Acta Chemica Scandinavica, 1998: 52: 1104–1109
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Syntheses and Crystal Structures of Salts of Hexabromotetraselenate(I) and Hexabromoselenate(IV)bis{dibromodiselenate(I)}

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Hauge, S., Janickis, V. and Marøy, K., 1998. Syntheses and Crystal Structures of Salts of Hexabromotetraselenate(I) and Hexabromoselenate(IV)-bis{dibromodiselenate(I)}. Acta Chem. Scand. 52: 1104–1109. © Acta Chemica Scandinavica 1998.

The title compounds have been prepared from elemental selenium and bromine, and phenyltrimethylammonium bromide or benzyltrimethylammonium bromide. The crystal structures of $[C_6H_5(CH_3)_3N]_2[Se_4Br_6]$ (**1**), $[C_6H_5CH_2(CH_3)_3N]_2[Se_4Br_6]$ (**2**) and $[C_6H_5(CH_3)_3N]_2[SeBr_6(Se_2Br_2)_2]$ (**3**) were determined by X-ray methods. Crystals of **1** and **2** are monoclinic, space group $P2_1/c$ (No. 14) with $Z=2$ and $a=8.618(2)$, $b=12.914(2)$, $c=13.609(3)$ Å and $\beta=95.13(2)°$ for **1**, and $a=8.417(2)$, $b=12.673(3)$, $c=14.813(3)$ Å and $\beta=$for 97.06(3)° for **2**. The crystals of **3** are monoclinic, space group $P2_1/n$ (No. 14) with $Z=2$ and $a=8.683(2)$, $b=12.762(3)$, $c=16.340(3)$ Å, $\beta=104.29(3)°$. The anions of **1** and **2** consist of two Br–Se–Se–Br units bonded together by two Br atom bridges between the Se atoms in such a way that a chair-shaped, six-membered ring is formed and the Se–Br bonds of the Br–Se–Se–Br units are pointing out of the ring. The anion of **3** is a nearly regular $SeBr_6$ octahedron where two *trans*-positioned Br atoms each have a weak bond to one of the Se atoms in a Se_2Br_2 molecule.

Selenium and bromine form the binary compounds Se_2Br_2, $SeBr_2$ and $SeBr_4$. In addition Se_3Br_2 and Se_4Br_2 are formed by disproportion of Se_2Br_2. Crystal structures of Se_2Br_2 and $SeBr_4$ are well known;[1,2] both compounds exist in allotrope modifications. $SeBr_2$ has not been isolated. Both $SeBr_2$ and $SeBr_4$ make series of complexes with bromide; with divalent selenium the anions $SeBr_4^{2-}$,[3,4] $Se_2Br_6^{2-}$,[3,5] $Se_4Br_{14}^{2-}$,[6,7] $Se_3Br_8^{2-}$,[7–9] and $Se_5Br_{12}^{2-}$,[7] and with tetravalent selenium the anions $SeBr_6^{2-}$,[8,10,11] $Se_2Br_9^{-}$,[8,12] $Se_2Br_{10}^{2-}$,[11–13] and $Se_3Br_{13}^{-}$.[14]

Selenium reacts with bromine in acetonitrile, and when the Se/Br_2 ratio is 2.0 the product is mainly Se_2Br_2:

$$2Se + Br_2 \rightleftharpoons Se_2Br_2$$

However, the reaction is not quantitative, since both Se_2Br_2 and Br_2 are parts of the equilibrium:

$$2SeBr_2 \rightleftharpoons Se_2Br_2 + Br_2$$

The K value for the last reaction in acetonitrile is 0.014–0.14.[15,16] Other compounds, such as $SeBr_4$, Se_3Br_2 and Se_4Br_2, will also be minor parts in the equilibrium. By adding bromide to the solution, the possibility of obtaining a complex with monovalent selenium should be good, but which species will crystallise from the solution depends on the concentration equilibrium and solubilities. This work reports the first complexes of univalent selenium.

Experimental

Preparations. The present compounds are among a series prepared by reactions between elemental selenium and bromine in the presence of complex cations.[4,5]

Preliminary reactions were done to find out how the presence of bromide will influence the oxidation state of Se in a selenium–bromine mixture.

To 4 mmol (0.639 g) Br_2 in 20 g of acetonitrile were added 8 mmol (0.632 g) of selenium. The mixture was stirred at room temperature for 1 h and 0.036 g (6%) of undissolved selenium was isolated.

To the same amount of selenium, bromine and acetonitrile as above were added 4 mmol (0.865 g) of $[C_6H_5(CH_3)_3N]Br$. The mixture was treated as above, and 0.230 g (28%) undissolved selenium was isolated.

Determination of selenium was done by treating the sample with a sulfite solution, adding bromide and oxidising with bromine. Excess bromine was removed,

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and the amount of selenium was determined iodometrically. Bromide was determined by potentiometric titration with silver nitrate. Densities were measured by the method of flotation, using a mixture of trichloromethane and tribromomethane.

$[C_6H_5(CH_3)_3]_2[Se_4Br_6]$ (**1**). To 6.0 mmol (0.474 g) of selenium and 3.0 mmol (0.648 g) of phenyltrimethylammonium bromide in 8.0 g of acetonitrile were added 4.5 mmol (0.72 g) bromine. After being stirred and heated to 40 °C, the solution was clear, dark brown. After being set aside for 3 h in a refrigerator, 1.0 g of dark red crystals of $[C_6H_5(CH_3)_3N]_2[SeBr_6 \cdot (Se_2Br_2)_2]$ was isolated. The filtrate was placed overnight in a freezer at −22 °C. Next day 0.49 g of a mixture of dark red and bright red crystals was isolated. The dark red crystals were $[C_6H_5(CH_3)_3N]_2[SeBr_6 \cdot (Se_2Br_2)_2]$ and the bright red crystals were $[C_6H_5(CH_3)_3N]_2[Se_4Br_6]$. It was easy to separate the bright red crystals. Found: Se 28.55, Br 44.80. Calc. for $[C_6H_5(CH_3)_3N]_2[Se_4Br_6]$: Se 29.58, Br 44.90.

$[C_6H_5CH_2(CH_3)_3N]_2[Se_4Br_6]$ (**2**). To 6.0 mmol (0.474 g) of selenium in 4.0 g of acetonitrile were added 3.0 mmol (0.479 g) of bromine. The mixture was stirred and heated to 60 °C. Small amounts of selenium did not react. 3 mmol (0.691 g) of benzyltrimethylammonium bromide were added to the mixture, and the temperature was raised to 75 °C. Some selenium was filtered off. After being left at room temperature for 2 h, 0.55 g of thin brown plates were isolated. The filtrate was placed in refrigerator for 6 h, and 0.31 g more of the compound was isolated. Found: Se 28.52, Br 43.30. Calc. for $[C_6H_5CH_2(CH_3)_3]_2[Se_4Br_6]$: Se 28.82, Br 43.75.

$[C_6H_5(CH_3)_3N]_2[SeBr_6 \cdot (Se_2Br_2)_2]$ (**3**). To 6.0 mmol (0.474 g) of selenium and 2.4 mmol (5.19 g) of phenyltrimethylammonium bromide in 8 g of acetonitrile were added 4.8 mmol (0.767 g) of bromine. The mixture was stirred and heated until the solution was clear with a dark brown colour. After 2 h at room temperature 0.14 mmol (0.12 g) of phenyltrimethylammonium hexabromoselenate(IV), $[C_6H_5(CH_3)_3N]_2[SeBr_6]$, was isolated. The filtrate was again left at room temperature for 2 h, and 0.58 mmol (0.85 g) of dark red prisms was isolated. Found: Se 26,57, Br 53.80. Calc. for $[C_6H_5(CH_3)_3N]_2[SeBr_6(Se_2Br_2)_2]$: Se 26.93, Br 54.49.

X-Ray structure analyses. The determination of unit-cell dimensions and data collections were carried out on an Enraf-Nonius CAD4 diffractometer. Data reductions were performed by XCAD4;[17] the structures were solved by direct methods using SHELXS86[18] and refined by SHELXL93.[19] The crystal data, conditions for data collection, and refinements are summarised in Table 1. Atomic scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 in Ref. 20.

The numerical absorption corrections in all cases led to reduced R- and $\Delta(\rho)$-values, but for compounds **2** and **3** the values are still larger than expected. The reason may be inaccurate indexing or measurements of the dimensions, since the specimens used were cut from larger crystals.

The data for compound **1** were first collected at 263 K and refined smoothly to $R=0.042$ for $I>2\sigma(I)$, but the displacement parameters were generally extremely high and especially for the methyl carbon atoms. A new set of data were then collected at 112 K, but the displacement parameters were still very high for most atoms. We then prepared the benzyltrimethylammonium salt, and the data collected at 114 K for this compound resulted in normal displacement parameters for all atoms.

The hydrogen atoms were in all structures placed geometrically and refined using a riding model with isotropic thermal parameters equal to $1.3U(eq)$ for the atom to which they are attached. All non-hydrogen atoms were refined anisotropically.

Final atomic coordinates and equivalent isotropic displacement parameters are listed in Tables 2 and 3. Complete lists of coordinates, bond lengths and angles, and anisotropic displacement parameters are available from the authors.

Results and discussion

It was mentioned in the introduction that selenium and bromine form many binary compounds, and addition of bromide as reactant increases the number of variants. The complex anions also set up many equilibria by disproportion and association. From the preliminary experiment where selenium is mixed with bromine in acetonitrile in the molar ratio 2:1, a small amount of selenium was undissolved, showing that a little of the selenium is present in a higher oxidation state than +1. When bromide is present in the reaction mixture much more selenium is undissolved, showing that a larger part of the dissolved selenium has reacted to a higher oxidation state. In complexes the bromine/selenium ratio generally increases with growing oxidation state. It is therefore necessary to keep the concentration of bromide low if complexes of univalent selenium are wanted. In the present synthesis of $[C_6H_5(CH_3)_3N]_2[SeBr_6 \cdot (Se_2Br_2)_2]$, 6 mmol of selenium is mixed with 2.4 mmol of bromide and 4.8 mmol of bromine. If all the bromine reacts with selenium, the average oxidation state of selenium is +1.6, in accordance with the chemical formula. However, the first compound that crystallizes is $[C_6H_5(CH_3)_3N]_2[SeBr_6]$, showing an equilibrium in the solution involving anions with selenium at +4 and with selenium at lower oxidation states than +1.6. In the synthesis of $[C_6H_5(CH_3)_3N]_2[Se_4Br_6]$ the average oxidation state of selenium is +1.5 and the bromide concentration is 25% higher. The effect of lowering of the average oxidation state from 1.6 to 1.5 seems to be enough to prevent the crystallization of the $SeBr_6^{2-}$ ion, in spite of the increase in the bromide concentration.

Table 1. Crystal data and structure refinement.

Identification code	**1**	**2**	**3**
Empirical formula	$C_{18}H_{28}Br_6N_2Se_4$	$C_{20}H_{32}Br_6N_2Se_4$	$C_{18}H_{28}Br_{10}N_2Se_5$
Formula weight	1067.72	1095.74	1466.32
Temperature/K	112(2)	114(2)	109(2)
Wavelength/Å	0.710 69	0.710 69	0.710 69
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	8.618(2)	8.417(2)	8.683(2)
b/Å	12.914(2)	12.673(3)	12.762(3)
c/Å	13.609(3)	14.813(3)	16.340(3)
β/°	95.13(2)	97.06(3)	104.29(3)
Volume/Å^3	1508.5(5)	1568(5)	1754.7(6)
Z	2	2	2
D_c/g cm^{-3}	2.35	2.32	2.78
D_o/g cm^{-3} (293 K)	2.31	2.26	2.58
F(000)	992	1024	1340
Crystal size/mm	0.15 × 0.27 × 0.31	0.09 × 0.12 × 0.40	0.10 × 0.17 × 0.27
θ range/°	2.4–26.3	2.9–29.9	2.4–28.0
hkl limits	$h=-10\rightarrow10$	$h=0\rightarrow11$	$h=0\rightarrow11$
	$k=0\rightarrow16$	$k=0\rightarrow17$	$k=0\rightarrow16$
	$l=0\rightarrow16$	$l=-20\rightarrow20$	$l=-21\rightarrow20$
Intensity decay (%)	18.6	8.7	8.0
Absorption coeff./mm^{-1}	12.93	12.41	16.62
Correction for absorption	Numerical	Numerical	Numerical
T_{min}/T_{max}	0.043/0.180	0.238/0.356	0.064/0.231
Independent reflections	3056	4538	4235
No. with $I>2\sigma(I)$	2109	3507	2673
Data/parameters	2934/137	4538/148	4233/164
Weight, $P=(F_o^2+2F_c^2)/3$	$[\sigma^2(F^2)+(0.075P)^2+33.24P]^{-1}$	$[\sigma^2(F^2)+(0.022P)^2+0.91P]^{-1}$	$[\sigma^2(F^2)+(0.102P)^2+51.44P]^{-1}$
Extinction coefficient	0.0031(5)		0.0008(3)
Refinement on	F^2	F^2	F^2
Goodness-of-fit on F^2	1.043	1.048	1.099
R (F) [$I>2\sigma(I)$]	0.0559	0.0858	0.0537
R (F) (all data)	0.0996	0.1152	0.1127
WR (F^2) [$I>2\sigma(I)$]	0.1440	0.2419	0.1598
WR (F^2) (all data)	0.1726	0.2779	0.2031
Max. and min. Δρ/e Å^{-3}	1.27 and −2.07	4.32 (near Se) and −4.69	4.91 (near Se) and −3.96

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (in Å^2 × 10^3) for **1** and **2**.

	$[C_6H_5(CH_3)_3N]_2[Se_4Br_6]$ (**1**)				$[C_6H_5CH_2(CH_3)_3N]_2[Se_4Br_6]$ (**2**)			
Atom	x	y	z	U(eq)[a]	x	y	z	U(eq)[a]
Se(1)	780(2)	1623(1)	5644(1)	34(1)	624(1)	1599(1)	5549(1)	14(1)
Se(2)	2624(1)	377(1)	5502(1)	26(1)	2610(1)	390(1)	5483(1)	15(1)
Br(1)	1578(2)	2301(1)	7268(1)	52(1)	1245(1)	2277(1)	7082(1)	19(1)
Br(2)	4714(2)	1560(1)	4862(1)	40(1)	4479(1)	1537(1)	4701(1)	21(1)
Br(3)	1038(2)	−1142(1)	6307(1)	39(1)	1065(1)	−1165(1)	6349(1)	19(1)
N	3339(11)	5587(9)	6997(7)	37(3)	3305(9)	5634(6)	7257(5)	15(1)
C(1)	1964(20)	5564(28)	7586(11)	132(13)	2742(13)	5776(9)	8187(7)	26(2)
C(2)	4161(29)	6590(14)	7152(13)	90(8)	4321(12)	6527(8)	7056(8)	26(2)
C(3)	4475(22)	4749(14)	7379(18)	91(8)	4204(12)	4630(8)	7267(7)	24(2)
C(4)					1769(10)	5586(8)	6574(6)	18(2)
C(5)	2809(13)	5409(9)	5921(8)	28(2)	2094(11)	5407(7)	5591(6)	18(2)
C(6)	2419(20)	6241(12)	5329(11)	56(4)	2240(11)	6258(8)	5011(7)	19(2)
C(7)	1944(23)	6066(16)	4348(12)	80(7)	2295(14)	6075(8)	4106(7)	26(2)
C(8)	1802(18)	5083(14)	3965(10)	55(4)	2276(11)	5066(8)	3757(7)	21(2)
C(9)	2170(27)	4279(14)	4582(11)	83(7)	2186(12)	4203(8)	4336(7)	22(2)
C(10)	2684(27)	4437(13)	5558(11)	74(6)	2072(11)	4375(7)	5261(6)	18(2)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (in $Å^2 \times 10^3$) for **3**.

Atom	*x*	*y*	*z*	*U*(eq)[a]
Se(1)	0	5000	5000	11(1)
Se(2)	−1587(2)	6651(1)	1273(1)	19(1)
Se(3)	590(2)	5696(1)	1907(1)	19(1)
Br(1)	−1000(2)	5384(1)	3415(1)	16(1)
Br(2)	2903(2)	5205(1)	4925(1)	18(1)
Br(3)	−107(2)	6975(1)	5303(1)	18(1)
Br(4)	−3529(2)	5352(1)	834(1)	28(1)
Br(5)	2013(2)	5521(1)	856(1)	27(1)
N	253(12)	2402(8)	1762(7)	14(2)
C(1)	−873(18)	2775(12)	2261(10)	27(3)
C(2)	−469(17)	2685(14)	852(9)	29(3)
C(3)	331(16)	1236(10)	1845(9)	20(3)
C(4)	1868(17)	2865(10)	2061(8)	18(3)
C(5)	2359(15)	3318(10)	2852(8)	17(3)
C(6)	3918(15)	3682(10)	3119(8)	16(2)
C(7)	4937(18)	3631(11)	2593(9)	24(3)
C(8)	4436(16)	3168(11)	1799(9)	20(3)
C(9)	2924(15)	2776(10)	1533(8)	15(2)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond lengths (in Å), bond angles and torsion angles (in °) of the anions in **1** and **2**.

Compound	**1**	**2**
Se(1)–Se(2)	2.282(2)	2.2787(12)
Se(1)–Br(1)	2.419(2)	2.4238(13)
Se(1)–Br(3a)	3.025(2)	3.041(2)
Se(2)–Br(2)	2.572(2)	2.5250(14)
Se(2)–Br(3)	2.681(2)	2.7632(13)
Se(2)···Br(2b)	3.460(2)	3.4934(14)
Se(2)···B(3a)	3.951(2)	3.979(2)
Se(2)···Se(1a)	4.111(2)	3.8824(14)
Se(2)–Se(1)–Br(1)	100.92(7)	101.76(5)
Se(2)–Se(1)–Br(3a)	95.20(6)	95.79(4)
Br(1)–Se(1)–Br(3a)	163.56(7)	162.31(5)
Se(1)–Se(2)–Br(2)	97.14(6)	97.72(5)
Se(1)–Se(2)–Br(3)	95.56(6)	94.00(4)
Br(2)–Se(2)–Br(3)	166.18(6)	168.25(5)
Se(2)–Br(3)–Se(1a)	91.98(5)	83.82(4)
Se(1)–Se(2)···Br(2b)	176.16(6)	177.02(4)
Se(1)–Se(2)···Br(3b)	49.69(5)	49.48(3)
Se(1)–Se(2)···Se(1a)	89.80(6)	88.32(4)
Br(1)–Se(1)–Se(2)–Br(2)	−85.33(7)	−97.30(5)
Br(1)–Se(1)–Se(2)–Br(3)	89.20(7)	81.96(5)
Br(2)–Se(2)–Se(1)–Br(3a)	97.97(6)	84.93(4)
Br(3a)–Se(1)–Se(2)–Br(3)	−87.50(5)	−95.81(4)
Se(1)–Se(2)–Br(3)–Se(1a)	84.58(6)	84.60(4)
Se(2)–Br(3)–Se(1a)–Se(2a)	−84.24(6)	−86.58(49)

Symmetry transformations: (a) $-x, -y, 1-z$; (b) $1-x, -y, 1-z$.

During the synthetic work it was observed that if more than one compound crystallized from the same solution, there was usually a break between the crystallization of the different compounds.

The anions of the present three structures all contain the Se_2Br_2 unit, which is known from the structures of α- and β-Se_2Br_2.[1] The two $Se_4Br_6^{2-}$ ions resemble the β-Se_2Br_2 molecule. Views of these three structures are shown in Fig. 1, and a view of the $SeBr_6(Se_2Br_2)_2^{2-}$ anion is shown in Fig. 2. Bond lengths and angles of the anions are listed in Tables 4 and 5, and selected dimensions, including those of α- and β-Se_2Br_2, are listed in Table 6.

The $Se_4Br_6^{2-}$ ion is the first isolated complex of univalent selenium. In the crystal structure two Se_2Br_2 units are bonded together by two bromine atom bridges between selenium atoms, resulting in a chair-shaped, six-membered, centrosymmetric ring of four selenium and two bromine atoms. The Se–Se bonds are a little, but significantly, longer in the present structures than in α- and β-Se_2Br_2. The selenium atoms of the present compounds are acting as central atoms in asymmetric, nearly linear 3*c*–4*e* systems. The bond lengths of the individual 3*c*–4*e* systems are 2.419(2)/3.025(2) Å and 2.572(2)/2.681(2) Å in **1** and 2.424(1)/3.041(2) Å and 2.525(1)/2.763(1) Å in **2**. The longer bonds are to the bridging bromine atoms in the six-membered ring. In α- and β-Se_2Br_2 the Se–Br bonds are in the range 2.357(2)–2.369(1) Å.[1] The corresponding bonds

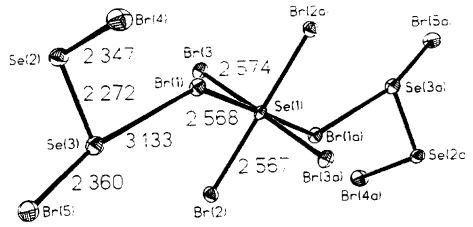

Fig. 2. View of the $SeBr_6(Se_2Br_2)_2^{2-}$ ion as found in the phenyltrimethylammonium salt.

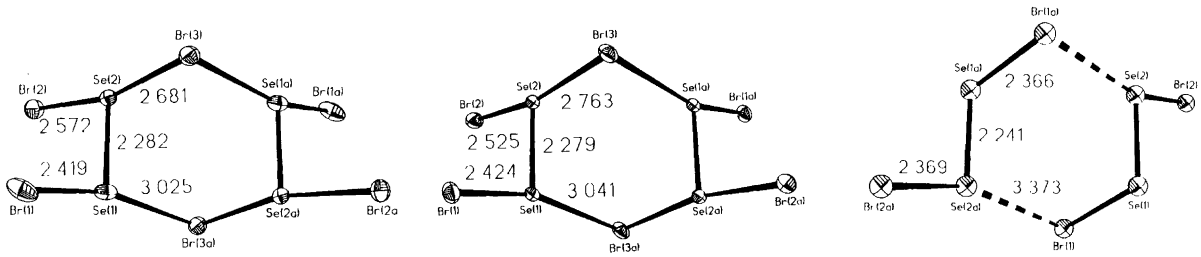

Fig. 1. View of the $Se_4Br_6^{2-}$ ion as found in the phenyltrimethylammonium salt (left) and the benzyltrimethylammonium salt (middle), and the Se_2Br_2 molecule as found in the β modification[1] (right).

Table 5. Bond lengths (in Å), bond angles and torsion angles (in °) of the anion in **3**.

Se(1)–Br(1)	2.5675(13)	Se(2)–Br(4)	2.347(2)
Se(1)–Br(2)	2.5673(14)	Se(3)–Br(5)	2.360(2)
Se(1)–Br(3)	2.5742(14)	Se(3)–Br(1)	3.133(2)
Se(2)–Se(3)	2.272(2)	Se(2)···Br(3b)	3.541(2)
Br(1)–Se(1)–Br(2)	91.37(5)	Se(3)–Se(2)–Br(4)	102.40(8)
Br(1)–Se(1)–Br(2a)	88.63(5)	Se(2)–Se(3)–Br(5)	104.22(7)
Br(1)–Se(1)–Br(3)	89.29(4)	Se(2)–Se(3)–Br(1)	87.03(6)
Br(1)–Se(1)–Br(3a)	90.71(4)	Br(5)–Se(3)–Br(1)	166.24(7)
Br(2)–Se(1)–Br(3)	89.53(4)	Se(1)–Br(1)–Se(3)	135.46(6)
Br(2)–Se(1)–Br(3a)	90.47(4)	Se(3)–Se(2)···Br(3b)	176.97(7)
Br(4)–Se(2)–Se(3)–Br(5)	97.49(8)		

Symmetry transformations: (a) $-x, 1-y, 1-z$; (b) $x-\frac{1}{2}, 1\frac{1}{2}-y, z-\frac{1}{2}$.

Table 6. Distances (in Å) and angles (in °) of Se_2Br_2 molecules and Se_2Br_2 units of other compounds.

	$Se_4Br_6^{2-}$ **1**	$Se_4Br_6^{2-}$ **2**	$Se_5Br_{10}^{2-}$ **3**	Se_2Br_2 **4**	β-Se_2Br_2 **5**
Se–Se	2.282(2)	2.279(1)	2.272(2)	2.258(2)	2.241(1)
Br–Se–Br–Se[a]	85.33(7)	97.31(5)	97.49(8)	85.0(1)	86.41(8)
Se–Br	2.419(2)	2.424(1)	2.347(2)	2.357(2)	2.366(1)
Se–Se–Br	100.92(7)	101.76(5)	102.40(8)	107.23(8)	103.86(5)
Se···Br	3.025(2)	3.041(2)			
Br–Se···Br	163.56(7)	162.31(5)			
Se–Br	2.572(2)	2.525(1)	2.360(2)		2.369(1)
Se–Se–Br	97.14(6)	97.72(5)	104.22(7)		104.51(5)
Se···Br	2.681(2)	2.763(1)	3.133(2)		3.373(1)
Br–Se···Br	166.18(6)	168.26(5)	166.24(7)		162.3
Ref.	This work	This work	This work	1	1

[a]Torsion angle.

in the present structures are considerably longer, 2.419(2)–2.572(2) Å, a pronounced effect of the 3*c*–4*e* systems. The Se–Se–Br(terminal) angles are in the range 97.14(6)–101.76(5)°. In accordance with observations in divalent and tetravalent selenium complexes the selenium atom which is involved in the most symmetrical 3*c*–4*e* system has the smallest angle, and when the two bonds are equal the angle is expected to be 90°. The largest observed differences between the two crystal structures are in the Se–Br–Se angles and some of the torsion angles. These differences might be a result of small differences in the packing caused by the different size of the cations. The Se(2)–Br(3) bond in **2** is longer than in **1**, whereas the *trans*-positioned Se(2)–Br(2) bond is shorter. A variation of this type is usual in 3*c*–4*e* bonds. At Se(1) there are only minor differences in angles and bond lengths between the two structures. In the direction of the Se–Se bond, Se(2) has a weak bond to Br(2) of an adjacent $Se_4Br_6^{2-}$ unit. The Se···Br distance is 3.460(2) Å in **1** and 3.493(2) Å in **2**, and the Se–Se···Br angle is 176.16(6)° in **1** and 177.02(4)° in **2**. Since Se(2) already is bonded to three atoms it can not accept more electrons and therefore probably acts as donor in this bond. Complex bonded divalent selenium has earlier been observed in this role.[6,7,21,22]

A comparison of Se–Br bond lengths in Se^{I}, Se^{II} and Se^{IV} complexes is not easy, since the asymmetric bonds show great variation, and bonds related through a centre of symmetry are not available for Se^{I}. For centrosymmetric tetravalent octahedral complexes the weighted mean value for 13 individual Se–Br bonds is 2.570(3) Å,[11] and when the asymmetry of a Br–Se–Br system is moderate, e.g. 2.483(3) and 2.670(3) Å,[23] the average is nearly the same, 2.577 Å. For centrosymmetric or near centrosymmetric square-planar divalent selenium complexes, the average Se–Br bond is 2.595 Å,[3,4] and also here the average of a moderate asymmetric system, e.g. 2.485(1) and 2.710(1) Å,[3] is nearly the same, 2.598 Å. The Br(2)–Se(2)–Br(3) system in **1** has Se–Br bonds 2.572(2) and 2.681(2) Å. This is an even more moderate asymmetry than in the former cases, and the bond of a symmetric system is expected to be only slightly less than the average value, 2.627 Å. One might conclude that in selenium complexes with bromine as ligands the length of the Se–Br bond decreases with increasing oxidation state of selenium, in accordance with the change in the coulomb attraction.

The complex ion $SeBr_6(Se_2Br_2)_2^{2-}$ is one of the most unique selenium complexes, built up of a nearly regular octahedral $SeBr_6^{2-}$ ion and using two of the bromine ligands as bridges to two Se_2Br_2 molecules. In the crystals, the tetravalent selenium lies in a centre of symmetry. The three crystallographically independent Se–Br bonds are equal within experimental error, with a

mean value of 2.570(4) Å, the same as that found earlier for $SeBr_6^{2-}$ ions.[11] The contact between Br(1) and Se(3) is probably a bond of the donor–acceptor adduct type, with Br(1) as donor and the Se_2Br_2 molecule as acceptor. Donor–acceptor adducts with bromine coordinated to Se^{IV} as donor have been observed earlier, but then with a bromine molecule as acceptor. In $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10}\cdot Br_2]_n$[11] the Se–Br–$Br_2$ angle is 114.23(8)°, with Se–Br bond length of 2.573(2) Å and a Br–Br_2 bond length of 3.097(2) Å. In $[(CH_3)_3HN]_{2n}[SeBr_6\cdot Br_2]_n$[10] the angle is 163.5(1)° and the bond lengths are 2.678(3) and 2.987(3) Å. In the first case the acceptor, Br_2, does not have an apparent influence on the length of the complex Se–Br bond. In the second case the Se–Br–Br_2 string is much more linear and the influence on the complex bond is obvious; the Se–Br bond is lengthened by 0.1 Å. In the present crystal structure the angle is 135.46(6)° and no influence on the complex bond is observed. It seems that the acceptor has to be co-linear with Br–Se–Br to have an influence on the Se–Br bond, and the influence is hardly detected when Se is situated in a centre of symmetry.

The Se_2Br_2 parts of the structure show a great resemblance to the structures of α- and β-Se_2Br_2, and $Se_4Br_6^{2-}$. However, β-Se_2Br_2 and $Se_4Br_6^{2-}$ both form six-membered rings, whereas the Se_2Br_2 parts of this ion have more open structures. It is mentioned above that the Se_2Br_2 parts are acceptors in a donor–acceptor adduct. In the two other adducts referred to, the two bromine atoms of the acceptor and the bromine donor are nearly linear. In the present compound the corresponding angle, Br(5)–Se(3)–Br(1), is 166.24(7)°. As usual, the bond within the acceptor is only a little affected by the contact, and the bond between the donor and the acceptor is long, 3.133(2) Å. Since Br(4) has no contact with any other atom than Se(2) and there is no contact to Se(2) *trans* to the Se(2)–Br(4) bond, this bond, 2.347(2) Å, may be regarded as covalent, indicating a covalent radius of about 1.21 Å for Se^{I}. The Se–Se bond lengths of the monovalent selenium compounds listed in Table 6 are shorter than the covalent Se–Se bond, 2.32 Å,[24] or 2.42 Å if the radius from above is used, and probably have some double bond character.

The dimensions of the cations of the present structures do not deviate from the usual values.

Acknowledgements. This work was supported by The Research Council of Norway.

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Received January 30, 1998.