



# The intermediary RTel as a source of new Te<sup>II</sup> and Te<sup>IV</sup> iodides by addition of (PyH)I and KI: Synthesis and structural features of [RTel]{RTel<sub>3</sub>}]<sub>n</sub>, [R<sub>2</sub>Te–TeIR], (PyH)[RTel<sub>2</sub>] and (PyH)<sub>n</sub>[RTel(μ-I)TeIR]<sub>n</sub> (R = 2,6-dimethylphenyl; Py = pyridine)

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## ABSTRACT

(DmephTe)<sub>2</sub> (dmeph = 2,6-dimethylphenyl) reacts with resublimed iodine or with pyridinium iodide under Ar atmosphere to yield [RTel]{RTel<sub>3</sub>}]<sub>n</sub> (**1**), [R<sub>2</sub>Te–TeIR] (**2**), (PyH)[RTel<sub>2</sub>] (**3**) and (PyH)<sub>n</sub>[RTel(μ-I)TeIR]<sub>n</sub> (**4**) (R = dmeph; Py = pyridine). While mesityl species analogue to **2** and **3** have been already described, the compounds **1** and **4** represent the first organotellurium iodides of their classes reported. In compound **4** a symmetrical, covalent iodine bridge links two RTel groups, attaining single [RTel(μ-I)TeIR] anions connected by Te···I secondary bonds and stabilized by pyridinium cations.

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## 1. Introduction

Because of rapid dismutation or disproportionation reactions, organytellurenyl halides RTeX (X = Cl, Br, I) are very unstable. Their stabilization arises, in general, by complexation with external neutral ligands, by addition of a second halide, or by functionalization of an organic ligand to provide a donor atom for intramolecular coordination (donor-stabilized tellurenyl halides) [1–4]. The stabilization can be achieved as well by the use of bulky substituents or coordinating functional groups [5,6]. It is also known that these species (RTeX) are relatively stable in solution, although in the literature few reports describe their characteristics in the solid state.

We have reported the synthesis and the structural characterization of PhTel (Ph = phenyl), the first organotellurenyl halide without additional functional groups [7,8]. The compound was obtained in the tetrameric form by the reaction between diphenylditelluride and the equivalent amount of iodine, and most of the experimental studies on the chemical and structural behaviour of organytellurium<sup>II/IV</sup> halogen compounds in our group are based upon the reactivity of the intermediary RTeX [9–12].

Since the chemistry of organotellurium iodides becomes more and more interesting and attractive, we have developed new

experimental routes to reach compounds with innovative architectural designs and (possibly) also with pharmacological applications.

Unusual compositions and configurations are characteristic for organotellurium iodides [13]. Many structures of Te<sup>II</sup> and Te<sup>IV</sup> iodide compounds attain secondary, interanionic I<sub>3</sub>···I–Te<sup>–</sup>, N<sup>+</sup>–H···I–Te<sup>–</sup> and N<sup>+</sup>–H···I<sub>3</sub> interactions, as well as Te···I, I···I or Te···π-aryl contacts [14–16]. Single monomers and dimers are often described, but also polymeric chains attaining 1D, 2D and 3D networks, as well rare polymeric structures with the chalcogen atoms presenting mixed valence states [17,18], like, for example, the recently reported neutral species [mesTel(μ-I)<sub>2</sub>(Telmes)<sub>2</sub>]<sub>n</sub> [12].

If the intermediary PhTel could be isolated as tetramer [7], Mes<sup>+</sup>TeI (Mes<sup>+</sup> = 2,4,6-tri-*tert*-butylphenyl) exhibits discrete molecules, without Te···I, Te···Te or I···I intermolecular interactions [19]. The compound represents a kinetically (sterically) stabilized arenetellurenyl iodide with a very bulky substituent. The molecule achieves an angular C–Te–I configuration {95.75(8)<sup>o</sup>} with a Te–I single bond {2.7181 (6) Å}.

Either the structure of the intermediary RTel or the structural features of the resulting products are dependent upon the substituent R. In our experiments in this field we have normally started from PhTel and MesTel (Mes = mesityl, 2,4,6-trimethylphenyl). To search more accurately the effects of small variations of the size of the R group on the stereochemistry of the obtained products, we have carried out some experiments starting from the intermediary (dmeph)Tel (dmeph = 2,6-dimethylphenyl). We report now

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the chemical and the structural features of the final products  $[\{\text{RTel}\}\{\text{RTel}_3\}]_n$  (**1**),  $[\text{R}_2\text{Te}-\text{TeIR}]$  (**2**),  $(\text{PyH})[\text{RTel}_2]$  (**3**) and  $(\text{PyH})_n[\text{RTel}(\mu\text{-I})\text{TeIR}]_n$  (**4**) ( $\text{R} = \text{dmeph}$ ;  $\text{Py} = \text{pyridine}$ ).

## 2. Results and discussion

The X-ray crystal data and the experimental conditions for the analyses of the complexes,  $[\{\text{RTel}\}\{\text{RTel}_3\}]_n$  (**1**),  $[\text{R}_2\text{Te}-\text{TeIR}]$  (**2**),  $(\text{PyH})[\text{RTel}_2]$  (**3**) and  $(\text{PyH})_n[\text{RTel}(\mu\text{-I})\text{TeIR}]_n$  (**4**) are given in Table 1. Table 2 summarizes selected bond distances and angles for the title compounds. Fig. 1 shows the polymerization of the compound **1**, with the multiple secondary interactions identified by dashed lines. Figs. 2 and 3 represent the molecular structures of compounds **2** and **3**, last attaining a pseudo dimeric configuration, indicated by the thicker dashed lines. Fig. 4 displays the one-dimensional assembly of **4**, attained through secondary interactions (dashed lines).

In  $[\{\text{RTel}\}\{\text{RTel}_3\}]_n$  (**1**),  $\{(\text{dmephTe})_2\text{I}_4\}$  moieties are connected through  $\text{Te}\cdots\text{I}$  {3.271(1) Å} and  $\text{I}\cdots\text{I}$  {3.817(2) Å} intermolecular interactions, assembling one-dimensional chains along the bisector of the  $bc$  axes (see Fig. 1).

The  $\text{Te}(1)-\text{I}(2)$  and  $\text{Te}(2)-\text{I}(2)$  bond lengths are very similar, with 3.0266(3) and 2.9130(3) Å, respectively. Formally, we consider the second bond as a covalent bond and assign to  $\text{Te}(1)$  the oxidation state +2 and to  $\text{Te}(2)$  the oxidation number +4 (because of the secondary bonding interactions the oxidation states are formal and approximative). The occurrence of chalcogen compounds with mixed valence states ( $\text{Te}^{\text{II}}/\text{Te}^{\text{IV}}$ ) is very uncommon, as we have already seen in the Section 1.

Compound **2**,  $[\text{R}_2\text{Te}-\text{TeIR}]$ , attains single  $\text{Te}^{\text{II}}$  molecules, with  $\text{Te}(1)-\text{Te}(2)$  distances equal to 3.2188(12) Å. The  $\text{Te}(1)-\text{I}(1)$  bond

is 2.8305(10) Å, the three center system  $\text{I}(1)-\text{Te}(1)-\text{Te}(2)$  is almost linear {171.082(13)°}, suggesting the occurrence of a charge transfer complex. The geometry about the  $\text{Te}(1)$  atom is a distorted T-shape, indicating the presence of a stereochemically active lone pair. In the analogous compound  $\text{Mes}(\text{I})\text{Te}(\text{TeMes}_2)$  [1] the presence of a somewhat bulkier R group is evident also in the  $\text{I}(1)-\text{Te}(1)-\text{Te}(2)$  bond angle {166.71(2)°}. The  $\text{Te}(1)-\text{Te}(2)$  and  $\text{Te}(1)-\text{I}(1)$  bond lengths are respectively 3.2834(15) and 2.8146(14) Å.

Since the  $\text{Te}^{\text{II}}$  compound  $(\text{PyH})[\text{RTel}_2]$  (**3**) also presents a T-shaped configuration, with a three center system attained by the almost linear atoms  $\text{I}(1)-\text{Te}(1)-\text{I}(2)$  {174.586(11)°}, the remarks made for compound **2** (with respect to the possible existence of a charge transfer complex, as well as the stereochemical activity of a lone pair) are appropriate also for **3**. The  $\text{Te}(1)-\text{I}(1)$  and  $\text{Te}(1)-\text{I}(2)$  bonds are very similar, with distances of 3.0082(10) and 2.9393(10) Å, respectively. Weak  $\text{Te}(1)\cdots\text{I}(1)$  interactions {4.050(13) Å} suggest a pseudo dimerization of the  $[\text{RTel}_2]$  anions. The interionic  $\text{I}(1)\cdots\text{H}(\text{Py})$  contacts measure 3.068(6) Å. These secondary interactions are situated in the limit of the sums of the van der Waals radii for  $\text{Te}/\text{I}$  and  $\text{I}/\text{H}$ , which are 4.04 and 3.07 Å, respectively [20].

The polymeric (also partially T-shaped) compound  $(\text{PyH})_n[\text{RTel}(\mu\text{-I})\text{TeIR}]_n$  (**4**) attains angular, five center moieties  $\{\text{I}(1)-\text{Te}(1)-(\mu\text{-I}(2)-\text{Te}(1)'\text{-I}(1)')\}$ . The  $\text{I}(1)-\text{Te}(1)-(\mu\text{-I}(2))$  bonds are almost linear {175.83(2)°}, while the  $\text{Te}(1)-(\mu\text{-I}(2)-\text{Te}(1)')$  atoms enclose an angle of 148.56(3)°. As a consequence of the asymmetry of the five center axis, in the lattice of **4** the extremities of the  $\text{I}(1)-\text{Te}(1)-(\mu\text{-I}(2)-\text{Te}(1)')-\text{I}(1)'$  moieties {the groups  $\text{I}(1)-\text{Te}(1)-(\mu\text{-I}(2))$  and  $\text{Te}(1)'\text{-I}(1)'$ }, are placed face to face in opposite sides, so that two pairs of  $\text{Te}\cdots\text{I}$  effective interactions with

**Table 1**  
Crystal data and structure refinement for **1**, **2**, **3** and **4**.

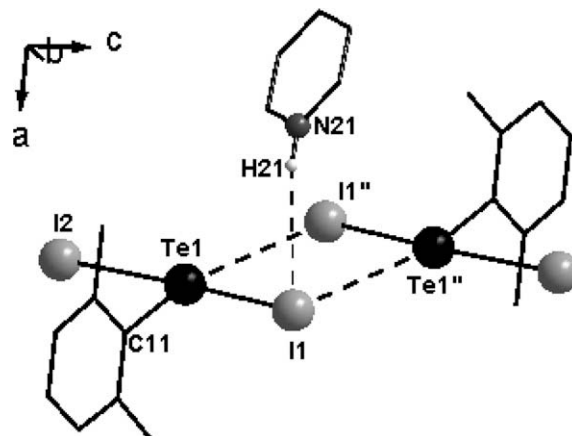
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	$\text{C}_{16}\text{H}_{18}\text{I}_4\text{Te}_2$	$\text{C}_{24}\text{H}_{27}\text{ITe}_2$	$\text{C}_{13}\text{H}_{15}\text{NI}_2\text{Te}$	$\text{C}_{21}\text{H}_{24}\text{NI}_3\text{Te}_2$
Formula weight	973.10	697.56	566.66	926.31
$T$ (K)	173(2)	173(2)	173(2)	173(2)
Radiation, $\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$
<i>Unit cell dimensions</i>				
$a$ (Å)	8.2922(2)	8.081(5)	8.464(5)	15.3911(11)
$b$ (Å)	11.5610(3)	14.093(5)	14.423(5)	7.7223(5)
$c$ (Å)	12.3596(3)	21.208(5)	14.093(5)	21.5657(14)
$\alpha$ (°)	98.4200(10)	90	90	90
$\beta$ (°)	104.1860(10)	99.482(5)	105.902(5)	92.279(4)
$\gamma$ (°)	93.8640(10)	90	90	90
$V$ (Å <sup>3</sup> )	1129.74(5)	2382.3(18)	1654.6(13)	2561.2(3)
$Z$ , $D_{\text{calc}}$ (g cm <sup>-3</sup> )	2, 2.861	4, 1.945	4, 2.275	4, 2.402
Absorption coefficient (mm <sup>-1</sup> )	8.043	3.751	5.512	5.901
$F(000)$	860	1312	1032	1680
Crystal size (mm)	0.252 × 0.136 × 0.132	0.21 × 0.123 × 0.084	0.645 × 0.162 × 0.138	0.264 × 0.178 × 0.109
$\theta$ Range (°)	1.72–29.58	1.74–29.13	2.06–28.72	1.94–24.79
Index ranges	–11 < $h$ < 11, –16 < $k$ < 16, –16 < $l$ < 17	–11 < $h$ < 10, –19 < $k$ < 12, –28 < $l$ < 29	–11 < $h$ < 11, –19 < $k$ < 19, –19 < $l$ < 19	–20 < $h$ < 20, –19 < $k$ < 10, –28 < $l$ < 29
Reflections collected	27224	24970	16094	15047
Reflections unique	6294 [ $R_{\text{int}} = 0.0206$ ]	6385 [ $R_{\text{int}} = 0.0326$ ]	4294 [ $R_{\text{int}} = 0.0246$ ]	3316 [ $R_{\text{int}} = 0.0617$ ]
Completeness to $\theta$ maximum (%)	99.5	99.8	99.9	99.8
<i>Absorption correction</i>				
Maximum and minimum transmission	0.7459 and 0.5946	0.4318 and 0.3889	0.7458 and 0.5278	0.7458 and 0.5372
<i>Refinement method</i>				
	Least-squares on $F^2$	Least-squares on $F^2$	Least-squares on $F^2$	Least-squares on $F^2$
Data/restraints/parameters	6294/0/200	6385/0/245	4294/0/155	3316/0/121
Goodness-of-fit on $F^2$	1.587	1.104	1.018	1.125
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0173$ , $wR_2 = 0.0383$	$R_1 = 0.0314$ , $wR_2 = 0.0811$	$R_1 = 0.0256$ , $wR_2 = 0.0534$	$R_1 = 0.0443$ , $wR_2 = 0.0989$
$R$ indices (all data)	$R_1 = 0.0203$ , $wR_2 = 0.0585$	$R_1 = 0.0439$ , $wR_2 = 0.0944$	$R_1 = 0.0400$ , $wR_2 = 0.0596$	$R_1 = 0.0730$ , $wR_2 = 0.1242$
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.582 and –0.820	0.880 and –0.965	0.746 and –0.636	1.517 and –1.207

**Table 2**  
Selected bond lengths [Å] and angles [°] for the compounds **1**, **2**, **3** and **4**.

<b>1</b>	
<i>Bond lengths</i>	
C(11)–Te(1)	2.141(3)
C(21)–Te(2)	2.137(4)
Te(1)–I(1)	2.7982(4)
Te(1)–I(2)	3.0266(3)
Te(2)–I(2)	2.9130(3)
Te(2)–I(3)	3.1682(3)
Te(2)–I(4)	2.8000(4)
Te(1)···I(3) <sup>y</sup>	3.271(1)
I(4)···I(4) <sup>z</sup>	3.817(2)
<i>Bond angles</i>	
C(11)–Te(1)–I(1)	91.10(9)
C(11)–Te(1)–I(2)	116.07(10)
C(21)–Te(2)–I(2)	115.02(11)
C(21)–Te(2)–I(3)	89.860(10)
C(21)–Te(2)–I(4)	91.250(10)
I(1)–Te(1)–I(2)	89.717(10)
Te(1)–I(2)–Te(2)	178.723(11)
I(3)–Te(2)–I(4)	178.880(12)
I(2)–Te(2)–I(3)	82.753(9)
I(2)–Te(2)–I(4)	96.909(11)
I(1)–Te(1)···I(3) <sup>y</sup>	173.290(0)
Te(2)–I(4)···I(4) <sup>z</sup>	150.130(0)
<b>2</b>	
<i>Bond lengths</i>	
C(11)–Te(1)	2.141(4)
C(21)–Te(2)	2.139(4)
C(31)–Te(2)	2.141(4)
Te(1)–I(1)	2.8305(10)
Te(1)–Te(2)	3.2188(12)
<i>Bond angles</i>	
I(1)–Te(1)–Te(2)	171.082(13)
C(11)–Te(1)–I(1)	93.94(10)
C(11)–Te(1)–Te(2)	77.29(10)
C(21)–Te(2)–Te(1)	94.83(10)
C(31)–Te(2)–Te(1)	118.95(10)
C(21)–Te(2)–C(31)	98.35(15)
<b>3</b>	
<i>Bond lengths</i>	
C(11)–Te(1)	2.132(4)
Te(1)–I(1)	3.0082(10)
Te(1)–I(2)	2.9393(10)
Te(1)···I(1) <sup>y</sup>	4.050(13)
I(1)···H(21) <sup>z</sup>	3.068(6)
<i>Bond angles</i>	
C(11)–Te(1)–I(1)	86.82(9)
C(11)–Te(1)–I(2)	87.83(8)
C(11)–Te(1)···I(1) <sup>y</sup>	159.230(1)
I(1)–Te(1)–I(2)	174.586(11)
N(21) <sup>z</sup> –H(21) <sup>z</sup> ···I(1)	135.920(2)
<b>4</b>	
<i>Bond lengths</i>	
C(11)–Te(1)	2.144(6)
Te(1)–I(1)	2.846(7)
Te(1)–I(2)	3.117(5)
Te(1)···I(1) <sup>z</sup>	3.963(4)
I(1)···H21	3.049(1)
<i>Bond angles</i>	
I(1)–Te(1)–I(2)	175.83(2)
Te(1)–I(2)–Te(1) <sup>y</sup>	148.56(3)
C(11)–Te(1)–I(1)	90.11(18)
C(11)–Te(1)–I(2)	85.79(18)
C(11)–Te(1)–I(1) <sup>z</sup>	166.81(0)
N(21)–H(21)···I(1)	149.68(1)

Symmetry transformations used to generate equivalent atoms:

**1** {<sup>y</sup> = 1 – x, –y, 2 – z; {<sup>z</sup> = 1 – x, –y, 1 – z}; **3** {<sup>y</sup> = 2 – x, –y, 2 – z; {<sup>z</sup> = 1 – x, –y, 2 – z}; **4** {<sup>y</sup> = –x, y, 0.5 – z; {<sup>z</sup> = 1 – x, 2 – y, 1 – z}.



There is a pronounced difference between the Te(1)–I(1) and Te(1)–I(2) bond lengths which are, respectively, 2.846(7) and 3.117(5) Å. This difference can be attributed to the bridging properties of the I(2) atoms. The interionic I(1)···H(Py) contacts measure, in the case of **4**, 3.049(1) Å.

### 3. Conclusion

The syntheses of the compounds **1**, **2**, **3** and **4** have shown that a relatively small modification of the size of R (substitution of the mesityl by the dmeph group) in the starting reagent (R<sub>2</sub>Te) led to new and different products, with exception of [R<sub>2</sub>Te–TeIR] (**2**) and (PyH)[R<sub>2</sub>Te] (**3**), both compounds analogue to already reported mesityl species [1,10]. In the case of compound **1**, we have recently described a similar polymer, [mes-Tel(μ-I)<sub>2</sub>(Telmes)<sub>2</sub>]<sub>n</sub> [12], the first clear molecular association between [mesTel<sub>3</sub>] and [mesTel] moieties (i.e., Te<sup>IV</sup>/Te<sup>II</sup>) ever reported in the solid state. However, besides the composition, also the structure of [mesTel(μ-I)<sub>2</sub>(Telmes)<sub>2</sub>]<sub>n</sub>, in which Te atoms attain double and triple bridge functions, is more complicated than the structure of [(R<sub>2</sub>Te){R<sub>2</sub>Te}]<sub>n</sub> (**1**), probably an stereochemical effect of the bulky mesityl groups. In both compounds the tellurium atoms attain mixed valence states in the same molecule, a very rare occurrence form of organochalcogen halides [17,18,21].

As already mentioned, we have previously reported a pseudo dimeric mesityl compound, (PyH)[mesTel<sub>2</sub>] [10], similar to the T-shaped complex described in this work, (PyH)[R<sub>2</sub>Te] (**3**). Both compounds seem to be unable to form authentic dimers, i.e., with dimeric interactions within the sum of the Te/I van der Waals radii {4.04 Å}. The secondary interactions Te(1)···I(1)<sup>y</sup> and Te(1)<sup>y</sup>···I(1) in (PyH)[mesTel<sub>2</sub>] measure 4.0712(16) Å, practically identical to the distance found in **3** {4.050(13) Å}.

Finally, the polymeric compound (PyH)<sub>n</sub>[R<sub>2</sub>Te(μ-I)TeIR]<sub>n</sub> (**4**) represents the first case described in the literature of a symmetrical, covalent iodine bridge, linking two R<sub>2</sub>TeI groups in a relatively opened angle {148.56(3)°}, to build single [R<sub>2</sub>Te(μ-I)TeIR] anions connected by two opposite pairs of Te···I secondary bonds, and stabilized by pyridinium cations. This occurrence can be associated with the differentiated stabilization of the species dmephTel in the course of the reaction.

### 4. Experimental

The syntheses and the recrystallizations of **1**, **2**, **3** and **4** were carried out under Ar atmosphere according to Scheme 1, by chemical additions to the intermediary (dmeph)TeI or by its rearrangement.

the same distance {3.963(4) Å} take place. These secondary, inter-anionic interactions, allow the one-dimensional propagation of the chains along the c-axis. The picture below reproduces the symmetric partial dimerization of I(1)–Te(1)–I(2).

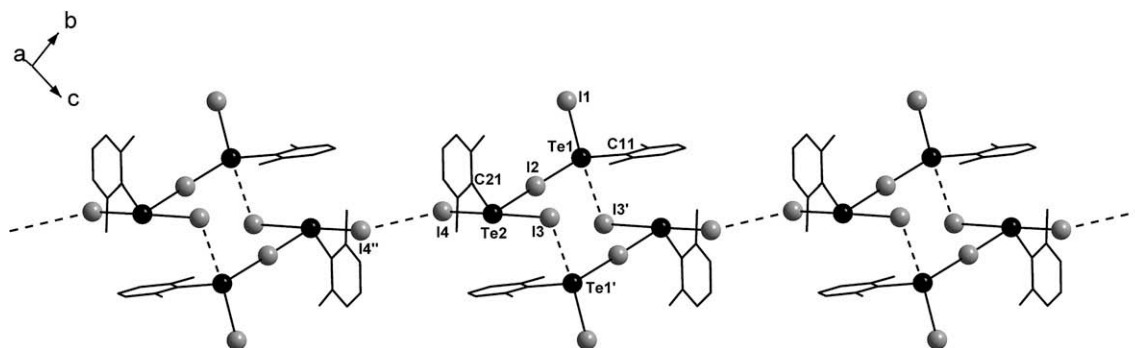


Fig. 1. Polymeric assembly of  $[(RTel)\{RTel_3\}]_n$  (**1**). Symmetry transformations used to generate equivalent atoms: (') =  $1 - x, 1 - y, 2 - z$ ; (") =  $1 - x, -y, 1 - z$ .

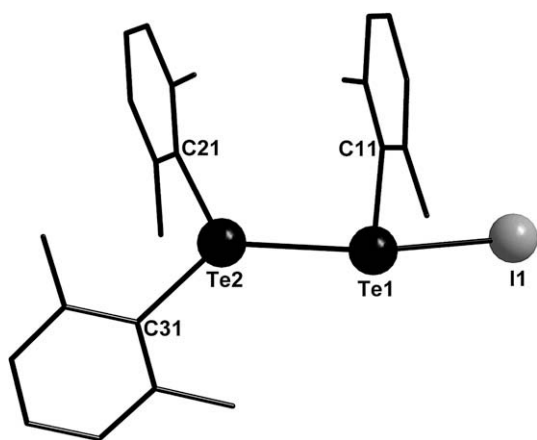


Fig. 2. Molecular structure (asymmetric unit) of  $[R_2Te-TeIR]$  (**2**).

was stirred for 5 h. The deep blue final solution was cleaned by filtration and kept under  $-18^\circ\text{C}$  for recrystallization. Yield: 88%.

*Properties:* black, crystalline solid.  $C_{16}H_{18}I_4Te_2$  (973.10). Melting point:  $81.6-82.4^\circ\text{C}$ . Anal. Calc.: C, 19.75; H, 1.86. Found: C, 20.34; H, 1.67%.

IR (KBr): 3052 [ $\nu(C-H)$ ], 2965 [ $\nu(C-H)$ ], 1628 [ $\nu(C=C)$ ], 1524 [ $\delta(C=C-H)$ ], 775, 738  $\text{cm}^{-1}$  [ $\delta_{\text{out pl.}}(C=C-H)$ ].

#### 4.2. Preparation of $[R_2Te-TeIR]$ (**2**)

To a solution of  $(dmephTe)_2$  (0.139 g, 0.3 mmol) in 5 mL of toluene, 0.076 g (0.3 mmol) of resublimed iodine was added. During the 30 min stirring the red solution turned indigo (formation of  $dmephTeI$ ). The system was warmed up at  $60^\circ\text{C}$  under stirring for 12 h. The precipitate of  $Te^0$  was removed by filtration and the solvent was extracted under vacuum. The remaining red powder was dissolved in a 1:1 mixture of dichloromethane/acetone e kept under  $-18^\circ\text{C}$  for recrystallization. Yield: 50% {very probably occurs also the formation of  $dmephTeI_3$  as subproduct}.

*Properties:* red, crystalline solid.  $C_{24}H_{27}ITe_2$  (697.56). Melting point:  $86.7-87.9^\circ\text{C}$ . Anal. Calc.: C, 41.32; H, 3.90. Found: C, 40.17; H, 4.11%.

IR (KBr): 3076 [ $\nu(C-H)$ ], 2966 [ $\nu(C-H)$ ], 1624 [ $\nu(C=C)$ ], 1519 [ $\delta(C=C-H)$ ], 762, 722  $\text{cm}^{-1}$  [ $\delta_{\text{out pl.}}(C=C-H)$ ].

#### 4.3. Preparation of $(PyH)[RTel_2]$ (**3**)

To a solution of  $(dmephTe)_2$  (0.139 g, 0.3 mmol) in 5 mL of toluene, 0.076 g (0.3 mmol) of resublimed iodine was added. During the 30 min stirring the red solution turned indigo (formation of  $dmephTeI$ ). Pyridinium iodide (0.124 g, 0.6 mmol) was then added. After 2 h stirring a red precipitate was isolated by filtration, dissolved in  $CH_2Cl_2$  and recrystallized at  $-18^\circ\text{C}$ . Yield: 97%.

*Properties:* black, hygroscopic crystalline solid.  $C_{13}H_{15}NI_2Te$  (566.66). Melting point:  $158.2-159.5^\circ\text{C}$ . Anal. Calc.: C, 27.55; H, 2.67; N, 2.47. Found: C, 28.01; H, 2.38; N, 2.25%.

IR (KBr): 3221 [ $\nu(N-H)$ ], 3070 [ $\nu(C-H)$ ], 2965 [ $\nu(C-H)$ ], 1629 [ $\nu(C=C)$ ], 1600 [ $\nu(C=N)$ ], 1531 [ $\delta(C=C-H)$ ], 1480 [ $\delta(C=N-H)$ ], 785, 729  $\text{cm}^{-1}$  [ $\delta_{\text{out pl.}}(C=C-H)$ ].

#### 4.4. Preparation of $(PyH)_n[RTel(\mu-I)TeIR]_n$ (**4**)

According to the preparation of **3**, with 0.062 g (0.3 mmol) of pyridinium iodide. Yield: 95%.

*Properties:* dark red, hygroscopic crystalline solid.  $C_{21}H_{24}NI_3Te_2$  (926.31). Melting point:  $124.3-125.7^\circ\text{C}$ . Anal. Calc.: C, 27.23; H, 2.61; N, 1.51. Found: C, 27.95; H, 2.31; N, 1.39%.

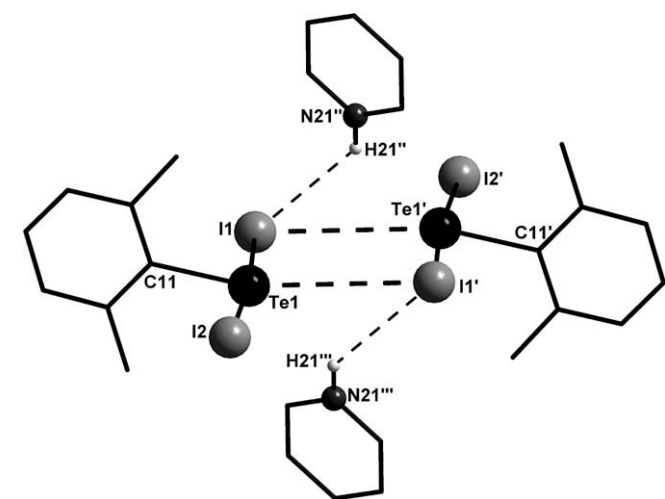
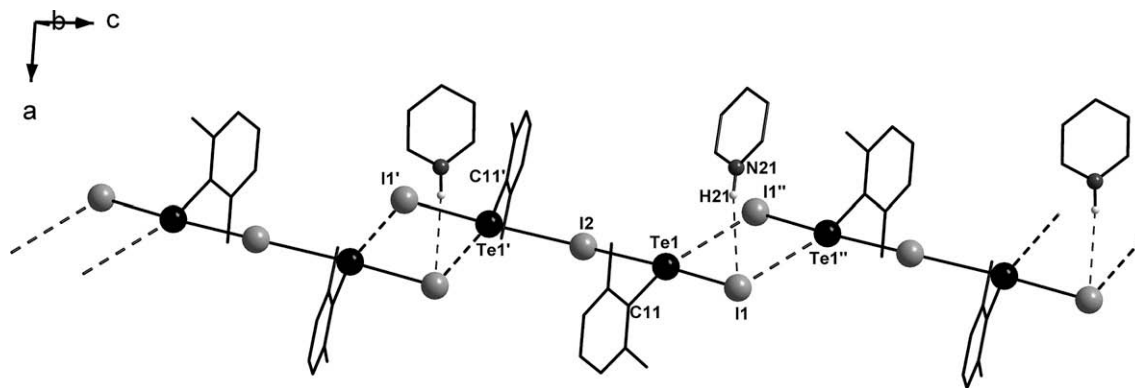


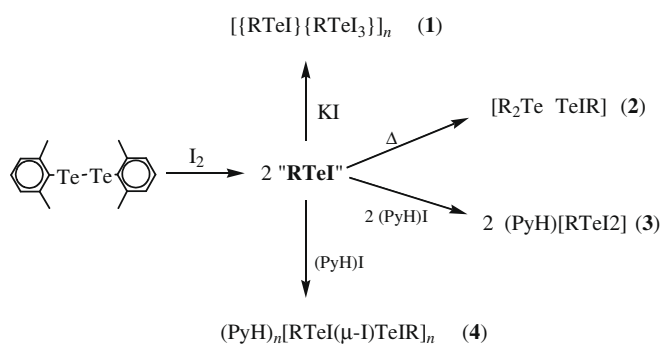
Fig. 3. Pseudo dimeric arrangement of  $(PyH)[RTel_2]$  (**3**). Symmetry transformations used to generate equivalent atoms: (') =  $2 - x, -y, 2 - z$ ; (") =  $1 - x, -y, 2 - z$ .

#### 4.1. Preparation of $[(RTel)\{RTel_3\}]_n$ (**1**)

To a solution of  $(dmephTe)_2$  (0.139 g, 0.3 mmol) in 5 mL of toluene, 0.076 g (0.3 mmol) of resublimed iodine was added. During the 30 min stirring the red solution turned indigo (formation of  $dmephTeI$ ). Thereafter 0.099 g (0.6 mmol) of KI plus 0.076 g (0.3 mmol) resublimed  $I_2$  were added, and the system



**Fig. 4.** One-dimensional assembly of  $(\text{PyH})_n[\text{RTeI}(\mu\text{-I})\text{TeIR}]_n$  (**4**) along the  $c$  axis. Symmetry transformations used to generate equivalent atoms: (') =  $1 - x, y, 0.5 - z$ ; (") =  $1 - x, 2 - y, 1 - z$ .



**Scheme 1.**

IR (KBr): 3194  $[\nu(\text{N-H})]$ , 3057  $[\nu(\text{C-H})]$ , 2965  $[\nu(\text{C-H})]$ , 1631  $[\nu(\text{C=C})]$ , 1599  $[\nu(\text{C=N})]$ , 1522  $[\delta(\text{C=C-H})]$ , 1478  $[\delta(\text{C=N-H})]$ , 775. 754  $\text{cm}^{-1}$   $[\delta_{\text{out pl.}}(\text{C=C-H})]$ .

#### 4.5. X-ray structure determinations

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo  $K\alpha$  radiation. The structures were solved by direct methods using SHELXS [22]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package [22]. 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. H atoms of the phenyl groups were positioned geometrically ( $\text{CH} = 0.93 \text{ \AA}$  for  $\text{Csp}^2$  atoms) and treated as riding on their respective C atoms, with  $U_{\text{iso}}(\text{H})$  values set at  $1.2U_{\text{eq}}\text{Csp}^2$ . Crystal data and more details of the data collections and refinements are contained in Table 1.

#### 5. Supplementary material

CCDC 710686, 710687, 710688, and 710689 contain the supplementary crystallographic data for **1**, **2**, **3**, and **4**, respectively. These

data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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