Properties of Chalcogen−Chalcogen Bonds, 23[+]

Novel Mesityltellurium Cations from Selenenation and Tellurenation Reactions of Dimesityl Telluride in the Presence of the $Br_2/AgSbF_6$ Reagent

Jörg Jeske,[a] Wolf-Walther du Mont,*[a] Frank Ruthe,[a] Peter G. Jones,[a] Laura M. Mercuri,[b] and Paola Deplano[b]

Dedicated to Professor Brigitte Sarry on the occasion of her 80th birthday

Keywords: Tellurium / Cations / Hypervalency / Secondary interactions / Selenium / Xerox process

The reaction of dimesityl telluride (**2**) with bis(pentafluorophenyl) diselenide (**1**), Br_2 and $AgSbF_6$ provides small amounts of crystalline $[Mes_2TeSeC_6F_5][SbF_6]$ (**3**). The main products, however, are $[Mes_2TeTeMes][SbF_6]$ (**4**) and $MesSeC_6F_5$ (**5**). Reactions of **2** with Br_2 and $AgSbF_6$ provide – depending on the stoichiometric ratio – **4** and $[Mes_3Te][SbF_6]$ (**6**) or $[Mes_2TeBr][SbF_6]$ (**7**). **2**, Mes_2Te_2, Br_2 and $AgSbF_6$ provide **4** in a fair yield. Addition of **2** to **4** leads to the tritellurium salt $[Mes_5Te_3][SbF_6]$ (**8**). Cation–anion interactions due to the α-heteroatom electrophilicity of RSe-, RTe- and Br-substituted telluronium salts are followed by structure determinations of **3**, **4**, **6**, **7** and **8** and by Raman-spectroscopic observations of the Te–Te vibrations in compounds **4** and **8**.

Introduction

In the course of the Xerox process, undesired residual charges can persist after exposure of amorphous Se/Te alloys to light. These residual charges may be due to charge separation by formation of chalcogenonium cations (with 3 covalent bonds) and chalcogenolate anions (with only 1 covalent bond) in the solid sate, as depicted schematically in Scheme 1 for tellurium chains.[1]

Such polar defects in Se/Te alloys should be metastable with respect to thermal reactions (i.e. collapsing of the ion pairs) leading to "classical" chalcogen chains involving only di-coordinated selenium and tellurium. We propose an alternative, namely that persistent "-onium" and "-ate" functionalities might interact with each other in a nonclassical way (Scheme 2), leading to structural moieties related to Böttcher's hypervalent polytellurides.[2−4] As organic model compounds for such interactions and as novel "isomers" of the stable diaryl tellurides that might mimic unusual soft−soft interactions, telluronium tellurolates Ph_3Te^+ TeR^- were studied with respect to their existence, structure and mode of decomposition.[5] These compounds exist in the solid state as dimers of ion pairs exhibiting weak cation−anion tellurium−tellurium interactions. At room temperature, the orange-red solids decompose into the more stable diaryl tellurides, accompanied by small amounts of the related ditellurides and biphenyl [Equation (1)]. Telluronium selenolates are slightly more stable than the tellurolates, but they exhibit similar structures and decomposition pathways.

$$(Ph_3TeER)_2 \rightarrow Ph_2Te + PhTeER + R_2E_2 + Ph_2$$

$$ER = p\text{-}CH_3C_6H_4Te,\ p\text{-}CH_3C_6H_4Se^{[5]} \qquad (1)$$

Intuitively, and from comparison with homonuclear cation−anion interactions by (n→σ*) overlap in iodophosphonium ions,[6] we expect that the cation−anion interactions and the colour of $[Ph_3TeER]_2$ (E = Se, Te) would be determined by n(E) → σ*(C−Te) interactions. These would also explain the VSEPR-consistent coordination geometries of the Te and Se atoms of the dimers of ion pairs.[5] The coordination geometries of pyramidal (3-Te-8) and hypervalent square-pyramidal (5-Te-12) tellurium atoms allow the application of extended (n→σ*) interactions (4 orthogonal 3-center-4-electron systems), involving p orbitals of the anions as donor functions and σ* (C−Te) energy levels as acceptors, as a qualitative bonding model. These cation−anion interactions, however, are much weaker than Te−Te contacts within "nonclassical" polytellurides[2−4,7] and polytellurium dications.[8]

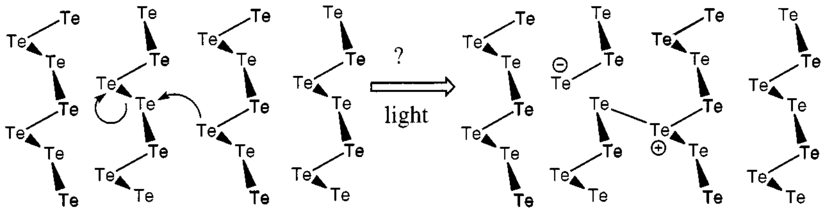
Calculations on $[R_3TeER]_n$ (R = H, Me; n = 1, 2) on the basis of the experimental Te···Te and Te···Se distances,

---

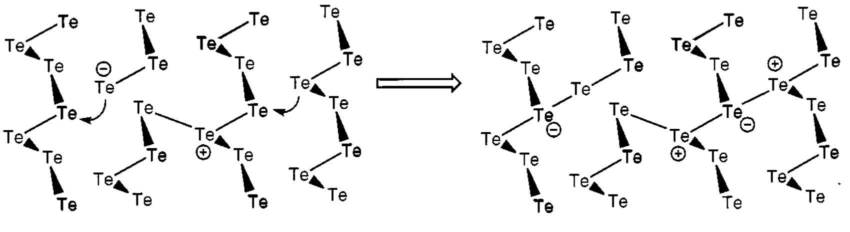
[+] Part 22: Ref.[21]

[a] Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig
Postfach 3329, 38023 Braunschweig, Germany
Fax: (internat.) + 49-(0)531/391-5387
E-mail: w.du-mont@tu-bs.de

[b] Dipartimento di Chimica Inorganica ed Analitica, Università di Cagliari,
Cittadella di Monserrato, 90131 Monserrato-Cagliari, Italy
Fax: (internat.) + 39-070/675-4499
E-Mail: deplano@vaxca1.unica.it



Scheme 1. The valence-alternation model ($2C_2^0 \rightarrow C_3^+ + C_1^-$) for localised gap states in lone-pair semiconductors applied to tellurium (Kastner−Adler−Fritzsche model)[1]



Scheme 2. "Classic" (8-Te-3 and 8-Te-1) (left) and "hypervalent" (8-Te-3 and 10-Te-3) (right) version of the Kastner−Adler−Fritzsche model

however, do not indicate a positive contribution of Te−Te and Te−Se orbital overlap to the overall energy.[9] The poor acceptor properties of R_3Te^+ towards RTe^- and RSe^- reflect the relative strength (a kind of "*trans* effect") of Te−C bonds, which do not offer low-lying σ* levels to facilitate the attack of donating nucleophiles.[10] Atoms that are more weakly bonded to the telluronium centre, however, would encourage the attack of donating nucleophiles, as shown by the increased electrophilicity of hypothetical $TeI_3^+$and $MeTeI_2^+$ cations relative to R_3Te^+ cations in Me_3Te^+ $MeTeI_4^-$ [11] and $(Ph_3Te^+)_2$ TeI_6^{2-}.[12] For this reason, we decided to synthesise telluronium ions containing one "soft" chalcogen atom adjacent to the formally positively charged tellurium atom of the cation. As an electron-withdrawing substituent we chose the pentafluorophenylseleno group. As further substituents, mesityl groups were selected to enhance crystallisation. An initial experiment explored whether bis(pentafluorophenyl) diselenide (**1**) would add oxidatively to dimesityl telluride (**2**) yielding an, as yet unknown, compound of the type $R_2Te(SeR')_2$ (formally regarded as an adduct of a $[R_2TeSeR']^+$ cation with a RSe^- anion). ^{77}Se- and ^{125}Te-NMR spectra of the reaction mixture, however, did not provide evidence for the presence of the compound $Mes_2Te(SeC_6F_5)_2$.[13] To elucidate whether the failure of the desired oxidative addition of **1** to the diaryl telluride **2** was really due to thermal instability of $Mes_2Te(SeC_6F_5)_2$ (and not to kinetic factors), we then attempted to generate an $[R_2TeSeR']^+$ cation by an independent route.

Reactions

Triorganylperoxonium ions $[R_2OOR]^+$,[13] -disulfonium ions $[R_2SSR]^+$,[14,15] related organoselenium cations such as $[(MeSe)_2SeMe]^+$ [15] and $[Ph_2Se_6]^{2+}$ [16] and oxytelluronium cations $[R_2TeOTeR_2]^{2+}$,[17,18] are well-known species; corresponding selenotelluronium salts $[R_2TeSeR']^+$ X^-, however, have not yet been reported in the literature,[5,12] Such compounds will undergo reductive elimination when the counterion X^- is a good nucleophile towards the $R'Se^+$ group. Salts of the type $[RR'TeTeR']^+$ X^- have been proposed as reactive intermediates when dialkyl ditellurides were activated by alkyl halides for one-pot reactions with carbon nucleophiles.[19] Oxidation of molecules that contain two R_2Te functions in the presence of poorly nucleophilic counteranions has led to a number of cyclic dications with $[R_2Te{-}TeR_2]^{2+}$ moieties;[20] in the presence of two R_2Se donor functions, hypervalent species with dicationic $[RR'Se{-}TeR''_2{-}SeRR']^{2+}$ functions have been generated.[20]

For the generation of $(Mes_2TeSeC_6F_5)^+$ SbF_6^- (**3**) we chose the oxidation of bis(pentafluorophenyl) diselenide (**1**) in the presence of dimesityl telluride (**2**), and SbF_6^- as a poorly nucleophilic counteranion. On addition of few drops of the Ag[SbF$_6$] solution in CH_2Cl_2 to the mixture of **1**, **2**, and Br_2, the solution became deep red; precipitation of AgBr occurred only after addition of the complete amount of Ag[SbF$_6$]. Crystallisation by diffusion of hexane first provided very dark crystals of a novel compound **4**, which did not contain selenium. Spectroscopic and analytical data and a crystal-structure determination confirmed that **4** is unexpectedly a dimesityl(mesityltelluro)telluronium salt [Mes$_2$TeTeMes][SbF$_6$].[21] At a later stage of the crystallisation procedure, a small amount of the originally desired orange-brown selenotelluronium salt **3** and further crystals of black **4** were isolated. An NMR investigation of the remaining oil revealed the presence of mesityl pentafluorophenyl selenide (**5**) [$\delta^{77}Se = +370$, $^3J(^{77}Se, ^{19}F) = \pm 11$ Hz]. Unexpected products **4** and **5** indicated cleavage of the Te−C bonds (loss of a mesityl group of **2**) and formation of a new Se−C bond by attachment of a mesityl group to selenium providing **5** [Equation (2)]. To gain more insight into the loss of a mesityl group from **2**, we treated **2** with 1/2 Br_2 and Ag[SbF$_6$] only. This reaction also provided crystals of compound **4**; however, these black crystals were accompanied by a small amount of greenish crystals of [Mes_3Te][SbF_6] (**6**) [Equation (3)]. This "aryl scrambling" could be associated with a disproportionation by aryl transfer between two R_2Te^+ cations or within an [$R_2Te{-}TeR_2$]$^{2+}$ dication, with an aryl cation transfer from R_2Te^{2+} to R_2Te providing R_3Te^+ and RTe^+, the latter being trapped by coordination with R_2Te. A somewhat related formal tellurium analogue to the pinacol−pinacolone rearrangement had previously been discussed when the rearrangement of Wöhler's "α-base $R_2Te(OH)_2$" into the "β-base"[22] was recognised as an alkyl transfer between tellurium atoms.

$$\underset{\mathbf{1}}{(C_6F_5)_2Se_2} + \underset{\mathbf{2}}{Mes_2Te} + Br_2 + 2\,AgSbF_6 \rightarrow \underset{\mathbf{3}}{(Mes_2TeSeC_6F_5)SbF_6} + \underset{\mathbf{4}}{(Mes_2TeTeMes)SbF_6} + \underset{\mathbf{5}}{MesSeC_6F_5} + 2\,AgBr \qquad (2)$$

$$2\,\mathbf{2} + Br_2 + 2\,AgSbF_6 \rightarrow \mathbf{4} + \underset{\mathbf{6}}{(Mes_3Te)SbF_6} + 2\,AgBr \qquad (3)$$

The observed partial decomposition of **2** upon oxidation with Br_2/$AgSbF_6$ into **4** and **6** would correspond to a dismutation 2 $R_2Te \rightarrow R_3Te^+ + RTe^-$,[6] if the cation of **4** were formally regarded as an adduct of the tellurolate anion $MesTe^-$ with the dication Mes_2Te^{2+}. Carrying out the bromination of **2** with *one* equivalent of Br_2 (Mes_2Te/Br_2, 1:1) and adding one equivalent of $AgSbF_6$ allowed the isolation of the bromotelluronium salt [Mes_2TeBr][SbF_6] (**7**) as yellow crystals [Equation (4)]. In the absence of the diselenide **1**, mesityl group transfer between **7** or the intermediate dication [Mes_2Te]$^{2+}$ and **2**, provided Mes_3Te^+ (the cation of compound **6**), whereas coordination of the remaining $MesTe^+$ moiety with **2** then led to stable **4** [Equation (5)]. In the presence of diselenide **1**, mesityl group transfer to the arylseleno group provided **5**, the remaining $MesTe^+$ moiety was again coordinated by **2** furnishing stable **4**. The latter type of reaction can indeed be verified using Mes_2Te_2, Br_2, $AgSbF_6$ and **2**: this synthesis is an excellent large-scale preparation of compound **4** [Equation (5)].[21] The isolation of compound **4** was favoured by its extremely low solubility; no solution-NMR data of **4** could be obtained.

$$\mathbf{2} + Br_2 + AgSbF_6 \rightarrow \underset{\mathbf{7}}{(Mes_2TeBr)SbF_6} + AgBr \qquad (4)$$

$$2\,\mathbf{2} + Mes_2Te_2 + Br_2 + AgSbF_6 \rightarrow 2\,\mathbf{4} + 2\,AgBr \qquad (5)$$

However, on addition of one further equivalent of **2** to suspended **4**, the black precipitate dissolved and provided the soluble novel [bis(dimesityltelluronio)mesityl tellurolate(II)] hexafluoroantimonate, $Mes_5Te_3SbF_6$ (**8**). The cation of **4** was obviously still coordinatively unsaturated and by adding one more equivalent of **2** "saturated" **8** was obtained, which contains a hypervalent central tellurium atom [Equation (6)]. This addition of **2** to **4** forming **8** is closely related to the well-known addition of I^- to I_2 to give I_3^-, which contains a hypervalent central iodine atom. Related homonuclear trichalcogen moieties with linearly coordinated central hypervalent sulfur or selenium atoms have been known since the detection of trithiapentalenes,[23] the tris(selenocyanate) monoanion and related species.[24] A related tetracationic system with approximately linear Se−Se···Se arrangements is formed by the interaction of one molecule of 1,2-bis(3-methyl-2-selenoxo-4-imidazolinyl)ethane ("ebis") with two [$(ebis)_2$]$^{2+}$ dications.[25] An organotellurium anion with an approximately linear triiodide-like Te_3 moiety related to **8**[21] was detected only recently.[26]

$$\mathbf{2} + \mathbf{4} \rightarrow \underset{\mathbf{8}}{[(Mes_2Te)_2TeMes]SbF_6} \qquad (6)$$

Spectroscopic and Structural Studies

Comparison of Selenotelluronium Salt 3 and Tellurotelluronium Salt 4

The description of the ditelluronium cation in **4** as a mesitylenetellurenyl cation $MesTe^+$, stabilised by the coordinating Lewis base **2**, is supported by the nature and extent of the various intermolecular interactions of the cations of **4** and of the closely related compound **3** with their SbF_6^- counteranions in the solid state. In solid **4** two cations and two anions form cyclic molecular dimers through secondary Te···F interactions,[21] in solid **3** similar sequences of Te···F and Se···F interactions lead to polymeric chains of cations and anions (Figure 1−4).

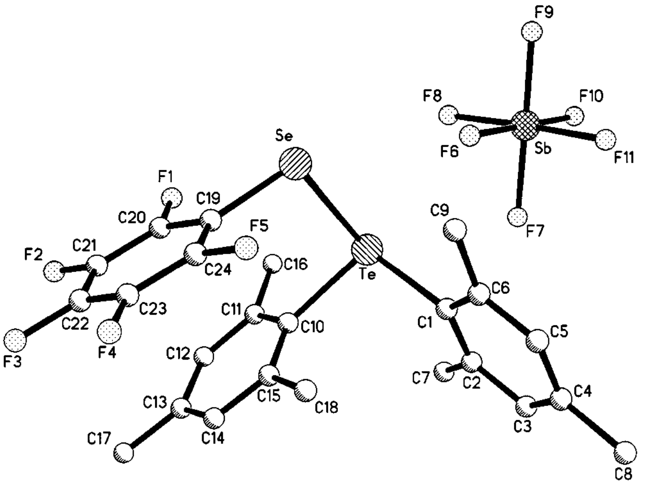


Figure 1. Molecular structure of **3** (cation−anion contacts neglected); selected distances [pm] and angles [°]: Te−C(10) 211.5(3), Te−C(1) 213.3(4), Se−C(19) 190.1(4), Te−Se 257.55(5), Sb−F(6) 189.1(2), Sb−F(7) 187.9(2), Sb−F(11) 185.8(2); C(10)−Te−C(1) 101.80(13), C(10)−Te−Se 96.10(9), C(19)−Se−Te 101.30(11)

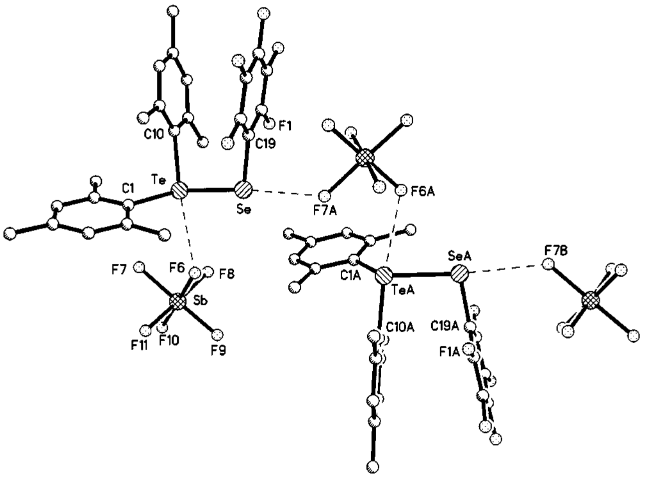


Figure 2. Cation−anion interactions in solid **3**; selected distances [pm] and angles [°]: Te−F(6) 296.2(2), Se−F(7)#1 301.1(2); C(10)−Te−F(6) 173.84(10), C(1)−Te−F(6) 81.28(10), Se−Te−F(6) 77.76(5), C(19)−Se−F(7)#1 84.25(12)

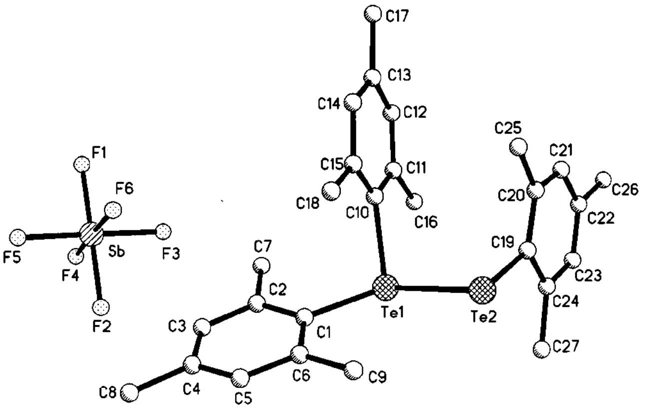


Figure 3. Molecular structure of **4** (cation−anion contacts neglected); selected distances [pm] and angles [°]: Te(1)−C(1) 214.1(4), Te(1)−C(10) 212.7(4), Te(2)−C(19) 213.1(5), Te(1)−Te(2) 276.45(5), Sb−F(1) 187.2(3), Sb−F(2) 186.7, Sb−F(5) 183.9(3); C(1)−Te(1)−Te(2) 112.76(12), C(10)−Te(1)−Te(2) 95.34(11), C(19)−Te(2)−Te(1) 86.18(12)

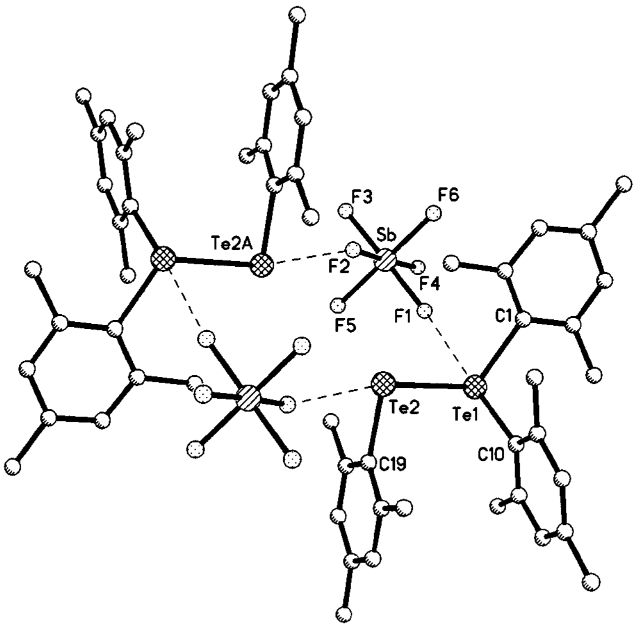
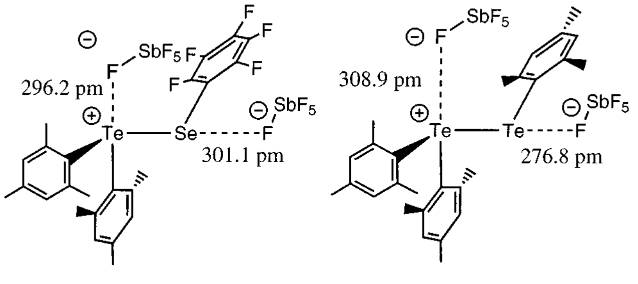


Figure 4. Intermolecular interactions within dimers of **4**; selected distances [pm] and angles [°]: Te(1)−F(1) 308.9(3), Te(2)−F(2A) 276.8(3); C(10)−Te(1)−F(1) 175.65(12), Te(2)−Te(1)−F(1) 88.94(6), Te(1)−Te(2)−F(2A) 168.27(9), C(19)−Te(2)−F(2A) 83.01(14)

The coordination geometry of all chalcogen atoms in **3** and **4** can be described as pseudo-trigonal-bipyramidal, when secondary Te···F and Se···F contacts are taken into consideration. When Te1 is considered as the central atom (*one* lone pair of electrons, 10-Te-4[27]), the neighbouring F atom adopts an apical position (C10−Te−F6 in **3**: 173.8°, C10−Te1−F1 in **4**: 175.6°), and the neighbouring "two-coordinated" chalcogen atom is equatorial. Regarding the Se atom in **3**, the gradual transition from two-coordination towards a "T-type" surrounding (10-Se-3[27]) can be recognised from the nearly linear arrangement Te−Se···F (Te−Se−F7A 173.8°, Te−Se−C19 101.3°, C19−Se−F7A 84.2°). For the "two-coordinated" Te atom in **4** the geometric features of a typical "T-type" structure (Te1−Te2−F2 168.3°, Te1−Te2−C19 86.2°, C19−Te2−F2 83°) are fully expressed. The typical T-type geometry is associated with a short contact between the "two-coordinated" Te atom and a fluorine atom of the counterion. This Te···F contact of the Te atom in the α-position to the telluronium centre of **4** (Te2···F2A 276.8 pm) is significantly shorter than the Te···F contact from the telluronium centre that bears the formal +1 charge (Te1−F1 308.9 pm) and is also shorter than the Se···F contact in **3** (**3**: Se···F7A 301.1 pm). The latter contact is longer (weaker) than the Te···F contact involving the telluronium centre, which is the predominant type of cation−anion interaction (Te···F6 296.2 pm) of the selenotelluronium salt; i.e. **3** is "the normal case" whereas **4** exhibits the unusual short Te···F contact involving the formally uncharged tellurium atom. This rather strong F→Te donor−acceptor interaction also coincides with a slight lengthening of the Te−Te bond in **4** (Mes_2Te_2: d = 270 pm;[28] **4**: d = 276.45 pm) and with a bathochromic shift of the Te−Te vibration mode in the Raman spectrum of **4** (143 cm^{-1}) compared with uncharged Me_2Te_2 [$\tilde{\nu}$(Te−Te) = 181 cm^{-1}] (Scheme 3).[29]



Scheme 3. Cation−anion interactions in **3** and **4**

Weakening of Te···Te bonds is to be expected when the F→Te donation leads to partial population of the σ* orbital of the Te−Te bond. The extent of the latter interaction allows the prediction that the Te atom involved, in the α-position to the telluronium centre, will have acceptor properties as a Lewis acid. Following this, **4** can be understood as a type of arenetellurenyl cation (RTe^+) that is coordinated but not yet coordinatively saturated by one diaryl telluride nucleophile.[10,30] The bridging of the cations of **3** and **4** by the SbF_6^- anions through donor−acceptor interactions correlates well with the expansion of the bridging Sb−F bonds of the anions [**3**: *d*(Sb−F) between 185.8 ppm (terminal) and 189.1 pm (bridging); **4**: *d*(Sb−F) between 183.9 (terminal) and 187.2 pm (bridging)]. As a test of the electrophilicity of **4**, the reaction of **4** with another molecule of **2** as a nucleophile was carried out. This led to the detection of the hypervalent cation **8**.[21]

Structures of Trimesityltelluronium Salt 6 and Bromodimesityltelluronium Salt 7

The propeller-like conformation of the cation of **6** with angles C−Te−C close to tetrahedral (104−109°) is very similar to that of the known compound Mes_3TeI.[31] Te···F contacts are very long (363−367 pm), i.e. cations and anions are well separated (Figure 5, 6).

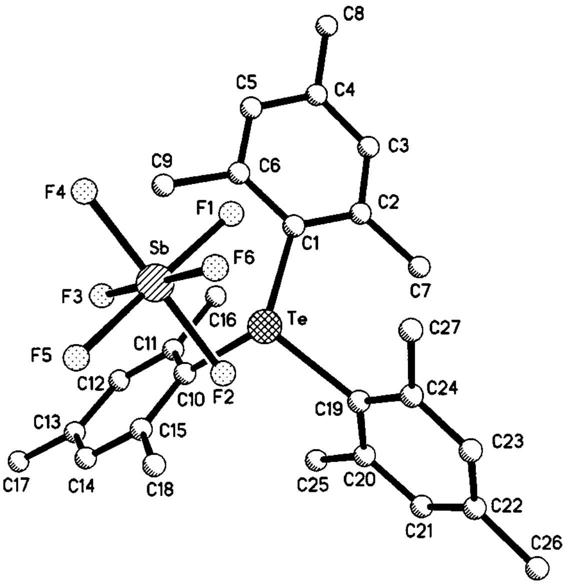


Figure 5. Molecular structure of **6**; selected distances [pm] and angles [°]: Te−C(1) 213.5(3), Te−C(10) 213.1(3), Te−C(19) 213.7(3), Te−F(1) 366.9(2), Te−F(2) 363.7(2), Te−F(3) 366.3(2) Sb−F(1) 187.3(2), Sb−F(4) 186.2(2); C(1)−Te−C(10) 104.42(11), C(1)−Te−C(19) 109.25(12), C(19)−TeC(19) 104.57(12)

The solid bromodimesityltelluronium salt **7** contains two independent ion pairs within the asymmetric unit. Since the fluorine atoms of both anions are disordered (they were refined on two different positions, see Figure 6), only a qualitative description of the cation−anion interactions can be given. The bromotelluronium salt **7** can be regarded as closely related to **3** and **4**: They contain telluronium cations with rather "soft" heteroatoms adjacent to the formally charged tellurium centre, offering two choices for cation−anion interactions. The shortest Te···F distances in **7** range from 262 to 324 pm, i.e., they are comparable to the Te···F distance of **3** and to that involving the formally charged telluronium centre of **4**. The coordination spheres of the Te atoms of **7** can be regarded as pseudo-trigonal-bipyramidal, with two carbon atoms and the lone pair in equatorial positions and an apical Te−F contact. The bromine atoms of the cations of **7** participate in the cation−anion interaction network by exhibiting contacts to (disordered) fluorine atoms of the SbF_6^- anions [Br(2)−F(3A) and Br(2)−F(3′A), depicted in Figure 6]. These Br···F distances, being shorter than the Se···F distances in **3**, indicate a certain Lewis acidity of the bromine atoms, a general property of heavy α-heteroatoms adjacent to onium centres.[5,12,21]

Compounds R_2TeBr_2 generally exist as molecular (10-Te-4) species with two apical Te−Br bonds, even when R is a very good electron-withdrawing substituent.[31] Being closer to an ideal 2c−2e bond, the Te−Br bond of **7** is significantly shorter than the apical Te−Br bonds of $(C_6F_5)_2TeBr_2$.[32]

Description of the Tritellurium Cation 8

Trialkyldisulfonium cations $[R_2SSR]^+$ do not tend to valence-shell expansion of sulfur by cation−anion interactions[14] or by addition of a second dialkyl sulfide nucleophile. The purple-black compound **4**, however, reacted in a straightforward manner with **2**, providing the novel brown-red "pentaaryltritelluranium" salt **8**. Due to its moderate solubility, a full set of solution-NMR data of **8** could be collected. The two Mes_2Te groups within the cation of **8** are NMR-equivalent; their ^{125}Te-NMR signal [$\delta(^{125}Te) = +854$] and the ^{125}Te-NMR signal of the central MesTe moiety of **8** [$\delta(^{125}Te) = +388$] are broadened to a somewhat different extent, and the Te−Te NMR coupling cannot be resolved. Dynamic exchange equilibria in solution were confirmed by addition of a small amount of **2** to a solution of **8**: from such a mixture, one averaged signal from free and coordinated **2** [$\delta(^{125}Te) = +842$] and a further signal from the unaffected central MesTe moiety [$\delta(^{125}Te) = +385$] were resolved. The related tritelluride anion $Ph_3Te_3^-$ [26] is also kinetically labile in solution. Crystalline **8**[21] contains $Mes_5Te_3^+$ cations, SbF_6^- anions and CH_2Cl_2. The cation contains an approximately linear Te_3 backbone. The two Te−Te distances are slightly different (Te1−Te2 304.9 pm, Te3−Te1 297.9 pm); they are both significantly longer in comparison with Te−Te single bonds such as those of **4** (Figure 7) or Mes_2Te_2. The average Te−Te distance of **8** (301.5 pm) is similar to that of $Ph_3Te_3^-$ (302.5 pm),[32] shorter than the typical Te−Te distances of linear Te−Te−Te moieties of "nonclassical" inorganic polytellurides, for instance the Te_5^{4-} ion within solid NaTe: *central*: *d*(TeTe) = 308 pm; *terminal*: *d*(TeTe) = 282 pm.[2,33] From the vibrational spectra of solid **8**, a strong Raman emission at 102 cm^{-1} can be assigned to the symmetric Te_3 stretching mode (Figure 8). The analogy of the position of this Raman emission to that of a slightly asymmetric triiodide anion is clear.[34,35] However, it is surprising, that the antisymmetric vibration is apparently not resolved in the IR spectrum.

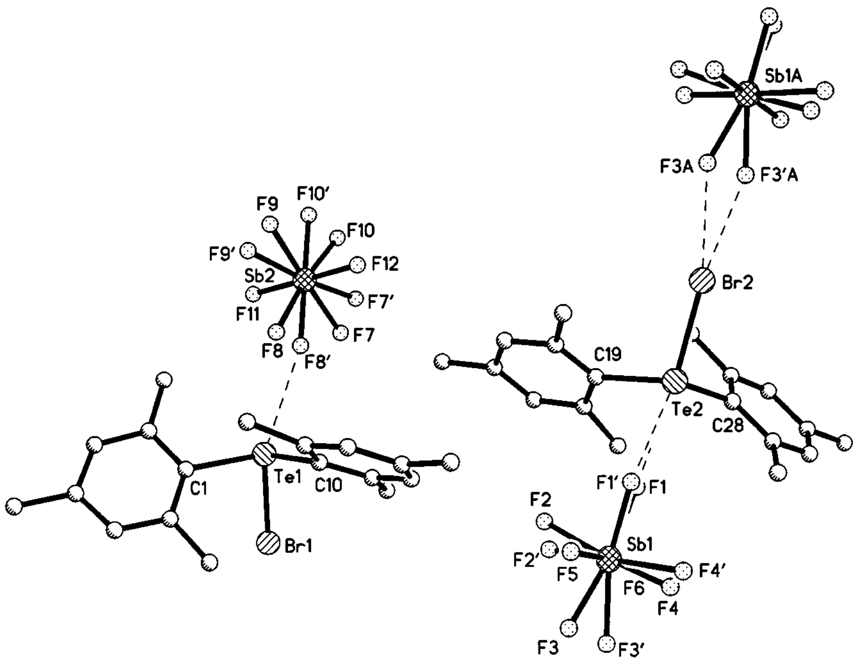


Figure 6. Structures of the two independent ion pairs and anion disorder of **7**; selected distances [pm] and angles [°], ion pair 1: Te(1)−C(1) 211.6(11), Te(1)−C(10) 212.9(10), Te(1)−Br(1) 250.9(2), Te(1)−F(8) 324(2), Te(1)−F(8′) 293(2); C(1)−Te(1)−C(10) 106.8(4), C(1(Te(1)−Br(1) 91.6(3), C(10)−Te(1)−Br(1) 101.8(3); ion pair 2: Te(2)−C(28) 213.9(12), Te(2)−C(19) 213.1(11), Te(2)−Br(2) 247.9(2), Te(2)−F(1) 262(2), Te(2)−F(1′) 266(2), Br(2)−F(3A) 269(2), Br(2)−F(3′A) 280(2); C(28)−Te(2)−C(19) 106.4(4), C(28)−Te(2)−Br(2) 93.4, C(19)−Te(2)−Br(2) 100.5(3)

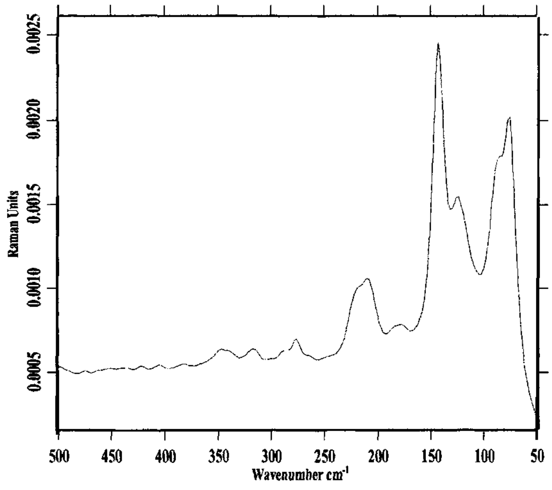


Figure 7. Raman emissions of solid **4**

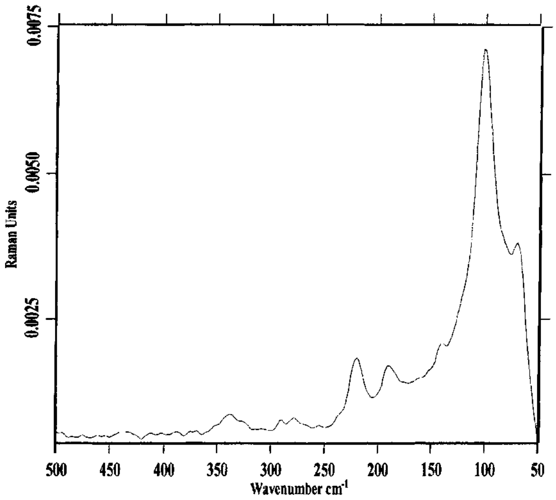
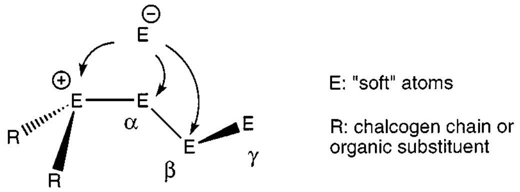


Figure 8. Raman emissions of solid **8**

A strong IR absorption at 289 cm^{-1} is observed in **8** and **4** (in the latter the band is less symmetric showing a shoulder at approximately 278 cm^{-1}). This band seems to confirm the presence of SbF_6 anions (it is present in all the samples containing this anion that we have investigated including $AgSbF_6$), while the vibrations expected in the Raman spectrum appear as weak peaks in **8** and **4**, the Raman spectra being dominated by the strong inter-tellurium vibrations. Surprisingly, to the best of our knowledge, a strong IR absorption at 289 cm^{-1} has not been reported previously in spite of numerous vibrational studies involving SbF_6 anions.[36] An (unassigned) strong IR absorption at 275 cm^{-1} has been reported for solid $[Cp_2ReCl_2](SbF_6)_3$.[37] For an SbF_6 anion in an octahedral structure, three Raman-active vibrations [$\nu_1(A_{1g})$ (668 cm^{-1}), ν_2 (E_g) (558 cm^{-1}) and ν_5 (F_{2g}) (294 cm^{-1})] and two infrared-active vibrations [$\nu_3(F_{1u})$ (669 cm^{-1}), ν_4 (F_{1u})(350 cm^{-1})] are expected.[38] The sixth vibration ν_6 (F_{2u}) calculated at 294 cm^{-1}, is predicted to be inactive in both the infrared and Raman spectra, but should become infrared-active in those structures that have lower symmetry than O_h.[39] We suggest that the band at 289 cm^{-1} is due to ν_4, and the presence of a shoulder at 278 cm^{-1} in **4** could be associated to ν_6, whose activity is related to the lowering of the symmetry as a result of the observed distortions in this anion (Figure 7).

The formation of nonclassical linear Te_3 moieties has been described theoretically as the hypothetical addition of Te^{2-} ions to Te_2^{2-} ions,[2,4] The above reaction of nucleophile **2** with electrophile **4** furnishing **8** is the first well-defined addition of two $8e^-$-tellurium species to form a linear $10e^-$-Te_3 species.[21,26] This model reaction provides an experimental approach to understanding how cationic defects in solid selenium−tellurium alloys (Scheme 1 and 2) may be stabilised by acceptor−donor interaction of adjacent two-coordinate tellurium atoms with tellurium atoms of neighbouring tellurium chains. However, it should be noted that soft heteroatoms (such as Se and Te) in β- and γ-positions from the onium centre can also exhibit certain Lewis-acidic properties (Scheme 4).



Scheme 4. Sites of nucleophilic attack in chalcogen cations

As in the stabilisation of onium-like cationic defects ("C-3") above, masking of the *negative* charges ("C-1") (Scheme 1) by local formation of hypervalent anionic Te_3 moieties (such as those in $LiTe_3$, $Ph_3Te_3^-$ or $NaTe_3$ [2,4,26,33,40]) will contribute to the stabilisation of anionic defects in tellurium.

Experimental Section

^{77}Se- and ^{125}Te-NMR spectra were run with a Bruker AM 200 spectrometer (38.2 MHz for ^{77}Se and 63.1 MHz for ^{125}Te) using CH_2Cl_2 as a solvent, if not otherwise specified. *J* values are given in Hz. − Raman spectra (resolution ± 4 cm^{-1}) were recorded with a Bruker RFS 100 FTR spectrometer (Nd:YAG laser excitation, 1064 nm). The solid samples, in the form of powders or crystals, were packed into glass capillary tubes and then fitted into the compartment designed for use with a 180° scattering geometry. The power level of the laser source was in the range of 70−150 mW. − Far-FTIR spectra (500−50 cm^{-1}) were recorded with a Bruker IFS 55 spectrometer (as polyethylene pellets). − Mass spectra were determined with Finnegan MAT 8430 and 4315 spectrometers [EI, 70 eV, CI, or FAB with *o*-nitrobenzylamine (NBA)]. − Melting points were determined with a Kofler hot-stage microscope and all values are uncorrected. − Elemental analyses were carried out by the Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie, Technische Universität Braunschweig. Solvents were dried by distillation under nitrogen from the appropriate drying agent, glassware was flame-dried and cooled under a stream of nitrogen.

3: A solution of $AgSbF_6$ (0.68 g, 2.0 mmol) in 10 mL of dichloromethane was added to a stirred mixture of Mes_2Te (1.1 g, 2.0 mmol), $(C_6F_5Se)_2$ (0.49 g, 1.0 mmol) and Br_2 (0.08 g, 0.50 mmol), dissolved in 30 mL dichloromethane. Upon addition of the first drops of the $AgSbF_6$ solution, the reaction mixture adopted an intense red colour. Precipitation of silver bromide occurred after all the $AgSbF_6$ had been added. After 30 min, the silver bromide was removed by filtration and a layer of 40 mL of hexane was carefully added to the red-brown solution. Within 18 h, the two phases had mixed by diffusion and black crystals (compound **4**) had separated from the mixture. The supernatant liquid was decanted and all volatiles were removed under vacuum until an oily residue remained. This residue was dissolved in a small amount of dichloromethane and a layer of hexane was again carefully added to the solution. Another crop of **4** (black crystals) was accompanied by a small amount of orange-brown crystals [m.p. 154 °C (dec.)] which were identified by X-ray crystallography as the desired compound **3**. Correct elemental analytical data were not obtained. Attempts to purify crude **3** by fractional crystallisation led to isolation of a further amount of **4**, which appeared to be a decomposition product of crude **3**. Evaporation of the solvents from the remaining slightly yellowish mother liquor furnished a viscous oil. ^{77}Se-NMR spectra and EI mass spectra allowed to the detection of mesityl (pentafluorophenyl) selenide (**5**) and bis(pentafluorophenyl) diselenide (**1**) in the the oily residue. − ^{77}Se NMR of the mixture: δ = 370 [$^3J(^{77}Se,^{19}F)$ = 11.0 Hz, $(C_6F_5)_2Se_2$ = **1**], 176 [$^3J(^{77}Se,^{19}F)$ = 14.3 Hz, $C_6F_5{-}Se{-}Mes$ = **5**]. − EI-MS of the mixture; *m*/*z* (%): 494 (50) [$(C_6F_5)_2Se_2^+$], 366 (84) [$C_6F_5{-}Se^+{-}Mes$], 247 (100) [$C_6F_5{-}Se^+$], 119 (35) [Mes^+].

4: Bromine (0.12 g, 0.75 mmol) was added to a solution of Mes_2Te (0.55 g, 1.5 mmol) and Mes_2Te_2 (0.49 g, 0.75 mmol) in 30 mL of dichloromethane, at room temperature. Subsequently, silver hexafluoroantimonate (0.50 g, 1.5 mmol), dissolved in 5 mL of dichloromethane, was added to the mixture. The colour of the solution turned from brown to deep red and precipitation of silver bromide began. Stirring was continued in the dark for 1 h for the reaction to reach completion. After removal of the precipitate by filtration, hexane was added to the brown solution. **4** separated from the solution as a brown-violet powder (0.94 g; 74%) that melted at 189 °C (dec.). Black single crystals suitable for X-ray diffraction[21] were obtained with help of the diffusion method (dichloromethane solution/hexane). Crystalline **4** was only slightly soluble in dichloromethane (intensely greenish-brown solution) and in methanol (colourless solution). − $C_{27}H_{33}F_6SbTe_2$ (848.5): calcd. C 38.22, H 3.92; found C 38.37, H 4.03. − ^{1}H NMR (CD_2Cl_2): δ = 7.05 (2 H), 2.34 (6 H), 2.32 (3 H). − ^{125}Te NMR: no signal observed due to low solubility. − Raman: $\tilde{\nu}$ = ν(Te−Te) 143 cm^{-1}. − FAB-MS (NBA), positive mode; *m*/*z* (%): 741 (5) [$Mes_3Te_3^+$], 613 (40) [$Mes_3Te_2^+$], 494 (22) [$Mes_2Te_2^+$], 368 (100) [Mes_2Te^+], 248 (24) [$MesTe^+{-}H$], 119 (70) [Mes^+]; negative mode; *m*/*z* (%): 494 (7) [$Mes_2Te_2^-$], 472 (2.5) [$Sb_2F_{12}^-$], 235 (100) [SbF_6^-], 216 (2) [SbF_5^-], 197 (2) [SbF_4^-]. − FT-IR: $\tilde{\nu}$ = 341 (2.8), 321 (2.8), 289 (10), 278 sh, 218 (3.4) 62 (2.2) cm^{-1}. − FT-Raman: $\tilde{\nu}$ = 210 (4.0), 143 (10.0), 124 (5.0), 85 (shoulder), 76 (8.0) cm^{-1}.

7: A solution of 1 mmol of Mes_2TeBr_2 was prepared by oxidation of Mes_2Te (0.37 g, 1.0 mmol), dissolved in 10 mL of dichloromethane, with a solution of bromine (0.16 g, 1.00 mmol) in 5 mL of dichloromethane at 0 °C. Addition of silver hexafluoroantimonate (0.38 g, 1.0 mmol) led to a deep red solution and to the precipitation of AgBr, which was removed by filtration after continued stirring for 15 min. Upon addition of 35 mL of hexane to the red solution, a yellow precipitate separated from the yellowish supernatant solution. In order to remove the remaining amounts of silver bromide from the yellow crude product, the latter was again treated with 5 mL of dichloromethane and the undissolved solid (AgBr) was removed by filtration. Precipitation by addition of 10 mL of hexane provided 0.54 g (79%) of yellow **7** (m.p. 148 °C, dec.). − $C_{18}H_{22}BrF_6SbTe$ (681.6): calcd. C 31.72, H 3.25; found C 30.98, H

3.25. – ^{1}H NMR (CD_2Cl_2): δ = 7.16 (2 H), 2.52 (6 H), 2.39 (3 H). – ^{125}Te NMR (CH_2Cl_2/C_6D_6): δ = 1128. – FAB-MS (NBA), positive mode; *m*/*z* (%): 617 (8) [$Mes_3Te_2^+$], 520 (45) [NBA(Mes_2Te^+ – H], 447 (45) [Mes_2TeBr^+], 368 (85) [Mes_2Te^+], 248 (40) [$MesTe^+$ – H], 119 (100) [Mes^+].

8: A solution of **8**, prepared by slight warming of a mixture of $Mes_2TeTeMes\ SbF_6$ (**4**) (0.43 g, 0.50 mmol) and Mes_2Te (**2**) (0.25 g, 0.70 mmol) in 2 mL of dichloromethane, was kept at −18 °C in order to obtain crystals that were suitable for X-ray diffraction.[21] After separation of the clear brownish-red needles from the solution by filtration, the solvent-containing single crystals decomposed under vacuum into a brown powder of **8** (0.45 g, 74%) which melted at 169 °C (dec.). The given yield and analytical data concern the solvent-free final product. **8** was fairly soluble in dichloromethane; addition of hexane to such a solution led to a precipitate of **4**. – $C_{45}H_{55}F_6SbTe_3$ (1214): calcd. C 44.50, H 4.56; found C 44.64, H 4.48. – ^{1}H NMR (CD_2Cl_2): δ = 7.04 (2 H), 2.32 (6 H), 2.30 (3 H). – ^{125}Te NMR (CH_2Cl_2/C_6D_6): δ = 854, 388; after addition of a 20% excess of **1**: δ = 842, 385. – FAB-MS (NBA), positive mode; *m*/*z*: 741 (2) [$Mes_3Te_3^+$], 613 (40) [$Mes_3Te_2^+$], 494 (14) [$Mes_2Te_2^+$], 368 (100) [Mes_2Te^+], 248 (20) [$MesTe^+$–H], 119 (55) [Mes^+]; negative mode; *m*/*z*: 494 (7) [$Mes_2Te_2^-$], 472 (3) [$Sb_2F_{12}^-$], 235 (100) [SbF_6^-], 216 (2) [SbF_5^-], 197 (2) [SbF_4^-]. – FT-IR: $\tilde{\nu}$ = 326 (3.2), 289 (10.0), 204 (3.8), 100 (shoulder), 78 (4.6) cm^{-1}. – FT-Raman: $\tilde{\nu}$ = 220 (2.0), 189 (1.9), 141 (2.5), 102 (10.0), 78 (shoulder), 70 (5.2) cm^{-1}.

Crystal Structure Determination of 3: Empirical formula: $C_{24}H_{22}F_{11}SbSeTe$, M = 847.73; orthorhombic, space group *Pbca*, a = 1452.73(12) pm, b = 1583.6(2) pm, c = 2405.6(2) pm; V = 5.5341(9) nm^3; Z = 8; $d_{calcd.}$ = 2.035 Mg m^{-3}; μ = 3.433 mm^{-1}, T = 173 K. An orange prism (0.62 × 0.42 × 0.20 mm) was mounted in an inert oil. 6933 intensities were measured (2θ = 6–50°, ω-scans; $-17 < h < 6$, $-18 < k < 0$, $-28 < l < 0$) using Mo-K_α radiation (graphite monochromator) with a Siemens P4 diffractometer. After absorption correction (ψ-scans; min. and max. transmission: 0.516, 1.000), 4877 reflections were unique (R_{int} = 0.0190) and used for all calculations (program SHELXL-93[41]). The structure was solved by direct methods and refined anisotropically by full-matrix least squares on $|F|^2$. Rigid methyl groups were employed, all other protons were refined using a riding model. The final $wR(F^2)$ was 0.0576, with conventional $R(F)$ 0.0268 for 349 parameters and 267 restraints (highest peak 754, deepest hole −463 e/nm^3).

Crystal Structure Determination of 6: Empirical formula: $C_{27}H_{33}F_6SbTe$, M = 720.88; orthorhombic, space group *Pbca*, a = 1616.55(10) pm, b = 1738.52(12) pm, c = 1985.6(2) pm; V = 5.5804(7) nm^3; Z = 8; $d_{calcd.}$ = 1.716 Mg m^{-3}, μ = 2.067 mm^{-1}, T = 173 K. A green prism (0.62 × 0.60 × 0.55 mm) was mounted in an inert oil. 4908 intensities were measured (2θ = 6–50°, ω-scans; $-19 < h < 6$, $-20 < k < 0$, $-0 < l < 23$) using Mo-K_α radiation (graphite monochromator) with a Siemens P4 diffractometer. After absorption correction (ψ-scans; min. and max. transmission: 0.821, 0.948), 4908 reflections were unique (R_{int} = 0.0190) and 4906 were used for all calculations (program SHELXL-93).[41] The structure was solved by direct methods and refined anisotropically by full-matrix least squares on $|F|^2$. Rigid methyl groups were employed, all other protons were refined using a riding model. The final $wR(F^2)$ was 0.0509, with conventional $R(F)$ 0.0242 for 326 parameters and 249 restraints (highest peak 344, deepest hole −488 e/nm^3).

Crystal Structure Determination of 7: Empirical formula: $C_{36}H_{44}Br_2F_{12}Sb_2Te_2$, M = 1363.23; monoclinic, space group $P2_1/n$, a = 1144.2(2) pm, b = 1210.3(2) pm, c = 3171.8(5) pm; V = 4.3860(13) nm^3; Z = 4; $d_{calcd.}$ = 2.064 Mg m^{-3}, μ = 4.434 mm^{-1}, T = 143 K. A yellow cut needle (0.80 × 0.42 × 0.38 mm) was mounted in an inert oil. 8158 intensities were measured (2θ = 6–50°; ω-scans; $-13 < h < 6$, $0 < k < 14$, $-37 < l < 37$; data are composed of independent set plus some Friedel pairs) using Mo-K_α radiation (graphite monochromator) with a Stoe STADI-4 diffractometer. After absorption correction (ψ-scans; min. and max. transmission: 0.460, 0.764), 7722 reflections were unique (R_{int} = 0.0498) and 7703 were used for all calculations (program SHELXL-93).[41] The structure was solved by direct methods and refined anisotropically by full-matrix least squares on $|F|^2$. Rigid methyl groups were employed, all other protons were refined using a riding model. The final $wR(F^2)$ was 0.1982, with conventional $R(F)$ 0.0675 for 457 parameters and 24 restraints (highest peak 1849, deepest hole −1561 e/nm^3).

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-121862 (**3**), -100165 (**4**),[21] -121863 (**6**), -121964 (**7**), -100165 (**8**).[21] Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the INTAS/RFBR program (95–126) for financial support.

[1] M. Kastner, D. Adler, H. Fritzsche, *Phys. Rev. Lett.* **1976**, *37*, 1504–1507; R. A. Street, N. F. Mott, *Phys. Rev. Lett.* **1975**, *35*, 1293.

[2] P. Böttcher, *Angew. Chem.* **1988**, *100*, 781–794; *Angew. Chem. Int. Ed. Engl.* **1988**, *27,* 759.

[3] M. G. Kanatzidis, *Angew. Chem.* **1995**, *107*, 2281–2283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2109–2111.

[4] Q. Liu, N. Goldberg, R. Hoffmann, *Chem. Eur. J.* **1996**, *2*, 390–397.

[5] W.-W. du Mont, J. Jeske, P. G. Jones, *Angew. Chem.* **1996**, *108*, 2822–2824; *Angew. Chem. Int. Ed. Engl.* **1996***, 35*, 2653–2655.

[6] M. Bätcher, W.-W. du Mont, S. Pohl, W. Saak, *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *49*/*50*, 147–150; W.-W. du Mont, F. Ruthe, *Coord. Chem. Rev.* **1999**, *189*, 101–133.

[7] B. Schreiner, K. Dehnicke, K. Moczek, D. Fenske, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1414.

[8] J. Beck, *Coord. Chem. Rev.* **1997**, *163*, 55–70.

[9] C. Janiak, Universität Freiburg, EHT and PM3 calculations, personal communication.

[10] I. Haiduc, R. B. King, M. G. Newton, *Chem. Rev.* **1994**, *94*, 301–326.

[11] F. Einstein, J. Trotter, C. Williston, *J. Chem. Soc. A* **1967**, 2018–2023.

[12] J. Jeske, Dissertation TU Braunschweig, **1997**; W.-W. du Mont, J. Jeske, P. G. Jones, VII. Int. Conf. on the Chemistry of Selenium and Tellurium, Vaalsbroek Castle (NL)/Aachen (D), **1997** (Abstract); *Phosphorus Sulfur Silicon Relat. Elem.* **1999**, *136–138*, 305–308; J. Beck, A. Fischer, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1042.

[13] G. A. Olah, G. Rasul, Burrichter, M. Hachoumy, G. K. Surya Prakash, R. I. Wagner, K. O. Christe, *J. Am. Chem. Soc.* **1997,** *119,* 9571–9573.

[14] T. P. Hilditch, S. Smiles, *J. Chem. Soc.* **1907**, *91*, 1394–1399; R. Minkwitz, H. Prenzel, H. Pritzkow, *Z. Naturforsch.* **1987**, *B42*, 750–755.

[15] R. Laitinen, R. Steudel, R. Weiss, *J. Chem Soc., Dalton Trans.* **1986**, 1095−1100.

[16] R. Faggiani, R. J. Gillespie, J. W. Kolis, *J. Chem. Soc, Chem. Commun.* **1987,** 592.

[17] F. L. Gilbert, T. M. Lowry, *J. Chem. Soc.* **1928,** 3179−3189; P. Nylen, *Z. Anorg. Allg. Chem.* **1941**, *246*, 227−242.

[18] K. Kobayashi, N. Deguchi, E. Horn, N. Furukawa, *Angew. Chem.* **1998**, *110*, 1031−1033; *Angew. Chem. Int. Ed.* **1998**, *37*, 1026−1028.

[19] V. A. Potapov, S. V. Amosova, V. Yu. Shestakova, A. R. Zhnikin, B. V. Petrov, *Recl. Trav. Chim. Pays-Bas* **1996**, *215*, 441−442.

[20] H. Fujihara, T. Ninoi, R. Akaishi, T. Erata, N. Furukawa, *Tetrahedron Lett.* **1991,** *32*, 4537; H. Fujihara, H. Ishitani, Y. Takaguchi, N. Furukawa, *Chem. Lett.* **1995**, 571−572

[21] J. Jeske, W.-W. du Mont, P. G. Jones, *Angew. Chem.* **1997**, *109*, 2304−2306; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2219−2221.

[22] H. D. K. Drew, *J. Chem. Soc.* **1929,** 560−569.

[23] S. Bezzi, M. Mammi, C. Garbagli, *Nature* **1958**, *182*, 247.

[24] O. Foss, *Pure Appl. Chem.* **1970**, *24*, 31.

[25] F. Bigoli, P. Deplano, F. A. Devillanova, A. Girlando, V. Lippolis, M. L. Mercuri, M. A. Pellinghelli, E. F. Trogu, *Inorg. Chem.* **1996**, *35*, 5403−5406.

[26] A. C. Hillier, S. Y. Liu, A. Sella, M. R. J. Elsegood, *Angew. Chem.* **1999**, *111*, 2918−2920, *Angew. Chem. Int. Ed. Engl.* **1999**, *38,* 2745−2747.

[27] (10-Te-4) means: 10 valence electrons at the central Te atom, that contains 4 substituents: C. W. Perkins, J. C. Martin, A. J. Arduengo III., W. Lau, A. Alegria, J. K. Kochi, *J. Am. Chem. Soc.* **1980**, *102*, 7753.

[28] A. Edelmann, S. Brooker, N. Bertel, M. Noltemeyer, H. W. Roesky, G. M. Sheldrick, F. T. Edelmann, *Z. Naturforsch.* **1992**, *B47*, 305−309.

[29] C. W. Sink, A. B. Harvey, *J. Mol. Struct.* **1969,** *4*, 203; W. R. McWhinnie, P. Thavornyutikarn, *J. Organomet. Chem.* **1972**, *35*, 149−154.

[30] S. Hauge, O. Vikane, *Acta Chem. Scand., Ser A* **1983**, *27,* 723; W.-W. du Mont, H.-H. Meyer, S. Kubiniok, S. Pohl, W. Saak, *Chem. Ber.* **1992**, *125*, 761−766.

[31] M. Wieber, R. Habersack, *Phosphorus Sulfur Silicon* **1995,** *106***,** 233−241.

[32] N. W. Alcock, W. D. Harrison, *J. Chem. Soc., Dalton Trans.* **1984**, 869; D. Naumann, L. Ehmanns, K.-F. Tebbe, W. Crump, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1269−1276.

[33] P. Böttcher, R. Keller, *J. Less-Common Met.* **1985**, *109*, 311−321.

[34] P. Deplano, F. A. Devillanova, J. R. Ferraro, M. L. Mercuri, V. Lippolis, E. F. Trogu, *Appl. Spectrosc.* **1994**, *48*, 1236.

[35] P. Deplano, J. R. Ferraro, M. L. Mercuri, E. F. Trogu, *Coord. Chem. Rev.* **1999**, *188*, 71−95.

[36] J. Passmore, T. S. Cameron, P. D. Boyle, G. Schatte, T. Way, *Can. J. Chem*. **1996**, *74*, 1671, and references therein.

[37] P. Gowik, T. M. Klapötke, I. Torniepoth-Oetting, *Chem. Ber.* **1989**, *122*, 2273.

[38] K. Nakamoto, in "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*", 4th ed., John Wiley & Sons, Inc., New York, **1986**.

[39] G. M. Begun, A. C. Ruthenberg, *Inorg. Chem*. **1967**, *6*, 2212.

[40] D. Y. Valentine, O. B. Cavin, H. L. Yakel, *Acta Crystallogr. B* **1977**, *33*, 1389−1396.

[41] G. M. Sheldrick, *SHELXL-93, A Program for Crystal Structure Refinement*, Göttingen, **1993.**

Received January 20, 2000
[I00020]