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Crystal structures of the products of unusual interactions between organotellurides and iodoacetylenes

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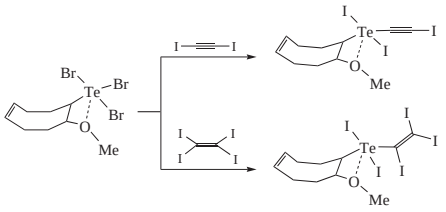
Unusual substitution of bromine atoms in organotellurium tribromide with 1,2-diiodoethyne and 1,1,2,2-tetraiodoethene and addition of diphenyl ditelluride to the triple bond of 1,2-diiodoethyne, is reported. In the solid state, halogen and chalcogen bonds assist self-assembly of the resulting molecules.

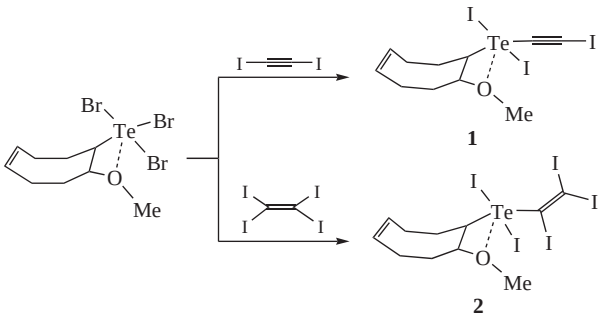


Iodoacetylenes and tetraiodoethene in combination with S, Se, N, O, P and halogen donors are the popular synthons in the supramolecular design strategies using halogen bonding as a tool.[1–4] In the course of our ongoing investigation of organotellurium halides as promising ligands in coordination chemistry[5,6] and building blocks for a crystal design, we intended to study co-crystallization of *trans*-8-methoxycyclooct-4-enyltellurium tribromide [*c*-C_8H_{10}(OMe)$TeBr_3$][7] with 1,2-diiodoethyne C_2I_2 and 1,1,2,2-tetraiodoethene $I_2C{=}CI_2$. The experiments were performed in CH_2Cl_2 solutions and allowed us to obtain well formed crystals suitable for the single crystal XRD investigation.† To our surprise, both **1** and **2** were not co-crystals, but the products of formal replacement of bromine atom of *c*-C_8H_{10}(OMe)$TeBr_3$ with iodoethynyl and triiodoethenyl groups, respectively (Scheme 1). Compound **2** co-crystallizes with molecules of C_2I_4 associated *via* I–I and C=C–C=C interactions into dimers of a parallel C_2I_4 plane molecules (see below).

Formal replacement of Br by the acetylide group in *c*-C_8H_{10}(OMe)$TeBr_3$, which occurred in the course of its interaction with diiodoethyne C_2I_2 (see Scheme 1), resembles the exchange of Br and Cl atoms in organotellurohalides by I,[7] N_3^-,[8] CN^-,[9] or SCN^- (ref. 10) anions. Taking into account the positive charge of the iodine atom bonded to a significantly more electronegative *sp*-hybridized carbon atom in diiodoethyne C_2I_2,[11] the exchange of Br for $IC{\equiv}C^-$ anionic moiety seems to be quite reasonable rationalization of formation of compound **1**. Similarly, the replacement of Br in *c*-C_8H_{10}(OMe)$TeBr_3$ with the 1,2,2-triiodoethenyl moiety may account for the formation of product **2**.

Under the similar conditions of attempted co-crystallization of iodoacetylenes with diphenyl ditelluride we obtained the crystals of the oxidative addition products 1,2- and 1,1-diodoethenes **3** and **4** (Scheme 2).

The intramolecular bond lengths and bond angles in the molecules of **1**–**4** are in good agreement with other reports on the similar tellurium compounds. Apart from the common Te···I intermolecular bonds, all four new compounds reveal remarkable intermolecular interaction of Te and I atoms with the π-systems of double, triple and aromatic C–C bonds (see Figures 1–4).‡ In the solid state structure of **1**, I···C≡C (3.697 Å) intermolecular interaction is just additional to Te–I, slightly distorting the Te–I dimeric arrangement (see Figure 1). In compound **2**, the I···C=C interaction (3.328 Å) is the major driving force assembling the



Scheme 1

† *General procedure*. Telluride reagent (0.1 mmol) and corresponding iodoacetylene in each pair **1**–**4** (0.3 mmol) were dissolved in purified CH_2Cl_2 (0.3 ml) in a 7-mm test tube, sealed with parafilm and left for slow evaporation. After 5–7 days, the crystals suitable for the single crystal XRD investigation were formed. They were isolated manually and used for XRD investigation without additional manipulations.

‡ *Crystallographic data for* **1**. Crystals of $C_{11}H_{15}I_3OTe$ (M = 671.55) are triclinic, space group $P\bar{1}$, at 293 K: a = 10.0285(7), b = 12.9430(9) and c = 16.0318(11) Å, α = 80.3110(10)°, β = 80.3110(10)°, γ = 73.1940(10)°, V = 1962.5(2) Å^3, two independent molecules, Z = 2 , d_{calc} = 2.273 g cm^{-3}, μ(MoKα) = 6.22 mm^{-1}, F(000) = 1200. 20784 reflections were measured and 9875 independent reflections (R_{int} = 0.0194) were used in a further refinement. The refinement converged to wR_2 = 0.0900 and GOF = 1.055 for all independent reflections [R_1 = 0.0322 was calculated against F for 8450 observed reflections with $I > 2\sigma(I)$].

Crystallographic data for **2**. Crystals of $C_{13}H_{15}I_9OTe$ (M = 1457) are triclinic, space group $P1$, at 293 K: a = 8.7222(15), b = 11.2356(19) and c = 15.266(3) Å, α = 97.898(3)°, β = 99.786(2)°, γ = 107.446(2)°, V = = 1377.9(4) Å^3, Z = 2, d_{calc} = 2.273 g cm^{-3}, μ(MoKα) = 11.17 mm^{-1}, F(000) = 1260. 14608 reflections were measured and 7057 independent reflections (R_{int} = 0.023) were used in a further refinement. The refinement converged to wR_2 = 0.092 and GOF = 1.026 for all independent reflections [R_1 = 0.037 was calculated against F for 5914 observed reflections with $I > 2\sigma(I)$].

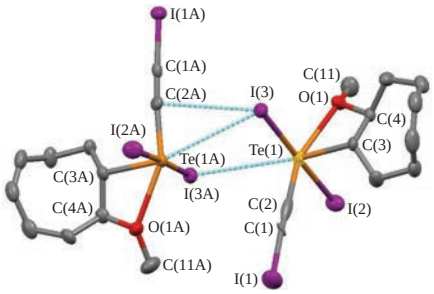


Figure 1 The solid-state structures of dimeric associates of **1** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected intramolecular distances (Å): C(2)–C(1) 1.17(1), C(1)–I(1) 2.032(9), O(1)–Te(1) 2.558(7), I(3)–Te(1) 2.897(1), Te(1)–I(2) 2.955(1), Te(1)–C(3) 2.194(8); and intermolecular distances (Å): Te(1A)–I(1) 4.926(1), C(2A)–I(3) 3.696(8), I(3)–Te(1A) 3.9224(9), Te(1)–I(3A) 3.9244(8), I(3)–Te(1A) 3.9224(9).

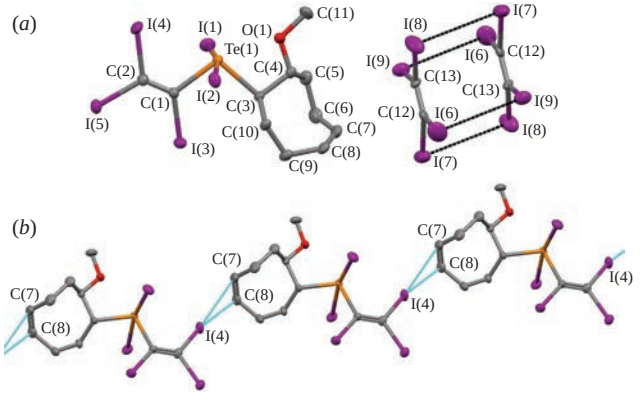
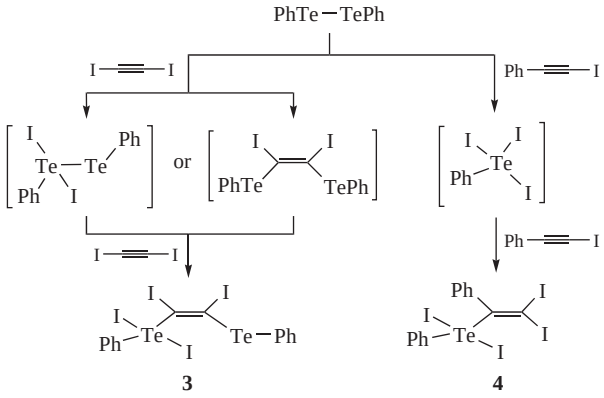


Figure 2 The solid-state structures of **2**·C_2I_4 and its 1-D chain packing arrangement showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected intramolecular distances (Å): C(1)–C(2) 1.32(1), C(3)–Te(1) 2.208(7), I(4)–C(2) 2.120(7), C(2)–I(5) 2.102(9), C(1)–I(3) 2.086(7), O(1)–Te(1) 2.630(6), Te(1)–I(1) 2.9227(7), Te(1)–I(2) 2.9299(8); intermolecular distances (Å): between the planes of C_2I_4 molecules 4.149, I(4)···[C(8)=C(7)]$_{centroid}$ 3.328.

molecules of **2** into 1-D chains (see Figure 2). Both **3** and **4** are featuring the Te···π_{Ph} (3.429 and 3.583 Å, respectively) intermolecular interactions, assembling their molecules into dimeric associates (see Figures 3, 4). Similar dimeric packing motif was



Scheme 2

described for 'Menshutkin complexes' $PhSbX_2$ (X = Cl, Br, I)[12] and π-complexation of post-transition metals by neutral aromatic hydrocarbons was generally reviewed[13] for IV–VA Groups elements and for Te.[14]

1,2-Dihalo-1,2-bis(arylchalcogenyl)ethene can be obtained by the substitution of halides in tetrahaloethene with the arylchalcogenate anion ArX^-,[15–17] or by addition of diorganyl dichalco-

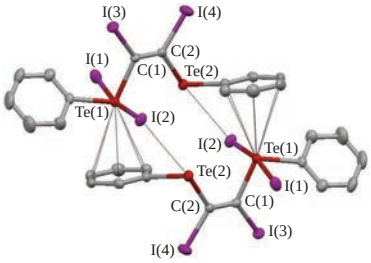


Figure 3 The solid-state structures of dimeric associates of **3** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected intramolecular distances (Å): C(1)–C(2) 1.317(6), C(1)–I(3) 2.095(4), C(2)–I(4) 2.106(4), C(1)–Te(1) 2.151(4), C(2)–Te(2) 2.128(4), Te(1)–I(2) 2.9171(4), Te(1)–I(1) 2.8994(4); intermolecular distances (Å): Te(1)–Ph$_{centroid}$ 3.429, Te(2)–I(2) 3.7708(4).

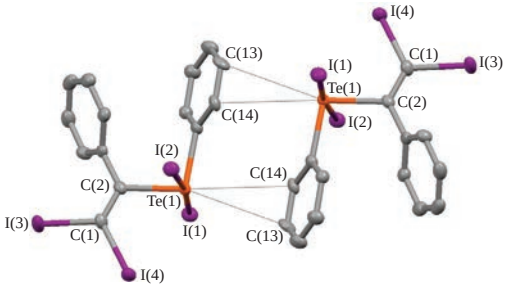


Figure 4 The solid-state structures of dimeric associates of **4** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected intramolecular distances (Å): I(4)–C(1) 2.087(5), I(3)–C(1) 2.107(5), C(2)–Te(1) 2.162(5), I(2)–Te(1) 2.9915(5), I(1)–Te(1) 2.8516(5), C(2)–C(1) 1.337(8); and intermolecular distances (Å): Te(1)–[C(14)=C(13)]$_{centroid}$ 3.583.

The measurements for crystals **1**, **2** were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = = 0.71073 Å). The structures were solved by direct methods, and the non-hydrogen atoms were located from the trial structures and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2. The hydrogen atom positions were fixed geometrically at calculated distances and allowed them to ride on the parent atoms. SQUEEZE procedure was used for the solvent.

Crystallographic data for **3**. Crystals of $C_{14}H_{10}I_4Te_2$ (M = 941) are orthorhombic, space group *Pbca*, at 150 K: a = 13.8366(2), b = 15.0009(2) and c = 19.7142(2) Å, V = 4091.91(9) Å^3, Z = 8, d_{calc} = 3.055 g cm^{-3}, μ(MoKα) = 8.88 mm^{-1}, F(000) = 3280. 34629 reflections were measured and 3597 independent reflections (R_{int} = 0.028) were used in a further refinement. The refinement converged to wR_2 = 0.048 and GOF = 1.156 for all independent reflections [R_1 = 0.021 was calculated against F for 3295 observed reflections with $I > 2\sigma(I)$].

Crystallographic data for **4**. Crystals of $C_{14}H_{10}I_4Te$ (M = 813.42) are monoclinic, space group $P2_1/n$ at 293 K: a = 10.4305(3), b = 15.7973(8) and c = 11.1670(3) Å, β = 93.824(3)°, V = 1835.93(12) Å^3, Z = 4, d_{calc} = = 2.943 g cm^{-3}, μ(MoKα) = 8.33 mm^{-1}, F(000) = 1432. 10497 reflections were measured and 3232 independent reflections (R_{int} = 0.030) were used in a further refinement. The refinement converged to wR_2 = = 0.071 and GOF = 1.061 for all independent reflections [R_1 = 0.027 was calculated against F for 2786 observed reflections with $I > 2\sigma(I)$].

The measurements for crystals **3**, **4** were made on an Oxford Diffraction CCD Agilent Technologies diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods, the non-hydrogen atoms were located from the trial structures and then refined anisotropically with CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.31.5 (release 28-08-2006 CrysAlis171 .NET) using a full-matrix least-squares procedure based on F^2. The hydrogen atom positions were fixed geometrically at calculated distances and allowed them to ride on the parent atoms.

CCDC 1454116–1454119 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

genides to the C≡C bond. In the most of the reported cases the latter reaction requires catalytic or photolytic conditions.[18–23] Therefore, similarly to the known examples of the addition of PhTeI[24] and $PhTeI_3$[25] to the triple C≡C bond, it can be rationalized as the result of the attack of triple bond of IC≡CI or PhC≡CI by the products of Ph_2Te_2 iodination with excess of these iodoalkynes (*i.e.*, $PhTeTeI_2Ph$ and $PhTeI_3$, respectively) (see Scheme 2).

Compound **1** is a rare, if not a unique, representative of iodoacetylenetellurium halides. Only (*n*-butyl)(dichloro)(phenylethynyl)tellurium[26] is structurally characterized. For the substituted triiodoethylenes, analogues of compound **2**, only three structures were found in the the Cambridge Structural Database (CSD).[27–29] In the absence of the strong experimental proof the mechanisms suggested above are quite speculative, and since compounds **1**–**4** are perspective reagents in organoelement, coordination and supramolecular chemistry, the detailed investigation of the reaction mechanisms, optimization of the reaction conditions and development of the universal synthetic procedure will be the focus of our further research.

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