

Synthesis of new T-shaped hypervalent complexes of tellurium showing Te– π -aryl interactions: X-ray characterization of [(mes)XTe(μ -X)Te(mes)(etu)] (X = Br, I) and [Ph(etu)Te(μ -I)Te(etu)Ph][PhTeI₄] (mes = mesityl; etu = ethylenethiourea)

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Abstract

Dimesityl ditelluride, (mesTe)₂, reacts with bromine/iodine and ethylenethiourea in methanol to give [(mes)XTe(μ -X)Te(mes)(etu)] {X = Br (**1**), I (**2**)}. The salt [Ph(etu)Te(μ -I)Te(etu)Ph][PhTeI₄] (**3**) is obtained by reflux of a mixture of (PhTe)₂, iodine, ethylenethiourea and PhTeI₃ in methanol. The new complexes were prepared in good yields by a one-pot procedure and characterized by single crystal X-ray diffraction. In the complexes **1** and **2**, the tellurium atoms perform Te– π -aryl interactions and attain T-shaped coordinations with a bridging halogen ligand. The [PhTeI₄][–] anions of complex **3** are associated in a quasi-dimeric configuration and the tellurium atoms achieve an octahedral coordination through secondary Te–I bonds.

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1. Introduction

Anionic complexes of organochalcogen halides such as [ArTeX₄][–] (X = Cl, Br, I) in form of polymeric chains or oligomeric structures, stabilized with a wide range of counter ions (protonated amines, alkali metal cations, etc.) are well known [1–5]. Most of these complex salts lie close to the ionic/covalent borderline and show properties of supramolecules due to interionic, fairly strong secondary bonds of the types NH \cdots X, E \cdots X (E = chalcogen) or X \cdots X. Cationic organochalcogen complexes are uncommon, since the covalent nature of the bonds as a result of the strong cation–anion approximation overcomes the ionic character of the salts, so they can be better depicted as neutral sub-

stances, like for example, (DMSeU)₂Te₂Br₆ (DMSeU = *N,N*-dimethylselenourea) [6] or Ph–Te(tmtu)I and β -naphthyl–Te(tmtu)I (tmtu = *N,N'*-tetramethylthiourea) [7].

Structural aspects of chalcogen compounds with mixed valences – Te^{II} and Te^{IV}, Se^{II} and Se^{IV} – were earlier discussed by Hauge [8], Pathirana and co-workers [6] and represent one of a series of different and interesting facets of a kind of compounds which overpass simple description, so that concepts like hypervalence, multicenter bonding, charge transfer interactions, secondary bonding, have been introduced in the understanding of their structural and chemical properties [9,10]. Recently, we have described [11] the one-pot synthesis and the structures of the compounds PhE^{II}(L)PhE^{IV}X₄ (E = Te, Se; E' = Te; X = Br, I; L = thiourea, *N,N'*-tetramethylthiourea): in the two salts of the four complexes [(tmtu)PhTe(μ -Br)TeBr₃Ph]₂, [(tu)PhTe(μ -I)TeI₃Ph]₂, [PhSe(tu)]–[PhTeI₄] and [PhSe(tu)][PhTeBr₄] (tu = thiourea), there

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are no simple (non-complex) counter ions, since both cation and anion are complexes themselves, with different oxidation states of the atomic centers, +2 and +4 for the cation and the anion, respectively.

We report now the synthesis of the novel compounds of tellurium(II) [(mes)BrTe(μ -Br)Te(mes)(etu)] (**1**) and [(mes)ITe(μ -I)Te(mes)(etu)] (**2**), also the mixed valence complex [Ph(etu)Te(μ -I)Te(etu)Ph][PhTeI₄] (**3**) {mes = mesityl(2,4,6-trimethylphenyl); etu = ethylenethiourea(2-imidazolidinethione); Ph = phenyl}. Such molecular assemblies (in the case of **1** and **2**) are yet unknown and the T-shaped [12,13] X–Te–X bonds are quite equal and linear. In the cation complex of **3**, the iodine bridge between two tellurium atoms suggest that the delocalization of the positive charge is limited to the two bicentric molecular orbitals localized at the three atoms Te–I–Te [14,15].

2. Experimental

All manipulations were partially conducted under nitrogen by use of standard Schlenk techniques. Methanol was dried with Mg/I₂ and distilled before use, according usual techniques [16].

2.1. [(mes)BrTe(μ -Br)Te(mes)(etu)] (**1**)

To a solution of 0.2465 g (0.5 mmol) of (mesTe)₂ (dimesityl ditelluride) in 15 ml of methanol, 0.08 g (0.5 mmol) of bromine dissolved in 5 ml of methanol were added and the mixture was stirred by 2 min. After the addition of 0.0510 g (0.5 mmol) of ethylenethiourea, the color of the solution changed instantaneously to orange. The reaction mixture was stirred by 2 h and then filtered. After evaporation of the solvent, in an opened flask, orange brownish crystals were obtained.

Properties: air stable, orange brownish crystalline substance; C₂₁H₂₆Br₂N₂STe₂ (753.52); Yield: 0.283 g, 75% based on (mesTe)₂; Melting point: 153–155 °C. C, H, N-Analysis, Found: C, 33.60; H, 3.54; N, 3.93. Calc.: C, 33.38; H, 3.74; N, 3.71%.

2.2. [(mes)ITe(μ -I)Te(mes)(etu)] (**2**)

To a solution of 0.2465 g (0.5 mmol) of (mesTe)₂ (dimesityl ditelluride) in 20 ml of methanol, 0.127 g (0.5 mmol) of resublimated iodine were added. After stirring the black solution for 2 min, 0.0510 g (0.5 mmol) of ethylenethiourea were added, changing the color of the solution to red. The mixture was stirred by 2 h at 40 °C and then filtered. Evaporation of the solvent in opened flask gives dark red crystals.

Properties: air stable, dark red crystalline substance; C₂₁H₂₆I₂N₂STe₂ (847.50); Yield: 0.305 g, 72% based on (mesTe)₂; Melting point: 140–142 °C. C, H, N-Analysis, Found: C, 29.88; H, 3.15; N, 3.49. Calc.: C, 29.69; H, 3.32; N, 3.30%.

2.3. [Ph(etu)Te(μ -I)Te(etu)Ph][PhTeI₄] (**3**)

To a solution of 0.2046 g (0.5 mmol) of (PhTe)₂ in 20 ml of methanol, 0.127 g (0.5 mmol) of iodine were added. After stirring for 2 min, 0.1021 g (1 mmol) of ethylenethiourea were added to the dark solution, changing its color instantaneously to red. After addition of 0.2926 g (0.5 mmol) of PhTeI₃ the temperature was increased and a slow reflux of the solvent was maintained by 1.5 h. Finally, the mixture is filtered and the dark solid is dissolved in hot methanol. The evaporation of the solvent in opened flask at room temperature gives dark crystals. The solid recrystallized from the mother solution (after the filtration) is also the title compound **3**.

Properties: air stable, dark crystalline substance; C₂₄H₂₃I₅N₄S₂Te₃ (1448.88); Yield: 0.543 g, 75% based on (PhTe)₂; Melting point: 147–149 °C. C, H, N-Analysis, Found: C, 20.02; H, 1.76; N, 4.05. Calc.: C, 19.84; H, 1.87; N, 3.86%.

2.4. Crystallography

X-ray data were collected on a Bruker SMART CCD diffractometer. The crystallographic structures of [(mes)BrTe(μ -Br)Te(mes)(etu)], [(mes)ITe(μ -I)Te(mes)(etu)] and [Ph(etu)Te(μ -I)Te(etu)Ph][PhTeI₄] were solved by direct methods (SHELXS-97) [17]. Refinements were carried out with the SHELXL-97 [18] package. 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.

2.5. ¹H-, ¹³C- and ¹²⁵Te NMR

The NMR spectral data were obtained in a Varian Mercury Plus 7.05 T spectrometer with 300.07 MHz (¹H), 75.46 MHz (¹³C) and 94.74 MHz (¹²⁵Te). The samples were dissolved in a 9:1 mixture of acetone-*d*₆ and DMSO-*d*₆, respectively. The solutions were measured in RMN tubes of 5 mm, at 300 K. The ¹H NMR chemical shifts are relative to Si(CH₃)₄ as internal reference. For the ¹³C measures the chemical shift of the carbon atom of the acetic methyl group was taken as internal reference (δ 29.3). The ¹²⁵Te NMR spectra were taken with reference to (CH₃)₂Te. A capillary containing Ph₂Te₂ dissolved in CDCl₃ (δ 450) was used as external reference. By convention, the chemical shift is positive when the resonance occurs at higher frequency than that of the reference.

3. Results and discussion

In the X-ray studies of the orthorhombic – (**1**) and (**2**) – and triclinic (**3**) title compounds, the space groups $P2_12_12_1$ (**1**, **2**) and $P\bar{1}$ (**3**) were chosen on the basis of statistics and later justified by the successful refinements. Crystal data

and experimental conditions are given in Table 1. Selected bond distances and angles of [(mes)BrTe(μ -Br)Te(mes)-(etu)] (**1**), [(mes)ITe(μ -I)Te(mes)(etu)] (**2**) and [Ph(etu)-Te(μ -I)Te(etu)Ph][PhTeI₄] (**3**) are listed in Tables 2 and 3, with dotted lines (Table 3) representing the secondary bonds. Figs. 1 and 2 display the asymmetric units of the compounds **1** and **2**, with the secondary Te– π interactions also identified by dotted lines. Fig. 3 represents the elementary cell of [Ph(etu)Te(μ -I)Te(etu)Ph][PhTeI₄] (**3**), whose assembly is related with the other half of the cell through a crystallographic inversion center, achieving additionally a quasi-dimeric arrangement by means of secondary, X-ray measured, interanionic Te–I bonds (dotted lines). The tellurium centers in **1** and **2** adopt a three-coordinate configuration, and the *trans* tellurium–halogen bonds are very similar, with distances of 2.7068(15) Å {Te(1)–Br(2)}, 2.8180(12) Å {Te(1)–Br(1)}, 2.9189(8) Å {Te(1)–I(2)} and 3.0125(8) Å {Te(1)–I(1)}. The symmetrical, T-shaped {(mes)TeX₂} fragments of **1** and **2** result probably from an oxidative addition of halogen molecules to a Te(I) atom and can be considered as hypervalent compounds of Te(II), for which the linearity of the X–Te–X system is expected, together with similar Te–X bond distances [19]. The small differences of the *trans* Te–X bond lengths in **1** and **2** can be attributed to the bridge function of Br1, in complex **1**,

and I1 in complex **2**, as showed in Figs. 1 and 2. Since these bridging bonds Te2–Br1 and Te2–I1 are fairly longer (3.1514(11) and 3.3163(6) Å, respectively) than the linear X–Te–X bonds, a reasonable but also frontier interpretation of the complexes **1** and **2** would be as ionic pairs

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

	1	2
<i>Bond lengths (Å)</i>		
S(1)–C(31)	1.721(13)	1.720(8)
S(1)–Te(2)	2.473(3)	2.4837(2)
C(21)–Te(2)	2.130(9)	2.122(6)
C(11)–Te(1)	2.125(8)	2.130(6)
N(32)–C(31)	1.312(14)	1.322(9)
N(35)–C(31)	1.340(13)	1.324(10)
Te(2)–X(2)	3.1514(11)	3.3163(6)
Te(1)–X(1)	2.7068(15)	2.9189(8)
Te(1)–X(2)	2.8180(12)	3.0125(8)
<i>Bond angles (°)</i>		
C(31)–S(1)–Te(2)	106.0(4)	106.3(2)
S(1)–Te(2)–X(2)	174.06(9)	172.94(5)
C(21)–Te(2)–S(1)	95.1(2)	95.56(16)
C(11)–Te(1)–X(1)	89.9(2)	89.78(18)
C(11)–Te(1)–X(2)	87.7(2)	87.57(18)
X(1)–Te(1)–X(2)	176.90(4)	176.09(2)
Te(1)–X(2)–Te(2)	107.57(3)	103.797(18)

Table 1
Crystal data and structure refinements for **1–3**

	1	2	3
Empirical formula	C ₂₁ H ₂₆ Br ₂ N ₂ STe ₂	C ₂₁ H ₂₆ I ₂ N ₂ STe ₂	C ₂₄ H ₂₃ I ₅ N ₄ S ₂ Te ₃
Formula weight	753.52	847.50	1448.88
<i>T</i> (K)	293(2)	273(2)	293(2)
Radiation, λ (Å)	Mo K α , 0.71073	Mo K α , 0.71073 Å	Mo K α , 0.71073
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Triclinic, <i>P</i> $\bar{1}$
Unit cell dimensions			
<i>a</i> (Å)	8.2740(10)	8.4508(2)	9.1687(3)
<i>b</i> (Å)	13.9100(10)	14.0226(3)	12.1183(3)
<i>c</i> (Å)	22.3870(10)	22.6044(6)	17.6893(5)
α (°)	90	90	81.424(2)
β (°)	90	90	76.142(2)
γ (°)	90	90	76.753(2)
<i>V</i> (Å ³)	2576.5(4)	2678.67(11)	1848.20(9)
<i>Z</i> , Calculated density (g cm ^{−3})	4, 1.943	4, 2.101	2, 2.604
Absorption coefficient (mm ^{−1})	5.457	4.571	6.662
<i>F</i> (000)	1424	1568	1296
Crystal size (mm)	0.12 × 0.12 × 0.1	0.32 × 0.3 × 0.3	0.3 × 0.24 × 0.21
θ range (°)	3.01–26.02	1.71–29.79	1.19–33.47
Index ranges	−10 ≤ <i>h</i> ≤ 8, −17 ≤ <i>k</i> ≤ 15, −27 ≤ <i>l</i> ≤ 27	−10 ≤ <i>h</i> ≤ 11, −14 ≤ <i>k</i> ≤ 16, −31 ≤ <i>l</i> ≤ 17	−12 ≤ <i>h</i> ≤ 14, −17 ≤ <i>k</i> ≤ 18, −24 ≤ <i>l</i> ≤ 27
Reflections collected	9249	11,707	21,271
Reflections unique	4949 [<i>R</i> _{int} = 0.0446]	6543 [<i>R</i> _{int} = 0.0190]	13,582 [<i>R</i> _{int} = 0.0233]
Completeness to theta maximum (%)	99.2	87.1	93.9
Refinement method	Full-matrix Least-squares on <i>F</i> ²	Full-matrix Least-squares on <i>F</i> ²	Full-matrix Least-squares on <i>F</i> ²
Data/restraints/parameters	4949/0/254	6543/0/254	13,582/0/343
Goodness-of-fit on <i>F</i> ²	0.968	1.169	0.963
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0419, <i>wR</i> ₂ = 0.0878	<i>R</i> ₁ = 0.0404, <i>wR</i> ₂ = 0.0951	<i>R</i> ₁ = 0.0371, <i>wR</i> ₂ = 0.0962
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0769, <i>wR</i> ₂ = 0.1023	<i>R</i> ₁ = 0.0540, <i>wR</i> ₂ = 0.1228	<i>R</i> ₁ = 0.0781, <i>wR</i> ₂ = 0.1239
Largest difference peak and hole (e Å ^{−3})	0.545 and −0.599	1.444 and −1.426	1.090 and −1.832

Table 3
Selected bond lengths (Å) and angles (°) for 3

Bond lengths (Å)	
Te(1)–I(1)	2.8723(5)
Te(1)–I(2)	2.9154(5)
Te(1)–I(3)	3.0040(6)
Te(1)–I(4)	2.9304(5)
Te(1)···I(1)′	3.8286(5)
Te(2)–S(1)	2.5190(17)
Te(2)–I(5)	3.2290(7)
Te(3)–S(2)	2.5910(17)
Te(3)–I(5)	3.0772(6)
Bond angles (°)	
C(11)–Te(1)–I(1)	91.67(13)
C(11)–Te(1)–I(2)	91.34(13)
C(11)–Te(1)–I(3)	89.24(13)
C(11)–Te(1)–I(4)	91.33(13)
C(11)–Te(1)···I(1)′	166.72(13)
I(1)–Te(1)–I(2)	90.517(18)
I(1)–Te(1)–I(3)	178.582(17)
I(1)–Te(1)–I(4)	90.470(17)
I(1)–Te(1)···I(1)′	89.548(13)
I(2)–Te(1)–I(3)	90.555(16)
I(2)–Te(1)–I(4)	177.126(16)
I(2)–Te(1)···I(1)′	101.870(15)
I(3)–Te(1)···I(1)′	89.323(12)
I(4)–Te(1)···I(3)	88.415(15)
I(4)–Te(1)···I(1)′	75.440(14)
Te(1)–I(1)–Te(1)′	90.452(13)
C(21)–Te(2)–S(1)	89.93(15)
C(21)–Te(2)–I(5)	87.46(15)
S(1)–Te(2)–I(5)	177.21(4)
C(31)–Te(3)–S(2)	89.04(15)
C(31)–Te(3)–I(5)	88.44(14)
S(2)–Te(3)–I(5)	177.31(5)
Te(3)–I(5)–Te(2)	108.622(16)

Symmetry transformations used to generate equivalent atoms: (′) $-x + 1$, $-y + 1$, $-z + 1$.

[(mes)Te(etu)][(mes)TeBr₂] and [(mes)Te(etu)][(mes)TeI₂], attaining a strong interaction between the [(mes)Te(etu)]⁺ cations and the T-shaped anions [(mes)TeX₂][−]. In a recent work, Aragoni et al. [20] analyzed 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 with the

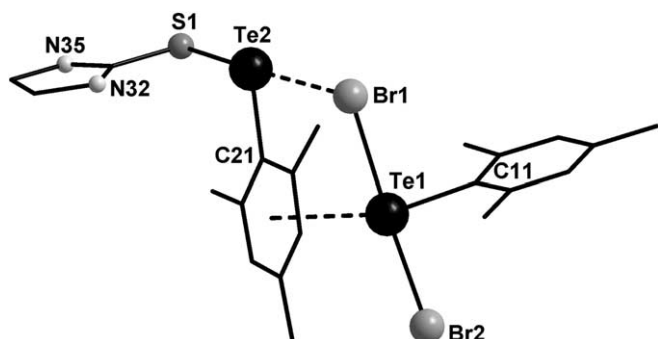


Fig. 1. Asymmetric unit of [(mes)BrTe(μ-Br)Te(mes)(etu)] (1). Dotted lines identify the secondary T–Br and Te–π interactions.

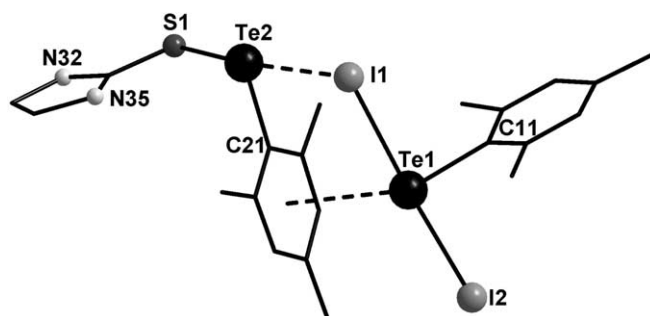


Fig. 2. Asymmetric unit of [(mes)ITe(μ-I)Te(mes)(etu)] (2). Secondary Te–I and Te–π bonds as dotted lines.

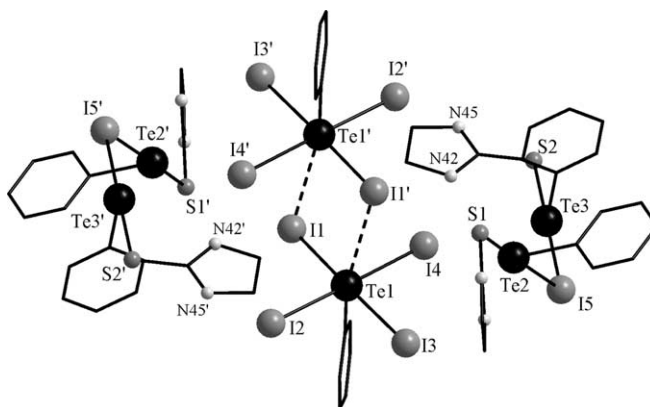


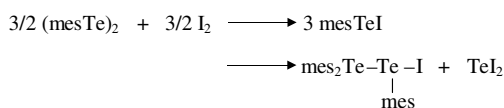
Fig. 3. Elementary cell of [Ph(etu)Te(μ-I)Te(etu)Ph][PhTeI₄] (3). The dotted lines represent the interanionic Te–I bonds. Symmetry transformations used to generate equivalent atoms: (′) $-x + 1$, $-y + 1$, $-z + 1$.

selenium atom in a partial hypervalent state. On the basis of these results, the authors have concluded that the compound can be described as product of a donor–acceptor interaction between I[−] and the selenium atom of the organic cation [RSeCN]⁺. These evidences give support to our molecular interpretation of the compounds 1 and 2, in which the fragments [(mes)TeX₂] result from an oxidative addition of halogen molecules to Te(I), nevertheless with a reasonably strong polarization of the bonds Te2–Br1 and Te2–I1, which have distances quite smaller than the sum of the van der Waals radii of the atoms Te/Br and Te/I. The fragment [(mes)TeS(R)] of 1 and 2 would correspond to the organic cation [RSeCN]⁺ of Aragoni and co-workers [20]. The occurrence of secondary bonds between the Te1 atoms and the π-electron systems of the overlooked mesityl groups indicates a presence of a partial positive charge on the Te atom, as expected in hypervalent adducts with halogens; the distances between the Te1 atoms and the centroid of the mesityl rings (dotted lines, see Figs. 1 and 2) are 3.681 Å for [(mes)BrTe(μ-Br)Te(mes)(etu)] and 3.762 Å for [(mes)ITe(μ-I)Te(mes)(etu)]. Not by chance, all aromatic substituents are perpendicular to the pseudo-apical bonds. Recently, Haiduc and Zukerman-Schpector have shown that many similar organotellurium compounds, in addition to secondary Te···halogen bonds, show intermolecular bonds of the type Te···π-aryl [21,22]. Several

authors have extended the Haiduc-Zukerman's nomenclature, describing, for example, self-assembled supramolecular arrays through tellurium– π -C₆H₅ interactions [23,24] or super molecules formed through Te \cdots X secondary bonds with intra-chain Te \cdots π -aryl interactions [25,26], among other classifications, depending on the type of the molecular aggregate and secondary interactions.

The complexes [(mes)BrTe(μ -Br)Te(mes)(etu)] and [(mes)ITe(μ -I)Te(mes)(etu)] cannot be classified as charge-transfer (CT) complexes. Indeed, on the basis of their structures and literature advices [27], they could be considered *compounds of the CT-type*, but the donor/acceptor interaction should occur between the μ -Br (or I) atom of the T-shaped [(mes)TeX₂] fragment, which acts as donor, and the empty sigma* molecular orbital located on the S–Te axis of the moiety [(mes)TeS(R)].

The mixed valence compound [Ph(etu)Te(μ -I)Te(etu)Ph][PhTeI₄] (**3**) is basically built up of [Ph(etu)Te(μ -I)Te(etu)Ph]⁺ cations and [PhTeI₄][−] anions. A probable reaction pathway involves the initial formation of 2 equivalents of the intermediary PhTe(etu)I, generated after the addition of ethylenethiourea to PhTeI, followed by transference of the iodide ion from 1 equivalent of PhTe(etu)I to the equimolar amount of PhTeI₃. Compound **3** was prepared by reaction of iodine with (PhTe)₂ instead of (mesTe)₂ because the reaction of the latter with iodine gives mesTe(mes₂Te)I, according to the following equation [28]:



The reaction of (PhTe)₂ with iodine gives 2 equivalents of PhTeI [29], whose further reactions lead to the formation of the multivalent complex **3**.

The fragments [PhTeI₄][−] of **3** {like in general most of the complex structures with the formula [PhTeX₄][−] (X = halogen)}, present a square pyramidal coordination at tellurium atom, with the halogen atoms in the basal positions and the organic group apical. As previously reported in many other examples [2,5], the lone electron pair of tellurium in a free octahedral position present a great ability to interact with surrounding iodine atoms to complete the coordination polyhedron, what explains the dimeric association of the anions [PhTeI₄][−] through TeI \cdots I' secondary bonds (see Fig. 3) in compound **3**. These secondary interactions have a distance of 3.8286(5) Å and the sum of the van der Waals radii of the atoms Te/I is 4.35 Å. The four Te–I primary bonds have a mean distance of 2.9305 Å. The anion is a distorted octahedron, since the four bonds Te–I are not fully planar, and this can be attributed to the stereoactivity of the lone electron pair at the tellurium atom, also recognizable in the deflection of the linearity of the C–Te–I bonds which achieve the octahedral coordination at tellurium: the angle of the bonds C(11) \cdots Te–I1' is 166.72(13)°. In the cation [Ph(etu)Te(μ -I)Te(etu)Ph], the central iodine

atom (I5) attains an asymmetrical bridge function: the bonds Te(2)–I(5) and Te(3)–I(5) measure, respectively, 3.2290(7) and 3.0772(6) Å, the Te2–S1 and Te3–S2 bonds have distances of 2.5190(17) and 2.5910(17) Å in that order. The Te2–I5–Te3 angle is 108.622(16)° and the bonds S1–Te2–I5 and S2–Te3–I5 are close to linear, with angles of 177.21(4) and 177.31(5)°. In the cationic units, the tellurium atoms achieve two T-shaped configurations, in which the iodine ligand is a common T vertex, and the two S-atoms the opposite ones.

Attempts to study the dissociation of the title complexes in solution by means of multinuclear NMR spectra and UV–visible spectroscopy were limited by the fact that the crystals of **1–3** are soluble only in polar solvents like acetone or dimethylsulfoxide (DMSO). Another limiting factor represents the occurrence of dynamic equilibrium in solution between the different forms of this sort of compound due to exchange between ligand and solvent molecules, predominantly with DMSO. To minimize this effect ¹H-, ¹³C- and ¹²⁵Te NMR studies were conducted in solutions of acetone-*d*₆ and DMSO-*d*₆ in a 9:1 proportion, respectively. The results, however, have been not fully conclusive. Complex **1** gives a ¹²⁵Te NMR singlet at 1396 and a broad signal at 1032 ppm. Complexes **2** and **3** generate each one a lone, wide peak localized in 778 (**2**) and 861 ppm (**3**). Recent experiments of ¹²⁵Te NMR with the neutral complex [(tmtu)PhTe(μ -Br)TeBr₃Ph]₂ [11] have showed similar results to those obtained for **1**. The occurrence of only one large signal for compounds **2** and **3** could be attributed to their probable dissociation and to the further solvation equilibrium of the species in solution. The ¹H- and ¹³C NMR signals of compounds **1** and **2** are: ¹H NMR, 9.07 ppm (**1**), 9.01 ppm (**2**) (s, broad, 2H (NH)); 7.01 ppm (**1**), 6.99 ppm (**2**) (s, 4H (CH_{arom.})); 3.85 ppm (**1**), 3.84 ppm (**2**) (s, 4H (CH₂)); 2.78 ppm (**1**), 2.74 ppm (**2**) (s, 12H (2,6-CH₃)); 2.284 ppm (**1**), 2.279 ppm (**2**) (s, 6H (4-CH₃)). ¹³C NMR, 175.77 ppm (**1**), 174.66 ppm (**2**) (CS); 144.74 ppm (**1**), 145.17 ppm (**2**) (C2, C6); 139.43 ppm (**1**), 139.66 ppm (**2**) (C4); 126.75 ppm (**1**), 126.82 ppm (**2**) (C3, C5); 45.66 ppm (**1**), 45.67 ppm (**2**) (CH₂); 30.00 ppm (**1**), 30.52 ppm (**2**) (2,6-methyl); 20.37 (**1**) 20.41 ppm (4-methyl). The Te–C1 signal could not be detached. The two aromatic mesityl rings are equivalent in compounds **1** and **2**, and this evidence should mean that in this case the Te \cdots π -aryl interactions are not differentiate through NMR spectroscopy. For compound **3**, the ¹H- and ¹³C NMR signals are: ¹H NMR, 10.3 ppm (broad, 1H (NH)), 9.5 ppm (broad, 1H (NH)), 8.21 ppm (d, *J* = 7 Hz, 6H (CH_{arom.})), 7.6 ppm (broad, 1H), 7.23 (t, *J* = 7.5 Hz) –7.11 ppm (t, *J* = 7.5 Hz, 9H), 4.60–4.25 and 4.0–3.8 (m, CH₂, ~8H). ¹³C NMR, 176.02 ppm (CS), 142.62 ppm (broad, C2, C6), 129.13 ppm (C3, C5), 128.15 ppm (C4), 51.90, 51.64, 46.56 and 42.52 ppm (**2**) (CH₂).

Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data

Centre CCDC nos. CSD 277353–277355 for compounds 1–3. Further details of the crystal structures investigations are available free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.08.037.

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