

# Crystal Structures of Phenyltrimethylammonium Salts of Hexabromodiselenate(II), $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_6]$ , Hexachlorodiselenate(II), $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Cl}_6]$ , and a Mixed Bromo/chlorodiselenate(II), $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_5\text{Cl}]$

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Hauge, S., Janickis, V. and Marøy, K., 1998. Crystal Structures of Phenyltrimethylammonium Salts of Hexabromodiselenate(II),  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_6]$ , Hexachlorodiselenate(II),  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Cl}_6]$ , and a Mixed Bromo/chlorodiselenate(II),  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_5\text{Cl}]$ . – Acta Chem. Scand. 52: 435–440. © Acta Chemica Scandinavica 1998.

The title compounds were prepared from elemental selenium and halogen and phenyltrimethylammonium halide. The crystal structures of  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_6]$  (**1**),  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_5\text{Cl}]$  (**2**) and  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Cl}_6]$  (**3**) have been determined by X-ray methods. Crystals of **1** and **2** are monoclinic, space group  $P2_1/c$  with  $Z=4$  and  $a=9.366(2)$ ,  $b=10.095(2)$ ,  $c=28.748(6)$  Å,  $\beta=91.54(3)^\circ$  for **1**, and  $a=9.371(2)$ ,  $b=10.054(2)$ ,  $c=28.685(6)$  Å,  $\beta=91.99(3)^\circ$  for **2**. Crystals of **3** are monoclinic, space group  $P2_1/n$  with  $Z=2$  and  $a=9.086(2)$ ,  $b=10.306(2)$ ,  $c=14.110(3)$  Å,  $\beta=96.89(3)^\circ$ . The  $\text{Se}_2\text{X}_6^{2-}$  ions consist of two edge-sharing distorted  $\text{SeX}_4$  squares. The terminal bonds are 2.404(2)–2.439(2) Å in **1** and 2.260(2)–2.261(2) Å in **3**, whereas the bridging bonds are 2.792(2)–2.899(2) Å in **1** and 2.590(4)–2.899(4) Å in **3**. In **2** each halogen position is partly occupied by bromine and partly by chlorine, the content of chlorine in one position varying from 7 to 28%. The observed effect on bond lengths by replacing some of the bromine by chlorine is small.

The  $\text{Se}_2\text{Br}_6^{2-}$  ion is known from the crystal structure of the tetraphenylphosphonium salt;  $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Se}_2\text{Br}_6]$ .<sup>1</sup> It is planar and consists of two edge-sharing distorted  $\text{SeBr}_4$  squares, and so being of the simple binuclear type of hexahalodichalcogenates(II) which is isoelectronic to  $\text{I}_2\text{Cl}_6$ . In  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Se}_2\text{Br}_4(\text{SCN})_2]$ ,<sup>2,3</sup> two of the terminal Br atoms are replaced by SCN groups, and in  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{X}_2(\text{SCN})_4]$ <sup>4</sup> and  $[(\text{CH}_3)_3\text{HN}]_2[\text{Se}_2\text{X}_2(\text{SCN})_4]$ <sup>4</sup> ( $\text{X}=\text{Cl}$  or  $\text{Br}$ ) all terminal X atoms are replaced by SCN groups. We wanted to look into the possibility of making similar complexes in which one or more of the Br ligands are exchanged with another halide. We report here the crystal structures of  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_6]$  (**1**),  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_5\text{Cl}]$  (**2**) and  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Cl}_6]$  (**3**).

## Experimental

**Preparations.** The compounds were prepared by reactions between elemental selenium and halogen in the presence

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of phenyltrimethylammonium halide. In the cases where Se and  $\text{Br}_2$  are used in a molar ratio 1:1 and with various amounts of  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]\text{Br}$ , the following compounds have been isolated and identified by X-ray methods:  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]$ ,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_4]$ ,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_4] \cdot [\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]\text{Br}$ ,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_6]$ ,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_4\text{Br}_6]$ ,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_5\text{Br}_{10}]$  and  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_4\text{Br}_{14}]$ . The formation of the different compounds depends on, in addition to the amount of  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]\text{Br}$ , the temperature of reaction and crystallisation. In most cases there is an equilibrium between different anions in the mother liquid, and the compounds are isolated by fractional crystallisation. More details about the synthetic work will be published in a separate article.

$[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_6]$  (**1**). Crystals of this composition were obtained after crystallisation of bis(phenyltrimethylammonium) tetrabromoselenate<sup>5</sup> prepared by reaction between selenium and bromine in acetonitrile and in the presence of phenyltrimethylammonium brom-

Table 1. Crystal data and structure refinement.

	<b>1</b>	<b>2</b>	<b>3</b>
Identification code	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>18</sub> H <sub>28</sub> Br <sub>6</sub> N <sub>2</sub> Se <sub>2</sub>	C <sub>18</sub> H <sub>28</sub> Br <sub>5</sub> ClN <sub>2</sub> Se <sub>2</sub>	C <sub>18</sub> H <sub>28</sub> Cl <sub>6</sub> N <sub>2</sub> Se <sub>2</sub>
Formula weight	909.80	865.34	643.04
Temperature/K	105(2)	93(2)	114(2)
Wavelength/Å	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	9.366(2)	9.371(2)	9.086(2)
<i>b</i> /Å	10.095(2)	10.054(2)	10.306(2)
<i>c</i> /Å	28.748(6)	28.685(6)	14.110(3)
β/°	91.54(3)	91.99(3)	96.89(3)
Volume/Å <sup>3</sup>	2717.0(9)	2700.8(9)	1311.7(5)
<i>Z</i>	4	4	2
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	2.224	2.128	1.628
<i>D</i> <sub>obs</sub> /g cm <sup>-3</sup>	2.15 (293 K)	2.00 (293 K)	1.59 (293 K)
<i>F</i> (000)	1712	1640	640
Crystal size/mm	0.19 × 0.23 × 0.25	0.10 × 0.18 × 0.18	0.15 × 0.15 × 0.40
θ-Range/°	2.4–28.1	1.4–24.0	2.8–26.3
Intensity decay (%)	18.6	27.8	4.0
Absorption coefficient/mm <sup>-1</sup>	11.55	10.24	3.44
Correction for absorption	Numerical	Empirical, ψ-scan	Empirical, ψ-scan
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.091/0.194	0.060/0.098	0.065/0.100
Independent reflections	4403	4233	2656
No. with <i>I</i> > 2σ( <i>I</i> )	3541	2277	1550
Data/restraints/parameters	5437/0/259	4233/6/272	2655/0/129
Weight, <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3	[σ <sup>2</sup> ( <i>F</i> <sup>2</sup> ) + (0.072 <i>P</i> ) <sup>2</sup> + 5.780 <i>P</i> ] <sup>-1</sup>	[σ <sup>2</sup> ( <i>F</i> <sup>2</sup> ) + (0.052 <i>P</i> ) <sup>2</sup> ] <sup>-1</sup>	[σ <sup>2</sup> ( <i>F</i> <sup>2</sup> ) + (0.077 <i>P</i> ) <sup>2</sup> + 10.317 <i>P</i> ] <sup>-1</sup>
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.222	0.970	1.126
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )]	0.0595	0.0671	0.0627
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.1510	0.1130	0.1515
Max. and min. Δρ/e Å <sup>-3</sup>	1.54 and -2.48	1.70 and -0.91	3.42 (near Se) and -0.73

ide. The filtrate after isolation of the main product was kept in an open beaker at -22 °C, whereby brown elongated prisms of compound **1** crystallised. Found: Se 16.72, Br 52.98. Calc. for [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[Se<sub>2</sub>Br<sub>6</sub>]: Se 17.36, Br 52.70.

[C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[Se<sub>2</sub>Br<sub>5</sub>Cl] (**2**). Crystals of this composition were obtained in the same way as for **1**, by replacing phenyltrimethylammonium bromide by chloride. Found: Se 19.07. Calc. for [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[Se<sub>2</sub>Br<sub>5</sub>Cl]: Se 18.25.

[C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[Se<sub>2</sub>Cl<sub>6</sub>] (**3**). 50 mmol (8.55 g) of phenyltrimethylammonium chloride were dissolved in a mixture of 10 g of concentrated hydrochloric acid and 10 g of acetonitrile. To the solution was added 50 mmol (3.95 g) of selenium. The suspension was chilled by ice water, stirred, and 50 mmol of chlorine gas were added. A yellowish precipitate was formed. The suspension was filtered, and the precipitate was washed with cold acetonitrile. Acetonitrile (15 g), at 45 °C, was used to extract the precipitate, and the solution was kept in a fridge overnight. The yellow-red crystals were washed with a small volume of acetonitrile followed by dichloromethane, and dried. The isolation procedure was carried out in argon gas, and 1.80 g were isolated. Found: Cl 32.83. Calc. for [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[Se<sub>2</sub>Cl<sub>6</sub>]: Cl 33.08.

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

Enraf-Nonius CAD4 diffractometer. The structures were solved by direct methods using SHELXS86,<sup>6</sup> and refinement and drawing by SHELXL93.<sup>7</sup> 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. 8.

In the structure of **2** each halogen position is mainly occupied by Br and partly by Cl. In each case Br and Cl were put into the same position and their individual occupancy factors refined by assuming a total of 1. An attempt was made to locate separate Cl positions from the difference Fourier synthesis, but without success. For **2** an extinction parameter *x* was refined by least squares, where *F*<sub>c</sub> was multiplied by *k*[1 + 0.001*x* × *F*<sub>c</sub><sup>2</sup> × λ<sup>3</sup>/sin(2θ)]<sup>-1/4</sup>, where *k* is the overall scale factor and *x* was found to be 2.3(9) × 10<sup>-4</sup>. In **3** the [Se<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> anion is situated on a centre of symmetry, but the bridging Cl atom was split into two positions, Cl(3) and Cl(4). The occupancy factors of these atoms were refined at an early stage to 0.502 and 0.482, respectively, keeping the sum equal to 1, and were then both fixed at 0.5. They were refined isotropically and the distance between them was found to be 0.703(5) Å. The hydrogen atoms were placed geometrically in all structures and refined using a riding model with isotropic thermal parameters equal to 1.3*U*(eq) for the atom to which they are attached. All non-hydrogen atoms, except Cl(3) and Cl(4) of **3**, were refined anisotropically.

Final atomic coordinates and equivalent isotropic displacement parameters are listed in Tables 2 and 3. Lists

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

Atom	[C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>3</sub> N] <sub>2</sub> Se <sub>2</sub> Br <sub>6</sub> ( <b>1</b> )				[C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>3</sub> N] <sub>2</sub> Se <sub>2</sub> Br <sub>5</sub> Cl ( <b>2</b> )			
	x	y	z	U(eq) <sup>a</sup>	x	y	z	U(eq) <sup>a</sup>
Se(1)	2233(1)	-3631(1)	3995(1)	15(1)	2271(2)	-3629(1)	3988(1)	25(1)
Se(2)	2084(1)	207(1)	3514(1)	15(1)	2079(2)	216(1)	3532(1)	27(1)
Br(1)	4030(1)	-4733(1)	4479(1)	19(1)	4072(2)	-4712(2)	4474(1)	31(1)
Br(2)	387(1)	-5290(1)	4116(1)	27(1)	473(2)	-5311(2)	4102(1)	42(1)
Br(3)	361(1)	-2157(1)	3384(1)	19(1)	390(2)	-2172(1)	3366(1)	31(1)
Br(4)	4188(1)	-1593(1)	3854(1)	21(1)	4207(2)	-1574(2)	3855(1)	32(1)
Br(5)	281(1)	1562(1)	3127(1)	24(1)	304(2)	1560(2)	3129(1)	37(1)
Br(6)	3729(1)	1998(1)	3658(1)	23(1)	3736(2)	1998(2)	3661(1)	38(1)
N(1)	8175(10)	-1767(10)	4741(4)	18(2)	8141(12)	-1799(10)	4721(4)	31(3)
C(11)	7581(16)	-2686(13)	4379(6)	36(4)	7630(18)	-2666(13)	4329(6)	57(6)
C(12)	7656(15)	-2195(15)	5204(5)	35(4)	7544(17)	-2305(16)	5167(6)	66(6)
C(13)	9769(13)	-1884(13)	4764(5)	21(3)	9737(14)	-1911(14)	4775(5)	40(4)
C(14)	7746(12)	-350(12)	4641(4)	14(2)	7784(15)	-360(13)	4627(4)	26(3)
C(15)	6958(13)	360(13)	4947(5)	22(3)	6967(14)	343(15)	4942(5)	33(4)
C(16)	6594(14)	1679(13)	4842(5)	26(3)	6603(16)	1635(14)	4852(5)	35(4)
C(17)	7029(15)	2231(14)	4436(5)	28(3)	7039(16)	2248(14)	4447(6)	42(4)
C(18)	7814(15)	1514(14)	4131(5)	26(3)	7837(17)	1564(13)	4130(5)	39(4)
C(19)	8183(13)	223(13)	4230(4)	19(3)	8171(15)	260(14)	4220(4)	31(4)
N(2)	3468(11)	4299(10)	2477(4)	15(2)	3447(12)	4281(11)	2462(4)	27(3)
C(21)	2247(13)	4730(14)	2774(5)	22(3)	2230(14)	4710(14)	2764(4)	32(4)
C(22)	3197(14)	2871(12)	2329(5)	25(3)	3167(15)	2874(12)	2315(4)	33(4)
C(23)	3441(14)	5143(14)	2047(5)	25(3)	3396(16)	5163(13)	2033(4)	36(4)
C(24)	4883(12)	4391(12)	2726(4)	15(2)	4886(14)	4375(12)	2709(4)	18(3)
C(25)	6083(12)	3967(13)	2479(5)	17(3)	6073(15)	3960(12)	2468(5)	27(4)
C(26)	7415(14)	4049(13)	2688(4)	21(3)	7392(16)	4052(14)	2700(5)	37(4)
C(27)	7577(15)	4544(13)	3140(5)	25(3)	7601(15)	4536(14)	3140(5)	32(4)
C(28)	6358(15)	4971(13)	3371(5)	25(3)	6356(17)	4943(14)	3367(5)	41(4)
C(29)	5015(14)	4905(13)	3163(4)	20(3)	5013(16)	4865(11)	3162(4)	28(4)

<sup>a</sup>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  $\text{\AA}^2 \times 10^3$ ) for **3**.

Atom	x	y	z	U(eq) <sup>a</sup>
Se	218(1)	8153(1)	5355(1)	38(1)
Cl(1)	2015(2)	7006(3)	6231(2)	48(1)
Cl(2)	-1443(3)	6518(3)	5347(2)	53(1)
Cl(3)	-2105(4)	9966(4)	4662(3)	31(1)
Cl(4)	-1907(5)	9510(4)	4329(3)	34(1)
N	-890(7)	4441(7)	7783(5)	34(2)
C(1)	-756(10)	3545(10)	8644(6)	43(2)
C(2)	271(9)	4038(11)	7173(7)	45(2)
C(3)	-574(10)	5824(10)	8111(8)	49(3)
C(4)	-2435(9)	4352(9)	7268(6)	35(2)
C(5)	-3585(10)	4777(10)	7759(6)	41(2)
C(6)	-5027(10)	4737(10)	7311(7)	46(2)
C(7)	-5318(10)	4274(10)	6384(7)	48(3)
C(8)	-4165(10)	3857(10)	5915(7)	43(2)
C(9)	-2710(10)	3904(9)	6353(6)	38(2)

<sup>a</sup>U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

of anisotropic temperature factors, hydrogen coordinates and least squares planes are available from the authors.

## Results and discussion

Selected bond lengths and angles are listed in Tables 4 and 5, and a view of the anion of compound **1** is shown in Fig. 1.

Compound **2** was prepared to find out if it is possible to replace one or more of the bromine atoms in the anion known from the crystal structure of [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]<sub>2</sub>[Se<sub>2</sub>Br<sub>6</sub>]<sup>4-</sup> by chlorine, whereas compounds **1** and **3** were prepared to compare dimensions of the mixed halide ion with dimensions of pure, and hopefully isomorphous, bromine and chlorine compounds. A similar replacement of bromine by thiocyanate has been successful. In [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>[Se<sub>2</sub>Br<sub>4</sub>(SCN)<sub>2</sub>]<sup>2,3</sup> two of the terminal Br atoms are replaced by SCN groups, and in [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[Se<sub>2</sub>X<sub>2</sub>(SCN)<sub>4</sub>]<sup>4</sup> and [(CH<sub>3</sub>)<sub>3</sub>HN]<sub>2</sub>[Se<sub>2</sub>X<sub>2</sub>(SCN)<sub>4</sub>]<sup>4</sup> all four terminal X atoms are replaced by SCN groups. We have also prepared the mixed halide tellurium compounds [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2n</sub>[Te<sub>2</sub>Cl<sub>10</sub>·Br<sub>2</sub>]<sub>n</sub> and [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>4n</sub>[Te<sub>2</sub>Cl<sub>10</sub>][Te<sub>2</sub>Cl<sub>11</sub>·I]<sub>n</sub>.<sup>12</sup>

The anion of compound **2** has the overall formula Se<sub>2</sub>Br<sub>5</sub>Cl<sup>2-</sup>, but the structure is disordered with mainly Br and a smaller part of Cl in each halogen position. The relative populations of Br/Cl are given in square brackets in Table 4. The highest population of Cl is found in one bridging atom, X(4), and one terminal atom, X(5), *trans*-positioned to one another. This is different from the mixed Br/SCN compounds<sup>2,4</sup> where only terminal Br atoms are replaced by SCN groups. Relative to the pure selenium–bromine bonds the observed selenium–halogen bonds are somewhat reduced by the Cl content, but to a lower degree than expected,

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

	<b>1</b>	<b>2<sup>a</sup></b>		<b>1</b>	<b>2</b>
Se(1)–Br(1)	2.425(2)	2.410(2) [88/12]	Br(1)–Se(1)⋯Br(1a) <sup>b</sup>	153.82(8)	153.57(9)
Se(1)–Br(2)	2.439(2)	2.418(2) [88/12]	Br(1)–Se(1)–Br(2)	95.03(6)	94.78(7)
Se(1)–Br(3)	2.865(2)	2.866(2) [93/7]	Br(1)–Se(1)–Br(4)	88.49(5)	88.16(7)
Se(1)–Br(4)	2.792(2)	2.784(2) [72/28]	Br(2)–Se(1)–Br(4)	175.81(6)	176.40(8)
Se(2)–Br(3)	2.899(2)	2.905(2) [93/7]	Br(1)–Se(1)–Br(3)	173.66(7)	173.47(8)
Se(2)–Br(4)	2.834(2)	2.819(2) [72/28]	Br(2)–Se(1)–Br(3)	91.11(5)	91.43(7)
Se(2)–Br(5)	2.421(2)	2.408(2) [73/27]	Br(4)–Se(1)–Br(3)	85.45(5)	85.70(6)
Se(2)–Br(6)	2.404(2)	2.391(2) [80/20]	Br(6)–Se(2)–Br(5)	95.19(6)	95.02(8)
Se(1)⋯Se(2)	4.115(2)	4.083(2)	Br(6)–Se(2)–Br(4)	89.21(6)	88.82(7)
Br(1)⋯Br(1a) <sup>a</sup>	3.501(3)	3.481(2)	Br(5)–Se(2)–Br(4)	172.06(7)	170.22(8)
			Br(6)–Se(2)–Br(3)	173.24(6)	172.53(8)
			Br(5)–Se(2)–Br(3)	91.54(6)	91.27(7)
			Br(4)–Se(2)–Br(3)	84.04(5)	84.34(6)
			Se(1)–Br(3)–Se(2)	91.10(5)	90.07(6)
			Se(1)–Br(4)–Se(2)	94.02(5)	93.56(7)

<sup>a</sup>The relative populations of Br/Cl are given in square brackets. <sup>b</sup>Symmetry transformation (a):  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ .

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

Se–Cl(1)	2.260(2)	Se–Cl(4)	2.666(4)
Se–Cl(2)	2.261(3)	Se–Cl(4a)	2.862(5)
Se–Cl(3)	2.899(4)	Se⋯Se(a)	3.944(2)
Se–Cl(3a)	2.590(4)	Cl(3)⋯Cl(4)	0.703(5)
Se–Cl(3)–Se(a)	91.70(12)	Cl(1)–Se–Cl(3)	166.04(13)
Se–Cl(4)–Se(a)	90.96(13)	Cl(2)–Se–Cl(3a)	179.15(11)
Cl(2)–Se–Cl(1)	92.92(10)	Cl(2)–Se–Cl(4)	87.09(12)
Cl(2)–Se–Cl(3)	91.17(11)	Cl(4)–Se–Cl(4a)	89.03(11)
Cl(3)–Se–Cl(3a)	88.30(13)	Cl(1)–Se–Cl(4a)	90.91(11)
Cl(1)–Se–Cl(3a)	87.76(11)	Cl(1)–Se–Cl(4)	179.72(13)
		Cl(2)–Se–Cl(4a)	166.67(13)

Symmetry transformations (a):  $-x, 2 - y, 1 - z$ .

and there is no good relationship between bond length and Cl content.

The dimensions of  $\text{Se}_2\text{X}_6^{2-}$  anions are given in Table 6. *Trans*-situated terminal and bridging bonds are listed on the same line. For (2), (3) and (4), where the anions are without symmetry elements, lines 1 and 3 contain data for Se(1), and lines 2 and 4 data for Se(2) (Fig. 1). The bonds of the nearly linear X–Se–X systems are of the three-centre, four-electron ( $3c-4e$ ) type with only one occupied bonding orbital. This electronic system, leading

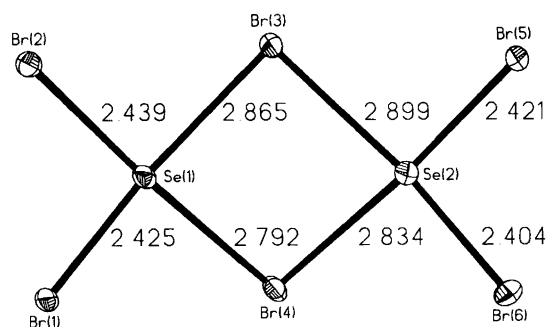


Fig. 1. View of the  $\text{Se}_2\text{Br}_6^{2-}$  anion as found in the phenyl-trimethylammonium salt (**1**).

to weak and long bonds, is easily polarisable and so easily influenced by interionic contacts and crystal fields. The two bonds are also easily influenced by each other in such a way that if one is elongated by some reason, the *trans*-situated bond is shortened. All terminal bonds are longer than the sum of the covalent radii, and all bridging bonds are considerably longer than the terminal bonds.

The anions presented in Table 6 can be looked upon as a result of nucleophilic attack of halide on selenium along the Se–X bonds of  $\text{SeX}_2$  molecules. One halide ion attacks the selenium atoms of two  $\text{SeX}_2$  molecules, and each selenium atom is attacked by two halide ions and so forming a stable four-membered ring. From the molecular structure of  $\text{SeCl}_2$  determined by electron diffraction<sup>14</sup> the Se–Cl bonds are 2.157(3) Å and the Cl–Se–Cl angle is 99.6(5)°. The  $\text{SeCl}_2$  parts of the  $\text{Se}_2\text{Cl}_6^{2-}$  ions are easily recognised, with bond lengths increased by 0.062–0.134 Å and bond angles decreased by 3.7–6.7°. From electron diffraction<sup>15</sup> and photoelectron<sup>16</sup> studies of  $\text{SeBr}_2$  similar changes of this unit are found in the  $\text{Se}_2\text{Br}_6^{2-}$  ions. The anions listed in the table represent intermediate states in the exchange reactions. The strength of the nucleophilic attack on selenium is here somewhat reduced, because each halide ion attacks two selenium atoms, and the linear X–Se–X systems will be asymmetric, with bridging bonds considerably longer than the terminal bonds.

Compounds (**1**) and (**2**) of Table 6, both of which are pure Br compounds, show some striking differences. In the centrosymmetric anion of (**1**) there is a pronounced asymmetry in the bonding system, the two terminal bonds differing by 0.086 Å and the two bridging bonds by 0.177 Å. In (**2**) these differences are reduced to maxima of 0.035 Å for the four terminal bonds and 0.107 for the four bridging bonds. The reason for this asymmetry, which occurs in several dihalogen bridged chalcogen(II) and chalcogen(IV) compounds,<sup>1,12,13</sup> is not clear. It was pointed out for (**1**), where the asymmetry

Table 6. Bond lengths (in Å) and angles (in °) in  $\text{Se}_2\text{Br}_6^{2-}$  and  $\text{Se}_2\text{Cl}_6^{2-}$  ions.

No.	Compound	Terminal bonds	Bridging bonds	X–Se–X <sup>a</sup> angle	Se···Se distance	Dihedral angle <sup>b</sup>	Ref.
(1)	$[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Se}_2\text{Br}_6]$	2.399(1) 2.485(1)	2.887(1) 2.710(1)	95.24(2)	4.100(1)	0	1
(2)	$[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_6]$	2.425(2) 2.404(2) 2.439(2) 2.421(2)	2.865(2) 2.899(2) 2.792(2) 2.834(2)	95.03(6) 95.19(6)	4.115(2)	22.33(5)	This work
(3)	$[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_5\text{Cl}]$	2.410(2) 2.391(2) 2.418(2) 2.408(2)	2.866(2) 2.905(2) 2.784(2) 2.819(2)	94.78(7) 95.02(8)	4.083(1)	22.55(5)	This work
(4)	$[\text{Se}_4\text{N}_3]_2[\text{Se}_2\text{Cl}_6]$	2.231(4) 2.219(4) 2.239(4) 2.270(4)	2.766(6) 2.827(6) 2.815(5) 2.688(5)	95.5(2) 95.7(2)	4.084	29.9	9
(5)	$[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Se}_2\text{Cl}_6]$	2.254(1) 2.291(1)	2.739(1) 2.620(1)	94.30(3)	3.938(1)	0	10
(6)	$[(\text{CH}_3)_3\text{SiN}(\text{H})\text{P}(\text{CH}_3)_3]_2[\text{Se}_2\text{Cl}_6]$	2.268(3) 2.268(4)	2.717(3) 2.752(4)	95.9(2)	4.071	0	11
(7)	$[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Cl}_6]$	2.260(2) 2.261(3) 2.261(3) 2.260(2)	2.899(4) 2.590(4) 2.862(5) 2.666(4)	92.9(1) 92.9(1)	3.944(2)	0	This work

<sup>a</sup>Terminal X atoms. <sup>b</sup>Angle between Se(1)X<sub>4</sub> and Se(2)X<sub>4</sub> planes.

is relatively large, that it may be initiated by interionic halogen–halogen contacts. However, in this case all terminal Br atoms have a closest interionic Br neighbour at a distance 3.752(1) Å, whereas in (2), with smaller asymmetry, only one of the terminal Br atoms has a short interionic contact, and this is even shorter, 3.586 Å. So one would expect a larger effect in the latter case. In the discussion of (5) it was pointed out that the  $\text{Se}_2\text{Cl}_6^{2-}$  ions, well separated by the large  $(\text{C}_6\text{H}_5)_4\text{P}^+$  cations, have no interionic Cl···Cl contacts below 4.4 Å, and still there is a pronounced asymmetry in the bridging system. One possible reason, also mentioned for (1) and (5), is the packing effect, but this may be difficult to verify. The planarity is also different in the two Br compounds. In (1) the maximum deviation of atoms from the  $\text{Se}_2\text{Br}_6$  plane is 0.03 Å only, whereas in (2) the maximum deviation of atoms from the two individual  $\text{SeBr}_4$  planes are 0.05 and 0.09 Å, and the angle between the two planes is 22.6°. In the centrosymmetric anion of (1) the bonds of the four-membered ring are alternately long and short, whereas in (2) the longest bond is situated opposite the shortest one (Fig. 1).

The dimensions of  $\text{Se}_2\text{Cl}_6^{2-}$  ions, compounds (4)–(6) in Table 6, give the impression of a great variation in bond lengths, especially in the four-membered ring bridging the two  $\text{SeCl}_4$  units. The terminal bonds are in the range 2.219(4)–2.291(1) Å, with differences within one compound in the range zero to 0.051 Å. Corresponding values for the bridging bonds are 2.620(1)–2.827(6) Å and 0.035–0.139 Å. The total

length of the individual linear Cl–Se–Cl systems is in the range 4.911–5.054 Å. The normal trend in such linear systems is that a short terminal bond leads to a long bridging bond, and extreme asymmetry leads to increasing total length. This tendency is not so clear in these compounds. Because of the disordered bridging Cl atoms in compound (7), it must be regarded as two different centrosymmetric  $\text{Se}_2\text{Cl}_6^{2-}$  ions. All terminal bonds are of the same length, whereas the bridging bonds in one ion are 2.899(4) and 2.590(4) Å, and in the other 2.862(5) and 2.666(4) Å. The  $3c-4e$  systems related to these bonds have Cl–Se–Cl bond angles of 166.04(13), 179.15(11), 166.67(13) and 179.72(13)°, respectively. The reduced possibility of overlap for the smallest angles is probably enough to account for the large differences in bond lengths in these four-membered rings.

The dimensions of the phenyltrimethylammonium ion do not deviate from the usual values.

*Acknowledgement.* This work was supported by The Research Council of Norway.

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Received June 30, 1997.