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Crystal Structures of Phenyltrimethylammonium Salts of Tetrabromoselenate(II) Bromide, $[C_6H_5(CH_3)_3N]_2[SeBr_4]\cdot[C_6H_5(CH_3)_3N]Br$ and a Mixed Tetra(bromo/chloro)selenate(II)

Sverre Hauge,[a,*] Vitalijus Janickis[b] and Kjartan Marøy[a,*]

[a]Department of Chemistry, University of Bergen, N-5007 Bergen, Norway and [b]Kaunas University of Technology, Kaunas, Lithuania

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The compounds were prepared from elemental selenium and halogen, and phenyltrimethylammonium halide. The crystal structures of $[C_6H_5(CH_3)_3N]_2[SeBr_4]\cdot[C_6H_5(CH_3)_3N]Br$ (**1**) and $[C_6H_5(CH_3)_3N]_2[SeBr_{4-x}Cl_x]\cdot[C_6H_5(CH_3)_3N]Br_{1-y}Cl_y$ (**2**) have been determined by X-ray methods. The crystals are orthorhombic, space group $P2_12_12_1$ with $Z=4$ and $a=9.061(2)$, $b=13.872(4)$, $c=25.894(5)$ Å for **1**, and $a=8.998(2)$, $b=13.787(3)$, $c=25.570(5)$ Å for **2**. The compounds have monomeric square-planar SeX_4^{2-} anions and the Se–Br distances for **1** are in the range 2.547(1)–2.616(1) Å.

The $SeBr_4^{2-}$ ion is known from the crystal structure of $[(C_6H_5)_4P]_2[SeBr_4]$,[1] and the $SeCl_4^{2-}$ ion from the crystal structure of $[(C_6H_5)_3(C_2H_4OH)P]_2[SeCl_4]\cdot CH_3CN$.[2] It has been possible to prepare the mixed bromine/thiocyanate selenium compounds $[(C_2H_5)_4N]_2[Se_2Br_4(SCN)_2]$,[3,4] where two terminal Br atoms in the dimeric $Se_2Br_6^{2-}$ ion are replaced by SCN^-, and $[C_6H_5(CH_3)_3N]_2[Se_2X_2(SCN)_4]$[5] and $[(CH_3)_3HN]_2[Se_2X_2(SCN)_4]$[5] (X = Cl or Br), where all terminal halogen atoms are replaced by SCN^-. We wanted to look into the possibility of making similar complexes where one or more of the Br ligands are exchanged with another halide. We report here the crystal structures of the isomorphous compounds $[C_6H_5(CH_3)_3N]_2[SeBr_4]\cdot[C_6H_5(CH_3)_3N]Br$ (**1**) and $[C_6H_5(CH_3)_3N]_2[SeBr_{4-x}Cl_x]\cdot[C_6H_5(CH_3)_3N]Br_{1-y}Cl_y$ (**2**).

Experimental

Preparations. The compounds were prepared by reactions between elemental selenium and halogen in the presence of phenyltrimethylammonium halide. In the cases where Se and Br_2 are used in the molar ratio 1:1 and with various amounts of $[C_6H_5(CH_3)_3N]Br$, the following compounds have been isolated and identified by X-ray methods: $[C_6H_5(CH_3)_3N]_2[SeBr_6]$, $[C_6H_5(CH_3)_3N]_2[SeBr_4]$, $[C_6H_5(CH_3)_3N]_2[SeBr_4]\cdot[C_6H_5(CH_3)_3N]Br$, $[C_6H_5(CH_3)_3N]_2[Se_2Br_6]$, $[C_6H_5(CH_3)_3N]_2[Se_4Br_6]$, $[C_6H_5(CH_3)_3N]_2[Se_5Br_{10}]$ and $[C_6H_5(CH_3)_3N]_2[Se_4Br_{14}]$. The formation of the different compounds depends on, in addition to the amount of $[C_6H_5(CH_3)_3N]Br$, 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 later article.

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

$[C_6H_5(CH_3)_3N]_2[SeBr_4]\cdot[C_6H_5(CH_3)_3N]Br$ (**1**). Light orange crystals of this composition were prepared by reaction between selenium and bromine in acetonitrile and in the presence of phenyltrimethylammonium bromide. Found: Se 9.08, Br 44.27. Calc. for $[C_6H_5(CH_3)_3N]_2[SeBr_4]$: Se 8.90, Br 45.04.

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[*] To whom correspondence should be addressed.

$[C_6H_5(CH_3)_3N]_2[SeBr_{4-x}Cl_x] \cdot [C_6H_5(CH_3)_3N]$-$Br_{1-y}Cl_y$ (**2**). Crystals of this composition were received in the same way as for **1**, by replacing phenyltrimethylammonium bromide by the chloride.

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[6] and refined by SHELXL93.[7] The crystal data, conditions for data collection, and refinements are summarised in Table 1.

In the structure of **2** each halogen position is partly 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. 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 Table 2. Complete lists of bond lengths and angles, anisotropic temperature factors, structure factors and hydrogen coordinates are available from the authors.

Results and discussion

Selected bond lengths and angles are listed in Table 3, and a view of the anion of compound **1** is shown in Fig. 1.

The crystal structure of compound **1** consists of isolated $SeBr_4^{2-}$, Br^- and $C_6H_5(CH_3)_3N^+$ ions, the shortest interionic contacts being Br···H = 2.74–2.95 Å, Br···Br = 4.58 Å and Se···Br = 6.00 Å. The $SeBr_4^{2-}$ ion consists of two linear three-centre, four-electron (3*c*–4*e*) Br–Se–Br systems and is nearly square-planar, the *cis* Br–Se–Br angles ranging from 87.45(3) to 93.80(3)° and the maximum deviation of an atom from the least-square plane being 0.052 Å. The two 3*c*–4*e* systems have Br–Se–Br angles 176.07(4) and 176.22(4)°, and Se–Br distances 2.547(1) and 2.616(1) Å, and 2.588(1) and 2.613(1) Å, respectively. The $SeBr_4^{2-}$ ion in this structure is thus different from the structure of $[(C_6H_5)_4P]_2[SeBr_4]$,[1] where two centrosymmetric ions in the asymmetric unit have Se–Br bonds in the narrow range 2.595(1)–2.604(1) Å.

A very similar case is the relation between the acentric $SeCl_4^{2-}$ ion as found in the structure of $[(C_6H_5)_3(C_2H_4OH)P]_2[SeCl_4] \cdot CH_3CN$,[2] where the individual 3*c*–4*e* systems have Se–Cl bond lengths 2.399(1) and 2.492(1) Å, and 2.412(1) and 2.462(1) Å, and the centrosymmetric $SeCl_4^{2-}$ ion in the structure of $[C_6H_5CH_2(CH_3)_3N]_2[SeCl_4]$,[8] where the Se–Cl bonds are 2.433(1) and 2.442(1) Å.

According to the VSEPR model[9] the ideal symmetry

Table 1. Crystal data and structure refinement.

Identification code	**1**	**2**
Empirical formula	$C_{27}H_{42}Br_5N_3Se$	$C_{27}H_{42}Br_{2.9}Cl_{2.1}N_3Se$
Formula weight	887.15	792.89
Temperature/K	105(2)	112(2)
Wavelength/Å	0.71069	0.71069
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	9.061(2)	8.998(2)
b/Å	13.872(4)	13.787(3)
c/Å	25.894(5)	25.570(5)
Volume/Å³	3254.7(12)	3172.1(11)
Z	4	4
D_c/g cm^{-3}	1.813	1.660
D_o/g cm^{-3}	1.78 (293 K)	1.64 (293 K)
F(000)	1736	1583
Crystal size/mm	0.19 × 0.23 × 0.25	0.34 × 0.49 × 0.55
θ-Range/°	2.4 to 28.1	1.6 to 28.0
Intensity decay (%)	9.3	15.2
Absorption coefficient/mm^{-1}	7.32	5.01
Correction for absorption	Empirical, ψ-scan	Empirical, ψ-scan
T_{min}/T_{max}	0.127/0.168	0.071/0.098
Independent reflections	4403	4271
No. with $I > 2\sigma(I)$	3472	2566
Data / restraints / parameters	4399 / 0 / 334	4271 / 5 / 344
Weight, $P = (F_o^2 + 2F_c^2)/3$	$[\sigma^2(F^2) + (0.042P)^2 + 5.832P]^{-1}$	$[\sigma^2(F^2) + (0.038P)^2]^{-1}$
Goodness-of-fit on F^2	1.181	0.995
$R[F^2 > 2\sigma(F^2)]$	0.0391	0.0678
$wR(F^2)$	0.0775	0.0979
Abs. struct. parameter	−0.04(2)	−0.04(3)
Max. and min. Δρ/e Å^{-3}	1.60 and −1.14	1.44 and −0.94

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

	$[C_6H_5(CH_3)_3N]_3[SeBr_4]Br$ (**1**)				$[C_6H_5(CH_3)_3N]_3[SeX_4]X$ (**2**)				
Atom	*x*	*y*	*z*	*U*(eq)[a]	*x*	*y*	*z*	*U*(eq)[a]	Br/Cl[b]
Se	4074(1)	9621(1)	8184(1)	14(1)	4042(1)	9580(1)	8207(1)	26(1)	
Br(1)	4001(1)	8776(1)	9057(1)	21(1)	4023(2)	8746(1)	9060(1)	34(1)	41/59
Br(2)	6725(1)	8977(1)	8045(1)	21(1)	6714(2)	8955(1)	8060(1)	40(1)	81/19
Br(3)	1360(1)	10166(1)	8358(1)	22(1)	1372(2)	10115(1)	8388(1)	37(1)	64/36
Br(4)	4044(1)	10585(1)	7316(1)	21(1)	3956(2)	10538(1)	7345(1)	42(1)	54/46
Br(5)	5820(1)	9644(1)	10841(1)	19(1)	5883(2)	9687(1)	10855(1)	27(1)	48/52
N(1)	3712(7)	13054(5)	8591(2)	18(1)	3783(10)	13042(7)	8570(3)	28(2)	
C(11)	4451(10)	12504(6)	8160(3)	28(2)	4584(14)	12524(9)	8136(4)	47(4)	
C(12)	4014(9)	14097(5)	8503(3)	20(2)	4067(14)	14106(8)	8488(4)	39(3)	
C(13)	2065(10)	12918(7)	8550(4)	32(2)	2138(14)	12885(11)	8526(6)	57(4)	
C(14)	4233(8)	12696(5)	9095(3)	19(2)	4314(12)	12694(8)	9092(4)	28(3)	
C(15)	4792(10)	13326(6)	9472(3)	23(2)	4871(12)	13332(8)	9450(4)	25(3)	
C(16)	5339(12)	12952(8)	9924(3)	36(2)	5442(14)	12952(9)	9925(4)	36(3)	
C(17)	5340(12)	11977(7)	10020(3)	36(2)	5399(15)	11972(10)	10026(5)	48(4)	
C(18)	4770(10)	11372(6)	9655(3)	28(2)	4847(12)	11345(9)	9647(5)	35(3)	
C(19)	4223(10)	11720(5)	9199(3)	24(2)	4283(13)	11701(8)	9190(4)	33(3)	
N(2)	8657(7)	8701(4)	9623(2)	16(1)	8644(9)	8708(6)	9644(3)	25(2)	
C(21)	7350(9)	8114(6)	9799(3)	24(2)	7320(13)	8153(8)	9830(4)	34(3)	
C(22)	9369(9)	8170(6)	9185(3)	23(2)	9348(12)	8152(8)	9202(4)	31(3)	
C(23)	8063(10)	9657(6)	9435(3)	29(2)	8103(13)	9658(8)	9450(4)	34(3)	
C(24)	9745(8)	8887(5)	10043(3)	14(1)	9789(12)	8887(8)	10071(4)	26(3)	
C(25)	9454(9)	8613(5)	10549(3)	18(2)	9507(13)	8624(8)	10580(4)	28(3)	
C(26)	10490(8)	8800(5)	10927(3)	21(2)	10595(11)	8773(8)	10956(4)	29(3)	
C(27)	11801(9)	9240(5)	10806(3)	21(2)	11929(12)	9198(8)	10828(5)	31(3)	
C(28)	12083(8)	9531(6)	10302(3)	24(2)	12177(12)	9474(8)	10315(4)	27(3)	
C(29)	11053(8)	9356(5)	9923(3)	19(2)	11129(12)	9337(7)	9931(4)	28(3)	
N(3)	−1228(7)	11793(4)	7262(2)	14(1)	−1214(10)	11753(6)	7257(3)	26(2)	
C(31)	356(9)	11932(6)	7094(3)	25(2)	290(15)	11936(12)	7064(6)	74(6)	
C(32)	−2243(9)	12216(6)	6862(3)	25(2)	−2366(15)	12100(12)	6879(5)	78(6)	
C(33)	−1506(9)	10725(5)	7273(3)	22(2)	−1376(17)	10678(8)	7286(5)	52(4)	
C(34)	−1446(8)	12268(5)	7774(3)	16(1)	−1424(11)	12239(7)	7778(4)	18(2)	
C(35)	−1367(8)	13260(5)	7795(3)	19(2)	−1337(12)	13238(7)	7797(4)	22(2)	
C(36)	−1506(9)	13717(6)	8269(3)	25(2)	−1481(11)	13709(8)	8268(4)	30(3)	
C(37)	−1733(9)	13191(6)	8712(3)	24(2)	−1677(12)	13203(9)	8723(4)	26(3)	
C(38)	−1845(10)	12202(6)	8680(3)	24(2)	−1758(16)	12185(9)	8705(4)	42(4)	
C(39)	−1708(8)	11735(6)	8215(3)	19(2)	−1625(13)	11695(8)	8229(4)	30(3)	

[a] *U*(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor. [b] Relative population of Br and Cl.

Table 3. Bond lengths (in Å) and angles (in °) of the anions in **1** and **2**.

	1	**2**
Se-Br(1)	2.5465(10)	2.467(2) [41/59]
Se-Br(3)	2.6126(12)	2.556(2) [64/36]
Se-Br(4)	2.6161(10)	2.569(2) [54/46]
Se-Br(2)	2.5875(11)	2.581(2) [81/19]
Br(1)-Se-Br(3)	87.45(3)	88.11(7)
Br(1)-Se-Br(4)	176.07(4)	176.17(8)
Br(3)-Se-Br(4)	89.45(3)	88.80(7)
Br(1)-Se-Br(2)	89.39(3)	88.82(7)
Br(3)-Se-Br(2)	176.22(4)	176.64(7)
Br(4)-Se-Br(2)	93.80(3)	94.32(7)

[a] The relative populations of Br/Cl are shown in square brackets.

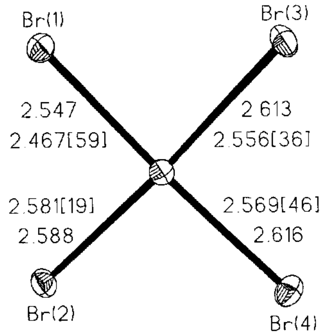

Fig. 1. View of the $SeBr_4^{2-}$ ion with bond lengths as found in the phenyltrimethylammonium salt. The bond lengths of the mixed Br/Cl ion are also given, with the relative amount of Cl in square brackets.

of these ions is D_{4h}. The total length of the individual 3*c*–4*e* systems in such compounds is nearly constant, and the deviation from D_{4h} symmetry is therefore more pronounced for ions without a crystallographic centre of symmetry. In the structures discussed here there is no indication that the deviation from the ideal symmetry is caused by direct interionic contacts, the shortest anion–

anion distance being 4.58 Å and the shortest $SeBr_4^{2-}$ anion–hydrogen distance being 2.83 Å. The reason for the deviation from the ideal symmetry, especially for the variation of Se–Br bond lengths, has to be sought among other interionic forces.

Compound **2** was prepared with the intention of having one or two of the Br atoms in the $SeBr_4^{2-}$ ion replaced by Cl atoms. The resulting structure has a Br/Cl ratio of 2.9/2.1, but instead of having some Br atoms totally replaced by Cl, each halogen position is partly occupied by Br and partly by Cl. In Tables 2 and 3 the ratios for the individual positions are given. As seen from Table 3 and Fig. 1, the position with highest content of Cl, (1), is related to the greatest reduction in Se–X distance and the position with the lowest content of Cl, (2), is related to the smallest reduction in Se–X distance compared to compound **1**. Position (4) has higher content of Cl than position (3), but has a smaller reduction of Se–X distance. This may be due to their *trans* bonding partners. *Trans* to (4) is the position with the highest content of Cl, and *trans* to (3) is the one with the lowest content of Cl. This may indicate a stronger *trans* bond lengthening effect of Br than of Cl.

From the two $SeBr_4^{2-}$ anions and the two $SeCl_4^{2-}$ anions discussed above, the average total lengths of the linear Br–Se–Br and Cl–Se–Cl systems are 5.189 and 4.879 Å, respectively. The linear system related to positions (2) and (3) in compound **2** with average Br/Cl ratio 72/28 has total length of 5.125 Å, and the linear system related to positions (1) and (4) with average Br/Cl ratio 48/52 has total length of 5.048 Å. These dimensions are thus reflecting the differences in Br/Cl ratios.

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

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