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One-Pot Synthesis and Structure of Organochalcogen Halides with Mixed Valence States

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Treatment of the diorganodichalcogenides PhEEPh (E = Se, Te) with one equivalent of elemental halogen (bromine or iodine) in methanol followed by addition of a sulfur donor and one more equivalent of the corresponding organochalcogen trihalide $PhTeX_3$ affords the mixed-oxidation-state organochalcogen halides $[PhE^{II}(L)PhE'^{IV}X_4]$ (E = Se, Te; E′ = Te; X = Br, I; L = thiourea, tetramethylthiourea) in a one-pot procedure. The X-ray structural analyses of these compounds suggest a strong dependence of the formation of supramolecular assemblies on the nature of the halogen bonded to the tellurium atom. The halogen can induce intramolecular and intermolecular secondary interactions among the heavy atoms simultaneously and, in addition to Te···X and X···X secondary bonds, intramolecular interactions of the type Te···η^6-π-aryl can be formed.

Introduction

The chemistry of organochalcogen halides is also the chemistry of secondary bonds and as such is the subject of considerable current interest. The bonding in these compounds eludes simple description, and concepts like hypervalence, multicenter bonding, charge-transfer interactions, and secondary bonds have been invoked to understand their structural and chemical properties.[1–9] Intermolecular bonding of the type E···X and X···X (E = Se, Te; X = Cl, Br, I) of various strengths leads to the formation of polymeric chains, dimeric structures, or monomers with fairly strong intermolecular interactions. Many of these halogen compounds lie close to the ionic/covalent borderline, and several identified species have been found to be dependent on the substituents R, the donor atom, the identity of the halogen, and, in some cases, also on the dielectric constant of the solvent in which they have been prepared.[10–12]

Recently, as part of our research on the coordination of organotellurium compounds, we have reported the syntheses and the molecular structures of organotellurium trihalides[13,14] and organotellurium monohalides,[11,15,16] as well as several studies involving structures of phenyltellurate halides stabilized by different cations.[17–19] Most of the crystal structures reported for the $RTeX_3$ species show that the occurrence of intra- and intermolecular interactions (secondary bonding), together with the nature of the organic groups bonded to the tellurium atoms, exert influence on the geometry around the tellurium(IV) center and consequently define the structural patterns of these compounds.[14,20–26] The apparent bisphenoidal coordination sphere of the central tellurium atom is extended by the presence of intermolecular Te···X and X···X secondary interactions. It has been assumed that for $RTeX_3$ compounds there is a tendency for the chlorides to be polymeric, the bromides either polymeric or dimeric, the iodides dimeric, and, if R is particularly bulky, monomeric structures would be the norm. Here, the size of the halogen should be the other determining factor, with dimeric structures preferred as the halogen size increases.[27,28] A comparison of the structure of $[(2,4,6\text{-}Ph_3C_6H_2)TeI_3]$ with the bonding situation in other organotellurium(IV) triiodides suggests a strong dependence of the formation of supramolecular assemblies on the nature of the organic substituents.[14]

More recently, we have extended our studies to investigate the reaction conditions needed to obtain and isolate the corresponding mono-iodide of the more bulky substituted ditellurides $(MesTe)_2$ or $(2,4,6\text{-}Ph_3C_6H_2Te)_2$. The presence of the methyl or phenyl groups on the aromatic rings probably prevents the formation of stable tetrameric subunits similar to $(PhTeI)_4$.[11] Attempts to crystallize the corresponding aryltellurenyl mono-iodide (RTeI) were un-

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successful as it decomposes to other aryltellurium derivatives.[11,15,16] Thus, for example, $(MesTe)_2$ [Mes = 2,4,6-$(CH_3)C_6H_2$] reacts with iodine to produce [MesTeI], which disproportionates to [$MesTeI_3$], elemental tellurium, and [$MesTe(TeMes_2)I$].[16] When the same reaction is carried out with [$(2,4,6\text{-}Ph_3C_6H_2)Te]_2$, the compound [$(2,4,6\text{-}Ph_3C_6H_2)TeI_3$][14] is formed as a result of a disproportion reaction under inert atmosphere or an oxo-bridged tellurium(IV) compound in the presence of air.[15] We are investigating this process further as it seems to have not only a steric influence but also an electronically directed behavior. The compound [$MesTe(TeMes_2)I$] is a representative example of a wider class of compounds of general formula [RTe(L)X] (where L is a neutral donor ligand), which were reported for the first time in the pioneering work of Foss and Huseby.[29] More recently, Godfrey,[12] Sadekov et al.,[30] and Singh et al.[31,32] have reported new examples.

Taking into account the unexpected reactivity and the interesting structural arrays previously obtained for several organochalcogen halides, we have turned our attention to the possibility of preparing organochalcogen halides with chalcogen atoms presenting mixed valence states in the same molecule.

There are only a few examples of this class of compounds in the literature. One of these is [$(DMSeU)_2Te_2Br_6$] (DMSeU = *N*,*N*-dimethylselenourea), which was obtained during the preparation of thin films of Te–Se alloys.[33] This compound contains both Te^{IV} and Te^{II} in the same molecule and there are no previously reported cases of such structures involving tellurium. Recently the synthesis and structural elucidation of [$Me_2TeCCTeMe$]I, the first alkynyltelluronium species, was reported.[34] A further search in the Cambridge Crystallographic Database reveals one more structure showing the coexistence of Ph_3TeI and MesTeI in a ratio of 4:2 in the same compound.[3,35] The iodine atoms bridge the Te^{IV} and Te^{II} atoms to build blocks containing six molecules.

In the light of these previous results and to expand our studies on the molecular structures and intermolecular bonding in organotellurium derivatives, we have prepared organic models which should allow the study of the interaction processes of tellurium(II) cations with tellurolate anions. In this paper we report the synthesis and the structural characterization of the four new complexes [(TMTU)PhTe(μ-Br)$TeBr_3Ph]_2$ (**1**), [(TU)PhTe(μ-I)$TeI_3Ph]_2$ (**2**), [PhSe(TU)][$PhTeI_4$] (**3**), and [PhSe(TU)][$PhTeBr_4$] (**4**).

Results and Discussion

The reactions between diaryl dichalcogenides and an equivalent amount of halogen in methanol at room temperature afford the corresponding arylchalcogen halides stabilized by a sulfur donor. The arylchalcogenide trihalide was added to the mixture and stirred at slow reflux for 2 h. The final solution was filtered and crystals suitable for X-ray analysis were achieved by slow evaporation of the solvent. Compounds **1**–**4** were obtained in yields of 63–85 % [Equation (1)].

$$1/2\ (PhE)_2 \xrightarrow{1/2\ X_2} PhEX \xrightarrow{L} PhE(L)X \xrightarrow{PhE'X_3} PhE(L)PhE'X_4 \qquad (1)$$

E = Se, Te; E′ = Te; X = Br, I; L = $(Me_2N)_2CS$ (TMTU), $(H_2N)_2CS$ (TU)

Several attempts to recrystallize **1**–**4** in order to obtain compounds with a high purity resulted in disproportionation to yield mainly Ph_2TeX_2 and $PhEX_3$ (E = Se, Te; X = Br, I).[11,16] Besides elucidating the structures of **1**–**4**, we were also interested in the structure of similar compounds containing chlorine. Attempts to obtain PhTeCl[36] by treatment of $(PhTe)_2$ with SO_2Cl_2 and then [$PhE(L)PhE'Cl_4$] according to Equation (1) failed; the analysis of the final material revealed merely the presence of [PhTe(TU)Cl][18] and the starting materials $PhTeCl_3$ or $PhSeCl_3$.

X-ray Crystallography

The X-ray studies showed that the asymmetric units of compounds **1** and **2** (Figures 1 and 2, respectively) present the general formula [$PhTe(L)PhTeX_4$] [**1**: L = TMTU (tetramethylthiourea), X = Br; **2**: L = TU (thiourea), X = I] Since the Te2–Br2 and Te2–I4 distances in **1** and **2** [3.1757(13) and 3.1687(8) Å] are similar to the Te1–Br2 and Te1–I4 distances, but much smaller than the Te1–Br3′ and Te1–I4′ bond lengths of 3.8471(13) and 3.7602(12) Å. According to Alcock's concept of secondary bonds,[1] the latter bonds are examples of this type of interaction. Thus, it is plausible to state that the asymmetric units are neutral monomers connected by secondary Te···X interactions into dimers with the formula [LPhTe(μ-X)$TeX_3Ph]_2$. The crystal structures of compounds **3** and **4** (Figures 3 and 4, respectively) are built up of discrete [$PhTeX_4]^-$ anions (**3**: X = I; **4**: X = Br) and the corresponding [$PhSe(TU)]^+$ cations. Considering the E···X secondary bonds, the complex salts **3** and **4** should be classified as pseudo-dimeric (**3**) or polymeric (**4**) assemblies.

The two $PhTe(TMTU)PhTeBr_4$ units in complex **1** are related by a center of inversion in the center of the rectangle formed by the atoms Te1, Br3, Te1′, and Br3′ (Figure 1). The Br3 and Br3′ atoms form secondary bonds to the Te1′ and Te1 atoms, respectively, thereby closing the dimeric arrangement. The geometry around the Te^{IV} atom (Te1) may be described as distorted octahedral with bonds to five bromine atoms (Br1, Br2, Br3, Br4, and Br3′) and to one aromatic carbon atom (C11). The geometry around the Te^{II} atom (Te2) presents a T-shape and involves a bromine atom (Br2), a sulfur atom, and an aromatic carbon (C21). The Br2 atom is shared by both tellurium atoms located in the same asymmetric unit, thereby suggesting the occurrence of a charge-transfer compound. The sum of the van der Waals radii of Te and Br is 4.0 Å.[37] The Te2–S bond length of 2.455(3) Å agrees with similar examples in the literature containing a Br–Te–S arrangement.[29] An intramolecular contact is observed between Te^{II} and the π-system of the phenyl ring C11–C16, resulting in a relatively short distance

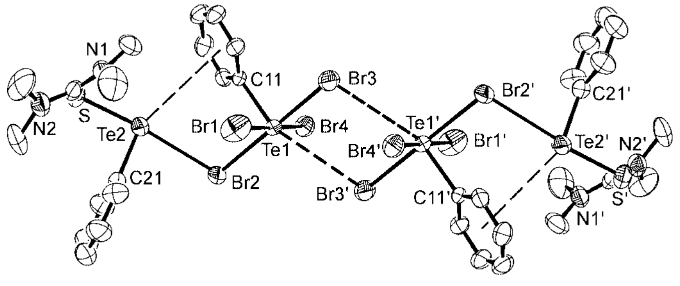

Figure 1. Crystal structure of **1** (hydrogen atoms omitted). Ellipsoids are drawn at 50 % probability. Selected bond lengths [Å] and angles [°]: Te1–Br1 2.6446(15), Te1–Br2 2.7728(14), Te1–Br3 2.6300(13), Te1–Br4 2.7090(16), Te1–Br3′ 3.8471(13), Te1–C11 2.142(7), Te2–Br2 3.1757(13), Te2–S 2.455(3), Te2–C21 2.097(9); Br1–Te1–Br2 88.53(4), Br1–Te1–Br3 90.49(5), Br1–Te1–Br4 177.58(4), Br1–Te1–Br3′ 81.18(4), C11–Te1–Br1 89.4(2), C11–Te1–Br2 89.4(2), C11–Te1–Br3 90.1(2), C11–Te1–Br4 88.9(2), Te1–Br2–Te2 102.27(4), Br2–Te2–S 173.38(7), Br2–Te2–C21 82.2(2), C21–Te2–S 91.2(2). Symmetry transformation used to generate equivalent atoms (′): –*x* – 1, –*y* + 1, –*z* + 1.

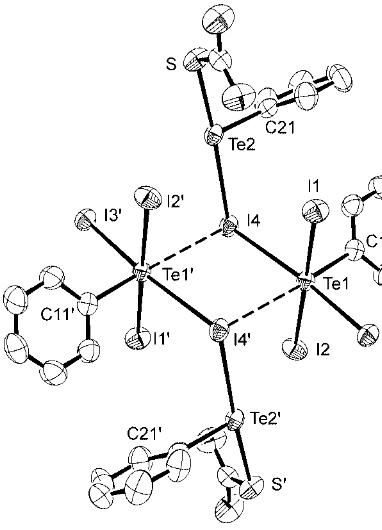

Figure 2. Crystal structure of **2** (hydrogen atoms omitted). Ellipsoids are drawn at 50 % probability. Selected bond lengths [Å] and angles [°]: Te1–I1 2.9053(8), Te1–I2 2.9519(8), Te1–I3 2.7953(7), Te1–I4 3.2651(7), Te1–I4′ 3.7602 (12), Te1–C11 2.144(6), Te2–I4 3.1687(8), Te2–S 2.4924(18), Te2–C21 2.110(6); I1–Te1–I2 178.21(2), I1–Te1–I3 88.36(2), I1–Te1–I4 90.52(17), I1–Te1–I4′ 82.31(2), C11–Te1–I1 91.88(17), C11–Te1–I2 89.85(17), C11–Te1–I3 94.40(17), Te1–I4–Te2 106.84(2), I4–Te2–S 176.11(5), I4–Te2–C21 90.19(17), C21–Te2–S 91.93(18). Symmetry transformation used to generate equivalent atoms (′): 1 – *x*, 1 – *y*, 1 – *z*.

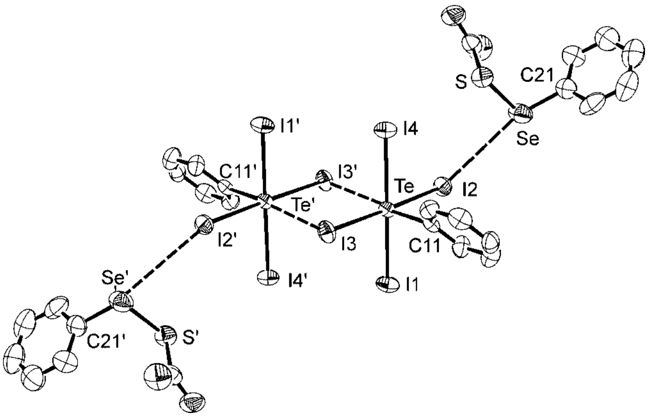

Figure 3. Crystal structure of **3** (hydrogen atoms omitted). Ellipsoids are drawn at 50 % probability. Selected bond lengths [Å] and angles [°]: Te–I1 2.9211(7), Te–I2 2.9614(8), Te–I3 2.9218(8), Te–I4 2.9521(7) Te–I3′ 3.8343(10), Te–C11 2.159(8), Se–I2 3.9485(12), Se–S 2.194(3), Se–C21 1,919(10); I1–Te–I2 89.64(2), I1–Te–I3 90.65(2), I1–Te–I4 176.89(3), I1–Te–I3′ 88.54(2), C11–Te–I1 91.93(18), C11–Te–I2 91.56(18), C11–Te–I3 90.97(18), Te–I2–Se 139.56(3), I2–Se–S 81.86(7), I2–Se–C21 154.2(3), C21–Se–S 100.0(3). Symmetry transformation used to generate equivalent atoms (′): –*x*, –*y*, –*z* + 2.

between Te^{II} and C12 [3.577(23) Å] in the solid-state structure of **1**. The distance between the Te^{II} atom and the centroid of the phenyl ring is 3.935(18) Å and can be interpreted as a Te–η^6-π-interaction.[38]

The $PhTe(TU)PhTeI_4$ units in complex **2** are also related by a center of inversion in the middle of the rectangle formed by the atoms Te1, I4, Te1′, and I4′. The dimer is connected through the I4 and I4′ atoms. The geometry around the Te1 atom may also be described as distorted octahedral, with bonds to five iodine atoms (I1, I2, I3, I4, and I4′) and to one aromatic carbon atom (C11). The Te1–I3 bond [2.7953(7) Å] is shorter than the *trans* Te1–I4 [3.2651(7) Å] and the Te2–I4 [3.1687(8) Å] bonds, probably due to the bridging role of the I4 atom,. The I4 atom is shared by both tellurium atoms located in the same asymmetric unit, which also suggests the occurrence of a charge-transfer process as in compound **1**.

In a recent work Aragoni et al.[6] discussed the ionic $\{[RSeCN]^+I^-\}$ or "T-shaped" hypervalent {R(I)SeCN} features of an ICN adduct with a selenium donor. Density functional theory (DFT) calculations, among other studies, have accounted for the strong polarity of the Se–I bond as being due to the selenium atom having a partial hypervalent state. These results allowed the authors to conclude that the compound can be described as the product of a donor–acceptor interaction between I and the selenium atom of the organic cation $[RSeCN]^+$. This evidence can also be used to support our molecular interpretation of the monomeric fragments $LPhTe(\mu\text{-}X)TeX_3Ph$ of compounds **1** and **2**, although with a reasonably strong polarization of the bonds Br2–Te2 in **1** and I4–Te1 in **2**. The $[PhTeS(R)]^+$ fragment of **1** and **2** would correspond to the organic cation $[RSeCN]^+$ of Aragoni and co-workers.[6] The dimerization

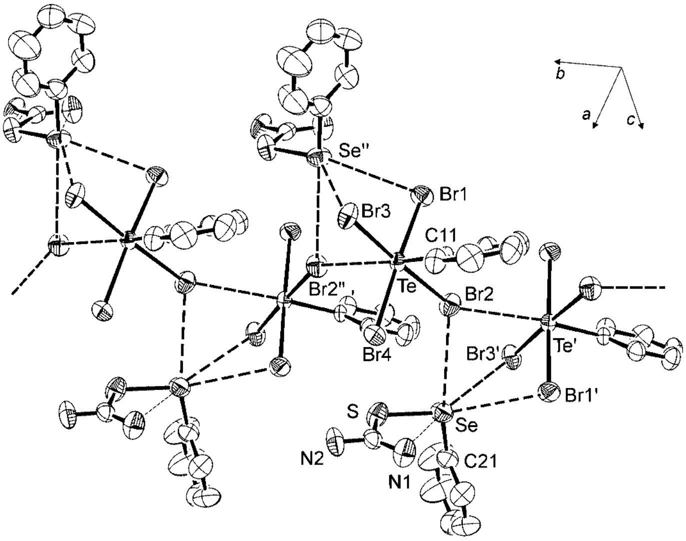

Figure 4. Crystal structure of **4** (hydrogen atoms omitted). Ellipsoids are drawn at 50 % probability. Selected bond lengths [Å] and angles [°]: Te–Br1 2.6535(12), Te–Br2 2.7688(12), Te–Br3 2.6163(12), Te–Br4 2.7309(12), Br2–Te′ 3.5775(13), Te–C11 2.148(9), Se–Br1′ 3.7113(18), Se–Br2 3.6853(16), Se–Br3′ 3.9395(17), Se–S 2.196(4), Se–C21 1.930(11), Se–N1 3.1681(97); Br1–Te–Br2 87.29(4), Br1–Te–Br3 89.69(4), Br1–Te–Br4 176.28(4), C11–Te–Br1 92.3(2), C11–Te–Br2 90.2(2), C11–Te–Br3 89.4(2), Te–Br1–Se′′ 94.02(4), Te–Br2–Se 124.00(5), Te–Br3–Se′′ 89.53(4), Br2–Se–S 93.87(10), Br2–Se–C21 156.1(3), C21–Se–S 100.3(4). Symmetry transformation used to generate equivalent atoms (′): –*x*, *y* – 0.5, –*z* + 1; (′′): –*x*, *y* + 0.5, –*z* + 1.

of the compounds through secondary Te···X bonds indicates the presence of a partial positive charge on the Te atom, as expected in hypervalent adducts with halogens. However, complexes **1** and **2** cannot be classified as charge-transfer (CT) complexes. Indeed, based on their structures and literature precedents[4,6] they should be considered CT-type compounds where the donor–acceptor interaction occurs from the μ-Br2 and μ-I4 atoms of the octahedral [PhTeX$_4$] fragment, which acts as donor, to the empty σ* molecular orbital located on the S–Te axis of the [PhTeS(R)]$^+$ moiety.

The crystal structure of complex **3** is built up of [PhTeI$_4$]$_2^{2-}$ anions stabilized by two [PhSeTU]$^+$ cationic units. The I3 and I3′ atoms connect the [PhTeI$_4$]$^-$ anionic units and the I2 and I2′ atoms present a weak interaction with the Se and Se′ atoms of cationic [PhSeTU]$^+$ units. The geometry around the Te atom can be described as distorted octahedral as it is bonded to five halogen atoms (I1, I2, I3, I4 and I3′) and to one aromatic carbon atom (C11). The geometry around the Se atom shows a distorted T-shaped form; the Se atom is bonded to one sulfur atom, one aromatic carbon atom (C21), and weakly bonded to one iodine atom [Se–I2 = 3.9485(12) Å]. The ionic formulation of compound **3** is supported by the fact that the Se–I bond length is much longer than analogous bond lengths in previously reported structures [Se–I = 2.564(1)–2.720(1) Å].[39,40] The structure of **3** is quite different from that of compound **1** with regards to the coordination sphere of the Te^{II} and Se^{II} atoms. The Te^{II} atom in **1** has a tendency to form an intramolecular bond of the type Te···η^6-π-aryl, while for **3** the Se^{II} atom coordinates preferentially to iodide atoms. Weak Se^{II}···I secondary interactions link the neighboring molecules into a chain along the crystallographic *b* axis. Also of interest in the structure of **3** is the presence of four identical weak I···I secondary interactions [3.7128(8) Å] with adjacent molecules to give a polymeric, double-zigzag chain along the crystallographic *a* axis. As in **2** and in other organotellurium triiodides,[14] intramolecular I···I and Te···I secondary interactions contribute to the formation of continuous supramolecular chains in the crystal packing.

The crystal structure of complex **4** is built up of discrete cationic [PhSeTU]$^+$ and anionic [PhTeBr$_4$]$^-$ units, with halogen atoms bridging secondary adjacent tellurium atoms to give a single zigzag polymeric chain along the crystallographic *b* axis. The chain character is additionally reinforced by three secondary bonds from cationic selenium atoms to the bromine ligands of the surrounding anionic units (Figure 4). The geometry around the Te atom, which is bonded to five bromine atoms (Br1, Br2, Br3, Br4, and Br2′′) and to one aromatic carbon atom (C11), may be described as distorted octahedral. The Se atom shows a highly distorted octahedral geometry, with secondary bonds to three bromine atoms (Br1, Br2′′, Br3) and primary bonds with one aromatic carbon atom (C21) and the sulfur/nitrogen atoms of the thiourea ligand. The interionic Se···Br secondary bonds of **4**, with distances varying from 3.6853(16) (Se–Br2) to 3.9395(17) Å (Se–Br3′) can be considered weak interactions when compared with the Se–Br bond lengths of 2.3331(8) Å in 2-Me$_2$NCH$_2$C$_6$H$_4$SeBr,[32,41] for example. The Se–N1 bond length of 3.1681(97) Å in **4** is also a very weak interaction when compared with Se–N bond lengths of other compounds such as 2-Me$_2$NCH$_2$C$_6$H$_4$SeX: [X = Cl: Se–N = 2.135(4) Å; Br: 2.143(6) Å; I: 2.172(3) Å].[42]

^{125}Te and ^{77}Se NMR Spectroscopy

Attempts to study the title complexes in noncoordinating solvents by means of NMR spectroscopy were unsuccessful due to their poor solubility. Since compounds **1**–**4**, as expected, do not show many significant features in their ^{1}H or ^{13}C NMR spectra, our attention turned to ^{125}Te and ^{77}Se NMR spectroscopy. A mixture of [D$_6$]acetone and [D$_6$]DMSO (9:1 by volume) was employed for the NMR studies. The two signals detected for **1** at δ = 1203.3 and 828.8 ppm (for **2** only one broad signal is observed at δ = 946 ppm) appear very close to the two peaks observed at δ = 1202.3 and 824.8 ppm for PhTeBr$_3$, whose spectrum was recorded under the same conditions for comparison purposes. The dissolution of PhTeBr$_3$ presumably produces the ionic species shown in Equation (2).

$$2\,\mathrm{PhTeBr_3} \xrightarrow{\mathrm{DMSO}} [\mathrm{PhTe^{IV}Br_2}]^+ + [\mathrm{PhTe^{IV}Br_4}]^- \qquad (2)$$

The major signal of compound **1** at δ = 1203.3 (s) ppm should correspond to the ionic form [PhTe^{IV}Br$_4$]$^-$, which occurs at δ = 1199.8 ppm for the standard compound (NEt$_4$)[PhTeBr$_4$]. This result allows also us to conclude that the dissolution of compound **1** (and probably also of **2**) leads to the cleavage of all the bonds represented by dotted lines in Figure 1 (e.g., the secondary Te1–Br3′ and the primary Te2–Br2 bonds). This also supports the assumption that the second signal of compound **1** [δ = 828.8 (s) ppm] should correspond to the cationic species [PhTe(L)]$^+$.

The selenium derivatives **3** and **4** seem to exhibit a different behavior in solution. While compound **4** presents only a sharp ^{125}Te resonance at δ = 1230.2 ppm, compound **3** does not show any NMR signal even though different windows were investigated. Furthermore, in the case of **4** two sharp ^{77}Se resonances are found at δ = 655.9 and 446.5 ppm in an approximate proportion of 1:1. This result supports the hypothesis of a partial disruption of the polymer according to Equation (3).

$$\{[\mathrm{PhSe(TU)}][\mathrm{PhTeBr_4}]\}_n \rightarrow n/2\ \{\mathrm{PhSe(TU)}[\mathrm{PhTeBr_4}]_2\}^- + n/2\ [\mathrm{PhSe(TU)}]^+ \qquad (3)$$

The anionic species might be fluxional and variable-temperature studies would be needed to characterize such a system. Unfortunately, we could not do this because of the limited solubility of all compounds in solvents adequate for low-temperature studies.

Conclusions

A good familiarity with the coordination chemistry and reactivity of organyl chalcogen compounds in the single oxidation states +2 and +4 is required and desirable for the adequate planning of different syntheses (one pot) to give good yields of organyl chalcogenides derivatives with mixed valence states.

The X-ray analytical data of the structures of compounds **1**–**4** show a strong tendency to dimerize for **1** and **2** and suggest that the formation of supramolecular assemblies depends on the nature of the halogen bonded to the tellurium atom. The halogen can induce simultaneous intra- and intermolecular secondary interactions among the heavy atoms and, in addition to Te···X and X···X secondary bonds, intramolecular interactions of the type Te···η^6-π-aryl can be formed. Secondary bonds are usually not strong enough to remain in solution, especially in coordinating solvents, but they can have spectacular effects in the building of a crystal by creating the secondary structure that defines the supramolecular arrangement in the solid state.[43,44] These findings also suggest further investigations of the steric influence of the organic substituents on the final architecture of the compounds.

Experimental Section

General Procedure: All manipulations were conducted under dinitrogen, using standard Schlenk techniques. Methanol was dried with sodium and distilled prior to use. Diphenyl diselenide and diphenyl ditelluride were prepared according to literature methods.[45,46]

X-ray Structural Determination: The structures were solved by direct methods using SHELXS-97.[47] Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL-97 package.[47] All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions. Crystal data and more details of the data collections and refinements are contained in Table 1.
CCDC-286671–286674 (**1**–**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

NMR Spectroscopy: All NMR spectra were recorded with a Varian Mercury plus spectrometer (7.05 T) operating at 94.74 MHz for ^{125}Te and 57.23 MHz for ^{77}Se. ^{125}Te and ^{77}Se NMR spectra were acquired in a mixture of [D$_6$]acetone and [D$_6$]DMSO (9:1 by volume) and were externally referenced to Me$_2$Te and Me$_2$Se checked against Te$_2$Ph$_2$ in CDCl$_3$ (δ = 450.0 ppm)[48] and Se$_2$Ph$_2$ in CDCl$_3$ (δ = 461.0 ppm),[49] respectively. The sample temperature was maintained at 300 K during the acquisitions.

General Procedure for the Synthesis of PhE(L)PhE′X$_4$. PhTe(TU)PhTeI$_4$: Iodine (1 mmol, 0.2538 g) was added to a solution of diphenyl ditelluride (1 mmol, 0.4092 g) in methanol at room temperature. The mixture was stirred for 10 min until the color changed from red to black. Thiourea (2 mmol, 0.1522 g) was then added to the mixture − the color of the solution changed from black to red − and soon afterwards PhTeI$_3$ (2 mmol, 1.1706 g) was added. The solution was kept at slow reflux for 2 h. The final solution was filtered at room temperature and crystals suitable for X-ray analysis were grown by slow evaporation.
1: Yield: 1.0141 g (65 %). M.p. 189–192 °C. C$_{17}$H$_{22}$Br$_4$N$_2$STe$_2$: calcd. C 23.71, H 2.57, N 3.25; found C 24.44, H 2.81, N 3.89. ^{125}Te NMR: δ 1203.3 (s), 828.8 (s) ppm.
2: Yield: 1.2907 g (63 %). M.p. 147–149 °C; C$_{13}$H$_{14}$I$_4$N$_2$STe$_2$: calcd. C 15.72, H 1.42, N 2.82; found C 16.00, H 1.47, N 2.73. ^{125}Te NMR: δ = 946 ppm (br).
3: Yield: 1.2840 g (68 %). M.p. 168–170 °C; C$_{13}$H$_{14}$I$_4$N$_2$SSeTe: calcd. C 16.53, H 1.49, N 2.97; found C 16.82, H 1.42, N 2.89.
4: Yield: 1.2853 g (85 %), Melting point: 178–180 °C; C$_{13}$H$_{14}$Br$_4$N$_2$SSeTe: calcd. C 20.64, H 1.87, N 3.70; found C 19.42, H 2.05, N 3.88. ^{125}Te NMR: δ = 1230.2 ppm (s). ^{77}Se NMR: δ = 655.9 (s), 446.5 (s) ppm.

Table 1. X-ray data collection and refinement parameters.

	1	**2**	**3**	**4**
Empirical formula	$C_{17}H_{22}Br_4N_2STe_2$	$C_{13}H_{14}I_4N_2STe_2$	$C_{13}H_{14}I_4N_2SSeTe$	$C_{13}H_{14}Br_4N_2SSeTe$
Mol. wt.	861.27	993.12	944.48	756.52
a [Å]	9.2793(13)	9.3392(16)	9.3920(4)	8.8030(3)
b [Å]	11.529(3)	10.7434(16)	9.7050(6)	9.2070(4)
c [Å]	12.249(2)	12.052(4)	13.2290(7)	13.0240(5)
α [°]	100.12(3)	91.833(14)	74.580(3)	
β [°]	103.511(14)	105.699(10)	73.040(3)	98.460(3)
γ [°]	93.40(2)	94.491(13)	88.710(3)	
V [Å^3]	1247.3(4)	1158.8(4)	1109.87(10)	1044.10(7)
Z	2	2	2	2
D_c [g cm^{-3}]	2.293	2.846	2.826	2.406
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1$
Cryst. size [mm]	0.15 × 0.1 × 0.05	0.14 × 0.1 × 0.08	0.14 × 0.1 × 0.05	0.13 × 0.1 × 0.07
$2\theta_{max}$ [°]	54	54	50	50
Linear absorption coefficient [mm^{-1}]	8.835	7.934	8.635	10.918
Absorption correction	DELABS[50]	DELABS[50]	SORTAV[51]	SORTAV[51]
T_{min}	0.3508	0.7003	0.3777	0.3310
T_{max}	0.6664	0.9413	0.6720	0.5327
Measured reflections	6413	5934	9872	7476
Independent reflections/R_{int}	5403/0.0662	5010/0.0243	3915/0.0479	3428/0.0876
Refined parameters	235	200	200	200
$R1$ (F)/$wR2$ (F^2) [$I > 2\sigma(I)$]	0.0597/0.1707	0.0401/0.1043	0.0380/0.1025	0.0429/0.1101
Device	CAD4	CAD4	BRUKER CCD	BRUKER CCD
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
GOF (F^2)	1.010	1.155	1.032	1.034

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[1] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1–58.

[2] B. Krebs, F.-P. Ahlers, *Adv. Inorg. Chem.* **1990**, *35*, 235–317.

[3] W.-W. Du Mont, J. Jeske, P. G. Jones, *Phosphorus, Sulfur Silicon Relat. Elem.* **1998**, *136–138*, 305–308.

[4] M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, F. Lelj, V. Lippolis, G. Verani, *Chem. Eur. J.* **2001**, *7*, 3122–3133.

[5] M. C. Aragoni, M. Arca, A. J. Blake, F. A. Devillanova, W. W. du Mont, A. Garau, F. Isaia, V. Lippolis, G. Verani, C. Wilson, *Angew. Chem.* **2001**, *113*, 4359–4362; *Angew. Chem. Int. Ed.* **2001**, *40*, 4229–4232.

[6] M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, P. Grimaldi, F. Isaia, F. Lelj, V. Vippolis, G. Verani, *Eur. J. Inorg. Chem.* **2004**, 2363–2368.

[7] P. C. Srivastava, S. Bajpai, S. Bajpai, C. Ram, R. Kumar, J. P. Jasinski, R. J. Butcher, *J. Organomet. Chem.* **2004**, *689*, 194–202.

[8] A. K. S. Chauhan, Anamika, A. Kumar, R. C. Srivastava, R. J. Butcher, J. Beckmann, A. Duthie, *J. Organomet. Chem.* **2005**, *690*, 1350–1355.

[9] P. C. Srivastava, *Phosphorus, Sulfur Silicon Relat. Elem.* **2005**, *180*, 969–983.

[10] P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, S. J. Teat, *J. Chem. Soc., Dalton Trans.* **1999**, 2845–2852.

[11] E. Schulz Lang, R. M. Fernandes Jr., E. T. Silveira, U. Abram, E. M. Vázquez-López, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1401–1404.

[12] P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, S. Sarwar, J. M. Sheffield, *Angew. Chem.* **2000**, *112*, 1866–1868; *Angew. Chem. Int. Ed.* **2000**, *39*, 1796–1798.

[13] E. Schulz Lang, G. Manzoni de Oliveira, E. T. Silveira, R. A. Burrow, E. M. Vázquez-López, *J. Organomet. Chem.* **2002**, *664*, 306–309.

[14] G. N. Ledesma, E. Schulz Lang, U. Abram, *J. Organomet. Chem.* **2004**, *689*, 2092–2095.

[15] E. Schulz Lang, U. Abram, J. Strähle, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1968–1972.

[16] G. N. Ledesma, E. Schulz Lang, E. M. Vázquez-López, U. Abram, *Inorg. Chem. Commun.* **2004**, *7*, 478–480.

[17] E. Schulz Lang, R. M. Fernandes Jr., C. Peppe, R. A. Burrow, E. M. Vázquez-López, *Z. Anorg. Allg. Chem.* **2003**, *629*, 215–218.

[18] E. Schulz Lang, G. Manzoni de Oliveira, R. M. Fernandes Jr., E. M. Vázquez-López, *Inorg. Chem. Commun.* **2003**, *6*, 869–872.

[19] E. Schulz Lang, G. Manzoni de Oliveira, R. M. Fernandes Jr., E. M. Vázquez-López, *Z. Anorg. Allg. Chem.* **2004**, *630*, 717–721.

[20] C. Knobler, J. D. McCullough, *Inorg. Chem.* **1977**, *16*, 612–615.

[21] R. K. Chadha, J. E. Drake, *J. Organomet. Chem.* **1985**, *293*, 37–43.

[22] N. Al-Salim, A. A. West, W. R. McWhinnie, T. A. Hamor, *J. Chem. Soc., Dalton Trans.* **1988**, 2363–2371.

[23] H. B. Singh, N. Sudha, R. T. Butcher, *Inorg. Chem.* **1992**, *31*, 1431–1435.

[24] J. Nvosad, K. W. Törnroos, M. Necas, A. M. Z. Slawin, J. D. Woollins, S. Huseby, *Polyhedron* **1999**, *18*, 2861–2867.

[25] M. Necas, J. Novosad, S. Huseby, *J. Organomet. Chem.* **2001**, *623*, 124–130.

[26] H. Fleischer, B. Mathiasch, D. Schollmeyer, *Organometallics* **2002**, *21*, 526–533.

[27] N. W. Alcock, W. D. Harrison, *Acta Crystallogr., Sect. B* **1982**, *38*, 2677–2679.

[28] N. W. Alcock, W. D. Harrison, *J. Chem. Soc., Dalton Trans.* **1984**, 869–875.

[29] O. Foss, S. Huseby, *Acta Chem. Scand.* **1966**, *20*, 132–142.

[30] I. D. Sadekov, V. I. Minkin, A. V. Zakharov, A. G. Starikov, G. S. Borodkin, S. M. Aldoshin, V. V. Tkachev, G. V. Shilov, F. J. Berry, *J. Organomet. Chem.* **2005**, *689*, 103–119.
[31] S. C. Menon, H. B. Singh, J. M. Jasinski, J. P. Jasinski, R. J. Butcher, *Organometallics* **1996**, *15*, 1707–1712.
[32] G. Mugesh, H. B. Singh, R. J. Butcher, *Tetrahedron: Asymmetry* **1999**, *10*, 237–242.
[33] H. M. K. K. Pathirana, J. H. Reibenspies, E. A. Meyers, R. A. Zingaro, *Acta Crystallogr., Sect. C* **1991**, *47*, 516–519.
[34] D. B. Werz, R. Gleiter, F. Rominger, *J. Organomet. Chem.* **2004**, *689*, 627–630.
[35] P. G. Jones, J. Jeske, *Private Communication*, **2004**, CCDC 239392.
[36] K. Giselbrecht, B. Bildstein, F. Sladky, *Chem. Ber.* **1989**, *122*, 1255–1256.
[37] *Periodic Table of the Elements*, VCH, Weinheim, **1986**.
[38] J. Zukerman-Schpector, I. Haiduc, *CrystEngComm* **2002**, *4*, 178–192.
[39] O. Vikane, *Acta Chem. Scand.* **1975**, *A29*, 787–793.
[40] S. M. Godfrey, D. G. Kelly, C. A. McAuliffe, A. G. Mackie, R. G. Pritchard, S. M. Watson, *J. Chem. Soc., Chem. Commun.* **1991**, 1163–1164.
[41] F. Cristiani, F. Demartin, F. A. Devillanova, F. Isaia, V. Lippolis, G. Verani, *Inorg. Chem.* **1994**, *33*, 6315–6324.
[42] T. M. Klapötke, B. Krumm, K. Polborn, *J. Am. Chem. Soc.* **2004**, *126*, 710–711.
[43] J. D. McCullough, C. Knobler, *Inorg. Chem.* **1976**, *15*, 2728–2731.
[44] J. D. McCullough, *Inorg. Chem.* **1977**, *16*, 2318–2321.
[45] H. J. Reich, J. M. Renga, I. L. Reich, *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447.
[46] a) K. J. Irgolic, *Houben-Weyl Methods of Organic Chemistry*, Vol. E 12b, Organotellurium Compounds (Ed.: D. Klamann), **1990**, 273; b) W. S. Haller, K. J. Irgolic, *J. Organomet. Chem.* **1972**, *38*, 97–103.
[47] G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, Programs for Crystal Structure Solution and Refinement; University of Göttingen, Germany, **1997**.
[48] M. Asahara, M. Tanaka, T. Erabi, M. Wada, *J. Chem. Soc., Dalton Trans.* **2000**, 3493–3499.
[49] S. Kumar, S. K. Tripathi, H. B. Singh, G. Wolmershäuser, *J. Organomet. Chem.* **2004**, *689*, 3046–3055.
[50] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158–166.
[51] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.

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