

Structure of *catena-μ*-Bromo-dibromo(phenyl)tellurium (IV)*

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Abstract. [TeBr₃(C₆H₅)], *M_r* = 444.41, triclinic, *P*1̄, *a* = 7.592 (1), *b* = 8.739 (2), *c* = 14.370 (3) Å, α = 98.85 (1), β = 92.78 (1), γ = 90.57 (1)°, *U* = 940.8 (3) Å³ at 173 K, *Z* = 4, *D_M* = 3.10 (floatation), *D_C* = 3.14 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 156.87 cm⁻¹, *F*(000) = 792, *R* = 0.067 for 3578 observed reflexions (*I*/*aI* ≥ 3.0). The compound is isomorphous with the trichloride and forms chains of square-based pyramidal CTeBr₄ units linked by *cis* basal μ-bromo bridges. [Mean Te–Br (terminal) 2.526 (5), (bridge) 2.839 (5), Te–C 2.140 (8) Å.]

Introduction. We have previously reported the structure of *catena-μ*-chloro-dichloro(phenyl)tellurium(IV) (Alcock & Harrison, 1982*b*) and have now investigated the structure of the tribromide and triiodide (Alcock & Harrison, 1982*c*). Organotellurium trihalides adopt contrasting structures; some are trigonal bipyramidal monomers, e.g. (2-biphenyl)tribromotellurium (Knobler & McCullough, 1977), whilst others, including the title compound, adopt square-based pyramidal oligomeric structures linked by μ-bromo bridges. The factors affecting the adoption of the contrasting structural types and the role of secondary bonding are discussed.

Experimental. Yellow crystals of C₆H₅TeBr₃ were obtained by treating diphenyl ditelluride with bromine in hot chloroform solution followed by recrystallization from hot chloroform. Initially examination was at ambient temperature but the crystal showed marked deterioration during data collection. [At 271 K *a* = 7.593 (2), *b* = 8.755 (2), *c* = 14.376 (5) Å, α = 98.80 (3), β = 92.88 (3), γ = 90.56 (2)°, *U* = 943.0 (5) Å³.] A second crystal was mounted in a Lindemann tube and examined at 173 K on a Syntex *P*2₁ diffractometer using the LT-1 attachment. Reflexions in the range 2θ = 3–60° were measured using a θ–2θ scan over a scan range (*K*α₁ – 1.05) to (*K*α₂ + 1.05) and a variable scan speed of 2–29.3° min⁻¹ depending on the intensity of a 2 s prescan. Background counts were measured for one quarter of the scan time at each end of the scan. The intensities of

Table 1. Atomic coordinates (× 10⁴; for Te × 10⁵), with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ² × 10 ³)
Te(1)	14834 (11)	3894 (10)	18482 (6)	22
Te(2)	65103 (11)	30325 (10)	18420 (6)	21
Br(11)	4181 (4)	1901 (3)	3083 (2)	64
Br(12)	3812 (2)	–1008 (2)	878 (1)	43
Br(13)	–1123 (2)	–994 (2)	907 (1)	45
Br(21)	–819 (3)	2177 (3)	3094 (2)	63
Br(22)	3900 (3)	3792 (2)	854 (1)	42
Br(23)	8798 (2)	4049 (2)	864 (1)	45
C(11)	1517 (17)	–1262 (14)	2805 (9)	22
C(12)	1529 (23)	–2801 (15)	2435 (11)	32
C(13)	1511 (27)	–3890 (20)	3058 (14)	46
C(14)	1444 (24)	–3390 (22)	4021 (14)	49
C(15)	1485 (26)	–1834 (25)	4365 (12)	50
C(16)	1517 (21)	–727 (18)	3771 (10)	32
C(21)	6500 (18)	5166 (15)	2798 (9)	23
C(22)	6527 (21)	5138 (18)	3755 (10)	31
C(23)	6467 (26)	6507 (20)	4371 (12)	40
C(24)	6419 (27)	7903 (20)	4011 (14)	44
C(25)	6418 (25)	7907 (19)	3026 (15)	45
C(26)	6447 (21)	6532 (16)	2432 (11)	33

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Te(1)–Br(11)	2.821 (3)	C(11)–C(12)	1.368 (17)
Te(1)–Br(12)	2.513 (2)	C(12)–C(13)	1.404 (25)
Te(1)–Br(13)	2.529 (2)	C(13)–C(14)	1.389 (28)
Te(1)–Br(21)	2.864 (3)	C(14)–C(15)	1.374 (28)
Te(2)–Br(21)	2.827 (3)	C(15)–C(16)	1.385 (27)
Te(2)–Br(22)	2.525 (2)	C(16)–C(11)	1.396 (19)
Te(2)–Br(23)	2.536 (2)	C(21)–C(22)	1.378 (20)
Te(2)–Br(11)	2.845 (3)	C(22)–C(23)	1.377 (21)
Te(1)–C(11)	2.140 (13)	C(23)–C(24)	1.397 (27)
Te(2)–C(21)	2.139 (12)	C(24)–C(25)	1.415 (30)
		C(25)–C(26)	1.363 (22)
		C(26)–C(21)	1.377 (21)
Br(11)–Te(1)–Br(12)	88.9 (1)	Br(21)–Te(2)–Br(22)	90.8 (1)
Br(11)–Te(1)–Br(13)	173.5 (1)	Br(21)–Te(2)–Br(23)	174.1 (1)
Br(11)–Te(1)–Br(21)	84.1 (1)	Br(21)–Te(2)–Br(11)	84.1 (1)
Br(11)–Te(1)–C(11)	84.4 (3)	Br(21)–Te(2)–C(21)	85.0 (4)
Br(12)–Te(1)–Br(13)	96.1 (1)	Br(22)–Te(2)–Br(23)	94.7 (1)
Br(12)–Te(1)–Br(21)	172.9 (1)	Br(22)–Te(2)–Br(11)	174.7 (1)
Br(12)–Te(1)–C(11)	92.7 (3)	Br(22)–Te(2)–C(21)	92.3 (4)
Br(13)–Te(1)–Br(21)	91.0 (1)	Br(23)–Te(2)–Br(11)	90.3 (1)
Br(13)–Te(1)–C(11)	91.1 (3)	Br(23)–Te(2)–C(21)	92.8 (4)
Br(21)–Te(1)–C(11)	87.0 (3)	Br(11)–Te(2)–C(21)	85.6 (4)
Te(1)–C(11)–C(12)	118.1 (10)	Te(2)–C(21)–C(22)	119.5 (10)
Te(1)–C(11)–C(16)	118.9 (10)	Te(2)–C(21)–C(26)	118.6 (10)
Te(1)–Br(11)–Te(2)	103.3 (1)	Te(2)–Br(21)–Te(1)	102.7 (1)
C(16)–C(11)–C(12)	123 (1)	C(26)–C(21)–C(22)	122 (1)
C(11)–C(12)–C(13)	118 (1)	C(21)–C(22)–C(23)	120 (1)
C(12)–C(13)–C(14)	120 (2)	C(22)–C(23)–C(24)	119 (2)
C(13)–C(14)–C(15)	120 (2)	C(23)–C(24)–C(25)	120 (2)
C(14)–C(15)–C(16)	122 (2)	C(24)–C(25)–C(26)	119 (2)
C(15)–C(16)–C(11)	117 (2)	C(25)–C(26)–C(21)	120 (2)

* Secondary Bonding. 11. Part 10: Alcock & Harrison (1982*a*).

three standard reflexions were measured every 300 reflexions and showed some random variability which could not be corrected. Of the 5586 reflexions collected 3578 were deemed observed ($I/\sigma I \geq 3.0$). An absorption correction was made using the program *ABSCOR* (Alcock, 1970). The trial structural solution was obtained by comparison with that of the isomorphous trichloride. Successive anisotropic thermal and positional least-squares refinements failed to reveal the positions of the hydrogen atoms which were input in calculated positions with fixed temperature factors. All calculations were carried out using the XRAY76 suite of programs (Stewart, 1976) on a Burroughs 6700 computer. Final atomic coordinates and bond lengths and angles with e.s.d.'s are listed in Tables 1 and 2,

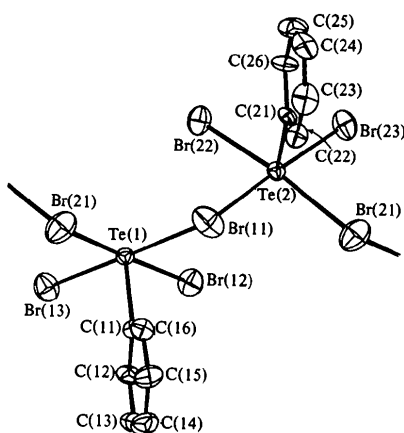


Fig. 1. Molecular structure and atom numbering.

Table 3. Summary of structural types adopted by organotellurium trihalides

Trigonal bipyramidal CTeX_3 units	Square-based pyramidal $(\text{CTeX}_4)_n$	
	$n = 2$	$n = \infty$
$\text{C}_{12}\text{H}_9\text{TeBr}_3^a$	$\text{EtOC}_6\text{H}_4\text{TeBr}_3^c$	$\text{EtOC}_6\text{H}_4\text{TeCl}_3^c$
$\text{C}_{12}\text{H}_9\text{TeI}_3^b$	$\text{MeOC}_6\text{H}_4\text{TeI}_3^c$	$\text{C}_6\text{H}_5\text{TeCl}_3^e$
	$\text{C}_6\text{H}_{10}\text{Te}_2\text{Br}_6^d$	$\text{C}_6\text{H}_5\text{TeBr}_3^f$
		$\text{ClC}_2\text{H}_4\text{TeCl}_3^g$

References: (a) Knobler & McCullough (1977); (b) McCullough & Knobler (1976); (c) Bird, Kumar & Pant (1980); (d) Hazell (1972); (e) Alcock & Harrison (1982b); (f) this work; (g) Kobelt & Paulus (1971).

respectively.* Fig. 1 illustrates the molecular structure and atom labelling scheme.

Discussion. *catena- μ -Bromo-dibromo(phenyl)tellurium(IV)* is isomorphous with the trichloride (Alcock & Harrison, 1982b) and the asymmetric unit contains two molecules of $\text{C}_6\text{H}_5\text{TeBr}_3$. The two molecules are linked by a μ -bridging bromine atom Br(11) and further linked to adjacent units by Br(21) to give infinite chains of molecules parallel to *a*.

The overall geometry at each Te atom is square-based pyramidal with an apical carbon atom and four bromine atoms in the basal plane. The bridging is in a *cis* basal fashion. The Te—C bonds are typical [mean 2.140 (8) Å]. At each Te atom the two terminal Te—Br bonds are short [mean 2.526 (5) Å] and Te— μ -Br bonds are longer [mean 2.839 (5) Å]. Secondary bonding is unimportant; there are no other Te—Br interactions significantly less than the sum of the van der Waals radii (3.91 Å). Some interactions (4.00–4.15 Å) cluster around the lone pair in the vacant octahedral site but as with the trichloride these are too long to be of major significance. The main non-bonded interactions are van der Waals interactions between benzene rings of adjacent parallel chains of molecules.

Three other organotellurium tribromide structures are known, di- μ -bromo-tetrabromo- μ -(1,2-cyclohexylene)-ditellurium(IV) [$\text{CHTeBr}_3\text{CHTeBr}_3(\text{CH}_2)_4$] (Hazell, 1972), (2-biphenyl)tribromotellurium (Knobler & McCullough, 1977) and tribromo(4-ethoxyphenyl)tellurium(IV) (Bird, Kumar & Pant, 1980). The structures of these and related compounds are summarized in Table 3, and relevant bond length data are compared in Table 4.

Simple VSEPR theory for a TeBr_3C system predicts a molecular shape based on a trigonal bipyramid with an equatorial lone pair. However, of the four compounds, only the biphenyl compound adopts this structure [with two longer axial Te—Br bonds and with a shorter Te—Br bond and a Te—C bond in the equatorial plane; $\text{Br}_{\text{ax}}\text{—Te—Br}_{\text{ax}}$ 178.46 (4) and

* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36909 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Selected bond lengths (Å) for organotellurium tribromides with e.s.d.'s in parentheses

	$\text{C}_6\text{H}_5\text{TeBr}_3$	$\text{CHTeBr}_3\text{CHTeBr}_3(\text{CH}_2)_4$	$\text{C}_{12}\text{H}_9\text{TeBr}_3$	$\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{TeBr}_3$
Te—Br _{terminal} (mean)	2.526 (2)	2.542 (9)	2.490 (1) Br _{eq} 2.661 (1) Br _{ax}	2.531 (3)
Te— μ -Br (mean)	2.839 (3)	2.880 (9)	—	2.932 (3)
Te—C (mean)	2.140 (8)	2.223 (50)	2.136 (8)	2.10 (2)
Te...Br	—	—	3.713 (1)	—

Br_{eq}—Te—C_{eq} 97.1 (3)°]. The molecules are held together by a single intermolecular secondary bond [3.713 (1) Å] between the Te atoms and the axial bromine atoms of adjacent pairs of molecules to give loose dimers.

The remaining tribromides all attain square-based pyramidal geometry at the tellurium atom by means of bridging bromine atoms. The geometries of the CTeBr₄ units are closely comparable in the three compounds but whereas the title compound adopts a polymeric chain structure, the presence of an ethoxy substituent on the phenyl ring in tribromo(4-ethoxyphenyl)-tellurium apparently leads to a dimeric structure (although the corresponding trichloride is polymeric). This structure is also adopted by the cyclohexene compound. None of these square-based pyramidal structures show significant secondary bonding because the 'vacant' coordination site at the tellurium atom is occupied by the lone pair. In the biphenyl compound a secondary Te...Br bond can be formed as a vacant site remains in the tellurium coordination sphere. In this case the bulky biphenyl group {with the second phenyl ring, not directly attached to the Te atom, making a close approach to the Te atom [Te...C = 2.945 (9) Å]} would appear to prevent a fourth bromine atom fully entering the tellurium coordination sphere, but it allows very asymmetric bridging by a bromine atom, with one primary Te—Br bond [2.675 (1) Å] and one secondary Te...Br bond [3.713 (1) Å]. The other examples all have almost symmetrical μ -bromo bridges with a mean Te— μ -Br = 2.90 Å.

On the evidence so far gathered (Table 3), the preferred structure for RTeBr₃ compounds appears to be that with bridging halogen atoms giving rise to square-based pyramidal geometry with oligomeric or dimeric structures. However, when a bulky organic group is present the trigonal bipyramidal geometry predicted by simple VSEPR is adopted.

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trans-Dichlorobis(triphenylphosphine)palladium(II)

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Abstract. C₃₆H₃₀Cl₂P₂Pd, *M_r* = 701.19, triclinic, *P*1̄, *a* = 9.690 (2), *b* = 10.325 (2), *c* = 9.194 (1) Å, α = 91.38 (1), β = 111.94 (1), γ = 72.51 (1)°, *V* = 809.71 Å³, *Z* = 1, *D_c* = 1.44 g cm⁻³, *F*(000) = 356, Mo *K* α radiation, λ = 0.71069 Å, μ (Mo *K* α) = 8.5 cm⁻¹. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to a final *R* of 0.024 for 4343 independent observed reflections [*I* > 3 σ (*I*)]. The crystal structure contains centrosymmetric, square-planar PdCl₂(PPh₃)₂ molecules with Pd—Cl 2.290 (1), Pd—P 2.337 (1) Å, and Cl—Pd—P 92.0 (1)°.

Introduction. In the course of studies of solvates of *trans*-Pd(Cl)(CH₂CN)(PPh₃)₂ (Ferguson, McAlees, McCrindle, Parvez & Roberts, 1982) we were surprised on interrogating the Cambridge Crystallographic Database to find no structure determination for *trans*-PdCl₂(PPh₃)₂ (1). As we had available a plentiful supply of crystals of (1) grown from acetonitrile, we undertook its X-ray analysis to determine precise values for the Pd—P and Pd—Cl bond lengths.

A crystal 0.50 × 0.35 × 0.25 mm was used for data collection with an Enraf-Nonius CAD-4 diffractometer. Following preliminary photographic studies, ac-