Journal of Organometallic Chemistry, 260 (1984) 73–80
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND CHARACTERISATION OF TRIETHYLTELLURONIUM SALTS. CRYSTAL STRUCTURE OF TRIETHYLTELLURONIUM BROMIDE

RAJ. K. CHADHA, JOHN E. DRAKE, MASOOD A. KHAN,
Chemistry Department, University of Windsor, Windsor, Ontario, N9B 3P4 (Canada)

and GURDEV SINGH
Chemistry Department, Panjab University, Chandigarh-160014 (India)

(Received July 28th, 1983)

Summary

Crystals of triethyltelluronium bromide are cubic with space group $I\bar{4}3m$ (No. 217), a 12.595(4) Å and $Z = 8$. The structure refined to a final R value of 0.0290 for 164 unique "observed" reflections and is disordered with respect to the carbon atoms of the ethyl groups. The bromine atoms are involved in weak secondary interactions with the tellurium atoms to form isolated cubane like tetramers with T_d symmetry. The crystal structure of Et_3TeBr is also consistent with the IR, conductivity measurements and mass spectrometry which shows the presence of Et_2TeBr^+, $EtTeBr^{+\cdot}$ and $TeBr^+$ fragments. Spectroscopic data and conductivity measurements are also reported for the other triethyltelluronium salts which are all ionic.

Introduction

Triorganotelluronium compounds were long considered to be ionic compounds [1]. Recent crystallographic studies on a few triphenyltelluronium pseudohalides [2,3] and solution studies on triorganotelluronium halides and carboxylates [4–7] have revealed that these compounds are not simple ionic compounds but exhibit cation–anion interactions. This has aroused fresh interest in this type of compound. As a part of our studies on the secondary interactions in organotellurium compounds [8–10], we now report the preparation, characterisation and crystal structure of triethyltelluronium bromide which shows Te...Br interactions in solution, gaseous and solid states. In addition, we describe the preparation and characterisation of triethyltelluronium salts of metal halides.

Experimental

Synthesis of compounds:

$MeTeBr_3$ [11] and Et_2Te [12] were prepared according to literature methods.

0022-328X/84/$03.00

Other reagents were prepared and purified by standard methods.

Et_3TeBr was prepared by treating Et_2Te with excess of EtBr and keeping the solution for ca. two weeks until the coloration of Et_2Te vanished. The excess of EtBr was then decanted and crystals washed with ether and dried. Recrystallisation from CH_2Cl_2 yielded Et_3TeBr.

Complexes of Et_3TeBr with $AsBr_3$, $SbBr_3$, $AlBr_3$ and $MeTeBr_3$ were prepared by adding CH_2Cl_2 solution of Et_3TeBr to the chilled and well stirred ether or CCl_4 solution of metal bromides in the molar ratio of 1/1. The similar complexes of Et_3TeBr with $SnBr_4$, $TeBr_4$, $TiBr_4$ and $TeCl_4$ were prepared in CH_2Cl_2 by mixing the components in the reverse order and in the mole ratio 2/1. In the latter case, the reaction mixture had to be refluxed before the reaction proceeded to completion.

Physical measurements

Conductance measurements were carried out on solution using glass cells with platinum electrodes and a Toshniwal conductivity bridge. Solvents used in conductance measurements had specific conductances well below the required range. IR spectra were recorded in Nujol mulls with Perkin–Elmer 621 and 180 spectrophotometers in CsI and polyethylene disks. The mass spectrum was recorded with an AEI double beam MS-30 spectrometer. The program BMASROS [13] was used to caluclate the theoretical isotope cluster of each fragment. ^1H NMR spectra were obtained at 60 MHz using a Varian A-60 instrument. Carbon and hydrogen microanalyses were performed by Guelph Chemical Laboratories Ltd. and Sh.L.K. Khullar of Panjab University. Tellurium and bromine were determined using standard gravimetric techniques. The density was measured by the flotation method in CCl_4/CH_3I.

X-Ray crystallographic analysis of Et_3TeBr

A crystal with approximate dimensions (0.15 × 0.17 × 0.17 mm) was mounted on a Syntex $P2_1$ diffractometer equipped with a Mo X-ray tube and a highly oriented graphite monochromator. The data were collected and processed as described earlier [14]. The intensities of three monitor reflections did not change significantly during data collection. Axial photographs obtained for the crystal showed $m3m$ Laue-symmetry. The systematic absences, hkl; $h+k+l=2n+1$, are consistent with $I432$ (No. 211), $I\bar{4}3m$ (No. 217) and $Im3m$ (No. 229) space groups. The $I\bar{4}3m$ was selected on the basis of Patterson vectors and later confirmed by successful refinement. The data were corrected for Lorentz and polarisation effects and an analytical absorption correction was also carried out. Details of X-ray data are given in Table 1.

The positions of the tellurium and bromine atoms were obtained from a sharpened Patterson synthesis and have the expected $3m$ site symmetry. Since there are eight molecules in the unit cell, the two carbon atoms are expected to be at the mirror plane. However, the difference Fourier map revealed that only the methylene carbon atom, C(1) was on the mirror plane and the methyl carbon atom, C(2), was disordered. Anisotropic refinement of Te, Br and C(1) atoms with fixed C(2) atomic position yielded unusually large U_{11} and U_{33} values for C(1) and chemically unreasonable C(1)–C(2) lengths and Te–C(1)–C(2) angles. It appears that the C(1) is also disordered across the mirror plane * with a small separation (0.76 Å) not

---

* We are thankful to the referee for pointing this out.

TABLE 1

CRYSTALLOGRAPHIC DATA

a	12.595(4) Å
V	1998(1) Å^3
Crystal system	cubic
Space group	$I\bar{4}3m$
Mol. wt.	294.5
Z	8
ρ_c (g cm^{-3})	1.96
ρ_o (g cm^{-3})	1.95
Radiation	Mo-K_α, λ 0.71069 Å
Monochromator	highly oriented graphite
Temperature	21°C
Abs. coeff. μ	66.27 cm^{-1}
Min.abs.corr.	4.816
Max.abs.corr.	8.209
2θ angle	4–50°
Scan type	coupled θ (crystal)/2θ (counter)
Scan width	$K_{\alpha_1} - 1°$ to $K_{\alpha_2} + 1°$
Scan speed	variable, 2.02–4.88° min^{-1}
Background time/scan time	0.5
Total reflections measured	918 ($+h$, $+k$, $+l$, R(I) 3.3%)
Unique data used	164 [$I > 2\sigma(I)$]
Number of parameters (NP)	16
R	0.0290
R_{wF}	0.0286

TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS (Å^2) FOR NON-HYDROGEN ATOMS OF Et_3TeBr WITH STANDARD DEVIATIONS IN PARENTHESES

	x	y	z	U_{11}
Te	0.1336(1)	0.1336(1)	0.1336(1)	0.0741(5)
Br	0.3514(1)	0.3514(1)	0.3514(1)	0.0881(7)
C(1)[a]	0.1146(15)	0.3004(15)	0.1575(15)	0.106(8)
C(2)[a]	0.1402(22)	0.3673(24)	0.0715(23)	0.145(9)

	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	0.0741(5)	0.0741(5)	−0.0019(4)	−0.0019(4)	−0.0019(4)
Br	0.0881(7)	0.0881(7)	−0.0105(6)	−0.0105(6)	−0.0105(6)

[a] Multiplicity = 0.5.

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Te–C(1)	2.14(2)	Te–C(1)–C(2)	117(2)
C(1)–C(2)	1.41(2)	C(1)–Te–C(1)[a]	89.3(6)
Te…Br′	3.564(1)	C(1)–Te…Br′[b]	80.1(4)
Te…Te[d]	4.759(1)	C(1)–Te…Br″[c]	168.3(4)
		Br′…Te…Br″	95.9(1)
		Te…Br′…Te[d]	83.8(2)

[a] Symmetry equivalent positions: z,x,y. [b] $-0.5+x$, $0.5-y$, $0.5-z$; [c] $0.5-x$, $-0.5+y$, $0.5-z$; [d] $-x$, y, $-z$.

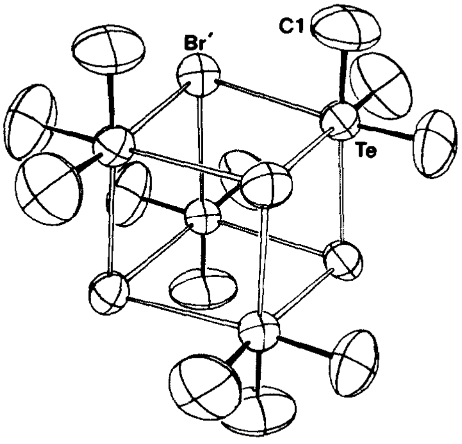

Fig. 1. ORTEP drawing of the tetramer $[Et_3TeBr]_4$. The ellipsoids correspond to 50% probability. The C(2) atoms are not drawn for simplicity and the C(1) atoms are plotted at the mean position of the disordered atoms. Te... Br secondary interactions are shown as open bonds.

detectable in the earlier difference map. Therefore, in the final refinement cycles, Te and Br were refined anisotropically and C(1) and C(2) atoms were refined isotropically assuming both are disordered. Convergence was achieved with this model with the final $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.0290$ and $R_{wF} = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.0286$ and this also yielded reasonable temperature factors and geometry for the carbon atoms. In the final cycle of refinement the largest shift/error ratio was 0.1 and the final difference map had no features of chemical significance with the largest peak being 0.3 eÅ^{-3}. The function $(|F_o| - |F_c|)^2$ was minimised during least squares refinement. Unit weights were used in the initial stages and in the final cycles, a weighting scheme of the form $w = 1/[\sigma^2(F) + 0.001F^2]$ was employed. A few low angle reflections were found to be affected by secondary extinction. An empirical isotropic extinction parameter, x, was used employing the equation $F_c = F[1 - 0.0001x(F^2/\sin\theta)]$ and refined to a value of 0.00095.

Computer programs and sources of scattering factor tables have been noted previously [8]. The final atomic coordinates and thermal parameters are given in Table 2 and important distances and angles in Table 3. Structure factor table may be obtained from R.K.C.

Discussion

Triorganotelluronium halides are generally prepared by the oxidative addition of organic halides to diorganotellurides [1]. Therefore, Et_3TeBr was prepared from Et_2Te and EtBr in quantitative yield. The product is highly soluble in polar solvents and completely insoluble in non-polar solvents. Its analytical, ^1H NMR and IR data are recorded in Table 4. ^{13}C [15] and ^{125}Te [16] NMR data have already been published.

The crystal structure analysis shows that tellurium and bromine atoms are involved in secondary interactions with one another to form isolated cubane like tetramers as shown in Fig. 1. These atoms occupy alternately the corners of a Te_4Br_4

cubane skeleton and the tetrameric unit, $Te_4Br_4(Et)_{12}$, has T_d symmetry imposed by the space group. The structure is thus similar to the Te_4Cl_{16} structure, though it has only approximate T_d symmetry [17]. The Te_4Br_4 core as with the Te_4Cl_4 unit in Te_4Cl_{16}, is much closer to a cube than usually found for cubane structures involving other elements as is evident from the difference of only 12.1° between Br′TeBr″ (95.9(1)°) and TeBr′Te′ (83.8(2)°) angles compared with a difference of 23.8° in cubane type $(Et_3P)_3 \cdot CuX$ compounds [18].

The organotellurium dibromides [9,19,20] and tribromides [21] show Te...Br secondary interactions with the distance between these atoms ranging from 3.59 to 3.93 Å (cf. the Van der Waals contact of 4.15 Å). The analogous contact of 3.564(1) Å in Et_3TeBr is thus the shortest such contact. This kind of secondary interaction is quite common in the tellurium compounds and usually results in the tellurium atom acquiring octahedral coordination and forming infinite chains or tetrameric clusters [8–10,17,22–24]. In Et_3TeBr, when Te–C primary bonds are coupled with Te...Br secondary bonds, the effective coordination of tellurium is also a distorted octahedron with C_{3v} symmetry. However, if only the primary bonds are considered, the tellurium atom has a trigonal pyramidal structure, with a CTeC bond angle of 89.3(6)°. This is as expected for a stereochemically inactive (pure *s*-character) lone pair of electrons with bonding essentially just involving the 5*p*-orbitals of tellurium. The Te–C bond length of 2.14(2) Å and CTeC bond angles of 89.3(6)° are comparable with the corresponding parameters of 2.07(6) Å and 95(2)° in the cation of $(Me_3Te)^+ (MeTeI_4)^-$ [18], 2.13(2) Å and 95.7(8)° in triphenyltelluronium cyanate·0.5 chloroform [2], 2.13(2) Å and 97.3(6)° in triphenyltelluronium thiocyanate [3] and 2.14(2) Å and 91.7(5)° in trimethyltelluronium tetraphenylborate [25].

Molar conductance values of 3.85, 67.36 and 3.37 ohm^{-1} cm^2 $mole^{-1}$ in nitrobenzene, CH_3CN and CH_2Cl_2 respectively are far below the required values (20–30, 90–130, 12–15 ohm^{-1} cm^2 $mole^{-1}$ respectively) for 1/1 electrolytes in these solvents [26]. This suggests that Et_3TeBr is a weak electrolyte in these solvents and this conclusion is consistent with the results obtained in the solid state.

The IR spectrum (600–50 cm^{-1}) shows only a single band (503 cm^{-1}) for the C–Te stretching frequency as might be expected for a CTeC bond angle of ~ 90°. The Te–Br stretching frequency is reported to occur in covalent bromides as a strong band in the region 220–172 cm^{-1} [27,28]. The lack of a strong band in this region is of course compatible with the crystal structure, since only weak Te...Br interactions are present. The strong absorption at 84 and 67 cm^{-1} can be assigned to the lattice modes. The IR spectrum in CH_2Cl_2 solution shows no extra features of interest.

The mass spectrum of Et_3TeBr (Table 5) is as might be expected on the basis of thermolysis products and it is interesting to note the presence of tellurium and bromine containing fragments, Et_2TeBr^+, $EtTeBr^{+\cdot}$ and $TeBr^+$. These fragments are confirmed by their isotopic cluster patterns. Though the relative abundances of these fragments are small, their presence indicates the Te...Br interaction is strong enough to be detected in the gaseous phase.

It is a general observation that for a large cation, the stability of the ionic bond increases if the anion is also large. Therefore, to stabilise the Et_3Te^+ cation, the complexes of Et_3TeBr with Sn^{IV}, Te^{IV}, As^{III}, Al^{III}, Sb^{III} bromides, Te^{IV} chloride and $MeTeBr_3$ have been prepared. The complexes **B**–**I**, which are crystalline solids possessing intense colours are recorded in Table 4, along with their melting points,

TABLE 4

ANALYTICAL DATA, IR SPECTRAL BANDS AND ^{1}H NMR SPECTRA OF TRIETHYLTELLURONIUM COMPOUNDS

Compound	Colour	M.p. (°C)	Analysis (Found (calcd.) (%))				Λ_M [a]	IR (cm^{-1})		^{1}H NMR [b]	
			C	H	Te	Br		ν(M–Br)	ν(C–Te)	CH_3	CH_2
A. Et_3TeBr	White	155(d) [c]	23.75 (24.45)	4.85 (5.09)	43.17 (43.33)	28.12 (27.13)	3.85 67.36 [d] 3.37 [e]		503s [f]	1.59	3.05
B. $(Et_3Te)_2^+(SnBr_6)^{2-}$	Yellow-green	166(d)	13.87 (14.02)	2.38 (2.92)	25.10 (24.84)	45.69 (46.67)	40.37	215s	560w	1.25	2.80
C. $(Et_3Te)_2^+(TeBr_6)^{2-}$	Orange	163(d)	16.12 (15.85)	3.22 (3.30)	28.29 (28.09)	52.24 (52.76)	42.94	180s 123w	550s	1.16	2.78
D. $(Et_3Te)_2^+(TeCl_4Br_2)^{2-}$	Yellow	155(d)	20.17 (19.70)	4.20 (4.10)	34.76 (34.91)	41.00 [g] (41.29)	43.69	185s 212s [i]	550s 515w	1.44	2.86
E. $(Et_3Te)_2^+(TiBr_6)^{2-}$ [h]	Red	80(d)	14.73 (15.05)	3.04 (3.14)	26.12 (26.68)	50.19 (50.12)	40.09	266s 248s	560m 472w	1.22	2.80
F. $(Et_3Te)^+(AsBr_4)^-$ [h]	Yellow	53	12.18 (11.82)	2.82 (2.46)	20.47 (20.95)	47.79 (52.47)	19.84	270s 260s 230s 220s	515m 475w	1.18	2.80
G. $(Et_3Te)^+(SbBr_4)^-$ [h]	Yellow	58	11.20 (10.98)	2.17 (2.29)	18.61 (19.45)	48.06 (48.72)	23.94	226m 210m 188s 167m	550w	1.16	2.84
H. $(Et_3Te)^+(AlBr_4)$ [h]	Deep yellow	45	12.19 (12.83)	3.10 (2.67)	21.47 (22.74)	56.13 (56.95)	20.68	398s	504m	1.25	2.78
I. $(Et_3Te)^+(MeTeBr_4)^-$	Light brown	151	12.20 (12.41)	2.95 (2.66)	37.54 (37.71)	47.70 (47.22)	24.97	221m 203s 185s 125m	550s	1.16 1.50	2.80

[a] Molar conductance (ohm^{-1} cm^2 mole^{-1}) in nitrobenzene. [b] Chemical shifts, in ppm from TMS, in DMSO-d_6, $J(CH_2-CH_3) \simeq 8$ Hz. [c] Lit. [34] 162°C. [d] In CH_3CN. [e] In CH_2Cl_2. [f] Other bands are 304m, 287m, 180w, 169w, 147w, 84s, 67s. [g] Total halide (%). [h] Extremely hygroscopic. [i] ν(Te–Cl).

TABLE 5

MASS SPECTRAL DATA FOR Et_3TeBr [a]

Species	Rel. int. (%).	Species	Rel. int. (%)
Et_2TeBr^+	1.2	$Te^{+\cdot}$	80.0
$EtTeBr^{+\cdot}$	0.5	$EtBr^{+\cdot}$	46.7
$TeBr^+$	0.7	$HBr^{+\cdot}$	33.3
$Te_2^{+\cdot}$	1.7	Br^+	10.1
$Et_2Te^{+\cdot}$	33.3	$C_4H_{10}^{+\cdot}$	6.7
$EtTe^+$	15.2	$C_2H_5^+$	100.0

[a] Relative to ^{130}Te.

elemental analyses, ^1H NMR data, some IR frequencies and molar conductance values in nitrobenzene. These values suggest ionic formulations of these compounds as represented in Table 4. High field methyl and methylene ^1H NMR signals in the compounds **B**–**I** as compared to the corresponding signals in Et_3TeBr also suggest that these compounds are more ionic in solution than Et_3TeBr. The interpretation of IR spectra of complexes **B**–**I** has been done according to literature [29–33] and the observed frequencies confirm the presence of the respective ions in these complexes. The appearance of two absorptions; one at 212 cm^{-1} corresponding to the Te–Cl asymmetric stretch (e_u), and the other at 185 cm^{-1} corresponding to the Te–Br asymmetric stretch (a_{2u}) indicate that the anion $[TeCl_4Br_2]^{2-}$ in **D** probably has trans configuration centrosymmetric with D_{4h} symmetry.

References

1 K.J. Irgolic, The Organic Chemistry of Tellurium, Gordon and Breach, New York, 1975.
2 D.D. Titus, J.S. Lee and R.F. Ziolo, J. Organomet. Chem., 120 (1976) 381.
3 J.S. Lee, D.D. Titus and R.F. Ziolo, Inorg. Chem., 16 (1977) 248.
4 N.S. Dance, W.R. McWhinnie, J. Mallaki and Z. Monsef-Mirzai, J. Organomet. Chem., 198 (1980) 131.
5 F.H. Musa and W.R. McWhinnie, J. Organamet. Chem., 159 (1978) 37.
6 W.R. McWhinnie and J. Mallaki, Polyhedron, 1 (1982) 13.
7 M.T. Chen and J.W. George, J. Am. Chem. Soc., 90 (1968) 4580.
8 R.K. Chadha, J.E. Drake and M.A. Khan, Acta Cryst. C, 39 (1983) 45.
9 R.K. Chadha, J.E. Drake and J.L. Hencher, Can. J. Chem., 61 (1983) 1222.
10 R.K. Chadha, J.E. Drake and M.A. Khan, Can. J. Chem., in press.
11 M.T. Chen and J.W. George, J. Organomet. Chem., 12 (1968) 401.
12 L. Tschugaeff and W. Chlopin, Chem. Ber., 47 (1914) 1269.
13 Obtained from J.M. Miller, Chem. Dept., Brock University, St. Catharines, Canada L2S 3A1.
14 M. Khan, R.C. Steevensz, D.G. Tuck, J.G. Noltes and P.W.R. Corfield, Inorg. Chem., 19 (1980) 3407.
15 R.K. Chadha and J.M. Miller, Can. J. Chem., 60 (1982) 596.
16 R.K. Chadha and J.M. Miller, Can. J. Chem., 60 (1982) 2256.
17 B. Buss and B. Krebs, Inorg. Chem., 10 (1971) 2795.
18 M.R. Churchill, B.G. DeBoer and S.J. Mendhak, Inorg. Chem., 14 (1975) 2041.
19 G. Christofferson and J.D. McCullough, Acta Crystal., 11 (1958) 249.
20 C. Knobler and J.D. McCullough, Inorg. Chem., 11 (1972) 3026.
21 C. Knobler and J.D. McCullough, Inorg. Chem., 16 (1977) 612.
22 F. Einstein, J. Trotter and C. Williston, J. Chem. Soc. A, (1967) 2018.
23 B. Krebs, B. Buss and D. Altena, Z. Anorg. Allgem. Chem., 386 (1971) 257.
24 B. Krebs and V. Paulat, Z. Naturforsch. B, 34 (1979) 900.

25 R.F. Ziolo and J.M. Troup, Inorg. Chem., 18 (1979) 2271.
26 D.A. Couch, P.S. Elmes, J.E. Fergusson, M.L. Greenfield and C.J. Wilkins, J. Chem. Soc. A, (1967) 1813.
27 P. Thavornyutikarn and W.R. McWhinnie, J. Organomet. Chem., 50 (1973) 135.
28 W.R. McWhinnie and P. Thavornyutikarn, J. Chem. Soc. (Dalton Trans.), (1972) 551.
29 N.N. Greenwood and B.P. Straughan, J. Chem. Soc. A, (1966) 962.
30 B.J. Brisdon, G.A. Ozin and R.A. Walton, J. Chem. Soc. A, (1969) 342.
31 G.Y. Ahlijah and M. Goldstein, J. Chem. Soc. A, (1970) 326.
32 R.H. Bradley, P.N. Brier and D.E.H. Jones, J. Chem. Soc. A, (1971) 1397.
33 N. Petragnani, L.T. Castellanos, K.J. Wynne and W. Maxwell, J. Organomet. Chem., 55 (1973) 295.
34 A. Marquardt and A. Michaelis, Chem. Ber., 21 (1888) 2042.