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The Reactions of Tellurium Tetrahalides with Triphenylphosphine under Ambient Conditions

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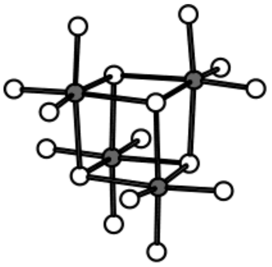
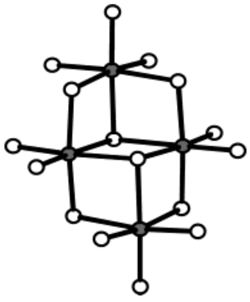
The reactions of tellurium tetrahalides and triphenylphosphine in tetrahydrofuran have been carried out under ambient conditions and afford $\{(Ph_3PO)_2H\}_2[Te_2X_{10}]$ [X = Cl (**1**), Br (**2**)] and $\{(Ph_3PO)_3(OH_3)\}_2[TeI_6]$ (**4**). The X-ray structures of **1** and **2** show that they are isostructural and contain discrete $[Te_2X_{10}]^{2-}$ anions exhibiting octahedral coordination around both tellurium atoms with one shared edge and $\{Ph_3POH\cdots OPPh_3\}^+$ cations that show strong hydrogen bonds (the O···O distances are 2.399 and 2.404 Å for **1** and **2**, respectively). The compound **4** is built up with discrete octahedral hexaiodotellurate anions and $\{(Ph_3PO)_3(OH_3)\}^+$ cations. The reaction of $TeBr_4$ and PPh_3 also results in the formation of formally zwitterionic $Ph_3PO(CH_2)_4TeBr_4$ (**3**). This reaction involves an unprecedented THF ring opening in which the oxygen atom becomes bonded to the phosphorus atom of triphenylphosphine and the carbon atom at the other end of the five-atomic chain becomes bonded to the tellurium atom of $TeBr_4$. The ring opening of the solvent THF is also taking place in the reaction involving tellurium tetraiodide, as indicated by the formation of $C_4H_8TeI_2$ (**5**). The reaction may initially lead to Ph_3PI_2 that reacts with THF yielding Ph_3PO and $ICH_2(CH_2)_2CH_2I$. The latter species reacts with elemental tellurium producing **5**. Depending on the conditions upon crystallization, two polymorphs of $C_4H_8TeI_2$ (**5a** and **5b**) are observed. While the molecular structures of the two forms are virtually identical, their packing and intermolecular contacts are different. Two further minor products (**6a** and **6b**) were isolated in the reaction of TeI_4 and PPh_3: Both are formally 1:1 adducts of **5** and TeI_4, but they differ considerably in their structures. **6a** can be formulated as $\{C_4H_8TeI^+\}_2[Te_2I_{10}{}^{2-}]$ and **6b** as $\{C_4H_8TeI^+\}_2(TeI_3{}^+)_2(I^-)_4$. The latter compound exhibits framework similar to that of the tetramers in γ- and δ-TeI_4.

Introduction

Tellurium forms tetrahalides with all four halogen elements. Especially $TeCl_4$, $TeBr_4$, and TeI_4 have seen considerable research activity because of their structural versatility and potential utility as synthons in many chemical reactions. The bonding in these compounds eludes simple description, and concepts like hypervalence, multicenter bonding, charge-transfer interactions, and secondary bonding have been evoked in the understanding of their structural and chemical properties (for a recent review of chalcogen halides, see ref 1).

The early electron diffraction studies suggested that $TeCl_4$(g) is a monomer displaying a Ψ-tbp structure with point group C_{2v}.[2] In the solid state $TeCl_4$[3,4] and $TeBr_4$[5] display a tetrameric cubane-like structure **I** in which the terminal Te−X bonds are shorter than those involving the triply bridging halogen atoms. The structure can be understood either as covalently bound (Te_4X_{16}) molecules or in terms of the ionic formulation $[(TeX_3{}^+X^-)_4]$.[3,6] The tellurium lone pairs show stereochemical activity directed toward the center of the cubane structure.





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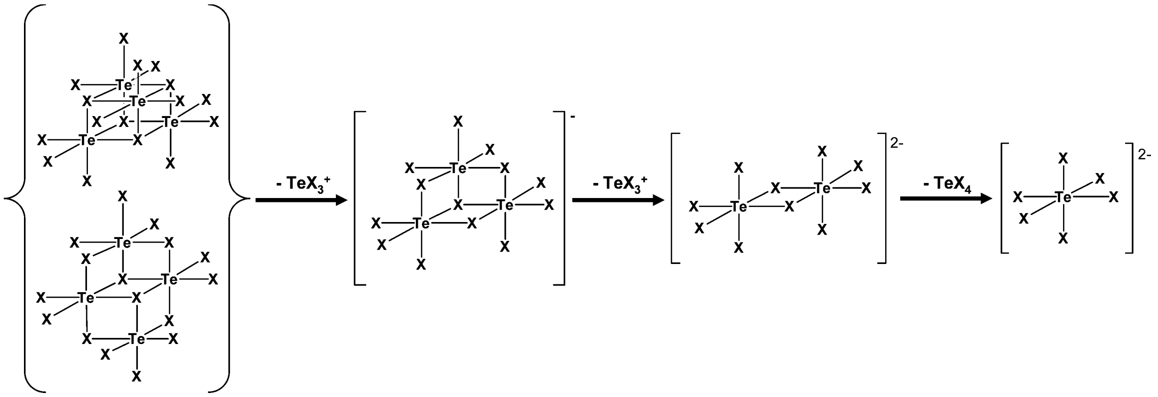
Scheme 1



TeI_4 differs from $TeCl_4$ and $TeBr_4$ by having five different polymorphs ($\alpha-\epsilon$) that can simultaneously be crystallized from the methanol solution of TeI_4 containing HI.[6] The orthorhombic δ-TeI_4 is the thermodynamically stable polymorph at normal conditions.[7] It shows another tetrameric structure (**II**) that can be formulated as $[(TeI_3^+I^-)_2(TeI_4)_2]$. The TeX_6 octahedra in **II** are less distorted than in the cubane structure (**I**). It has been suggested,[1] that the formation of the structure type **II** is a consequence of a smaller electronegativity difference between tellurium and iodine compared to that between tellurium and chlorine or tellurium and bromine, since the cubane structure (**I**) favors larger charge separation with the formation of more polar bonds. Indeed, orthorhombic β-TeI_4 and monoclinic γ-TeI_4 also exhibit the structure **II**.[6] Trigonal α-TeI_4 shows a continuous 2H-CdI_2 structure that can also be understood in terms of a repeating structural unit similar to **II**.[6] Interestingly, only the thermodynamically least-stable tetragonal ϵ-TeI_4 shows the cubane structure **I**.[6]

The tetrameric tellurium tetrachlorides, -bromides, and -iodides undergo a systematic stepwise degradation in the presence of stoichiometric amounts of halides in nonpolar solvents and form oligonuclear halogenotellurates(IV) (see Scheme 1). There are numerous examples of the formation and equilibria between the different anions (for a detailed discussion, see ref 1).

Tellurium tetrahalides can react with both Lewis bases and Lewis acids. There are several examples of adducts where tellurium tetrahalides have acted both as acceptors and as donors (see ref 1 and references therein). This amphoteric behavior can be understood in terms of the partially ionic Te−X bonding. We are interested in the reactivity trends of tellurium tetrahalides TeX_4 (X = Cl, Br, I) and revisited their reactions with Ph_3P in tetrahydrofuran. In an inert atmosphere, the reaction of $TeCl_4$ with Ph_3P has been reported to afford Ph_3PCl_2 and Te(0),[8] or $TeCl_2$, Te(0), and Ph_3PO.[9] The last product was assumed to be formed upon hydrolysis of Ph_3PCl_2 during the workup of the product mixture. In this work we explored the reactions in air. We found that under these conditions the reaction of $TeCl_4$ with Ph_3P in tetrahydrofuran affords $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$ (**1**) and that of $TeBr_4$ yields $\{(Ph_3PO)_2H\}_2[Te_2Br_{10}]$ (**2**) and $Ph_3PO(CH_2)_4TeBr_4$ (**3**).[10] The reaction of TeI_4 produces mainly $\{(Ph_3PO)_3H_3O\}_2[TeI_6]$ (**4**), but small amounts of $C_4H_8TeI_2$ (**5**) and $C_4H_8Te_2I_6$ (**6**) were also obtained. The products have been characterized by ^{125}Te and ^{31}P NMR spectroscopy, as well as by X-ray crystallography.

Experimental Section

General Procedures. All reactions were carried out in air. Ph_3P (Fluka), $TeCl_4$ (Alfa), $TeBr_4$ (Aldrich), and TeI_4 (Aldrich) were used without further purification.

Spectroscopic Methods. The $^{31}P\{^1H\}$ and ^{125}Te spectra were recorded on a Bruker DPX400 spectrometer operating at 161.98 and 126.24 MHz, respectively. The spectra were recorded unlocked. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. For ^{125}Te a saturated solution of H_6TeO_6(aq) was used as an external reference. The chemical shifts are reported relative to neat Me_2Te [$\delta(Me_2Te) = \delta(H_6TeO_6) + 712$]. All spectra were recorded in THF.

Reaction of $TeCl_4$ with Ph_3P. Ph_3P (313 mg, 1.19 mmol) was added into a stirred solution of 308 mg (1.14 mmol) of $TeCl_4$ in 6.0 mL of THF. The reaction mixture was further mixed for 1 h. During this time a black precipitate was obtained. It was removed by filtration, and the solvent was evaporated from the green filtrate. The remaining mixture of pale green crystals and dark oil was washed with diethyl ether. Yield: 322 mg (63%, based on triphenylphosphine.) Anal. Calcd for $C_{72}H_{62}O_4P_4Te_2Cl_{10}$ (**1**): C 50.13, H 3.62. Found: C 49.82, H 3.45.

Reaction of $TeBr_4$ with Ph_3P. $TeBr_4$ (499 mg; 1.12 mmol) was dissolved in 10.0 mL of THF, and 295 mg (1.13 mmol) of Ph_3P was added to the resulting solution. The mixture turned yellow, and a black precipitate was formed. After 1 h the reaction mixture was filtered, the solvent was evaporated from the reddish filtrate, and some hexane was added. The addition of hexane resulted in the formation of orange crystals and reddish brown oil. The crystals

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Table 1. Details of the Structure Determination of $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$ (**1**), $\{(Ph_3PO)_2H\}_2[Te_2Br_{10}]$ (**2**), $\{(Ph_3PO)_3H_3O\}_2[TeI_6]$ (**4**), $(CH_2)_4TeI_2$ (**5b**), and $(CH_2)_4Te_2I_6$ (**6**a and **6b**)[a]

	1	**2**	**4**	**5b**	**6a**	**6b**
formula	$C_{36}H_{31}O_2P_2Cl_5Te$	$C_{36}H_{31}O_2P_2Br_5Te$	$C_{108}H_{96}O_8P_6TeI_6$	$C_8H_{16}Te_2I_4$	$C_4H_8Te_2I_6$	$C_4H_8Te_2I_6$
fw	862.40	1084.70	2596.67	875.01	1072.70	1072.70
crystal system	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$Pba2$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	11.637(2)	11.837(2)	18.445(4)	9.860(5)	9.387(2)	9.589(2)
b, Å	12.429(3)	12.509(3)	32.344(7)	18.785(5)	9.593(2)	19.365(4)
c, Å	14.026(3)	14.069(3)	17.452(4)	9.639(5)	19.369(4)	9.616(2)
α, deg	72.11(3)	71.90(3)				
β, deg	72.12(3)	72.50(3)		93.972(5)	94.46(3)	98.64(3)
γ, deg	84.09(3)	83.07(3)				
V	1837.2(6)	1887.5(7)	10412(4)	1781(1)	1738.7(6)	1765.2(6)
Z	2	2	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.559	1.909	1.657	3.263	4.098	4.036
μ(Mo Kα), mm^{-1}	1.292	6.196	2.211	10.183	13.976	13.767
$F(000)$	860	1040	5072	1520	1816	1816
crystal size (mm^3)	0.30 × 0.30 × 0.15	0.40 × 0.20 × 0.20	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.15 × 0.12	0.25 × 0.15 × 0.08
θ range (deg)	1.72−26.00	2.31−26.00	2.48−25.00	2.07−25.99	2.18−25.99	2.99−24.99
reflns collected	13227	23344	42516	23526	27050	19133
unique reflns	6859	6942	15266	3492	3416	3085
R_{int}	0.0596	0.0406	0.0689	0.0837	0.0513	0.0630
R_1[b]	0.0452	0.0277	0.0473	0.0290	0.0286	0.0544
wR_2[c]	0.1254	0.0753	0.0892	0.0705	0.0708	0.1437
GOF on F^2	1.013	0.985	0.979	1.065	1.163	1.239

[a] $T = 150(2)$ K. [b] $R_1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ $[I \geq 2\sigma(I)]$. [c] $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ [all data].

were washed with acetone. Yield: 217 mg (35%). Anal. Calcd for $C_{72}H_{62}O_4P_4Te_2Br_{10}$ (**2**): C 39.86, H 2.88. Found: C 39.58, H 2.55.

Reaction of TeI_4 with Ph_3P. The reaction of TeI_4 (705 mg; 1.11 mmol) and Ph_3P (291 mg; 1.11 mmol) was carried out similarly to those of other tellurium tetrahalides. A mixture of three compounds was obtained. $\{(Ph_3PO)_3H_3O\}_2[TeI_6]$ (**4**) is the most abundant product, and $(CH_2)_4TeI_2$ (**5**) and $(CH_2)_4Te_2I_6$ (**6**) are formed in small amounts. **5** and **6** crystallize as two different crystal modifications (**5a**, **5b** and **6a**, **6b**). The separation and isolation of the three products was attempted by extraction with different solvents. Crystals for X-ray structure determination were obtained in these experiments, but the complete isolation of the products was not successful. **4**, **5b**, and **6b** were obtained from toluene and THF, **5a** was obtained from hexane and diethyl ether, and **6a** was obtained from toluene.

X-ray Crystallography. Diffraction data for **1**−**6** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data and the details of the structure determinations are given in Table 1. All structures were solved by direct methods using SHELXS-97[11] and refined using SHELXL-97.[12] After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in the aromatic rings of **1**, **2**, and **4** (C−H = 0.95 Å), and in the methylene groups of **5** and **6** (C−H = 0.98 Å). In the final refinement the calculated hydrogen atoms were riding with the carbon atom they were bonded to. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon atom.

The bridging hydrogen atoms in the dimeric cations $\{(Ph_3PO)_2H\}^+$ of **1** and **2** could be located and refined in the conventional way by using a fixed isotropic thermal parameter of 0.04. The hydrogen atoms of the oxonium ion in the trimeric cation $\{(Ph_3PO)_3(OH_3)\}^+$ of **4**, however, could not be observed in the final difference Fourier synthesis. The scattering factors for the neutral atoms were those incorporated with the programs.

Results and Discussion

General. The reaction of PPh_3 and $TeCl_4$ in air affords $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$ (**1**) in good yield. The precipitation of elemental tellurium was also observed in the course of the reaction. The ^{125}Te NMR spectrum of $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$ (**1**) shows one resonance at 1540 ppm. It is in agreement with the previously reported value of $[Te_2Cl_{10}]^{2-}$ at 1570 ppm that was recorded in acetonitrile for $[Ni(NCMe)_6][Te_2Cl_{10}]$.[13] The $^{31}P\{^1H\}$ spectrum of **1** displayed one resonance in the region 37−47 ppm due to $\{(Ph_3PO)_2H\}^+$. This chemical shift is strongly dependent on the concentration.

Analogously, the reaction of PPh_3 and $TeBr_4$ yields $\{(Ph_3PO)_2H\}_2[Te_2Br_{10}]$ (**2**). In addition, $Ph_3PO(CH_2)_4TeBr_4$ (**3**) is also formed in this reaction, as we have recently reported.[10] It is interesting to note that the yields of **2** and **3** seem to be dependent on each other. With increasing amount of **3**, the yield of **2** becomes smaller.[14] A typical isolated yield of **2** was 35%, and that of **3** was 13−50% depending on the reaction time.[10]

$[(Ph_3PO)_2H]_2[Te_2Br_{10}]$ (**2**) exhibits a ^{125}Te NMR resonance due to $[Te_2Br_{10}]^{2-}$ at 1200 ppm. The resonance of $Ph_3PO(CH_2)_4TeBr_4$ was observed at 1210 in THF (1225 ppm in acetonitrile[10]). The assignment was carried out by recording the spectra from solutions obtained by redissolving the pure crystalline products. In the $^{31}P\{^1H\}$ spectrum of **2**, a concentration dependent resonance due to $\{(Ph_3PO)_2H\}^+$ was observed in the region 36−47 ppm. The resonance at 62.6 ppm is due to **3**.

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(14) The relative concentrations of **2** and **3** in the reaction solution were monitored by ^{31}P NMR spectroscopy.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$ (**1**) and $\{(Ph_3PO)_2H\}_2[Te_2Br_{10}]$ (**2**)

	1	**2**		**1**	**2**
Te(1)−X(1)	2.457(1)	2.6467(11)	P(1)−O(1)	1.530(3)	1.523(2)
Te(1)−X(2)	2.332(1)	2.5541(7)	P(2)−O(2)	1.523(3)	1.520(2)
Te(1)−X(3)	2.472(1)	2.6067(8)	O(1)−H(1)	1.092(2)	1.024(2)
Te(1)−X(4)	2.504(1)	2.6744(11)	O(2)−H(2)	0.886(3)	0.966(2)
Te(1)−X(5)	2.609(1)	2.8606(9)			
Te(1)−X(5)[a]	3.071(1)	2.9683(8)			
X(1)−Te(1)−X(2)	87.95(5)	89.90(3)	X(3)−Te(1)−X(5)	179.25(4)	175.39(1)
X(1)−Te(1)−X(3)	90.05(5)	90.47(3)	X(3)−Te(1)−X(5)[a]	95.22(5)	88.85(3)
X(1)−Te(1)−X(4)	176.20(4)	177.17(1)	X(4)−Te(1)−X(5)	89.02(5)	88.42(3)
X(1)−Te(1)−X(5)	89.67(5)	88.76(3)	X(4)−Te(1)−X(5)[a]	94.83(5)	92.05(3)
X(1)−Te(1)−X(5)[a]	88.62(5)	87.74(3)	X(5)−Te(1)−X(5)[a]	85.47(4)	86.58(3)
X(2)−Te(1)−X(3)	89.18(5)	91.64(3)	Te(1)−X(5)−Te(1)[a]	94.53(4)	93.42(3)
X(2)−Te(1)−X(4)	88.49(5)	90.28(3)	O(1)−H(1)−O(2)	167.7(2)	163.7(2)
X(2)−Te(1)−X(5)	90.12(5)	92.90(3)	O(2)−H(2)−O(1)	170.0(2)	166.9(2)
X(2)−Te(1)−X(5)[a]	174.43(3)	177.60(1)	H(1)−O(2)−P(2)	128.3(2)	125.2(2)
X(3)−Te(1)−X(4)	91.22(5)	92.34(3)	H(2)−O(1)−P(1)	129.8(2)	127.2(2)

[a] Symmetry operation: $-x + 1, -y, -z + 1$.

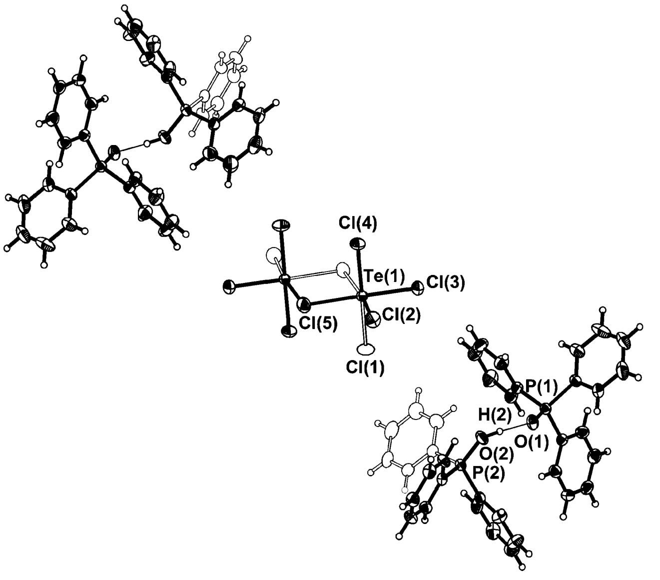

Figure 1. The crystal structure of $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$ (**1**) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at the 50% probability level. $\{(Ph_3PO)_2H\}_2[Te_2Br_{10}]$ (**2**) is isostructural with **1**.

The reaction of TeI_4 and PPh_3 seems to be somewhat more complicated. After the precipitation of elemental tellurium, $\{(Ph_3PO)_3H_3O\}_2[TeI_6]$ (**4**) was obtained together with small amounts of $(CH_2)_4TeI_2$ (**5**) and $(CH_2)_4Te_2I_6$ (**6**). Only one resonance at 870 ppm was observed in the ^{125}Te NMR spectrum of the reaction mixture. It was assigned to $[TeI_6]^{2-}$. The concentrations of **5** and **6** were probably too low for the detection of the ^{125}Te resonances.[15] Like in the case of other tetrahalides, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of TeI_4 and PPh_3 displayed a concentration dependent resonance at 29−39 ppm that was assigned to the $\{(Ph_3PO)_2H_3O\}^+$ cation on the basis of the X-ray structure.

$\{(Ph_3PO)_2H\}_2[Te_2X_{10}]$ (X = Cl, Br). $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$ (**1**) and $\{(Ph_3PO)_2H\}_2[Te_2Br_{10}]$ (**2**) are isomorphic. The crystal structure of **1** with the atomic numbering scheme is shown in Figure 1. That of **2** is identical. The selected bond lengths and angles are shown in Table 2.

The structures of **1** and **2** consist of discrete $[Te_2X_{10}]^{2-}$ (X = Cl, Br) anions and $\{(Ph_3PO)_2H\}^+$ cations. The anions are composed of two slightly distorted TeX_6 octahedra sharing an edge. The terminal Te−X bonds lengths are in the ranges 2.332(1)−2.504(1) Å and 2.5541(7)−2.6744(11) Å for **1** and **2**, respectively. The bridging bonds lengths in **1** are 2.609(9) and 3.071(1) Å. Those in **2** are 2.8606(9) and 2.9683(8) Å. The bond parameter data are expectedly in accord with those reported previously for various salts containing $[Te_2X_{10}]^{2-}$ anions.[13,17] Krebs et al.[17a] have noted the decreasing stereochemical influence of the tellurium lone pair, as the halogen becomes heavier. As a consequence, the bonding arrangement involving the bridging halido ligands is more symmetric, and the relative lengths of the bridging Te−X bonds compared to those of the terminal bonds are smaller in **2** than in **1** (see Table 2).

The $\{(Ph_3PO)_2H\}^+$ cation consists of a Ph_3POH^+ cation and a Ph_3PO molecule that are linked together by a strong hydrogen bond [the O(1)···O(2) distances are 2.399 Å and 2.404 Å in **1** and **2**, respectively].[18] The disordered hydrogen atom lies in two alternative locations with the site occupation factors being 50% in both cases. One of the positions is at the single bond distance from O(1), and the other position is at that from O(2) (see Table 2). Only one of the two alternative positions has been shown in Figure 1. The P−O bond lengths are 1.530(3) and 1.523(3) Å in **1** and 1.523(2) and 1.520(2) Å in **2**. They are somewhat longer than the P−O bonds in $Ph_3PO\cdot H_2O$ [1.483(10)−1.485(2) Å] that does not show as strong hydrogen bonding.[20]

$\{(Ph_3PO)_3OH_3\}_2[TeI_6]$ (4). The crystal structure of $\{(Ph_3PO)_3OH_3\}_2[TeI_6]$ (**4**) with the atomic numbering scheme is

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(15) The ^{125}Te chemical shift of $(CH_2)_4TeI_2$ (**5**) has been reported at 929.2 ppm in DMSO-d_6[16a] and 782 ppm in $CDCl_3$.[16b]

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(17) (a) Krebs, B.; Büschner, K. *Z. Anorg. Allg. Chem.* **1980**, *463*, 56. (b) Hauge, S.; Marøy, K. *Acta Chem. Scand.* **1998**, *52*, 445. (c) Hauge, S.; Marøy, K. *Acta Chem. Scand.* **1999**, *53*, 992. (d) James, M. A.; Knop, O.; Cameron, T. S. *Can. J. Chem.* **1992**, *70*, 1795. (e) Hauge, S.; Marøy, K. *Acta Chem. Scand.* **1996**, *50*, 1095. (f) Krebs, B.; Paulat, V. *Z. Natursforsch.* **1979**, *34B*, 900. (g) Beck, J.; Hormel, A.; Koch, M. *Eur. J. Inorg. Chem.* **2002**, 2271.

(18) The $\{(Ph_3PO)_2H\}^+$ cation has been characterized on few occasions and has been shown to involve a strong hydrogen bond.[19]

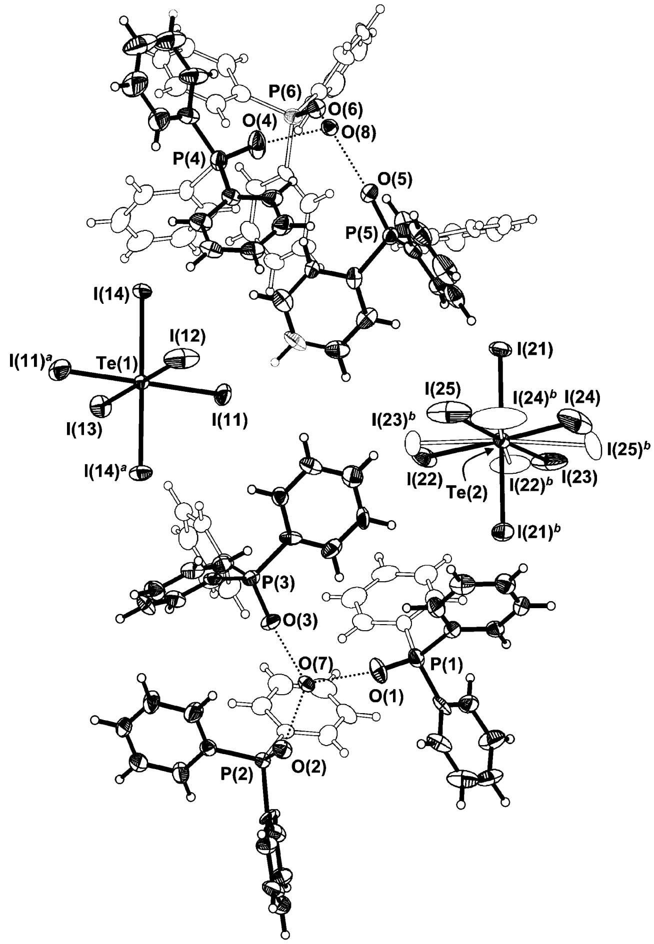

Figure 2. The crystal structure of $\{(Ph_3PO)_3H_3O\}_2[TeI_6]$ (**4**) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at the 50% probability level. The disorder of the other anion is displayed.

shown in Figure 2. The bond lengths and angles are presented in Table 3.

The lattice is composed of discrete $[TeI_6]^{2-}$ anions and $\{(Ph_3PO)_3OH_3\}_2\}^+$ cations. The tellurium atoms in both of the two crystallographically independent anions lie in the special positions. The $[TeI_6]^{2-}$ octahedron around Te(1) is composed of four independent iodine atoms [I(11)−I(14)], the octahedral coordination being completed by symmetry (see Figure 2). The octahedron involving Te(2) analogously contains independent iodine atoms I(21)−I(25), the octahedron being completed by symmetry-equivalent atom I(21)^b (the symmetry operation b is $-x + 1, -y + 1, z$). The $[TeI_6]^{2-}$ octahedron involving Te(2) is disordered. The symmetry operation $-x + 1, -y + 1, z$ for the atoms I(22)−I(25) creates another square-planar TeI_4 fragment that is rotated approximately 30° about the common I(21)−Te(2)−I(21)^b axis. The site occupation factors of iodine atoms I(22)−I(25) and their symmetry-related counterparts are 50%.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $\{(Ph_3PO)_3H_3O\}_2[TeI_6]$ (**4**)

Te(1)−I(11)	2.9136(6)	P(3)−O(3)	1.510(5)
Te(1)−I(12)	2.9002(12)	P(4)−O(4)	1.503(6)
Te(1)−I(13)	2.9485(11)	P(5)−O(5)	1.493(6)
Te(1)−I(14)	2.9368(5)	P(6)−O(6)	1.491(5)
Te(2)−I(21)	2.9427(5)	O(7)···O(1)	2.464(7)
Te(2)−I(22)	2.9400(16)	O(7)···O(2)	2.469(7)
Te(2)−I(23)	2.8558(17)	O(7)···O(3)	2.458(7)
Te(2)−I(24)	2.8787(17)	O(8)···O(4)	2.452(8)
Te(2)−I(25)	2.937318)	O(8)···O(5)	2.463(7)
P(1)−O(1)	1.503(6)	O(8)···O(6)	2.484(7)
P(2)−O(2)	1.499(5)		
I(11)−Te(1)−I(11)^a	179.70(5)	I(21)−Te(2)−I(22)	88.64(4)
I(11)−Te(1)−I(12)	90.15(2)	I(21)−Te(2)−I(23)	89.59(4)
I(11)−Te(1)−I(13)	89.85(2)	I(21)−Te(2)−I(24)	92.27(4)
I(11)−Te(1)−I(14)	90.08(2)	I(21)−Te(2)−I(25)	94.98(4)
I(11)−Te(1)−I(14)^a	89.92(2)	I(22)−Te(2)−I(23)	90.02(10)
I(12)−Te(1)−I(11)^a	90.15(2)	I(22)−Te(2)−I(24)	176.74(10)
I(12)−Te(1)−I(13)	180.00(5)	I(22)−Te(2)−I(25)	87.42(8)
I(12)−Te(1)−I(14)	90.16(2)	I(22)−Te(2)−I(21)^b	91.00(4)
I(12)−Te(1)−I(14)^a	90.15(2)	I(23)−Te(2)−I(24)	93.12(9)
I(13)−Te(1)−I(14)	89.84(2)	I(23)−Te(2)−I(25)	174.71(7)
I(13)−Te(1)−I(14)^a	89.84(2)	I(23)−Te(2)−I(21)^b	90.19(4)
I(13)−Te(1)−I(11)^a	89.85(2)	I(24)−Te(2)−I(25)	89.38(12)
I(14)−Te(1)−I(14)^a	179.68(5)	I(24)−Te(2)−I(21)^b	88.10(4)
I(11)^a−Te(1)−I(14)^a	90.08(2)	I(25)−Te(2)−I(21)^b	85.23(4)
I(21)−Te(2)−I(21)^b	179.58(4)		

^{a} Symmetry operation: $-x + 2, -y + 1, z$. ^{b} Symmetry operation: $-x + 1, -y + 1, z$.

The Te−I bond lengths span a narrow range of 2.867(1)−2.949(1) Å, and the bond angles depict only slightly distorted octahedra (see Table 3 and Figure 2). These values are quite typical for $[TeI_6]^{2-}$, as exemplified by $(Et_4N)_2[TeI_6]$ [2.945(10)−2.948(6) Å][21] and $H_2TeI_6{\cdot}8H_2O$ [2.938(1)−2.942(2) Å].[22] It has been suggested that in the case of electronegative monatomic ligands the almost ideal octahedral coordination geometry of the 14-electron AX_6E species can be explained by interligand repulsions and that the lone electron pair of tellurium resides in the stereochemically inactive 6s orbital (for a more detailed discussion, see ref 1).

The three Ph_3PO molecules in the cation are linked together by the H_3O^+ ion. While the three hydrogen atoms involving the oxonium ion could not be located, the three short O···O distances involving both O(7) and O(8) of 2.452(8)−2.484(7) Å imply strong hydrogen bonds (see Table 3) like in the case of the $\{(Ph_3PO)_2H\}^+$ cation in **1** and **2** or in the analogous cation $\{(Ph_3PO)_2(OH_3)\}^+$ found in $\{(Ph_3PO)_2(OH_3)\}_2[AuCl_4]$.[23] The existence of $\{(Ph_3PO)_3(OH_3)\}^+$ has also been reported previously.[24]

$C_4H_8TeI_2$ (5). It turned out that the small amounts of **5** that are formed in the reaction of TeI_4 and PPh_3 in THF can be crystallized as two polymorphs, **5a** and **5b**, depending

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(19) (a) Jones, P. G.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1978**, *34*, 1353. (b) Antipin, M. Yu.; Kalinin, A. E.; Struchkov, Yu. T.; Matrosov, E. J.; Kabachnik, M. I. *Kristallografiya* **1980**, *25*, 514. (c) Arens, G.; Sundermeyer, W.; Pritzkow, H. *Chem. Ber.* **1986**, *119*, 3631. (d) Carmalt, C. J.; Norman, N. C.; Farrugia, L. J. *Polyhedron* **1993**, *12*, 2081. (e) Lane, H. P.; Godfrey, S. M.; McAuliffe, C. A; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1994**, 3249. (f) De Aurajo, M. P.; Queiroz, S. L.; Alzir, A.; Panepuzzi, E. H.; Oliva, G.; Castellano, E. E. *Transition Met. Chem.* **2002**, *27*, 110.

(20) (a) Baures, P. W.; Silverton, J. V. *Acta Crystallogr., Sect. C* **1990**, *46*, 715. (b) Baures, P. W. *Acta Crystallogr., Sect. C* **1991**, *47*, 2715.

(21) Srivastava, P. C.; Schmidt, H.-G.; Roesky, H. W. *Z. Naturforsch.* **1995**, *50*, 695.

(22) Katryniok, D.; Kniep, R.; Mootz, D. *Z. Anorg. Allg. Chem.* **1980**, *461*, 96.

(23) Jiang, D.-H.; Yang, Y.-H.; Gao, Z.-L.; Sun, S.-X.; Shen, J.-L. *Acta Chim. Sin.* **1982**, *50*, 1091.

(24) Auerswald, T. H.; Engelhardt, C.; Zentralinst, G. *J. Prakt. Chem.* **1979**, *321*, 835.

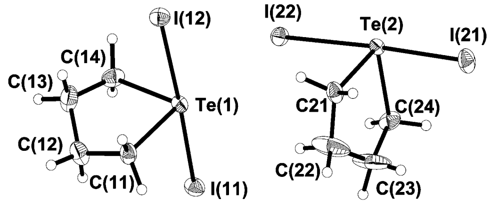

Figure 3. The molecular structures of $C_4H_8TeI_2$ (**5b**) displaying the two molecules in the asymmetric unit. The thermal ellipsoids have been drawn at the 50% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $(CH_2)_4TeI_2$ (**5b**)

Te(1)−I(11)	2.866 (2)	Te(2)−I(21)	2.8442(9)
Te(1)−I(12)	3.003(2)	Te(2)−I(22)	3.0140(9)
Te(1)−C(11)	2.153(6)	Te(2)−C(21)	2.162(6)
Te(1)−C(14)	2.163(6)	Te(2)−C(24)	2.160(6)
I(11)−Te(1)−I(12)	177.72(2)	I(21)−Te(2)−I(22)	177.21(2)
I(11)−Te(1)−C(11)	89.0(2)	I(21)−Te(2)−C(21)	90.6(2)
I(11)−Te(1)−C(14)	91.3(2)	I(21)−Te(2)−C(24)	89.9(2)
I(12)−Te(1)−C(11)	90.0(2)	I(22)−Te(2)−C(21)	86.8(2)
I(12)−Te(1)−C(14)	86.6(2)	I(22)−Te(2)−C(24)	88.8(2)
C(11)−Te(1)−C(14)	84.7(2)	C(21)−Te(2)−C(24)	84.9(2)

on the crystallizing conditions. Orange-red crystals of **5a** were obtained from hexane and diethyl ether, and those of **5b** exhibiting deeper red color were obtained from toluene and THF. It has been reported already in the 1930s that $C_4H_8TeI_2$ (**5**) can exist as two different polymorphs,[25] but the crystal structure of only **5a** has previously been known.[26]

The molecular structure of **5b** together with the atomic numbering scheme is shown in Figure 3, and the bond lengths and angles are presented in Table 4. Like in **5a**,[16b,27] the asymmetric unit in **5b** also consists of two crystallographically independent $C_4H_8TeI_2$ molecules. In both cases the geometries of individual molecules are quite similar. The coordination polyhedron of tellurium is based on a trigonal bipyramid with two iodine atoms occupying the axial positions and the two carbon atoms lying in two equatorial positions. The tellurium lone pair occupies the third equatorial position. As a consequence, the I−Te−I fragment has slightly deviated from linearity, the iodine atoms leaning away from the lone pair [the I−Te−I bond angles in the two independent molecules are 177.72(2)° and 177.21(2)°]. Similarly, the C−Te−C bond angles are rather small [84.7(2)° and 84.9(2)°]. The Te−I bond lengths in **5b** are in the range 2.8442(9)−3.0140(9) Å, and the Te−C bond lengths are in the range 2.153(6)−2.163(6) Å. The corresponding values in **5a** are 2.875(1)−2.942(1) Å and 2.155(7)−2.163(6) Å, respectively (see Supporting Information). There are a number of related R_2TeI_2 species[28] for which the geometry of the tellurium environment is similar. In all species the Te−I bonds are somewhat longer than the single bond, as expected for the axial bonds in trigonal-bipyramidal geometry.[29]

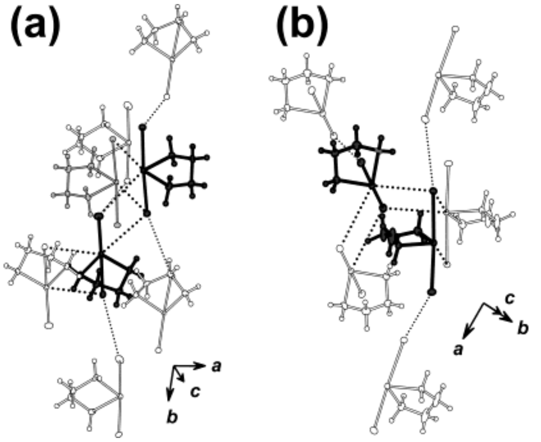

Figure 4. The packing of the molecules in (a) **5a** and (b) **5b**.

The $C_4H_8TeI_2$ molecules in both **5a** and **5b** are linked together by Te···I and I···I secondary bonding interactions. The short Te···I intermolecular contacts in **5a** span a range of 3.6483(8)−3.948(1) Å and those in **5b** the range 3.626(2)−3.937(1) Å. These secondary bonds expand the coordination polyhedra of tellurium in both cases to an AX_4Y_2E (X = primary bond, Y = secondary bond, E = lone pair) octahedron and are shown in Figure 4. The differences in the packing of the $C_4H_8TeI_2$ molecules in the two lattices are also apparent in Figure 4. The short I···I contacts are 3.916(1) and 3.982(1) Å for **5a**, and 3.821(2) and 3.975(1) Å for **5b**. The complete network of Te···I and I···I intermolecular interactions in both **5a** and **5b** is also shown in Figure 4.

There is a qualitative correlation between the lengths of the Te−I bonds in R_2TeI_2 and the strength of the secondary bonding interactions (see Supporting Information),[28] though the bond lengths are also affected by the organic group. McCullough et al.[28l] have correlated the secondary bonds with the color of the crystalline material. In absence of I···I close contacts the crystals appear orange. With increasing influence of the I···I interactions the color becomes deeper red and tends toward purple and black. The slight change of color from orange-red in **5a** to deeper red in **5b** is consistent

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(25) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1931**, 180.

(26) Both previous crystal structure determinations of **5a** have been carried out at room temperature.[16b, 27] Since the X-ray data of **5b** were collected at 150 K, we have also redetermined the crystal structure of **5a** at low temperature in order to facilitate the direct comparison of bond parameters between the two forms (see Supporting Information).

(27) Srivastava, P. C.; Bajpai, S.; Lath, R.; Butcher, R. J. *J. Organomet. Chem.* **2000**, *608*, 96.

(28) (a) Chao, G. Y.; McCullough, J. D. *Acta Crystallogr.* **1962**, *15*, 887. (b) Knobler, C.; McCullough, J. D.; Hope, H. *Inorg. Chem* **1970**, *9*, 797. (c) Chan, L. Y. Y.; Einstein, F. W. B. *J. Chem. Soc., Dalton Trans.* **1972**, 316. (d) Hope, H.; Knobler, C.; McCullough, J. D. *Inorg. Chem.* **1973**, *12*, 2665. (e) McCullough, J. D. *Inorg. Chem.* **1973**, *12*, 2669. (f) McCullough; J. D. *Inorg. Chem.* **1975**, *14*, 1142. (g) Ziolo, R. F.; Gunther, W. H. H. *J. Organomet. Chem.* **1978**, *146*, 245. (h) Knobler, C.; Ziolo, R. F. *J. Organomet. Chem.* **1979**, *178*, 423. (i) Pritzkow, H. *Inorg. Chem.* **1979**, *18*, 311. (j) Singh, H. B.; McWhinnie, W. R.; Hamor, T. A. Jones, R. H. *J. Chem. Soc., Dalton Trans.* **1984**, 23. (k) Alcock, N. W.; Harrison, W. D. *J. Chem. Soc., Dalton Trans.* **1984**, 869. (l) McCullough, J. D.; Knobler, C.; Ziolo, R. F. *Inorg. Chem.* **1985**, *24*, 1814. (m) Hu, N.-H.; Jin, Z.-S.; Li, Z.-S. *Acta Crystallogr., Sect. C.* **1991**, *47*, 1858. (n) Al-Rubaie, A. Z.; Uemura, S.; Masuda, H. *J. Organomet. Chem.* **1991**, *410*, 309. (o) Morkved, E. H.; Faccin, G.; Manfrotto, D.; Kjosen, H.; Becker, J. Y.; Shapiro, L.; Ellern, L.; Bernstein, J.; Khodorkovsky, V. *J. Mater. Chem.* **1997**, *7*, 1697. (p) Farran, J.; Alvarez-Larena, A.; Capparelli, M. V.; Piniella, J. F.; Germain, G.; Torres-Castellanos, L. *Acta Crystallogr., Sect. C* **1998**, *54*, 995. (q) Schulz Lang, E.; Fernandes, R. M., Jr.; Silveira, E. T.; Abram, U.; Vazquez-Lopez, E. M. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1401. (r) Asahara, M.; Tanaka, M. Erabi, T. Wada, M. *J. Chem. Soc., Dalton Trans.* **2000**, 3493.

(29) The sum of the covalent radii of tellurium and iodine is 2.70 Å.[30]

(30) Emsley, J. *The Elements*, 3rd ed.; Clarendon Press: Oxford, 1998.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in $(CH_2)_4Te_2I_6$ (**6a** and **6b**)

	6a	**6b**		**6a**	**6b**
Te(1)−I(11)	2.7338(8)	2.755(2)	Te(2)−I(22)	2.7982(8)	2.767(1)
Te(1)−C(11)	2.141(8)	2.171(14)	Te(2)−I(23)	2.7982(8)	2.777(1)
Te(1)−C(14)	2.152(9)	2.154(18)	Te(2)−I(24)	2.8743(8)	2.783(1)
Te(1)−I(21)	3.3270(9)	3.261(2)	Te(2)−I(25)	3.1514(9)	3.197(1)
Te(2)−I(21)	3.0270(8)	3.328(1)	Te(2)−I(25)[a]	3.1579(9)	3.249(1)
I(11)−Te(1)−C(11)	96.8(2)	95.0(5)	I(21)−Te(2)−I(25)[a]	87.10(3)	92.67(3)
I(11)−Te(1)−C(14)	93.3(2)	93.2(5)	I(22)−Te(2)−I(23)	95.35(2)	96.17(4)
C(11)−Te(1)−C(14)	83.7(4)	84.1(6)	I(22)−Te(2)−I(24)	92.56(3)	92.78(4)
I(11)−Te(1)−I(21)	173.83(2)	169.65(5)	I(22)−Te(2)−I(25)	86.55(2)	89.46(4)
I(21)−Te(1)−C(11)	88.3(2)	94.7(5)	I(22)−Te(2)−I(25)[a]	172.78(2)	177.74(4)
I(21)−Te(1)−C(14)	83.8(2)	84.1(5)	I(23)−Te(2)−I(24)	91.36(2)	93.15(5)
Te(1)−I(21)−Te(2)	124.61(2)	95.22(4)	I(23)−Te(2)−I(25)	177.10(2)	174.09(4)
I(21)−Te(2)−I(22)	92.86(4)	86.30(4)	I(23)−Te(2)−I(25)[a]	91.86(2)	85.87(3)
I(21)−Te(2)−I(23)	87.41(2)	91.78(5)	I(24)−Te(2)−I(25)	86.36(2)	84.76(5)
I(21)−Te(2)−I(24)	174.53(2)	175.06(4)	I(24)−Te(2)−I(25)[a]	87.62(3)	88.08(3)
I(21)−Te(2)−I(25)	94.70(2)	90.37(4)	I(25)−Te(2)−I(25)[a]	86.25(2)	88.53(3)

[a] Symmetry operations: **6a** $-x + 1, -y + 2, -z + 1$; **6b** $-x + 1, -y + 1, -z + 2$.

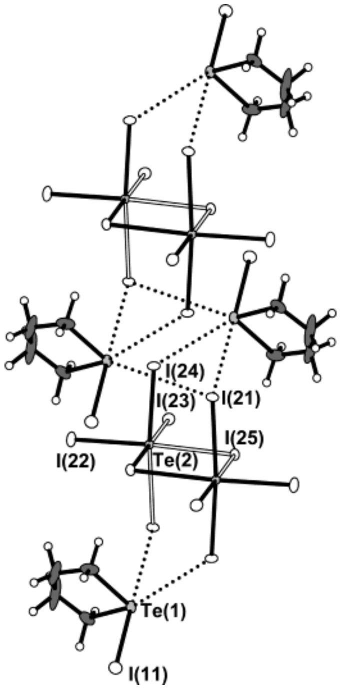

Figure 5. The crystal structure of **6a**. The compound can be formulated as $\{C_4H_8TeI^+\}_2[Te_2I_{10}{}^{2-}]$. The thermal ellipsoids have been drawn at the 50% probability level.

with this scheme, since the I⋯I contacts are shorter in **5b** than in **5a**. These colors are consistent with the initial report of Morgan and Burstall.[25]

$C_4H_8Te_2I_6$ (6). There are two distinct forms of $C_4H_8Te_2I_6$ (**6a** and **6b**) that are formed depending on the crystallizing conditions. Though both compounds can formally be considered as 1:1 adducts of TeI_4 and $C_4H_8TeI_2$, their structures differ considerably from that of a simple straightforward adduct. Though superficially similar, the structures of **6a** and **6b** also differ from each other.

The crystal structure of **6a** is presented in Figure 5 together with the atomic numbering scheme. The most important bond lengths and angles are presented in Table 5. The compound can be formulated as $\{C_4H_8TeI^+\}_2[Te_2I_{10}{}^{2-}]$. The bond lengths and angles in the $[Te_2I_{10}]^{2-}$ anion are virtually identical to those found in $\{(C_7H_7)(C_2H_5)_3N^+\}_2[Te_2I_{10}{}^{2-}]$.[5] The Te(1)−I(11) bond of 2.7338(8) Å found in the $\{C_4H_8TeI\}^+$ cation is shorter than the Te−I bonds in **5a** or **5b** and is close to the single bond length,[29] as expected for the 8-electron AX_3E cation. The I−Te−C bond angles of 93.3(2)° and 96.8(2)° and the C−Te−C bond angle of 83.7(4)° are also consistent with the three-coordinate telluronium cation. The structural differences in **5** and the cation in **6a** can be compared to those observed in Cl_2TeSeN_2S[31] and $(ClTeTeN_2S^+)(Cl^-)$.[32] The axial Te−Cl bond lengths in the former are 2.403(2) and 2.782(2) Å, and the coordination environment of tellurium is a trigonal bipyramid [Cl−Te−Cl = 173.6(1)°].[31] In the cationic species, the Te−Cl bond length of 2.336(4) Å is shorter and the coordination is based on the tetrahedron [the bond angles around tellurium span 88.7(4)−101.1(1)°].[32]

The Te(1)−I(21) distance of 3.3270(9) Å in **6a** is very long for covalent interaction. It is comparable to the $I_3Te^+\cdots(\mu\text{-}I^-)$ distances of 3.187−3.343 Å found in γ- and δ-TeI_4[6,7] and somewhat shorter than the $R_3Te^+\cdots I^-$ distances, for instance, in Me_3TeI[33] and Et_3TeI.[34]

The cations and anions in **6a** are further linked together by weaker Te(1)⋯I(21) and Te(1)⋯I(24) contacts of 3.937(1) and 3.887(1) Å, respectively (see Figure 5). There are also several I⋯I contacts between the $[Te_2I_{10}]^{2-}$ anions in the range 3.609(1)−3.900(1) Å.

The formal presentation of **6b** is somewhat more complex. The crystal structure is shown in Figure 6 together with the numbering of the atoms. The bond parameters are presented in Table 5. The interatomic distances in the Te_2I_{10} fragment differ considerably from the corresponding distances in **6a** and from those in $\{(C_7H_7)(C_2H_5)_3N^+\}_2[Te_2I_{10}{}^{2-}]$[5] and do not imply the presence of a discrete $[Te_2I_{10}]^{2-}$ anion. Comparing all bond parameters in **6b** with those found in γ- and δ-TeI_4,[6,7] the following inferences can be made.

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(31) Haas, A.; Kasparowski, J.; Pryka, M. *Chem. Ber.* **1992**, *125*, 789.

(32) (a) Haas, A.; Kasparowski, J.; Pryka, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1144. (b) Haas, A.; Pryka, M.; Schäfers, M. *Chem. Ber.* **1994**, *127*, 1865.

(33) (a) Collins, M. J.; Ripmeester, J. A.; Sawyer, J. F. *J. Am. Chem. Soc.* **1988**, *110*, 8583. (b) Zhou, Z.-L.; Huang, Y.-Z.; Tang, Y.; Chen, Z.-H.; Shi, L.-P-; Jin, X.-L.; Yang, Q.-C. *Organometallics* **1994**, *13*, 1575.

(34) Chadha, R. K.; Drake, J. E. *J. Organomet. Chem.* **1986**, *299*, 331.

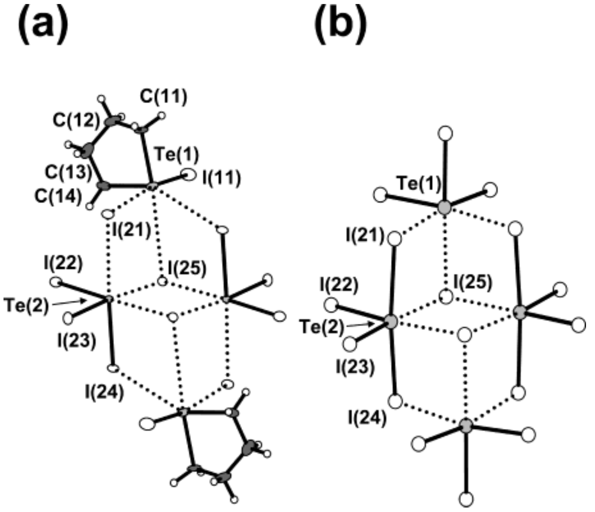

Figure 6. (a) The crystal structure of **6b**. The compound can be formulated as $\{C_4H_8TeI^+\}_2(TeI_3^+)_2(I^-)_4$. The thermal ellipsoids have been drawn at the 50% probability level. (b) The crystal structure of δ-TeI_4 (adapted from the data taken from ref 7).

Table 6. The Comparison of Te−I Distances in $(CH_2)_4Te_2I_6$ (**6b**) and in γ- and δ-TeI_4[a]

	6b	γ-TeI_4 [b]	δ-TeI_4 [c]
Te(1)−I(21)	3.261(2)	3.252, 3.337	3.231
Te(1)−I(24)	3.900(2)	3.265, 3.343	3.279
Te(1)−I(25)	3.676(2)	3.187, 3.207	3.200, 3.214
Te(2)−I(21)	3.328(1)	2.921, 3.035	2.933
Te(2)−I(22)	2.767(1)	2.743, 2.751	2.766
Te(2)−I(23)	2.777(1)	2.753, 2.785	2.770
Te(2)−I(24)	2.783(1)	2.897, 3.002	2.989
Te(2)−I(25)	3.197(1), 3.249(1)	3.228−3.257	3.241, 3.247

[a] The tellurium and iodine atoms in γ- and δ-TeI_4 have been renumbered to correspond to the numbering of **6b** (see Figure 5). [b] Reference 6. [c] Reference 7.

It can be seen from Figure 6 that the structural framework of **6b** is very similar to that of the tetramers in γ- and δ-TeI_4 [6,7] implying the structure type **II**. Krebs and Ahlers[1] have formulated the $(TeI_4)_4$ tetramer as $(TeI_3^+)_2(I^-)_2(TeI_4)_2$ based on the interatomic distances. Using the same arguments, **6b** can be considered as $\{C_4H_8TeI^+\}_2(TeI_3^+)_2(I^-)_4$ (the ionic and molecular fragments of **6b** and the TeI_4 tetramer are indicated in Figure 6). The relevant framework Te−I distances in **6b** and in the two polymorphs of TeI_4 are compared in Table 6.

It can be seen from Figure 6 that whereas the TeI_4 exhibits a $(TeI_3)^+$ cation both at the top and bottom of the molecule, **6b** contains two $\{C_4H_8TeI\}^+$ cations in the corresponding locations. The Te(1)−I(11) bond length of 2.755(2) Å in the cation is again close to that of the single bond,[29] and the I−Te−C bond angles of 93.2(5)° and 95.0(5)°, as well as the C−Te−C angle of 84.1(6)° (see Table 5), indicate a pyramidal telluronium ion.

In both γ- and δ-TeI_4 the two $(TeI_3)^+$ cations show close contacts of 3.231−3.279 Å to two TeI_4 molecules.[6,7] These interatomic distances are in good agreement with the cation−anion contacts in **6a**. The two TeI_4 fragments in γ- and δ-TeI_4 show the expected trigonal-bipyramidal geometry, with the axial Te(2)−I(21) and Te(2)−I(24) bonds [2.921−3.035 Å] longer than the equatorial Te(2)−I(22) and Te(2)−I(23) bonds [2.743−2.785 Å]. It can be seen from Figure 6 that in **6b** two $(TeI_3)^+$ cations can be found in the locations where γ- and δ-TeI_4 contain two TeI_4 molecules. This inference is based on the differences in the corresponding interatomic distances and angles. The three Te−I bonds in question [Te(2)−I(22), Te(2)−I(23), and Te(2)−I(24)] span virtually equal single bond[29] lengths of 2.767(1)−2.783(1) Å and are close to those of 2.753−2.789 Å and 2.738−2.773 Å reported for the two $(TeI_3)^+$ fragments in γ- and δ-TeI_4, respectively.[6,7] It should be noted that the axial Te(2)−I(24) in γ- and δ-TeI_4[6,7] is significantly longer than that in **6b**. Conversely, the Te(2)−I(21) distance that represents the other axial bond of the TeI_4 molecule, and is therefore of comparable length to the Te(2)−I(24) bond in γ- and δ-TeI_4,[6,7] is significantly longer in **6b** [3.261(2) Å] and can be inferred as the cation−anion distance.

The two types of the cations in **6b** are linked together by two bridging μ_2−I^- anions and two μ_3−I^- anions that together build up the framework of the structure type **II**. It can be seen from Table 6 that the Te(2)−I(25) bonds in **6b** and in γ- and δ-TeI_4 are of comparable length, in the range 3.197(1)−3.257 Å. Whereas the long Te(1)−I(25) distance of 3.676(2) Å represents a secondary bonding interaction in **6b**, the corresponding interatomic separation is shorter in γ- and δ-TeI_4 (3.187−3.214 Å).[6,7] They represent typical cation−anion distances.

We note that the two polymorphs of Me_2TeI_2 also show significantly differing structures. α-Me_2TeI_2 is composed of discrete molecules,[35] while β-Me_2TeI_2 is ionic and contains $(Me_3Te)^+$ cations and $[MeTeI_4]^-$ anions.[36]

Reaction Pathways. The reactions between tellurium tetrahalides and triphenylphosphine in tetrahydrofuran in air are very versatile. Early reports under an inert atmosphere have suggested that, in the case of $TeCl_4$ and Ph_3P, Ph_3PCl_2 and Te(0)[8] or Ph_3PO, $TeCl_2$, and Te(0)[9] are formed. In the latter case, the formation of Ph_3PO was explained by the hydrolysis of Ph_3PCl_2. We have observed that under ambient conditions the reactions of $TeCl_4$ or $TeBr_4$ and Ph_3P afford $\{(Ph_3PO)_2H\}_2[Te_2X_{10}]$ [X = Cl (**1**), Br (**2**)] in good yields. The main product in the reaction involving TeI_4 is $\{(Ph_3PO)_3(OH_3)\}_2[TeI_6]$ (**4**).[37]

The cations in **1**, **2**, and **4** that consist of Ph_3PO molecules linked into dimeric or trimeric units by bridging H^+ or H_3O^+ cations, respectively, are probably produced by hydrolysis of Ph_3PX_2 due to atmospheric moisture, as suggested by Arens et al.[19c] and Lane et al.[19e] The formation of various

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(35) Chan, L. Y. Y.; Einstein, F. W. B. *J. Chem. Soc., Dalton Trans.* **1972**, 316.

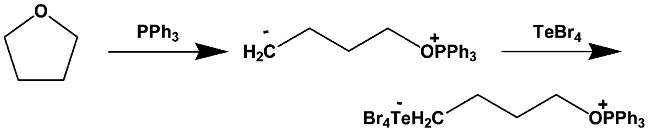
(36) Einstein, F.; Trotter, J.; Williston, C. S. *J. Chem. Soc. A* **1967**, 2018.

(37) For comparison, we also tested the reaction of $TeCl_4$ and PPh_3 in an argon atmosphere. After the dark precipitate was filtered off, two resonances could be observed in the ^{31}P NMR spectrum of the remaining solution. The resonance at 66.5 ppm is probably due to Ph_3PCl_2.[38] The second resonance falls within the range assigned to **1** and indicates that even traces of adventitious water play a role in the reaction.

(38) (a) Wiley, G. A.; Stine, W. R. *Tetrahedron Lett.* **1967**, 2321. (b) Dillon, K. B.; Lynch, R. J.; Reeve, Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1976**, 1243. (c) Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sheffield, M. *Chem. Commun.* **1996**, 2521. (d) Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sheffield, M.; Thompson, G. M. *J. Chem. Soc., Dalton Trans.* **1997**, 4823.

anions from tellurium tetrahalides and the structural relationships between them have been explained by Krebs and Paulat,[17f] and are depicted in Scheme 1. It is not quite clear what factors determine the product distribution and isolation of the actual anions. The ^{125}Te NMR spectra of different reaction solutions only indicate the presence of one type of anion in each case. This has also been recently observed for the reaction of Te and SO_2Cl_2.[13] Different chlorotellurate anions are produced depending on the solvent, but only one type of anion is observed in every case.

We have recently observed that in the case of $TeBr_4$ the reaction with PPh_3 in THF results also in the opening of the tetrahydrofuran ring with the formation of $Ph_3PO(CH_2)_4TeBr_4$ (**3**) that is formally zwitterionic.[10] The ring opening is probably initiated by the attack of PPh_3 at the THF oxygen in the same fashion as the reaction of PPh_3 with elemental sulfur.[39] The open-chain intermediate reacts with $TeBr_4$ to afford **3**.[10]



Anderson and Freenor[40] have established that Ph_3PBr_2 also effects a THF ring opening and produces Ph_3PO and $BrCH_2(CH_2)_2CH_2Br$ in good yield. It is reasonable to assume that TeI_4 reacts with PPh_3 and affords elemental tellurium and Ph_3PI_2 in an analogous manner to $TeCl_4$.[8,9] Ph_3PI_2 then reacts with THF and produces Ph_3PO and $ICH_2(CH_2)_2CH_2I$. The reaction between the elemental tellurium and $ICH_2(CH_2)_2CH_2I$ leads to the formation of $(CH_2)_4TeI_2$ (**5**), as reported by Morgan and Burstall.[25]

The formation of **6a** and **6b** can most conveniently be viewed as a simple interaction between $(CH_2)_4TeI_2$ (**5**) and TeI_4. It is possible that the structural and bonding differences between the two forms originate only upon crystallization of the two species.

Conclusions

The reaction of tellurium tetrachloride and triphenylphosphine has been reported to form elemental tellurium and Ph_3PCl_2,[8] or Te(0), $TeCl_2$, and Ph_3PO.[9] In this contribution we have shown that under ambient conditions the reactions afford $\{(Ph_3PO)_2H\}_2[Te_2X_{10}]$ [X = Cl (**1**), Br (**2**)] and $\{(Ph_3PO)_3OH_3\}_2[TeI_6]$ (**4**). Compounds **1** and **2** are isostructural and contain discrete $[Te_2X_{10}]^{2-}$ anions and dimeric $\{Ph_3POH\cdots OPPh_3\}^+$ cations. Compound **4** contains octahedral hexaiodotellurate anions and trimeric $\{(Ph_3PO)_3(OH_3)\}^+$ cations.

In addition to the products mentioned above, $TeBr_4$ and PPh_3 afford zwitterionic $Ph_3PO(CH_2)_4TeBr_4$ (**3**). This reaction involves an unprecedented THF ring opening in which the oxygen atom is bonded to phosphorus and the carbon atom is bonded to tellurium. A THF ring opening is probably also effected in the formation of the side product $(CH_2)_4TeI_2$ (**5**) during reaction of TeI_4 and PPh_3. This product can be crystallized as two different polymorphs **5a** and **5b** that differ only in the packing of the molecules. **5** can be explained to be formed from elemental tellurium and $ICH_2(CH_2)_2CH_2I$. Tellurium is produced in the initial reaction of TeI_4 and PPh_3. The latter product is obtained as a consequence of the attack of Ph_3PI_2 at the THF molecule resulting also in the formation of Ph_3PO. Most Ph_3PO, however, is probably produced by the influence of atmospheric moisture.

The reaction of TeI_4 and PPh_3 leads upon crystallization to the formation of two different forms of $(CH_2)_4Te_2I_6$ (**6a** and **6b**) that can both formally be considered as 1:1 adducts of TeI_4 and $(CH_2)_4TeI_2$. They are superficially similar, but their structures differ from each other. **6a** can be formulated as $\{(CH_2)_4TeI^+\}_2[Te_2I_{10}{}^{2-}]$ and **6b** as $\{(CH_2)_4TeI^+\}_2(TeI_3{}^+)_2(I^-)_4$. Though the interatomic distances vary, the structural framework of **6b** is very similar to that of the tetramers in γ- and δ-TeI_4.

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Supporting Information Available: Seven X-ray crystallographic files in CIF format, two tables containing crystal data and selected bond lengths and angles of **5a**, and a figure illustrating the effect of intermolecular I···I and I···Te interactions on the corresponding Te−I bond lengths in R_2TeI_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) Bartlett, P. D.; Meguerian, G. *J. Am. Chem. Soc.* **1956**, *78*, 3710.
(40) Anderson, A. G.; Freenor, F. J. *J. Org. Chem.* **1972**, *37*, 626.