

# Synthesis and crystal structure of novel selected bromochalcogenates(IV/I)

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Compounds  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$  (**1**),  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$  (**2**) and  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6]\cdot\text{CH}_3\text{CN}$  (**3**) were prepared from elemental selenium, bromine and benzyltrimethylammonium bromide (**1**), and from elemental selenium, bromine, tellurium dioxide and benzyltrimethylammonium bromide (**2**, **3**), respectively. The constitution of the compounds was confirmed by the chemical analysis and X-ray crystal structure determination. The cation and  $\text{Se}_2\text{Br}_2$  molecule in compounds (**1**) and (**2**) are disordered. The crystals of (**1**) are trigonal, the space group  $R\bar{3}$  (No. 148) with  $Z = 1$  and  $a = 12.8161(15)$  Å,  $\alpha = 41.644(17)^\circ$ . The crystals of (**2**) are trigonal, the space group  $R\bar{3}$  or  $R3$  (No. 148 or 146, the values of statistics closer to  $R3$ ) with  $Z = 1$  and  $a = 12.9365(15)$  Å,  $\alpha = 41.436(17)^\circ$ . The crystal structure of **3** has been determined by the X-ray method and refined to  $R = 0.0596$  and  $0.0709$  for 2768 and 3183 reflections, respectively. The crystals are monoclinic, the space group  $I 2/a$  with  $Z = 4$  and  $a = 15.114(3)$ ,  $b = 9.3244(19)$ ,  $c = 22.437(5)$  Å,  $\beta = 95.22(3)^\circ$ . The  $[\text{TeBr}_6]^{2-}$  octahedron of **3** is centrosymmetric with  $\text{Te(IV)}-\text{Br} = 2.7101(8)$ ,  $2.6788(8)$ ,  $2.7084(10)$  Å and  $\text{BrTe(IV)}-\text{Br} = 89.44(3)$ ,  $90.38(2)$ ,  $91.00(2)^\circ$ . The length of  $\text{Se(IV)}-\text{Br}$  bonds in **1** are  $2.565(2)$  Å and the mean value of  $\text{Te(IV)}-\text{Br}$  bonds in **2** is  $2.698(6)$  Å.

**Key words:** bromochalcogenate(IV){dibromodiselenate(I)}, bromotellurate(IV), synthesis, crystal structure

## INTRODUCTION

The binary compound of Te(IV) with bromine  $\text{TeBr}_4$  is very stable and like other tellurium(IV) halides was characterized structurally [1, 2]. It makes a series of complexes with bromide: anions  $[\text{TeBr}_6]^{2-}$  [3–7],  $[\text{TeBr}_5]^-$  [8],  $[\text{Te}_2\text{Br}_{10}]^{2-}$  [9, 10],  $[\text{Te}_2\text{Br}_9]^-$  [11],  $[\text{Te}_3\text{Br}_{13}]^-$  [6]. All these anions are based on  $\text{TeBr}_6$  octahedra and in the oligomeric species the octahedra are connected by common edges.

In our earlier studies [12–17], we have investigated the reaction between elemental selenium and bromine in a solution of acetonitrile in the presence of bromides of various cations. It had been shown [12–17] that the formation of the species that crystallize from the solution when bromide ions are added after the primary reaction of selenium with bromine, depends on the equilibrium concentrations and solubilities, respectively, and especially it depends on the nature of the cation, the bromide of which has been used for the synthesis. If phenyltrimethylammonium bromide,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]\text{Br}$ , or benzyltrimethylammonium bromide,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]\text{Br}$ , were used, the first halochalcogenates(I), hexabromotetraselenates(I),  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_4\text{Br}_6]$  and  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{Se}_4\text{Br}_6]$ , were isolated [12]. In the

case of phenyltrimethylammonium bromide, depending on the stoichiometry of elemental selenium, bromine and bromide, tetrabromo-selenate(II) bromide,  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_4]\cdot[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]\text{Br}$  [13], hexabromodiselenate(II),  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{Se}_2\text{Br}_6]$  [14], and hexabromoselenate(IV)-bis{dibromodiselenate(I)},  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$  [12], were synthesized too. When tetramethylammonium bromide,  $[(\text{CH}_3)_4\text{N}]\text{Br}$ , was used, red crystals of unique tetramethylammonium octadecabromohexadecaselenate(I),  $[(\text{CH}_3)_4\text{N}]_2[\text{Se}_{16}\text{Br}_{18}]$  [15], with a high yield were isolated, and in the case when tetraethylammonium bromide,  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$ , was used the brown crystals of tetraethylammonium octabromotriselenate(II)-{dibromodiselenate(I)},  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Se}_3\text{Br}_8(\text{Se}_2\text{Br}_2)]$ , the first salt of a mixed-valence bromoselenate(II,I) with a high yield were obtained [16]. When benzyltrimethylammonium bromide,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]\text{Br}$ , was used, benzyltrimethylammonium hexabromoselenate(IV) acetonitrile solvate,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]\cdot\text{CH}_3\text{CN}$ , was synthesized [17]. All the synthesized bromoselenates were characterized by the X-ray crystal structure determination [12–17].

In a number of studies [18–21], reactions between elemental selenium and bromine in acetonitrile solution in the presence of tellurium(IV) oxide and bromides of

various cations have been studied too. It has been shown [18–21] again that the formation of the species that crystallize from the solution when bromide ions are added after the primary reaction of selenium with bromine and tellurium(IV) oxide especially depends on the nature of the cation, the bromide of which was used for the synthesis. If phenyltrimethylammonium bromide,  $[C_6H_5(CH_3)_3N]Br$ , was used, phenyltrimethylammonium hexabromotellurate(IV)-bis{dibromoselenate(I)},  $[C_6H_5(CH_3)_3N]_2[TeBr_6(Se_2Br_2)_2]$ , the first complex of bromotellurate(IV)-selenate(I), i. e. the first complex of univalent selenium with bromotellurate containing one chalcogen atom – selenium in oxidation state +1 and another – tellurium in oxidation state +4, was synthesized [19]. In the cases of ethyltriphenylphosphonium and tetraphenylphosphonium bromides,  $[C_2H_5(C_6H_5)_3P]Br$  and  $[(C_6H_5)_4P]Br$ , hexabromotellurate(IV)-bis{dibromodiselenates(I)} of these cations,  $[C_2H_5(C_6H_5)_3P]_2[TeBr_6(Se_2Br_2)_2]$  and  $[(C_6H_5)_4P]_2[TeBr_6(Se_2Br_2)_2]$ , were isolated too [19]. If methyltriphenylphosphonium bromide,  $[CH_3(C_6H_5)_3P]Br$ , was used, another mixed-valence bromochalcogenate compound, bis(methyltriphenylphosphonium) bromotellurate(IV)-selenate(II) – hexabromotellurate(IV)-bis{dibromoselenate(II)},  $[CH_3(C_6H_5)_3P]_2[TeBr_6(SeBr_2)_2]$ , was synthesized for the first time [20]. And when methyltriethylammonium bromide,  $[CH_3(C_2H_5)_3N]Br$ , was used, bis(methyltriethylammonium), tellurate(IV)-tris{dibromoselenate(II)},  $[CH_3(C_2H_5)_3N]_3[TeBr_6(SeBr_2)_3]$ , containing a chain-polymeric mixed-valence bromotellurate(IV)-selenate(I) anion was isolated [21]. All the synthesized bromotellurates-selenates were also characterized by the X-ray crystal structure determination [18–21].

In continuation of the earlier studies in the area of halogenochalcogenates [12–22], 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,  $[C_6H_5CH_2(CH_3)_3N]Br$ , looking for the formation of another mixed-valence bromoselenate(IV,I) – hexabromoselenate(IV)-{dibromodiselenate(I)},  $[C_6H_5CH_2(CH_3)_3N]_2[SeBr_6(Se_2Br_2)]$  (1). We also have investigated the same reaction but in the presence of tellurium(IV) oxide, like in our previous studies [18–21].

In this paper we also present the preparation of the new salts: mixed-valence bromoselenate(IV,I) – hexabromoselenate(IV)-{dibromodiselenate(I)} anion,  $[C_6H_5CH_2(CH_3)_3N]_2[SeBr_6(Se_2Br_2)]$  (1), analogous tellurium(IV)-Se(I) complex – hexabromotellurate(IV)-{dibromodiselenate(I)} anion,  $[C_6H_5CH_2(CH_3)_3N]_2[TeBr_6(Se_2Br_2)]$  (2), and of the monomeric bromotellurate(IV) anion,  $[C_6H_5CH_2(CH_3)_3N]_2[TeBr_6] \cdot CH_3CN$  (3), as well as the crystal structure of (3).

## EXPERIMENTAL

The determination of selenium was performed by treating the sample with a sulfite solution, adding bromide

and oxidising with bromine. The excess bromine was removed, and the amount of selenium was determined iodometrically. Bromide was determined by potentiometric titration with silver nitrate. The determination of tellurium was done by atomic absorption spectrometry (Perkin-Elmer-503). The following conditions for the tellurium determination by AAS method were used: absorption line of 214.3 nm, electric current density of 15 mA, flame, oxidizing (lemon, blue), limit of detection of 1 µg/ml. Densities were measured by the method of floatation using a mixture of trichloromethane and tribromomethane.

## X-ray structural analysis

The determinations of unit cell dimensions and data collections were carried out on an Enraf-Nonius CAD4 diffractometer, using the graphite-monochromated Mo  $K\alpha_1$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The reflections were collected in  $\theta$  range 2–30° for 1 and 2, and from 2 to 26° for 3, with an  $\omega$  scan mode, scan speed 2.75° min<sup>-1</sup> and min. scan width 1.30°. The direct methods employing SHELXS97 [23] were used to determine the structure solutions.

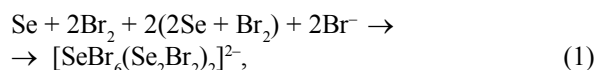
The structure of  $[C_6H_5CH_2(CH_3)_3N]_2[TeBr_6] \cdot CH_3CN$  (3) was refined by the SHELXL97 [24]. Atomic scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 in [25].

## RESULTS AND DISCUSSION

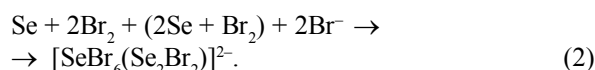
### $[C_6H_5CH_2(CH_3)_3N]_2[SeBr_6(Se_2Br_2)]$ (1)

As mentioned above, the interaction of selenium and bromine in the presence of phenyltrimethylammonium bromide leads to the isolation of phenyltrimethylammonium hexabromoselenate(IV)-bis{dibromodiselenate(I)},  $[C_6H_5(CH_3)_3N]_2[SeBr_6(Se_2Br_2)]$  [12]. It has been pointed out [16] that the reactions of selenium with bromine in acetonitrile lead to a number of equilibria in which several selenium bromide species are involved, and that the nature of the cation, the bromide of which is introduced into the Se/Br<sub>2</sub> system, may determine the composition of the bromochalcogenate anion which crystallises from the solution.

In the present study we have used another stoichiometry of selenium interaction with bromine and bromide than in the earlier work [12]: instead of the stoichiometry of the equation



the amounts of the reactants were chosen in accordance with the equation

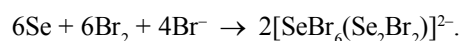


We decreased the amounts of elemental selenium and bromine expecting that the number of Se<sub>2</sub>Br<sub>2</sub> molecules formed in the reaction mixture would decrease from

about 2 to about 1. In a series of experiments we tested various bromide salts in order to find the cation that would form a fairly stable crystal lattice involving the anions of the composition  $[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]^{2-}$ . So far, only benzyltrimethylammonium bromide,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]\text{Br}$ , was found to be suitable for this purpose, and therefore phenyltrimethylammonium bromide formerly used for the synthesis and isolation of bromochalcogenates(IV/I),  $[\text{NMe}_3\text{Ph}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)_2]$  [12], and  $[\text{NMe}_3\text{Ph}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]$  [18], was replaced by benzyltrimethylammonium bromide,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]\text{Br}$ .

In an experimental study, the direct synthesis of the new mixed valence bromoselenate(IV,I) complex (**1**) has been worked out. The new anion was isolated as a benzyltrimethylammonium salt,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$  (**1**), in about 80% yield.

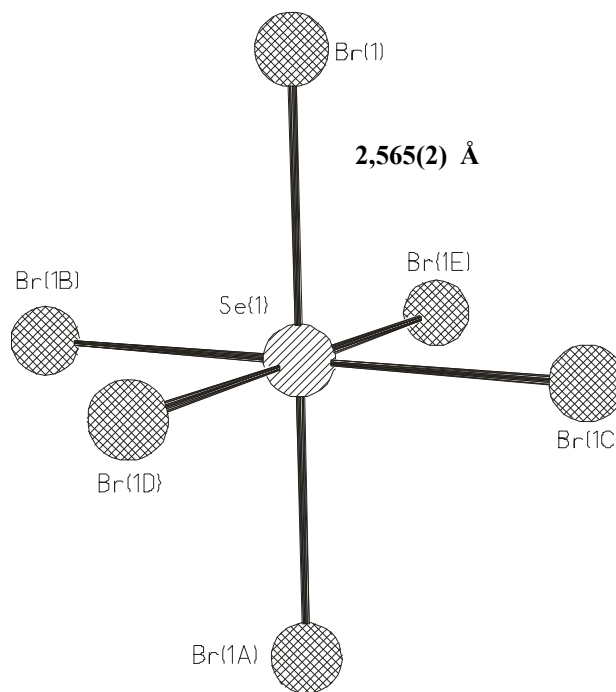
To a solution of 6.0 mmol (0.96 g) of bromine in 4 g of acetonitrile 6.0 mmol (0.474 g) of selenium were added. The suspension was heated under stirring up to 60 °C until selenium reacted. Then 4 mmol (0.92 g) of benzyltrimethylammonium bromide was added. The dark brown clear solution was left to stand at room temperature. After being left for 3 h, 1.57 g of thin or thick six-sided red plate-like crystals, sensitive to water (a gradual liberation of red selenium because of the compounds unstable in water containing Se(I)) were isolated. The filtrate was placed into a refrigerator and left at 0 °C for 5 h, and another 0.22 g of the compound was isolated. The total yield was 1.79 g, 76% of the theoretical value calculated from the equation



Found: Se 20.18, 19.80, 20.23; Br 51.72, 54.26, 55.25, 54.34. Calc. for  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$ : Se 20.13; Br 54.33.

A number of attempts (three data collections on different crystals) were undertaken at 263 K to determine the crystal structure of compound (**1**). The crystals are trigonal, the space group  $R\bar{3}$  (No. 148) with  $Z = 1$  and  $a = 12.8161(15)$  Å,  $\alpha = 41.644(17)^\circ$ , volume = 840.22 Å<sup>3</sup>,  $D_{\text{calculated}}$  (263 K) = 2.325 g·cm<sup>-3</sup>,  $D_{\text{observed}}$  (293 K) = 2.25 g·cm<sup>-3</sup> and  $F(000) = 548.0$ . The reflections were collected in  $\theta$  range 2.15–29.97°.

It was found that the benzyl molecule of the cation and the  $\text{Se}_2\text{Br}_2$  molecule of the complex anion were disordered by the threefold inversion symmetry axis. Only the nitrogen atom, carbon atoms of 3 methyl groups and of  $\text{CH}_2$  group and one carbon atom of a ring connected to  $\text{CH}_2$  group could be located and refined: the N and C atoms of  $\text{CH}_3$ -groups – anisotropically, and the last 2 C atoms of the  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]^+$  cation – isotropically. All atoms of the  $[\text{SeBr}_6]^{2-}$  octahedra, one Se atom and the Br atom of the  $\text{Se}_2\text{Br}_2$  molecule connected to it were refined anisotropically too. Numerical absorption correction (absorption coefficient 12.81 mm<sup>-1</sup>) was applied, but because of the disorder other atoms could not be found in the electron density difference



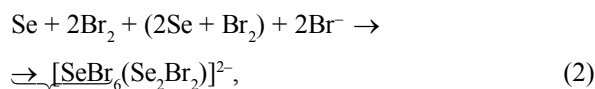
**Fig. 1.** View of the  $[\text{SeBr}_6]^{2-}$  ion as found in the crystal structure of  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$

map and the structure could be refined only to the value of  $R = 0.1060$  for 731 unique reflections with  $F_o > 4\sigma(F_o)$ . All Se(IV)–Br bond lengths in the regular octahedral  $[\text{SeBr}_6]^{2-}$  ion are 2.565(2) Å. A view of the  $[\text{SeBr}_6]^{2-}$  ion of compound **1** is shown in Fig. 1.

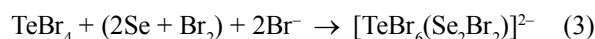
The results of the present work (Se(IV)–Br = 2.565(2) Å) are in good agreement with the dimensions of the anions in other known monomeric hexabromoselenates(IV) (the average values of Se(IV)–Br = 2.562(1)–2.577(2) Å) [17] and coincide with the average length of Se(IV)–Br bond 2.565(2) Å in bis(benzyltrimethylammonium) hexabromoselenate(IV),  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6] \cdot \text{CH}_3\text{CN}$  [17].

#### $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$ (**2**) and $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6] \cdot \text{CH}_3\text{CN}$ (**3**)

For the synthesis of compound (**2**), in equation (2)



we replaced the fragment  $\text{Se} + 2\text{Br}_2$  by  $\text{TeBr}_4$



and used the stoichiometry of equation (3).

To a solution of 3.0 mmol (0.4794 g) of bromine in 4 g of acetonitrile 6.0 mmol (0.474 g) of selenium was added. The suspension was heated under stirring up to 60 °C until selenium almost reacted. Then 3.0 mmol (1.342 g) of tellurium tetrabromide was added under stirring and heating, and finally 6 mmol (1.381 g) of benzyltrimethylammonium bromide was added. An

intensive reaction started and many small red crystals separated. The mixture was diluted with 24.0 g of acetonitrile, brought to the boil and hot filtered. About 2.2 g of brown-red plate-like small crystals were isolated (fraction 1). They were sensitive to water (a gradual liberation of red selenium because of the compounds unstable in water, containing Se(I)), what indicates the presence of selenium(I) bromide,  $\text{Se}_2\text{Br}_2$ , molecules in the crystals. The obtained dark brown filtrate was left to stand at room temperature. After being left for 2 h, 0.95 g of irregular six-sided brown plate-like crystals of  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$  (**2**) sensitive to water (a gradual liberation of red selenium because of the compounds unstable in water, containing Se(I)), slightly contaminated with the yellow crystals of  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}][\text{TeBr}_6]\cdot\text{CH}_3\text{CN}$  (**3**), were isolated (fraction 2). The filtrate was placed into a refrigerator and left at 0 °C overnight, and another 0.15 g of thin or thick six-sided brown plate-like crystals of (**2**) were isolated (fraction 3): they slowly liberated red selenium (decomposition of  $\text{Se}_2\text{Br}_2$ ) under the influence of water and under the action of a strong reductor  $\text{H}_3\text{PO}_2$ , black elemental tellurium was liberated. A well-developed crystal from the product received in fraction 3 was later used for data collection for the X-ray crystal structure determination. The last filtrate was again placed into a refrigerator and kept there at -23 °C for a few weeks, and 0.26 g of large yellow well-developed bipyramidal prisms of (**3**) were isolated (fraction 4): under the action of  $\text{H}_3\text{PO}_2$ , they liberated black elemental tellurium, and under the action of water, they gradually became colorless because of hydrolysis to  $\text{TeO}_2\cdot\text{H}_2\text{O}$ . The crystal from the product of fraction 4 was later used for the analysis and data collection for the X-ray crystal structure determination.

While analysing the six-sided brown plate-like crystals of (**2**), Te 20.18 and Br 52.54 were found. The calculations for  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$  are the following: Te 20.41 and Br 52.17.

An attempt (low temperature data collection on the well-developed crystal from the product of fraction 3) was undertaken at 161 K to determine the crystal structure of compound (**2**). The crystals are trigonal, the space group  $R\bar{3}$  or  $R3$  (No. 148 or 146, the values of the statistics closer to  $R3$ ) with  $Z = 1$  and  $a = 12.9365(15)$  Å,  $\alpha = 41.436(17)^\circ$ , volume = 856.72 Å<sup>3</sup>,  $D_{\text{calculated}}$  (161 K) = 2.374 g·cm<sup>-3</sup>,  $D_{\text{observed}}$  (293 K) = 2.26 g·cm<sup>-3</sup> and  $F(000) = 566.0$ . The reflections were collected in  $\theta$  range 2.15–30.00°.

It was found again that the benzyl molecule of the cation and the  $\text{Se}_2\text{Br}_2$  molecule of the complex anion were disordered. Only the nitrogen atom, carbon atoms of 3 methyl groups and of  $\text{CH}_2$  group and one carbon atom of a ring, connected to  $\text{CH}_2$  group could be located and refined: the N atom – anisotropically and C atoms of the  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]^+$  cation were located isotropically. All atoms of the  $[\text{TeBr}_6]^{2-}$  octahedra, Se and Br atoms of the  $\text{Se}_2\text{Br}_2$  molecule were refined

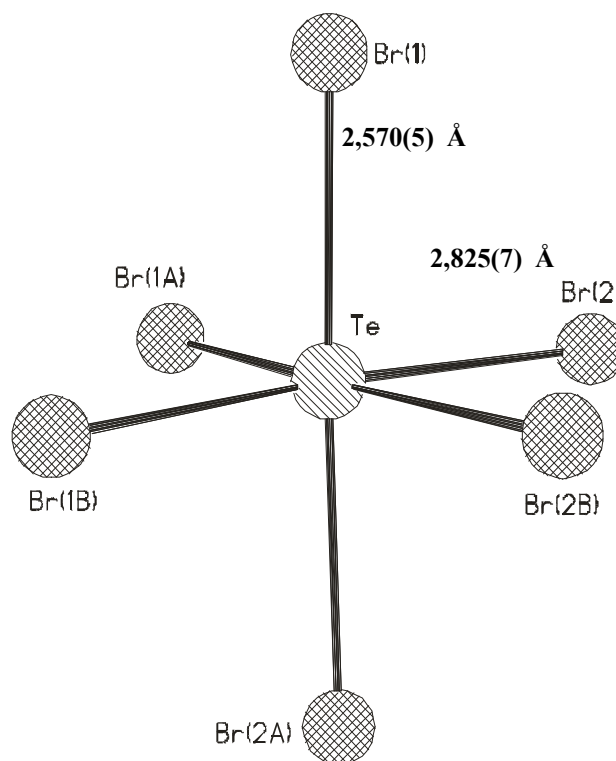


Fig. 2. View of the  $[\text{TeBr}_6]^{2-}$  ion as found in the crystal structure of  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$

anisotropically, but the last ones which had very large thermal parameters, what directly indicated a disorder. Numerical absorption correction (absorption coefficient 12.33 mm<sup>-1</sup>) was applied, but because of the disorder other atoms could not be found in the electron density difference map, and the structure could be refined only to the value of  $R = 0.1726$  for 1134 unique reflections with  $F_o > 4\sigma(F_o)$ . The Te(IV)–Br bond lengths in the irregular octahedral  $[\text{TeBr}_6]^{2-}$  ion are 2.570(5) and 2.825(7) Å (average 2.6975 Å). A view of the  $[\text{TeBr}_6]^{2-}$  ion of compound **2** is shown in Fig. 2.

As mentioned above, the product of fraction 4 isolated during the synthesis of compound (**2**), according to the preliminary analytical qualitative reactions, could be bis(benzyltrimethylammonium) hexabromotellurate(IV) acetonitrile solvate,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6]\cdot\text{CH}_3\text{CN}$ , the crystals of which could be isomorphous with the crystals of analogous selenium compound – bis(benzyltrimethylammonium) hexabromoselenate(IV) acetonitrile solvate,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6]\cdot\text{CH}_3\text{CN}$  [17]. The analysis and the X-ray crystal structure determination confirmed this suggestion. While analysing the yellow well-developed bipyramidal prisms of (**3**), Te 13.18 with calculations for  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}][\text{TeBr}_6]$  – Te 13.45 was found isolated in fraction 4.

*X-ray structural analysis.* The crystal data, conditions for data collection and refinement are summarised in Table 1. The extinction parameter  $x$  was refined by the least squares in which  $F_c$  was multiplied by  $k[1 + 0.001x \times F_c \times \lambda^3/\sin(2\theta)]^{-1/4}$ , where  $k$  was the overall scale factor and  $x$  was found to be 0.0012(2). The

Table 1. Crystal data and structure refinement for compound **3**

Identification code	<b>3</b>
Empirical formula	C <sub>22</sub> H <sub>35</sub> N <sub>3</sub> TeBr <sub>6</sub>
Formula weight	948.57
Temperature/K	111(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	<i>I</i> 2/a
<i>a</i> /Å	15.114(3)
<i>b</i> /Å	9.3244(19)
<i>c</i> /Å	22.437(5)
β/°	95.22(3)
Volume/Å <sup>3</sup>	3148.9(11)
<i>Z</i>	4
<i>D</i> <sub>c</sub> /g·cm <sup>-3</sup>	1.921
<i>D</i> <sub>o</sub> /g·cm <sup>-3</sup> (293 K)	1.960
<i>F</i> (000)	1800
Crystal size/mm	0.176 × 0.220 × 0.310
θ range/°	2.37 to 26.28
<i>hkl</i> limits	<i>h</i> = -18 → 0 <i>k</i> = -11 → 0 <i>l</i> = -27 → 27
Absorption coeff./mm <sup>-1</sup>	8.568
Correction for absorption	Numerical
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.2709/0.1735
Reflections collected/unique	3569/3183
Data/restraints/parameters	3183/ 0 / 152
Extinction coefficient	0.0012(2)
Refinement on	<i>F</i> <sup>2</sup>
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.069
<i>R</i> ( <i>F</i> ) [ <i>I</i> > 2σ( <i>I</i> )]	0.0596
<i>R</i> ( <i>F</i> ) (all data)	0.0709
<i>WR</i> ( <i>F</i> <sup>2</sup> ) [ <i>I</i> > 2σ( <i>I</i> )]	0.1635
<i>WR</i> ( <i>F</i> <sup>2</sup> ) (all data)	0.1776
Max. and min. Dr/e Å <sup>3</sup>	2.599 and -3.431 (close to Te or Br)

hydrogen atoms of the cation were placed geometrically and refined using a riding model with isotropic thermal parameters equal to 1.3 *U*(eq) for the atom they had been attached to. All non-hydrogen atoms were refined anisotropically.

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

Bond lengths and angles of the [TeBr<sub>6</sub>]<sup>2-</sup> ion in **3** are listed in Table 3, and a view of the molecular structure of compound **3** is shown in Fig. 3.

The tellurium atom of the mononuclear anion in compound **3** is situated in the centre of symmetry, and there are very small deviations from the regular octahedral geometry.

The [TeBr<sub>6</sub>]<sup>2-</sup> ion is known from a number of structural determinations. Like in other structures, it is built up of a regular or nearly regular octahedron. In the present structure, the central TeBr<sub>6</sub> octahedron has a nearly ideal octahedral symmetry too with the largest deviation of Br–Te(IV)–Br angles (89.44(3), 91.00(2) and 90.38(2)°) 1.0°, and the three independent Te(IV)–Br bond lengths are 2.7101(8), 2.6788(8) and 2.7084(10) Å (average 2.699 Å); thus, the largest difference is 0.0313 Å. The crystals of compound **3** are isomorphous with crystals of the analogous selenium compound bis(benzyltrimethylammonium) hexabromoselenate(IV) acetonitrile solvate, [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[SeBr<sub>6</sub>]·CH<sub>3</sub>CN [17].

For comparison, data of the structural determinations of monomeric hexabromotellurates(IV) are listed in Table 4.

In compounds (1) and (4) from the above table, the [TeBr<sub>6</sub>]<sup>2-</sup> ion has a highest symmetry, and so all the Te(IV)–Br bonds are identical – (2.681(2) and 2.695(4) Å, respectively), and all the Br–Te(IV)–Br angles are exactly 90°.

In compounds (2), (3), (5) and (6) from the same table, the [TeBr<sub>6</sub>]<sup>2-</sup> ion has the centre of symmetry. So

Table 2. Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for compound **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Te	2500	2500	2500	13(1)
Br(1)	1626(1)	691(1)	1705(1)	21(1)
Br(2)	3480(1)	294(1)	295(1)	18(1)
Br(3)	1294(1)	2026(1)	3300(1)	21(1)
N	-1067(4)	2505(5)	1486(2)	16(1)
C(1)	-875(6)	2888(8)	2137(3)	30(2)
C(2)	-966(5)	921(7)	1402(3)	21(1)
C(3)	-1995(5)	2934(7)	1277(3)	23(2)
C(4)	-390(4)	3331(7)	1144(3)	18(1)
C(5)	-511(4)	3175(7)	484(3)	16(1)
C(6)	-47(5)	2126(8)	192(3)	25(2)
C(7)	-156(5)	2037(8)	-420(3)	28(2)
C(8)	-656(5)	3016(8)	-760(3)	28(2)
C(9)	-1099(4)	4092(8)	-483(3)	21(1)
C(10)	-1025(4)	4177(7)	138(3)	18(1)
N(1)	-2500	665(12)	0	50(3)
C(11)	-2500	-591(12)	0	35(3)
C(12)	-2500	-2130(14)	0	52(4)

<sup>a</sup>*U*(eq) is defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

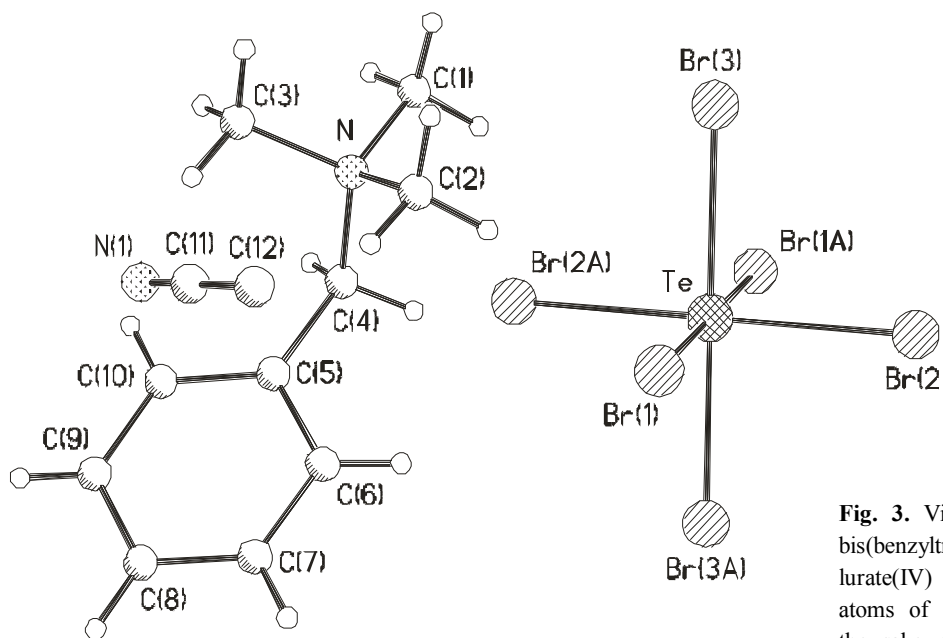


Fig. 3. View of the molecular structure of bis(benzyltrimethylammonium) hexabromotellurate(IV) acetonitrile solvate (the hydrogen atoms of  $\text{CH}_3\text{CN}$  molecule are omitted for the sake of clarity)

Table 3. Bond lengths (in Å) and bond angles (in °) in the anion of compound 3, with e. s. d. s in parentheses

Te(IV)–Br(1)	2.7101(8)	Br(1)–Te(IV)–Br(2)	89.44(3)
Te(IV)–Br(2)	2.6788(8)	Br(1)–Te(IV)–Br(3)	91.00(2)
Te(IV)–Br(3)	2.7084(10)	Br(2)–Te(IV)–Br(3)	90.38(2)

Table 4. Bond Te(IV)–Br lengths (in Å) in hexabromotellurate(IV) ions

No.	Compound	Bond range	Average	Ref.
1.	$[\text{NH}_4]_2[\text{TeBr}_6]$	2.681(2)	2.681	4
2.	$[\text{H}_9\text{O}_4]_2[\text{TeBr}_6]$	2.671(4)–2.716(4)	2.696	6
3.	$\text{K}_2[\text{TeBr}_6]$	2.687(6)–2.698(6)	2.692	3
4.	$\text{Cs}_2[\text{TeBr}_6]$	2.695(4)	2.695	4
5.	$[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6]$	2.6931(5)–2.7056(6)	2.701	7
6.	$[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6]\cdot\text{CH}_3\text{CN}$	2.6788(8)–2.7101(8)	2.699	This work

the *trans* Te(IV)–Br bonds are identical, and the *trans* Br–Te(IV)–Br angles as it was pointed out in [26] when discussing the structures of hexabromoselenates(IV) (BrSe(IV)–Br), are exactly 180°. In the anions of compounds (1) and (4), the Te(IV)–Br bond lengths are in the range of 2.681(2)–2.695(4) Å, with the mean value of 2.688 Å. In the less symmetric anion of compound (3) Te(IV)–Br bond lengths are in a narrow range too: 2.687(6)–2.698(6) Å, with the mean length of 2.692(6) Å, which is only slightly longer than in compounds (1) and (4), and the deviations of all the BrTe(IV)–Br angles lie only within 0.3° of 90°. In the less symmetric  $[\text{TeBr}_6]^{2-}$  anions of (2), (5) and (6), the ranges are wider (2.671(4)–2.716(4) Å (average 2.696 Å), (2.6931(5)–2.7056(6) Å (average 2.701 Å) and 2.6788(8)–2.7101(8) Å (average 2.699 Å), respectively), and the deviations of the BrTe(IV)–Br angle from 90° are larger – 0.9, 1.28 and 1.00°, respectively. It seems that there is a tendency of an increasing asymmetry in the  $[\text{TeBr}_6]^{2-}$  anion with an increase in the deviation of the Br–Te(IV)–

Br angle from the ideal of 90°. In the sequence of hexabromoselenate(IV) ions of compounds (1) and (4), (3), (2), (6), (5), the values of the largest deviation of Br–Te(IV)–Br angle from 90° are 0.00, 0.30, 0.90, 1.00 and 1.28°, respectively, and correspondingly the average length of the Te(IV)–Br bonds are 2.688, 2.692, 2.696, 2.699 and 2.701 Å.

The average length of the Te(IV)–Br bonds in compound (6) (this work) 2.699 Å is about by 0.20 Å longer than the sum of the covalent radii [26–28] probably because of the interionic contacts. The variation of the bond lengths in 3c-4e systems is common. The results of the present work (Te(IV)–Br = 2.6788–2.7101 Å) are in good agreement with the dimensions of the anions in other known hexabromotellurates(IV) 2.671–2.716 Å.

The dimensions of the benzyltrimethylammonium cation are within the following ranges: N–C = 1.494(9)–1.539(8) Å, C–C = 1.371(11)–1.484(9) Å, CN–C = 106.7(5)–111.0(5)°, NC–C = 114.9(5) and CC–C = 118.8(6)–121.8(7)°.

## CONCLUSIONS

As a result of the reaction between selenium and bromine in acetonitrile and between selenium, bromine and tellurium dioxide in acetonitrile in the presence of benzyltrimethylammonium bromide, the bis(benzyltrimethylammonium) hexabromoselenate(IV) {dibromodiselenate(I)},  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$ , hexabromotellurate(IV) {dibromodiselenate(I)},  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$ , and hexabromotellurate(IV) acetonitrile solvate,  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6]\cdot\text{CH}_3\text{CN}$ , are isolated. The X-ray structure determinations showed that the cations and  $\text{Se}_2\text{Br}_2$  molecules in the first two compounds are disordered. The crystals of  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$  are trigonal, the space group  $R\bar{3}$  with  $Z = 1$  and  $a = 12.8161(15)$  Å,  $\alpha = 41.644(17)^\circ$ . The crystals of  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$  are trigonal, the space group  $R\bar{3}$  or  $R3$  (No. 148 or 146, the values of statistics closer to  $R3$ ) with  $Z = 1$  and  $a = 12.9365(15)$  Å,  $\alpha = 41.436(17)^\circ$ . The crystal structure of  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6]\cdot\text{CH}_3\text{CN}$  has been determined by the X-ray methods and refined to  $R = 0.0596$  and  $0.0709$  for 2768 and 3183 reflections, respectively. The crystals are monoclinic, the space group  $I 2/a$  with  $Z = 4$  and  $a = 15.114(3)$ ,  $b = 9.3244(19)$ ,  $c = 22.437(5)$  Å,  $\beta = 95.22(3)^\circ$ . The  $[\text{TeBr}_6]^{2-}$  octahedron of **3** is centrosymmetric with  $\text{Te(IV)}-\text{Br} = 2.7101(8)$ ,  $2.6788(8)$ ,  $2.7084(10)$  Å and  $\text{BrTe(IV)}-\text{Br} = 89.44(3)$ ,  $90.38(2)$ ,  $91.00(2)^\circ$ . The lengths of the  $\text{Se(IV)}-\text{Br}$  bonds in  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$  are  $2.565(2)$  Å and the mean value of the  $\text{Te(IV)}-\text{Br}$  bonds in  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$  is  $2.698(6)$  Å.

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### NAUJUŲ RINKTINIŲ BROMOCHALKOGENATŲ(IV/I) SINTEZĖ IR KRISTALINĖ STRUKTŪRA

#### Santrauka

Junginiai  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{SeBr}_6(\text{Se}_2\text{Br}_2)]$  (**1**),  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)]$  (**2**) ir  $[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6]\cdot\text{CH}_3\text{CN}$  (**3**) gauti atitinkamai, seleniui sąveikaujant su bromu ir benziltrimetilamonio bromidu acetonitrile (**1**), ir seleniui sąveikaujant su bromu, benziltrimetilamonio bromidu ir telūro dioksidu acetonitrile (**2** ir **3**). Junginių sudėtis patvirtinta chemine ir rentgenostruktūriniu analize. Katijonai ir  $\text{Se}_2\text{Br}_2$  molekulės junginiuose (**1**) ir (**2**) yra netvarkingi. (**1**) junginio kristalai yra trigonaliniai, erdvinė grupė  $R\bar{3}$  (Nr. 148),  $Z = 1$  ir  $a = 12,8161(15)$  Å,  $\alpha = 41,644(17)^\circ$ . Junginio (**2**) kristalai taip pat trigonaliniai, erdvinė grupė  $R\bar{3}$  arba  $R3$  (Nr. 148 arba 146, statistikos duomenys artimesni  $R3$ ),  $Z = 1$  ir  $a = 12,9365(15)$  Å,  $\alpha = 41,436(17)^\circ$ . Junginio **3** kristalinė ir molekulinė struktūra nustatyta monokristalų rentgenostruktūriniu analize ir išstobulinta

iki  $R = 0,0596$  ir  $0,0709$  atitinkamai 2768 ir 3183 atspindžiams. Kristalai yra monoklininės singonijos, erdvinė grupė  $I 2/a$  su  $Z = 4$  ir  $a = 15,114(3)$ ,  $b = 9,3244(19)$ ,  $c = 22,437(5)$  Å,  $\beta = 95,221(3)$  °. **3** junginio nija yra beveik taisyklingas ok-

taedras: jungtys Te(IV)–Br yra 2,7101(8), 2,6788(8), 2,7084(10) Å, o valentiniai kampai Br–Te(IV)–Br = 89,44(3), 90,38(2), 91,00(2) °. Jungtys Se(IV)-Br junginyje **1** yra 2,565(2) Å, o vidutinė jungties Te(IV)-Br vertė junginyje **2** – 2,698(6) Å.