An Aryltellurium Mixed Halide Anion. Preparation and Crystal and Molecular Structure of $[NBu^n_4][PhTeCl_3I]$ †

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The crystal and molecular structure of the title compound has been determined from diffractometer data by the heavy-atom method. The crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 11.449(4), b = 11.606(4), c = 12.060(3) Å, α = 94.33(2), β = 93.22(2), γ = 113.33(3)°, U = 1 460.8(8) Å^3, and Z = 2; R = 0.059 for 2 633 observed reflections [$I/\sigma(I) \geqslant 3.0$]. The $PhTeCl_3I^-$ anion is a square-based pyramid with a lone pair in the sixth position of an octahedron: Te–C 2.15(1), Te–Cl 2.565(4)—2.663(3), and Te–I 2.837(2) Å. Allowing for disorder, corrected values for Te–Cl and Te–I are 2.51 and 3.04 Å respectively.

The reported structures of aryltellurium trihalides [1] all contain square-pyramidal $RTeX_4$ units with halogen atoms bridging adjacent tellurium atoms to give dimeric or polymeric structures (except with very bulky aryl groups), and the presence of the lone pair in the vacant sixth octahedral position prevents significant secondary bonding. As well as forming links between individual molecules, these compounds can act as halide ion acceptors, to give $RTeX_4^-$ ions, and it is of interest to discover whether these share the geometry of the parent $RTeX_3$ species, or whether they form additional bridges. Hitherto, only one structure of this type has been determined, the special case of $[TeMe_3][MeTeI_4]$ [2] which is an isomer of Me_2TeI_2. The preparation of a range of $RTeX_4^-$ ions has been reported,[3] including some in which the halogens are not identical, and their spectra appear consistent with square-pyramidal geometry, though the spectra are too complex for complete certainty.

We report here the crystal structure of the $PhTeCl_3I^-$ ion, a mixed halide not among those originally studied; it was produced in an attempt to prepare $PhTeI_4^-$ from $PhTeCl_3$.

Experimental

Addition of an excess of a methanolic solution of tetra-n-butylammonium iodide to phenyltellurium trichloride in methanol gave an immediate precipitate of red crystals. These were filtered off and the mother-liquor allowed to evaporate slowly to yield red crystals of $[N(C_4H_9)_4]^+[C_6H_5TeCl_3I]^-$ (Found: C, 38.45; H, 6.0; N, 2.15. Calc. for $C_{22}H_{41}Cl_3INTe$: C, 38.85; H, 6.05; N, 2.05%).

Crystal Data.—$C_{22}H_{41}Cl_3INTe$, M = 680.44, Triclinic, space group $P\bar{1}$, a = 11.449(4) b = 11.606(4) c = 12.060(3) Å, α = 94.33(2), β = 93.22(2), γ = 113.33(2)°, U = 1 460.8(8) Å^3, D_m = 1.53 g cm^{-3}, Z = 2, D_c = 1.55 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 23.51 cm^{-1}, $F(000)$ = 692, T = 290 K.

Data were obtained using a Syntex $P2_1$ diffractometer with unit-cell dimensions obtained from the positions of 15 high-angle reflections. Reflections were measured using θ—2θ scans over a scan range (2θ) (K_{α_1} − 1.0°) to (K_{α_2} + 1.0°) to a maximum of 2θ of 50°. A variable scan rate of 2—29.3° min^{-1}, depending on the intensity of a 2.5-s prescan, was used. Backgrounds were recorded at the end of each scan, each for one quarter of the scan time. The intensities of three check reflections were monitored every 297 reflections and they showed slight systematic decay for which a correction was made. Of the 5 471 reflections collected 2 633 were deemed observed [$I/\sigma(I) \geqslant 3.0$] and were used in refinement. Lorentz, polarization, and absorption corrections were applied, the last with the program ABSCOR.[4]

A Patterson synthesis revealed the positions of two heavy atoms which were input as iodine and tellurium atoms and a trial structure in space group $P\bar{1}$ obtained. This trial structure proved unsatisfactory and the space group was relaxed to $P1$ with two Te atoms and two iodine atoms. Successive isotropic refinement and difference-Fourier syntheses enabled most of the light atoms to be located and it was found that the two cations and anions were related by inversion through a centre. The structure was then returned to $P\bar{1}$ and anisotropic refinement on the heavy atoms and difference-Fourier syntheses revealed all the light atoms. Anisotropic refinement on all atoms gave R = 0.11, and this value could not be lowered until it was realised that the halogen atoms were disordered. Refinement of their population parameters showed that although iodine is present to the greatest extent at the position of the I atom, it partly occupies the positions of each of the chlorine atoms. Although such a refinement has dangers, because of the correlation between population and thermal parameters, in this case the temperature factors for Cl(1)—Cl(3) are satisfactorily close in value (Table 1), while a calculation of the number of electrons represented by the populations obtained gives almost precisely the expected result (Table 2). With this check, the actual occupancies of each site by iodine and chlorine can be determined (Table 2). Refinement including population parameters for the halogen atoms resulted in R = 0.065 and revealed most of the hydrogen atoms. All the hydrogen atoms were then input in calculated positions with fixed temperature factors. A final least-squares refinement in large blocks on all the non-hydrogen atoms after application of an empirical weighting scheme gave R = 0.059.

The scattering factors used in refinement were taken in their analytical form from ref. 5. Computing was carried out using the X-RAY 76 suite of programs [6] on a Burroughs B6700 computer. Final positional parameters are given in Table 1, and bond lengths and angles are in Table 3; Figure 1 shows the anion with the atomic numbering, and Figure 2 gives a packing diagram.

Discussion

The compound exists as discrete tetra-n-butylammonium cations and trichloroiodophenyltellurate anions. The geometry of the anion is that of a square-based pyramid, with

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† Tetra-n-butylammonium trichloroiodophenyltellurate.

Supplementary data available (No. SUP 23653, 19 pp.): structure factors and thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Atomic co-ordinates (× 10^4), with standard deviations in parentheses *

Atom	*X/a*	*Y/b*	*Z/c*	*U*
Te	2 146.8(8)	−1 570.9(8)	2 618.9(8)	57
I	3 160(2)	−2 354(2)	4 478(1)	111
Cl(1)	3 174(3)	−2 700(3)	1 234(3)	91
Cl(2)	1 087(3)	−494(3)	3 909(3)	97
Cl(3)	1 180(3)	−842(3)	880(2)	97
C(1)	437(12)	−3 280(12)	2 493(13)	65
C(2)	−35(13)	−3 919(14)	1 459(16)	84
C(3)	−1 197(18)	−5 037(18)	1 375(23)	117
C(4)	−1 747(21)	−5 418(20)	2 375(33)	148
C(5)	−1 226(22)	−4 746(20)	3 397(25)	130
C(6)	−98(17)	−3 656(15)	3 492(16)	102
C(11)	−2 136(14)	−1 130(13)	1 463(12)	71
C(12)	−3 130(16)	−2 334(14)	802(13)	84
C(13)	−2 502(17)	−2 880(15)	−24(15)	99
C(14)	−3 396(21)	−4 105(19)	−636(19)	126
C(15)	−3 444(13)	−1 440(12)	3 120(13)	69
C(16)	−2 743(14)	−2 166(13)	3 660(13)	80
C(17)	−3 745(18)	−3 172(16)	4 312(14)	101
C(18)	−4 666(20)	−4 286(17)	3 510(17)	114
C(19)	−3 515(12)	32(12)	1 743(11)	67
C(110)	−4 032(13)	769(12)	2 481(12)	73
C(111)	−4 902(14)	1 241(14)	1 791(14)	83
C(112)	−5 442(18)	1 982(16)	2 528(18)	115
C(113)	−1 533(13)	549(12)	3 054(11)	69
C(114)	−659(15)	1 584(14)	2 455(14)	87
C(115)	339(17)	2 577(16)	3 340(17)	103
C(116)	1 297(22)	3 604(22)	2 839(22)	142
N(1)	−2 648(9)	−509(9)	2 335(8)	57
H(2)	392	−3 634	817	82
H(3)	−1 581	−5 502	673	82
H(4)	−2 505	−6 167	2 341	82
H(5)	−1 637	−5 027	4 048	82
H(6)	287	−3 194	4 194	82
H(111)	−1 759	−538	948	82
H(112)	−1 500	−1 340	1 826	82
H(121)	−3 522	−2 936	1 304	82
H(122)	−3 761	−2 136	413	82
H(131)	−2 163	−2 294	−553	82
H(132)	−1 826	−3 008	366	82
H(141)	−3 735	−4 691	−108	82
H(142)	−4 072	−3 976	−1 026	82
H(143)	−2 999	−4 450	−1 159	82
H(151)	−3 665	−980	3 696	82
H(152)	−4 200	−2 031	2 702	82
H(161)	−2 441	−2 574	3 102	82
H(162)	−2 043	−1 608	4 161	82
H(171)	−3 304	−3 471	4 831	82
H(172)	−4 217	−2 786	4 701	82
H(181)	−5 107	−3 987	2 991	82
H(182)	−4 194	−4 672	3 121	82
H(183)	−5 271	−4 894	3 904	82
H(191)	−3 034	570	1 229	82
H(192)	−4 219	−655	1 348	82
H(1101)	−4 515	246	3 004	82
H(1102)	−3 341	1 474	2 868	82
H(1111)	−4 416	1 767	1 271	82
H(1112)	−5 588	534	1 399	82
H(1121)	−5 928	1 456	3 048	82
H(1122)	−4 756	2 689	2 920	82
H(1123)	−5 976	2 272	2 105	82
H(1131)	−1 886	919	3 598	82
H(1132)	−1 035	174	3 417	82
H(1141)	−239	1 255	1 943	82
H(1142)	−1 133	1 962	2 062	82
H(1151)	−95	2 923	3 823	82
H(1152)	760	2 169	3 759	82
H(1161)	1 731	3 258	2 356	82
H(1162)	876	4 012	2 420	82
H(1163)	1 909	4 213	3 381	82

* Average isotropic *U* (× 10^3) is given for anisotropic atoms. Populations: 1.0; except I, 0.677(5), Cl(1), 1.359(15); Cl(2), 1.189(15); Cl(3), 1.490(15).

Table 2. Populations and occupancies for halogen atoms

Atom	Refined population parameter	Equivalent number of electrons	Fractional occupancy		Weighted fraction [a]		Distance [b]	
			I	Cl	I	Cl	Obs.	Calc.
I	0.677(5)	35.9	0.53	0.47	0.628	0.372	2.837	2.838
Cl(1)	1.359(15)	23.1	0.17	0.83	0.235	0.765	2.645	2.630
Cl(2)	1.189(15)	20.2	0.09	0.91	0.129	0.871	2.565	2.573
Cl(3)	1.490(15)	25.3	0.23	0.77	0.309	0.691	2.663	2.670
Totals		104.5 [c]	1.02	1.98				

[a] Weighted fractional occupancies (W_I and W_{Cl}) are related to fractional occupancies (f_I and f_{Cl}) by $W_I = f_I \times 1.2/(f_I \times 1.2 + f_{Cl} \times 0.8)$ and $W_{Cl} = f_{Cl} \times 0.8/(f_I \times 1.2 + f_{Cl} \times 0.8)$ [$1.2 = 53/\frac{1}{2}(53 + 35.5)$ and $0.8 = 35.5/\frac{1}{2}(53 + 35.5)$]. [b] Calculated distances = $3.036W_I + 2.505W_{Cl}$. [c] Total electron count = 3 × Cl(17) + 1 × I(53) = 104.

four halogen atoms and the tellurium atom in the basal plane, and an apical carbon atom; Te is only 0.015 Å out of the plane of the halogen atoms (away from the apex). This geometry is also found in most aryltellurium trihalides which share halogen atoms between neighbouring molecules, giving rise to dimeric or polymeric structures. For both the present compound and these trihalides, no significant secondary bonding to the tellurium is present, because the lone pair blocks the sixth position of the co-ordination pseudo-octahedron.

The tellurium–halogen bond lengths should provide useful information on the change from a neutral square-pyramidal species to an anionic species, but unfortunately they are severely affected by disorder. It is possible to obtain corrected Te–Cl and Te–I distances * if it is assumed that the observed distances are given by equations of the form $d_{obs.} = d_{Te-I}W_I + d_{Te-Cl}W_{Cl}$ where W_I and W_{Cl} are the fractional occupancies of the halogen atom site, weighted for the relative numbers of electrons (see Table 2). The four such observations can be used in a linear least-squares calculation to give Te–Cl 2.505 and Te–I 3.036 Å (using unweighted fractional occupancies, 2.529 and 3.112 Å). These values reproduce the observed distances rather well (Table 2), but it is not very

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* We thank one of the referees for suggesting this approach.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Te–I	2.837(2)	C(3)–C(4)	1.41(5)	N(1)–C(113)	1.54(1)	C(19)–C(110)	1.49(2)
Te–Cl(1)	2.645(4)	C(4)–C(5)	1.37(4)	C(11)–C(12)	1.53(2)	C(110)–C(111)	1.55(2)
Te–Cl(2)	2.565(4)	C(5)–C(6)	1.40(2)	C(12)–C(13)	1.50(3)	C(111)–C(112)	1.51(3)
Te–Cl(3)	2.663(3)	C(6)–C(1)	1.40(2)	C(13)–C(14)	1.49(2)	C(113)–C(114)	1.49(2)
Te–C(1)	2.15(1)	N(1)–C(11)	1.50(2)	C(15)–C(16)	1.53(2)	C(114)–C(115)	1.55(2)
C(1)–C(2)	1.36(2)	N(1)–C(15)	1.54(2)	C(16)–C(17)	1.57(2)	C(115)–C(116)	1.46(3)
C(2)–C(3)	1.44(2)	N(1)–C(19)	1.54(2)	C(17)–C(18)	1.53(2)		

I–Te–Cl(1)	90.73(9)	C(2)–C(3)–C(4)	117(2)	N(1)–C(11)–C(12)	115(1)
I–Te–Cl(2)	90.95(10)	C(3)–C(4)–C(5)	122(2)	C(11)–C(12)–C(13)	110(1)
I–Te–Cl(3)	179.59(8)	C(4)–C(5)–C(6)	121(2)	C(12)–C(13)–C(14)	113(2)
I–Te–C(1)	90.2(4)	C(5)–C(6)–C(1)	116(2)	N(1)–C(15)–C(16)	114(1)
Cl(1)–Te–Cl(2)	178.01(11)	C(2)–C(1)–Te	118(1)	C(15)–C(16)–C(17)	106(1)
Cl(1)–Te–Cl(3)	89.54(11)	C(6)–C(1)–Te	117(1)	C(16)–C(17)–C(18)	111(1)
Cl(1)–Te–C(1)	89.8(4)	C(11)–N(1)–C(15)	112(1)	N(1)–C(19)–C(110)	116(1)
Cl(2)–Te–Cl(3)	88.78(12)	C(11)–N(1)–C(19)	109(1)	C(19)–C(110)–C(111)	111(1)
Cl(2)–Te–C(1)	89.1(4)	C(11)–N(1)–C(113)	110(1)	C(110)–C(111)–C(112)	112(1)
Cl(3)–Te–C(1)	89.5(4)	C(15)–N(1)–C(119)	108(1)	N(1)–C(113)–C(114)	116(1)
C(6)–C(1)–C(2)	125(1)	C(15)–N(1)–C(113)	108(1)	C(13)–C(114)–C(115)	108(1)
C(1)–C(2)–C(3)	118(2)	C(19)–N(1)–C(113)	110(1)	C(114)–C(115)–C(116)	113(2)

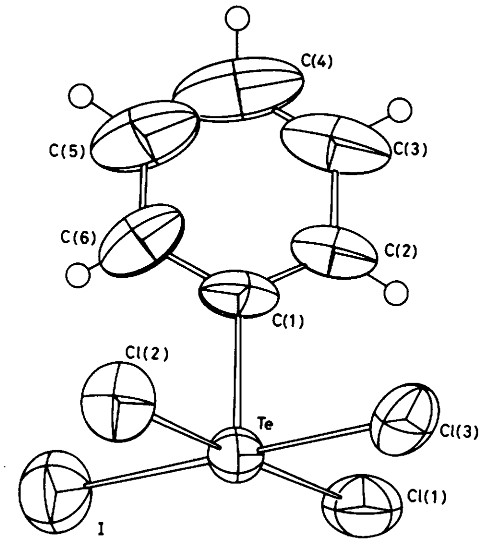

Figure 1. Structure of the $[PhTeCl_3I]^-$ ion showing the atomic numbering

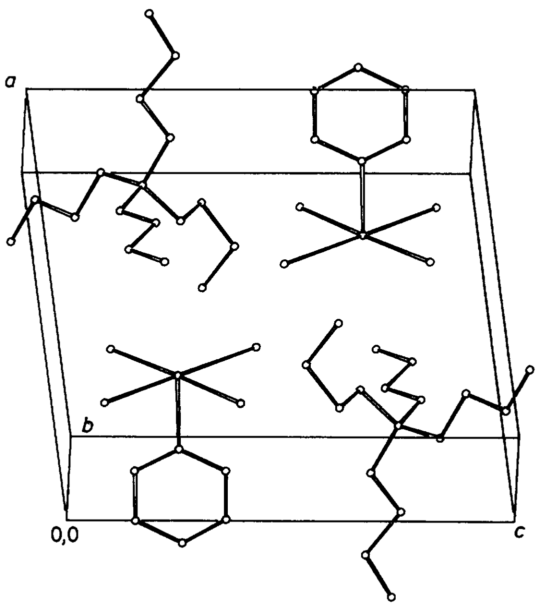

Figure 2. Packing diagram for $[NBu^n_4]^+[PhTeCl_3I]$

easy to judge their real validity or accuracy. Comparative figures are given in Table 4. The Te–C distance shows a slight increase over the values in $PhTeX_3$, probably on the limit of significance. The effect on the Te–Cl(terminal) distance is in the same direction and is much more substantial; the shortest of these uncorrected distances [Te–Cl(2)] is not far removed from Te–Cl(corrected) and so the effect is almost certainly real. Similarly, Te–I (both uncorrected and corrected) is lengthened in relation to $PhTeI_3$, though the difference between the distance found here and that in $MeTeI_4^-$ is disturbing. The overall lengthening in the anion in comparison to the neutral molecules can be understood straightforwardly in terms of increased repulsion from the additional electron. An alternative view can be based on consideration of the bridging halogen atoms in $PhTeX_3$. Te–X(bridge) is substantially longer than Te–X(terminal) either in the neutral or the anionic species. It is possible therefore to see Te in both compounds achieving an approximately constant 'bond valence',[7] either as the sum of four bonds of equal bond order (anion) or of two shorter and two longer bonds (neutral). Further

Table 4. Comparison of bond lengths (Å)

Compound	$PhTeCl_3I^-$	$MeTeI_4^-$	$PhTeCl_3$	$PhTeI_3$
Reference	*a*	2	1	*b*
Te–I(terminal)	2.837(2) [c] 3.036 [d]	2.840(7)— 2.984(7)		2.780(1)
Te–I(bridge)				3.285(1)
Te–Cl(terminal)	2.565(4)— 2.663(3) [c] 2.505 [d]		2.377(1)	
Te–Cl(bridge)			2.755(1)	
Te–C	2.15(1)	2.15(8)	2.122(4)	2.12(2)

[a] This work. [b] N. W. Alcock and W. D. Harrison, unpublished work. [c] Affected by disorder. [d] Corrected for disorder (see text)

examination of this approach requires a more extensive survey of bridge and terminal bond lengths and strengths.

In the cation, all the arms form extended chains with almost ideal 180° dihedral angles, with the single exception of C(15)-C(16)-C(17)-C(18) [76(2)°], which is bent to avoid contact with I. Apart from this, there are no close cation–anion or anion–anion approaches; this undoubtedly underlies the disorder of the halogen atoms, whose very weak contacts do not provide enough discrimination to prevent the disorder. This packing is in notable contrast to that in [$TeMe_3$][$MeTeI_4$], which has a strong secondary bond between cation and anion.[2] This is also exceptional in that it does form a secondary bond from the anion to another anion. The value of the angle C–Te · · · I is rather low (166°), presumably so that the Te · · · I interactions can avoid the lone pair.

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