Secondary Bonding. Part 7.† Crystal and Molecular Structures of Diphenyltellurium Dichloride and Phenyltellurium Trichloride

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The crystal and molecular structures of the title compounds have been determined from diffractometer data by the heavy-atom method. The crystals of diphenyltellurium dichloride (1) are orthorhombic, space group *Pbca*, with unit-cell dimensions (173 K) $a = 7.644(2)$, $b = 18.160(3)$, $c = 18.014(3)$ Å, $Z = 8$, from 1 552 observed reflections [$I/\sigma(I) \geqslant 3.0$], $R = 0.036$. Crystals of phenyltellurium trichloride (2) are triclinic, space group $P\bar{1}$, with unit-cell dimensions (290 K) $a = 7.468(1)$, $b = 8.610(1)$, $c = 13.987(2)$ Å, $\alpha = 98.89(1)$, $\beta = 92.10(1)$, $\gamma = 90.81(1)$°, $Z = 4$, from 2 903 observed reflections, $R = 0.018$. The primary geometry about Te in (1) is based on a trigonal bipyramid with a vacant equatorial position, whereas (2) exhibits square-based pyramidal geometry for its two independent Te atoms; these are bridged by Cl atoms, to give a chain structure. Both structures exhibit longer Te $\cdots$ Cl interactions, though these are weak and perhaps of little significance in (2).

We present the crystal structures of diphenyltellurium dichloride (1) and phenyltellurium trichloride (2) as part of a series of studies of secondary interactions in Te compounds. The structure of (1) is closely comparable to that of other compounds of the type R_2TeX_2 [1–4] consisting of R_2TeX_2 molecules loosely linked by secondary interactions, Te $\cdots$ X, to adjacent molecules. The structure of (2), like those of (*p*-ethoxyphenyl)tellurium trichloride [5] and (2-chloroethyl)tellurium trichloride,[6] is a Cl-bridged polymer.

EXPERIMENTAL

Compound (1) was prepared by reaction of diphenylmercury with tellurium tetrachloride in refluxing benzene (1 : 1 mol ratio). The cooled solution was filtered and the benzene removed under vacuum. Recrystallisation of the crude product (85—90% yield) from ethanol afforded colourless crystals of $(C_6H_5)_2TeCl_2$ (m.p. 159—160 °C). These were stored in the dark to prevent discolouration and decomposition. Compound (2) was prepared by the reaction of phenylmagnesium bromide on tellurium powder (1 : 1 mol ratio) in refluxing tetrahydrofuran. The resultant solution was cooled and poured into cold saturated aqueous NH_4Cl. Red diphenyl ditelluride was extracted into chloroform. The chloroform solution, after drying, was treated with a slight excess of SO_2Cl_2 solution (25% in $CHCl_3$) at 5 °C. The crude precipitate of (2) (80% yield) was filtered off. The filtrate gradually deposited well formed crystals.

Crystallographic Study.—Crystal data are given in Table 1. Unit-cell constants were determined by least-squares fit to the positions of 15 reflections using the standard programmes of a Syntex $P2_1$ four-circle diffractometer. For both compounds, data were collected to $2\theta = 50°$ with variable scan rates of 3—29° min^{-1} (1) and 2—29° min^{-1} (2) depending on the intensity for a 2-s prescan; the total background time was half the scan time. The intensity of three standards was measured every 300 reflections. The check reflections for (2) showed a slight but systematic change in intensity during data collection, for which a correction was made. The check reflections for (1) decreased significantly during data collection at room temperature so data were re-determined at 173 K with a new crystal. At this temperature the check reflections showed no significant change during the data collection. Lorentz, polarization, and absorption corrections were applied (the last with the program ABSCOR [7]) and refinement carried out on the observed reflections ($I/\sigma I \geqslant 3.0$). The positions of one Te atom in (1) and two Te atoms in (2) were found from Patterson functions. For both, the remaining non-hydrogen atoms were located by difference-Fourier synthesis and isotropic least-squares refinements using the '*X*-Ray-76' [8] programs. Anisotropic least-squares refinement on all non-hydrogen atoms and difference-Fourier syntheses revealed the hydrogen atoms, which were refined isotropically. Empirical weighting schemes were used giving reduced weight to reflections with high and low *F* and sin θ values. Final *R* values were 0.036 and 0.018, for (1) and (2) respectively. Scattering factors were taken from ref. 9 in the analytical form, and all computing was done on a Burroughs B6700 computer. Table 2 contains atomic coordinates and Table 3 bond lengths and angles. Structure factors and temperature factors are listed in Supplementary Publication No. SUP 23189 (31 pp.).‡

TABLE 1

Crystal data

	Compound		
	(1)		(2)
Formula	$C_{12}H_{10}Cl_2Te$		$C_6H_5Cl_3Te$
M	352.7		311.1
System	orthorhombic		triclinic
Absences	0 *k l*	*k* ≠ 2*n*	none
	h 0 *l*	*l* ≠ 2*n*	
	h k 0	*h* ≠ 2*n*	
Space group	*Pbca*		$P\bar{1}$
Cell dimensions	at 173 K	at 290 K	at 290 K
a/Å	7.644(2)	7.696(2)	7.468(1)
b/Å	18.160(3)	18.091(4)	8.610(1)
c/Å	18.014(3)	18.196(4)	13.987(2)
α/°			98.89(1)
β/°			92.10(1)
γ/°			90.81(1)
U/Å^3	2 500(1)	2 533(1)	887.0(2)
Z	8		4
D_c/g cm^{-3}	1.85		2.33

DISCUSSION

Compound (1) adopts a primary four-co-ordinate geometry based on a trigonal bipyramid around Te, with

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† Part 6: N. W. Alcock and J. F. Sawyer, *J. Chem. Soc., Dalton Trans.*, 1980, 115.

‡ For details, see Notices to Authors, No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 2

Atomic co-ordinates (× 10^4) for compounds (1) and (2) [a]

Atom	X	Y	Z
(a) Ph_2TeCl_2 (1)			
Te	558.4(6)	1 536.9(3)	1 340.7(2)
Cl(1)	3 252(3)	2 061(1)	1 960(1)
Cl(2)	−1 930(3)	963(1)	672(1)
C(1)	1 938(10)	1 557(4)	334(4)
C(2)	1 238(10)	1 980(4)	−239(4)
C(3)	2 131(11)	2 011(5)	−904(4)
C(4)	3 673(11)	1 630(5)	−994(4)
C(5)	4 357(10)	1 210(5)	−414(4)
C(6)	3 495(10)	1 177(4)	255(4)
C(7)	1 304(9)	477(4)	1 710(4)
C(8)	1 305(10)	−133(4)	1 246(4)
C(9)	1 773(11)	−824(4)	1 510(4)
C(10)	2 238(11)	−901(5)	2 252(5)
C(11)	2 208(10)	−297(4)	2 711(4)
C(12)	1 739(10)	393(4)	2 454(4)
H(1)	8(215)	2 281(85)	−171(85)
H(2)	1 604(207)	2 397(90)	−1 254(86)
H(3)	4 613(222)	1 753(85)	−1 426(87)
H(4)	5 600(220)	865(87)	−503(86)
H(5)	4 040(215)	821(89)	758(89)
H(6)	1 113(217)	−64(89)	850(85)
H(7)	1 492(213)	−1 318(86)	1 305(86)
H(8)	2 587(225)	−1 453(82)	2 339(90)
H(9)	2 397(229)	−347(87)	3 274(83)
H(10)	1 701(221)	714(85)	2 786(85)
(b) $PhTeCl_3$ (2) [b]			
Te(1)	1 397.0(3)	387.8(3)	1 774.8(2)
Te(2)	6 429.7(3)	3 005.7(3)	1 759.3(2)
Cl(1)	4 014.6(14)	1 936.5(12)	2 980.8(7)
Cl(2)	−959.4(14)	2 073.1(12)	2 989.1(7)
Cl(3)	3 980.7(14)	3 777.8(13)	822.0(7)
Cl(4)	3 687.6(14)	−946.9(13)	856.6(7)
Cl(5)	8 642.2(15)	4 015.1(14)	836.6(7)
Cl(6)	−1 038.3(14)	−1 029.6(13)	866.6(7)
C(1)	1 435(5)	−1 248(4)	2 761(3)
C(2)	1 433(6)	−2 840(5)	2 380(3)
C(3)	1 423(6)	−3 925(5)	3 018(4)
C(4)	1 402(6)	−3 426(6)	4 000(4)
C(5)	1 437(6)	−1 849(6)	4 369(3)
C(6)	1 449(5)	−731(5)	3 751(3)
C(7)	6 422(5)	5 142(4)	2 750(3)
C(8)	6 477(5)	5 109(5)	3 735(3)
C(9)	6 450(6)	6 525(5)	4 361(3)
C(10)	6 362(6)	7 926(5)	3 993(4)
C(11)	6 330(7)	7 932(5)	3 011(4)
C(12)	6 362(6)	6 536(4)	2 370(3)
H(2)	1 437(74)	−3 129(63)	1 689(40)
H(3)	1 502(92)	−5 097(78)	2 698(49)
H(4)	1 427(115)	−4 411(97)	4 314(62)
H(5)	1 290(67)	−1 604(57)	5 041(36)
H(6)	1 481(73)	527(62)	4 016(39)
H(8)	6 491(66)	4 097(56)	3 980(36)
H(9)	6 390(72)	6 506(61)	5 043(39)
H(10)	6 361(82)	8 863(70)	4 478(44)
H(11)	6 292(79)	8 976(66)	2 717(42)
H(12)	6 310(43)	6 452(37)	1 573(23)

[a] Estimated standard deviations are in parentheses in Tables 2—4. [b] Compound (2) is numbered as a dimer.

TABLE 3

Interatomic bond lengths (Å) and angles (°) for compounds (1) and (2)

(1)		(2)	
Te–Cl(1)	2.529(3)	Te(1)–Cl(1)	2.726(1)
Te–Cl(2)	2.482(2)	Te(1)–Cl(2)	2.760(1)
Te · · · Cl(1′)	3.677(2)	Te(1)–Cl(4)	2.378(1)
		Te(1)–Cl(6)	2.387(1)
		Te(2)–Cl(1)	2.772(1)
		Te(2)–Cl(2′)	2.762(1)
		Te(2)–Cl(3)	2.373(1)
		Te(2)–Cl(5)	2.369(1)
		Te(1) · · · Cl(3)	3.905(1)
		Te(1) · · · Cl(5′)	4.118(1)
		Te(1) · · · Cl(6′)	3.820(1)
		Te(2) · · · Cl(4)	3.957(1)
		Te(2) · · · Cl(6″)	4.028(1)
		Te(2) · · · Cl(4′)	3.809(1)
Te–C(1)	2.111(7)	Te(1)–C(1)	2.118(4)
Te–C(2)	2.102(7)	Te(2)–C(7)	2.125(3)
Cl(1)–Te–Cl(2)	175.54(7)	Cl(1)–Te(1)–Cl(2)	85.33(3)
Cl(1)–Te–C(1)	88.41(20)	Cl(1)–Te(1)–Cl(4)	88.28(3)
Cl(1)–Te–C(7)	88.63(20)	Cl(1)–Te(1)–Cl(6)	174.03(4)
Cl(2)–Te–C(1)	88.06(20)	Cl(1)–Te(1)–C(1)	84.79(4)
Cl(2)–Te–C(7)	89.21(20)	Cl(2)–Te(1)–Cl(4)	173.56(3)
C(1)–Te–C(7)	99.01(29)	Cl(2)–Te(1)–Cl(6)	90.74(3)
Cl(1′) · · · Te–Cl(1)	85.47(6)	Cl(2)–Te(1)–C(1)	86.45(10)
Cl(1′) · · · Te–C(7)	95.47(20)	Cl(4)–Te(1)–Cl(6)	95.56(4)
Cl(1′) · · · Te–Cl(2)	98.63(6)	Cl(4)–Te(1)–C(1)	92.17(10)
Cl(1′) · · · Te–C(1)	164.13(21)	Cl(6)–Te(1)–C(1)	90.48(10
		Cl(1)–Te(2)–Cl(3)	98.06(4)
		Cl(1)–Te(2)–Cl(5)	175.05(3)
		Cl(1)–Te(2)–C(7)	84.80(10)
		Cl(1)–Te(2)–Cl(2′)	85.40(3)
		Cl(3)–Te(2)–Cl(5)	94.54(4)
		Cl(3)–Te(2)–C(7)	92.41(10)
		Cl(3)–Te(2)–Cl(2′)	174.30(11)
		Cl(5)–Te(2)–C(7)	91.64(11)
		Cl(5)–Te(2)–Cl(2′)	90.92(4)
		C(7)–Te(2)–Cl(2′)	85.81(10)
		Te(1)–Cl(1)–Te(2)	104.83(3)
		Te(2)–Cl(2′)–Te(1)	104.58(3)
C(2)–C(1)–Te	117.5(5)	C(2)–C(1)–Te(1)	117.7(3)
C(6)–C(1)–Te	120.8(5)	C(6)–C(1)–Te(1)	120.4(3)
C(8)–C(7)–Te	121.8(5)	C(8)–C(7)–Te(2)	120.0(3)
C(12)–C(7)–Te	118.1(5)	C(2)–C(7)–Te(2)	117.7(3)

	(1)	(2)
C(1)–C(2)	1.396(10)	1.392(5)
C(2)–C(3)	1.399(11)	1.388(7)
C(3)–C(4)	1.374(12)	1.375(7)
C(4)–C(5)	1.399(11)	1.376(7)
C(5)–C(6)	1.386(11)	1.389(7)
C(6)–C(1)	1.386(11)	1.387(5)
C(7)–C(8)	1.386(11)	1.382(5)
C(8)–C(9)	1.381(11)	1.388(6)
C(9)–C(10)	1.400(11)	1.385(7)
C(10)–C(11)	1.371(11)	1.374(8)
C(11)–C(12)	1.376(11)	1.385(6)
C(12)–C(7)	1.399(10)	1.386(6)
C(1)–C(2)–C(3)	118.8(7)	118.3(4)
C(2)–C(3)–C(4)	120.3(7)	120.4(4)
C(3)–C(4)–C(5)	120.1(7)	120.8(5)
C(4)–C(5)–C(6)	120.5(7)	120.4(4)
C(5)–C(6)–C(1)	118.7(7)	118.4(4)
C(6)–C(1)–C(2)	126(7)	121.8(4)
C(7)–C(8)–C(9)	120.3(7)	118.5(4)
C(8)–C(9)–C(10)	119.3(7)	119.9(4)
C(9)–C(10)–C(11)	120.1(8)	120.6(4)
C(10)–C(11)–C(12)	121.1(7)	120.7(4)
C(11)–C(12)–C(7)	119.1(7)	118.1(4)
C(12)–C(7)–C(8)	120.1(7)	122.3(3)

an equatorial lone pair. The Cl atoms occupy the axial positions with a Cl–Te–Cl angle of 175.5°. The angle between the equatorial phenyl groups (99.0°) is less than the normal 120°, presumably due to the repulsion of the aromatic groups by the equatorial lone pair, as predicted by valence shell electron-pair repulsion (VSEPR) theory.

The Te–Cl distances of 2.53 and 2.48 Å are close to those observed for Me_2TeCl_2 [3] (2.54 and 2.48 Å) and $(C_{12}H_8O)TeCl_2$ [4] (2.47—2.58 Å), but longer than those of $TeCl_4$ (mean 2.31 Å).[10] The Te–C distances are similar to values reported for other R_2TeX_2 compounds. The halogen atoms are both bent slightly towards the phenyl rings, as a result of lone-pair–bond-pair repulsions predicted by VSEPR, and as found in most R_2TeX_2 systems (except Ph_2TeBr_2,[2] where the Br atoms are bent away from the phenyl rings). Relevant bond lengths and angles for five R_2TeX_2 compounds are presented in Table 4.

TABLE 4

Bond lengths (Å) and bond angles (°) in some R_2TeX_2 compounds [a]

	$(C_6H_5)_2TeCl_2$	$(C_6H_5)_2TeF_2$ [1]	$(C_6H_5)_2TeBr_2$ [2]	$(CH_3)_2TeCl_2$ [3]	$(C_{12}H_8O)TeCl_2$ [4]
Te–C	2.111(7), 2.102(7)	2.115(3)	2.18(3) 2.14 [b]	2.10 2.08	2.087(3), 2.103(3)
Te–X	2.529(2), 2.482(2)	2.006(2)	2.682(3)	2.541(10), 2.480(10)	2.576(3), 2.478(3), 2.501(3), 2.563(3)
Te · · · X	3.677(2)	3.208(2)	3.93	3.46, 3.52	3.368(4)—3.504(4)
C–Te–C	99.0(3)	96.9(1)	94.4(12), 96.3 [b]	98.2(11)	90.7(3)
X–Te–X	175.5(1)	173.1(1)	177.9(2)	172.3(3)	176.8(1)
C–Te–X	88.1—88.6(2)	87.6(1)	90.7(6)	86.4—88.0(8)	86.0(3), 88.5(3), 90.8(3), 91.2(3)
Difference (Te · · · X) — (Te–X)	1.148	1.202	1.25	0.92, 1.04	*ca.* 0.92

[a] Some standard deviations not quoted in original sources. [b] Calculation based on centroid of phenyl ring.

Secondary interactions in different R_2TeX_2 compounds give rise to differing overall structures. In the case of phenoxatellurin-10,10-dichloride[4] four molecules are held together to form discrete tetrameric units, whereas all the other compounds are loosely packed in sheets or chains. The relative strengths of the secondary bonds in the different compounds are difficult to ascertain but they are probably of least significance in Ph_2TeF_2.[1] In (1) there is just one secondary interaction, Te · · · Cl(1′) 3.677(2) Å, approximately *trans* to C(1) [Cl(1′) · · · Te–C(1) = 164.1(2)°], giving a distorted octahedral arrangement about Te, with the sixth position vacant (Figure 1). The crystal packing of (1), including secondary bonds, is shown in Figure 2.

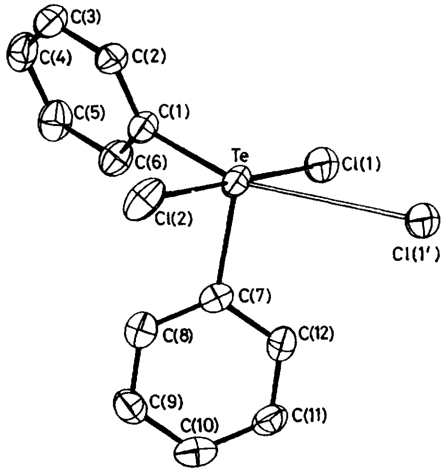

FIGURE 1 Structure of Ph_2TeCl_2 showing the atom numbering

These secondary bonds link the molecules into chains parallel to *a*, which are seen ' sideways-on ' in Figure 2(*a*), and ' end-on ' in Figure 2(*b*). Benzene ring–benzene ring interactions holding the chains together are also apparent in the structures. The molecular structure of phenyltellurium trichloride (2) contains two independent distorted square-based pyramidal $CTeCl_4$ units in the asymmetric unit (Figure 3). Chlorine atoms form bridges between the units in a *cis* basal fashion giving infinite chains, $(PhTeCl_3)_n$. The relevant bond lengths and angles are given in Table 3. Two structures are closely similar to this: $(p\text{-}EtOC_6H_4)TeCl_3$ [5] and $(ClCH_2CH_2)TeCl_3$,[6] both of which are polymeric with Cl bridges as in (2). Table 5 summarises the data for the three compounds. The polymeric structures of the trichlorides contrast with those adopted by a variety of tri-iodides and tribromides, all of which, whilst exhibiting the square-based pyramidal geometry, are dimeric with basal edge-sharing of two halogens. This contrast is presumably due to the smaller size of Cl, making a double bridge less favourable than for Br or I.

The marked contrast in the structures adopted by R_2TeCl_2 and $RTeCl_3$ must result from the replacement of a C atom with a much more electronegative Cl atom, leading to greater polarity in the Te–Cl bond. The two short Te–Cl bonds and the third longer one suggest a tendency for the compound to exist as $PhTeCl_2^+Cl^-$. This goes much further in solution, as shown by the conductivity of organotellurium trihalides in polar non-aqueous solvents.[11]

The possible secondary Te · · · Cl bonds in this compound raise the problem of defining the limits for these. The sum of the van der Waals radii for Te and Cl is 3.81 Å but interactions that are even longer than the van der Waals distance have occasionally been considered significant (*e.g.* in Et_2SnI_2 [12]). In (2), only the Te(2) · · · Cl(4′) contact of 3.809 Å is within this limit. However, five further interactions occur between 3.820 and 4.118 Å. They have no obvious geometrical rationale, except that they all occur on the vacant side of the Te co-ordination polyhedron (Figure 3).

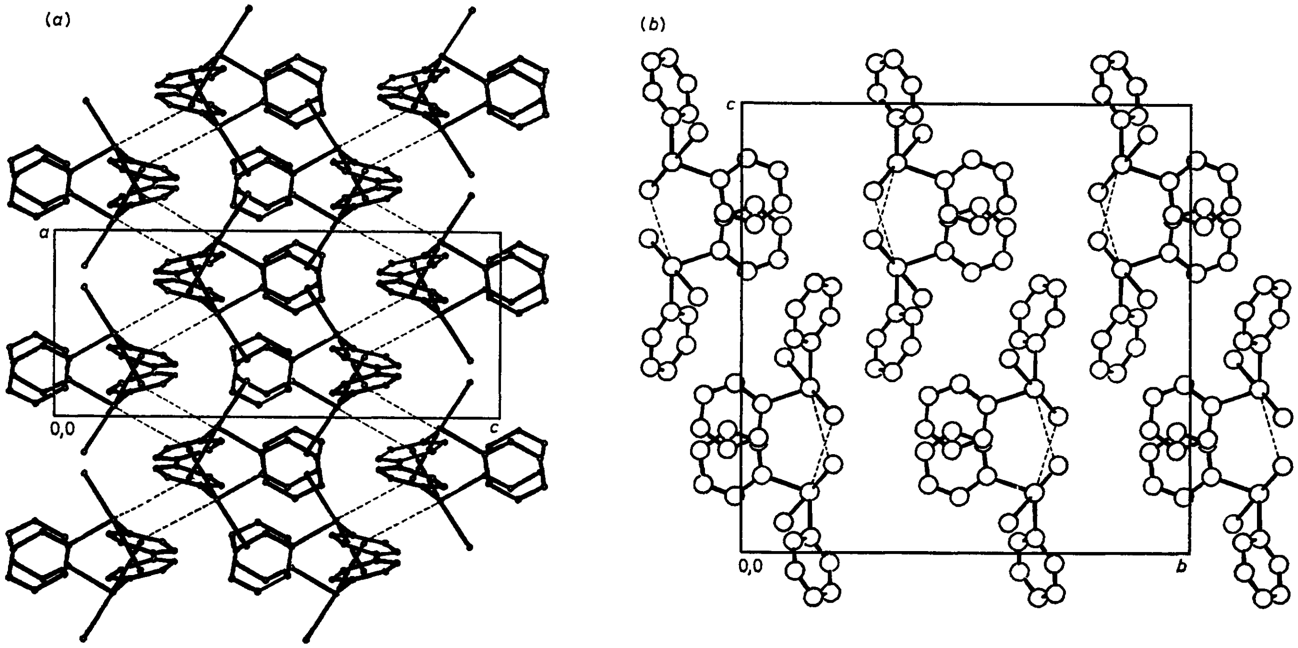

FIGURE 2 Packing diagrams for Ph_2TeCl_2, viewed (*a*) down *b*; (*b*) down *a*. Secondary bonds are shown as dashed lines

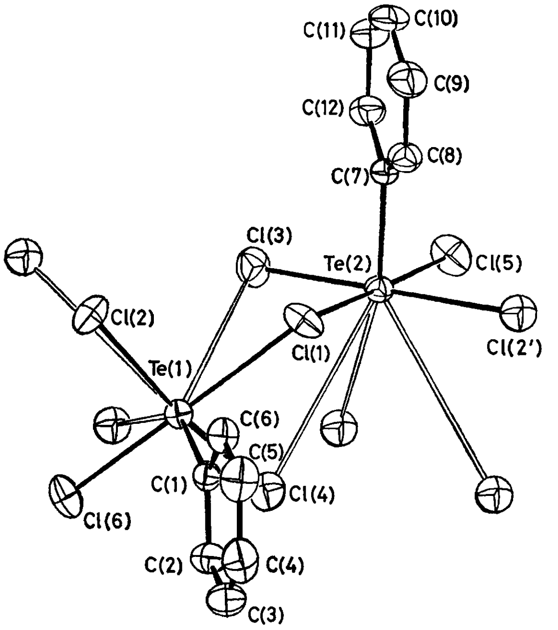

FIGURE 3 Structure of $PhTeCl_3$ showing the two independent molecules, the long Te···Cl contacts, and the atomic numbering. Cl(2') is related to Cl(2) by a unit translation along *x*

TABLE 5

Mean bond lengths (Å) and bond angles (°) in some $RTeCl_3$ compounds *

	$(C_6H_5)TeCl_3$	$(p\text{-}EtOC_6H_4)\text{-}TeCl_3$ [5]	$(ClCH_2CH_2)\text{-}TeCl_3$ [6]
Te–Cl (bridge)	2.755(1)	2.749(6)	2.717(3)
Te–Cl (terminal)	2.377(1)	2.396(6)	2.386(3)
Te–C	2.122(4)	2.12(3)	2.164(13)
C–Te–Cl (bridge)	85.46(10)	88.2	82.5
C–Te–Cl (terminal)	91.68(10)	91.0	92.7

* Some standard deviations not quoted in original sources.

The contrast with the single relatively strong secondary bond in (1) may perhaps be attributed to the difference between the five-electron-pair trigonal-bipyramidal geometry in (1) and the six electron pairs in (2), in which the vacant position of the octahedron is occupied by a lone pair, inhibiting formation of a short secondary bond. A similar situation is found in XeF_5^+ and IF_5 species [11] in which the vacant side of the octahedron is occupied by several interactions arranged around the lone-pair direction.

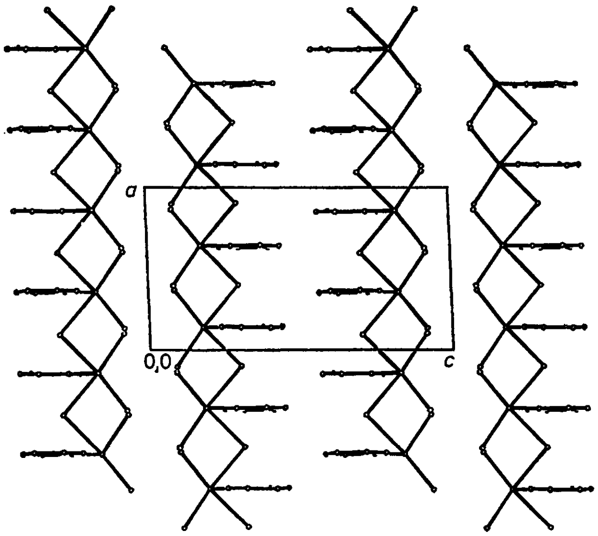

FIGURE 4 Packing diagram for $PhTeCl_3$, viewed down *b*

The overall packing of (2) is dominated by face-to-face benzene ring interactions (Figure 4). There are also Te–Te contacts of 4.369 and 4.358 Å, similar to that in

p-EtOC$_6$H$_4$TeCl$_3$ (4.265 Å),[5] which are slightly less than the sum of the van der Waals radii (4.40 Å). These contacts may account for the ease with which these trichlorides are reduced to ditellurides; this occurs on standing at room temperature in the solid state (shown by the gradual production of the characteristic red colour of the ditelluride).

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