

Synthesis and crystal structure of bis(benzyltrimethylammonium) Hexabromoselenate(IV), $[C_6H_5CH_2(CH_3)_3N]_2[SeBr_6] \cdot CH_3CN$

Vitalijus Janickis

*Department of Inorganic Chemistry,
Faculty of Chemical Technology,
Kaunas University of Technology,
Radvilėnų 19, LT-50254 Kaunas,
Lithuania*

The compound $[C_6H_5CH_2(CH_3)_3N]_2[SeBr_6] \cdot CH_3CN$ (**1**) was prepared from elemental selenium and bromine, and benzyltrimethylammonium bromide. The crystal structure of **1** has been determined by X-ray methods and refined to $R = 0.0554$ and 0.1072 for 1772 and 2591 reflections, respectively. The crystals were monoclinic, space group was $I 2/a$ with $Z = 4$ and $a = 15.064(3)$, $b = 9.2617(19)$, $c = 22.161(4)$ Å, $\beta = 93.91(3)^\circ$. The $[SeBr_6]^{2-}$ octahedron of **1** is centrosymmetric with $Se-Br = 2.5445(11)$, $2.5756(11)$, $2.5740(12)$ Å and $Br-Se-Br = 90.34(4)$, $90.56(4)$, $90.07(3)^\circ$. It has been confirmed that the individual $Se-Br$ bond lengths in hexabromoselenate(IV) anions vary within a wide range, whereas the total length of the linear $Br-Se-Br$ bonding systems in these ions is almost constant, which is in accordance with the three-centre-four electron bond model.

Key words: bromoselenate(IV), syntheses, crystal structure

INTRODUCTION

Selenium and bromine form the binary compounds Se_2Br_2 , $SeBr_2$ and $SeBr_4$. The crystal structures of Se_2Br_2 and $SeBr_4$ are well known [1, 2]; both compounds exist in allotrope modifications. $SeBr_4$ makes a series of complexes with bromide; the monomeric $[SeBr_6]^{2-}$ ion [3–12], the dimeric $[Se_2Br_9]^-$ anion formed by two octahedra sharing one face [5, 11, 13], the dimeric $[Se_2Br_{10}]^{2-}$ ion formed by two octahedra sharing one edge [6, 8, 13, 14], the trimeric $[Se_3Br_{13}]^-$ ion formed by three octahedra each of them sharing one face with the two others [15].

In 1998 the first complex dianion of mixed-valency bromoselenate(IV,I) containing selenium in the oxidation states +4 and +1 was reported [16]: hexabromoselenate(IV)-bis{dibromodiselenate(I)} dianion, $[SeBr_6(Se_2Br_2)_2]^{2-}$, containing a nearly regular $SeBr_6$ octahedron where two *trans*-positioned bromo ligands each form a weak bond to one of the Se^I atoms of an additional Se_2Br_2 molecule [16]. The hexabromoselenate(IV)-bis{dibromodiselenate(I)} dianion, $[SeBr_6(Se_2Br_2)_2]^{2-}$, was

isolated only as phenyltrimethylammonium salt, $[C_6H_5(CH_3)_3N]_2[SeBr_6(Se_2Br_2)_2]$, from the reaction between elemental selenium and bromine in the presence of phenyltrimethylammonium bromide [16].

In our earlier studies [16–20], we have investigated the reaction between elemental selenium and bromine in a solution of acetonitrile in the presence of bromides of various cations. And it has been shown [16–20] that the formation of the species that are to crystallize from the solution when bromide ions are added after the primary reaction of selenium and bromine, depends on equilibrium concentrations and solubilities, and especially on the nature of the cation the bromide of which was used for the synthesis.

In continuation of the earlier studies in the area of halogenochalcogenates [16–24], in the present study we have investigated the reaction between elemental selenium and bromine in the solution of acetonitrile in the presence of benzyltrimethylammonium bromide, $[C_6H_5CH_2(CH_3)_3N]Br$. The present paper also gives a report on the preparation and the crystal structure of a new salt of the monomeric bromoselenate(IV) anion, $[C_6H_5CH_2(CH_3)_3N]_2[SeBr_6] \cdot CH_3CN$ (**1**).

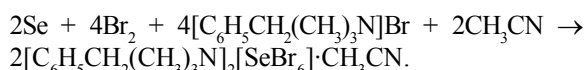
Corresponding author. E-mail: vitalijus.janickis@ktu.lt

EXPERIMENTAL

The determination of selenium was done by treating the sample with a sulphite solution, adding bromide and oxidizing with bromine. Bromine excess was removed and the amount of selenium was determined iodometrically. The density was measured by floatation, using a mixture of trichloromethane and tribromomethane.

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

4.0 mmol (0.64 g) of bromine were added to 2.0 mmol (0.158 g) of selenium in 8.0 g of acetonitrile. The mixture was stirred and heated to 65 °C until selenium reacted. 4.0 mmol (0.92 g) of benzyltrimethylammonium bromide were added to the mixture under stirring and heating. The clear solution was set aside at room temperature for a few hours, and 1.36 mmol (1.22 g) of brown plate-like crystals of bis(benzyltrimethylammonium) hexabromoselenate(IV) acetonitrile solvate, $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]\cdot\text{CH}_3\text{CN}$, were isolated. The yield was about 70% of the theoretical value calculated from the following equation:



Found: Se 8.62. Calc. for $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]\cdot\text{CH}_3\text{CN}$: Se 8.77.

X-ray structure analyses

The determination of unit cell dimensions and data collection was carried out on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods using a SHELXS97 [25] and refined by a SHELXL97 [26]. The atomic scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 in ref. [27]. The crystal data, conditions for data collection and refinement are summarised in Table 1. An extinction parameter x was refined by least squares, where F_o was multiplied by $k[1 + 0.001x \times F_o \times \lambda^3/\sin(2\theta)]^{-1/4}$, where k was the over-all scale factor, and x was found to be 0.00011(15). The hydrogen atoms of the cation were placed geometrically and refined using a riding model with the isotropic thermal parameters equal to 1.3 $U(\text{eq})$ for the atom to which they are attached. All the non-hydrogen atoms except the disordered nitrogen and carbon atoms in the solvate molecule CH_3CN , which were found to be disordered, were refined anisotropically.

Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2.

RESULTS AND DISCUSSION

Bond lengths and angles of the $[\text{SeBr}_6]^{2-}$ ion in **1** are listed in Table 3, and bond lengths in the known hexabromoselenate(IV) ions are listed in Table 4. The view of the molecular structure of compound **1** is shown in Fig. 1.

The selenium atom of the mononuclear anion in compound **1** is situated in the centre of symmetry, and there

Table 1. Crystal data and structure refinement

Identification code	1
Empirical formula	$\text{C}_{22}\text{H}_{35}\text{N}_3\text{SeBr}_6$
Formula weight	899.95
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$I 2/a$
$a/\text{Å}$	15.064(3)
$b/\text{Å}$	9.2617(19)
$c/\text{Å}$	22.161(4)
$\beta/^\circ$	93.91(3)
Volume/Å ³	3084.8(11)
Z	4
$D_c/\text{g}\cdot\text{cm}^{-3}$	1.938
$D_o/\text{g}\cdot\text{cm}^{-3}$ (293 K)	1.930
$F(000)$	1728
Crystal size/mm	0.160.256'0.28
θ range/ $^\circ$	2.71 to 24.63
hkl limits	$h = 0 \rightarrow 17$ $k = 0 \rightarrow 10$ $l = -25 \rightarrow 25$
Absorption coeff./mm ⁻¹	9.005
Correction for absorption	Numerical
$T_{\text{min}}/T_{\text{max}}$	0.2726/0.1462
Reflections collected/unique	2702/2591
Data/restraints/parameters	2591 / 0 / 151
Extinction coefficient	0.00049(8)
Refinement on	F^2
Goodness-of-fit on F^2	1.090
$R(F)$ [$>2\sigma(I)$]	0.0554
$R(F)$ (all data)	0.1072
$WR(F^2)$ [$>2\sigma(I)$]	0.1447
$WR(F^2)$ (all data)	0.1589
Max. and min. $\Delta\rho/e \text{ Å}^{-3}$	3.720 and -1.073

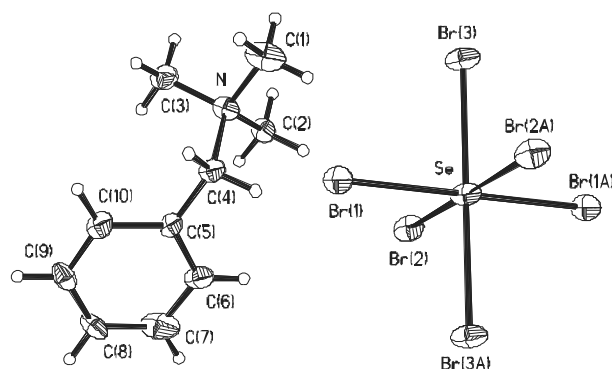


Fig. 1. View of the molecular structure of bis(benzyltrimethylammonium) hexabromoselenate(IV)

are very small deviations from the regular octahedral geometry.

The $[\text{SeBr}_6]^{2-}$ ion is known from a number of structural determinations. Like in other known structures it is built up of a nearly regular octahedron. In the present structure, the central SeBr_6 octahedron has a nearly

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

Atom	x	y	z	$U(\text{eq})^{**}$
Se	2500	2500	2500	23(1)
Br(1)	3426(1)	407(1)	2941(1)	26(1)
Br(2)	3303(1)	4244(1)	3260(1)	28(1)
Br(3)	3676(1)	2979(1)	1734(1)	29(1)
N	6008(6)	2504(8)	3492(4)	23(2)
C(1)	5794(9)	2147(11)	2846(5)	40(3)
C(2)	5876(8)	4085(10)	3583(5)	26(2)
C(3)	6950(7)	2128(11)	3664(5)	31(3)
C(4)	5372(7)	1630(10)	3860(4)	25(2)
C(5)	5504(6)	1782(10)	4521(4)	20(2)
C(6)	5063(7)	2821(11)	4839(5)	31(3)
C(7)	5182(10)	2885(12)	5468(6)	47(4)
C(8)	5711(8)	1917(11)	5781(4)	29(3)
C(9)	6145(7)	893(11)	5474(5)	28(2)
C(10)	6057(7)	795(10)	4855(5)	29(3)
N(1)	2500	5670(20)	5000	86(6)
C(11)	2500	2850(40)	5000	117(11)
C(12)	2500	4480(30)	5000	69(6)
C(13)	2597(7)	3756(11)	4484(4)	22(2)
N(2)	2722(12)	2350(20)	4573(8)	32(4)

** $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond lengths (in \AA) and bond angles (in $^\circ$) in the anion of **1**, with e.s.d.s in parenthesis

Se-Br(1)	2.5445(11)	Br(1)–Se–Br(2)	90.34(4)
Se-Br(2)	2.5756(11)	Br(1)–Se–Br(3)	90.07(3)
Se-Br(3)	2.5740(12)	Br(2)–Se–Br(3)	90.56(4)

Table 4. Bond lengths (in \AA) in hexabromoselenate(IV) ions

No.	Compound	Bond range	Average	Ref.
1.	$[\text{NH}_4]_2[\text{SeBr}_6]$	2.577(2)	2.577	4
2.	$[\text{H}_3\text{O}]_2[\text{SeBr}_6]$	2.562(1)	2.562	8, 10
3.	$[\text{H}_5\text{O}_2]_2[\text{SeBr}_6] \cdot 2\text{H}_2\text{O}$	2.553(2)–2.579(2)	2.565	3
4.	$[\text{H}_3\text{O}(\text{Crown})^a]_2[\text{SeBr}_6]$	2.549(1)–2.584(1)	2.572	8, 12
5.	$[\text{H}_3\text{O}(\text{Crown})^b]_2[\text{SeBr}_6] \cdot \text{CH}_3\text{CN}$	2.564(2)–2.582(2)	2.572	8
6.	$[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_2]_2[\text{SeBr}_6]$	2.547(2)–2.595(2)	2.571	4
7.	$[\text{H}_9\text{O}_4][\text{H}_3\text{O}][\text{SeBr}_6] \cdot 2/2\text{C}_4\text{H}_8\text{O}_2$	2.483(3)–2.670(3)	2.574	7
8.	$[(\text{CH}_3)_3\text{NH}]_{2n}[\text{SeBr}_6 \cdot \text{Br}_2]_n$	2.454(3)–2.682(4)	2.571	5
9.	$[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]$	2.570(1)–2.574(1)	2.572	9
10.	$5[(\text{H}_2\text{N})(\text{CH}_3)_2\text{NCBr}]^+[\text{SeBr}_6]^{2-}[\text{Se}_2\text{Br}_9] \cdot 2[\text{Br}_3]^-$	2.5664(8)–2.5820(1)	2.572	11
11.	$[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6] \cdot \text{CH}_3\text{CN}$	2.5445(11)–2.5756(11)	2.565	This work

^a Dibromobenzo-15-crown-5. ^b Bis(dibromobenzo)-18-crown-6.

ideal octahedral symmetry too with the largest deviation of angles 0.56° , and the three independent bond lengths are 2.5445(11), 2.5756(11) and 2.5740(12) \AA (average 2.565 \AA); thus, the largest difference is 0.0311 \AA .

For comparison, the data of the structural determinations of hexabromoselenates(IV), like it was done in the work of S. Hauge and K. Maroy 10 years ago [9], are listed in Table 4. In compounds (1)–(6), (9)–(11), the $[\text{SeBr}_6]^{2-}$ ion has the centre of symmetry, and so the

trans Se-Br bonds are identical and the *trans* Br-Se-Br angles, as was pointed out in [9] are exactly 180° . In these ions the Se-Br bond lengths are in the range of 2.545(1)–2.595(2) \AA with a mean value of 2.566 \AA . In the asymmetric ions of (7) and (8), the ranges are wider (2.483(3)–2.670(3) and 2.454(3)–2.682(4) \AA , respectively), but the deviations from the octahedral angles are a maximum of 2.4 and 2.8° , respectively. In (8), as was pointed out in [9], there are two Se-Br bonds of

lengths 2.678(3) and 2.628(4) Å. The Br atoms involved are each in a bonding contact with the Br₂ molecule, the polymeric chains of the composition [SeBr₆²⁻·Br₂]_n are formed, and these contacts should have a lengthening effect on the Se-Br bonds. In (7) there are also 2 long Se-Br bonds, 2.610(3) and 2.670(3) Å. S. Hauge and K. Marøy have admitted [9], that each of the six bromine atoms is taking part in nearly linear interionic Se-Br...Br systems, with Br...Br distances 3.522(3)–3.698(4) Å. But according to [9], these moderate variations cannot explain the differences of the individual Se-Br bond lengths, since in all cases the average of each pair of *trans* situated bonds is within the range of the centrosymmetrical [SeBr₆]²⁻ ions.

We agree with S. Hauge and K. Marøy to their conclusion that the individual Se-Br bond lengths vary within a wide range, whereas the total length of the linear Br-Se-Br bonding systems is almost constant. This is in accordance with the three-centre-four electron bond model, and therefore, is the mean Se-Br bond length of 2.570 Å, which is about 0.27 Å longer than the sum of the covalent radii of Se and Br, probably because of the interionic contacts.

The dimensions of the benzyltrimethylammonium cation are within the following ranges: N–C = 1.482(13)–1.531(12) Å, C–C = 1.359(16)–1.472(14) Å, C–N–C = 107.0(8)–111.1(8)°, N–C–C = 115.7(8) and C–C–C = 117.9(9)–122.4(9)°.

CONCLUSIONS

As a result of the reaction between selenium and bromine in acetonitrile in the presence of benzyltrimethylammonium bromide, bis(benzyltrimethylammonium) hexabromoselenate(IV) acetonitrile monosolvate is isolated. X-ray structure determination showed that the crystals of [C₆H₅CH₂(CH₃)₃N]₂[SeBr₆]²⁻·CH₃CN are monoclinic, space group is I 2/a with Z = 4 and a = 15.064(3), b = 9.2617(19), c = 22.161(4) Å, β = 93.91(3)°. The octahedral monomeric anion [SeBr₆]²⁻ is centrosymmetric with Se–Br = 2.5445(11), 2.5756(11), 2.5740(12) Å and Br–Se–Br = 90.34(4), 90.56(4), 90.07(3)°. It is confirmed that the individual Se-Br bond lengths vary within a wide range, whereas the total length of the linear Br-Se-Br bonding systems in hexabromoselenate(IV) anion is almost constant, what is in accordance with the three-centre-four electron bond model.

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Vitalijus Janickis

**BIS(BENZILTRIMETILAMONIO)-
HEKSABROMOSELENITO(IV),
[C₆H₅CH₂(CH₃)₃N]₂[SeBr₆]·CH₃CN, SINTEZĖ IR
KRISTALINĖ STRUKTŪRA**

S a n t r a u k a

Junginys [C₆H₅CH₂(CH₃)₃N]₂[SeBr₆]·CH₃CN (**1**) gautas seleni sąveikaujant su bromu ir benziltrimetilamonio bromidu acetone nitrile. Jo kristalinė ir molekulinė struktūra nustatyta monokris-

talų rentgenostruktūrine analize ir išstobulinta iki $R = 0,0554$ ir $0,1072$ atitinkamai 1772 ir 2591 atspindžiams. Kristalai yra monoklininės singonijos, erdvinė grupė I 2/a su $Z = 4$ ir $a = 15,064(3)$, $b = 9,2617(19)$, $c = 22,161(4)$ Å, $\beta = 93,91(3)^\circ$. **1** junginio nijaonas yra beveik taisyklingas oktaedras: jungtys Se(IV)-Br yra 2,5445(11), 2,5756(11), 2,5740(12) Å, o valentiniai kampai BrSe-Br = 90,34(4), 90,56(4), 90,07(3)°. Patvirtinta, kad individualių SeBr jungčių ilgis heksabromoselenito(IV) anijone kinta plačiame intervale, nors suminis linijinių Br-Se-Br jungčių sistemų ilgis išlieka beveik pastovus, ir tai atitinka tricentrinį keturių elektronų ryšio modelį.