# Syntheses and Crystal Structures of Phenyltrimethylammonium Salts of a Mixed Hexabromoselenate/tellurate(IV), $[C_6H_5(CH_3)_3N]_2[Se_{0.75}Te_{0.25}Br_6]$, and a Mixed *catena*-poly[(Di-μ-bromobis{tetrabromoselenate/tellurate(IV)})-μ-bromine], $[C_6H_5(CH_3)_3N]_{2n}[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]_n$

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The title compounds were prepared from elemental selenium and bromine and tellurium tetrabromide, and phenyltrimethylammonium bromide. The crystal structures of $[C_6H_5(CH_3)_3N]_2[Se_{0.75}Te_{0.25}Br_6]$ (1) and $[C_6H_5(CH_3)_3N]_{2n}$-$[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]_n$ (2) have been determined by X-ray methods and refined to $R = 0.056$ and 0.044 for 1450 and 2469 reflections, respectively. In both compounds each chalcogen position is partly occupied by selenium and partly by tellurium. The content of tellurium in one position in both anions is 25%. Crystals of 1 are monoclinic, space group $P2_1/c$ with $Z = 2$ and $a = 8.8060(18)$, $b = 10.675(2)$, $c = 14.200(3)$ Å, $\beta = 104.16(3)°$. Crystals of 2 are triclinic, space group $P\bar{1}$ with $Z = 1$ and $a = 8.6676(17)$, $b = 8.8614(18)$, $c = 11.473(2)$ Å, $\alpha = 94.13(3)$, $\beta = 102.19(3)$, $\gamma = 90.47(3)°$. The $[Se_{0.75}Te_{0.25}Br_6]^{2-}$ octahedron of 1 is centrosymmetric with Se(Te)–Br(1) = 2.6048(11), 2.5990(11), 2.5995(11) Å and Br–Se(Te)–Br = 90.24(4), 89.92(4), 89.06(4)°. The dimeric, centrosymmetric $[Se_{1.5}Te_{0.5}Br_{10}]^{2-}$ unit of 2, consisting of two edge-sharing Se(Te)Br$_6$ octahedra, has Se(Te)–Br dimensions 2.4310(11) and 2.4566(12) Å for equatorial terminal, 2.9107(12) and 2.8189(12) Å for equatorial bridging, and 2.5888(11) and 2.5898(11) Å for axial bonds. One of the axial bromine atoms in each Se(Te)Br$_6$ octahedron is linked to an equivalent Br atom by a Br$_2$ molecule, thus forming a polymeric chain, $[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]_n^{2n-}$, with Br–Br$_2$ = 3.0699(14) Å, Br–Br' = 2.336(2) Å, Br–Br–Br' = 172.67(6)°.

Selenium(IV) and tellurium(IV) form six-coordinated octahedral or distorted octahedral complexes with bromide. The known modifications of such complexes are the monomeric anions $[SeBr_6]^{2-}$,[1–8] $[TeBr_6]^{2-}$,[4,9,10] $[TeBr_5]^-$,[7] a number of dimeric forms $[Se_2Br_9]^-$,[3,11] $[Te_2Br_9]^-$,[12,13] $[Se_2Br_{10}]^{2-}$,[4,6,11,14] $[Te_2Br_{10}]^{2-}$,[12,15–17] one trimeric form $[Se_3Br_{13}]^-$,[18] $[Te_3Br_{13}]^-$,[9,12] and tetrameric neutral molecules, $[Se_4Br_{16}]$[19] and $[Te_4Br_{16}]$.[20,21] Polymeric anions are also known. In the crystals of $[(CH_3)_3NH]_{2n}$ $[SeBr_6 \cdot Br_2]_{2n}$,[3,4] the SeBr$_6$ octahedra are polymerised by Br$_2$ molecules connected to two *cis*-positioned Br atoms. The anion $[Te_2Br_9]_n^{n-}$[12] consists of Te$_2$Br$_{10}$ units with one axial Br atom of each octahed-

ron situated on a twofold axis. The crystals of $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10} \cdot Br_2]_n$[8] and $[C_6H_5(CH_3)_3N]_{2n}$-$[Te_2Br_{10} \cdot Br_2]_n$[10] contain centrosymmetric $[Se_2Br_{10}]^{2-}$ or $[Te_2Br_{10}]^{2-}$ units, consisting of two edge-sharing distorted SeBr$_6$ or TeBr$_6$ octahedra. One of the axial bromine atoms in each SeBr$_6$ or TeBr$_6$ octahedron is linked to an equivalent Br atom by a Br$_2$ molecule, and so forming a polymeric chain, $[Se_2Br_{10} \cdot Br_2]_n^{2n-}$ or $[Te_2Br_{10} \cdot Br_2]_n^{2n-}$. Many salts of analogous selenium and tellurium bromide complexes form isomorphous crystals; for instance, $[C_6H_5(CH_3)_3N]_2[SeBr_6]$ and $[C_6H_5(CH_3)_3N]_2[TeBr_6]$, $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10} \cdot Br_2]_n$[8] and $[C_6H_5(CH_3)_3N]_{2n}[Te_2Br_{10} \cdot Br_2]_n$.[10] We wanted to look into the possibility of making analogues to the two last mentioned Se$^{IV}$- and Te$^{IV}$-polymeric complexes but containing in the same anion both Se$^{IV}$-

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and $Te^{IV}$-atoms as the central ones. We report here the crystal structures of the compound $[C_6H_5(CH_3)_3N]_2$-$[Se_{0.75}Te_{0.25}Br_6]$, which is isomorphous with the earlier described compounds $[C_6H_5(CH_3)_3N]_2[SeBr_6]$ and $[C_6H_5(CH_3)_3N]_2[TeBr_6]$, and of the compound $[C_6H_5(CH_3)_3N]_{2n}[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]_n$, which is isomorphous with the abovementioned analogues pure selenium and pure tellurium polymeric compounds, $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10} \cdot Br_2]_n,$[8] and $[C_6H_5(CH_3)_3N]_{2n}$-$[Te_2Br_{10} \cdot Br_2]_n$.[10]

## Experimental

*Preparations.* Compounds $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10} \cdot Br_2]_n$ and $[C_6H_5(CH_3)_3N]_{2n}[Te_2Br_{10} \cdot Br_2]_n$ were prepared by reactions in acetonitrile of selenium or tellurium, bromine and phenyltrimethylammonium bromide[8,10] using an excess of bromine according to the equations:

$$2Se + 5Br_2 + 2Br^- = Se_2Br_{10} \cdot Br_2^{2-}$$

$$2Te + 5Br_2 + 2Br^- = Te_2Br_{10} \cdot Br_2^{2-}$$
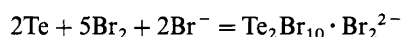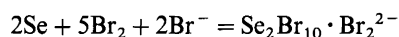
In this work elemental selenium and $TeBr_4$ were used in

addition to bromine and phenyltrimethylammonium bromide, looking for the possibility of making a similar complex containing selenium and tellurium, according to the equation

$$Se + 3Br_2 + TeBr_4 + 2Br^- = TeSeBr_{10} \cdot Br_2^{2-}$$
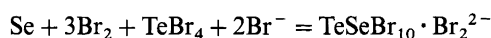
Determination of selenium was done by treating the sample with a sulfite solution, adding bromide and oxidizing with bromine. Excess of bromine was removed, and the amount of selenium was determined iodometrically. Bromine was determined by potentiometric titration with silver nitrate. Densities were measured by flotation, using a mixture of trichloromethane and tribromomethane.

*$[C_6H_5(CH_3)_3N]_2$ $[Se_{0.75}Te_{0.25}Br_6]$* (1). Crystals of this composition were obtained after crystallisation of compound **2**. The filtrate was placed in a refrigerator for few days, and homogeneous brown plate-like crystals were isolated. Yield 0.45 g, 18% of selenium used. Found: Se 6.42, Br 56.66. Calc. for $[C_6H_5(CH_3)_3N]_2$-$[Se_{0.75}Te_{0.25}Br_6]$: Se 7.02, Br 56.87.

*Table 1.* Crystal data and structure refinement.

| Identification code | 1 | 2 |
| --- | --- | --- |
| Empirical formula | $C_{18}H_{28}Br_6N_2Se_{0.75}Te_{0.25}$ | $C_{18}H_{28}Br_{12}N_2Se_{1.5}Te_{0.5}$ |
| Formula weight | 843.00 | 1413.58 |
| Temperature/K | 263(2) | 112(2) |
| Wavelength/Å | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| a/Å | 8.8060(18) | 8.6676(17) |
| b/Å | 10.675(2) | 8.8614(18) |
| c/Å | 14.200(3) | 11.473(2) |
| $\alpha/°$ | | 94.13(3) |
| $\beta/°$ | 104.16(3) | 102.19(3) |
| $\gamma/°$ | | 90.47(3) |
| Volume/Å³ | 1294.3(4) | 858.9(3) |
| Z | 2 | 1 |
| $D_c$/g cm$^{-3}$ | 2.163 | 2.733 |
| $D_o$/g cm$^{-3}$ (293 K) | 2.16 | 2.65 |
| F(000) | 797 | 647 |
| Crystal size/mm | 0.42 × 0.44 × 0.55 | 0.19 × 0.20 × 0.25 |
| θ range/° | 2.39–24.97 | 2.3–25.01 |
| hkl limits | h=0→10 | h= -10→10 |
| | k=0→12 | k= -10→10 |
| | l= -16→16 | l=0→13 |
| Absorption coefficient/mm$^{-1}$ | 10.674 | 16.054 |
| Correction for absorption | Numerical | Empirical, $\psi$-scan |
| $T_{min}/T_{max}$ | 0.017/0.078 | 0.087/0.154 |
| Independent reflections | 2280 | 3018 |
| No. with $I>2\sigma(I)$ | 1450 | 2469 |
| Data/restraints/parameters | 2280/1/130 | 3018/1/160 |
| Weight, $P=(F_o^2+2F_c^2)/3$ | $[\sigma^2(F^2)+(0.1012P)^2]^{-1}$ | $[\sigma^2(F^2)]^{-1}$ |
| Extinction coefficient | 0.0038(8) | 0.0035(10) |
| Refinement on | $F^2$ | $F^2$ |
| Goodness-of-fit on $F^2$ | 0.963 | 0.721 |
| $R(F)$ $[I>2\sigma(I)]$ | 0.056 | 0.0441 |
| $R(F)$ (all data) | 0.1126 | 0.0583 |
| $WR(F^2)$ $[I>2\sigma(I)]$ | 0.1398 | 0.1212 |
| $WR(F^2)$ (all data) | 0.1527 | 0.1648 |
| Max. and min. $\Delta\rho/e$ Å$^{-3}$ | 2.048 and −1.237 | 1.436 and −1.612 |

$[C_6H_5(CH_3)_3N]_{2n}[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]_n$ (2). To 2.0 mmol (0.158 g) selenium in 3.2 g acetonitrile was added 6.4 mmol (1.023 g) bromine. The suspension was stirred until all selenium had reacted. 2.0 mmol (0.8944 g) of tellurium tetrabromide and 19 g acetonitrile, and 4 mmol (0.8645 g) phenyltrimethylammonium bromide was added. The suspension was heated to boiling until all solid was dissolved and then set aside at room temperature. After a few hours a mixture of mainly well developed brown prisms and of some small brown–yellow plate-like crystals of $[C_6H_5(CH_3)_3N]_2$-$[Se_{0.75}Te_{0.25}Br_6]$ (which crystallised from the filtrate later as main product of the second fraction) were isolated. Yield 1.4 g, 72% of selenium used. The brown prisms were $[C_6H_5(CH_3)_3N]_{2n}[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]_n$ and it was easy to separate them. Found: Se 8.12, Br 62.67. Calc. for $[C_6H_5(CH_3)_3N]_{2n}[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]_n$: Se 8.38, Br 67.83. The reduced content of bromine determined may be explained by contaminations with $[C_6H_5(CH_3)_3N]_2$-$[Se_{0.75}Te_{0.25}Br_6]$.

*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 SHELXS97[22] and refined by SHELXL97.[23] Atomic scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 of Ref. 24. The crystal data, conditions for data collection and refinements are summarised in Table 1.

In both structures each chalcogen position is mainly occupied by Se and partly by Te. In each case Se and Te were put into the same position and their individual occupancy factors refined (for Se −0.37756 and 0.76277, for Te −0.12243 and 0.23723 in 1 and 2, respectively) by assuming a total of 0.5 for 1 and total of 1 for 2, since the chalcogen atoms of $[Se_{0.75}Te_{0.25}Br_6]^{2-}$ anion of 1 are situated on a centre of symmetry. For both structures an extinction parameter $x$ was refined by least squares, where $F_c$ was multiplied 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 0.0038(8) for 1 and 0.0035(10) for 2. The hydrogen atoms were in all structures placed geometrically 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 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, hydrogen coordinates and least squares planes are available from the author.

## Results and discussion

Selected bond lengths and angles are given in Table 3, and a view of the anion of compound 2 is shown in Fig. 1. Compound 1 is isomorphous with the compounds

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

| Atom | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| $[C_6H_5(CH_3)_3N]_2[Se_{0.75}Te_{0.25}Br_6]$ (1) | | | | |
| Se | 5000 | 0 | 5000 | 26(1) |
| Te | 5000 | 0 | 5000 | 26(1) |
| Br(1) | 5302(1) | 1169(1) | 6646(1) | 41(1) |
| Br(2) | 4934(1) | 2131(1) | 4105(1) | 45(1) |
| Br(3) | 8023(1) | −33(1) | 5269(1) | 43(1) |
| N | 1790(9) | −359(7) | 8012(6) | 35(2) |
| C(1) | 1789(13) | −1207(12) | 7164(8) | 54(3) |
| C(2) | 1455(13) | 968(11) | 7640(10) | 57(3) |
| C(3) | 3380(13) | −363(11) | 8674(9) | 54(3) |
| C(4) | 576(11) | −789(8) | 8497(7) | 33(2) |
| C(5) | 969(13) | −1445(11) | 9355(8) | 52(3) |
| C(6) | −196(14) | −1886(12) | 9758(8) | 61(3) |
| C(7) | −1732(13) | −1696(11) | 9334(8) | 47(3) |
| C(8) | −2131(13) | −1080(12) | 8460(9) | 56(3) |
| C(9) | −977(12) | −616(12) | 8054(8) | 51(3) |
| $[C_6H_5(CH_3)_3N]_2[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]$ (2) | | | | |
| Se | 3811(1) | 9827(1) | 1397(1) | 17(1) |
| Te | 3811(1) | 9827(1) | 1397(1) | 17(1) |
| Br(1) | 1062(1) | 9856(1) | 1566(1) | 23(1) |
| Br(2) | 4832(1) | 9783(1) | 3561(1) | 25(1) |
| Br(3) | 3836(1) | 12756(1) | 1536(1) | 21(1) |
| Br(4) | 3759(1) | 6896(1) | 1192(1) | 25(1) |
| Br(5) | 2944(1) | 9909(1) | −1107(1) | 21(1) |
| Br(6) | 4645(1) | 14283(1) | 4085(1) | 25(1) |
| N | 9001(8) | 5282(7) | 2235(6) | 20(1) |
| C(1) | 8669(13) | 6199(11) | 1168(8) | 35(2) |
| C(2) | 10276(12) | 4201(12) | 2080(9) | 35(2) |
| C(3) | 7546(11) | 4348(11) | 2224(8) | 31(2) |
| C(4) | 9479(9) | 6319(9) | 3356(7) | 21(2) |
| C(5) | 8329(11) | 6855(10) | 3927(9) | 29(2) |
| C(6) | 8781(12) | 7842(11) | 4954(9) | 37(2) |
| C(7) | 10335(11) | 8266(9) | 5375(8) | 27(2) |
| C(8) | 11445(11) | 7752(11) | 4773(9) | 31(2) |
| C(9) | 11027(10) | 6773(11) | 3757(8) | 29(2) |

[a] $U$(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

$[C_6H_5(CH_3)_3N]_2[SeBr_6]$[8] and $[C_6H_5(CH_3)_3N]_2[TeBr_6]$.[10] The Se and Te atoms of 1 are situated on a centre of symmetry, and the $[Se_{0.75}Te_{0.25}Br_6]^{2-}$ anion has very nearly ideal octahedral symmetry with largest deviation of angles 0.94°, and the three independent bond lengths 2.5955(11), 2.5990(11) and 2.6048(11) Å. Thus the largest difference is 0.0093 Å. The smallest deviation of analogous chalcogen(IV)–Br bonds was found in the structure of the isomorphous pure selenium compound,[8] and the largest in the structure of the isomorphous pure tellurium compound,[10] 0.0045 and 0.0125 Å, respectively. The average value of chalcogen–Br bond length in 1 2.600 Å is in between the average values of Se–Br and Te–Br bond lengths in compounds $[C_6H_5(CH_3)_3N]_2[SeBr_6]$[8] and $[C_6H_5(CH_3)_3$-$N]_2[TeBr_6]$,[10] 2.5717 and 2.701 Å, respectively, and is very close to the expected value of 2.604 Å. Thus the results are in good agreement with the dimensions of the

*Table 3.* Distances (in Å) and angles (in °) in $[Se_{0.75}Te_{0.25}Br_6]^{2-}$ and $[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]^{2-}$ ions.

**(1) $[Se_{0.75}Te_{0.25}Br_6]^{2-}$**

| | | | |
|---|---|---|---|
| Se(Te)–Br(1) | 2.6048(11) | Br(1)–Se(Te)–Br(2) | 90.24(4) |
| Se(Te)–Br(2) | 2.5990(11) | Br(1)–Se(Te)–Br(3) | 89.92(4) |
| Se(Te)–Br(3) | 2.5995(11) | Br(2)–Se(Te)–Br(3) | 89.06(4) |

Interionic contact:

| | | | |
|---|---|---|---|
| Br(3)···Br(3a) | 3.743(2) | Se(Te)–Br(3)···Br(3a) | 160.28(5) |

Symmetry operation: (a) $-x+2$, $-y$, $-z+1$

**(2) $[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]^{2-}$**

| | | | |
|---|---|---|---|
| Se(Te)–Br(1) | 2.4310(10) | Se(Te)–Br(5a) | 2.9107(12) |
| Se(Te)–Br(2) | 2.4566(12) | Br(3)–Br(6) | 3.0699(14) |
| Se(Te)–Br(3) | 2.5888(11) | Br(6)–Br(6f) | 2.336(2) |
| Se(Te)–Br(4) | 2.5898(11) | Se(Te)···Se,Te(a) | 4.188(2) |
| Se(Te)–Br(5) | 2.8189(12) | | |
| Br(1)–Se(Te)–Br(2) | 94.04(5) | Br(3)–Se(Te)–Br(4) | 178.35(4) |
| Br(1)–Se(Te)–Br(3) | 88.75(4) | Br(3)–Se(Te)–Br(5) | 87.60(4) |
| Br(1)–Se(Te)–Br(4) | 91.23(4) | Br(3)–Se(Te)–Br(5a) | 86.03(4) |
| Br(1)–Se(Te)–Br(5) | 91.45(4) | Br(4)–Se(Te)–Br(5) | 90.76(4) |
| Br(2)–Se(Te)–Br(3) | 91.89(5) | Br(5)–Se(Te)–Br(5a) | 86.07(4) |
| Br(2)–Se(Te)–Br(4) | 89.76(5) | Se(Te)–Br(5)–Se,Te(a) | 93.93(4) |
| Br(2)–Se(Te)–Br(5) | 174.48(4) | Se(Te)–Br(3)–Br(6) | 115.16(4) |
| Br(2)–Se(Te)–Br(5a) | 88.41(4) | Br(3)–Br(6)–Br(6f) | 172.67(6) |

Interionic contacts:

| | | | |
|---|---|---|---|
| Br(1)···Br(1b) | 3.703(2) | Se(Te)–Br(1)···Br(1b) | 102.66(5) |
| Br(1)···Br(5b) | 3.4106(13) | Se(Te)–Br(1)···Br(5b) | 166.33(4) |
| | | Se(Te)–Br(5)···Br(1b) | 101.98(4) |
| | | Se,Te(a)–Br(5)···Br(1b) | 162.33(3) |
| Br(2)···Br(2c) | 3.247(2) | Se(Te)–Br(2)···Br(2c) | 162.53(5) |
| Br(3)···Br(4d) | 3.7177(13) | Se(Te)–Br(3)···Br(4d) | 170.61(3) |
| | | Se(Te)–Br(4)···Br(3e) | 168.98(4) |

Symmetry operations: (a) $-x+1$, $-y+2$, $-z$; (b) $-x$, $-y+2$, $-z$; (c) $-x+1$, $-y+2$, $-z+1$; (d) $x$, $y+1$, $z$; (e) $x$, $y-1$, $z$; (f) $-x+1$, $-y+3$, $-z+1$.
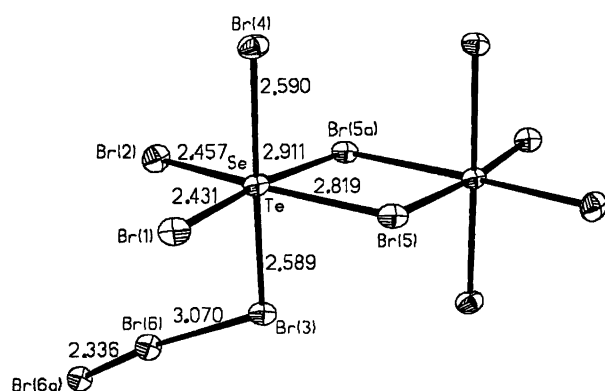


*Fig. 1.* View of the $[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]^{2-}$ ion as found in the phenyltrimethylammonium salt.

anions in the isomorphous pure selenium and pure tellurium compounds.

Compound **2** is isomorphous with $[C_6H_5(CH_3)_3N]_{2n}$-$[Se_2Br_{10} \cdot Br_2]_n$[8] and $[C_6H_5(CH_3)_3N]_{2n}[Te_2Br_{10} \cdot Br_2]_n$[10] and also with $[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10} \cdot Br_2]_n$.[25] Its $[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]^{2-}$ are double-bridged centrosym-

metric $Se_{1.5}Te_{0.5}Br_{10}$ dimers that are polymerised by bonding contacts between axial Br atoms and $Br_2$ molecules situated on symmetry centres. The bond lengths of the anions of these first three compounds are given in Table 4. *Trans* situated terminal and bridging bonds are listed on the same line. The axial bond lengths in **2** are equal, 2.590(1) and 2.589(1) Å, and confirm the conclusion[8,10] that they are unaffected by the contacts to the $Br_2$ molecule. They are very close to the bond lengths found in **1** (average 2.600 Å). Similar insensitivity of hexabromoselenate(IV) Se–Br bond lengths on coordination was found also in the structure of $[C_6H_5(CH_3)_3N]_2[SeBr_6(Se_2Br_2)_2]$,[26] where two *trans*-positioned Br atoms of a nearly regular $SeBr_6$ octahedron each have a weak bond to one of the Se atoms in a $Se_2Br_2$ molecule. The dinuclear complexes are polymerised through bromine molecules, probably by charge transfer bonds where bromide ligands bonded to selenium or tellurium are donors and the bromine molecules are acceptors. The $Br–Br_2–Br$ sequences are almost linear, with $X–Br–Br$ angles of 172.67(6)–174.23(6)°. In general, the bond lengths in the $[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]^{2-}$ anion are in between the corresponding bond lengths in

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*Table 4.* Selected bond lengths (in Å) and angles (in °) in $[Y_2Br_{10} \cdot Br_2]^{2-}$ ions (Y = Se or Te).

| Compound | Equatorial terminal X-Y bonds | Equatorial bridging Y-X bonds | Axial Y-X bonds | X-Br$_2$ bonds | Br-Br bonds | Y-X-Br$_2$ angle | X-Br-Br angle | Ref. |
|---|---|---|---|---|---|---|---|---|
| $[C_6H_5(CH_3)_3N]_2[Se_2Br_{10} \cdot Br_2]$ | 2.384(2) | 2.943(2) | 2.562(2) | 3.097(2) | 2.339(3) | 114.23(8) | 173.0(2) | |
| | 2.423(2) | 2.792(2) | 2.573(2)[a] | | | | | 8 |
| $[C_6H_5(CH_3)_3N]_2[Se_{1.5}Te_{0.5}Br_{10} \cdot Br_2]$ | 2.431(1) | 2.911(1) | 2.590(1) | 3.070(1) | 2.336(2) | 115.16(4) | 172.7(1) | This |
| | 2.457(1) | 2.819(1) | 2.589(1)[a] | | | | | work |
| $[C_6H_5(CH_3)_3N]_2[Te_2Br_{10} \cdot Br_2]$ | 2.538(1) | 2.967(1) | 2.678(1) | 3.122(2) | 2.332(2) | 112.17(3) | 174.3(1) | |
| | 2.542(1) | 2.959(1) | 2.696(1)[a] | | | | | 10 |

[a] X atom connected to Br$_2$.

the analogous pure selenium and pure tellurium compounds, and, as expected, closer to the bond lengths in the $[Se_2Br_{10} \cdot Br_2]^{2-}$ ion.

In the equatorial planes of Se(Te) coordination, each of the chalcogen atoms has, like in the $[Se_2Br_{10} \cdot Br_2]^{2-}$ and $[Te_2Br_{10} \cdot Br_2]^{2-}$ ions, a distorted square planar arrangement, being bonded to two terminal bromine atoms with rather strong $3c$–$4e$ bonds, the average bonds being about 0.15 Å shorter than the axial bonds. The *trans*-situated bridging bonds, as is common in linear $3c$–$4e$ systems, are asymmetric in such way that the shortest terminal bonds have the longest *trans*-bridging bond partners. In the structure of **2** the difference between the lengths of the two bridging bonds of one chalcogen atom is 0.092 Å. The smallest deviation of analogous bridging chalcogen(IV)–Br bonds was found in the structure of the isomorphous pure tellurium compound, $[C_6H_5(CH_3)_3N]_{2n}[Te_2Br_{10} \cdot Br_2]_n$,[10] 0.008 Å, and the longest in the structure of the isomorphous pure selenium compound, $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10} \cdot Br_2]_n$,[8] 0.151 Å. The average of the total lengths of the two $3c$–$4e$ systems in the structure of **2** is 5.309(1) Å, compared with the analogous values in the structures of $[C_6H_5(CH_3)_3N]_{2n}$-$[Se_2Br_{10} \cdot Br_2]_n$[8] and $[C_6H_5(CH_3)_3N]_{2n}[Te_2Br_{10} \cdot Br_2]_n$,[10] are 5.271(2) and 5.503(1) Å, respectively. There is also a noticeable change in the length of Br–Br bonds in the $Br_2$ molecule. In the pure isomorphous tellurium compounds $[C_6H_5(CH_3)_3N]_{2n}[Te_2Br_{10} \cdot Br_2]_n$[10] and $[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10} \cdot Br_2]_n$[25] it is 2.332(2) and 2.302(1) Å, respectively. In the structure of the pure isomorphous selenium compound $[C_6H_5(CH_3)_3N]_{2n}$-$[Se_2Br_{10} \cdot Br_2]_n$[8] it is 2.339(3) Å and in the mixed selenium/tellurium compound it is 2.336(2) Å. Thus the results, as in the case of the structure of $[C_6H_5(CH_3)_3N]_2$-$[Se_{0.75}Te_{0.25}Br_6]$, are in agreement with the dimensions of the anions in the isomorphous pure selenium and pure tellurium compounds.

Data obtained in this work in comparison with selected data of the known dimeric bromotellurate(IV) anions[10] and of decabromodiselenate(IV) ions[8] confirm that the presence of the charge transfer bond does not seem to have any significant influences on the crystal structure of the $[Y_2Br_{10}]^{2-}$ ion.

The dimensions of the phenyltrimethylammonium ion are within the following ranges: N–C = 1.480(12)–

1.516(13) Å, C–C = 1.36(2)–1.38(2) Å, C–N–C = 107.3(9)–112.5(8)°, N–C–C = 119.9(8) and 121.1(9)°, C–C–C = 118.7(10)–122.0(10)° in compound **1** and N–C = 1.496(11)–1.507(11) Å, C–C = 1.361(14)–1.399(13) Å, C–N–C = 107.0(7)–112.5(6)°, N–C–C = 118.8(7) and 120.0(7)°, C–C–C = 118.4(8)–120.6(9)° in compound **2**.

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