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Syntheses and Crystal Structures of Phenyltrimethylammonium Salts of Hexachlorotellurate(IV), $[C_6H_5(CH_3)_3N]_2[TeCl_6]$, *catena*-poly[(Di-μ-chlorobis{tetrachlorotellurate(IV)})-μ-bromine], $[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10}\cdot Br_2]_n$, and Di-μ-chlorobis{tetrachlorotellurate(IV) *catena*-poly[(μ-chlorobis{pentachlorotellurate(IV)})-μ-iodine(I)], $[C_6H_5(CH_3)_3N]_{4n}[Te_2Cl_{10}]_n[Te_2Cl_{11}\cdot I]_n$

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The title compounds were prepared from tellurium tetrachloride, phenyltrimethylammonium chloride and halogens. The crystal structures of $[C_6H_5(CH_3)_3N]_2[TeCl_6]$ (**1**), $[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10}\cdot Br_2]_n$ (**2**) and $[C_6H_5(CH_3)_3N]_{4n}[Te_2Cl_{10}]_n[Te_2Cl_{11}\cdot I]_n$ (**3**) have been determined by X-ray methods and refined to $R=0.018$, 0.029 and 0.032 for 2648, 3025 and 1883 observed reflections, respectively. Crystals of **1** are monoclinic, space group $P2_1/a$ with $Z=2$ and $a=13.965(3)$, $b=10.292(2)$, $c=8.608(2)$ Å, $\beta=104.51(2)°$. Crystals of **2** are triclinic, space group $P\bar{1}$ with $Z=1$ and $a=8.672(1)$, $b=8.785(1)$, $c=11.565(1)$ Å, $\alpha=95.93(2)°$, $\beta=103.27(2)°$, $\gamma=90.44(2)°$. Crystals of **3** are orthorhombic, space group $Pnnm$ with $Z=2$ and $a=11.952(1)$, $b=16.475(2)$, $c=16.923(2)$ Å. The $[TeCl_6]^{2-}$ of **1** is a centrosymmetric and nearly perfect octahedron. The dimeric, centrosymmetric $[Te_2Cl_{10}]^{2-}$ anion of **3** consists of two edge-sharing distorted $TeCl_6$ octahedra. The same dimeric unit occurs in **2**, but here one of the axial Cl atoms in each $TeCl_6$ octahedron is linked to an equivalent Cl atom by a Br_2 molecule, and so forming a polymeric chain, $[Te_2Cl_{10}\cdot Br_2]_n^{2n-}$. The $[Te_2Cl_{11}\cdot I]^{2-}$ anion of **3** consists of a distorted $TeCl_6$ octahedron with one Cl atom on a centre of symmetry and one Cl atom (*cis* to the central Cl atom) bonded to an I^+ ion, also situated on a centre of symmetry, and so forming a polymeric chain, $[Te_2Cl_{11}\cdot I]_n^{2n-}$.

Tellurium(IV) chlorides have been found in various structural forms. In all known structures the tellurium atoms are coordinated to six chlorine atoms in an octahedral or distorted octahedral arrangement. The monomeric dianion $TeCl_6^{2-}$ is known from numerous salts (see Ref. 1 and references therein), the dimeric dianion $Te_2Cl_{10}^{2-}$ consists of two octahedra sharing one edge,[2–7] the trimeric anion $Te_3Cl_{13}^{-}$ consists of three octahedra, each sharing one edge with each of the two others and so forming a trigonal unit with idealised C_{3v} symmetry,[8] the tetrameric neutral molecule Te_4Cl_{16} consists of four octahedra, each sharing one edge with each of the three others in a cubane-like structure,[9,10] the polymeric ion $[TeCl_5]_n^{n-}$ consists of a chain of octahedra, each sharing two *cis*-oriented corners with two different neighbours,[11,12] and the polymeric ion $[Te_2Cl_9]_n^{n-}$ consists of Te_2Cl_{10} units with one axial Cl atom of each octahedron situated on a twofold axis.[13] We report here the structure of a new salt of the monomeric dianion, $[C_6H_5(CH_3)_3N]_2[TeCl_6]$ (**1**), and two new structure variants of tellurium(IV) halides, $[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10}\cdot Br_2]_n$ (**2**) and $[C_6H_5(CH_3)_3N]_{4n}[Te_2Cl_{10}]_n[Te_2Cl_{11}\cdot I]_n$ (**3**).

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Experimental

Preparations

$[C_6H_5(CH_3)_3N]_2[TeCl_6]$. To a solution of 4 mmol (0.687 g) $[C_6H_5(CH_3)_3N]Cl$ in 3 g CH_3OH was added 2 mmol (0.539 g) $TeCl_4$ dissolved in 3 g CH_3CN. The solution was set aside in a refrigerator for one day. Yield 0.95 g (77.5%) yellow prisms with a woof of green.

$[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10}{\cdot}Br_2]_n$. A solution of 4 mmol (0.687 g) $[C_6H_5(CH_3)_3N]Cl$ and 2 mmol + 200% (0.96 g) Br_2 in 3.0 g CH_3CN was added to 4 mmol (1.078 g) $TeCl_4$. From the clear solution orange prisms deposited. After 2 days in a refrigerator the yield was 1.10 g, 53% of the theoretical value from the equation

$$2\,TeCl_4 + 2\,[C_6H_5(CH_3)_3N]Cl + Br_2$$
$$= [C_6H_5(CH_3)_3N]_2[Te_2Cl_{10}\cdot Br_2]$$

$[C_6H_5(CH_3)_3N]_{4n}[Te_2Cl_{10}]_n[Te_2Cl_{11}\cdot I]_n$. The first crystals of this compound were obtained in an attempt to prepare $[C_6H_5(CH_3)_3N]_2[Te_2Cl_{10}\cdot I_2]$ by a method similar to the one used to prepare $[C_6H_5(CH_3)_3N]_2$-$[Te_2Cl_{10}\cdot Br_2]$. Later the compound was prepared in the following way: 0.50 mmol (0.127 g) I_2 and 4 mmol (0.687 g) $[C_6H_5(CH_3)_3N]Cl$ was suspended in 3.0 g CH_3CN. To the suspension was added 0.50 mmol (0.4 g) Cl_2 and 4 mmol (1.087 g) $TeCl_4$. By heating, the resulting light yellow suspension turned into a clear solution from which yellow prisms deposited. The crystals were washed with CH_2Cl_2 and dried. Yield 1.00 g, 52% of theoretical value from the equation

$$8\,TeCl_4 + 8\,[C_6H_5(CH_3)_3N]Cl + Cl_2 + I_2$$
$$= 2\,[C_6H_5(CH_3)_3N]_4[Te_2Cl_{10}][Te_2Cl_{11}\cdot I]$$

X-Ray structure analyses. The determination of unit cell parameters and the data collections were carried out on an Enraf-Nonius CAD4 diffractometer, using monochromated MoKα radiation ($\lambda = 0.710\,69$ Å). Crystal data and conditions for data collections are given in Table 1. The cell parameters were based on a least-squares fit of accurate setting angles for 21–24 reflections. Intensities were corrected for Lorentz and polarization effects, decay and absorption. Reflections with $I > 2\sigma(I)$ were regarded as observed.

The structures of compounds **1** and **2** were solved by

Table 1. Crystallographic data.

No.	**1**	**2**	**3**
Formula	$C_{18}H_{28}N_2Cl_6Te$	$C_{18}H_{28}N_2Br_2Cl_{10}Te_2$	$C_{36}H_{56}N_4Cl_{21}ITe_4$
M	612.8	1042.0	1926.7
System	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/a$	$P\bar{1}$	$Pnnm$
a/Å	13.965(3)	8.672(1)	11.952(1)
b/Å	10.292(2)	8.785(1)	16.475(2)
c/Å	8.608(2)	11.565(1)	16.923(2)
α/°		95.93(2)	
β/°	104.51(2)	103.27(2)	
γ/°		90.44(2)	
V/Å^3	1197.7(9)	852.5(3)	3332.2(1.0)
Z	2	1	2
T/K	93	293	293
D_x/g cm^{-3}	1.699	2.029	1.920
D_o/g cm^{-3}	1.64[a]	1.95	1.90
$F(000)$	608	494	1836
Θ_{max}	28	28	28
Scan mode	ω	ω	ω
Min scan width/°	1.00	1.00	1.00
Loss of intensity (%)	5.8	4.2	2.0
μ (MoKα)/cm^{-1}	19.3	48.4	30.8
Crystal size/mm	0.14 × 0.22 × 0.26	0.11 × 0.29 × 0.14	0.08 × 0.08 × 0.25
Crystal volume/mm^3		0.0059	0.0018
Correction for absorption	Empirical[b]	Numerical	Numerical
Transmission factors		0.50–0.58	0.75–0.81
Correction factors	0.96–1.12		
No. of ind. meas.	2887	4096	4137
No. with $I > 2\sigma(I)$	2648	3025	1883
No. of parameters refined	124	155	165
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.018	0.029	0.032
$R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$	0.022	0.034	0.032
$S = [\Sigma w(F_o - F_c)^2/(n - m)]^{1/2}$	1.573	1.569	1.182
Max. $\Delta(\rho)$/e Å^{-3}	0.63	0.65	0.49

[a] Measured at room temperature. [b] Ref. 15.

Table 2. Fractional atomic coordinates with e.s.d.s in parentheses.

Atom	x	y	z	B_{eq}/Å^{2a}
(**1**) $[C_6H_5(CH_3)_3N]_2[TeCl_6]$				
Te	0	0	0	0.570(2)
Cl(1)	−0.16506(3)	0.11481(4)	−0.02884(4)	1.073(6)
Cl(2)	0.08498(3)	0.21861(4)	0.00259(4)	1.154(6)
Cl(3)	0.03004(3)	0.00436(4)	0.30241(4)	1.146(6)
N	0.19881(12)	0.53233(12)	0.31259(15)	0.93(2)
C(1)	0.12997(12)	0.53780(16)	0.14796(18)	1.21(3)
C(2)	0.23345(12)	0.39319(16)	0.34270(18)	1.38(3)
C(3)	0.28695(11)	0.61718(17)	0.31310(18)	1.41(3)
C(4)	0.15074(10)	0.57864(14)	0.44043(16)	0.86(2)
C(5)	0.20044(11)	0.55893(16)	0.59975(17)	1.14(3)
C(6)	0.15908(11)	0.60517(16)	0.71967(17)	1.29(3)
C(7)	0.06945(12)	0.67056(16)	0.68139(18)	1.28(3)
C(8)	0.02179(11)	0.68999(17)	0.52220(19)	1.44(3)
C(9)	0.06158(11)	0.64464(16)	0.39887(18)	1.25(3)
(**2**) $[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10}\cdot Br_2]_n$				
Te	0.37956(3)	0.48594(3)	0.13772(2)	2.626(5)
Cl(1)	0.11324(13)	0.49070(16)	0.15265(12)	5.02(3)
Cl(2)	0.47320(17)	0.49115(17)	0.34707(10)	5.03(3)
Cl(3)	0.37565(15)	0.77231(13)	0.15446(11)	4.18(3)
Cl(4)	0.36173(19)	0.19806(14)	0.12182(13)	5.45(3)
Cl(5)	0.29824(14)	0.48427(15)	−0.11353(12)	4.61(3)
Br	0.46177(6)	0.92947(7)	0.40802(5)	5.22(1)
N	0.1145(4)	0.9618(4)	0.7828(3)	3.6(1)
C(1)	0.1392(11)	0.8687(7)	0.8841(5)	8.1(2)
C(2)	0.2598(8)	1.0536(8)	0.7875(6)	7.7(2)
C(3)	−0.0069(8)	1.0791(8)	0.7988(6)	7.8(2)
C(4)	0.0698(5)	0.8618(5)	0.6678(4)	3.6(1)
C(5)	−0.0966(6)	0.8154(7)	0.6292(5)	5.6(1)
C(6)	−0.1458(8)	0.7216(8)	0.5220(6)	6.9(2)
C(7)	−0.0418(8)	0.6725(7)	0.4569(5)	6.3(2)
C(8)	0.1144(8)	0.7173(7)	0.4962(5)	6.8(2)
C(9)	0.1661(6)	0.8100(7)	0.6026(5)	5.5(1)
(**3**) $[C_6H_5(CH_3)_3N]_{4n}[Te_2Cl_{10}]_n[Te_2Cl_{11}\cdot I]_n$				
Te(1)	0.88539(5)	0.09724(4)	1/2	3.09(1)
Cl(11)	0.8762(2)	0.09988(13)	0.35322(10)	5.58(4)
Cl(12)	1.1313(2)	0.0675(2)	1/2	5.57(6)
Cl(13)	0.6898(2)	0.1097(2)	1/2	7.08(9)
Cl(14)	0.9086(3)	0.2422(2)	1/2	6.54(8)
Te(2)	0.35058(5)	0.37264(4)	1/2	3.24(1)
I	0	1/2	1/2	6.63(3)
Cl(21)	0.3522(2)	0.36528(12)	0.35303(10)	5.55(4)
Cl(22)	0.2036(3)	0.2777(2)	1/2	7.97(8)
Cl(23)	0.2088(3)	0.5250(3)	1/2	8.7(1)
Cl(24)	0.4910(3)	0.2753(2)	1/2	7.36(8)
Cl(25)	1/2	1/2	1/2	9.4(1)
N	0.2109(5)	0.1472(3)	0.2319(3)	4.1(1)
C(1)	0.1450(7)	0.1833(7)	0.2976(6)	8.9(3)
C(2)	0.1573(7)	0.0696(5)	0.2105(7)	8.7(3)
C(3)	0.2001(8)	0.2054(6)	0.1650(6)	8.9(3)
C(4)	0.3307(6)	0.1329(4)	0.2536(4)	4.0(2)
C(5)	0.3575(7)	0.1215(5)	0.3310(5)	6.5(2)
C(6)	0.4682(8)	0.1074(6)	0.3488(5)	8.5(3)
C(7)	0.5471(7)	0.1019(5)	0.2923(6)	7.8(2)
C(8)	0.5195(7)	0.1125(5)	0.2155(6)	7.2(2)
C(9)	0.4096(6)	0.1266(5)	0.1964(5)	5.8(2)

[a] $B_{eq} = 4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

using the coordinates of the heavy atoms in the isomorphous selenium bromine compounds,[14] compound **3** by direct methods (MULTAN). C and N atoms were located from Fourier difference maps, and the structures were refined by full-matrix least-squares calculations, using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atom positions were calculated with bond lengths C–H = 0.95 Å, and held fixed with thermal parameters equal to $1.3B_{eq}$ for the atom to which they are attached. A secondary extinction coeffisient, g, in $F_{corr} = F_c(1 + gI_c)^{-1}$, was included as a variable and refined to 4.85×10^{-7} for compound **2**, but was found to be negligible for **1** and **3**. For the mixed halogen anions, Cl and Br in **2**, and Cl and I in **3**, the population parameters for the halogen atoms were refined, but there was no indication of disorder.

The programs used were Enraf-Nonius' Structure Determination Package 1987. All refined atomic coordinates are given in Table 2. Lists of structure factors, anisotropic displacement parameters and complete lists of bond lengths and angles are available from the authors.

Results and discussion

Bond lengths and angles are given in Table 3, and views of the anions are shown in Figs. 1 and 2.

The centrosymmetric $TeCl_6^{2-}$ anion of compound **1** has nearly ideal octahedral symmetry with largest deviation of angles 1.06°, and bond lengths in the range 2.5313(3)–2.5465(3) Å. This is in accordance with other centrosymmetric $TeCl_6^{2-}$ anions[1] and in contrast to $TeCl_6^{2-}$ anions in general positions where the range is much wider, as for example in the structure of dimethylammonium tetramethylformamidinium hexachlorotellurate(IV),[16] where the bonds are in the range 2.463(3)–2.618(2) Å.

The $[Te_2Cl_{10}\cdot Br_2]^{2-}$ anions of compound **2** are double bridged Te_2Cl_{10} dimers that are polymerized by bonding contacts between axial Cl atoms and Br_2 molecules situated on symmetry centres. The compound is isomorphous with $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10}\cdot Br_2]_n$.[14]

The double salt of compound **3** has a double bridged $[Te_2Cl_{10}]^{2-}$ anion which is known from other salts,[4–7] and a $[Te_2Cl_{11}\cdot I]^{2-}$ anion which represents a new modification in the series of chalcogen-halide compounds.

The bond lengths of the anions of compounds **2** and **3** are given in Table 4 along with bond lengths of similar anions. Data of some further known structures are not included in this table because the compounds are assumed to be partly hydrolyzed, whereby some Cl atoms are replaced by OH groups and so the dimensions are less reliable.[5] The anions in (1)–(4) are separate Te_2Cl_{10} units, in (5) and (6) Te_2Cl_{10} units polymerized by two axial Cl atoms forming Te–Cl–Te and Te–Cl–Br_2–Cl–Te bridges, respectively, in (7) $TeCl_6$ units polymerized by two *cis* Cl atoms forming Te–Cl–Te bridges, and in (8) $TeCl_6$ units polymerized by one of two *cis* Cl atoms

Table 3. Distances (in Å) and angles (in °) of the anions with e.s.d.s in parentheses.

(**1**) $[C_6H_5(CH_3)_3N]_2[TeCl_6]$

Te-Cl(1)	2.5465(3)	Cl(1)-Te-Cl(2)	89.97(1)
Te-Cl(2)	2.5411(3)	Cl(1)-Te-Cl(3)	90.27(1)
Te-Cl(3)	2.5313(3)	Cl(2)-Te-Cl(3)	91.06(1)

Interionic contact:

Cl(3)···Cl(3a)	3.703(1)	Te-Cl(3)···Cl(3a)	157.96(2)

Symmetry operation: (a) −*x*, −*y*, 1−*z*.

(**2**) $[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10}\cdot Br_2]_n$

Te-Cl(1)	2.3574(10)	Te-Cl(5a)	2.8819(11)
Te-Cl(2)	2.3714(10)	Cl(3)-Br	3.0341(10)
Te-Cl(3)	2.5041(9)	Br-Br(b)	2.3015(9)
Te-Cl(4)	2.5178(11)	Te···Te(a)	4.2066(4)
Te-Cl(5)	2.8213(11)		

Cl(1)-Te-Cl(2)	92.03(4)	Cl(3)-Te-Cl(4)	175.56(4)
Cl(1)-Te-Cl(3)	86.85(4)	Cl(3)-Te-Cl(5)	88.49(3)
Cl(1)-Te-Cl(4)	88.71(4)	Cl(3)-Te-Cl(5a)	86.90(3)
Cl(1)-Te-Cl(5)	93.32(4)	Cl(4)-Te-Cl(5)	91.94(4)
Cl(1)-Te-Cl(5a)	173.56(4)	Cl(4)-Te-Cl(5a)	97.54(4)
Cl(2)-Te-Cl(3)	90.91(4)	Cl(5)-Te-Cl(5a)	84.95(4)
Cl(2)-Te-Cl(4)	89.07(4)	Te-Cl(5)-Te(a)	95.05(3)
Cl(2)-Te-Cl(5)	174.58(4)	Te-Cl(3)-Br	115.05(4)
Cl(2)-Te-Cl(5a)	89.63(4)	Cl(3)-Br-Br(b)	173.73(4)

Interionic contacts:

Cl(1)···Cl(1c)	3.646(2)	Te-Cl(1)···Cl(1c)	104.40(5)
Cl(1)···Cl(5c)	3.504(1)	Te-Cl(1)···Cl(5c)	167.99(5)
		Te-Cl(5)···Cl(1c)	98.39(4)
		Te(a)-Cl(5)···Cl(1c)	163.90(4)
Cl(2)···Cl(2d)	3.447(2)	Te-Cl(2)···Cl(2d)	167.95(6)
Cl(3)···Cl(4e)	3.798(1)	Te-Cl(3)···Cl(4e)	169.97(6)
		Te-Cl(4)···Cl(3f)	170.06(6)

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

(**3**) $[C_6H_5(CH_3)_3N]_{4n}[Te_2Cl_{10}]_n[Te_2Cl_{11}\cdot I]_n$

Te(1)-Cl(11)	2.4866(16)	Te(1)-Cl(13)	2.3472(25)
Te(1)-Cl(12)	2.9793(28)	Te(1)-Cl(14)	2.4046(26)
Te(1)-Cl(12a)	2.7212(28)	Te(1)···Te(1a)	4.2155(11)

Cl(11)-Te(1)-Cl(11b)	174.57(9)	Cl(12)-Te(1)-Cl(13)	175.56(11)
Cl(11)-Te(1)-Cl(12)	92.65(5)	Cl(12)-Te(1)-Cl(14)	92.83(10)
Cl(11)-Te(1)-Cl(12a)	90.82(5)	Cl(12a)-Te(1)-Cl(13)	90.83(11)
Cl(11)-Te(1)-Cl(13)	87.40(5)	Cl(12a)-Te(1)-Cl(14)	177.56(10)
Cl(11)-Te(1)-Cl(14)	89.29(5)	Cl(13)-Te(1)-Cl(14)	91.61(12)
Cl(12)-Te(1)-Cl(12a)	84.73(8)	Te(1)-Cl(12)-Te(1a)	95.27(8)

Te(2)-Cl(21)	2.4902(16)	Te(2)-Cl(24)	2.3208(30)
Te(2)-Cl(22)	2.3525(28)	Te(2)-Cl(25)	2.7554(6)
Te(2)-Cl(23)	3.0277(35)	Cl(23)-I	2.5295(35)

Cl(21)-Te(2)-Cl(21b)	174.35(9)	Cl(22)-Te(2)-Cl(24)	94.62(14)
Cl(21)-Te(2)-Cl(22)	88.47(5)	Cl(22)-Te(2)-Cl(25)	172.09(11)
Cl(21)-Te(2)-Cl(23)	92.55(5)	Cl(23)-Te(2)-Cl(24)	167.72(12)
Cl(21)-Te(2)-Cl(24)	87.76(5)	Cl(23)-Te(2)-Cl(25)	74.42(8)
Cl(21)-Te(2)-Cl(25)	91.84(5)	Cl(24)-Te(2)-Cl(25)	93.29(10)
Cl(22)-Te(2)-Cl(23)	97.67(13)	Te(2)-Cl(23)-I	114.67(15)

Interionic contacts between $[Te_2Cl_{10}]$ and $[Te_2Cl_{11}\cdot I]$ groups:

Cl(11)···Cl(21c)	3.549(2)	Te(1)-Cl(11)···Cl(21c)	171.41(9)
		Te(2)-Cl(21)···Cl(11d)	167.17(8)
Cl(12)···Cl(22e)	3.569(4)	Te(1)-Cl(12)···Cl(22e)	94.55(10)
		Te(1a)-Cl(12)···Cl(22e)	170.18(12)
		Te(2)-Cl(22)···Cl(12f)	145.71(17)
Cl(13)···Cl(24)	3.618(4)	Te(1)-Cl(13)···Cl(24)	136.08(15)
		Te(2)-Cl(24)···Cl(13)	174.74(16)
Cl(14)···Cl(22e)	3.573(5)	Te(1)-Cl(14)···Cl(22e)	106.05(12)
		Te(2)-Cl(22)···Cl(14f)	147.72(17)

Symmetry operations: (a) 2−*x*, −*y*, 1−*z*; (b) *x*, *y*, 1−*z*; (c) ½+*x*, ½−*y*, ½−*z*; (d) *x*−½, ½−*y*, ½−*z*; (e) 1+*x*, *y*, *z*; (f) *x*−1, *y*, *z*.

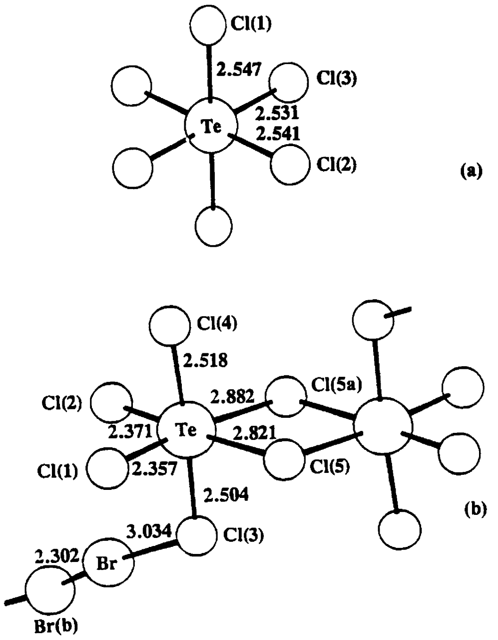

Fig. 1. Views of the $TeCl_6^{2-}$ anion (above) and the $Te_2Cl_{10}\cdot Br_2^{2-}$ anion (below) as found in the phenyltrimethylammonium salts.

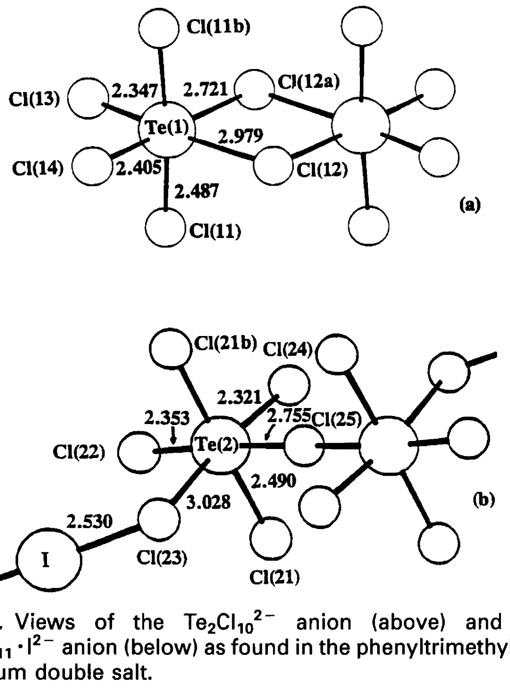

Fig. 2. Views of the $Te_2Cl_{10}^{2-}$ anion (above) and the $Te_2Cl_{11}\cdot I^{2-}$ anion (below) as found in the phenyltrimethylammonium double salt.

forming a linear Te–Cl–Te bridge and the other a Te–Cl–I–Cl–Te bridge. In each of the eight anions there are three categories of bond lengths; two short terminal equatorial bonds, two long bridging equatorial bonds, and two axial bonds of intermediate lengths. *Trans* situated terminal and bridging bonds are listed on the same line. In compounds (2), (4), (7) and (8) the axial bonds are related by symmetry.

The bonds in such complexes are usually explained as of the three-centre four-electron (3*c*–4*e*) type. The linear X–Y–X system has only one occupied bonding orbital. The total lengths of the systems are, both from the 3*c*–4*e* model and the observations in crystal structures, considerably longer than the sum of the covalent radii of the atoms. The two bonds are mutually influenced by each other in such a way that if one for some reason is longer than the bonds of a symmetric system, the other is shorter, and vice versa. The average of two unsymmetrical bonds is equal to or longer than symmetrical bonds. The variation in bond lengths points towards a rather flat energy curve.

The most investigated bridges between two chalcogen(IV) nucleus are of the type $Y_2X_{10}^{2-}$, as represented here by compounds (1)–(4) in Table 4 and shown in Fig. 2a, and by the two polymeric anions in compounds (5) and (6). The Te–Cl–Te angles, from the model expected to be 90°, are in the range 90.6(1)–95.3(1)°. The bridging atoms have long bonds to the Te atoms; they are the weak bonds of an asymmetric 3*c*–4*e* system with correspondingly strong bonds in *trans* positions. The two bridging bonds are in all cases of different lengths, but with individual differences in a wide range, from 0.066 Å in (6) to 0.357 Å in (1). The ratio of the average bridging bond lengths to the average equatorial terminal ones is nearly constant, ranging from 1.18 in (2) to 1.21 in (6).

In the polymeric anion of compound (7) the Te–Cl–Te angles are 152.0(3) and 158.6(3)°, the average bridging bond length is 2.795 Å, and the average Te···Te distance is 5.453 Å. In the polymeric anion of compound (8), shown in Fig. 2b, the Te–Cl–Te bridges are linear and symmetric with bond lengths 2.755(1) Å, Te···Te distance 5.510 Å. The average bridging bond lengths of the angular double-bridged compounds, (1)–(6), are in the range 2.821–2.852 Å, and the Te···Te distances 4.033–4.216 Å. The large Te–Cl–Te angles and long bridging bonds in the angular double bridged compounds is usually explained by electrostatic repulsion between the central atoms. The long bridging bonds in the single-bridged compounds must be due to some other effects.

Compound (8), Fig 2b, may be described as dimeric single bridged $Te_2Cl_{11}^{3-}$ units polymerized by I^+ bridges between Cl atoms in *cis* positions to the Te–Cl–Te bridges. The Te–Cl–I angle is 114.67(15)°. The Cl–I–Cl bridges are linear symmetric with I–Cl distances of 2.530(4) Å as compared to 2.54 Å in the linear symmetric ICl_2^- ion in the tetramethylammonium salt.[17] The Cl atoms involved in this bridge belong to the Cl–I–Cl as well as the Cl–Te–Cl 3*c* systems. The latter system is extremely asymmetric with terminal bond 2.321(3) Å, which is a little shorter than the sum of the covalent radii, and the bridging bond is 3.028(4) Å. The Cl–Te–Cl angle is 167.72(12)°.

In compound (6), Fig. 1b, the bridging I^+ ion of compound (8), Fig. 2b, is replaced by a Br_2 molecule. The Te–Cl–Br angle is 115.05(4)°, virtually the same as corresponding angle in compound (8). The Cl–Te–Cl

Table 4. Bond lengths (in Å) in dimeric and polymeric chlorotellurate(IV) ions.

No.	Compound	Equatorial terminal Te–Cl bonds	Equatorial bridging Te–Cl bonds	Axial Te–Cl bonds	Te···Te distance	Te–Cl–Te angle	Ref.
(1)	$[(C_6H_5)_4As]_2[Te_2Cl_{10}]_2$	2.336(1)	3.010(1)	2.478(2)	4.033(1)	90.6(1)	4
		2.436(1)	2.653(1)	2.517(1)		—	
(2)	$(H_2O)_2(15\text{-Crown-}5)_3][Te_2Cl_{10}]_2$	2.361(2)	2.970(4)	2.494(2)	4.138(2)	93.8(1)	7
		2.416(2)	2.689(3)	—		—	
(3)	$[C_{16}H_{11}NS]_2[Te_2Cl_{10}]_2$	2.349(2)	2.937(2)	2.470(2)	4.050[a]	92.0(1)	6
		2.413(2)	2.715(2)	2.527(2)		—	
(4)	$[C_6H_5(CH_3)_3N]_{4n}[\mathbf{Te_2Cl_{10}}]_n[Te_2Cl_{11}\cdot I]_n$	2.347(3)	2.979(3)	2.487(2)	4.216(1)	95.3(1)	This work
		2.405(3)	2.721(3)	—		—	
(5)	$[H_9O_4]_n[Te_2Cl_9]_n$	2.337(2)	2.867(2)	2.355(3)	4.046(2)	91.7(1)	13
		2.375(2)	2.774(2)	2.775(2)[b]		—	
(6)	$[C_6H_5(CH_3)_3N]_{2n}[Te_2Cl_{10}\cdot Br_2]_n$	2.357(1)	2.882(1)	2.518(1)	4.207(1)	95.1(1)	This work
		2.371(1)	2.821(1)	2.504(1)[c]		—	
(7)	$[PCl_4]_n[TeCl_5]_n$	2.345(8)	2.852(8)[d]	2.498(5)			12
		2.375(5)	2.783(7)[d]	—			
		2.357(7)	2.852(8)[d]	2.489(4)			
		2.382(8)	2.693(8)[d]	—			
(8)	$[C_6H_5(CH_3)_3N]_{4n}[Te_2Cl_{10}]_n[\mathbf{Te_2Cl_{11}\cdot I}]_n$	2.321(3)	3.028(4)[e]	2.490(2)			This work
		2.353(3)	2.755(1)[f]	—			

[a] Calculated from coordinates given. [b] μ_2Cl on twofold axis. [c] Cl attached to Br_2. [d] Single μ_2Cl bridges. [e] Cl attached to I. [f] μ_2Cl on centre of symmetry.

system which was extremely asymmetric in (8) is here nearly symmetric, with Te–Cl bonds 2.518(1) and 2.504(1) Å, and Cl–Te–Cl angle 175.56(4)°. The Br–Br distance, 2.302(1) Å, is only slightly longer than a covalent bond, 2.28 Å, whereas the Br–Cl bridge is long, 3.034(1) Å. The Br–Br–Cl angle is 173.73(4)°. In the isomorphous compound $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10}\cdot Br_2]_n$[14] the molecular Br–Br bond is 2.339(4) Å and the bridging Br–Br bond is 3.097(3) Å. Taking into account the difference in covalent radii this bridging bond is a little stronger than the corresponding Br–Cl bond in the Te compound.

In the polymeric anion of $[(CH_3)_3HN]_{2n}[SeBr_6\cdot Br_2]_n$[1,18] each $SeBr_6^{2-}$ unit has two *cis* Br atoms bridged to neighbouring $SeBr_6^{2-}$ units by Br_2 molecules in such a way that an almost linear Br–Se–Br···Br–Br···Br–Se–Br string is formed. The angles are in the range 163.5(2)–179.2(1)°, and Br–Se = 2.454(3) Å, Se–Br = 2.678(3) Å, Br···Br = 2.987(3) Å, and Br–Br = 2.330(3) Å. The bridging Br_2 molecule has a clear elongating effect on the Se–Br bond, and the *trans* Br–Se bond is correspondingly shorter. In $[C_6H_5(CH_3)_3N]_{2n}[Se_2Br_{10}\cdot Br_2]_n$[14] and $[C_6H_5(CH_3)_3N]_2[Te_2Cl_{10}\cdot Br_2]$ (6) there is no such effect (Br–Se = 2.562 Å, Se–Br = 2.573 Å, and Cl–Te = 2.518 Å, Te–Cl = 2.504 Å). In the latter compounds the bridges are angular, Se–Br···Br = 114.23(8)° and Te–Cl···Br = 115.05(4)°, and the contacts to Br_2 are weaker, Br···Br = 3.097(2) Å, Cl···Br = 3.034(1) Å.

From compound **1** and Ref. 1, the average of the total lengths of the linear 3*c*–4*e* systems in the mononuclear $TeCl_6^{2-}$ ions is 5.08 Å. The corresponding average of the dimeric and polymeric compounds of Table 4, for systems where none of the Cl atoms participates in bridge bonding, is 4.99 Å. This indicates an effect of the bridging system in the equatorial plane on the axial bonds, which may be unexpected for a 3*c*–4*e* bonding system.

The linear $Cl_{terminal}$–Te–Cl_{bridge} string is usually referred to as an asymmetric 3*c*–4*e* system, but the terminal bonds are in some cases of about the same lengths as a normal covalent Te–Cl bond, 2.35 Å, or even shorter. This fact should accordingly tell us that this is a 2*c*–2*e* bond, but the atom in the *trans* position is clearly within bonding distance from the Te atom and the short terminal bonds can therefor hardly be regarded as covalent 2*c*–2*e* bonds.

The dimensions of the phenyltrimethylammonium ion are within the following ranges: N–C = 1.501(2)–1.513(2) Å, C–C = 1.380(2)–1.389(2) Å, C–N–C = 107.4(1)°–112.4(1)°, N–C–C = 118.2(1) and 120.6(1)°, C–C–C = 118.6(1)°–121.3(1)° in compound **1**, N–C = 1.475(5)–1.507(6) Å, C–C = 1.347(8)–1.393(7) Å, C–N–C = 104.3(4)°–113.0(3)°, N–C–C = 120.0(4)° and 120.5(3)°, C–C–C = 119.3(5)°–121.2(51)° in compound **2**, N–C = 1.475(9)–1.497(8) Å, C–C = 1.345(13)–1.376(12) Å, C–N–C = 105.4(7)–112.7(6)°, N–C–C = 118.9(6) and 120.2(6)°, C–C–C = 117.4(9)–122.0(9)° in compound **3**. In compound **1** each Cl atom is surrounded by 6–9 C atoms from methyl and phenyl groups, at distances 3.61–3.98 Å and the shortest Cl···H distance is 2.91 Å. In compound **2** there are 12 Cl···C distances in the range 3.39–3.98 Å and 6 Br···C distances in the range 3.68–3.98 Å. All Cl atoms are involved and the shortest Cl···H distance is 2.83 Å. In compound **3** there are 26 Cl···C distances in the range 3.54–4.00 Å and all Cl atoms except Cl(25) are involved. The shortest Cl···H distance is 2.80 Å.

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