Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(triphenyltelluronium) hexachlorotellurate

Sari M. Närhi,[a] Raija Oilunkaniemi,[a]* Risto S. Laitinen[a] and Markku Ahlgrén[b]

[a]Department of Chemistry, PO Box 3000, FIN-90014 University of Oulu, Finland, and [b]Department of Chemistry, University of Joensuu, PO Box 111, FIN-80101 Joensuu, Finland

Correspondence e-mail:
raija.oilunkaniemi@oulu.fi

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.007 Å
R factor = 0.032
wR factor = 0.083
Data-to-parameter ratio = 17.3

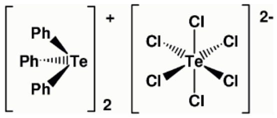
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 26 March 2004
Accepted 2 April 2004
Online 17 April 2004

The title compound, $(Ph_3Te)_2[TeCl_6]$ or $2C_{18}H_{15}Te^+\cdot TeCl_6^{2-}$, was obtained as yellow hexagonal crystals from the reaction of Ph_3TeCl with $[(Ph_3PO)_2H]_2[Te_2Cl_{10}]$. The structure consists of discrete octahedral $[TeCl_6]^{2-}$ anions, with site symmetry $\overline{3}$, and trigonal pyramidal $(Ph_3Te)^+$ cations, with site symmetry 3. The weak Te$\cdots$Cl secondary bonds of 3.527 (1) Å between the cation and anion expand the $TePh_3E$ coordination of the telluronium tellurium into a distorted $TePh_3Cl_3E$ trigonal prism (E = electron lone pair).

Comment

The structural features of organotelluronium salts R_3TeX are governed by weak secondary tellurium-anion interactions that expand the TeX_3E (X = bonding pair and E = lone pair) trigonal pyramidal geometry around tellurium into a five- or six-coordinate entity. Due to these various secondary interactions between the Te atom and the anions, the coordination chemistry of tellurium(IV) is far more complicated than would be predicted by the stoichiometry of these salts (Lee *et al.*, 1977; Ziolo & Extine, 1980; Collins *et al.*, 1988; Silvestru *et al.*, 1995, and references therein; Oilunkaniemi *et al.*, 2001, and references therein; Klapötke *et al.*, 2002).



(I)

In this contribution, we report the crystal structure of $(Ph_3Te)_2[TeCl_6]$, (I), formed by the reaction of Ph_3TeCl with

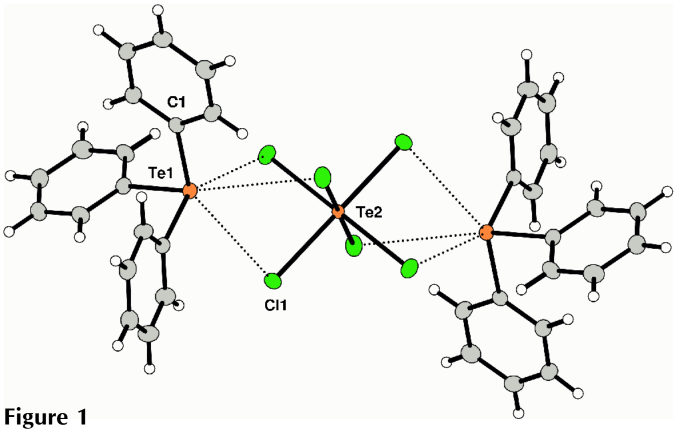


Figure 1
The molecular structure of $(Ph_3Te)_2[TeCl_6]$, showing the numbering of the unique atoms. Displacement ellipsoids are drawn at the 50% probability level.

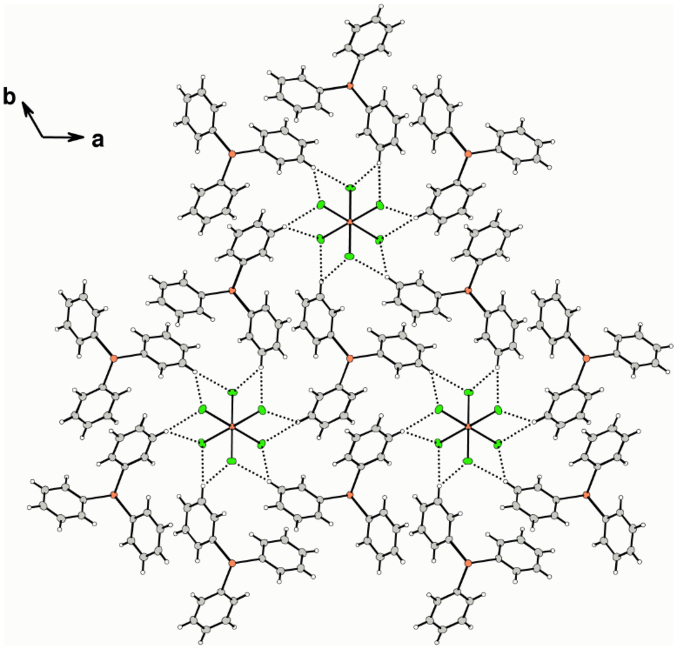


Figure 2
The hydrogen-bond network in $(Ph_3Te)_2[TeCl_6]$. The cations lie on threefold rotation axes and the anions have crystallographic site symmetry $\overline{3}$.

$[(Ph_3PO)_2H]_2[Te_2Cl_{10}]$. The molecular structure is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1.

The cations lie on threefold rotation axes and the anions have crystallographic site symmetry $\overline{3}$. The Te—C bond length in the Ph_3Te^+ cation is 2.120 (4) Å. This value compares well with those in related telluronium salts, as exemplified by the mean Te—C bond length of 2.130 (4) Å in Ph_3TeCl (Ziolo & Extine, 1980). The Te—C bonds expectedly depict a trigonal pyramidal coordination polyhedron with C—Te—C bond angles of 97.72 (13)°. This angle is comparable with the corresponding angles in other Ph_3Te^+ cations (Lee *et al.*, 1977; Ziolo & Extine, 1980; Silvestru *et al.*, 1995; Oilunkaniemi *et al.*, 2001; Klapötke *et al.*, 2002).

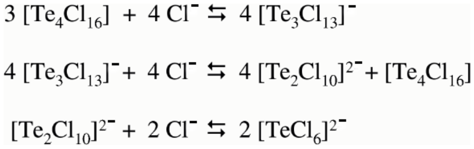
The $[TeCl_6]^{2-}$ anion shows an almost ideal octahedral coordination despite being a 14-electron TeX_6E species. It has been suggested that with electronegative monoatomic ligands the stereochemistry is dominated by interligand repulsions and that the lone electron pair of tellurium resides in the stereochemically inactive 6*s* orbital [for more detailed discussion, see Brown (1964)]. The Te—Cl bond shows a length of 2.545 (1) Å and the Cl—Te—Cl bond angles are 91.01 (3)° and 88.99 (3)°. These values are in good agreement with those reported for a large number of species containing the $[TeCl_6]^{2-}$ anion (Krebs & Ahlers, 1990, and references therein).

The crystal structure contains discrete $(Ph_3Te)_2[TeCl_6]$ units, in which the cations and anions are linked by secondary Te···Cl interactions, as shown in Fig. 1. The three chloro ligands at the corners of a trigonal face of the octahedral $[TeCl_6]^{2-}$ anion exhibit short Te···Cl contacts of 3.527 (1) Å with one Ph_3Te^+ cation. Another Ph_3Te^+ is linked in a similar fashion on the opposite trigonal face. These interactions expand the coordination number of the telluronium tellurium to six. The coordination polyhedron of the tellurium atom in Ph_3Te^+ can therefore be considered a distorted trigonal prism TeX_3Y_3E (*Y* is a secondary bonding pair). This arrangement is very common for these compounds (Collins *et al.*, 1988). There are also three H···Cl close contacts of 2.81–3.00 Å. The two shortest contacts are involved in weak bifurcated hydrogen bonds, as shown in Fig. 2.

The packing is expectedly dependent on the size and geometry of the anion. The cation-anion interactions are similar in $(Ph_3Te)_2[MCl_6]$ (*M* = Pt, Ir), the anion of which also shows a regular octahedron, but differ from those in $(Ph_3Te)_2[AuCl_4]$ (Oilunkaniemi et al., 2001).

The ^{125}Te NMR spectrum of $(Ph_3Te)_2[TeCl_6]$ was recorded from a solution in acetonitrile and shows two resonances at 757 and 1469 p.p.m. These resonances are due to the Te atoms in Ph_3Te^+ and $[TeCl_6]^{2-}$ ions, respectively. The former chemical shift is close to values recorded earlier for the Ph_3Te^+ ion [754 p.p.m. in nitric acid; 788 p.p.m. in ethanol (Oilunkaniemi *et al.*, 2001)]. The chemical shift of the $[TeCl_6]^{2-}$ ion can be compared to those of $[(Me_2SO)_2H][TeCl_6]$ in tetrahydrofuran (1548 p.p.m.) (Pietikäinen *et al.*, 2002) and $(Et_2NH_2)_2[TeCl_6]$ in DMSO (1531.7 p.p.m.) (Chadha & Miller, 1982).

The formation of the $[TeCl_6]^{2-}$ anion in the reaction of Ph_3TeCl with $[(Ph_3PO)_2H]_2[Te_2Cl_{10}]$ is consistent with the equilibria proposed by Hasche *et al.* (1997) (see scheme below).



$$3\,[Te_4Cl_{16}] + 4\,Cl^- \leftrightarrows 4\,[Te_3Cl_{13}]^-$$

$$4\,[Te_3Cl_{13}]^- + 4\,Cl^- \leftrightarrows 4\,[Te_2Cl_{10}]^{2-} + [Te_4Cl_{16}]$$

$$[Te_2Cl_{10}]^{2-} + 2\,Cl^- \leftrightarrows 2\,[TeCl_6]^{2-}$$

Experimental

$(Ph_3Te)_2[TeCl_6]$ was obtained upon dissolving 236 mg (0.14 mmol) $[(Ph_3PO)_2H]_2[Te_2Cl_{10}]$ (Oilunkaniemi *et al.*, 2002) and 110 mg (0.28 mmol) Ph_3TeCl (Gunther *et al.*, 1974) in dichloromethane and combining the two solutions. The salt started to precipitate almost immediately (yield: 78%, 115 mg) Analysis calculated for $C_{36}H_{30}Cl_6Te_3$: C 40.86, H 2.86%, found: C 41.87, H 2.71%. The ^{125}Te NMR spectrum was recorded from isolated $(Ph_3Te)_2[TeCl_6]$ that was dissolved in acetonitrile. The spectrum was recorded on a Bruker DPX400 spectrometer operating at 126.24 MHz. A saturated solution of H_6TeO_6(aq) was used as an external reference. Chemical shifts are reported relative to neat Me_2Te. [$\delta(Me_2Te) = \delta(H_6TeO_6) + 712$ p.p.m.]. The spectrum was recorded unlocked.

Crystal data

$2C_{18}H_{15}Te^+\cdot Cl_6Te^{2-}$
$M_r = 1058.10$
Trigonal, $R\overline{3}$
$a = 14.217$ (2) Å
$c = 15.852$ (3) Å
$V = 2774.8$ (8) Å^3
$Z = 3$
$D_x = 1.900$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1137 reflections
$\theta = 3.1$–26.0°
$\mu = 2.81$ mm^{-1}
$T = 150$ (2) K
Block, yellow
0.25 × 0.20 × 0.18 mm

Acta Cryst. (2004). E**60**, o798–o800 Sari M. Närhi *et al.* • $2C_{18}H_{15}Te^+\cdot Cl_6Te^{2-}$ **o799**

Data collection

Bruker–Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2001)
$T_{\min} = 0.513$, $T_{\max} = 0.600$
14235 measured reflections
1210 independent reflections
1137 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.068$
$\theta_{\max} = 26.0°$
$h = -17 \rightarrow 17$
$k = -17 \rightarrow 17$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.083$
$S = 1.10$
1210 reflections
70 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 22.1387P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.85$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00072 (16)

Table 1
Selected geometric parameters (Å, °).

Te1—C1$^{\rm i}$	2.120 (4)	Te2—Cl1$^{\rm i}$	2.5451 (10)
C1$^{\rm i}$—Te1—C1	97.72 (13)	Cl1$^{\rm ii}$—Te2—Cl1$^{\rm iii}$	88.99 (3)
Cl1$^{\rm i}$—Te2—Cl1$^{\rm ii}$	91.01 (3)	Cl1$^{\rm ii}$—Te2—Cl1$^{\rm iv}$	180

Symmetry codes: (i) $-x+y, 1-x, z$; (ii) $y-\frac{1}{3}, \frac{1}{3}-x+y, \frac{4}{3}-z$; (iii) $\frac{2}{3}-x, \frac{4}{3}-y, \frac{4}{3}-z$; (iv) $1-y, 1+x-y, z$.

The H atoms were placed in calculated positions (C—H = 0.95 Å) and refined in the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The largest peak in the final difference Fourier map is 1.72 Å from atom Te1.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Financial support from the Academy of Finland and the Ministry of Education in Finland (Graduate School of Inorganic Materials Chemistry) is gratefully acknowledged.

References

Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Brown, I. D. (1964). *Can. J. Chem.* **42**, 2758–2767.

Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Chadha, R. K. & Miller, J. M. (1982). *Can. J. Chem.* **60**, 2256–2258.

Collins, M. J., Ripmeester, J. A. & Sawyer, J. F. (1988). *J. Am. Chem. Soc.* **110**, 8583–8590.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gunther, W. H. H., Nepywoda, J. & Chu, J. Y. C. (1974). *J. Organomet. Chem.* **74**, 79–84.

Hasche, S., Reich, O., Beckmann, I. & Krebs, B. (1997). *Z. Anorg. Allg. Chem.* **623**, 724–734.

Klapötke, T. M., Krumm, B., Mayer, P., Piotrowski, H., Schwab, H. & Vogt, M. (2002). *Eur. J. Inorg. Chem.* pp. 2701–2709.

Krebs, B. K & Ahlers, F.-P. (1990). *Adv. Inorg. Chem.* **35**, 235–317.

Lee, J.-S., Titus, D. D. & Ziolo, R. F. (1977). *Inorg. Chem.* **16**, 2487–2492.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Oilunkaniemi, R., Kunnari, S. M., Laitinen, R. S. & Ahlgrén, M. (2002). *XXXVth International Conference on Coordination Chemistry*. Book of Abstracts, p. 627. Heidelberg, Germany.

Oilunkaniemi, R., Pietikäinen, J., Laitinen, R. S. & Ahlgrén, M. (2001). *J. Organomet. Chem.* **640**, 50–56.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pietikäinen, J., Maaninen, A., Laitinen, R. S., Oilunkaniemi, R. & Valkonen, J. (2002). *Polyhedron*, **21**, 1089–1095.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Silvestru, A., Haiduc, I., Toscano, R. A. & Breunig, H. J. (1995). *Polyhedron*, **14**, 2047–2053.

Ziolo, R. F. & Extine, M. (1980). *Inorg. Chem.* **19**, 2964–2967.

o800 Sari M. Närhi *et al.* • $2C_{18}H_{15}Te^{+}\cdot Cl_6Te^{2-}$ *Acta Cryst.* (2004). E**60**, o798–o800