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# Synthesis and crystal structure of bis(phenyltrimethylammonium) hexabromotellurate(IV)bis{dibromodiselenate(I)}, [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]

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The compound [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>] (**1**) was prepared from elemental selenium and tellurium tetrabromide and bromine, and phenyltrimethylammonium bromide. The crystal structure of **1** has been determined by X-ray methods and refined to R = 0.0292 and 0.0387 for 10074 and 12059 reflections, respectively. The crystals are monoclinic, space group *Pn* with *Z* = 2 and *a* = 8.8390(18), *b* = 12.759(3), *c* = 16.617(3) Å, β = 104.57(3)°. The anion of **1** is a nearly regular octahedron where two *trans*-positioned Br atoms each have a bond to one of the Se atoms in a Se<sub>2</sub>Br<sub>2</sub> molecule. The Te(IV)-Br distances are in the range 2.6828(17)–2.704(2) Å. The bond lengths in coordinated Se<sub>2</sub>Br<sub>2</sub> molecules are: Se(I)-Se(I) = 2.266(2) and 2.272(2) Å, Se(I)-Br = 2.380(2), 2.361(2), 2.346(2) and 2.346(2) Å.

**Key words:** bromotellurate(IV)-dibromodiselenate(I), synthesis, crystal structure

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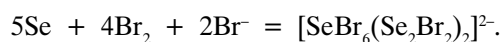
## INTRODUCTION

In contrast to monoselenium dibromide SeBr<sub>2</sub> which has not been isolated, but makes a series of complexes with bromide [1], the binary compound of Se(I) with bromine Se<sub>2</sub>Br<sub>2</sub> is stable as a pure liquid or solid. It exists in α- and β-Se<sub>2</sub>Br<sub>2</sub> allotropic modifications which have been characterized by full low-temperature crystal structure analysis [2]. But only in 1998 the first two complexes of Se<sub>2</sub>Br<sub>2</sub> with bromide ion were reported; the hexabromotetratellurate(IV) [Se<sub>4</sub>Br<sub>6</sub>]<sup>2-</sup> ion consisting of two Br-Se-Se-Br units bound together by two bromide ion bridges between the selenium atoms in such a way that a chair-shaped, six-membered ring is formed [3], and the dianion [SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> which is a nearly regular SeBr<sub>6</sub> octahedron where two *trans*-positioned Br atoms each have a weak bond to one of the Se atoms in a Se<sub>2</sub>Br<sub>2</sub> molecule [3]. This dianion

[SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> was the first example of bromotellurates (I, IV) containing selenium in oxidation states +1 and +4.

The binary compound of Te(IV) with bromine TeBr<sub>4</sub> is very stable and like other tellurium(IV) halides was characterized structurally [4, 5]. It makes a series of complexes with bromide: the anions [TeBr<sub>6</sub>]<sup>2-</sup> [1, 6, 7], [TeBr<sub>5</sub>]<sup>-</sup> [8], [Te<sub>2</sub>Br<sub>10</sub>]<sup>2-</sup> [9, 10], [Te<sub>2</sub>Br<sub>9</sub>]<sup>-</sup> [11], [Te<sub>3</sub>Br<sub>13</sub>]<sup>-</sup> [6]. All these anions are based on TeBr<sub>6</sub> octahedra, and in the oligomeric species the octahedra are connected by common edges.

The dianion [SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> was isolated as the phenyltrimethylammonium salt by reaction between elemental selenium and bromine in the presence of phenyltrimethylammonium bromide [3]. The amounts of reactants used were in accordance with the equation



In this work, elemental selenium and TeBr<sub>4</sub> were used in addition to bromine and phenyltrimethylammonium bromide, looking for the possibility of making a similar complex containing selenium and tellurium. The amounts of reactants used were in accordance with the equation

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$\text{TeBr}_4 + 4\text{Se} + 2\text{Br}_2 + 2\text{Br}^- = [\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$ , since the product of selenium reaction with bromine in acetonitrile when Se/Br<sub>2</sub> ratio is 2.0 is mainly Se<sub>2</sub>Br<sub>2</sub> [3].

This work reports 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.

## EXPERIMENTAL

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

**Preparation.** [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>] (**1**). To 4.8 mmol (0.379 g) of selenium in 4.0 g of acetonitrile 2.4 mmol (0.384 g) of bromine were added. The mixture was stirred and heated to 65 °C. Small amounts of selenium did not react. 1.2 mmol (0.537 g) of tellurium tetrabromide and 2.4 mmol (0.519 g) of phenyltrimethylammonium bromide were added to the mixture under stirring and heating. Soon a red-orange precipitate formed, and in spite of 8 g more acetonitrile added it did not dissolve. The hot suspension was filtered, and 0.57 mmol (0.48 g) of small orange crystals of phenyltrimethylammonium hexabromotellurate [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>] were isolated. The filtrate was left at room temperature for 2 h, and 0.31 mmol (0.46 g) of red short prisms was isolated. The filtrate was placed first in a refrigerator for 12 h and then in a freezer for 12 h, and 0.19 mmol (0.28 g) more of the compound was isolated. Found: Se 20.41. Calc. for [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]: Se 20.85.

**X-ray structure analyses.** The determination of unit cell dimensions and data collection were carried out on a BRUKER -AXS SMART 2K diffractometer. The structure was solved by direct methods using SHELXS97 [12] and refined by SHELXL97 [13]. Atomic scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 in ref. [14]. Since the unit cell dimensions and volume were similar and somewhat larger than of the analogous pure selenium compound [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>], we expected that the compound isolated was isomorphous with the former one, and tried to solve the structure in the centric space group *P*2<sub>1</sub>/*n*, but unsuccessfully. 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*<sub>*c*</sub> was multi-

plied by  $k[1 + 0.001x \times F_c \times \lambda^3/\sin(2\theta)]^{-1/4}$ , where *k* is the overall scale factor and *x* was found to be 0.00049(8). The hydrogen atoms were found in the difference electron density map 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 one carbon atom C(16) of the phenyl ring were refined anisotropically. After all atoms had been located, the value of the Flack absolute structure parameter *x* was close to 0.5, and following the program suggestion racemic twinning was refined. The final value of the absolute structure parameter refined in this way was 0.478(19).

The final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Complete lists of bond lengths and angles, anisotropic displacement parameters, structure factors,

Table 1. Crystal data and structure refinement

Identification code	<b>1</b>
Empirical formula	C <sub>18</sub> H <sub>28</sub> N <sub>2</sub> Se <sub>4</sub> Br <sub>10</sub> Te
Formula weight	1514.96
Temperature/K	123(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	<i>Pn</i>
<i>a</i> /Å	8.8390(18)
<i>b</i> /Å	12.759(3)
<i>c</i> /Å	16.617(3)
β/°	104.57(3)
Volume/Å <sup>3</sup>	1813.7(6)
<i>Z</i>	2
<i>D</i> <sub>x</sub> /g cm <sup>-3</sup>	2.774
<i>D</i> <sub>m</sub> /g cm <sup>-3</sup> (293 K)	2.67
<i>F</i> (000)	1376
Crystal size/mm	0.23 × 0.32 × 0.40
θ range/°	1.60 to 31.54
<i>hkl</i> limits	<i>h</i> = -12→12 <i>k</i> = -18→18 <i>l</i> = -24→24
Absorption coeff./mm <sup>-1</sup>	15.864
Correction for absorption	Numerical
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.01754/0.11645
Reflections collected/unique	34606/12059
No with <i>I</i> > 2σ( <i>I</i> )	10074
Data/restraints/parameters	12059/2/313
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> ) + (0.0388 <i>P</i> ) <sup>2</sup> + 0.0000 <i>P</i> ] <sup>-1</sup>
Extinction coefficient	0.00049(8)
Refinement on	<i>F</i> <sup>2</sup>
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.016
<i>R</i> ( <i>F</i> ) [ <i>I</i> > 2σ( <i>I</i> )]	0.0292
<i>R</i> ( <i>F</i> ) (all data)	0.0387
<i>WR</i> ( <i>F</i> <sup>2</sup> ) [ <i>I</i> > 2σ( <i>I</i> )]	0.0717
<i>WR</i> ( <i>F</i> <sup>2</sup> ) (all data)	0.0746
Absolute structure parameter	0.478(19)
Max. and min. Δρ/e Å <sup>3</sup>	0.741 and -1.16

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

Atom	x	y	z	$U(\text{eq})^a$
Te	2005(2)	2501(1)	3264(1)	12(1)
Br(1)	939(1)	2125(1)	1621(1)	18(1)
Br(2)	2193(2)	4576(1)	2974(1)	20(1)
Br(3)	3071(2)	2877(1)	4908(1)	19(1)
Br(4)	4984(2)	2254(1)	3194(1)	21(1)
Br(5)	-990(2)	2760(1)	3334(1)	21(1)
Br(6)	1842(2)	428(1)	3551(1)	21(1)
Se(1)	1417(1)	3193(1)	6381(1)	17(1)
Se(2)	3601(2)	4096(1)	7011(1)	19(1)
Br(7)	29(2)	3009(1)	7429(1)	24(1)
Br(8)	5490(2)	2764(1)	7428(1)	26(1)
Se(3)	387(2)	904(1)	-492(1)	18(1)
Se(4)	2575(1)	1811(1)	138(1)	17(1)
Br(9)	-1458(2)	2246(1)	-907(1)	28(1)
Br(10)	3981(2)	1972(1)	-880(1)	25(1)
N(1)	1791(9)	-144(8)	6442(5)	11(1)
C(11)	1726(14)	-1236(9)	6434(9)	19(2)
C(12)	2817(12)	278(9)	5975(6)	17(2)
C(13)	2433(15)	151(11)	7449(7)	23(2)
C(14)	69(13)	322(9)	6124(7)	12(2)
C(15)	-272(13)	760(10)	5411(8)	16(2)
C(16)	-1864(14)	1198(9)	5138(7)	17(2)
C(17)	-2943(15)	1066(9)	5665(8)	18(2)
C(18)	-2461(13)	667(11)	6352(7)	16(2)
C(19)	-919(14)	230(11)	6701(8)	19(2)
N(2)	7310(11)	-5065(8)	5001(6)	15(2)
C(21)	7458(14)	-6335(9)	5130(8)	17(2)
C(22)	6083(17)	-4780(12)	5514(9)	42(4)
C(23)	6538(15)	-4791(11)	4223(6)	23(2)
C(24)	8811(14)	-4634(9)	5290(6)	12(2)
C(25)	9447(14)	-4176(10)	6145(7)	17(2)
C(26)	10901(16)	-3876(9)	6407(8)	26(3)
C(27)	11859(16)	-3847(10)	5927(9)	25(3)
C(28)	11351(15)	-4373(11)	5035(7)	18(2)
C(29)	9876(14)	-4724(10)	4838(7)	18(2)

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

hydrogen coordinates and least square planes are available from the authors.

## RESULTS AND DISCUSSION

Bond lengths and angles of the  $[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$  ion are listed in Table 3, and selected dimensions of  $\text{Se}_2\text{Br}_2$  units in the present structure and in an analogous anion of a pure selenium compound including those of  $\alpha$ - and  $\beta$ - $\text{Se}_2\text{Br}_2$  modifications are listed in Table 4. A view of the anion of compound **1** is shown in Figure 1.

The  $[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$  ion is a unique tellurium complex like the ion  $[\text{SeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$  is one of the most unique selenium complexes. Like the last one,

it is built up of a nearly regular octahedral  $\text{TeBr}_6^{2-}$  ion and using two of the bromine ligands as bridges to two  $\text{Se}_2\text{Br}_2$  molecules. Thus this structure closely resembles the structure of the analogous pure selenium anion. The difference between them is that in the crystals the tetravalent selenium lies in the centre of symmetry and the asymmetric unit is half of the anion and one cation. In the present structure the tellurium atom is situated in a general position, but the anion is approximately centrosymmetric. The central  $\text{TeBr}_6$  octahedron has a nearly ideal octahedral symmetry with largest deviation of angles  $1.84^\circ$ , and the six independent bond lengths are 2.6828(17), 2.6978(19), 2.698(2), 2.6988(19), 2.6994(17) and 2.704(2)  $\text{\AA}$  (average 2.6968  $\text{\AA}$ ); thus the largest difference is 0.0212  $\text{\AA}$ . The smallest deviations of angles and lengths of Te(IV)-Br bonds were found in the structure of the hexabromotellurate(IV) of the same phenyltrimethylammonium cation [7]  $1.28^\circ$  and 0.0125  $\text{\AA}$ , respectively, but in the latter structure the Te atom is situated in the centre of symmetry, and in such cases smaller deviations from ideal symmetry are usually observed [1]. Variation of the bond lengths in  $3c-4e$  systems is common, and the dimensions are in agreement with those in the compounds  $[\text{H}_3\text{O}_4]_2[\text{TeBr}_6]$  and  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6]$ , with bond lengths in the ranges 2.671(4)–2.716(4)  $\text{\AA}$  [6] and 2.6931(5)–2.7056(6)  $\text{\AA}$  (average 2.701  $\text{\AA}$ ) [7], respectively. Thus the coordination of two  $\text{Se}_2\text{Br}_2$  molecules does not have an apparent influence on the length of the complex Te–Br bond. The contacts of two bromine ligands of  $\text{TeBr}_6$  octahedra and Se(1) and Se(4) atoms of  $\text{Se}_2\text{Br}_2$  molecules, 3.177(2) and 3.180(2)  $\text{\AA}$ , are slightly longer as compared with analogous contacts in the  $[\text{SeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$  ion, 3.133(2)  $\text{\AA}$ , and are probably, as in the latter structure, of the donor–acceptor adduct type, with the Br(1) and Br(3) atoms as donors and the Se atoms of the  $\text{Se}_2\text{Br}_2$  molecules as acceptors. It was pointed out [3] in the discussion on adducts with bromine coordinated to Se(IV) as donor, with a bromine molecule as acceptor, that the acceptor has to be co-linear with the Br–Se–Br se-

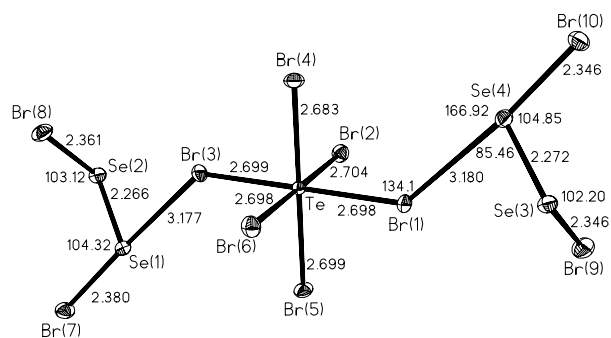


Figure. View of the  $[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$  ion as found in the phenyltrimethylammonium salt

Te-Br(1)	2.6978(19)	Se(2)-Br(8)	2.361(2)
Te-Br(2)	2.704(2)	Se(1)-Br(3)	3.177(2)
Te-Br(3)	2.6988(19)	Se(2) ... Br(2a)	3.599(2)
Te-Br(4)	2.6828(17)	Se(3)-Se(4)	2.272(2)
Te-Br(5)	2.6994(17)	Se(3)-Br(9)	2.346(2)
Te-Br(6)	2.698(2)	Se(4)-Br(10)	2.346(2)
Se(1)-Se(2)	2.266(2)	Se(4)-Br(1)	3.180(2)
Se(1)-Br(7)	2.380(2)	Se(3) ... Br(6b)	3.567(2)
Br(1)-Te-Br(2)	90.87(6)	Br(5)-Te-Br(6)	90.90(6)
Br(1)-Te-Br(3)	179.99(9)	Se(1)-Se(2)-Br(8)	103.12(9)
Br(1)-Te-Br(4)	91.84(6)	Se(2)-Se(1)-Br(7)	104.32(8)
Br(1)-Te-Br(5)	88.23(6)	Se(2)-Se(1)-Br(3)	85.26(6)
Br(1)-Te-Br(6)	89.10(6)	Br(7)-Se(1)-Br(3)	166.63(8)
Br(2)-Te-Br(3)	89.14(6)	Te-Br(3)-Se(1)	133.73(6)
Br(2)-Te-Br(4)	90.12(6)	Se(1)-Se(2) ... Br(2a)	176.88(8)
Br(2)-Te-Br(5)	89.59(6)	Se(4)-Se(3)-Br(9)	102.20(8)
Br(2)-Te-Br(6)	179.51(8)	Se(3)-Se(4)-Br(10)	104.85(8)
Br(3)-Te-Br(4)	88.17(6)	Se(3)-Se(4)-Br(1)	85.46(6)
Br(3)-Te-Br(5)	91.76(6)	Br(10)-Se(4)-Br(1)	166.92(8)
Br(3)-Te-Br(6)	90.89(6)	Te-Br(1)-Se(4)	134.05(6)
Br(4)-Te-Br(5)	179.70(9)	Se(4)-Se(3) ... Br(6b)	177.26(8)
Br(4)-Te-Br(6)	89.39(6)		
Br(7)-Se(1)-Se(2)-Br(8)	97.03(9)	Br(8)-Se(2)-Se(1)-Br(3)	-73.50(7)
Br(9)-Se(3)-Se(4)-Br(10)	-97.62(9)	Br(9)-Se(3)-Se(4)-Br(1)	74.20(7)
Symmetry transformations: (a) $x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ ; (b) $x - \frac{1}{2}, -y, z + \frac{1}{2}$ .			

Se<sub>2</sub>Br<sub>2</sub> parts of the [TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> ion, as of [SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> ion, have more open structures. The Se<sub>2</sub>Br<sub>2</sub> parts of the present structure are acceptors in a donor-acceptor adduct. As usual, the bond within the acceptor is weakly influenced by the contact; the bond between the donors Br(1) and Br(3) atoms and the acceptors – Se(1) and Se(4) atoms of the Se<sub>2</sub>Br<sub>2</sub> molecules is long, 3.177(2) and 3.180(2) Å, *i.e.* even longer than in the [SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> ion.

The Se–Se bonds, like in the structure of [SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup>, are a little, but significantly, longer in the present structure than in the Se<sub>2</sub>Br<sub>2</sub> modifications. The Se(1) and Se(4) atoms of the present compound are acting as central atoms in the asymmetric, nearly linear 3c–4e Br(3)–Se(I)–Br(7) and Br(1)–Se(4)–Br(10) systems. The bond lengths of the individual 3c–4e systems are 2.380(2)/3.177(2) Å and 2.346(2)/3.180(2) Å; the longer bonds are to the bridging bromine atoms. In the directions of the Se(1)–Se(2) and Se(4)–Se(3) bonds,

quence to have influence on the length of the complex Se–Br bond. In the crystal structure of [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>] the angle Se(IV)–Br–Se(I) is 135.46(6)°, and no influence on the complex bond was observed. In the present structure of [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>] the angles Te(IV)–Br–Se(I) are similar, 133.73(6) and 134.05(6)°, and no influence on the complex bond Te–Br is observed, either.

The Se<sub>2</sub>Br<sub>2</sub> parts of the [TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> ion show a resemblance to the structures of the two solid Se<sub>2</sub>Br<sub>2</sub> modifications [2] and to Se<sub>2</sub>Br<sub>2</sub> units of the [Se<sub>4</sub>Br<sub>6</sub>]<sup>2-</sup> ion [3], and especially to the Se<sub>2</sub>Br<sub>2</sub> parts of the [SeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> ion. However, β-Se<sub>2</sub>Br<sub>2</sub> and [Se<sub>4</sub>Br<sub>6</sub>]<sup>2-</sup> both form six-membered rings, whereas the

	α-Se <sub>2</sub> Br <sub>2</sub>	β-Se <sub>2</sub> Br <sub>2</sub>	[SeBr <sub>6</sub> (Se <sub>2</sub> Br <sub>2</sub> ) <sub>2</sub> ] <sup>2-</sup>	[TeBr <sub>6</sub> (Se <sub>2</sub> Br <sub>2</sub> ) <sub>2</sub> ] <sup>2-</sup>
Se–Se	2.258(2)	2.241(1)	2.272(2)	2.266(2) 2.272(2)
Br–Se–Se–Br <sup>a</sup>	85.0(1)	86.41(8)	97.49(8)	97.03(9) 97.62(9)
Se–Br	2.357(2)	2.366(1)	2.347(2)	2.361(2) 2.346(2)
Se–Se–Br	107.23(8)	103.86(5)	102.40(8)	103.12(9) 102.20(8)
Se–Br		2.369(1)	2.360(2)	2.380(2) 2.346(2)
Se–Se–Br		104.51(5)	104.22(7)	104.32(8) 104.85(8)
Se ... Br		3.373(1)	3.133(2)	3.177(2) 3.180(2)
Br–Se ... Br		162.3(6)	166.24(7)	166.63(8) 166.92(8)
Ref.	2	2	3	This work
<sup>a</sup> Torsion angle.				

Se(2) has a contact to Br(2) and Se(3) a contact to Br(6) atoms of adjacent  $[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$  ions. The Se(2) ... Br(2) distance is 3.599(2) Å and the Se(3) ... Br(6) distance is 3.567(2) Å, and the Se(1)-Se(2) ... Br(2) angle is 176.88(8) ° and the Se(4)-Se(3) ... Br(6) angle is 177.26(8) °. In addition, Se(2) and Se(3) have contacts to phenyl carbon atoms of the adjacent molecule, C(27) and C(17), respectively. The Se(2) ... C(27) and Se(3) ... C(17) distances are 3.333 and 3.281 Å, respectively. These weak bonds complete the distorted square-planar coordination geometries of Se(2) and Se(3) atoms. The Se(1) and Se(4) atoms have weak contacts each to two hydrogen atoms of methyl groups of the adjacent molecule, H(21B), H(21C) and H(11B), H(11C), respectively. The Se(1) ... H(21B), Se(1) ... H(21C), Se(4) ... H(11B), Se(4) ... H(11C) distances are 3.219, 3.323, 3.401 and 3.464 Å, respectively. Thus these contacts complete the distorted square-planar coordination of the Se(1) and Se(4) atoms.

The dimensions of the phenyltrimethylammonium cations are within the following ranges: N-C = 1.347(13)–1.670(13) Å, C-C = 1.225(17)–1.586(17) Å, C-N-C = 101.5(9)–116.3(9) °, N-C-C = 115.6(10)–124.8(10) ° and C-C-C = 111.4(11)–127.4(11) °.

## CONCLUSIONS

As a result of the reaction between selenium and bromine, and tellurium tetrabromide in acetonitrile in the presence of phenyltrimethylammonium bromide, a bis(phenyltrimethylammonium) hexabromotellurate(IV)bis{dibromodiselenate(I)} is isolated.

X-ray structure analysis has shown that the crystals of  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]$  are monoclinic, space group  $Pn$  with  $Z = 2$  and  $a = 8.8390(18)$ ,  $b = 12.759(3)$ ,  $c = 16.617(3)$  Å,  $\beta = 104.57(3)$  °.

The anion  $[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$  is built up of a nearly regular octahedral  $[\text{TeBr}_6]^{2-}$  ion, using two of the *trans*-positioned Br ligands as bridges to two  $\text{Se}_2\text{Br}_2$  molecules. The Te(IV)-Br distances are in the range 2.6828(17)–2.704(2) Å, and the coordination of two  $\text{Se}_2\text{Br}_2$  molecules does not have an apparent influence on the length of the complex Te–Br bond.

The bond lengths in coordinated  $\text{Se}_2\text{Br}_2$  molecules are: Se(I)–Se(I) = 2.266(2) and 2.272(2) Å, Se(I)–Br = 2.380(2), 2.361(2), 2.346(2) and 2.346(2) Å. The  $\text{Se}_2\text{Br}_2$  parts of  $[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]^{2-}$  structure are acceptors in a donor–acceptor adduct, and as usual the bond within the acceptor is weakly influenced by the contact.

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## BIS(FENILTRIMETILAMONIO)

## HEKSABROMOTELURITO(IV)BIS{DIBROMODISELENITO(I)}, [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>], SINTEZĖ IR KRISTALINĖ STRUKTŪRA

S a n t r a u k a

Junginys  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2[\text{TeBr}_6(\text{Se}_2\text{Br}_2)_2]$  (1) gautas seleni sąveikaujant su bromu, telūro tetrabromidu ir feniltrimetilamonio bromidu acetonitrile. Jo kristalinė ir molekulinė struktūra nustatyta monokristalų rentgenostruktūrine analize ir išstobulinta iki  $R = 0,0292$  ir  $0,0387$  atitinkamai 10074 ir 12059 atspindžiams. Kristalai yra monoklininės singonijos, erdvinė grupė  $Pn$  su  $Z = 2$  ir  $a = 8,8390(18)$ ,  $b = 12,759(3)$ ,  $c = 16,617(3)$  Å,  $\beta = 104,57(3)$  °. 1 junginio anijonas yra beveik taisyklingas oktaedras, kurio du *trans*-pozicijose esantys Br atomai kiekvienas turi jungtį su vienu  $\text{Se}_2\text{Br}_2$  molekulės Se atomu. Jungčių Te(IV)-Br

ilgiai yra intervale 2,6828(17)–2,704(2) Å. Jungčių ilgiai koordinuotose  $\text{Se}_2\text{Br}_2$  molėkulėse yra tokie:  $\text{Se(I)-Se(I)} = 2,266(2)$  ir  $2,272(2)$  Å,  $\text{Se(I)-Br} = 2,380(2)$ ,  $2,361(2)$ ,  $2,346(2)$  ir  $2,346(2)$  Å.

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**СИНТЕЗ И КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА  
ГЕКСАБРОМОТЕЛЛУРИПА(IV)БИСДИБРОМОДИСЕЛЕНИТА(IV)  
БИС(ФЕНИЛТРИМЕТИЛАММОНИЯ),  
[C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>]**

Резюме

Соединение [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>2</sub>[TeBr<sub>6</sub>(Se<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>] (**1**) получено в результате взаимодействия селена с бромом, тетрабромидом теллура и бромидом фенилтриметил-

аммония в ацетонитриле. Кристаллическая структура установлена рентгеноструктурным анализом монокристаллов и уточнена до  $R = 0,0292$  и  $0,0387$  для соответственно 10074 и 12059 рефлексов. Кристаллы относятся к моноклинной сингонии, пространственная группа симметрии  $Pn$  с  $Z = 3$  и  $a = 8,8390(18)$ ,  $b = 12,759(3)$ ,  $c = 16,617(3)$  Å,  $\beta = 104,57(3)^\circ$ . Анион соединения **1** представляет собой почти правильный октаэдр, два атома брома которого, находящиеся в *транс*-позициях, имеют каждый связь с одним атомом селена молекул  $\text{Se}_2\text{Br}_2$ . Межатомные расстояния Te(IV)–Br находятся в интервале 2,6828(17)–2,704(2) Å. Межатомные расстояния в координированных молекулах  $\text{Se}_2\text{Br}_2$  таковы:  $\text{Se(I)-Se(I)} = 2,266(2)$  и  $2,272(2)$  Å,  $\text{Se(I)-Br} = 2,380(2)$ ,  $2,361(2)$ ,  $2,346(2)$  и  $2,346(2)$  Å.