Telluranes: potential synthons for charge-transfer complexes (involving hypervalent Te–I bonds) and serendipitous synthesis of the first triphenyl methyl phosphonium salts containing $[C_4H_8TeI_4]^{2-}$ and $[TeI_6]^{2-}$ anions

Prakash C. Srivastava [a,*], Sangeeta Bajpai [a], Smriti Bajpai [a], Chhabi Ram [a],
Rajesh Kumar [a], Jerry P. Jasinski [b], Ray J. Butcher [c]

[a] Chemistry Department, Lucknow University, Lucknow 226007, India
[b] Chemistry Department, Keene State University, Keene, NH, USA
[c] Chemistry Department, Howard University, Washington, DC 20059, USA

Abstract

Hypervalent Te–I bonds of telluranes ($C_4H_8TeI_2$, $C_5H_{10}TeI_2$ and α-Me_2TeI_2) have been utilised to form the charge transfer (CT) complexes (**1–3**). The reaction of cyclic tellurane (1,1-diiodotetrahydro tellurophene, $C_4H_8TeI_2$) with I_2/ICl yields $C_8H_{16}Te_2I_6$ [$IC_4H_8TeI–I–I–ITeC_4H_8I$] (**1**); an unusual dinuclear species while the reaction of another cyclic tellurane (1,1-diiodo telluracyclohexane, $C_5H_{10}TeI_2$) with I_2 yields $C_5H_{10}TeI_4$ (**2**) possessing different structural motif than **1**. In **2** the iodine molecules are on both sides bonded to iodine atom of hypervalent Te–I bond of $C_5H_{10}TeI_2$ which is analogous to the structural type present in Me_2TeI_4 (**3**) obtained by the reaction of α-Me_2TeI_2 with ICl. The reaction of $C_4H_8TeI_2$ with PPh_3, serendipitously, yields the first triphenyl methyl phosphonium salts $[PPh_3Me]_2^{2+}[C_4H_8TeI_4]^{2-}$ (**4**) and $[PPh_3Me]_2^{2+}[TeI_6]^{2-}$ (**5**), indicating the oxidation of PPh_3 whereas $C_4H_8TeI_2$ itself, is converted into $[C_4H_8TeI_4]^{2-}$ and $[TeI_6]^{2-}$ anions. All the complexes **1–5** have been characterised through single crystal X-ray diffraction studies.
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1. Introduction

From the beginning of 20th century, it is known that diorganyl chalcogenides R_2Y (Y = S, Se, Te) interact with dihalogens (X_2) to form compounds of type R_2YX_2 [diorganyldihalo-thiane (Y = S), selenane (Y = Se) and tellurane (Y = Te)] [1a]. In last few years these interactions have received attention by many research groups due to structural diversities associated with R_2YX_2 in the solid state [1b]. Two distinct structural motifs are possible: R_2YX_2 could be a charge transfer (CT) complex $R_2Y–X–X$ or it may correspond to Ψ trigonal bipyramidal (TBP) structure. For example Me_2SBr_2 is a

CT complex $Me_2S–Br–Br$ [2] while Me_2SeBr_2 [3] and Me_2TeBr_2 [4] adopt ΨTBP structure. Me_2SI_2 [1], Me_2SeI_2 [3] are CT complexes and Me_2TeI_2 [5,6] corresponds to ΨTBP structure. Among cyclic selenanes and telluranes, $C_4H_8SeI_2$ adopts a CT structure $C_4H_8Se–I–I$ [9] while $C_4H_8TeI_2$ possesses ΨTBP structure [10]. These observations are in conformity with the previous study [3] where it has been shown that in R_2YX_2 the structural type (CT or ΨTBP) is dependent on R or Y or X and, in general, on the nature of R_2Y. The less electronegative the Y atom in R_2YX_2, the more likely is the ΨTBP structure. Further, R_2YX_2 correspond to hypervalent compounds [11], which is one of the characteristics of organic heteroatom chemistry and we [4,10,12] and others [13], in recent years, have reported telluranes (R_2YX_2) and their derivatives

* Corresponding author. Tel.: +05222358473.
E-mail address: pcsrivastava31@rediffmail.com (P.C. Srivastava).

possessing TBP geometry, having the two apical ligands and the central Te constructing a three-center-four-electron hypervalent bond with ca. 180° bond angle and its use in the synthesis of supramolecular associations. The formation of hypervalent Te–X bonds in telluranes has also been explained by the use of $n \rightarrow \sigma^*$ orbital interaction and they have been used for the synthesis of macrocycles [14]. Besides, interactions of $Ph_2Se_2I_2$ and $Ph_4Te_4I_4$ with PPh_3 have resulted in the formation of CT complexes $Ph_3PSe(Ph)I$ [15] and $Ph_3PTe(Ph)I$ [16], respectively. Herein we describe the synthesis and structures of the first CT complexes, containing cyclic telluranes (involving hypervalent Te–I bonds), prepared by the reactions of cyclic telluranes viz. $C_4H_8TeI_2$ with I_2/ICl and $C_5H_{10}TeI_2$ with I_2 and the serendipitous synthesis of the first triphenyl methyl phosphonium salts containing $[C_4H_8TeI_4]^{2-}$ or $[TeI_6]^{2-}$ anion (exception to VSEPR rules) [17], obtained by the reaction of $C_4H_8TeI_2$ with PPh_3.

2. Experimental

2.1. Synthesis

$C_4H_8TeI_2$ [18], $C_5H_{10}TeI_2$ [19], α-Me_2TeI_2 [7] were prepared by the literaure methods and $PPh_3Me^+I^-$ was obtained by the reaction of PPh_3 with MeI in solvent ether. Iodine (E-Merck), ICl (Qualigens), PPh_3, MeI and Tellurium (Aldrich) were commercially obtained. I_2 was sublimed and the purity of PPh_3 was confirmed prior to use by elemental analysis, ^1H and ^{31}P {H}NMR spectroscopy. The solvents $CHCl_3$, CH_2Cl_2, $(CH_3)_2CO$, C_6H_6 and Et_2O were dried by standard procedures and freshly distilled before use. Elemental analyses, UV–Vis, NMR spectroscopy were carried out as already reported [12].

2.1.1. Complex (1)

$C_4H_8TeI_2$ (2.00 g, 4.57 mmol) and iodine (1.16 g, 4.57 mmol) were suspended in dry $CHCl_3$ (40 ml), stirred for about 2 h and refluxed for 1 h. It was then filtered and the filtrate was reduced and kept for 1 day when orange red plates suitable for X-ray diffraction appeared. Complex **1** yield : 2.32 g (45%), m.p. 110 °C. *Anal.* Calc. for $C_8H_{16}I_6Te_2$: C, 8.5; H, 1.4; Te, 22.6. Found: C, 8.7; H, 1.6; Te, 22.5%. ^1H NMR: δ_H (CDCl$_3$) 3.94 (4H, t, Te CH$_2$), 3.00 (4H, m, Te CH$_2$CH$_2$).

The reaction of $C_4H_8TeI_2$ (2.00 g, 4.57 mmol) and iodine (2.32 g, 9.14 mmol) in $CHCl_3$ (1:2) molar ratio gave complex **1** (m.p. 110 °C).

2.1.2. Complex (2)

$C_5H_{10}TeI_2$ (2.00 g, 4.42 mmol) and iodine (1.25 g, 4.42 mmol) were suspended in dry $CHCl_3$ (35 ml), stirred for about 6 h and refluxed for 2 h. The reaction

mixture was then filtered and the filtrate was reduced from which dark red needle shaped crystals suitable for X-ray diffraction were obtained after 1 day. Complex **2** yield: 1.62 g (52%), m.p. 68 °C. *Anal.* Calc. for $C_5H_{10}I_4Te$: C, 8.5; H, 1.4; Te, 18.0. Found: C, 8.3; H, 1.1; Te, 18.2%. ^1H NMR: δ_H (CDCl$_3$) 3.66 (4H, t, Te CH$_2$), 2.34 (4H, m, Te CH$_2$CH$_2$), 1.99 (2H, m, Te CH$_2$CH$_2$CH$_2$).

2.1.3. Complex (3)

α-$(CH_3)_2TeI_2$ (1.65 g, 4 mmol) and ICl (0.2 ml, 4 mmol) were suspended in dry $CHCl_3$ (60 ml), stirred for 1 h and refluxed for few minutes. The reaction mixture was filtered and the filtrate was reduced and kept for 1 day. Large crop of red brown plate suitable for X-ray diffraction separated. Complex **3** yield: 1.10 g (83%), m.p. 75 °C. *Anal.* Calc. for $C_2H_6I_4Te$: C, 3.6; H, 0.9; Te, 19.1. Found: C, 3.4; H, 0.8; Te, 19.0%. ^1H NMR: δ_H (CDCl$_3$) 3.35 (6H, s, Te CH$_3$).

2.1.4. Complex (4) and (5)

To a suspension of $C_4H_8TeI_2$ (2.00 g, 4.57 mmol) in dry Et_2O (40 ml), PPh_3 (4.79 g, 18.28 mmol) was added against a stream of dry N_2 at ambient temperature. After stirring for about 1 h under N_2, the wine red solid changed to sticky orange yellow mass which was dissolved in Et_2O/CH_2Cl_2 (1:2) at 50 °C and filtered leaving behind some sticky mass. The filtrate was reduced and kept for 1 day after which the mixture of yellow and dark brown crystals separated. When they were dissolved in CH_2Cl_2, the yellow crystals had dissolved whereas dark brown crystals of **5** m.p. 172 °C. *Anal.* Calc. for $C_{38}H_{36}I_6P_2Te$: C, 31.6; H, 2.5; Te, 8.8. Found: C, 31.5; H, 2.6; Te, 8.7%. ^1H NMR: [δ_H (CDCl$_3$) 3.14, 3.10 (6H, d, PCH$_3$ ^2J(PH) 12 Hz), 7.74 (30H, m, PPh] remained insoluble and they were separated. The CH_2Cl_2 solution was reduced and kept for 1 day when yellow crystals of **4** m.p. 144 °C. *Anal.* Calc. for $C_{42}H_{44}I_4P_2Te$: C, 40.5; H, 3.5; Te, 10.2. Found: C, 40.3; H, 3.7; Te, 10.4%. ^1H NMR: [δ_H (CDCl$_3$) 3.28, 3.24 (6H, d, PCH$_3$ ^2J(PH) 12Hz), 3.94 (4H, t, Te CH$_2$), 3.01 (4H, m, Te CH$_2$CH$_2$), 7.78 (30H, m, PPh)] suitable for X-ray diffraction appeared.

2.2. X-ray measurements

A summary of the crystal data and refinement parameters for $C_4H_8I_3Te$ (**1**), $C_5H_{10}I_4Te$ (**2**), $C_2H_6I_4Te$ (**3**), $C_{21}H_{22}I_2PTe$ 0.50 (**4**), $C_{19}H_{18}I_3PTe0.50$ (**5**) is given in Table 1. The crystals were mounted on a Bruker SMART CCD diffractrometer using graphite-mono-chromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cells were determined from 25 randomly selected reflections using the automatic search index and least squares refinement. The structure of **1** was solved in space group $P\bar{1}$, **2** in space group $P2(1)/n$, **3** in space
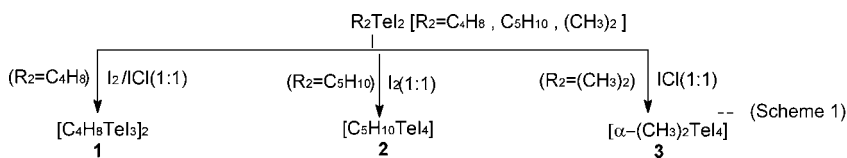
Table 1
Crystal data and refinement details for complexes **1–5**

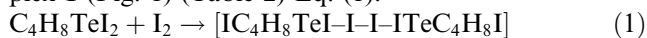|	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_4H_8I_3Te$	$C_5H_{10}I_4Te$	$C_2H_6I_4Te$	$C_{21}H_{22}I_2PTe_{0.50}$	$C_{19}H_{18}I_3PTe_{0.50}$
Formula weight	564.40	705.33	665.27	622.96	721.80
Temperature (K)	293(2)	93(2)	93(2)	93(2)	93(2)
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P-1$	$P2(1)/n$	$P-1$	$C2/c$	$C2/c$
a (Å)	7.4770(4)	8.4344(4)	6.4895(10)	15.773(2)	23.457(5)
b (Å)	8.9244(5)	10.4910(5)	7.3786(12)	12.6338(16)	14.064(3)
c (Å)	9.5233(5)	15.7163(7)	12.465(2)	21.747(3)	15.474(3)
α (°)	89.8550(10)	90	73.461(2)	90	90
β (°)	68.1750(10)	99.0410(10)	81.774(3)	91.702(2)	122.144(3)
γ (°)	70.6090(10)	90	76.119(2)	90	90
V (Å³)	551.13(5)	1373.38(11)	553.65(15)	4331.8(10)	4332.3(15)
Z	2	4	2	8	8
μ (mm⁻¹)	11.032	11.109	13.766	3.639	5.073
Index ranges	$-9 \leftarrow h \leftarrow 9,$	$-11 \leftarrow h \leftarrow 11,$	$-8 \leftarrow h \leftarrow 7,$	$-18 \leftarrow h \leftarrow 18,$	$-31 \leftarrow h \leftarrow 27,$
	$-11 \leftarrow k \leftarrow 11,$	$-13 \leftarrow k \leftarrow 12,$	$-9 \leftarrow k \leftarrow 9,$	$-13 \leftarrow k \leftarrow 14,$	$-18 \leftarrow k \leftarrow 18,$
	$-12 \leftarrow 1 \leftarrow 12$	$-20 \leftarrow 1 \leftarrow 20$	$-16 \leftarrow 1 \leftarrow 16$	$-25 \leftarrow 1 \leftarrow 24$	$-19 \leftarrow 1 \leftarrow 17$
Reflections collected	4336	10 541	4339	12 992	12 730
Independent reflections	2633	3354	2626	3680	4366
	($R_{int} = 0.0522$)	($R_{int} = 0.0429$)	($R_{int} = 0.0320$)	($R_{int} = 0.0340$)	($R_{int} = 0.0388$)
Final R indices [$I > 2\sigma(I)$] $R_1 = 0.0404$	$R_1 = 0.0317$	$R_1 = 0.0274$	$R_1 = 0.0202$	$R_1 = 0.0488$	
	$wR_2 = 0.1102$	$wR_2 = 0.0805$	$wR_2 = 0.0707$	$wR_2 = 0.0455$	$wR_2 = 0.1207$
R indices (all data)	$R_1 = 0.0500$	$R_1 = 0.0375$	$R_1 = 0.0297$	$R_1 = 0.0226$	$R_1 = 0.0535$
	$wR_2 = 0.1154$	$wR_2 = 0.0836$	$wR_2 = 0.0718$	$wR_2 = 0.0464$	$wR_2 = 0.1233$

group $P\bar{1}$ and **4** and **5** in space group $C2/c$. The data were corrected for Lorentz, polarisation and absorption effects. The data were monitored by measuring three standard reflections at every 97 reflections. The structures were solved by the routine heavy atom method SHELXS-97 [20] and Fourier methods and refined by full-matrix least-squares using the SHELXL-97 program [20] with the non-hydrogen atoms anisotropic and hydrogen atoms having fixed isotropic thermal parameters of 0.08 Å².

3. Results and discussion

The complexes (**1–3**) have ben synthesised by the following reactions (Scheme 1):

So far no CT complex containing cyclic diorganyldiiodo tellurane involving hypervalent Te–I bond has been reported either in solution or in solid state. **1** is the first CT complex containing 1,1-diiodo tetrahydro tellurophene in the solid state. The I(3)–I(3A) bond length is 2.77 Å and I(1)–I(3A) bonds are 3.39 Å while in I_2 the covalent radius of I–I is 2.67 Å [21] and van der Waals radius is 4.30 Å. The I(1)–I(3)–I(3A) angle is 175.8°. The lengthening of I–I bonds in **1** is comparable to those observed for cyclic thioether-diiodine CT complexes [22] and I–I secondary bond distance 3.39 Å is comparable to 3.32 Å in $Bu_3^tPI_2$, CT complex reported by du Mont et al. [23], indicating sufficient interaction in solid state. The elongations of I–I bond in **1** can be attributed to the donation of electron density from filled nonbonding orbitals of I to the antibonding LUMO (lowest unoccupied molecular orbital) of diiodine molecule which is

-- (Scheme 1)

The interaction of $C_4H_8TeI_2$ with I_2 in 1:1 molar ratio in chloroform yields unusual dinuclear CT complex **1** (Fig. 1) (Table 2) Eq. (1).

$$C_4H_8TeI_2 + I_2 \rightarrow [IC_4H_8TeI–I–I–ITeC_4H_8I] \qquad (1)$$

an antibonding σ^* orbital lying along the main axis of diiodine ($n \rightarrow \sigma^*$ orbital interaction) [22a,22b]. The structure may be somewhat likened to [$Ph_3PCl^+–Cl^-$ $+ ClPPh_3$]Cl containing long Cl–Cl contacts [24].
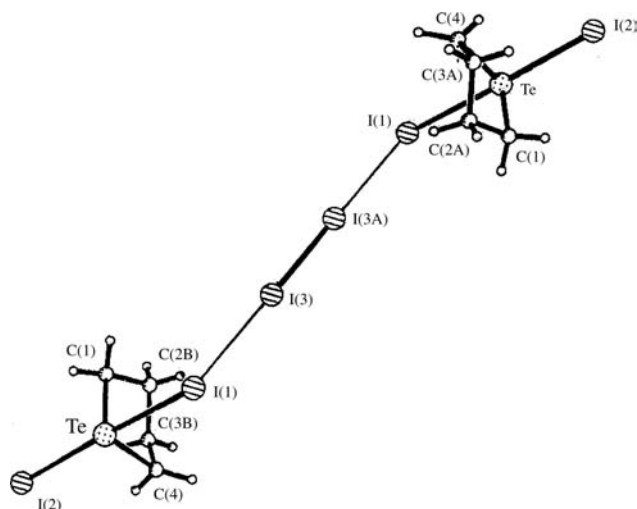
Fig. 1. Crystal structure of **1**.

Table 2
Bond lengths (Å) and angles (°) for **1**

Bond lengths			
Te–I(2)	2.889(1)	Te–I(1)	2.954(1)
Te–C(4)	2.148(1)	Te–C(1)	2.186(1)
C(1)–C(2B)	1.527(2)	C(1)–C(2A)	1.532(1)
C(2A)–C(3A)	1.521(2)	C(3A)–C(4)	1.535(2)
C(2B)–C(3B)	1.510(3)	C(3B)–C(4)	1.530(2)
I(1)–I(3A)	3.394(1)	I(3)–I(3A)	2.775(1)
Bond angles			
C(4)–Te–C(1)	84.3(3)	C(4)–Te–I(2)	92.1(2)
C(1)–Te–I(2)	90.7(2)	C(4)–Te–I(1)	90.9(2)
C(1)–Te–I(1)	89.5(2)	I(2)–Te–I(1)	176.9(2)
C(2B)–C(1)–Te	108.0(13)	C(2A)–C(1)–Te	102.6(7)
C(3A)–C(2A)–C(1)	109.2(14)	C(2A)–C(3A)–C(4A)	106.9(13)
C(3B)–C(2B)–C(1)	108.0(2)	C(2B)–C(3B)–C(4)	116.0(3)
C(3B)–C(4)–Te	105.2(7)	C(3A)–C(4)–Te	105.8(8)
I(1)–I(3)–I(3A)	175.8		

Thus the building block is CT complex **1** ($C_8H_{16}Te_2I_6$), an unusual dinuclear species (IC$_4$H$_8$TeI–I–I–ITeC$_4$H$_8$I), whose bridging I$_2$ acts as a supramolecular glue. One of the I atom of this I$_2$ molecule is *exo* bound to Te of another $C_4H_8TeI_2$ molecule through weak Te–I contact (3.855 Å) making (formally) a trinuclear species. In the unit cell such two trinuclear species are connected together through weak Te–I contact (3.825 Å) (the covalent radius of Te–I is 2.70 Å [25] and van der Waals radius is 4.35 Å [26]), resulting in overall extended strucure (formally) hexanuclear species containing Te$_2$I$_2$ square somewhat similar to Te$_4$ square reported by Godfrey and coworkers [16] in Ph$_4$Te$_4$I$_4$. Apart from these, weak C(sp^3)–H–I contacts [H–I = 3.21 Å, C–I = 4.16 Å, C–H = 0.97 Å, ∠C–H–I = 167.9°] are also seen (Fig. 2).

When $C_4H_8TeI_2$ was reacted with ICl (1:1 molar ratio) in chloroform, CT complex **1** (same cell constants)
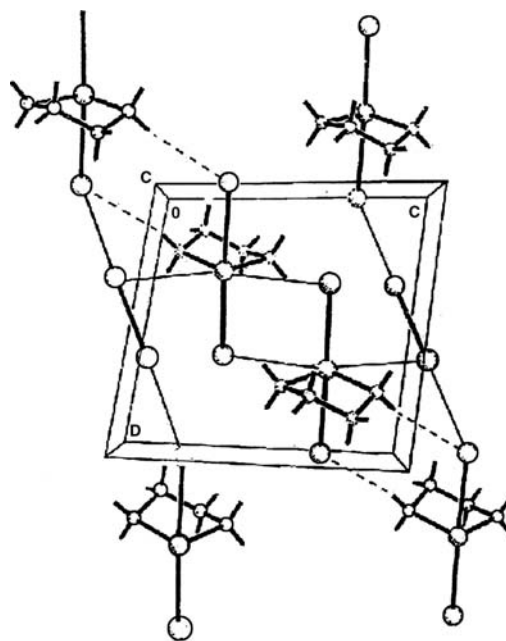
Fig. 2. The unit cell of **1** illustrating the I – I, Te – I and H – I contacts linking the structure into ($C_4H_8TeI_3$)$_2$ dimers and Te$_2$I$_2$ square.

was obtained instead of $C_4H_8TeI_2 \cdot$ ICl adduct. A possible explanation is that ICl in solutions dissociates as **2** ICl = I$^+$ + ICl$_2^-$ [27] hence the interacting species is I$^+$ (iodonium ion) which interacts with hypervalent Te–I bond of $C_4H_8TeI_2$ resulting in the formation of $C_4H_8TeI_3$, which exists as a dimer, an unusual dinuclear species **1**.

Srivastava et al. [28] erroneously described the reaction products of $C_4H_8TeI_2$ with I$_2$ and ICl as $C_4H_8TeI_4$ and $C_4H_8TeI_2 \cdot$ ICl adducts, respectively. Their conclusions were based on elemental analysis, UV and ^{1}H NMR data. In contrast we have found a different product ($C_4H_8TeI_3$)$_2$ CT complex **1** (X-ray evidence) from these reactions.

CT complex **1** is air stable and there is no change [loss of iodine] when **1** is kept in vacuum for several hours at room temperature. Reactions of **1** with Ag salts (AgCl, AgBr) result in almost quantitative precipitation of AgI.

Solution of complex **1** in CH$_2$Cl$_2$ is dark brown in contrast to the violet solution of I$_2$ in CH$_2$Cl$_2$. The change of colour indicates formation of charge-transfer complex. The UV–Vis spectrum of **1** shows bands at 336 and 271 nm which are also found when I$_2$ is added to $C_4H_8TeI_2$ (in 1:2 molar ratio) in CH$_2$Cl$_2$. The UV–Vis spectrum of $C_4H_8TeI_2$ shows bands at 330 and 270 nm. I$_2$ in CH$_2$Cl$_2$ absorbs at 501 nm. The absence of free I$_2$ in solution of the CT complex **1** appears to suggest that **1** remains intact in solution.

It is thus evident that we have been successful in the formation of CT complex **1** by the interaction of $C_4H_8TeI_2$ with I$_2$ and ICl which exhibits the charge transfer from I of hypervalent Te–I bond of $C_4H_8TeI_2$

to I_2 molecule and simultaneously the charge transfer between Te–I and this study will form the basis of obtaining CT complexes of varied structural varities by the interaction of other cyclic diorganyl diiodotelluranes with dihalogens/interhalogens.

In order to check the generality of the above reaction product (CT complex) obtained by the reaction of cyclic tellurane $C_4H_8TeI_2$ (1,1-diiodotetrahydro tellurophene) with I_2/ICl, we reacted another cyclic tellurane $C_5H_{10}TeI_2$ (1,1-diiodo telluracyclohexane) with I_2 and surprisingly the product $C_5H_{10}TeI_4$ **2** corresponded to complex of different structural motif where iodine mol-
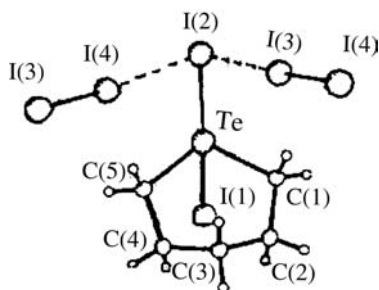

Fig. 3. Crystal structure of **2**.

Table 3
Bond lengths (Å) and angles (°) for **2**

Bond lengths			
Te–I(1)	2.791(1)	Te–I(2)	3.086(1)
Te–C(5)	2.162(1)	Te–C(1)	2.160(1)
C(1)–C(2)	1.523 (8)	C(2)–C(3)	1.513(9)
C(3)–C(4)	1.528 (10)	C(4)–C(5)	1.512(9)
I(3)–I(4)	2.744(1)	I(2)–I(3)	3.327(1)
I(2)–I(4)	3.509(1)		
Bond angles			
C(1)–Te–C(5)	95.4(2)	C(1)–Te–I(1)	92.9(1)
C(5)–Te–I(1)	92.1(1)	C(1)–Te–I(2)	88.8(1)
C(5)–Te–I(2)	87.7(1)	I(1)–Te–I(2)	178.4(2)
C(2)–C(1)–Te	114.5(4)	C(3)–C(2)–C(1)	114.2(5)

ecules are on both sides bonded to iodine atom of hypervalent Te–I bond of $C_5H_{10}TeI_2$ molecule (Fig. 3) (Table 3) which is analogous to the structural type present in the I_2 adduct of acyclic dimethyl diiodotellurane Me_2TeI_4 (**3**) (Fig. 4). The I–I bond is lengthened and it is 2.74 Å. The I(2)–I(3) secondary bond is 3.33 Å and I(2)–I(4) secondary bond length is 3.51 Å. The solution of **2** in CH_2Cl_2 is dark brown hence $C_5H_{10}TeI_4$ is also a CT complex and in UV–Vis spectrum of **2** in CH_2Cl_2 the bands appear at 504, 338, 336, 330 and 275 nm (cf. the bands in UV–Vis spectrum of $C_5H_{10}TeI_2$ at 344, 340, 331 and 276 nm). The interaction of $C_5H_{10}TeI_2$ with ICl in chloroform did not result in a clean product. Gilbert and Lowry [29] formulated $C_5H_{10}TeI_4$ as $[C_5H_{10}TeI] I_3$ on the basis of conductivity data.

Me_2TeI_4 (**3**) is obtained by the interaction of α-Me_2TeI_2 with ICl in chloroform. Srivastava et al. [28] also erroneously described the reaction product of –$(CH_3)TeI_2$ with ICl as $(CH_3)TeI_2 \cdot$ ICl adduct on the basis of elemental analysis and ^{1}HNMR data. The X-ray structure (Fig. 4) (Table 4) of red brown crystals of **3** shows that it is essentially similar (only unit cell angles are differing) to Me_2TeI_4 obtained by Vernon [30] by the interaction of α-Me_2TeI_2 with I_2 and characterised through single crystal X-ray diffraction studies by Pritzkow [31]. The I–I bond in both the cases is lengthened and it is 2.75 Å. Although they did not describe Me_2TeI_4 as CT complex, we argue that Me_2TeI_4 is a CT complex because of the specific characteristics [32]. Vernon [30] originally formulated Me_2TeI_4 as $[Me_2TeI_2]I_2$. In subsequent solution studies Gilbert and coworkers [33] indicated it to correspond $[Me_2TeI]I_3$. On the basis of spectroscopic data Thayer et al. [34] reported it to be an adduct of α-Me_2TeI_2 with I_2.

In view of the interesting CT complexes obtained by the reactions of $Ph_2Se_2I_2$ and $Ph_4Te_4I_4$ with PPh_3 [15,16], $C_4H_8TeI_2$ was reacted with PPh_3 at ambient temperature in 1:4 stoichiometric ratio and instead of
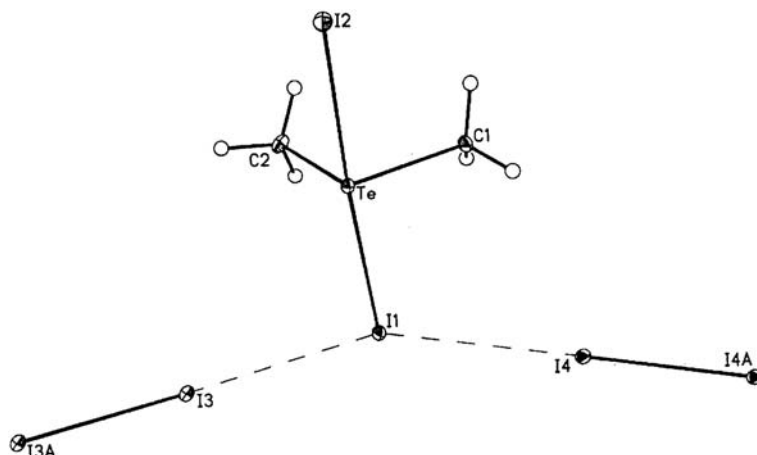
Fig. 4. Crystal structure of **3**.

Table 4
Bond lengths (Å) and angles (°) for **3**

Bond lengths			
Te–C(2)	2.116(6)	Te–C(1)	2.124(6)
Te–I(2)	2.802(1)	Te–I(1)	3.068(1)
I(3)–I(3)#1	2.759(1)	I(4)–I(4)#2	2.748(1)
Bond angles			
C(2)–Te–C(1)	95.5(3)	C(2)–Te–I(2)	90.5(2)
C(1)–Te–I(2)	89.9(2)	C(2)–Te–I(1)	85.9(17)
C(1)–Te–I(1)	85.7(2)	I(2)–Te–I(1)	174.0(2)

CT complexes we obtained triphenyl methyl phosphonium salts (**4** and **5**) (Scheme 2).

$$\text{C}_4\text{H}_8\text{TeI}_2 \ + \ 4\text{PPh}_3 \longrightarrow$$

[PPh₃Me]₂²⁺ — structure **4**
[PPh₃Me]₂²⁺ — structure **5**

+ sticky mass – (Scheme 2)
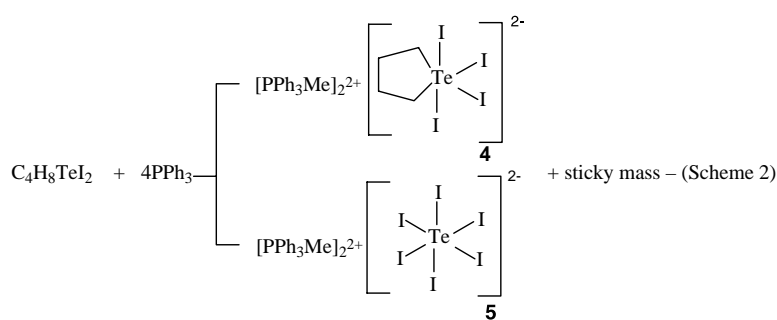
C$_4$H$_8$TeI$_2$ reacts with PPh$_3$ in Et$_2$O to produce sticky orange yellow mass which on extraction and crystallisation with Et$_2$O/CH$_2$Cl$_2$ yields yellow crystals of **4** and dark brown crystals of **5** and some sticky mass is left behind. When acetone or chloroform, in place of Et$_2$O, was used in Scheme 2 the yellow crystal of **4** (m.p. 144 °C) could be obtained but dark brown crystals of **5** did not appear. When benzene was used as a solvent the reaction did not yield even **4**. The reaction of C$_4$H$_8$TeI$_2$ (0.54 g, 1.23 mmol) with PPh$_3$Me$^+$I$^-$ (1.00 g, 2.47 mmol) in chloroform under nitrogen atmosphere yielded yellow solid corresponding to [PPh$_3$Me]$_2^{2+}$ [C$_4$H$_8$TeI$_4$]$^{2-}$ (m.p. 144 °C, authentic ^{1}H NMR).

The X-ray crystal structure of **4** reveals it to be [PPh$_3$Me]$_2^{2+}$[C$_4$H$_8$TeI$_4$]$^{2-}$ (Fig. 5) (Table 5). **4** is the dianionic complex [C$_4$H$_8$TeI$_4$]$^{2-}$ (Te–I = Te–I#1 = 2.926 Å, ∠I–Te–I#1 = 179.0°, ∠C(1)–Te–C(1)#1 = 83.9°, Te–I(2)$^-$ = Te–I(2)$^-$#1 = 3.748 Å, ∠I(2)$^-$–Te–I(2)$^-$#1 = 123.2°), containing stereochemically active electron lone pair [10] with triphenyl methyl phosphonium cations. We are aware of the reports of the structures of mono-anionic tetrahalo organyl tellurate(IV) complexes only [8,11].

The X-ray crystal structure of [PPh$_3$Me]$_2^{2+}$[TeI$_6$]$^{2-}$ (**5**) (Fig. 6) (Table 6) shows that it contains discrete octahedral [TeI$_6$]$^{2-}$ anion, all the Te–I bonds of which are in the range of 2.97–2.98 Å and the I–Te–I bond angles are in the range of 87.4°–92.6°, indicating that the coordination octahedron of Te(IV) atom is practically

regular and the data are comparable to those in K$_2$TeI$_6$ [35] and our previous report of the first tetraalkyl ammonium salt containing discrete octahedron of [TeI$_6$]$^{2-}$ anion in [Et$_4$N]$_2^{2+}$[TeI$_6$]$^{2-}$ [36]. **5** accounts for the first example of triphenyl methyl phosphonium salt containing regular octahedron of a discrete [TeI$_6$]$^{2-}$ anion where the lone pair of electrons at Te appears to be stereochemically inactive and because of ligand–ligand repulsion the lone pair of electrons is forced inside the valency shell into a spherical s type orbital. Such an example is an exception to valence shell electron pair repulsion rules and is rare in tellurium(IV) complexes [17]. Most of the tellurium(IV) complexes, otherwise, contain stereochemically active electron lone pair which affects their geometry in a significant way [37].

There are no interactions between cations and dianions in **4** and **5**. The presence of cations [PPh$_3$Me]$^+$ in **4** and **5** indicates that oxidation of PPh$_3$ takes place. The presence of PCH$_3$ signals in ^{1}H NMR as doublet with
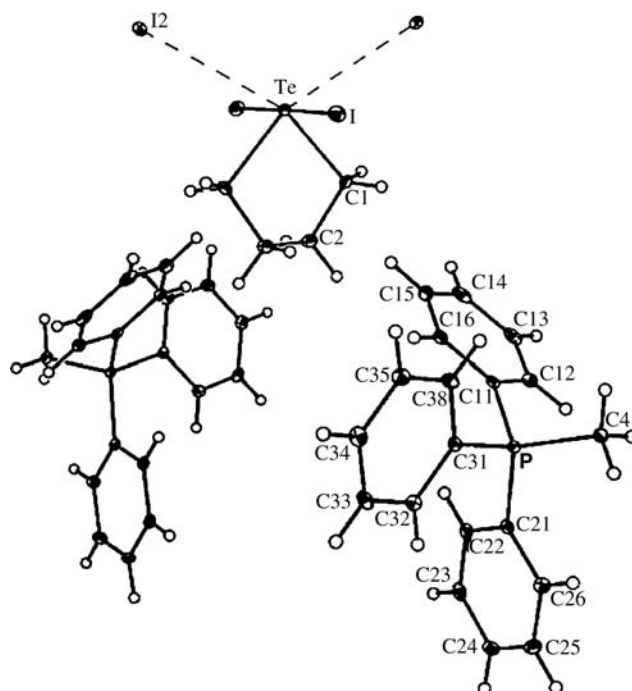

Fig. 5. Crystal structure of **4**.

Table 5
Bond lengths (Å) and angles (°) for **4**

Bond lengths			
Te–C(1)#1	2.159(3)	Te–C(1)	2.159(3)
Te–I	2.926(1)	Te–I#1	2.926(1)
Te–I2)$^-$	3.748	Te–I(2)$^-$#1	3.748
P–C(41)	1.783(3)	P–C(31)	1.789(3)
P–C(21)	1.790(3)	P–C(11)	1.793(3)
Bond angles			
C(1)#1–Te–C(1)	83.9(2)	C(1)#1–Te–I	87.9(1)
C(1)–Te–I	91.4(1)	C(1)#1–Te–I#1	91.4(1)
C(1)–Te–I#1	87.9(1)	I–Te–I#1	179.0(1)
C(41)–P–C(31)	108.5(1)	C(41)–P–C(21)	109.9(1)
C(31)–P–C(21)	110.4(1)	C(41)–P–C(11)	110.1(1)
C(31)–P–C(11)	110.3(1)	C(21)–P–C(11)	107.7(1)
I(2)$^-$–Te–I(2)$^-$#1	123.2		
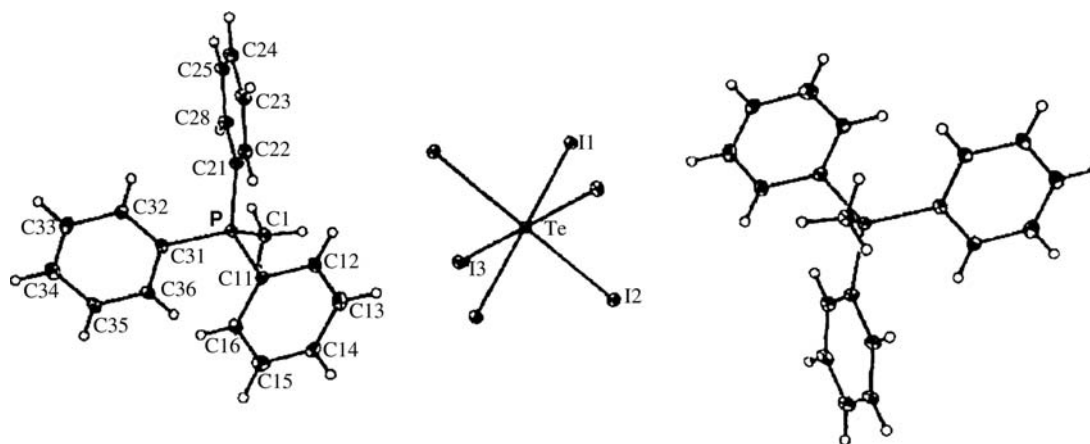
Fig. 6. Crystal structure of **5**.

Table 6
Bond lengths (Å) and angles (°) for **5**

Bond lengths			
Te–I(1)	2.979(1)	Te–I(2)	2.971(1)
Te–I(3)	2.974(1)	Te–I(2)#1	2.971(1)
Te–I(3)#1	2.974(1)	Te–I(1)#1	2.979(1)
P–C(1)	1.783(8)	P–C(31)	1.802(9)
P–C(21)	1.806(8)	P–C(11)	1.809(9)
Bond angles			
I(2)–Te–I(2)#1	180.0(2)	I(2)–Te–I(3)	88.8(2)
I(2)#1–Te–I(3)	91.2(2)	I(2)–Te–I(3)#1	91.2(2)
I(2)#1–Te–I(3)#1	88.8(2)	I(3)–Te–I(3)#1	180.0
I(2)–Te–I(1)	87.4(2)	I(2)#1–Te–I(1)	92.6(2)
I(3)–Te–I(1)	87.9(2)	I(3)#1–Te–I(1)	92.1(2)
I(2)–Te–I(1)#1	92.6(2)	I(2)#1–Te–I(1)#1	87.4(2)
I(3)–Te–I(1)#1	92.1(2)	I(3)#1–Te–I(1)#1	87.9(2)
I(1)–Te–I(1)#1	180.0	C(1)–P–C(31)	109.7(4)
C(1)–P–C(21)	110.4(4)	C(31)–P–C(21)	107.9(4)
C(1)–P–C(11)	109.0(4)	C(31)–P–C(11)	110.0(4)
C(21)–P–C(11)	109.8(4)		

^{2}JPH $= 12$ Hz in **4** and ^{2}JPH $= 12$ Hz in **5** indicates the presence of –CH$_3$ group attached to phosphorus. We therefore, attribute the synthesis of **4** and **5** as serendipitous and the only products we have been able to identify out of, probably, many products formed through Scheme 2.

We have thus not only synthesised the first CT complexes (**1** and **2**) containing cyclic telluranes involving hypervalent Te–I bonds but also demonstrated that **1** is the unusual dinuclear species which is structurally different from **2**. Hypervalent bonds of telluranes can thus, serve as potential synthons for CT complexes. **4** and **5** are the first serendipitously synthesised triphenyl methyl phosphonium salts having dianions containing cyclic tellurane [C$_4$H$_8$TeI$_4$]$^{2-}$ and discrete octahedron of [TeI$_6$]$^{2-}$ respectively, indicating, probably, the oxidation of PPh$_3$ by cyclic tellurane while C$_4$H$_8$TeI$_2$ itself is being converted to uncommon dianions.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 207163, 207164, 207165, 207166 and 207167 for complexes **1**, **2**, **3**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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[32] (i) In X-ray of Me$_2$TeI$_4$ there is lengthening of I–I bond (2.75 Å) [31] in comparison to 2.67 Å, in diiodine molecule; (ii) we prepared Vernon's large bluish black crystals of Me$_2$TeI$_4$ [30] in ethyl

acetate and dissolved them in CH_2Cl_2. The colour of the solution was wine red. The colour of our red brown crystals of Me_2TeI_4 in CH_2Cl_2 was also wine red in contrast to violet solution of I_2 in CH_2Cl_2. The change of colour also indicates formation of charge-transfer complex.

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