and angles are given in Table 3, and views of the anions are shown in Fig. 1.

The Se atom of the mononuclear  $[\text{SeBr}_6]^{2-}$  anion in compound 1 is situated on a centre of symmetry, and there are only small deviations from regular octahedral geometry. The largest deviation from octahedral angles is  $1.17^\circ$  and the Se–Br bonds are 2.5695(3)–2.5740(3) Å.

For comparison data of structure determinations of hexabromoselenates are listed in Table 4. In compounds (1)–(6) the  $[\text{SeBr}_6]^{2-}$  ion has at least a centre of symmetry, and so the *trans* Se–Br bonds are identical and the *trans* Br–Se–Br angles are exactly  $180^\circ$ . In these ions the Se–Br bond lengths are in the range 2.549(1)–2.582(1) Å, with a weighted mean value<sup>11</sup> for 13 individual measurements of 2.570(3) Å.

In (7) the ion has mirror plane symmetry and a little wider bond range, and in the asymmetric ions of (8) and (9) the ranges are much wider, but the deviations from

octahedral angles are a maximum of  $2.4$  and  $2.8^\circ$ , respectively. In (9) there are two *cis*-oriented Se–Br bonds of lengths 2.678(3) and 2.682(4) Å. The Br atoms involved are each in bonding contact with a  $\text{Br}_2$  molecule such that polymer chains of composition  $[\text{SeBr}_6^{2-} \cdot \text{Br}_2]_n$  results, and these contacts may have a lengthening effect on the Se–Br bonds. In (8) there are also two long *cis*-oriented Se–Br bonds, 2.610(3) and 2.670(3) Å. Here each of the six Br atoms is taking part in one nearly linear interionic Se–Br $\cdots$ Br system, with Br $\cdots$ Br distances in the range 3.522(3)–3.698(4) Å, and these moderate variations can hardly explain the differences of the individual Se–Br bond lengths. In all cases the average of each pair of *trans* situated bonds is within the range of the centrosymmetrical ions.

It may be concluded that the individual bonds are likely to vary within a wide range, whereas the total length of a linear Br–Se–Br bonding system is nearly constant. This is in accordance with the three-centre–four-electron bond model, and so is the mean Se–Br bond length of 2.570(3) Å, which is about 0.27 Å longer than the sum of the covalent radii.

According to the Valence Shell Electron Pair Repulsion (VSEPR) theory the central atom in  $\text{TeX}_6^{2-}$  and  $\text{SeX}_6^{2-}$

Table 2. Fractional atomic coordinates with e.s.d.s in parentheses.

Atom	x	y	z	$B_{\text{eq}}/\text{Å}^2$
(1) $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]$				
Se	0	0	0	0.586(7)
Br(1)	–0.03033(4)	0.11670(3)	–0.16443(2)	0.867(5)
Br(2)	0.00792(4)	0.21338(3)	0.08982(2)	0.898(6)
Br(3)	0.30365(4)	0.00158(4)	0.02666(2)	0.888(5)
N	0.3195(3)	0.5336(3)	0.1971(2)	0.83(5)
C(1)	0.1553(4)	0.5349(4)	0.1305(3)	1.12(6)
C(2)	0.3537(4)	0.4001(3)	0.2347(3)	1.18(7)
C(3)	0.3197(4)	0.6194(4)	0.2835(3)	1.24(7)
C(4)	0.4438(4)	0.5794(4)	0.1479(2)	0.77(6)
C(5)	0.6022(4)	0.5656(4)	0.1964(2)	1.03(6)
C(6)	0.7199(4)	0.6120(4)	0.1544(3)	1.27(7)
C(7)	0.6777(4)	0.6721(4)	0.0637(3)	1.09(6)
C(8)	0.5197(4)	0.6862(4)	0.0168(3)	1.37(7)
C(9)	0.4011(4)	0.6399(3)	0.0574(3)	1.12(7)
(2) $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_{2n}[\text{Se}_2\text{Br}_{10} \cdot \text{Br}_2]_n$				
Se	0.37703(20)	0.48752(18)	0.13995(15)	1.90(4)
Br(1)	0.10766(21)	0.49001(19)	0.15469(18)	3.36(5)
Br(2)	0.47947(24)	0.48647(21)	0.35122(16)	3.74(5)
Br(3)	0.38075(21)	0.77651(18)	0.15227(16)	2.95(4)
Br(4)	0.37224(24)	0.19967(19)	0.11754(17)	3.76(5)
Br(5)	0.29745(20)	0.49125(18)	–0.10635(16)	2.42(4)
Br(6)	0.46332(24)	0.92964(21)	0.40836(19)	4.08(5)
N	0.1049(15)	0.9654(13)	0.7754(11)	2.7(3)
C(1)	0.1321(32)	0.8810(23)	0.8796(17)	8.0(8)
C(2)	0.2425(24)	1.0592(20)	0.7745(20)	6.7(6)
C(3)	–0.0160(25)	1.0756(21)	0.7934(21)	7.1(7)
C(4)	0.0552(17)	0.8644(16)	0.6670(16)	2.8(4)
C(5)	–0.0965(25)	0.8206(20)	0.6264(18)	5.7(6)
C(6)	–0.1498(24)	0.7273(21)	0.5233(17)	5.2(6)
C(7)	–0.0398(22)	0.6763(19)	0.4642(17)	4.5(5)
C(8)	0.1159(25)	0.7119(19)	0.4982(17)	5.3(6)
C(9)	0.1647(20)	0.8064(19)	0.6023(17)	4.2(5)

Table 3. Distances (in Å) and angles (in °) in the anionic selenium-bromine species, with e.s.d.s in parentheses.

(1) [SeBr <sub>6</sub> ] <sup>2-</sup>			
Se-Br(1)	2.5740(3)	Br(1)-Se-Br(2)	90.47(1)
Se-Br(2)	2.5706(3)	Br(1)-Se-Br(3)	90.13(1)
Se-Br(3)	2.5695(3)	Br(2)-Se-Br(3)	91.17(1)
Interionic contact:			
Br(3)···Br(3a)	3.666(1)	Se-Br(3)···Br(3a)	160.42(2)
Symmetry operations: (a) 1 - x, -y, -z			
(2) [Se <sub>2</sub> Br <sub>10</sub> ·Br <sub>2</sub> ] <sup>2-</sup>			
Se-Br(1)	2.3840(22)	Se-Br(5a)	2.9428(21)
Se-Br(2)	2.4228(23)	Br(3)-Br(6)	3.0973(23)
Se-Br(3)	2.5727(22)	Br(6)-Br(6b)	2.3385(35)
Se-Br(4)	2.5617(22)	Se···Se(a)	4.2497(32)
Se-Br(5)	2.7920(22)		
Br(1)-Se-Br(2)	95.27(8)	Br(3)-Se-Br(4)	177.41(10)
Br(1)-Se-Br(3)	89.19(7)	Br(3)-Se-Br(5)	87.46(7)
Br(1)-Se-Br(4)	91.31(7)	Br(3)-Se-Br(5a)	86.47(6)
Br(1)-Se-Br(5)	91.77(8)	Br(4)-Se-Br(5)	89.99(7)
Br(1)-Se-Br(5a)	174.33(8)	Br(4)-Se-Br(5a)	92.86(7)
Br(2)-Se-Br(3)	92.11(8)	Br(5)-Se-Br(5a)	84.40(6)
Br(2)-Se-Br(4)	90.37(8)	Se-Br(5)-Se(a)	95.60(6)
Br(2)-Se-Br(5)	172.94(9)	Se-Br(3)-Br(6)	114.23(8)
Br(2)-Se-Br(5a)	88.55(7)	Br(3)-Br(6)-Br(6b)	173.00(19)
Interionic contacts:			
Br(1)···Br(1c)	3.700(4)	Se-Br(1)···Br(1c)	103.99(9)
Br(1)···Br(5c)	3.460(2)	Se-Br(1)···Br(5c)	166.51(8)
Br(2)···Br(2d)	3.373(3)	Se-Br(5)···Br(1c)	101.56(6)
Br(3)···Br(4e)	3.833(2)	Se(a)-Br(5)···Br(1c)	161.73(7)
		Se-Br(2)···Br(2d)	164.17(11)
		Se-Br(3)···Br(4e)	171.04(8)
		Se-Br(4)···Br(3f)	168.47(8)
Symmetry operations: (a) 1 - x, 1 - y, -z; (b) 1 - x, 2 - y, 1 - z; (c) -x, 1 - y, -z; (d) 1 - x, 1 - y, 1 - z; (e) x, 1 + y, z; (f) x, y - 1, z.			

Table 4. Bond lengths (in Å) in hexabromoselenate(IV) ions.

No.	Compound	Bond range	Average	Ref.
(1)	[NH <sub>4</sub> ] <sub>2</sub> [SeBr <sub>6</sub> ]	2.577(2)	2.577	3
(2)	[H <sub>3</sub> O] <sub>2</sub> [SeBr <sub>6</sub> ]	2.562(1)	2.562	5
(3)	[H <sub>5</sub> O <sub>2</sub> ] <sub>2</sub> [SeBr <sub>6</sub> ]·4H <sub>2</sub> O	2.553(2)-2.579(2)	2.565	2
(4)	[H <sub>3</sub> O(Crown) <sup>a</sup> ] <sub>2</sub> [SeBr <sub>6</sub> ]	2.549(1)-2.584(1)	2.572	5
(5)	[H <sub>3</sub> O(Crown) <sup>b</sup> ] <sub>2</sub> [SeBr <sub>6</sub> ]·CH <sub>3</sub> CN	2.564(2)-2.582(2)	2.572	5
(6)	[C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>3</sub> N] <sub>2</sub> [SeBr <sub>6</sub> ]	2.570(1)-2.574(1)	2.572	This work
(7)	[H <sub>3</sub> N(CH <sub>2</sub> ) <sub>3</sub> NH <sub>3</sub> ] <sub>2</sub> [SeBr <sub>6</sub> ]	2.547(2)-2.595(2)	2.571	3
(8)	[H <sub>9</sub> O <sub>4</sub> ][H <sub>3</sub> O][SeBr <sub>6</sub> ]·2½C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	2.483(3)-2.670(3)	2.574	4
(9)	[(CH <sub>3</sub> ) <sub>3</sub> NH] <sub>2n</sub> [SeBr <sub>6</sub> ·Br <sub>2</sub> ] <sub>n</sub>	2.454(3)-2.682(4)	2.564	6

<sup>a</sup> Dibromobenzo-15-crown-5. <sup>b</sup> Bis(dibromobenzo)-18-crown-6.

ions (X = Cl, Br or I) is surrounded by one lone electron pair in addition to the six bonding pairs. Such AB<sub>6</sub>E systems should possess distorted, non-octahedral geometry with the lone-pair electrons pointing to the seventh position.<sup>12</sup> In the majority of known crystal structures, however, the ion has at least a centre of symmetry and octahedral or nearly octahedral geometry. It has been concluded that these ions are exceptions to the VSEPR rule. The possible role of the lone-pair electrons in such

ions has been discussed on the basis of structural and spectroscopic data, and theoretical calculations.<sup>3,13,14</sup> Abriel,<sup>15</sup> in an article on symmetry rules of the lone-pair electrons in TeX<sub>6</sub><sup>2-</sup> (X = Cl, Br, I), concludes: "(a) Packing of cations and anions fixes the point symmetry of the Te atom. (b) With a centre of symmetry for this Te position a nondistorted TeX<sub>6</sub><sup>2-</sup> ion results. Only small deviations from ideal *m*3̄*m* symmetry will be allowed when the point group is of lower symmetry than

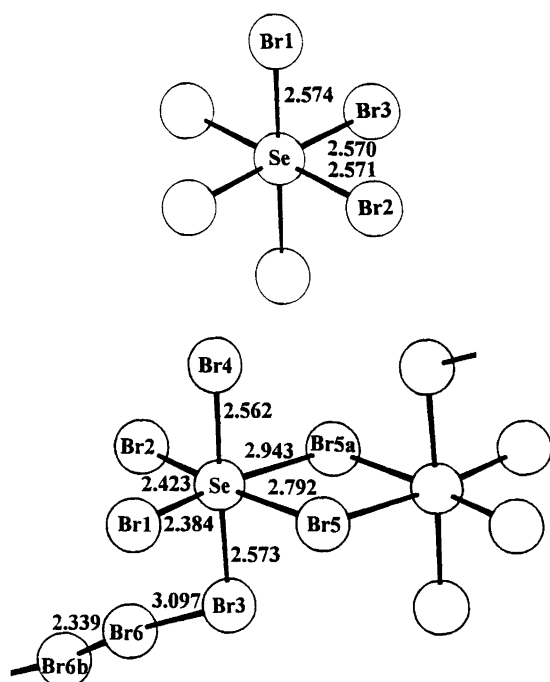


Fig. 1. Views of the  $\text{SeBr}_6^{2-}$  anion (above) and the  $\text{Se}_2\text{Br}_{10}^{2-}$  anion (below) as found in the phenyltrimethylammonium salts.

$m\bar{3}m$ . The octahedrally enforced dynamic structure is stabilized by this crystal field. (c) With a non-centrosymmetric point symmetry for the Te atom the  $\text{TeX}_6^{2-}$  group will be statically distorted.”

From theoretical studies on hexachlorides of selenium and tellurium and their dianions<sup>14</sup> it was, however, concluded that  $\text{SeCl}_6^{2-}$  and  $\text{TeCl}_6^{2-}$  ions possess the symmetry of a regular octahedron in the ground electron states.

In the  $[\text{Se}_2\text{Br}_{10} \cdot \text{Br}_2]^{2-}$  anion in compound **2** the two Se atoms are related by a centre of symmetry and so are the atoms of the  $\text{Br}_2$  molecule (Br6 and Br6b). The  $\text{Br}_2$  molecules are in bonding contacts with two axial positioned Br atoms of the  $\text{Se}_2\text{Br}_{10}$  unit, one of each Se atom, such that an endless chain of composition  $[\text{Se}_2\text{Br}_{10}^{2-} \cdot \text{Br}_2]_n$  is formed. The  $\text{Br} \cdots \text{Br} - \text{Br} \cdots \text{Br}$  unit has a  $\text{Br}-\text{Br}$  distance of 2.339(4) Å,  $\text{Br} \cdots \text{Br}$  distance of 3.097(2) Å, a  $\text{Br}-\text{Br} \cdots \text{Br}$  angle of 173.0(2)° and a  $\text{Se}-\text{Br} \cdots \text{Br}$  angle of 114.2(1)°. These contacts between the  $\text{Br}_2$  molecules and the dimeric ions do not seem to

influence the geometry of the  $\text{Se}_2\text{Br}_{10}$  unit, as the axial  $\text{Se}-\text{Br}$  bond with Br connected to  $\text{Br}_2$  is only slightly longer than the *trans* situated  $\text{Se}-\text{Br}$  bond. The present compound is a donor-acceptor adduct where bromine, complex-bonded to selenium, is donor and the bromine molecule is acceptor. As usual, the bond length in the acceptor is only a few hundredths of an ångström longer than in the free molecule, and the rather long distance between donor and acceptor represents a weak bond. As mentioned above, the participation of bromine as donor atom does not have an apparent influence on the length of the complex  $\text{Se}-\text{Br}$  bond. This is in contrast to what was found in (9) of Table 4, where the contacts seem to have a strong lengthening effect on the adjacent  $\text{Se}-\text{Br}$  bonds. In this compound the  $\text{Se}-\text{Br} \cdots \text{Br}-\text{Br}$  is nearly linear, while in the present structure  $\text{Se}-\text{Br} \cdots \text{Br}$  is 114.23(8)° and  $\text{Br} \cdots \text{Br}-\text{Br}$  is 173.00(19)°. The main deviations from octahedral symmetry of the present  $\text{SeBr}_6$  unit are: the terminal equatorial  $\text{Se}-\text{Br}$  bonds are 0.14–0.18 Å shorter than the axial bonds, the bridging bonds are 0.22–0.38 Å longer than the axial bonds, the angle between the terminal equatorial bonds is 95.27(8)°, the angle between the bridging bonds is 84.40(6)°, and the angles between *trans* situated bonds are 172.94(9)–177.41(10)°. For comparison the bond lengths of the known structures of  $[\text{Se}_2\text{Br}_{10}]^{2-}$  ions are listed in Table 5. *Trans* situated terminal and bridging bonds are listed on the same line. In all cases the shortest terminal equatorial bond has the longest bridging bond as the *trans* bonding partner. The asymmetry of the bridging bonds, assumed to indicate influence of the lone-pair electrons,<sup>1</sup> varies from 0.051 Å in (2) to 0.151 Å in (3). The axial bonds are identical in (1), very slightly different in (3), and differ by 0.147 Å in (2). Some further details of these structures will be discussed in a paper on analogous tellurium compounds.<sup>16</sup>

The dimensions of phenyltrimethylammonium ion are:  $\text{N}-\text{C}=1.489(4)\text{--}1.514(4)$  Å,  $\text{C}-\text{C}=1.376(5)\text{--}1.390(5)$  Å,  $\text{C}-\text{N}-\text{C}=107.6(3)\text{--}112.9(3)^\circ$ ,  $\text{C}-\text{C}-\text{C}=118.3(3)\text{--}121.3(3)^\circ$  in compound **1** and  $\text{N}-\text{C}=1.452(19)\text{--}1.481(19)$  Å,  $\text{C}-\text{C}=1.347(23)\text{--}1.404(20)$  Å,  $\text{C}-\text{N}-\text{C}=103.6(1.4)\text{--}113.6(1.3)^\circ$ ,  $\text{C}-\text{C}-\text{C}=116.4(1.9)\text{--}123.9(1.9)^\circ$  in compound **2**. In **1** each Br atom is surrounded by 5–8 C atoms from methyl and phenyl groups, at distances 3.615(4)–3.969(4) Å and the shortest  $\text{Br} \cdots \text{H}$  distance is 2.94 Å. In **2** there are 15

Table 5. Bond lengths (in Å) in decabromodiselenate(IV) ions.

No.	Compound	Equatorial bonds	Bridging bonds	Axial bonds	Se...Se distance	Ref.
(1)	$[(\text{C}_2\text{H}_5)_3\text{N}]_4[\text{Se}_2\text{Br}_{10}][\text{Se}_2\text{Br}_9]_2$	2.393(3) 2.433(4)	2.877(4) 2.755(4)	2.566(3)	4.239(4)	7
(2)	$[\text{C}_4\text{H}_{10}\text{NO}]_2[\text{Se}_2\text{Br}_{10}]$	2.370(2) 2.391(1)	2.923(1) 2.872(1)	2.503(2) 2.650(2)	4.243(2)	5
(3)	$[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_{2n}[\text{Se}_2\text{Br}_{10} \cdot \text{Br}_2]_n$	2.384(2) 2.423(2)	2.943(2) 2.792(2)	2.562(2) 2.573(2)	4.250(3)	This work

Br...C distances between 3.49 and 4.00 Å, and all Br atoms are involved. The shortest Br...H distance is 2.97 Å.

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## References

1. Krebs, B. and Ahlers, F.-P. *Adv. Inorg. Chem.* 35 (1990) 235.
2. Krebs, B. and Hein, M. *Z. Naturforsch., Teil B* 34 (1979) 1666.
3. Abriel, W. *Z. Naturforsch., Teil B* 42 (1987) 415.
4. Bonmann, S., Eidenschink, I. and Krebs, B. *Z. Kristallogr. Suppl. Nr. 5* (1992) 29.
5. Beckmann, I. *Ph. D. Thesis.* University of Münster, 1994.
6. Lührs, E. *Ph. D. Thesis.* University of Münster, 1987.
7. Ahlers, F.-P., *Ph. D. Thesis.* University of Münster, 1991.
8. Ahlers, F.-P., Lührs, E. and Krebs, B. *Z. Anorg. Allg. Chem.* 594 (1991) 7.
9. Born, P., Kniep, R. and Mootz, D. *Z. Anorg. Allg. Chem.* 451 (1979) 12.
10. Walker, N. and Stuart, D. *Acta Crystallogr., Sect. A* 39 (1983) 159.
11. Domenicano, A., Vaciago, A. and Coulson, C. A. *Acta Crystallogr., Sect. B* 31 (1975) 221.
12. Gillespie, R. J. and Hargittai, I. *The VSEPR Model of Molecular Geometry*, Allyn and Bacon, Boston 1991.
13. Abriel, W. and Zehnder, E.-J., *Z. Naturforsch. Teil B* 42 (1987) 1273.
14. Klobulowski, M. *Can. J. Chem.* 71 (1993) 141.
15. Abriel, W. *Acta Crystallogr., Sect. B* 42 (1986) 449.
16. Hauge S. and Marøy, K. *To be published.*

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