Inorganic Chemistry
Communication

Inorg. Chem. **2009,** *48,* 4607–4609 **4607**
DOI:10.1021/ic900193k

New Aryltellurenyl Iodides with Uncommon Valences: Synthetic and Structural Characteristics of [$RTeTeI_2R$], [R_2TeTeR_2][Te_4I_{14}], and [$RTe(I)I_2$] (R = 2,6-Dimethoxyphenyl)

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Received January 29, 2009

$(RTe)_2$ (R = 2,6-dimethoxyphenyl) reacted with iodine to give [$RTeTeI_2R$] (**1**), [R_2TeTeR_2][Te_4I_{14}] (**2**), and [$RTe(I)I_2$] (**3**). The synthesis of the mixed-valent, neutral complex **1** occurred easily through the reaction of $(RTe)_2$ with mesTeI (mes = 2,4,6-trimethylphenyl), which proved the ability of mesTeI to act as a selective oxidation reagent. In the cationic species $[R_2TeTeR_2]^{2+}$ as well in the counterion $[Te_4I_{14}]^{2-}$ of compound **2**, tellurium occurs in the rare oxidation state 3+.

The halogenation of diarylditellurides $(RTe)_2$ has been experimentally studied in recent years with the purpose of obtaining Te^{II} and Te^{IV} compounds, as well as mixed-valent aryltellurenyl halides and related charge-transfer complexes.

Because the chemistry of organyltellurenyl iodides is becoming more and more interesting and attractive, new experimental routes to synthesize compounds with innovative architectural designs − and possibly also with pharmacological applications − have been attempted worldwide.

Unusual compositions and configurations are characteristic for these types of organyltellurenyl halides.[1] Many structures of tellurium(II) and -(IV) iodide compounds attain secondary, interionic $I_3^-\cdots I{-}Te^-$, $N^+{-}H\cdots I{-}Te^-$, and $N^+{-}H\cdots I_3^-$ interactions, as well as $Te\cdots I$, $I\cdots I$, or $Te\cdots\pi{-}$aryl contacts.[2,3] 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[4] like, for example, the recently reported neutral species $[mesTeI(\mu\text{-}I)_2(TeImes)_2]_n$ (mes = 2,4,6-trimethylphenyl),[5] are often described.

The chemical and structural versatility of organyltellurenyl halides, combined with the already observed 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.

Earlier studies[6] 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 as key compounds in the synthesis of Te^{II} and Te^{IV} products. Recently, we have attained the selective oxidation of $(PhTe)_2$ with I_2 with the formation of $(PhTeI)_4$.[7] Because the oxidation of Te^{II} to Te^{IV} occurs relatively easily, the stabilization of Te^{II} compounds can be valuable in many cases. We have investigated the ability of the mesityl group to stabilize tellurium(II) iodides as mesTeI, and the obtained results were undoubted and reproducible.[5,8] This finding aroused our interest for the possibility of using mesTeI as a selective oxidation reagent, an hypothesis that was proven also in the case of the preparation of [$RTeTeI_2R$] (**1**; R = 2,6-dimethoxyphenyl) by the reaction of $(RTe)_2$ with mesTeI at room temperature (see Scheme 1). The specific mixed-valence state of **1** is also promoted by the organic substituent R (2,6-dimethoxyphenyl) because the direct reaction with I_2 can also be carried out, although under controlled conditions (−10 °C). Some reactions of bis(2,6-dimethoxyphenyltellurium) with I_2 under different conditions presented in this work are summarized in Scheme 1.

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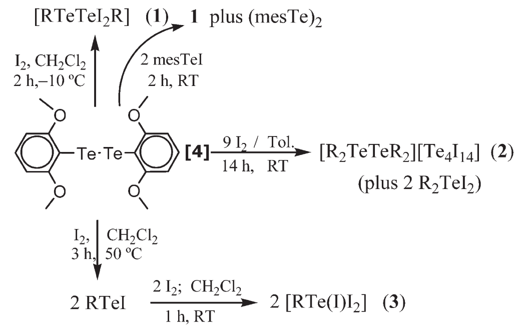
Scheme 1. Reactions of $(RTe)_2$ (R = 2,6-Dimethoxyphenyl) with Iodine and also with mesTeI (mes = 2,4,6-Trimethylphenyl) for **1**



Because all of the reactions should occur with the formation of the relatively unstable intermediary RTeI,[1b] we can presume that the two methoxy groups of 2,6-dimethoxyphenyl are particularly able to stabilize tellurium iodides in mixed-valent, unusual compositions.

The structure of compound **1**, also the pseudodimeric association of the molecules (in dashed lines), is represented in Figure 1. The reciprocal Te2···I2 interactions, with a distance of 4.016(8) Å, are less than the sum of the van der Waals radii for Te/I (4.04 Å).[9] Compound **1**, with vicinal, asymmetrically substituted Te atoms with oxidation numbers 1+ and 3+, exemplifies the steric effect of the 2,6-dimethoxyphenyl group in regard to the stabilization of unusual structures, as well as the selective oxidative character of the mesTeI species. Compounds analogous to **1**, with Cl and Br instead I, have already been obtained by Beckmann and co-workers,[10] by the reaction of $(PhTe)_2$ with Br_2, such as through halogenation of the bulky diarylditelluride $(RTe)_2$ {R = 2,6-(mes)-C_6H_3} with bromine or sulfuryl chloride.

The structure of the complex salt $[R_2TeTeR_2][Te_4I_{14}]$ (**2**) is shown in Figure 2. On the basis of the geometry and bond lengths, the anion tetramer $[Te_4I_{14}]^{2-}$ can be considered as assembled by two $[Te_2I_6]^{2-}$ dianions connected by two I^+, generating two Te−I−Te fragments (with 3.012 and 3.041 Å) having a 3c−4e bond system. In turn, each $Te_2I_6^{2-}$ dianion can be seen as formed by two neutral TeI_2 connected by two bridging I^-. The structurally analogous dianion $[Se_4Br_{14}]^{2-}$ was earlier reported by Krebs and co-workers.[11] In the cation $[R_2TeTeR_2]^{2+}$, the Te−Te bond is 2.855 Å and the R−Te−R bonds have different distances (2.162 and 2.093 Å). In both ionic species, the Te atoms occur in the rare oxidation state 3+. Figure 3 shows the supramolecular, 2D lattice of the anion $[Te_4I_{14}]^{2-}$ in the *ab* plane. This configuration was attained through Te1···I6, Te2···I3 (both 3.899 Å), and I1···I6 (3.906 Å) secondary interactions. In the synthesis of **2**, light-red crystals of R_2TeI_2 were also identified.

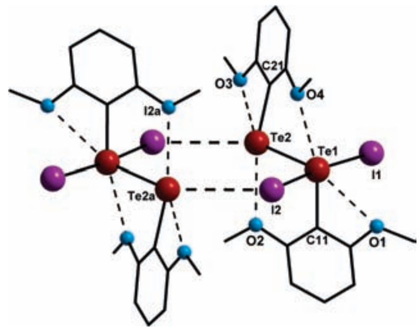


Figure 1. Molecular structure of **1** and the pseudodimeric association of the molecules. H atoms have been omitted for clarity. Symmetry code: a = $-x, 2-y, z$. Selected bond lengths [Å] and angles [deg]: Te1−C11 2.110(4), Te1−Te2 2.757(4), Te1−I2 2.922(5), Te1−I1 2.984(5), Te2−C21 2.126(5), Te2···I2a 4.016(8), Te1···O1 2.925(5), Te1···O4 2.904(5), Te2···O2 2.886(5), Te2···O3 2.916(4); C11−Te1−Te2 101.02(13), C11−Te1−I1 89.18(13), C11−Te1−I2 89.13(13), Te2−Te1−I2 94.78 (14), Te2−Te1−I1 92.05(14), I1−Te1−I2 173.15(15), C21−Te2−Te1 95.54(13), Te1−Te2···I2a 157.38(11), Te1−I2···Te2a 100.61(11).

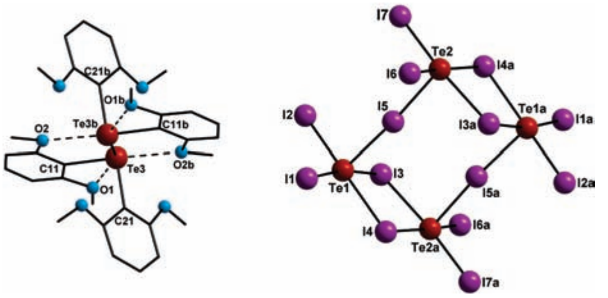


Figure 2. Molecular structure of **2**. H atoms have been omitted for clarity. Symmetry codes: a = $1-x, 1-y, 1-z$; b = $3-x, -y, -z$. Selected bond lengths [Å] and angles [deg]: C11−Te3 2.162(13), C21−Te3 2.093(13), Te3−Te3b 2.855(16), Te1−I1 2.798(12), Te1−I2 2.838(14), Te1−I3 3.129(12), Te1−I4 3.097(13), Te1−I5 3.012(13), Te2−I5 3.041 (13), Te2−I6 2.828(12), Te2−I7 2.826(14), Te2−I3a 3.077(12), Te2−I4a 3.115(12), Te3···O1 2.765(4), Te3···O2b 2.905(5); C11−Te3−C21 95.10(5), C11−Te3−Te3b 97.90(4), C21−Te3−Te3b 94.90(4), Te1−I5−Te2 175.65(4), I1−Te1−I2 97.04(4), I1−Te1−I5 95.79(4), I2−Te1−I5 90.32(4), I1−Te1−I4 89.35(4), I2−Te1−I4 172.72(4), I5−Te1−I4 92.513, I1−Te1−I3 170.02(5), I2−Te1−I3 89.12(4), I5−Te1−I3 92.01(3), I4−Te1−I3 84.08(3), Te2a−I3−Te1 95.19(3), I7−Te2−I6 96.79(4), I7−Te2−I5 92.23(4), I6−Te2−I5 92.84(4), I7−Te2−I3a 174.21(4), I6−Te2−I3a 87.76(4), I5−Te2−I3a 91.11(3), I7−Te2−I4a 90.45(4), I6−Te2−I4a 170.29(4), I5−Te2−I4a 93.35(3), I3a−Te2−I4a 84.64(3), Te1−I4−Te2a 95.09(3).

As is also depicted in Scheme 1, our reaction of $(RTe)_2$ (R = 2,6-dimethoxyphenyl) with I_2 at 50 °C affords initially 2 equiv of RTeI, which reacts stoichiometrically with iodine to give $[RTe(I)I_2]$ (**3**), whose structure is shown in Figure 4. Secondary Te···I and I···I contacts hold pairs of $RTe(I)I_2$ moieties in a 1D arrangement along the *b* axis. The Te1−I1 bond [2.757(16) Å] is shorter than the Te1−I2 one [2.825(14) Å], and the I2−I3 bond measures 3.098(15) Å. The I1−Te1−I2 angle presents 96.25(2)°, and the Te1−I2−I3 axis is predominantly linear, with 171.15(18)°. The reciprocal Te1···I3a interactions have a distance of 3.345(5) Å, and the associated, chain-forming I1*x*···I3*y* interactions measure 3.892(6) Å. A similar compound, 2,6-(mes) $C_6H_3TeI\cdots I_2$, has also been reported by the group previously mentioned,[10] but the chaining of the pairs of molecules occurs in the form of stairs because the bonds analogous to Te1−I1···I3 in **3** [in our case with 147.179(14)°] present, in the charge-transfer complex 2,6-(mes)-$C_6H_3TeI\cdots I_2$,[10] an open angle of 170.97(2)°, holding the molecule pairs almost parallel to each other. The six-membered rings of compound **3**, delimited by Te1, Te1a, I3, and I3a (see Figure 4), suggest two different pictures for its structure, represented by the dimers $[RTeI(I_2)]_2$ and $[RTeI_3]_2$. In both formulations, however, the Te atoms occur in the oxidation number 3+.

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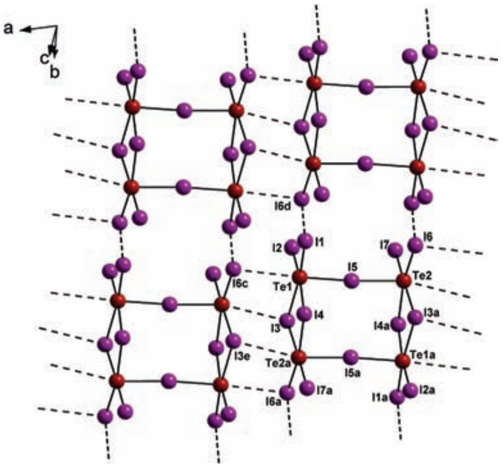


Figure 3. 2D assembly of the anions $[Te_4I_{14}]^{2-}$ (**2**) in the *ab* plane (dashed lines). Symmetry codes: a = $1 - x, 1 - y, 1 - z$; c = $1 + x, y, z$; d = $1 - x, -y, 1 - z$; e = $2 - x, 1 - y, 1 - z$. Selected bond lengths [Å] and angles [deg]: Te1···I6c 3.899(5), I1···I6d 3.906(5); I5−Te1···I6c 176.72(1), I5a−Te2a···I3e 166.06(1).

Complex **1** has a trigonal-bipyramidal (TBP) configuration of the type $RR'E{\cdot}X_2$,[12] and the I1−Te1−I2 (X−E−X) bonds are hypervalent 3c−4e. According to the N−X−L notation proposed by Martin and co-workers,[13] the hypervalent atoms in X−E−X (TBP) are represented by 10−E−4. The apical I1−Te1−I2 bonds are appropriately longer than the two equatorial ones. In the dication $[R_2TeTeR_2]^{2+}$ (**2**), the three-coordinated Te centers would be classified as 8−E−3 (onium ions). Through strong interaction with O2 and O2b [2.905(5) Å], both atoms assume a 10−E−4 TBP configuration, with C11−Te3−O2b and C11b−Te3b−O2 as apical axes [167.653(4)°]. The Te centers in $[Te_4I_{14}]^{2-}$ (**2**) present a square-pyramidal geometry, typical of both R_5Te^+ (10−Te−5) and R_5Te^- (12−Te−5) ions.

Also, the open Te1−I2−I3 angle [171.15(18)°] of **3** allows us to consider the species $RTe(I)I_2$ as a $RR'E{\cdot}X_2$, three-coordinated molecular complex (MC).[12] The hypervalent 3c−4e atoms in E−X−X (MC) are represented by 10−X−2. An alternative configuration for **3** would be the TBP $RTeI_3$ (10−E−4). Probably, this realizable form was hindered by 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.[14]

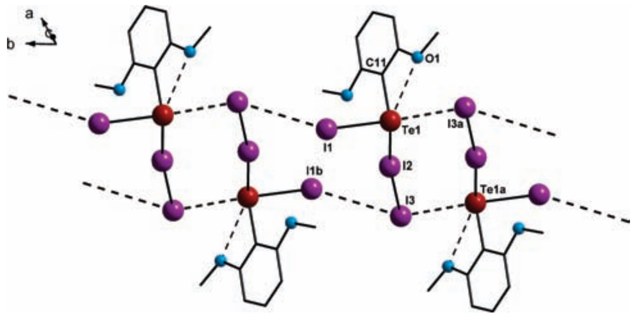
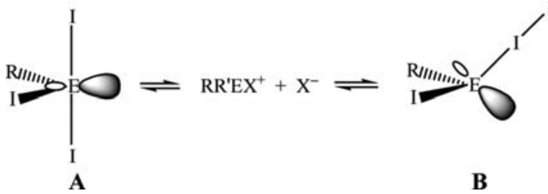


Figure 4. Molecular structure and the 1D assembly along the *b* axis (in dashed lines) of **3**. H atoms have been omitted for clarity. Symmetry codes: a = $1 - x, 1 - y, 1 - z$; b = $1 - x, 2 - y, 1 - z$. Selected bond lengths [Å] and angles [deg]: Te1−C11 2.096(5), Te1−I1 2.757(16), Te1−I2 2.825(14), I2−I3 3.098(15), Te1···I3a 3.345(5), I3···I1b 3.892(6), Te1···O1 2.986(14); C11−Te1−I1 93.14(14), C11−Te1−I2 108.50(15), Te1−I2−I3 171.15(18), I1−Te1−I2 96.25(2), C11−Te1···I3a 82.64(1), I1−Te1···I3a 174.26(1), Te1a···I3···I1b 141.82(1).

Scheme 2. TBP and MC Configurations for $RR'E{\cdot}X_2$



The interactions between the Te centers and the O atoms of the methoxy groups in 2,6-dimethoxyphenyltellurium compounds have been studied by Wada and co-workers.[15] These interactions in our title compounds are remarkably shorter than the sum of the Te/O van der Waals radii (3.58 Å)[9] and are also depicted as dashed lines in Figures 1, 2, and 4. A torsion of the 2,6-dimethoxyphenyl rings is observed in compound **1** (Figure 1) due to the double interaction of the two methoxy groups of both rings with Te1 and Te2.

Acknowledgment. This work was supported with funds from PRONEX-CNPq/FAPERGS (Brazil).

Supporting Information Available: A detailed experimental section including the synthetic procedures and information of the equipment used, crystallographic information, ORTEP projections, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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