Tellurium Cations by Lewis Acid-Base Reactions: Syntheses and Crystal Structures of (Te$_4^{2\oplus}$)(Zr$_2$Br$_{10}^{2\ominus}$) and (TeBr$_3^\oplus$)(Zr$_2$Br$_9^\ominus$)

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ZrBr$_4$ reacts with Te$_2$Br in a sealed evacuated ampoule at 210°C in quantitative yield to afford (Te$_4^{2\oplus}$)(Zr$_2$Br$_{10}^{2\ominus}$) as blue-black, moisture-sensitive crystals. The crystal-structure determination shows, that (Te$_4$)(Zr$_2$Br$_{10}$) consists of planar, nearly square Te$_4^{2\oplus}$ and Zr$_2$Br$_{10}^{2\ominus}$ ions, that form edge-sharing double octahedra. Both ions possess crystallographic $2/m$ (C_{2h}) symmetry. At temperatures above 250°C (Te$_4$)(Zr$_2$Br$_{10}$) decomposes with cleavage of Te−Te bonds into (TeBr$_3^\oplus$)(Zr$_2$Br$_9^\ominus$), which forms yellow, hygroscopic crystals. (TeBr$_3$)(Zr$_2$Br$_9$) can also be obtained by the reaction of two equivalents of ZrBr$_4$ with TeBr$_4$ at 260°C. The crystal structure is built of Zr$_2$Br$_9^\ominus$ ions, that form face-sharing double octahedra, and of pyramidal TeBr$_3^\oplus$ ions. Each TeBr$_3^\oplus$ ion exhibits three Te−Br contacts to two different Zr$_2$Br$_9^\ominus$ ions, resulting in a strongly deformed octahedral coordination for the Te atom. The Zr$_2$Br$_9$ double octahedra and the TeCl$_6$ octahedra are connected by common edges and corners to infinite chains.

Metal halides in high oxidation states can act as selective oxidants for tellurium. Depending on the amount of tellurium used, oxidation with WCl$_6$ yields the cations Te$_4^{2\oplus}$ and Te$_8^{2\oplus}$ in the ionic compounds Te$_4^{2\oplus}$(WCl$_6^\ominus$)$_2$[1] and Te$_8^{2\oplus}$(WCl$_6^\ominus$)$_2$[2]. By using MoOCl$_4$ and two equivalents of tellurium one obtains Te$_4^{2\oplus}$(MoOCl$_4$)$_2^{2\ominus}$ [3].

A new way to compounds containing tellurium polycations is now found. Ditellurium monobromide, that already contains tellurium in the formal oxidation state +0.5, acts as a Lewis base toward ZrBr$_4$ and yields the Te$_4^{2\oplus}$ ion. The resulting compound (Te$_4^{2\oplus}$)(Zr$_2$Br$_{10}^{2\ominus}$) is thermally unstable and decomposes with loss of elemental tellurium to (TeBr$_3^\oplus$)(Zr$_2$Br$_9^\ominus$).

Preparation and Properties of (Te$_4$)(Zr$_2$Br$_{10}$) and (TeBr$_3$)(Zr$_2$Br$_9$)

Te$_2$Br reacts with ZrBr$_4$ in a Lewis acid-base reaction with ZrBr$_4$ acting as an acceptor for Br$^\ominus$.

$$2\ \mathrm{Te_2Br} + 2\ \mathrm{ZrBr_4} \longrightarrow (\mathrm{Te_4^{2\oplus}})(\mathrm{Zr_2Br_{10}^{2\ominus}})$$

This reaction is carried out in a sealed evacuated ampoule (temperature gradient 230 → 210°C). (Te$_4$)(Zr$_2$Br$_{10}$) is obtained in the colder part of the ampoule in quantitative yield as blue-black crystals, which are easily hydrolyzed in moist air. At temperatures above 250°C (Te$_4$)(Zr$_2$Br$_{10}$) decomposes into a black melt, from which yellow, very hygroscopic crystals of (TeBr$_3$)(Zr$_2$Br$_9$) sublime. At 290°C this decomposition is complete after some days, leaving solid tellurium in the hot part of the ampoule. The decomposition is not reversible. The reformation of (Te$_4$)(Zr$_2$Br$_{10}$) from (TeBr$_3$)(Zr$_2$Br$_9$) and tellurium at temperatures below 230°C has not been observed.

(TeBr$_3$)(Zr$_2$Br$_9$) is also obtained by the reaction of TeBr$_4$ with two equivalents of ZrBr$_4$ at 260°C.

$$\mathrm{TeBr_4} + 2\ \mathrm{ZrBr_4} \longrightarrow (\mathrm{TeBr_3^\oplus})(\mathrm{Zr_2Br_9^\ominus})$$

ZrBr$_4$ acts in this reaction again as an acceptor for Br$^\ominus$.

Crystal Structure of (Te$_4^{2\oplus}$)(Zr$_2$Br$_{10}^{2\ominus}$)

The crystal structure of (Te$_4^{2\oplus}$)(Zr$_2$Br$_{10}^{2\ominus}$) is built of Te$_4^{2\oplus}$ and Zr$_2$Br$_{10}^{2\ominus}$ ions. Figure 1 gives a view of the two ions, Table 1 contains selected distances and angles, Table 3 the crystal data, and Table 4 the atomic coordinates. The planar Te$_4^{2\oplus}$ ions possess $2/m$ (C_{2h}) symmetry with the atoms Te1 and Te(1$^{\text{II}}$) located on the twofold axis and the atoms Te2 and Te(2$^{\text{II}}$) located in the mirror plane. All four Te−Te

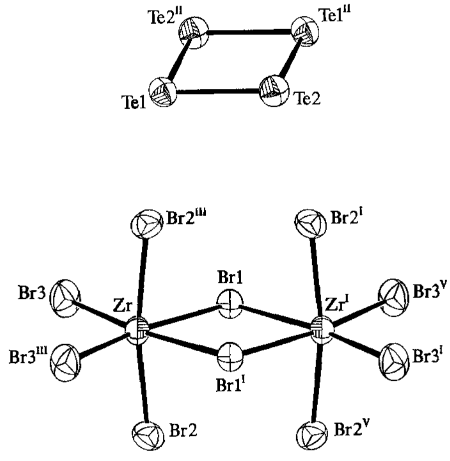

Figure 1. Te$_4^{2\oplus}$ and the Zr$_2$Br$_{10}^{2\ominus}$ ions in the structure of (Te$_4$)(Zr$_2$Br$_{10}$); thermal ellipsoids are scaled to enclose 70% of the probability density (ORTEP[19])

0009−2940/91/0404−0677 $ 3.50+.25/0

bonds have the equal length of 269.5 pm, but the Te—Te—Te angles of 88.3 and 91.7° show a distortion form ideal square geometry. Bond length and angels, however, show no marked difference to other halogenometallates with $Te_4^{2\oplus}$ ions[1,4,5]. The $Zr_2Br_{10}^{2\ominus}$ ions form edge-sharing double octahedra and possess $2/m$ (C_{2h}) symmetry with the two Zr atoms located on the twofold axis and Br1 and $Br(1^I)$ located in the mirror plane. The so far unknown anion is isostructural to its chlorine-containing analogue $Zr_2Cl_{10}^{2\ominus}$ [6]. Due to the symmetry only three independent Zr—Br distancess are observed in the $Zr_2Br_{10}^{2\ominus}$ ion. These distances differ markedly. The longest is observed between Zr and the bridging Br1 with 275.6 pm, the terminal bromine atoms Br2 and Br3 exhibit shorter distances of 261.1 and 251.7 pm. The zirconium atoms are displaced out of the centers of their octahedra toward the outer edges of the double octahedron. Besides the differences in the Zr—Br distances, this can also be seen from the angles Br1—Zr—$Br(3^{III})$ (170.8°) and Br2—Zr—$Br(2^{III})$ (169.5°), which are both bent by about 10° from the ideal linear geometry.

Table 1. Selected interatomic distances [pm] and angles [°] for $(Te_4)(Zr_2Br_{10})$; standard deviations are 0.1 pm and 0.1°

Distances			
Zr - Zr^I	420.7	Te1 - Br2	318.2
Zr - Br1	275.6	Te1 - $Br(3^{VII})$	388.9
Zr - Br2	261.1	Te2 - Br2	381.7
Zr - Br3	251.7	Te2 - $Br(2^{VIII})$	392.5
Te1 - Te2	269.5	Te2 - Br3	393.0
Angles			
Br1 - Zr - Br2	85.6	Br2 - Zr - Br3	91.8
Br1 - Zr - $Br(2^{III})$	86.4	Br3 - Zr - $Br(3^{III})$	98.6
Br1 - Zr - $Br(1^I)$	80.5	Zr1 - Br1 - Zr^I	99.5
Br1 - Zr - Br3	90.5	Te1 - Te2 - $Te1^{II}$	88.3
Br1 - Zr - $Br(3^{III})$	170.8	Te2 - Te1 - $Te2^{II}$	91.7
Br2 - Zr - $Br(2^{III})$	169.5		

Symmetry operations:

I: $-x, -y, -z,$
II: $-x + 1, -y + 1, -z$
III: $-x, y, -z$
IV: $-x + 1, y, -z$
V: $x, -y, z$
VI: $x, -y + 1, z$
VII: $1/2 - x, 1/2 - y, 1/2 - z$
VIII: $1/2 - x, 1/2 - y, (1/2 - z) - 1$
IX: $1/2 - x, 1/2 + y, (1/2 - z) - 1$
X: $1/2 + x, 1/2 - y, (1/2 + z) - 1$

Several contacts shorter than the sum of the van der Waals radii (415 pm[7]) are observed between the bromine atoms of the anions and the $Te_4^{2\oplus}$ ions. The coordination of the $Te_4^{2\oplus}$ ion by the surrounding bromine atoms shown in Figure 2 is typical of all compounds with $Te_4^{2\oplus}$ ions that have been stucturally investigated so far. There are always four halogen atoms with relatively short distances bridging the edges of the Te_4 square and additional terminal halogen atoms with longer distances above and under the Te_4 plane[8]. The atoms Te1 and $Te(1^{II})$ exhibit remarkable short contacts of 318.2 pm to the four bridging Br atoms, while all other Te···Br contacts are longer than 380 pm. The shortest Te···Cl contacts of 319 pm are found in $(Te_4)(Nb_2OCl_{10})$[5] and in $(Te_4)(WCl_6)_2$[1]. In $(Te_4)(Zr_2Br_{10})$ Zr···Br contacts are of the same order of magnitude.

Figure 3 gives a view of the packing of ions in the unit cell. Cations and anions each form a body-centered lattice. These lattices penetrate each other. Every ion is located in a distorted octahedral hole that is formed by the counter ions. The packing of the ions in $(Te_4)(Zr_2Br_{10})$ is equivalent to that found in $(Te_4)(MoOCl_4)_2$[3].

Crystal Structure of $(TeBr_3^{\oplus})(Zr_2Br_9^{\ominus})$

Table 2 contains selected distances and angels, Table 3 the crystal data, and Table 5 the atomic coordinates. The

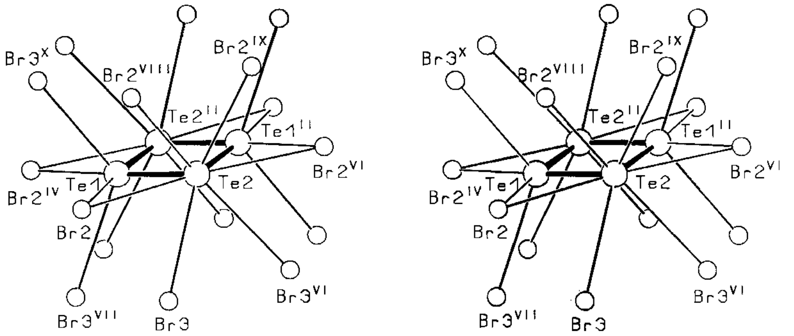

Figure 2. Stereoscopic view of the $Te_4^{2\oplus}$ ion in the structure of $(Te_4)(Zr_2Br_{10})$ with all Te···Br contacts up to 400 pm

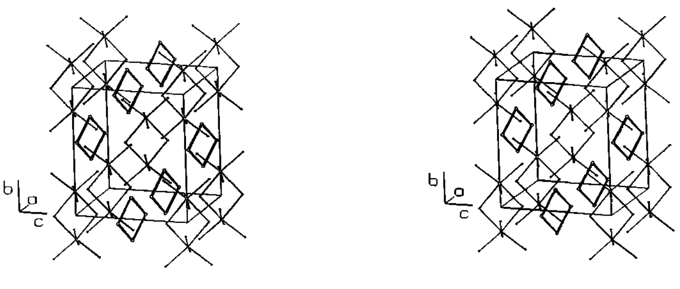

Figure 3. Stereoscopic view of the unit cell of $(Te_4)(Zr_2Br_{10})$

crystal structure of $(TeBr_3^{\oplus})(Zr_2Br_9^{\ominus})$ is built of $TeBr_3^{\oplus}$ and $Zr_2Br_9^{\ominus}$ ions. Figure 4 shows a detailed view of the structure and the connection of the ions. The $Zr_2Br_9^{\ominus}$ ions form double octahedra with a common face. Zr—Br distances in the wide range from 246.5 to 282.1 pm are observed in the anions. The Zr—Br distances to the three bridging bromine atoms Br4, Br5, and Br6 with an average length of 274.8 pm are much longer than the terminal Zr—Br bonds with an average of 252.6 pm. The overall Zr—Br distance, however, of 263.7 pm is close to 262.8 pm found in the $Zr_2Br_{10}^{2\ominus}$ ion. The $TeBr_3^{\oplus}$ ions are pyramidal with an average Te—Br distance of 247.0 pm and an average Br—Te—Br angle of 96.8°. Comparable values are found in $(TeBr_3)(AsF_6)$[9] (Te—Br 243.2 pm, Br—Te—Br 97.9°) and in $(TeBr_3)(AuBr_4) \cdot \frac{1}{2} Br_2$[10] (Te—Br 246.3 pm, Br—Te—Br 96.0°). Like in nearly all compounds containing $EX_3^{\oplus}$ ions (E = S, Se, Te; X = F, Cl, Br, I) strong cation-anion interactions are observed in $(TeBr_3)(Zr_2Br_9)$. The atoms Br1 and Br3 of one and the atom Br7 of another neighboring $Zr_2Br_9^{\ominus}$ unit exhibit contacts of an average length of 318.8 pm to each $TeBr_3^{\oplus}$ group. The resulting coordination environment for the Te atom is a strongly deformed octahedron with three secondary Te···Br contacts *trans* to the three primary Te—Br bonds. This distortion of the $TeBr_6$ octahedron is interpreted with the stereochemical active lone electron pair on the tellurium atom sticking out toward the longer distant face of the octahedron[11]. The $ZrBr_6$ and $TeBr_6$ octahedra are linked to infinite chains that run along the *c* axis (Figure 5). All three possible kinds of linkage between octahedra, common faces, edges, and corners are found in these chains. The concept of closest packings of spheres allows an alternative description of the structure. The bromine atoms of $(TeBr_3)(Zr_2Br_9)$ form a closest packing with the triangular nets of bromine atoms spanned parallel to the *a*-*b* plane. These nets are stacked perpendicular to the *c* axis with the layer sequence *A B A C A C B C B, A*.... According to the symbolism introduced by Zhdanov[12] this layer sequence is a rhombohedral $(1 \cdot 2)_3$ packing. The zirconium and tellurium atoms together occupy one quarter of the octahedral holes. On one interlayer space, filled with one quarter of the possible number of zirconium atoms, follow two interlayer spaces, each filled with one quarter of the possible number of zirconium and tellurium atoms in equal amounts. The complete packing symbol is $A_{\gamma/4(Zr)}B_{\gamma/4(Zr,Te)}A_{\beta/4(Zr,Te)}C_{\beta/4(Zr)}A_{\beta/4(Zr,Te)}C_{\alpha/4(Zr,Te)}B_{\alpha/4(Zr)}C_{\alpha/4(Zr,Te)}B_{\gamma/4(Zr,Te)}, A\ldots$

Table 2. Selected interatomic distances [pm] and angles [°] for $(TeBr_3)(Zr_2Br_9)$; standard deviations are 0.1 pm and 0.1°

Distances			
Zr1 - Zr2	369.2	Zr2 - Br6	269.2
Zr1 - Br1	258.1	Zr2 - Br7	259.3
Zr1 - Br2	246.9	Zr2 - Br8	246.5
Zr1 - Br3	257.5	Zr2 - Br9	247.5
Zr1 - Br4	268.5	Te - Br1	311.1
Zr1 - Br5	268.0	Te - Br3	311.9
Zr1 - Br6	279.7	Te - Br(7^I)	318.6
Zr2 - Br4	282.1	Te - Br10	245.7
Zr2 - Br5	281.0	Te - Br11	248.0
		Te - Br12	247.2
Angles			
Br1 - Zr1 - Br2	97.3	Br4 - Zr2 - Br8	168.3
Br1 - Zr1 - Br3	93.5	Br4 - Zr2 - Br9	90.8
Br1 - Zr1 - Br4	90.1	Br5 - Zr2 - Br6	79.5
Br1 - Zr1 - Br5	166.6	Br5 - Zr2 - Br7	84.6
Br1 - Zr1 - Br6	87.6	Br5 - Zr2 - Br8	91.0
Br2 - Zr1 - Br3	97.7	Br5 - Zr2 - Br9	168.1
Br2 - Zr1 - Br4	94.3	Br6 - Zr2 - Br7	159.8
Br2 - Zr1 - Br5	94.6	Br6 - Zr2 - Br8	94.9
Br2 - Zr1 - Br6	172.2	Br6 - Zr2 - Br9	94.2
Br3 - Zr1 - Br4	166.9	Br7 - Zr2 - Br8	97.8
Br3 - Zr1 - Br5	91.0	Br7 - Zr2 - Br9	99.1
Br3 - Zr1 - Br6	88.0	Br8 - Zr2 - Br9	99.6
Br4 - Zr1 - Br5	82.9	Zr1 - Br4 - Zr2	84.2
Br4 - Zr1 - Br6	79.5	Zr1 - Br5 - Zr2	84.5
Br5 - Zr1 - Br6	79.9	Zr1 - Br6 - Zr2	84.5
Br4 - Zr2 - Br5	78.2	Br10 - Te - Br11	96.9
Br4 - Zr2 - Br6	79.0	Br10 - Te - Br12	96.7
Br4 - Zr2 - Br7	85.6	Br11 - Te - Br12	96.7

Symmetry operations:
I: *x*, 1/2 − *y*, 1/2 + *z*   II: *x*, 1/2 − *y*, (1/2 + *z*) − 1

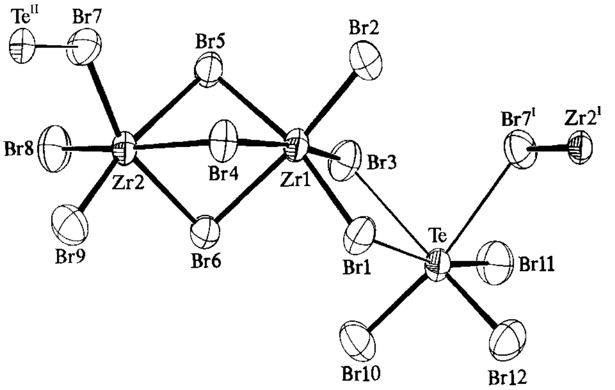

Figure 4. Detailed view of the structure of $(TeBr_3^{\oplus})(Zr_2Br_9^{\ominus})$; thermal ellipsoids are scaled to enclose 70% of the probability density (ORTEP[19])

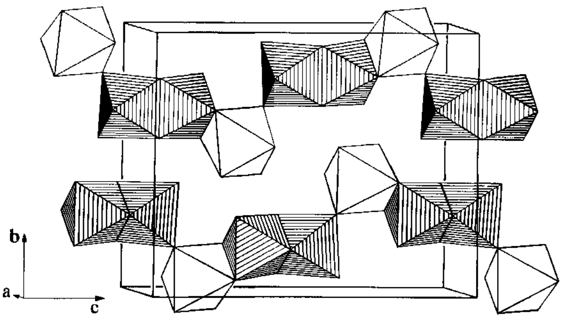

Figure 5. The unit cell of $(TeBr_3)(Zr_2Br_9)$ showing the connection of $ZrBr_6$ and $TeBr_6$ octahedra (STRUPLO[20]); $ZrBr_6$ octahedra are shaded, $TeBr_6$ octahedra are blank

Experimental

All experiments were carried out under dry nitrogen or argon. Glass ampoules were heated to 300°C in vacuo prior to use. Charging and opening of the ampoules were performed in an argon-filled glove box. Zirconium tetrabromide[13], tellurium tetrabromide[13], and ditellurium monobromide[14] were prepared according to literature procedures.

Tetratellurium(2+) Di-μ-bromooctabromodizirconate-(2−) [($Te_4^{2\oplus}$)($Zr_2Br_{10}^{2\ominus}$)]: Ditellurium monobromide (0.84 g, 2.5 mmol) and zirconium tetrabromide (1.03 g, 2.5 mmol) are filled in a glass ampoule, which is evacuated and sealed. The ampoule is placed in a horizontal tube furnace (temperature gradient 230 → 210 °C). Blue-black crystals are slowly formed in the colder part of the ampoule within 2 weeks.

Br_5Te_2Zr (745.94) Calcd. Br 53.56 Found Br 54.88

Tribromotellurium(+) Tri-μ-bromohexabromodizirconate(−) [($TeBr_3^{\oplus}$)($Zr_2Br_9^{\ominus}$)]: Tellurium tetrabromide (0.45 g, 1 mmol) and zirconium tetrabromide (0.82 g, 2 mmol) are filled in a glass ampoule, which is sealed in vacuo. The components are melted at 350 °C and then cooled to 290 °C below the melting point. In a temperature gradient (290 → 260 °C) orange crystals are formed in the colder parts of the ampoule within 3 d.

$Br_{12}TeZr_2$ (1268.89) Calcd. Br 75.57 Found Br 75.04

Table 3. Crystal structure determinations for (Te_4)(Zr_2Br_{10}) and ($TeBr_3$)(Zr_2Br_9)

	(Te_4)(Zr_2Br_{10})	($TeBr_3$)(Zr_2Br_9)
Formula	Br_5Te_2Zr	$Br_{12}TeZr_2$
M_r	795.94	1268.89
a, pm	964.7(2)	676.18(8)
b, pm	1126.0(2)	1560.4(2)
c, pm	1012.5(3)	1923.8(3)
β, °	95.49(1)	97.91(1)
V, pm^3	$1094.8 \cdot 10^6$	$2010.5 \cdot 10^6$
Z	4	4
$\varrho_{calcd.}$, $g \cdot cm^{-3}$	4.52	4.19
Space group	$I2/m$ (no.12)	$P2_1/c$ (no. 14)
Instrument	Four circle diffractometer	Siemens–Stoe AED2
Radiation	Mo-K_α	
T, °C	−60	21
Reflections collected	5437, $3° < 2\theta < 60°$	8092, $3° < 2\theta < 55°$
Scan mode	ω/θ	$\omega/2\theta$
Unique reflections	1677	3899
R_{merge}	0.035	0.030
Reflections used in refinements	1530, $I > 1.5 \cdot \sigma(I)$	3449, $I > 1.5 \cdot \sigma(I)$
Refined parameters	42	137
R [a]	0.041	0.045
R_w [b]	0.032	0.036
ϱ_{fin}(max/min), $e/10^6 pm^3$	+1.70/−1.42	+1.40/−1.22

[a] $R = \Sigma(|F_o - |F_c||)/\Sigma|F_o|$. – [b] $R_w = \Sigma\sqrt{w}(|F_o - |F_c||)/\sqrt{w}\Sigma|F_o|$ with $w = 1/\sigma^2(F_o)$.

Table 4. Fractional atomic coordinates and equivalent isotropic temperature parameters for (Te_4)(Zr_2Br_{10}); the coefficient B of the Debye-Waller factor $\exp(-B \times \sin^2\theta/\lambda^2)$ is given in units of [10^4 pm^2]; standard deviations of the last significant digits are given in parentheses

Atom	x	y	z	B
Zr	0	0.18679(8)	0	2.08(4)
Te1	0.5	0.33324(6)	0	2.37(3)
Te2	0.30530(6)	0.5	-0.06621(8)	2.53(3)
Br1	0.08363(9)	0	0.1647(1)	2.05(4)
Br2	0.24294(7)	0.16566(7)	-0.09134(8)	2.75(3)
Br3	0.08112(8)	0.33260(7)	0.17939(9)	3.30(4)

Crystal-Structure Determination of (Te_4)(Zr_2Br_{10})[15]: Table 3 contains the crystal data and details of the data collection. The unconventional space-group setting $I2/m$ is chosen to avoid an extreme monoclinic angle in the standard $C2/m$ setting (lattice constants of the $C2/m$ cell: a = 1330.0, b = 1126.0, c = 964.7 pm; β = 130.7°). An empirical absorption correction based on ψ scans of 9 reflections is applied to all data (crystal size: 0.08 × 0.17 × 0.14 mm; μ = 236.5 cm^{-1}, transmission factors 0.168–0.050). The structure was solved by combined Patterson and Direct Methods[16] and refined by full-matrix least squares[17]. All atoms are refined with anisotropic displacement parameters.

Crystal-Structure Determination of ($TeBr_3$)(Zr_2Br_9)[15]: Table 3 contains the crystal data and details of data collection, which is performed by the learnt-profile method[18]. An empirical absorption correction based on ψ scans of 10 reflections is applied to all data (crystal size; 0.07 × 0.16 × 0.24 mm; μ = 237.8 cm^{-1}, transmission factors 0.059–0.009). The structure is solved by Direct Methods[16] and refined by full-matrix least squares[17]. All atoms are refined with anisotropic displacement parameters.

Table 5. Fractional atomic coordinates and equivalent isotropic temperature parameters for ($TeBr_3$)(Zr_2Br_9); the coefficient B of the Debye-Waller factor $\exp(-B \times \sin^2\theta/\lambda^2)$ is given in units of [10^4 pm^2]; standard deviations of the last significant digits are given in parentheses

Atom	x	y	z	B
Zr1	0.8169(1)	0.19225(7)	0.67324(5)	2.42(4)
Zr2	0.7422(1)	0.18288(6)	0.47964(5)	2.38(5)
Te	0.6570(1)	0.04093(4)	0.84040(4)	2.44(3)
Br1	0.5047(1)	0.18706(8)	0.73668(6)	3.20(5)
Br2	0.9956(2)	0.30651(8)	0.74526(6)	3.76(6)
Br3	0.9822(1)	0.06308(7)	0.74146(6)	3.24(5)
Br4	0.6294(1)	0.30106(7)	0.57795(6)	3.01(5)
Br5	1.0818(1)	0.18457(7)	0.58184(5)	2.78(4)
Br6	0.6233(1)	0.07627(7)	0.57582(6)	2.96(5)
Br7	0.9101(1)	0.31265(8)	0.42719(6)	3.31(5)
Br8	0.8889(1)	0.06896(8)	0.41412(6)	3.94(6)
Br9	0.4072(1)	0.19237(9)	0.40961(6)	4.04(6)
Br10	0.4932(2)	-0.06323(8)	0.75552(7)	4.11(6)
Br11	0.8558(2)	-0.06396(8)	0.91775(6)	3.87(6)
Br12	0.3799(2)	0.05483(9)	0.91113(7)	4.07(6)

CAS Registry Numbers

Te_2Br: 12514-37-3 / $ZrBr_4$: 13777-25-8 / $TeBr_4$: 10031-27-3 / ($Te_4^{2\oplus}$)($Zr_2Br_{10}^{2\ominus}$): 131216-27-8 / ($TeBr_3^{\oplus}$)($Zr_2Br_9^{\ominus}$): 131216-29-0

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