Ammonium iron(III) oxalate ($(NH_4)_3[Fe(C_2O_4)_3]\cdot 3H_2O$, $M_W = 428$; 2.568 g, 6 mmol) was dissolved in hot distilled water (3 mL, 50 °C) contained in a foil-covered flask. Finely powdered potassium ferricyanide ($K_3[Fe(CN)_6]$, $M_W = 329$; 0.987 g, 3 mmol) was added to the hot solution with vigorous stirring for 20 min and then sonicated for 2 min. The solution was left to cool in the dark for several hours. Green crystals of $K_3[Fe(C_2O_4)_3]$ were removed by filtration in the dark from the mixture of $(NH_4)_3[Fe(C_2O_4)_3]$ and $(NH_4)_3[Fe(CN)_6]$ solutions. We used this procedure specifically to remove potassium ions from the reaction mixture as ammonium cyanometallate is significantly more stable than the potassium salt of Prussian blue. The solution was then diluted to 10 mL with distilled water to give an equimolar mixture of $(NH_4)_3[Fe(C_2O_4)_3]$ and $(NH_4)_3[Fe(CN)_6]$ at a concentration of 0.3 M.

A small amount (0.09–0.36 mL) of the $(NH_4)_3[Fe(C_2O_4)_3]$ and $(NH_4)_3[Fe(CN)_6]$ mixture (0.01–0.3 M in water) was added to an isooctane solution of NaAOT (10 mL, 0.1 M in isooctane) at room temperature in the dark to produce an AOT water-in-oil microemulsions at $w = 5-20$. Higher water levels ($w = 15-20$) resulted in a slight phase separation of the water in the microemulsion due to the high ionic strength of the reaction solution. This separation could be prevented by using lower concentrations of the reactants. The microemulsions were exposed to daylight for various periods to slowly photoreduce the $[Fe(C_2O_4)_3]^{3-}$ ions to $[Fe(C_2O_4)_3]^{4-}$, which serve as a source of $Fe^{II}$ ions for treatment with aqueous $[Fe(CN)_6]^{3-}$. This latter process is analogous to the Turnbull method for producing Prussian blue.

Samples for analytical TEM and UV/Vis spectroscopy were taken over two weeks. For TEM, droplets of the microemulsion were air-dried onto Formvar-coated, carbon-reinforced, 3 mm diameter, copper electron microscope grids.

Control experiments used equivalent amounts of the $(NH_4)_3[Fe(C_2O_4)_3]$ and $(NH_4)_3[Fe(CN)_6]$ aqueous mixture (0.3 M) added to 10 mL of isooctane or water in the absence of NaAOT.

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# Synthesis and Characterization of $Ph_4Te_4I_4$, Containing a $Te_4$ Square, and $Ph_3PTe(Ph)I$

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Charles A. McAuliffe, Robin G. Pritchard,
Shamsa Sarwar, and Joanne M. Sheffield

The interaction of organoelement compounds of Group 16 with dihalogens is a subject of considerable current interest. For example, the dihalogen adducts of organoselenium compounds[1, 2] and selenoamides[3–5] have all been intensively studied by a variety of research groups in the last few years. In addition, we have recently reported the structure of $Ph_3PSe(Ph)I$, formed from the reaction of $Ph_3P$ with $Ph_2Se_2I_2$.[6] Many of the dihalogen compounds formed lie close to the ionic/covalent borderline, and several structural types have been identified which are dependent on the substituents R, the donor atom, the identity of the halogen, and, in some cases, the dielectric constant of the solvent in which such compounds are prepared. For example, dimethylselenide diiodine adopts a three-coordinate charge-transfer (CT) structure, $Me_2SeI{-}I$,[1] whereas the corresponding dibromide adopts a disphenoidal "see-saw" structure, $Me_2SeBr_2$. On the other hand, $Me_2SBr_2$ is a CT complex, $Me_2SBr{-}Br$, thus illustrating the importance of the donor atom on the nature of the dihalogen adduct produced.[7] Also of relevance to the present study is the isolation of the first stable alkanetellurenyl pseudohalides by Fimml and Sladky, who reported on compounds of formula $(Me_3Si)_3CTeX$ (X = CN, SCN, SeCN, NCO, $N_3$).[8]

The interaction of $Ph_2Se_2$ with diiodine has been described by du Mont and co-workers, and a very interesting CT complex was observed in the solid state.[9] The X-ray crystal structure of this molecule revealed a dimeric centrosymmetric moiety containing short and long iodine–iodine distances (2.775(1) and 3.588(1) Å, Figure 1). In view of this interesting (and unexpected) structure, we were interested in synthesizing the analogous tellurium compound from the stoichiometric reaction of $Ph_2Te_2$ and molecular iodine in diethyl ether in order to determine if the compound produced is isomorphous with $Ph_2Se_2I_2$ or whether a new structural motif would be revealed.

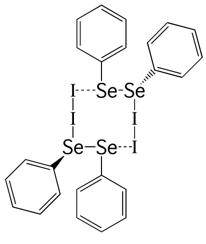

Figure 1. The structure of $Ph_2Se_2I_2$ as described by du Mont et al.[13]

Diphenyl ditelluride reacts rapidly with diiodine to produce an intensely violet-black product. Elemental analysis of this material revealed the stoichiometry "PhTeI", suggesting a product analogous to $Ph_2Se_2I_2$ from du Mont et al.[9] We were nevertheless interested in crystallographically characterizing the compound for comparative purposes. The X-ray crystal

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structure[10] revealed a novel structural modification not previously observed for organoelement – halogen compounds of Group 16: Individual PhTeI units are weakly linked into a tetramer through weak tellurium – tellurium bonds, the structure being best represented as $Ph_4Te_4I_4$ (**1**, Figure 2). This compound is quite different from $Ph_2Se_2I_2$ and illustrates the sensitivity of the structure of such systems on the Group 15 or 16 atom, a phenomenon previously described by other workers and us.[1, 7, 9]

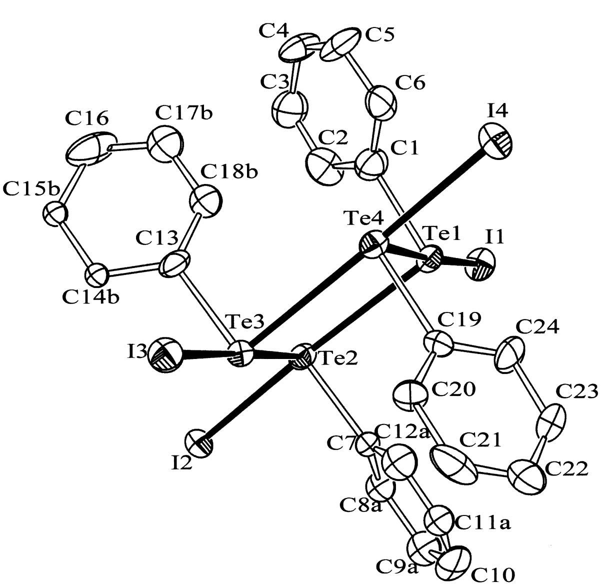

Figure 2. The X-ray crystal structure of **1**. Selected bond lengths [Å] and angles [°]: Te1–I1 2.799(2), Te2–I2 2.8181(14), Te3–I3 2.822(2), Te4–I4 2.830(2), Te1–Te2 3.1474(14), Te2–Te3 3.125(2), Te3–Te4 3.1627(14), Te4–Te1 3.175(2), I1–I4[a] 3.841(3), I1–I2[b] 3.852(3), I2–I3[c] 3.898(3), I3–I4[d] 3.856(3)—where [a] denotes $x + 1/2, y - 1/2, z$; [b] denotes $x + 1/2, y + 1/2, z$; [c] denotes $x + 1/2, y - 1/2, z$; and [d] denotes $1/2 - x, y - 1/2, z$; I1-Te1-Te(2) 94.09(4), I1-Te1-Te4 176.12(4), Te2-Te1-Te4 89.78(3), I2-Te2-Te1 175.56(5), I2-Te2-Te3 93.75(4), Te1-Te2-Te3 90.49(3), I3-Te3-Te2 175.77(4), I3-Te3-Te4 93.70(4), Te2-Te3-Te4 90.40(3), I4-Te4-Te1 93.92(4), I4-Te4-Te3 176.77(5), Te1-Te4-Te3 89.31(3).

The Te–Te bonds in **1** range from 3.125(2) to 3.175(2) Å, and are thus considerably longer than *d*(Te–Te) in diphenyl ditelluride (2.705(1) Å).[11] The coordination around tellurium may be interpreted by postulating the presence of a stereochemically active lone pair on the tellurium atom, giving rise to a pseudo-trigonal-bipyramidal geometry. The existence of a compound of formula PhTeI was first reported by Schulz and Klar in 1974, who proposed a halide-bridged structure for the compound to explain its low solubility.[12] Similarly, Alcock and Harrison reported the formation of PhTeI in chloroform; however, attempted recrystallization of this product resulted in the isolation of the decomposition products $Ph_2TeI_2$ and $PhTeI_3$ from hot toluene and toluene at room temperature, respectively.[13] Both structures exhibit halide bridges.

Also of interest in the structure of **1** is the presence of weak secondary I⋯I interactions ranging from 3.841(3) to 3.898(3) Å, which is shorter than the sum of the van der Waals radii for two iodine atoms (4.3 Å). These very weak, but significant, contacts help to stabilize **1** and link the structure as a whole into a network of small $Te_4$ squares and larger $I_4$ square (Figure 3). Although no organotelluride – halogen compound that adopts this structure has been previously described, two compounds that contain the $Te_4$ unit have been reported quite recently. du Mont and co-workers have described the structure of $Ph_3TeTe(p\text{-tol})$ (tol = tolyl) in which cyclic units of composition $R_8Te_4$ are revealed, linked through weak Te–Te interactions.[14] The compound as a whole may be thought of as a tetramer of diaryltellurium. The Te–Te distances for this compound range from 3.3233(13) to 3.5958(13) Å, and are considerably longer than those observed in **1** (3.125(2) – 3.175(2) Å) but may still be regarded as Te–Te bonds when compared to the sum of the van der Waals radii for two tellurium atoms (4.40 Å). One other compound that also contains the $Te_4$ unit is the organometallic complex ($\mu$-4-cyclotetratellurido) icosacarbonyltetrachromium, in which the tellurium atoms form a $Te_4$ square, each of which is also bonded to a $Cr(CO)_5$ unit.[15] The values for *d*(Te–Te) for this complex range from 2.818(1) to 2.895 (1) Å, and are thus considerably shorter than those observed in **1**, as expected.

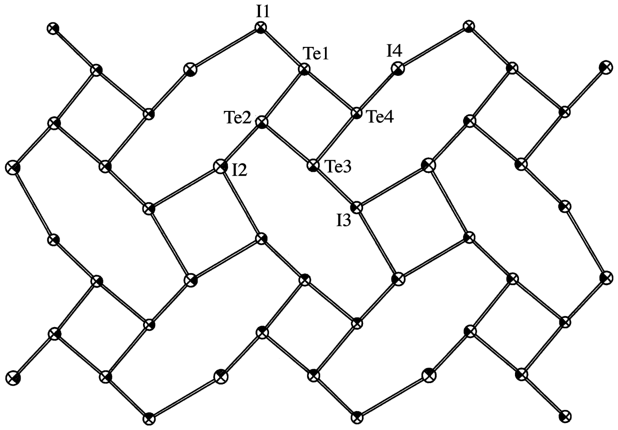

Figure 3. The crystal packing of **1** illustrating the long-range I⋯I contacts linking the structure into small ($Te_4$) and large squares ($I_4$), *d*(I–I) = 3.841(3) – 3.898(3) Å; phenyl rings are omitted for clarity.

As well as elucidating the structure of **1**, we were interested in examining whether it would react with a tertiary phosphine at ambient temperatures. Consequently, **1** was treated with $PPh_3$ in a 1:4 stoichiometric ratio [Eq. (1)].

$$\underset{\mathbf{1}}{Ph_4Te_4I_4} + 4\,PPh_3 \xrightarrow{Et_2O} 4\,\underset{\mathbf{2}}{Ph_3PTe(Ph)I} \qquad (1)$$

Compound **1** reacts very rapidly with $PPh_3$ to produce the deep yellow $Ph_3PTe(Ph)I$ (**2**). The X-ray crystal structure[16] of this material reveals a CT complex (Figure 4). The Te–I distances (3.0930(9) Å) clearly represents a CT interaction when compared to the sum of the van der Waals radii of the two atoms and is similar to the I–I distance in $Ph_3PI_2$ (3.142(2) Å).[17] The CT nature of **2** is confirmed by the geometry at the tellurium center, which is T-shaped (C1-Te1-P1 91.0(2)°, C1-Te1-I1 89.2(2)°) and not bent, as would be expected for an ionic compound. Additionally, angle P1-Te1-I1 is essentially linear (179.45(5)°).

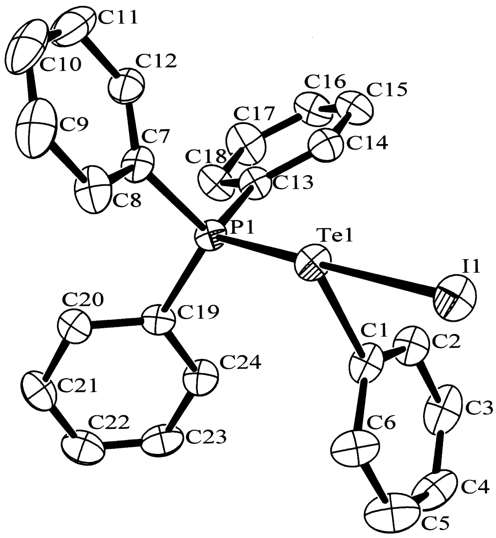

Figure 4. The X-ray crystal structure of **2**. Selected bond lengths [Å] and angles [°]: I1–Te1 3.0930(9), Te1–C1 2.109(7), Te1–P1 2.568(2); C1-Te1-P1 91.0(2), C1-Te1-I1 89.2(2), P1-Te1-I1 179.45(5), C19-P1-C7 109.2(3), C19-P1-Te1 118.3(2), C2-C1-Te1 121.3(6).

Only one compound of formula $R_3PTe(R)I$ has previously been described, $Ph_3PTe(2\text{-Naphthyl})I$, by Petragnani and Moura Campos in 1965.[18] However, no single-crystal X-ray structure determination was attempted on this material. A wider class of compounds of general formula LTe(R)X (where L is a neutral donor ligand) has been long recognized, having first been reported in the pioneering work of Foss and Husebye,[19] who investigated the structures of PhTe(tu)X (tu = thiourea; X = Br, Cl). Both structures contain divalent tellurium atoms bonded to a phenyl group, a thiourea molecule, and, in *trans* position to the latter, a halogen atom. In common with **2**, the Te–X bonds are rather long in these structures (Te–Cl 3.00(15), Te–Br 3.11(1) Å).

The $^{31}P\{^1H\}$ NMR spectrum of **2** reveals a single peak at $\delta = 26.9$, which is shifted to higher field than that exhibited by $Ph_3PI_2$ ($\delta = 44.2$), which is known to ionize in $CDCl_3$ to produce $[Ph_3PI]I$. This result suggests that **2** may retain its molecular CT structure in solution, however, no $^{125}Te$ satellites were observed. Work is currently underway to investigate whether the reaction of compounds of the general type $R_3PTe(R)I$ with crude metal powders will provide a novel route to new tellurium-bound metal complexes, analogous to our recent results concerning the reaction of $R_3EI_2$ with metal powders: For example in the reaction of $Me_3PI_2$ with gold metal powder the novel trigonal-bipyramidal complex $AuI_3(PMe_3)_2$ is produced.[20]

## *Experimental Section*

**1**: $Ph_2Te_2$ (Aldrich; 1.00 g, 2.44 mmol) was dissolved in dry $Et_2O$ (ca. 75 mL), and subsequently $I_2$ (0.62 g, 2.44 mmol) was added against a stream of dry $N_2$. After stirring for about 2 d under $N_2$, the dark purple **1** was isolated using standard Schlenk techniques. The yield was essentially quantitative. After drying in vacuo, **1** was transferred to predried nitrogen-filled ampules, which were flame-sealed. Crystals suitable for X-ray diffraction were easily obtained by dissolving the bulk solid in refluxing $Et_2O$ and leaving the mixture to cool to room temperature. A large crop of black crystals formed after about 3 d. Elemental analysis of $Ph_4Te_4I_4$: found (calcd): C 22.0 (21.8), H 1.9 (1.5), I 38.2 (38.4), Te 37.9 (38.3).

**2**: Compound **1** (0.5 g, 0.38 mmol) was dissolved in dry $Et_2O$ (ca. 50 mL), and subsequently $Ph_3P$ (0.40 g, 1.50 mmol) was added against a stream of dry $N_2$. Almost instantaneously a color change from deep burgundy (due to **1**) to bright yellow was noted. After stirring for 1 d under $N_2$, the bright yellow **2** was isolated using standard Schlenk techniques (yield ca. 90%). After drying in vacuo, **2** was transferred to predried nitrogen-filled ampules, which were flame-sealed. Crystals suitable for X-ray diffraction were obtained by dissolution of the bulk solid in $Et_2O/CH_2Cl_2$ (1/1) at 50 °C. On cooling to room temperature large well-formed yellow-orange crystals were apparent in the reaction vessel after about 2 d.

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[10] a) Crystal data for **1** ($C_{24}H_{20}I_4Te_4$): $M_r = 1326.40$, monoclinic, space group *Cc*, $a = 13.759(4)$, $b = 13.812(4)$, $c = 16.451(5)$ Å, $\beta = 101.62(3)$, $V = 3062.3(16)$ Å$^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.877$ Mg m$^{-3}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), crystal dimensions $0.25 \times 0.25 \times 0.10$ mm$^3$. Of 6769 reflections collected on a Rigaku AFC 6S diffractometer, 3551 were observed ($R_{\text{int}} = 0.0994$) and used for all calculations (programme SHELXL 93). After absorption correction (psi scans) the structure was solved by direct methods and refined anisotropically on $F^2$. Final residuals $R_1 = 0.0603$, $wR_2 = 0.1642$ ($I > 2\sigma(I)$); $R_1 = 0.0650$, $wR_2 = 0.1700$ (all data), 287 parameters. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141820 and -141821. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] Crystal data for **2** ($C_{24}H_{20}IPTe$):[10b] $M_r = 593.87$, triclinic, space group $P\bar{1}$, $a = 9.780(2)$, $b = 9.780(2)$, $c = 12.412(3)$ Å, $\alpha = 76.21(2)$, $\beta = 73.03(2)$, $\gamma = 87.79(2)°$, $V = 1102.3(4)$ Å$^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.789$ Mg m$^{-3}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), crystal dimensions $0.30 \times 0.20 \times 0.20$ mm$^3$. Of 4097 reflections collected on a Nonius MAC 3 CAD4 diffractometer, 3847 were observed ($R_{\text{int}} = 0.0739$) and used for all calculations (programme SHELXL 93). After absorption correction (psi scans) the structure was solved by direct methods and refined anisotropically on $F^2$. Final residuals $R_1 = 0.0549$, $wR_2 = 0.1376$ ($I > 2\sigma(I)$); $R_1 = 0.0692$, $wR_2 = 0.1491$ (all data), 244 parameters.

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