Synthesis and structural features of new aryltellurenyl iodides

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ARTICLE INFO

ABSTRACT

$(TmpTe)_2$ (tmp = 2,3,5,6-tetramethylphenyl) reacts with I_2 to yield the sterically stabilized arenetellurenyl iodide $[tmpTeI]_2$ (**1**). The reaction of **1** with I_2 gives $[tmpTe(I)I_2]$ (**2**), which formally results from the association of the intermediary RTeI with I_2 under oxidation to Te^{III}. Compound **1** reacts also with (PyH)I to give the hypervalent, 3c−4e, T-shaped complex $(PyH)[tmpTeI_2]$ (**3**). The reaction of **3** with I_2 gives $(PyH)[tmpTeI_3(I_3)]$ (**4**), a rare example of Te^{IV} compound in which a I_3^- chain appears as component of the complex and not as solvate. Complex **3** reacts also with I_2 in the presence of water with hydrolysis of the R−Te bond, leading to the structurally rare compounds $(PyH)_2[TeI_4(\mu\text{-}I)_2TeI_4]$ (**5**), $[(tmp)_2TeI_2]$ (**6**) and $(PyH)_2[TeI_6]\cdot I_2$ (**7**). The structural features of the products are discussed, as well as the synthetic procedures.

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1. Introduction

The increasingly interesting and attractive chemistry of organyltellurenyl iodides affords worldwide the emergence of new experimental routes to achieve compounds with innovative architectural designs. The reactions of diaryldtellurides $(RTe)_2$ with iodine have been experimentally studied with the purpose of obtaining Te^{II} and Te^{IV} compounds, as well as mixed-valent aryltellurenyl iodides and related charge-transfer complexes. It is well known that uncommon compositions and configurations are characteristic for these types of compounds [1,2]. Almost as a rule, tellurium(II) and tellurium(IV) iodide compounds attain all possible combinations of secondary, interionic interactions. Single monomers and dimers and also polymeric chains attaining 1D, 2D and 3D networks, as well as rare polymeric structures with chalcogen atoms presenting mixed-valence states are often described [3,4], like, for example, the recently reported [5] neutral species [mesTeI(μ_3-I)(TeImes)$_2$]$_n$ (mes = 2,4,6-trimethylphenyl). The chemical and structural versatility of organyltellurenyl iodides, combined with the noticeable effect of the ligand R on the stabilization of mixed-valent aryltellurenyl iodides, led us to the development of functionalized organic substituents to stabilize Te centers in uncommon and useful assemblies. Recently we have shown that the two methoxy groups of the unstable intermediary RTeI (R = 2,6-dimethoxiphenyl) are particularly able to stabilize tellurium iodides in mixed-valent, unusual compositions [6].

Either the structure of the intermediary RTeI or the structural features and oxidation states of the resulting products are dependent upon the substituent R. After working with PhTeI (Ph = phenyl) and mesTeI, newly we have carried out some experiments starting from the intermediary (dmeph)TeI [2], to search more accurately the effects of small variations of the size of the R group on the stereochemistry of the reaction products. The new Te^{II} and Te^{IV} iodides obtained from these reactions were [{RTeI}{RTeI$_3$}]$_n$, [R2Te−TeIR], (PyH)[RTeI$_2$] and (PyH)$_n$[RTeI(μ-I)TeIR]$_n$ (R = dmeph = 2,6-dimethylphenyl; Py = pyridine). Former studies [7] on the influence of the substituent R on the controlled oxidation of the Te atom have shown that the aryltellurenyl iodides ArTeI can be viewed also as key compounds in the syntheses of Te^{II} and Te^{IV} products. Since the mesityl group allows the stabilization of tellurium(II) iodides as mesTeI [5,8,9], the possibility of using mesTeI as a selective oxidation reagent has been studied and demonstrated also in the case of the preparation of the mixed-valent complex [RTeTeI$_2$R] (R = 2,6-dimethoxiphenyl) [7]. As part of our research on further effects of the ligand R on the stabilization and structure of aryltellurenyl iodides, we describe in this work the syntheses and the structural characterization of the intermediary $[tmpTeI]_2$ (**1**) and of the new complexes $[tmpTe(I)I_2]$ (**2**), $(PyH)[tmpTeI_2]$ (**3**), $(PyH)[RTeI_3(I_3)]$ (**4**), $(PyH)_2[TeI_4(\mu\text{-}I)_2TeI_4]$ (**5**), $[R_2TeI_2]$ (**6**) and $(PyH)_2[TeI_6]\cdot I_2$ (**7**) (tmp = 2,3,5,6-tetramethylphenyl). The new products corroborate again the versatility of aryltellurenyl iodides regarding reactivity and structure, as well as the close dependence of these factors with the substituent R.

2. Experimental

The preparation of all complexes mentioned and discussed in this wok is resumed in Scheme 1. $(TmpTe)_2$ was prepared by modification of known routes [10]. The syntheses and recrystallizations of compounds **1**−**4** were carried out under Ar atmosphere.

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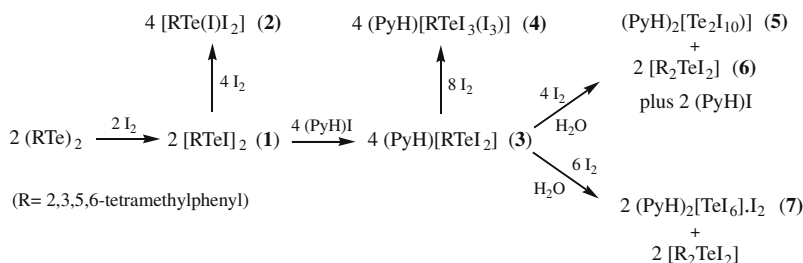
Scheme 1. Reactions of (RTe)$_2$ (R = 2,3,5,6-tetramethylphenyl), [RTeI]$_2$ and (PyH)[RTeI$_2$] with I$_2$/(PyH)I discussed in this work.

2.1. Preparation of [tmpTeI]$_2$ (**1**)

To a solution of 0.104 g (0.2 mmol) of (TmpTe)$_2$ in 5 mL of toluene, 0.051 g (0.2 mmol) of resublimed iodine were added. After stirring by 30 min the red solution turned blue. The mixture was filtered and the concentrated solution was cooled at −18 °C to give black crystals. Yield: 0.153 g (98%).

Properties: black, crystalline solid. C$_{10}$H$_{13}$ITe (775.41). Melting point: 103.5–105.3 °C. Anal. Calc.: C, 30.98; H, 3.38. Found: C, 30.87; H, 3.41%.

IR (KBr): 2997 [ν(=C−H)], 2968 [ν(−C−H)], 1630 [ν(C=C)], 1535 [δ(C=C−H)], 782, 704 [$\delta_{out\ pl.}$(C=C−H)].

2.2. Preparation of [tmpTe(I)I$_2$] (**2**)

To 0.156 g (0.4 mmol) of **1**, 0.101 g (0.4 mmol) of resublimed iodine dissolved in 5 mL of toluene were added. After 1 h stirring a red precipitate was filtered, dissolved in CH$_2$Cl$_2$ and recrystallized at −18 °C, giving red crystals. Yield: 0.247 g (96%).

Properties: red, crystalline substance. C$_{10}$H$_{13}$I$_3$Te$_1$ (641.50): Melting point: 141.9–142.7 °C. Anal. Calc.: C, 18.72; H, 2.04. Found: C, 18.47; H, 1.99%.

IR (KBr): 2965 [ν(=C−H)], 2924 [ν(−C−H)], 1630 [ν(C=C)], 1529 [δ(C=C−H)], 802 [$\delta_{out\ pl.}$(C=C−H)]

2.3. Preparation of (PyH)[tmpTeI$_2$] (**3**)

To 0.156 g (0.4 mmol) of **1**, 0.083 g (0.4 mmol) of pyridinium iodide dissolved in 5 mL of toluene were added. After 2 h stirring a red precipitate was filtered, dissolved in a 2:1 mixture of CH$_2$Cl$_2$/acetone and recrystallized at −18 °C, giving hygroscopic red crystals. Yield: 0.231 g (97%)

Properties: red, hygroscopic crystalline solid. C$_{15}$H$_{19}$N$_1$I$_2$Te$_1$ (594.71). Melting point: 152.1–154.1 °C. Anal. Calc.: C, 30.29; H, 3.22; N, 2.36. Found: C, 30.48; H, 3.17; N, 2.35%.

IR (KBr): 3207 [ν(N−H)], 3063 [ν(=C−H)], 2954 [ν(−C−H)], 1631 [ν(C=C)], 1599 [ν(C=N)], 1527 [δ(C=C−H)], 1478 [δ(C=N−H)], 740, 670 [$\delta_{out\ pl.}$(C=C−H)].

2.4. Preparation of (PyH)[tmpTeI$_3$(I$_3$)] (**4**)

To 0.238 g (0.4 mmol) of **3**, 0.203 g (0.8 mmol) of resublimed iodine dissolved in 10 mL of toluene were added. After 1 h stirring a dark red precipitate was filtered, dissolved in a 2:1 mixture of CH$_2$Cl$_2$/acetone and recrystallized at −18 °C, giving hygroscopic black crystals. Yield: 0.414 g (94%).

Properties: black, hygroscopic crystalline substance. C$_{30}$H$_{38}$N$_1$I$_2$Te$_1$ (1102.31). Melting point: 168.1–169.3 °C. Anal. Calc. C, 16.34; H, 1.74; N, 1.27. Found: C, 16.48; H, 1.69; N, 1.25%.

IR (KBr): 3209 [ν(N−H)], 3053 [ν(=C−H)], 2916 [ν(−C−H)], 1628 [ν(C=C)], 1596 [ν(C=N)], 1524 [δ(C=C−H)], 1476 [δ(C=N−H)], 776, 669 [$\delta_{out\ pl.}$(C=C−H)].

2.5. Preparation of (PyH)$_2$[TeI$_4$(μ-I)$_2$TeI$_4$] (**5**) and [(tmp)$_2$TeI$_2$] (**6**)

To 0.238 g (0.4 mmol) of **3**, 0.101 g (0.4 mmol) of resublimed iodine dissolved in 10 mL of toluene were added. After 1 h stirring a dark red precipitate was isolated by filtration and dissolved in 4 mL

Table 1
Crystallographic data and refinement parameters for **1**, **2**, **3**, **4**, **5**, **6** and **7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	C$_{20}$H$_{26}$I$_2$Te$_2$	C$_{10}$H$_{13}$I$_3$Te	C$_{15}$H$_{19}$I$_2$NTe	C$_{15}$H$_{19}$I$_6$NTe	C$_{10}$H$_{12}$I$_{10}$N$_2$Te$_2$	C$_{20}$H$_{26}$I$_2$Te	C$_{10}$H$_{12}$I$_8$N$_2$Te
Fw	775.41	641.50	594.71	1102.31	1684.42	647.81	1303.02
T (K)	170(2)	170(2)	170(2)	170(2)	170(2)	170(2)	170(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2/n$	$P2/n$	$Pbca$	$P2_1/n$	$C2/c$
a/Å	7.44810(10)	6.3246(13)	9.5051(3)	12.082(3)	12.26970(10)	9.9186(2)	18.1474(5)
b/Å	9.1083(2)	23.879(6)	8.8133(3)	8.861(2)	12.9259(2)	14.9060(4)	10.2878(3)
c/Å	9.3839(2)	9.888(3)	11.2052(4)	24.180(5)	19.0862(2)	14.3917(4)	14.8906(4)
α/°	92.9190(10)	90	90	90	90	90	90
β/°	111.4130(10)	99.853(11)	109.3250(10)	102.702(3)	90	95.257(2)	107.6620(10)
γ/°	109.8660(10)	90	90	90	90	90	90
V/Å^3	546.142(18)	1471.3(6)	885.79(5)	2525.3(10)	3027.01(6)	2118.81(10)	2648.99(13)
Z	1	4	2	4	4	4	4
ρ_{calcd} (g cm^3)	2.358	2.896	2.230	2.899	3.696	2.031	3.267
μ (Mo Kα) (mm^1)	5.498	8.284	5.153	8.512	12.128	4.317	10.443
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
F (0 0 0)	356	1136	548	1944	2880	1216	2248
Collected reflns.	5165	11,863	6970	17,935	18,271	19,544	13,505
Unique reflectionns	3097	3252	2292	5014	4084	4682	2787
GOF (F^2)	1.157	0.936	1.063	1.016	1.031	0.959	1.020
R_1[a]	0.0191	0.0426	0.0222	0.0601	0.0206	0.0367	0.0224
wR_2[b]	0.0522	0.0836	0.0550	0.1924	0.0373	0.0872	0.0446

[a] $R_1 = ||F_o| − |F_c||/|F_o|$.
[b] $wR_2 = \{\sum w(F_o^2 − F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$.

of CH$_2$Cl$_2$, with further addition of 2 mL of water. Hygroscopic black crystals of **5** (Yield: 0.152 g, 45%) grew at the interface of the solvents CH$_2$Cl$_2$/H$_2$O. In the organic phase red crystals of **6** (Yield: 0.146 g, 43%) were formed, also with colourless crystals of (PyH)I.

Properties of **5**: black, hygroscopic crystalline solid. C$_{10}$H$_{12}$N$_2$I$_{10}$Te$_2$ (1684.42). Melting point: 168.6–169.8 °C. Anal. Calc.: C, 7.13; H, 0.72; N, 1.66. Found: C, 7.16; H, 0.69; N, 1.65%.

IR (KBr): 3215 [ν(N–H)], 3057 [ν(=C–H)], 1628 [ν(C=C)], 1597 [ν(C=N)], 1528 [δ(C=C–H)], 1479 [δ(C=N–H)], 729, 666 [$\delta_{out\ pl.}$(C=C–H)].

Properties of **6**: red, crystalline solid. C$_{20}$H$_{26}$I$_2$Te$_1$ (647.81). Melting point: 157.2–159.1 °C. Anal. Calc.: C, 26.97; H, 1.88. Found: C, 26.79; H, 1.94%.

IR (KBr): 3962 [ν(=C–H)], 2917 [ν(–C–H)], 1618 [ν(C=C)], 1537 [δ(C=C–H)], 783 [$\delta_{out\ pl.}$(C=C–H)].

2.6. Preparation of) (PyH)2[TeI6]·I2 (7)

To 0.238 g (0.4 mmol) of **3**, 0.152 g (0.6 mmol) of resublimed iodine dissolved in 10 mL of toluene were added. After 1 h stirring a dark red precipitate was isolated by filtration and dissolved in 4 mL of CH$_2$Cl$_2$, with further addition of 2 mL of water. Hygroscopic black crystals grew at the interface of the solvents CH$_2$Cl$_2$/H$_2$O. In the organic phase occurred also the formation of a significant amount of **6**. Yield: 0.179 g (46%).

Properties: black, hygroscopic crystalline substance. C$_{10}$H$_{12}$N$_2$I$_8$Te (1303.02). Melting point: 159.5–160.8 °C. Anal. Calc.: C, 9.22; H, 0.93; N, 2.15. Found: C, 9.37; H, 0.96; N, 2.12%.

IR (KBr): 3203[ν(N–H)], 3055 [ν(=C–H)], 1629 [ν(C=C)], 1598 [ν(C=N)], 1527 [δ(C=C–H)], 1481 [δ(C=N–H)], 744, 675 [$\delta_{out\ pl.}$(C=C–H)].

2.7. X-ray structure determinations

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo Kα radiation. The structure was solved by direct methods using SHELXS [11]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package [11]. 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 collection and refinements are contained in Table 1.

3. Results and discussion

Because of rapid dismutation or disproportionation, the compounds RTeX (X = Cl, Br, I) are very unstable. Their stabilization can also be achieved by using bulky substituents or coordinating functional groups [12,13]. It is also known that these species present a relative stability in solution, although in the literature few reports describe their characteristics in the solid state. We have reported the synthesis and the tetrameric structure of PhTeI (Ph = phenyl), the first organotellurenyl halide without additional functional groups [14,15]. The use of a very bulky R allowed the isolation of Mes*TeI (Mes* = 2,4,6-tri-*tert*-butylphenyl), which exhibits discrete molecules, without Te···I, Te···Te or I···I intermolecular interactions [16]. The compound [tmpTeI]$_2$ (**1**) (tmp = 2,3,5,6-tetramethylphenyl), whose structure is displayed in Fig. 1, represents also a sterically stabilized arenetellurenyl iodide with a bulky substituent. Since the sum of the Te–Te covalent/van der Waals radii [17,18] are 2.94 and 4.12 Å, respectively, the Te1–Te1a distance of 3.1458(4) Å in **1** allows its formulation as a dimer. Double, reciprocal Te···I secondary contacts, with a distance of 3.898(2) Å, hold the dimers in a one-dimensional, polymeric association along the *a* axis.
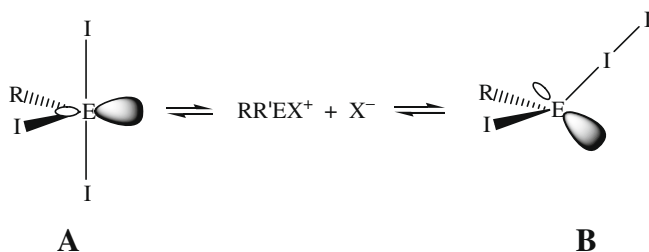
As is also depicted in Scheme 1, our reaction of (RTe)$_2$ (R = 2,3,5,6-tetramethylphenyl) with I$_2$ affords initially 2 equiv of [RTeI]$_2$ (**1**), which reacts with 4 equiv of iodine under splitting of the Te–Te bond to give [tmpTe(I)I$_2$] (**2**), whose structure is shown in Fig. 2. Single molecules of **2**, which formally result from the gathering of the intermediary RTeI with I$_2$ under oxidation to Te^{III}, act upon one another through secondary Te1···I3a (3.4769(0)) and I3c···Te1b (3.7569(0) Å) bonds. These interactions keep the molecules of **2** in a two-dimensional, supramolecular assembly in the *ac* plane. Single, also network-forming molecules analog to the new compound [RTe(I)I$_2$] (**2**) were already obtained, with R = 2,6-dimethoxiphenyl [6] and 2,6-dimesitylphenyl [19]. Nevertheless, compound **2** is the unique of its species to perform a two-dimensional assemblage of the molecules. The relatively open Te1–I2–I3 angle (173.85(3)°) allows us to consider the species RTeI(I$_2$) (**2**) as a RR′E·X$_2$ (R′ = I), three-coordinated molecular complex (MC) [20,21]. According to the N–X–L notation proposed by Martin and co-workers [22], the hypervalent 3c–4e atoms in X–E–X trigonal-bipyramidal configurations (TBP) [20,21] are represented by 10–E–4, and the 3c–4e atoms in E–X–X configurations (MC), as in the case of compound **2**, are represented by 10–X–2. An alternative configuration for **2** would be the TBP RTeI$_3$ (10–E–4). As in the case of the early reported [6] compound [RTe(I)I$_2$] (R = 2,6-dimethoxyphenyl), probably this realizable form was hindered by
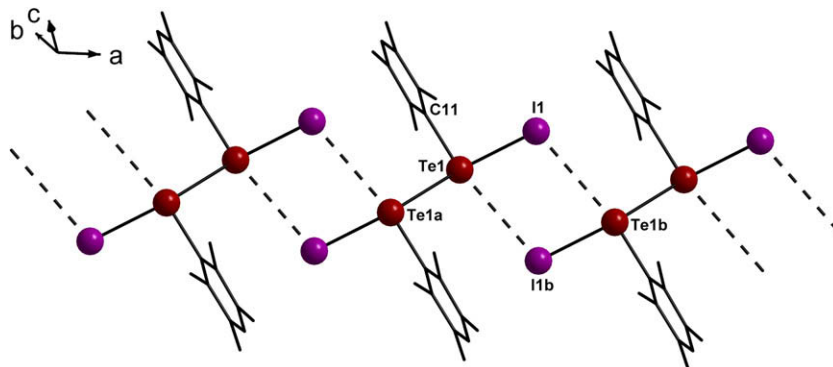
Fig. 1. Molecular structure of [tmpTeI]$_2$ (**1**) and the one-dimensional assembling of the dimers along the *a* axis. Hydrogen atoms have been omitted by clarity. Dashed lines represent secondary interactions. Symmetry code: (a) = −x, −y, 1 − z; (b) = 1 − x, −y, 1 − z. Selected bond lengths [Å] and angles [°]: Te1–C11 2.145(3), Te1–I1 2.7743(3), Te1–Te1a 3.1458(4), Te1···I1b 3.898(2); C11–Te1–I1 95.08(7), C11–Te1–Te1a 93.23(7), I1–Te1–Te1a 147.247(11), C12–C11–Te1 118.77(19), C16–C11–Te1 119.07(19), Te1a–Te1···I1b 96.32(11).
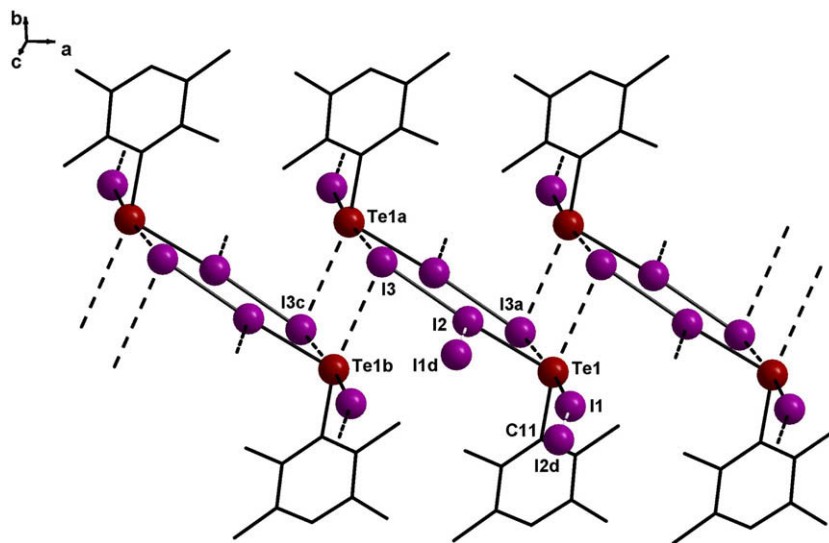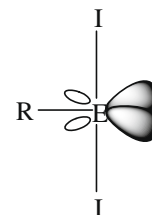
Fig. 2. Molecular structure of [tmpTe(I)I$_2$] (**2**) and the two-dimensional assembling of the molecules along the *ac* plane through Te$\cdots$I and I$\cdots$I secondary interactions (dashed lines). Hydrogen atoms have been omitted by clarity. Symmetry code: (a) = 1 − x, −y, −z; (b) = −1 + x, y, z; (c) −x, −y, −z; (d) = 2 − x, −y, 1 − z. Selected bond lengths [Å] and angles [°]: I2–I3 3.0169(10), I1–Te1 2.7316(12), Te1–C11 2.140(9), Te1–I2 2.8977(10), Te1$\cdots$I3a 3.4769(0), I1$\cdots$I2d 3.8156(0), Te1a$\cdots$I3c 3.7569(0), I2$\cdots$I1d 3.8156(0); C11–Te1–I1 94.10(3), C11–Te1–I2 113.20(3), I1–Te1–I2 98.78(3), Te1–I2–I3 173.85(3), I1–Te1$\cdots$I3a 174.53(1), I2–Te1$\cdots$I3a 77.58(1), Te1–I1$\cdots$I2d 163.11(1), I2–I3$\cdots$Te1b 77.61(0).

Scheme 2. TBP and MC configurations for RR′E·X$_2$.

the species [tmpTeI$_2$]$^-$ (**3**) as a RE·X$_2$, three-coordinated trigonal-bipyramidal compound [20,21], with the two iodine atoms occupying the apical sites, and the Martin notation X−E−X to a TBP three-coordinated configuration (also with basis on the VSEPR theory), can be now represented by 10−E−3, according to Chart 1 [22,25].

The complex (PyH)[tmpTeI$_3$(I$_3$)] (**4**) represents a rare example of Te^{IV} compound in which a I$_3^-$ chain appears as component of the complex and not as solvate, as normally occurs [1,5]. The reciprocal association of single [tmpTeI$_3$(I$_3$)]$^-$ anions through I2−I6 secondary interactions with a distance of 3.587(3) Å produces

the interactions with bulky neighbor molecules, forcing the preferential three-coordinated configuration (**B**, Scheme 2) because the increased bulkiness around E prefers MC to TBP [23].

The hypervalent, 3c−4e T-shaped compound (PyH)[tmpTeI$_2$] (**3**), represented in Fig. 3, does not shows the tendency of the analog complex (PyH)[mesTeI$_2$] (mes = 2,4,6-trimethylphenyl) [24] to undergo dimerization through secondary and reciprocal Te$\cdots$I interactions. The open I1a−Te1−I1 angle (173.963(12)°), as well as the somewhat open orthogonal angles C11−Te1−I1a (93.019(6)) and C11−Te1−I1 (93.019(6)°), allow us to consider

Chart 1. TBP configuration for a three-coordinated RE·X$_2$ complex (X−E−X≡10−E−3).
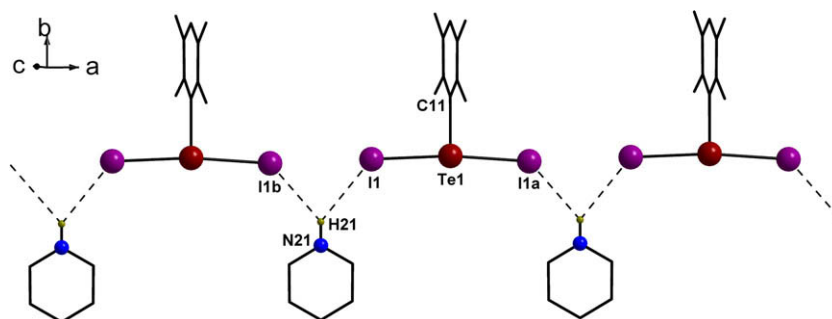
Fig. 3. Molecular structure of (PyH)[tmpTeI$_2$] (**3**) and the one-dimensional assembling of the T-shaped molecules along the *a* axis. Hydrogen atoms have been omitted by clarity. Dashed lines represent secondary, interionic interactions. Symmetry code: (a) = 0.5 − x, y, 1.5 − z; (b) = −0.5 − x, y, 1.5 − z. Selected bond lengths [Å] and angles [°]: Te1–C11 2.153(4), Te1–I1a 2.9787(2), Te1–I1 2.9787(2), N21–H21 0.860(0), H21$\cdots$I1 3.196(1), H21$\cdots$I1b 3.196(1); C11–Te1–I1a 93.019(6), C11–Te1–I1 93.019(6), I1a–Te1–I1 173.963(12), N21–H21$\cdots$I1 133.580(1).
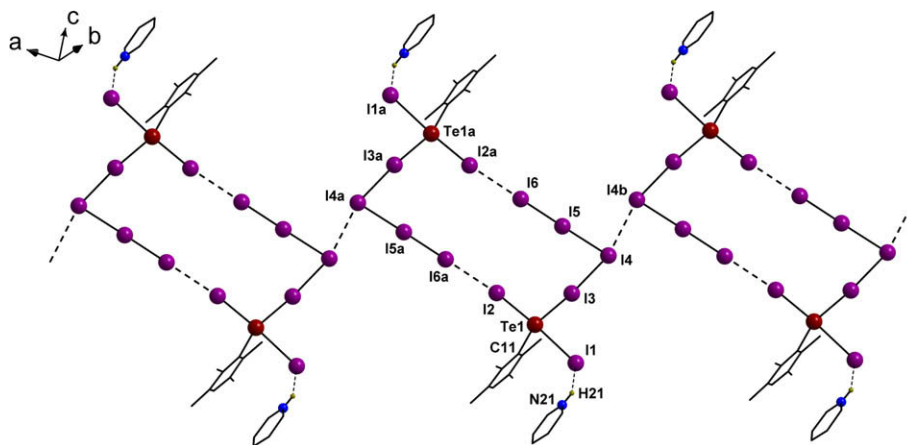
Fig. 4. Molecular structure of (PyH)[tmpTeI$_3$(I$_3$)] (**4**) and the one-dimensional assembling of the molecules. Hydrogen atoms have been omitted by clarity. Dashed lines represent secondary interactions. Symmetry code: (a) = 1 − *x*, 1 − *y*, 1 − *z*; (b) = −*x*, 2 − *y*, 1 − *z*. Selected bond lengths [Å] and angles [°]: Te1–C11 2.175(16), Te1–I1 3.075(18), Te1–I2 2.805(17), Te1–I3 2.853(2), I5–I6 2.807(18), I5–I4 3.065(17), I4–I3 3.016(2), N21–H21 0.860(1), I2···I6a 3.587(3), I4···I4b 3.750(1), H21···I1 3.025(1); I6–I5–I4 179.30(7), I3–I4–I5 85.60(5), C11–Te1–I2 88.2(4), C11–Te1–I3 118.6(7), I2–Te1–I3 91.25(6), C11–Te1–I1 85.3(4), I2–Te1–I1 172.93(5), I3–Te1–I1 89.28(6), Te1–I3–I4 173.07(6), Te1–I2···I6a 171.81(1), I3–I4···I4b 163.34(1), N21–H21···I1 132.25(2).

12-membered rings with an inversion center, as shown in Fig. 4. The linkage of the rings through I4$_{x'}$···I4$_y$ contacts (3.750(1) Å) promotes a pseudo polymeric, one-dimensional chaining of the ions chiefly along the *a* axis.

Complex (PyH)$_2$[TeI$_4$(µ-I)$_2$TeI$_4$] (**5**), whose structure is shown in Fig. 5, represents the first main product of this work obtained in the presence of water. The aryltellurenyl iodides synthesized in these conditions undergo stoichiometric rearrangement of the R–Te^{II} bond, with its partial cleavage under oxidation to Te^{IV} and subsequent addition of the R group to a Te^{III} substrate (**6**, to be discussed further). The occurrence of I–I secondary interactions {3.5206(0) and 3.6751(0) Å} between the octahedral configured [TeI$_4$(µ-I)$_2$TeI$_4$]$^{2-}$ moieties and neighboring ions leads to the three-dimensional arrangement of the ionic species in the lattice, as represented in Fig. 6, in the cell projection 2*xa*, 2*xb* and 1*xc*. We have earlier reported the structure of the [TeI$_4$(µ-I)$_2$TeI$_4$]$^{2-}$ anion in [{TeI$_6$}{Te$_2$I$_{10}$}][Co(NH$_3$)$_6$]$_2$·2I·6H$_2$O [1], although in this compound the bulky complex counter ion does not allows the three-dimensional assembly of the species. Other authors have been described as well the dioctahedral structure of the [Te$_2$X$_{10}$]$^{2-}$ anion {X = Cl, Br, I [26]; X = Cl [27]; X = I [28]}, with diverse cationic species.

Complex [(tmp)$_2$TeI$_2$] (**6**), although its formulation allows presuming, is not a tetra-coordinated Te^{IV} compound, but instead, a tri-coordinated Te^{III} species, as represented in Fig. 7. The structural interpretation of this compound is exactly the same proposed for complex **2**, from which **6** can be derivatized by substitution of the single iodine atom by R. The measured bond distances and angles of **6** correspond also to those of **2**. Tetra-coordinated Te^{IV} complexes of the type R$_2$TeX$_2$ (X = Cl, Br, I) have been extensively discussed by Beckmann and co-workers [29–32], and the distorted tetrahedral seems to be the preferential configuration for R$_2$TeI$_2$ compounds. We can attribute the RR'E·X$_2$, three-coordinated MC [20,21] configuration of **6** (see discussion of compound **2**), to the cleavage of the R–Te bond occurred in the starting complex (PyH)[tmpTeI$_2$] (**3**), from which **5** and **6** are formed.

The reaction of (PyH)[tmpTeI$_2$] (**3**) with a little excess of iodine, also with addition of water to the crude product, leads as well to the cleavage of the R–Te bond and to the formation of Te^{IV} and Te^{III} products, (PyH)$_2$[TeI$_6$]I$_2$ (**7**) and complex **6**, respectively. The structure of compound **7** is shown in Fig. 8. The octahedral [TeI$_6$]$^{2-}$ anion is well known in the chemistry of aryltellurenyl iodides,

however the structure of complex **7** is noteworthy because of the rare assemblage of its crystalline lattice. The [TeI$_6$]$^{2-}$ anions are linked through secondary interactions {3.2821(0) Å} of I$_2$ bridging molecules with equatorial iodine ligands, in a zig-zag, one-dimensional assembly along the *a* axis. The apical iodine ligands attain also secondary interactions with pyridinium cations.
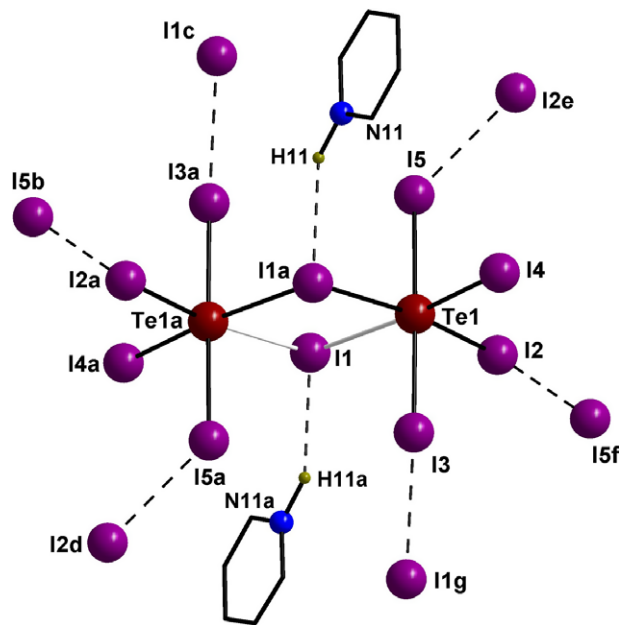
Fig. 5. Molecular structure of (PyH)$_2$[TeI$_4$(µ-I)$_2$TeI$_4$] (**5**) and the secondary interactions with PyH$^+$ and the neighboring iodine atoms (dashed lines). Hydrogen atoms have been omitted by clarity. Symmetry code: (a) = 2 − *x*, −*y*, 1 − *z*; (b) = 2.5−*x*, −*y*, −0.5 + *z*; (c) = 0.5 + *x*, −0.5 − *y*, 1 − *z*; (d) = 1.5 − *x*, −*y*, −0.5 + *z*; (e) = 0.5 + *x*, *y*, 1.5 − *z*; (f) = −0.5 + *x*, *y*, 1.5 − *z*; (g) = 1.5 − *x*, 0.5 + *y*, *z*. Selected bond lengths [Å] and angles [°]: Te1–I1 3.0918(3), Te1–I2 2.7912(3), Te1–I3 2.8991(3), Te1–I4 2.8213(3), Te1–I5 2.9797(3), Te1–I1a 3.2590(3), I1···H11a 3.0230(1), I2a···I5b 3.5206(0), I3a···I1c 3.6751(0), I5a···I2d 3.5206(0), I2···I5f 3.5206(0), I3···I1g 3.6751(0); I2–Te1–I4 97.465(11), I2–Te1–I5 88.787(10), I4–Te1–I3 92.038(11), I2–Te1–I5 89.625(10), I4–Te1–I5 90.586(10), I3–Te1–I5 177.090(11), I2–Te1–I1 89.528(9), I4–Te1–I1 172.971(12), I3–Te1–I1 88.801(10), I5–Te1–I1 88.747(9), Te1–I1–Te1a 92.803(1), N11–H11···I1a 129.904(0).
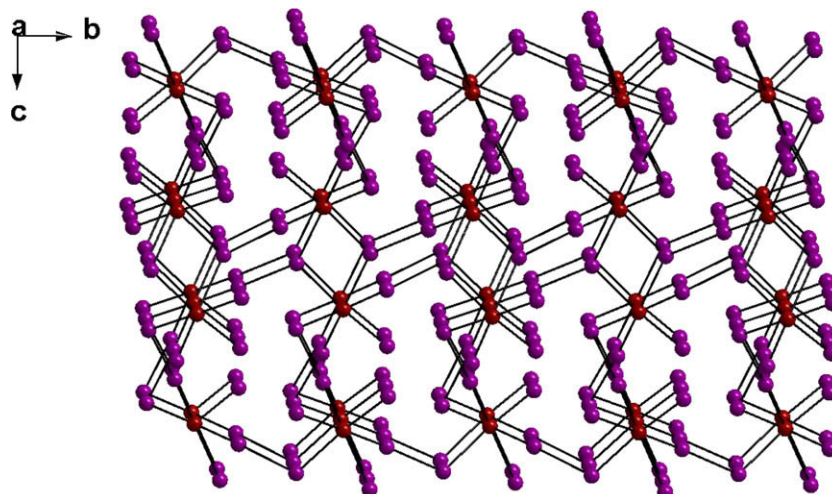
Fig. 6. Three-dimensional assembly of $(PyH)_2[TeI_4(\mu\text{-}I)_2TeI_4]$ (**5**) in the cell projection 2*xa*, 2*xb*, 1*xc*. Hydrogen atoms and the pyridinium ions have been omitted by clarity. The piridinium ions are placed in the spaces between the anionic moieties.
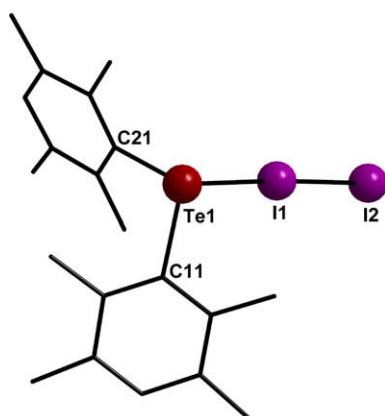

Fig. 7. Molecular structure of $[(tmp)_2TeI_2]$ (**6**). Hydrogen atoms have been omitted by clarity. Selected bond lengths [Å] and angles [°]: I1–I2 2.9226(6), I1–Te1 2.9804(5), Te1–C21 2.147(5), Te1–C11 2.157(5); Te1–I1–I2 177.433(17), C21–Te1–C11 104.56(19), C21–Te1–I1 95.03(14), C11–Te1–I1 100.88(13).

Compounds **5**, **6** and **7** were obtained in the presence of an excess of water (on the contrary of the preceding discussed compounds), and the hydrolysis of the R–Te bond led to the occurrence of redox rearrangements. An interesting study would be the investigation of reactions performed in conditions situated between these two procedures, i.e., in the presence of small amounts of water. A reaction of **3** with I_2 conducted without addition of water, but in opened vessel, gave two main products, one of them very unstable, which could not be analyzed accurately. Nevertheless, some preliminary results indicate the occurrence of partial hydrolysis of the R–Te bond in $(PyH)[tmpTeI_2]$ (**3**), and the formation of a mixed-valent anion containing the species $[RTe^{(II)}I_2]^-$ and $[Te^{(IV)}I_6]^{2-}$. Compound **6** could also be identified as the other main product.

Acknowledgment
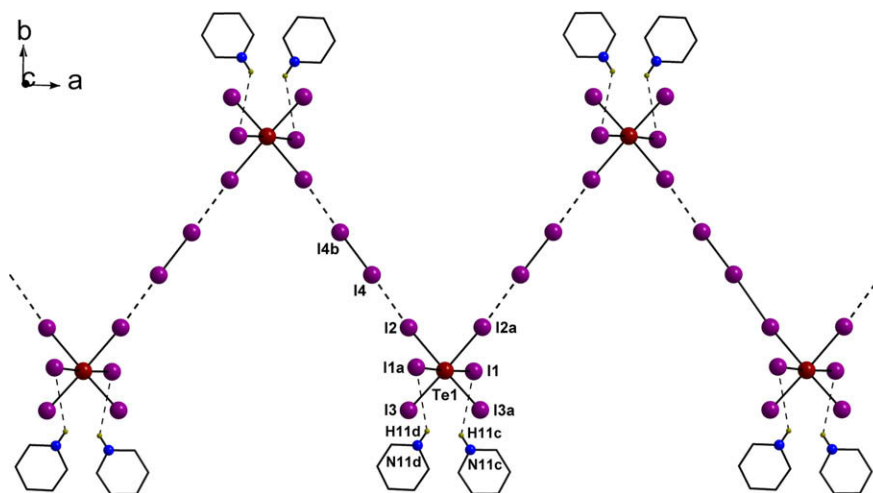
Fig. 8. Molecular structure of $(PyH)_2[TeI_6]\cdot I_2$ (**7**) and the secondary interactions (dashed lines) with PyH^+ ions and I_2 solvate molecules, last producing the one-dimensional assembly of the molecules along the *a* axis. Hydrogen atoms of the pyridine rings have been omitted by clarity. Symmetry code: (a) = $1 - x, y, 2.5 - z$; (b) = $0.5 - x, 2.5 - y, 2 - z$; (c) = $1 - x, 1 - y, 2 - z$; (d) = $x, 1 - y, 0.5 + z$. Selected bond lengths [Å] and angles [°]: Te1–I1 2.9279(3), Te1–I1a 2.9279(3), Te1–I2 3.0463(4), Te1–I2a 3.0463(4), Te1–I3 2.8445(4), Te1–I3a 2.8445(4), I4–I4b 2.7712(6), I2···I4 3.2821(0), I1···H11c 3.2817(1), I1a···H11d 3.2817(1), N11c–H11c 0.860, N11d–H11d 0.860; I3–Te1–I3a 91.676(17), I3–Te1–I1a 90.270(11), I3–Te1–I1 91.652(11), I3a–Te1–I1 90.270(11), I1a–Te1–I1 177.242(18), I3–Te1–I2a 178.197(12), I3–Te1–I2 89.805(10), I1a–Te1–I2 89.369(10), I1–Te1–I2 88.659(10), I2a–Te1–I2 88.734(16), Te1–I2···I4 167.58(10), I2···I4–I4b 174.29(10), I1···H11–N11 136.09(10).

Appendix A. Supplementary material

CCDC 761171, 761172, 761173, 761174, 761175, 761175, 761176 and 761177 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.004.

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