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Reaction of $TeBr_4$ with $SbBr_3$ in the Presence of $[C_6H_5(CH_3)_3N]Br$: Crystal Structures of $[C_6H_5(CH_3)_3N]_2[Te_2Br_{10}]$ and $[C_6H_5(CH_3)_3N][SbTeOBr_6]$

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The title compounds have been isolated from a solution of $TeBr_4$, $SbBr_3$ and $C_6H_5(CH_3)_3NBr$ in acetonitrile. The crystal structures were determined by X-ray methods. Crystals of $[C_6H_5(CH_3)_3N]_2[Te_2Br_{10}]$ (**1**) are monoclinic, space group $P2_1/n$ (No. 14) with $Z=2$ and $a=8.354(2)$, $b=11.683(2)$, $c=17.753(4)$ Å and $\beta=99.52(3)°$. Crystals of $[C_6H_5(CH_3)_3N][SbTeOBr_6]$ (**2**) are monoclinic, space group $P2_1/m$ (No. 11) with $Z=2$ and $a=7.689(2)$, $b=12.672(3)$, $c=10.459(2)$ Å and $\beta=99.81(3)°$. The anion of **1** consists of two edge-sharing distorted $TeBr_6$ octahedra, whereas the anion of **2** consists of the two face-sharing ψ-octahedral units $SbOBr_4$ (lone pair) and $TeOBr_4$ (lone pair) with the oxygen and two bromine atoms in the common face.

Tellurium(IV) forms tetra-, tri-, di- and mononuclear complexes with bromide, Te_4Br_{16}, $Te_3Br_{13}^-$, $Te_2Br_{11}^{3-}$, $Te_2Br_{10}^{2-}$, $Te_2Br_9^-$ and $TeBr_6^{2-}$, and these are well characterised by X-ray methods.[1-7] Antimony(III) has a similar tendency to form bromide complexes, and among the known species are $Sb_4Br_{16}^{4-}$, $Sb_2Br_9^{3-}$ and $Sb_2Br_8^{2-}$.[8-11] We wanted to look into the possibility of making bromide complexes in which both antimony(III) and tellurium(IV) are present. We report here the result of a reaction between equimolar amounts of $SbBr_3$, $TeBr_4$ and $[C_6H_5(CH_3)_3N]Br$ dissolved in acetonitrile. The products are characterised by X-ray methods.

Experimental

Preparation of $[C_6H_5(CH_3)_3N]_2[Te_2Br_{10}]$ (**1**) *and $[C_6H_5(CH_3)_3N][SbTeOBr_6]$* (**2**). To 2.0 mmol (0.894 g) of $TeBr_4$ and 2.0 mmol (0.723 g) of $SbBr_3$ in 5 ml of acetonitrile was added 2.4 mmol (0.518 g) of $[C_6H_5(CH_3)_3N]Br$. The reaction mixture was stirred and the temperature raised to 75 °C. Another 9 ml of acetonitrile was needed to obtain a clear orange solution. After 2 h at room temperature 0.70 g of orange crystals of compound **1** was isolated. The filtrate was placed in a refrigerator for a few days, and then 0.35 g of light yellow crystals of compound **2** was isolated. Each fraction was somewhat contaminated by crystals from the other one, but single crystals were picked out and used for X-ray analyses.

The preparations were repeated under different conditions with the aim of better separation of the two compounds. The attempts also included separation by hand, but chemical analyses of antimony and tellurium by atomic absorption spectrometry were not satisfactory. The only conclusion that can be made from chemical analyses is that the contents of antimony and tellurium in compound **2** are of the same size.

X-Ray structure analyses. The determination of unit-cell dimensions and data collections were carried out on an Enraf-Nonius CAD4 diffractometer. Data reductions were performed by XCAD4,[12] the structures solved by direct methods using SHELXS86[13] and refinement and drawing by SHELXL97.[14] The crystal data, conditions for data collection, and refinements are summarised in Table 1. Atomic scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 in Ref. 15.

Since compound **2** contains both Sb and Te it may mean that one or both independent central positions are partly occupied by Sb and partly by Te, or that one position is occupied by Sb only and the other by Te. Since Sb and Te are so close, nos. 51 and 52 in the Periodic Table, the refinements are equivalent, independent of the choice made.

The hydrogen atoms in **1** were placed geometrically and refined using a riding model with isotropic thermal

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Table 1. Crystal data and structure refinement.

Compound	1	2
Empirical formula	$C_{18}H_{28}Br_{10}N_2Te_2$	$C_9H_{14}Br_6NOSbTe$
Formula weight	1326.72	881.02
Temperature/K	263(2)	263(2)
Wavelength/Å	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/m$
a/Å	8.354(2)	7.689(2)
b/Å	11.683(3)	12.672(3)
c/Å	17.753(4)	10.459(2)
β/°	99.52(3)	99.81(3)
Volume/Å^3	1708.8(6)	1004.2(3)
Z	2	2
D_c/g cm^{-3}	2.58	2.91
D_o/g cm^{-3} (293 K)	2.54	2.88
$F(000)$	1208	792
Crystal size/mm	0.20 × 0.26 × 0.40	0.14 × 0.28 × 0.36
θ-range/°	2.1–25.0	2.0–25.1
hkl limits	$h=0\rightarrow9$ $k=0\rightarrow13$ $l=-21\rightarrow20$	$h=0\rightarrow9$ $k=0\rightarrow15$ $l=-12\rightarrow12$
Intensity decay (%)	1.8	2.0
Absorption coeff./mm^{-1}	13.41	14.73
Correction for absorption	Numerical	Numerical
T_{min}/T_{max}	0.290/0.367	0.032/0.154
Independent reflections	2985	1834
No. with $I>2\sigma(I)$	1622	1150
Data/parameters	2985/149	1834/90
Weight, $P=(F_o^2+2F_c^2)/3$	$[\sigma^2(F^2)+(0.158P)^2$	$[\sigma^2(F^2)+(0.153P)^2$
Extinction coefficient	0.0012(4)	0.0028(12)
Refinement on	F^2	F^2
Goodness-of-fit on F^2	0.946	1.074
$R(F)$ $[I>2\sigma(I)]$	0.0740	0.0756
$R(F)$ (all data)	0.1725	0.1410
$WR(F^2)[I>2\sigma(I)]$	0.1985	0.2102
$WR(F^2)$ (all data)	0.2261	0.2385
Max. and min. $\Delta\rho$/e Å^{-3}	2.29 and −2.38	1.85 and −2.07

parameters equal to $1.3U$(eq) for the atom to which they are attached. The hydrogen atoms in **2** were not included. All non-hydrogen atoms, except C(1) and C(2) in **2**, were refined anisotropically. As seen from Table 1, the R- and $\Delta\rho$-values are relatively high. The crystals were not well developed, and inaccurate indexing or measurement of the dimensions of the crystals may be some of the reasons for the high values. The space group of compound **2**, $P2_1/m$ rather than $P2_1$, was determined by intensity statistics and refinements in both space groups, and confirmed by the program PLATON[16] by use of refined coordinates in space group $P2_1$.

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

Results

Bond lengths and angles of the anions are listed in Table 3, and views of the anions with atomic numbering are shown if Figs. 1 and 2.

The anion of compound **1** consists of two $TeBr_6$ octahedra sharing one edge, and so forming a double bridged centrosymmetric $Te_2Br_{10}{}^{2-}$ dimer as known from several structure determinations.[3–6] All dimensions are within the ranges found for this anion.[6]

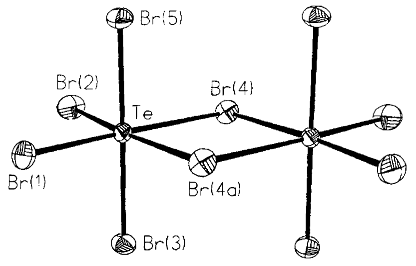

Fig. 1. View of the $[Te_2Br_{10}]^{2-}$ ion as found in compound **1** with atomic numbering.

The anion of compound **2** is a dinuclear complex, bridged by two bromine atoms and one oxygen atom. Taking into account the lone electron pair of each central atom the structure comprises two face-sharing ψ-octahedral $Sb/TeOBr_4$ (lone pair) units, with four bromine atoms in the equatorial plane and the lone electron pairs *trans* to the oxygen atom. As expected from the VSEPR theory[17] the central atoms are situated on the lone electron pair side of the planes through their

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (in $Å^2 \times 10^3$).

Atom	*x*	*y*	*z*	*U*(eq)[a]
$[C_6H_5(CH_3)_3N]_2[Te_2Br_{10}]$ (**1**)				
Te	−4627(1)	3204(1)	9822(1)	36(1)
Br(1)	−6435(4)	1454(2)	9738(1)	83(1)
Br(2)	−2162(3)	2056(2)	9585(1)	73(1)
Br(3)	−3838(2)	2843(2)	11350(1)	55(1)
Br(4)	−2651(2)	5319(2)	9942(1)	51(1)
Br(5)	−5440(3)	3520(2)	8337(1)	60(1)
N	−4335(16)	118(13)	7287(8)	43(3)
C(1)	−4660(2)	−972(19)	6822(14)	75(7)
C(2)	−5660(2)	234(18)	7756(13)	60(6)
C(3)	−4510(3)	1094(18)	6762(11)	59(5)
C(4)	−2722(19)	14(14)	7781(10)	42(4)
C(5)	−2540(2)	−791(15)	8352(10)	46(4)
C(6)	−950(3)	−906(17)	8806(11)	60(6)
C(7)	250(2)	−203(18)	8712(13)	64(6)
C(8)	50(2)	611(18)	8175(12)	59(6)
C(9)	−1490(2)	758(16)	7694(11)	50(5)
$[C_6H_5(CH_3)_3N][SbTeOBr_6]$ (**2**)				
Te	2801(2)	2500	7954(2)	43(1)
Sb	−1410(2)	2500	6468(2)	40(1)
Br(1)	3268(3)	1054(2)	9693(2)	71(1)
Br(2)	1455(4)	1027(2)	5932(2)	64(1)
Br(3)	−3091(3)	1040(2)	7424(2)	58(1)
O	340(2)	2500	8081(16)	43(4)
N	−1150(4)	2500	11850(2)	65(7)
C(1)	−1540(10)	2500	10560(8)	170(3)
C(2)	380(7)	1570(4)	12280(5)	190(2)
C(3)	−2570(4)	2500	12670(2)	46(7)
C(4)	−3230(3)	1578(15)	12990(2)	55(5)
C(5)	−4610(3)	1577(19)	13760(2)	69(7)
C(6)	−5300(4)	2500	14160(3)	58(8)

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

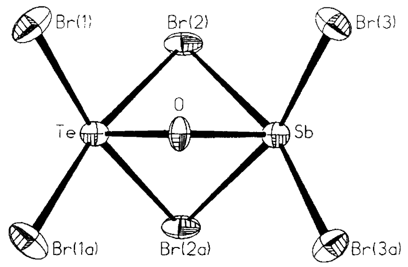

Fig. 2. View of the $[SbTeOBr_6]^-$ ion as found in compound **2** with atomic numbering.

four coordinating bromine atoms, 0.36 and 0.28 Å from the planes. In each ψ-octahedral unit the equatorial plane has two approximately linear 3*c*–4*e* Br–Sb/Te–Br bonding systems at nearly right angles. Perpendicular to the equatorial plane is a covalent Sb/Te–O bond. The covalent Sb/Te–O bonds are 1.92 and 1.97 Å as compared to the sums of single-bond radii 2.03 and 2.07 Å for Te–O and Sb–O.[18] As usual in dinuclear halogen complexes of antimony and tellurium the Br–Sb/Te–Br systems are asymmetric with short terminal bonds and long bridging bonds. The total lengths of the two independent 3*c*–4*e* systems are 5.442 and 5.568 Å. The shortest bond is within ranges found for dinuclear tellurium(IV)–bromine complexes (see compound **1** and Ref. 6) and the longest one is within ranges found for dinuclear antimony(III)–bromine complexes (see e.g. Ref. 19). The shortest Sb/Te–O bond and the shortest 3*c*–4*e* bond systems are to the same Sb/Te atom. Since compound **2** has one $[C_6H_5(CH_3)_3N]^+$ cation per anion consisting of two central atoms, six Br^- and one O^{2-}, the central atoms have an average charge of +3.5. In accordance with this fact and the chemical analyses we conclude that the central atoms are 50% Te^{4+} and 50% Sb^{3+}. As mentioned earlier there is no evidence from the refinement as to whether each of the central positions is partly occupied by antimony and partly by tellurium or one position by antimony only and the other one by tellurium, but the dimensions discussed above indicate the latter alternative. The tables of bond lengths and angles and the figure are in accordance with this alternative. Structures similar to the anion of compound **2**, where both central atoms are antimony, are known,[20–25] but so far no such structure with tellurium has been published.

Trans to the Te–O bond are two equivalent weak contacts, Te···Br = 3.782(3) Å and O-Te···Br = 150.23(9)°. Opposite to the Sb–O bond there are weak

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

$[C_6H_5(CH_3)_3N]_2[Te_2Br_{10}]$ (**1**)			
Te–Br(1)	2.532(2)	Te–Br(4a)	2.940(2)
Te–Br(2)	2.550(2)	Te–Br(5)	2.637(2)
Te–Br(3)	2.717(2)	Te···Te	4.304(2)
Te–Br(4)	2.959(2)		
Br(1)–Te–Br(2)	93.17(10)	Br(5)–Te–Br(4^{i})	89.04(7)
Br(1)–Te–Br(5)	90.12(8)	Br(3)–Te–Br(4^{i})	90.81(7)
Br(2)–Te–Br(5)	89.46(8)	Br(1)–Te–Br(4)	177.09(9)
Br(1)–Te–Br(3)	88.68(8)	Br(2)–Te–Br(4)	89.72(8)
Br(2)–Te–Br(3)	90.78(8)	Br(5)–Te–Br(4)	90.22(7)
Br(5)–Te–Br(3)	178.78(8)	Br(3)–Te–Br(4)	90.98(6)
Br(1)–Te–Br(4^{i})	90.83(9)	Br(4a)–Te–Br(4)	86.29(6)
Br(2)–Te–Br(4^{i})	175.73(8)	Te–Br(4)–Te(a)	93.71(6)
$[C_6H_5(CH_3)_3N][SbTeOBr_6]$ (**2**)			
Te–O	1.920(17)	Sb–Br(3)	2.556(2)
Te–Br(1)	2.564(2)	Sb–Br(2)	3.012(3)
Te–Br(2)	2.878(2)	Te···Sb	3.344(3)
Sb–O	1.970(14)		
O–Te–Br(1)	88.4(3)	Br(3)–Sb–Br(3^{ii})	92.73(12)
Br(1a)–Te–Br(1)	91.27(4)	Br(3)–Sb–Br(2^{ii})	162.94(9)
O–Te–Br(2)	79.4(4)	O–Sb–Br(2)	75.3(4)
Br(1a)–Te–Br(2)	166.98(11)	Br(3)–Sb–Br(2)	93.37(7)
Br(1)–Te–Br(2)	92.69(8)	Br(2)–Sb–Br(2^{ii})	76.60(10)
Br(2)–Te–Br(2^{ii})	80.88(10)	Te–Br(2)–Sb	69.15(6)
O–Sb–Br(3)	89.0(4)	Te–O–Sb	118.5(9)

Symmetry transformation ^{i} $-1-x$, $1-y$, $2-z$; ^{ii} x, $\frac{1}{2}-y$, z.

Table 4. Selected bond lengths (in Å) and angles (in °) for the anion of **2** and related structures.

Complex	Ref.	Sb–Cl/Br (terminal)	Sb–Cl/Br (bridge)	Sb–O/S	Sb–Cl/Br–Sb/Te	Sb–O/S–Sb/Te	Sb···Sb/Te
$[SbTeOBr_6]^-$	This work	2.56	3.01	1.97	69.2	118.9	3.34
$[SbTeOCl_6]^-$	20, 21	2.44	2.89	1.95	71.3	119.5	3.37
$[Sb_2OCl_6]^{2-}$	22	2.43	2.89	1.94	70.1	117.1	3.32
$[Sb_2OCl_6]^{2-}$	23	2.44	2.86	1.92	69.9	116.3	3.26
$[Sb_2SBr_6]^{2-}$	24	2.63	3.05	2.50	71.6	92.3	3.57
$[Sb_2SCl_6]^{2-}$	25	2.49	2.89	2.42	76.2	95.2	3.58

contacts to the carbon atoms of the benzene ring of the cation. The distances are 3.51(3)–3.92(2) Å and the O–Sb···C angles are 150.7(7)–165.1(8)°. The latter contacts are similar to those found in the structure of $[H_3O \cdot (\text{dibenzo-18-crown-6})][Te_2Br_9]$.[7]

The dimensions of the supposed antimony part of the anion and the corresponding dimensions of known similar structures are listed in Table 4. Comparison of the structures shows that the dimensions of the present anion do not deviate much from corresponding dimensions of the others, except for the terminal Sb–Br bonds, which are somewhat shorter than in $[Sb_2SBr_6]^{2-}$. When the bridging oxygen is exchanged with sulfur, the bond to antimony is increased by more than the difference in covalent radii, 0.38 Å,[18] the bond angle of the bridge is decreased from nearly 120° to close to 90°, and the Sb···Sb distance is increased by about 0.25 Å.

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

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