

# New versatile organytellurium(IV) halides: Synthesis and X-ray structural features of the telluronium telluroate salts $[\text{PhTe}(\text{CH}_3)_2]_2[\text{TeX}_6]$ ( $\text{X} = \text{Cl}, \text{Br}$ ) and $[\text{Ph}_3\text{Te}][\text{PhTeX}_4]$ ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )

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## Abstract

$\text{TeX}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ) react in  $\text{HCl}/\text{HBr}$  with  $[\text{Ph}(\text{CH}_3)_2\text{Te}]\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) to give  $[\text{PhTe}(\text{CH}_3)_2]_2[\text{TeCl}_6]$  (**1**) and  $[\text{PhTe}(\text{CH}_3)_2]_2[\text{TeBr}_6]$  (**2**). The reaction of  $\text{PhTeX}_3$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) in cooled methanol with  $[(\text{Ph})_3\text{Te}]\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) leads to  $[\text{Ph}_3\text{Te}][\text{PhTeCl}_4]$  (**3**),  $[\text{Ph}_3\text{Te}][\text{PhTeBr}_4]$  (**4**) and  $[\text{Ph}_3\text{Te}][\text{PhTeI}_4]$  (**5**). In the lattices of the telluronium telluroate salts **1** and **2**, octahedral  $\text{TeCl}_6$  and  $\text{TeBr}_6$  dianions are linked by telluronium cations through  $\text{Te} \cdots \text{Cl}$  and  $\text{Te} \cdots \text{Br}$  secondary bonds, attaining bidimensional (**1**) and three-dimensional (**2**) assemblies. The complexes **3**, **4** and **5** show two kinds of  $\text{Te} \cdots \text{halogen}$  secondary interactions: the anion–anion interactions, which form centrosymmetric dimers, and two identical sets of three telluronium–telluroate interactions, which accomplish the centrosymmetric fundamental moiety of the supramolecular arrays of the three compounds, with the tellurium atoms attaining distorted octahedral geometries. Also phenyl  $\text{C}–\text{H} \cdots \text{halogen}$  secondary interactions are structure forming forces in the crystalline structures of compounds **3**, **4** and **5**.

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## 1. Introduction

The possible ways of interaction of telluronium cations with telluroate anions have been a very exciting matter of search. According to du Mont and co-workers [1], “onium” and “ate” functions might interact with each other in a non-classical way leading to structural moieties related to Böttcher’s hypervalent polytellurides (tellurium-rich tellurides which are characterized without exception by directed  $\text{Te}–\text{Te}$  bonds, representing a link between the Zintl phases on the one hand, and molecular compounds on the other) [2,3]. The telluroate anions would

be nucleophiles that may attack the formally charged three-coordinated telluronium center, leading to a collapse of the ion pairs and to the formation of polytellurides. However, if the organic telluronium ion  $\text{Ph}_3\text{Te}^+$  and the cationic  $\text{TeI}_3^+$  moiety are compared [1] toward (soft) iodide nucleophilic attack, the iodide ions prefer to attack the latter one. Thus, nucleophilic ( $\text{I}^- \rightarrow \text{TeI}_3^+$ ) attacks lead to the stable brown prismatic salt  $(\text{Ph}_3\text{Te})_2[\text{TeI}_6]$  with cation–anion  $\text{Te} \cdots \text{I}$  contacts of 3.897 Å (see Section 3). Comproving the very weak electrophilic character of the telluronium cation  $\text{Ph}_3\text{Te}^+$  – and the failure of the ion pair collapsing theory – the same authors have compared the reactivity of the electrophiles  $\text{Ph}_3\text{Te}^+$  and  $\text{RTeI}$  against iodide ions. They prefer to attack the latter one, i.e. formally uncharged dicoordinated tellurium atoms with one  $\text{Te}–\text{I}$  bond are stronger electrophiles toward “soft” iodide ions than

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triorganotelluronium cations. An explanation to this apparent anomaly should be the fact that compared with  $R_3Te^+$ , the weaker Te–I bonds of  $TeI_3^+$  and  $RTeI$  are more susceptible to the  $n \rightarrow \sigma^*$  attack by nucleophiles because of their low-lying  $\sigma^*$  energy levels.

Even though the ion pairs retain their individualities in telluronium tellurolate salts, these compounds surely play an important role in the supramolecular synthesis [4,5], due to their remarkable ability to act as supermolecules-building tectons. We have already described some examples of this tendency for the anionic species  $[RTeX_4]^-$  ( $R = \text{aryl}$ ;  $X = \text{halogen}$ ) [6–9],  $[TeCl_6]^{2-}$  and  $[TeBr_6]^{2-}$ , although no one of the reported compounds have been stabilized by telluronium cations. Another interesting characteristic of  $[RTeX_4]^-$  anions is their trend to be also stabilized by  $Se^{II}$  and  $Te^{II}$  cationic complexes to form mixed valence complex salts. We have newly reported some

structures of this kind of compounds, such as  $[PhSe(tu)][PhTeI_4]$ ,  $[PhSe(tu)][PhTeBr_4]$  [10] and  $[Ph(etu)Te(\mu-I)Te(etu)Ph][PhTeI_4]$  [11]. In these cases, however, the tectonic character of the  $[RTeX_4]^-$  ion – i.e. its ability to build supermolecules through secondary interactions – is very limited, probably due to stereochemical effects associated with the size of the cation complex. Also in the mixed valence complex salts  $[p-CH_3O(C_6H_4)Te(etu)][p-CH_3O(C_6H_4)TeI_4]$  and  $[p-PhO(C_6H_4)Te(tu)][p-PhO(C_6H_4)TeI_4]$  [12] the  $Te^{IV}$  anions  $[p-CH_3O(C_6H_4)TeI_4]^-$  and  $[p-PhO(C_6H_4)TeI_4]^-$  have confirmed their tectonic character. In both compounds the anions are linked in the well-known dimeric association through reciprocal  $Te \cdots I$  secondary interactions which assure the octahedral coordination of the Te atoms. Single  $I \cdots I$  interactions in the first complex generate a polymeric chain, in the second one the dimers are linked through “double”  $I \cdots I$  bonding in a curious

Table 1  
Crystal data and structure refinement for  $[PhTe(CH_3)_2][TeX_6]$  { $X = Cl$  (1),  $Br$  (2)} and  $[Ph_3Te][PhTeX_4]$  { $X = Cl$  (3),  $Br$  (4),  $I$  (5)}

	1	2	3	4	5
Empirical formula	$C_{16}H_{22}Cl_6Te_3$	$C_{16}H_{22}Br_6Te_3$	$C_{24}H_{20}Cl_4Te_2$	$C_{24}H_{20}Br_4Te_2$	$C_{24}H_{20}I_4Te_2$
Formula weight	809.84	1076.60	705.40	883.24	1071.20
$T$ (K)	273(2)	273(2)	295(2)	295(2)	293(2)
Radiation, $\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Unit cell dimensions $a, b, c$ (Å)	$a = 16.4146(5)$	$a = 9.1355(3)$	$a = 9.0986(3)$	$a = 9.2156(2)$	$a = 11.9225(2)$
	$b = 8.5127(2)$	$b = 11.9744(4)$	$b = 11.1814(3)$	$b = 11.3434(2)$	$b = 13.7885(2)$
	$c = 18.8996(6)$	$c = 12.3706(4)$	$c = 13.4233(5)$	$c = 13.7079(3)$	$c = 18.3355(3)$
$\alpha, \beta, \gamma$ (°)	$\beta = 106.6540(10)$	$\beta = 107.421(2)$	$\alpha = 0.3530(10)$ $\beta = 7.3380(10)$ $\gamma = 78.0460(10)$	$\alpha = 1.3140(10)$ $\beta = 6.8210(10)$ $\gamma = 77.8220(10)$	$\beta = 106.7590(10)$
$V$ (Å <sup>3</sup> )	2530.11(13)	1291.17(7)	1257.83(7)	1326.78(5)	2886.21(8)
$Z, D_{\text{calc}}$ (g cm <sup>-3</sup> )	4, 2.126	2, 2.769	2, 1.862	2, 2.211	4, 2.465
Absorption coefficient (mm <sup>-1</sup> )	4.070	12.652	2.754	8.232	6.310
$F(000)$	1504	968	672	816	1920
Crystal size (mm)	$0.23 \times 0.20 \times 0.09$	$0.12 \times 0.09 \times 0.07$	$0.36 \times 0.13 \times 0.12$	$0.21 \times 0.15 \times 0.11$	$0.21 \times 0.14 \times 0.12$
$\theta$ Range (°)	1.45–30.65	2.89–30.50	1.61–30.55	2.66–30.57	1.78–31.37
Index ranges	$-23 \leq h \leq 23$ , $-10 \leq k \leq 12$ , $-27 \leq l \leq 26$	$-13 \leq h \leq 12$ , $-16 \leq k \leq 17$ , $-17 \leq l \leq 16$	$-12 \leq h \leq 12$ , $-15 \leq k \leq 15$ , $-19 \leq l \leq 19$	$-13 \leq h \leq 13$ , $-16 \leq k \leq 16$ , $-19 \leq l \leq 19$	$-17 \leq h \leq 17$ , $-20 \leq k \leq 20$ , $-26 \leq l \leq 26$
Reflections collected	32,409	15,267	34,954	43,702	41,124
Reflections unique	7758 [ $R_{\text{int}} = 0.0319$ ]	3933 [ $R_{\text{int}} = 0.0234$ ]	7678 [ $R_{\text{int}} = 0.0255$ ]	8108 [ $R_{\text{int}} = 0.0388$ ]	9494 [ $R_{\text{int}} = 0.0366$ ]
Completeness to theta maximum	99.1%	99.7%	99.6%	99.5%	99.8%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Maximum and minimum transmission	0.7108 and 0.4545	0.4713 and 0.3121	1 and 0.484359	1 and 0.357927	1 and 0.528502
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	7758/0/228	3933/0/117	7678/0/271	8108/0/272	9494/0/272
Goodness-of-fit on $F^2$	0.995	1.036	0.994	1.04	1.005
Final $R$ indices [ $I > 2 \sigma(I)$ ]	$R_1 = 0.0278$ , $wR_2 = 0.0827$	$R_1 = 0.0140$ , $wR_2 = 0.0302$	$R_1 = 0.0208$ , $wR_2 = 0.0654$	$R_1 = 0.0266$ , $wR_2 = 0.0600$	$R_1 = 0.0321$ , $wR_2 = 0.0797$
$R$ indices (all data)	$R_1 = 0.0545$ , $wR_2 = 0.1067$	$R_1 = 0.0167$ , $wR_2 = 0.0308$	$R_1 = 0.0310$ , $wR_2 = 0.0820$	$R_1 = 0.0420$ , $wR_2 = 0.0643$	$R_1 = 0.0550$ , $wR_2 = 0.1042$
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.700 and -0.961	0.549 and -0.466	0.432 and -0.759	0.955 and -1.049	1.735 and -1.413

polymeric conformation. The strong cation–anion interaction existing in  $[p\text{-PhO}(\text{C}_6\text{H}_4)\text{Te}(\text{tu})][p\text{-PhO}(\text{C}_6\text{H}_4)\text{TeCl}_4]$  suggests further its molecular association. Finally, in the compounds  $(2\text{-Br-C}_5\text{NH}_5)_2[\text{TeCl}_6]$  and  $(2\text{-Br-C}_5\text{NH}_5)_2\text{-}[\text{TeBr}_6]$  [13] the pyridinium cations are linked to the  $\text{TeX}_6$ -anions through hydrogen bondings, in  $(2\text{-Br-C}_5\text{NH}_5)_2[\text{TeBr}_6]$  there are additional weak interionic  $\text{Br} \cdots \text{Br}$  contacts; the effective interactions hold the lattices of both ionic species in supramolecular, bidimensional arrays.

In the light of the commented experiments and results we report now on the synthesis and structural characterization of the telluronium telluroate salts  $[\text{PhTe}(\text{CH}_3)_2]_2\text{-}[\text{TeX}_6]$   $\{\text{X} = \text{Cl}$  (**1**),  $\text{Br}$  (**2**) $\}$  and  $[\text{Ph}_3\text{Te}][\text{PhTeX}_4]$   $\{\text{X} = \text{Cl}$  (**3**),  $\text{Br}$  (**4**),  $\text{I}$  (**5**) $\}$ . While in **1** and **2** only  $\text{Te} \cdots \text{X}$  secondary interactions determine the profile of the supramolecular assembling, in **3**, **4** and **5** the nature of the supermolecules is determined also by  $\text{H} \cdots \text{X}$  secondary bonding. As will be demonstrated, the telluronium cations  $\text{Ph}(\text{CH}_3)_2\text{Te}^+$  and  $\text{Ph}_3\text{Te}^+$  are much more interactive toward secondary contacts with the anions  $[\text{TeX}_6]^{2-}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) and  $[\text{PhTeX}_4]^-$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) than any other before investigated cationic species.

## 2. Experimental

All reactions were conducted under nitrogen by use of standard Schlenk techniques, but recrystallizations of the complexes were carried out in air. Methanol was dried with  $\text{Mg/I}_2$ , acetonitrile with  $\text{CaH}_2$  and both were distilled prior to use. Commercially available hydrochloric and hydrobromic acids were used as received. Tellurium(IV) halides were prepared by the literature procedures [14]. The compound iodide dimethyl phenyltellurium(IV) was prepared according to Smith and co-workers [15], the analogous chloride and bromide derivatives were prepared by ion exchange with the appropriate silver halide in hot methanol. Chlorotriphenyltellurium(IV) was prepared according to Günther's procedure [16], the analogous iodide and bromide derivatives were prepared by ion exchange with the appropriate sodium halide in cooled water. Trihalophenyltellurium(IV) compounds were prepared following the literature procedures [17].

### 2.1. General procedure for the preparation of $[(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{Te}]_2[\text{TeX}_6]$ $\{\text{X} = \text{Cl}$ (**1**), $\text{Br}$ (**2**) $\}$

To a solution of 1.5 mmol of  $\text{TeX}_4$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) in 15 mL of concentrated hydrohalic acid, 3.0 mmol of solid  $[(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{Te}]\text{X}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) were added. Precipitation of the desired products occurs immediately. After stirring for 30 min the powdered products were collected by filtration, dried under vacuum and recrystallized from acetonitrile.

$[(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{Te}]_2[\text{TeCl}_6]$  (**1**). Properties: air stable, yellow crystalline substance.  $\text{C}_{16}\text{H}_{22}\text{Te}_3\text{Cl}_6$  (809.84). Yield: 87% based on  $\text{TeCl}_4$ . Melting point: 106–107 °C.

$\text{C}$ ,  $\text{H}$ -Analysis, Found:  $\text{C}$ , 23.69;  $\text{H}$ , 2.90. Calc.:  $\text{C}$ , 23.73;  $\text{H}$ , 2.74%.

$^1\text{H}$  NMR: the multiplet (a sharp “singlet” in the center of a width, very weak “duplet”) centered in 2.413 ppm evinces the  $^1\text{H}\text{-}^{125}\text{Te}$  satellite coupling, characteristic of the methyl groups.  $^2J_{\text{HTe}} = 24.501$  Hz.

$[(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{Te}]_2[\text{TeBr}_6]$  (**2**). Properties: air stable, orange-yellowish crystalline substance.  $\text{C}_{16}\text{H}_{22}\text{Te}_3\text{Br}_6$  (1076.60). Yield: 89% based on  $\text{TeBr}_4$ . Melting point: 104–105 °C.  $\text{C}$ ,  $\text{H}$ -Analysis, Found:  $\text{C}$ , 17.83;  $\text{H}$ , 2.80. Calc.:  $\text{C}$ , 17.85;  $\text{H}$ , 2.48%.

$^1\text{H}$  NMR: the multiplet with midpoint in 2.417 ppm indicates the  $^1\text{H}\text{-}^{125}\text{Te}$  satellite coupling characteristic of the methyl groups.  $^2J_{\text{HTe}} = 24.811$  Hz.

### 2.2. General procedure for the preparation of $[(\text{C}_6\text{H}_5)_3\text{Te}][(\text{C}_6\text{H}_5)\text{TeX}_4]$ $\{\text{X} = \text{Cl}$ (**3**), $\text{Br}$ (**4**), $\text{I}$ (**5**) $\}$

To a solution of 1.5 mmol of  $(\text{C}_6\text{H}_5)\text{TeX}_3$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) in 20 mL of methanol cooled to 0 °C, 1.5 mmol of  $[(\text{C}_6\text{H}_5)_3\text{Te}]\text{X}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ), dissolved in 20 mL of methanol were added dropwise. Precipitation of the desired products occurs immediately. After stirring for 30 min, the powdered products were collected by filtration and recrystallized from acetonitrile.

$[(\text{C}_6\text{H}_5)_3\text{Te}][(\text{C}_6\text{H}_5)\text{TeCl}_4]$  (**3**). Properties: air stable, colorless crystalline substance.  $\text{C}_{24}\text{H}_{20}\text{Te}_2\text{Cl}_4$  (705.40). Yield: 92% based on  $(\text{C}_6\text{H}_5)\text{TeCl}_3$ . Melting point: 190–191 °C.  $\text{C}$ ,  $\text{H}$ -Analysis: Found:  $\text{C}$ , 41.04;  $\text{H}$ , 2.83. Calc.:  $\text{C}$ , 40.86;  $\text{H}$ , 2.86%.

Table 2

Selected bond lengths (Å) and angles (°) for  $[\text{PhTe}(\text{CH}_3)_2]_2[\text{TeCl}_6]$  (**1**) and  $[\text{PhTe}(\text{CH}_3)_2]_2[\text{TeBr}_6]$  (**2**)

<b>1</b>		<b>2</b>	
<i>Bond lengths</i>		<i>Bond lengths</i>	
Te(1)–Cl(6)	2.4958(10)	Te(21)–Br(22)	2.698(19)
Te(1)–Cl(4)	2.5097(10)	Te(21)–Br(21)	2.704(18)
Te(1)–Cl(2)	2.5145(11)	Te(21)–Br(23)	2.717(18)
Te(1)–Cl(5)	2.5335(13)	Te(22)–C(27)	2.113(17)
Te(1)–Cl(3)	2.5721(11)	Te(22)–C(21)	2.113(16)
Te(1)–Cl(1)	2.6009(11)	Te(22)–C(28)	2.114(19)
<i>Bond angles</i>		Te(22) $''$ –Br(21)	3.729(1)
Cl(6)–Te(1)–Cl(4)	87.89(4)	Te(22) $''$ –Br(21)	3.719(1)
Cl(6)–Te(1)–Cl(2)	88.26(4)	<i>Bond angles</i>	
Cl(4)–Te(1)–Cl(2)	85.49(4)	Br(22) $'$ –Te(21)–Br(22)	180.000(5)
Cl(6)–Te(1)–Cl(5)	89.51(5)	Br(22)–Te(21)–Br(21) $'$	87.630(6)
Cl(4)–Te(1)–Cl(5)	90.81(4)	Br(22)–Te(21)–Br(21)	92.370(6)
Cl(2)–Te(1)–Cl(5)	175.74(5)	Br(21) $'$ –Te(21)–Br(21)	180.000(11)
Cl(6)–Te(1)–Cl(3)	88.99(4)	Br(21) $'$ –Te(21)–Br(23)	91.246(5)
Cl(4)–Te(1)–Cl(3)	174.90(4)	Br(21)–Te(21)–Br(23)	88.754(5)
Cl(2)–Te(1)–Cl(3)	90.39(4)	Br(22) $'$ –Te(21)–Br(23) $'$	90.748(6)
Cl(5)–Te(1)–Cl(3)	93.20(5)	Br(22)–Te(21)–Br(23) $'$	89.252(6)
Cl(6)–Te(1)–Cl(1)	177.82(5)	Br(23)–Te(21)–Br(23) $'$	180.000(4)
Cl(4)–Te(1)–Cl(1)	90.89(4)	C(27)–Te(22)–C(21)	96.68(7)
Cl(2)–Te(1)–Cl(1)	89.85(5)	C(27)–Te(22)–C(28)	94.77(7)
Cl(5)–Te(1)–Cl(1)	92.31(5)	C(21)–Te(22)–C(28)	96.51(7)
Cl(3)–Te(1)–Cl(1)	92.09(4)	Te(22) $''$ –Br(21)–Te(22)	118.17(1)

For **2**, symmetry transformations used to generate equivalent atoms: ( $'$ ) $-x + 2, -y, -z$ ; ( $''$ ) $-x + 1, -y, -z$ .

$[(C_6H_5)_3Te][(C_6H_5)TeBr_4]$  (**4**). Properties: air stable, orange-yellowish crystalline substance.  $C_{24}H_{20}Te_2Br_4$  (883.24). Yield: 94% based on  $(C_6H_5)TeBr_3$ . Melting point: 196–197 °C. C, H-Analysis: Found: C, 32.95; H, 2.21. Calc.: C, 32.63; H, 2.29%.

$[(C_6H_5)_3Te][(C_6H_5)TeI_4]$  (**5**). Properties: air stable, black crystalline substance.  $C_{24}H_{20}Te_2I_4$  (1071.20). Yield: 96% based on  $(C_6H_5)TeI_3$ . Melting point: 201–202 °C. C, H-Analysis: Found: C, 27.24; H, 2.06. Calc.: C, 26.91; H, 1.89%.

Table 3

Selected bond lengths (Å) and angles (°) for  $[Ph_3Te][PhTeCl_4]$  (**3**),  $[Ph_3Te][PhTeBr_4]$  (**4**) and  $[Ph_3Te][PhTeI_4]$  (**5**)

<b>3</b>		<b>4</b>		<b>5</b>	
<i>Bond lengths</i>		<i>Bond lengths</i>		<i>Bond lengths</i>	
Te(1)–Cl(1)	2.4930(7)	Br(11)–Te(1)	2.7065(3)	Te(1)–I(4)	2.8767(4)
Te(1)–Cl(4)	2.5146(7)	Br(12)–Te(1)	2.6746(3)	Te(1)–I(1)	2.9373(4)
Te(1)–Cl(2)	2.5266(7)	Br(13)–Te(1)	2.6542(4)	Te(1)–I(3)	2.9374(4)
Te(1)–Cl(3)	2.5443(7)	Br(14)–Te(1)	2.6920(3)	Te(1)–I(2)	3.0058(4)
H(12)···Cl(4)	2.743(2)	H(16)···Br(14)	2.886(2)	H(2)···I(4)	3.086(1)
H(16)···Cl(2)	2.786(2)	H(12)···Br(12)	2.826(2)	H(6)···I(2)	3.113(0)
H(216)···Cl(3)	2.863(2)	H(26)···Br(12)'	2.770(2)	Te(1)···I(3)'	3.827(0)
H(226)···Cl(4)	2.693(2)	Te(2)···Br(12)'	3.620(1)	Te(2)···I(3)	3.853(2)
Te(1)···Cl(3)'	3.615(2)	Te(2)···Br(11)'	3.662(3)	Te(2)···I(1)'	3.724(1)
Te(2)···Cl(2)'	3.657(2)	Te(2)···Br(14)	3.752(2)	Te(2)···I(2)'	3.673(1)
Te(2)···Cl(3)	3.541(3)	Te(1)···Br(11)'	3.684(2)	<i>Bond angles</i>	
Te(2)···Cl(4)	3.472(1)	<i>Bond angles</i>		I(4)–Te(1)–I(1)	89.054(12)
<i>Bond angles</i>		Br(13)–Te(1)–Br(12)	89.240(13)	I(4)–Te(1)–I(3)	90.846(11)
Cl(1)–Te(1)–Cl(4)	89.31(3)	Br(13)–Te(1)–Br(14)	89.200(13)	I(1)–Te(1)–I(3)	176.054(12)
Cl(1)–Te(1)–Cl(2)	89.44(3)	Br(12)–Te(1)–Br(14)	177.733(13)	I(4)–Te(1)–I(2)	177.223(14)
Cl(4)–Te(1)–Cl(2)	178.45(3)	Br(13)–Te(1)–Br(11)	178.596(12)	I(1)–Te(1)–I(2)	92.313(12)
Cl(1)–Te(1)–Cl(3)	177.06(2)	Br(12)–Te(1)–Br(11)	92.046(12)	I(3)–Te(1)–I(2)	87.624(11)
Cl(4)–Te(1)–Cl(3)	91.36(3)	Br(14)–Te(1)–Br(11)	89.531(12)	Te(1)–I(3)···Te(1)'	98.87(1)
Cl(2)–Te(1)–Cl(3)	89.85(3)	Te(1)–Br(11)···Te(1)'	90.78(1)	I(3)···Te(2)···I(2)'	77.72(1)
Te(1)···Cl(3)'···Te(2)'	81.61(1)	Te(2)···Br(12)'–Te(1)'	102.70(2)	I(3)···Te(2)···I(1)'	82.97(1)
Te(1)–Cl(2)···Te(2)'	96.57(2)	Te(2)···Br(11)'–Te(1)'	100.97(1)	Te(1)'···I(3)···Te(2)	70.32(1)
Te(2)'···Cl(4)'–Te(1)'	104.52(2)	Te(2)···Br(14)–Te(1)	96.11(1)	I(1)'–Te(1)'···I(3)	94.93(1)
Cl(2)···Te(2)'···Cl(4)'	80.82(2)	Te(1)···Br(11)'···Te(2)	82.52(1)	I(4)'–Te(1)'···I(3)	90.88(1)
Te(1)···Cl(3)'–Te(1)'	93.81(2)	Br(12)···Te(2)'···Br(14)'	76.97(1)	I(2)'–Te(1)'···I(3)	86.59(1)

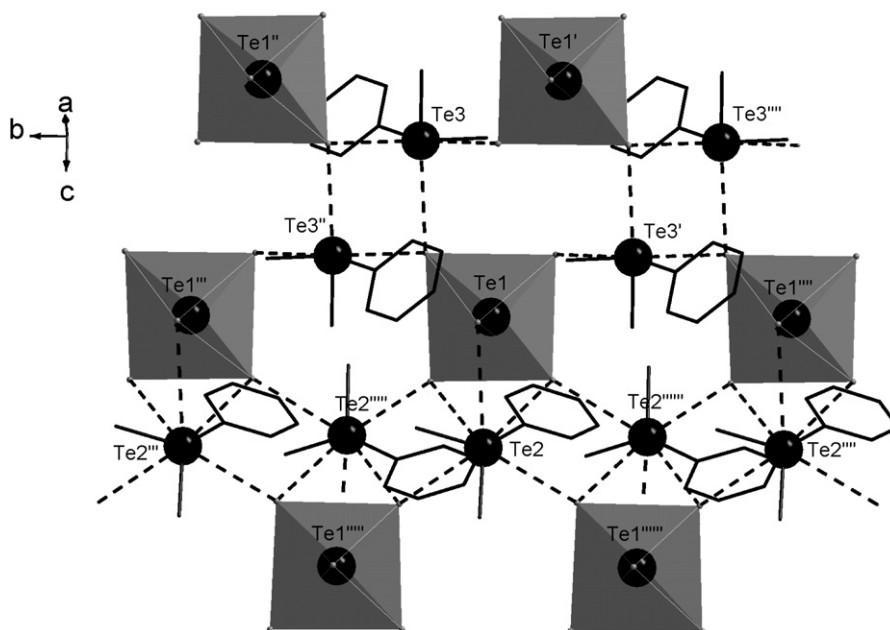
For **3**: symmetry transformations used to generate equivalent atoms (')  $-x, 1-y, 1-z$ .For **4**: symmetry transformations used to generate equivalent atoms (')  $1-x, 1-y, 1-z$ .For **5**: symmetry transformations used to generate equivalent atoms (')  $-x, 1-y, -z$ .

Fig. 1. Bidimensional arrangement of the octahedral  $[TeCl_6]^{2-}$  anions linked by telluronium bridges (dashed lines) in  $[(C_6H_5)(CH_3)_2Te]_2[TeCl_6]$  (**1**). Symmetry transformations used to generate equivalent atoms: (')  $1-x, -y, -z$ ; (")  $1-x, 1-y, -z$ ; (""')  $x, 1+y, z$ ; (""")  $x, -1+y, z$ ; (""")  $1/2-x, 1/2+y, 1/2-z$ ; (""")  $1/2-x, -1/2+y, 1/2-z$ .

### 2.3. Crystallography

X-ray data were collected on a Bruker Kappa X8 APEX II CCD diffractometer using Mo K $\alpha$  radiation (0.71073 Å). The crystallographic structures of **1**, **2**, **3**, **4** and **5** were solved by direct methods (SHELXS-97) [18]. Refinements were carried out with the SHELXL-97 package [19]. 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.

### 2.4. $^1\text{H}$ NMR

The spectral data were obtained in a Bruker DPX 400 MHz device. The samples were dissolved in DMSO- $d_6$ , in a 5 mm tube at 300 K.

## 3. Results and discussion

Crystal data and experimental conditions are given in Table 1. Selected bond distances and angles of [(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>Te]<sub>2</sub>[TeCl<sub>6</sub>] (**1**), [(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>Te]<sub>2</sub>[TeBr<sub>6</sub>] (**2**), [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Te][(C<sub>6</sub>H<sub>5</sub>)TeCl<sub>4</sub>] (**3**), [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Te][(C<sub>6</sub>H<sub>5</sub>)TeBr<sub>4</sub>] (**4**) and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Te][(C<sub>6</sub>H<sub>5</sub>)TeI<sub>4</sub>] (**5**) are resumed in Tables 2 and 3, with dashed lines representing the secondary bonds. Fig. 1 shows the bidimensional arrangement of the octahedral [TeCl<sub>6</sub>]<sup>2-</sup> anions, linked through Te···Cl secondary bonds (dashed lines), in the lattice of [(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>Te]<sub>2</sub>[TeCl<sub>6</sub>] (**1**). Fig. 2 represents the expanded asymmetric unit of [(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>Te]<sub>2</sub>[TeBr<sub>6</sub>] (**2**), including the telluronium cation and three tellurium atoms of the

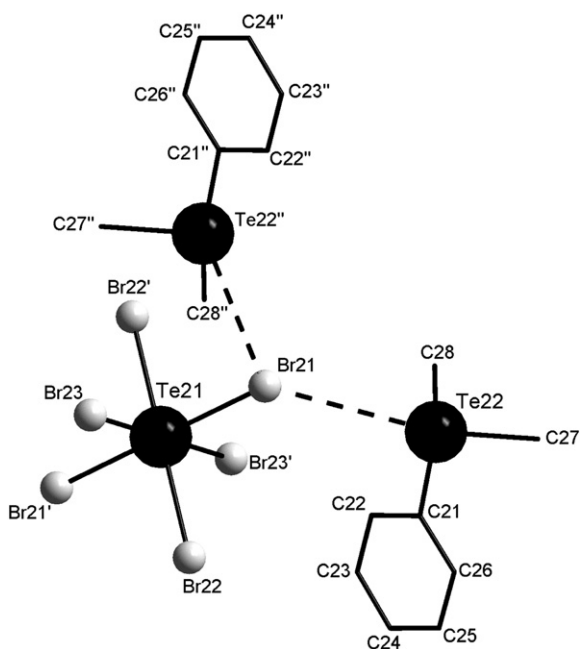


Fig. 2. Asymmetric unit (expanded) of [(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>Te]<sub>2</sub>[TeBr<sub>6</sub>] (**2**). Secondary interactions in dashed lines. Symmetry transformations used to generate equivalent atoms: (')  $2 - x, -y, -z$ ; (")  $1 - x, -y, -z$ .

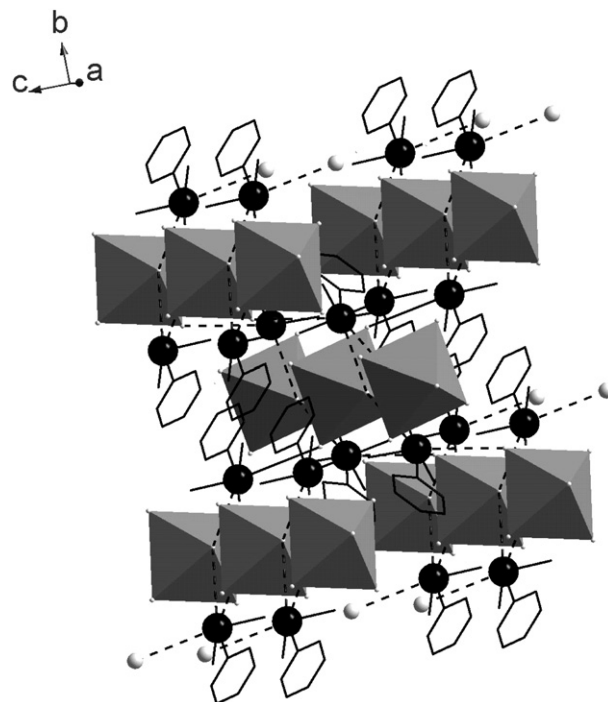


Fig. 3. Three-dimensional supramolecular assembly of [PhTe(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[TeBr<sub>6</sub>] (**2**). The octahedral TeBr<sub>6</sub> anions are linked through Te···Br contacts attained by the telluronium cations (dashed lines). The central chain of octahedra (along the *a* axis) is quadratic surrounded by four adjacent chains with a different spatial arrangement.

TeBr<sub>6</sub> moiety, generated by the symmetry transformations (')  $\{2 - x, -y, -z\}$  and (")  $\{1 - x, -y, -z\}$  on the real asymmetric unit. Fig. 3 displays the interesting three-dimensional supramolecular assembling of **2**, with the octahedral TeBr<sub>6</sub> anions linked through Te···Br contacts attained by the telluronium cations (dashed lines). Figs. 4–6 display sections of the bidimensional assemblies of complexes **3**, **4** and **5**, with secondary H–X and Te–X (X = Cl, Br, I) bonds in dashed lines.

The mean distance of the six Te–Cl bonds in complex **1** is 2.538 Å. The [TeCl<sub>6</sub>]<sup>2-</sup> anions are distorted octahedra and the Cl–Te–Cl angles in the three orthogonal axes are 175.74(5), 174.90(4) and 177.82(5)° (see Table 2). The orthogonal angles present also small deviations, which are expected for a [TeX<sub>6</sub>E]<sup>2-</sup> anion (X = halogen; E = lone electron pair) [20,21]. In **1**, the TeCl<sub>6</sub><sup>2-</sup> anions are linked by telluronium cations in a bidimensional array, forming chains of the ABAB... type, in which appear two different modes of secondary Te···Cl bonds. The mean distance of the five Te···Cl contacts between the AB chains is 3.580 Å, and that of the three Te···Cl bonding is 3.617 Å. These values are lower than the sum of the van der Waals radii of tellurium and chlorine, 3.681 Å [22], therefore we can assume that the Te···Cl interactions play an important role as structure forming forces in the lattice of **1**. In complex **2**, each two telluronium cations attain four secondary bonds toward two adjacent TeBr<sub>6</sub> octahedra. One of the two bond pairs is shown in Fig. 2, with distances

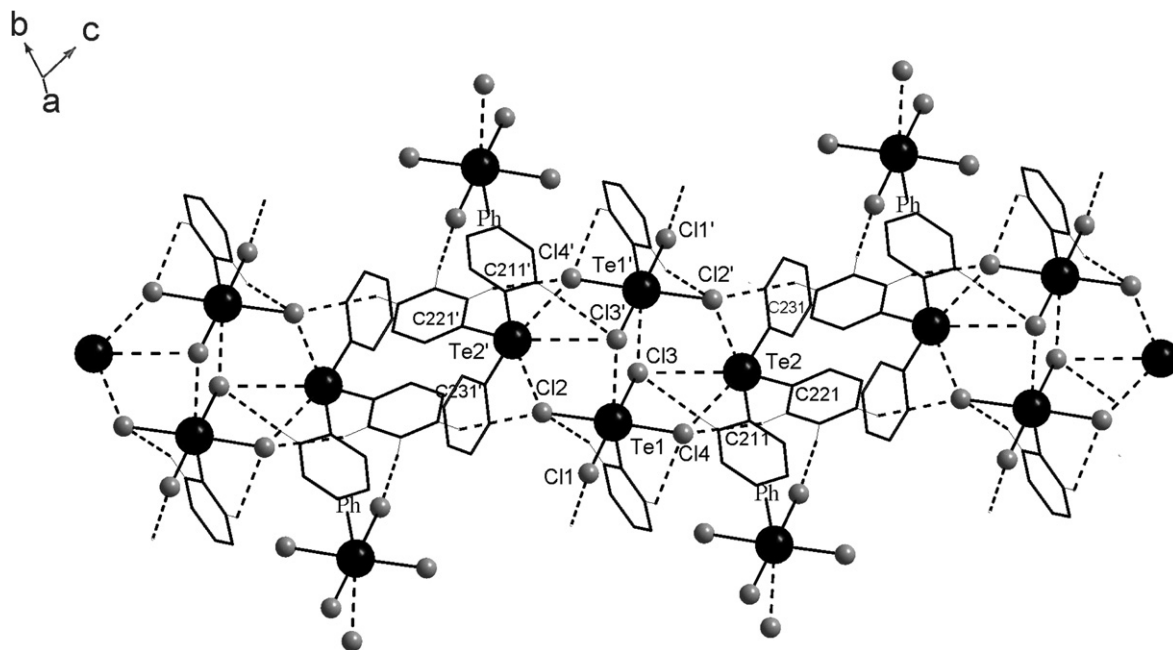


Fig. 4. Section of the bidimensional assembly of the lattice of  $[\text{Ph}_3\text{Te}][\text{PhTeCl}_4]$  (3). Secondary H–Cl and Te–Cl bonds in dashed lines. Symmetry transformations used to generate equivalent atoms: (')  $-x, 1-y, 1-z$ .

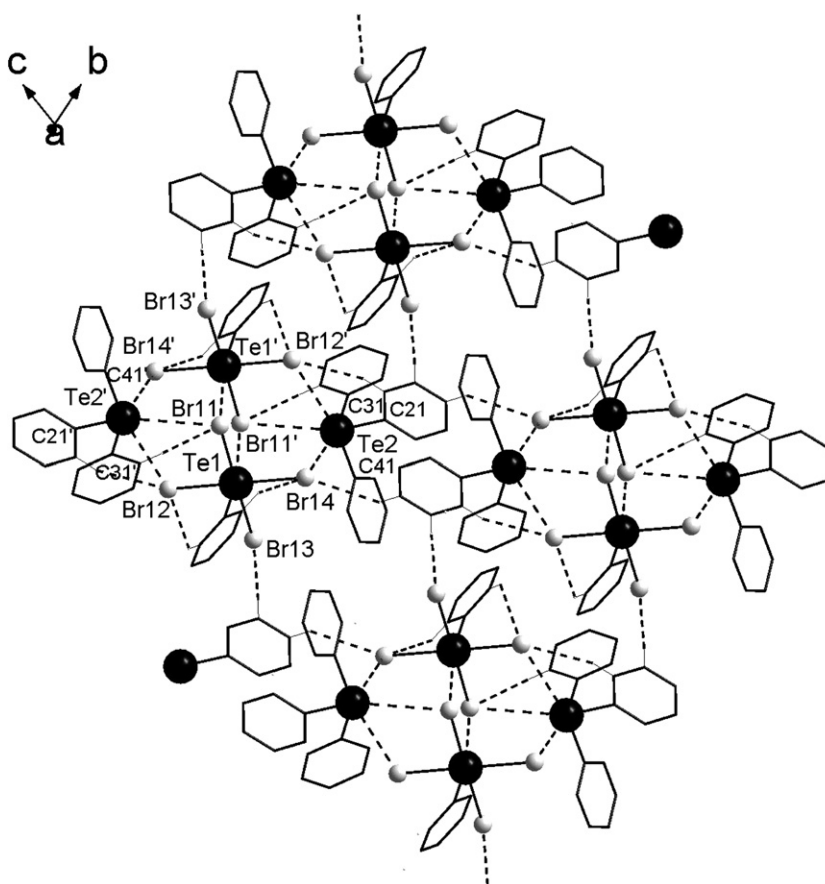


Fig. 5. Bidimensional arrangement of  $[\text{Ph}_3\text{Te}][\text{PhTeBr}_4]$  (4) along the  $a$  axis. Secondary H–Br and Te–Br bonds in dashed lines. Symmetry transformations used to generate equivalent atoms: (')  $1-x, 1-y, 1-z$ .

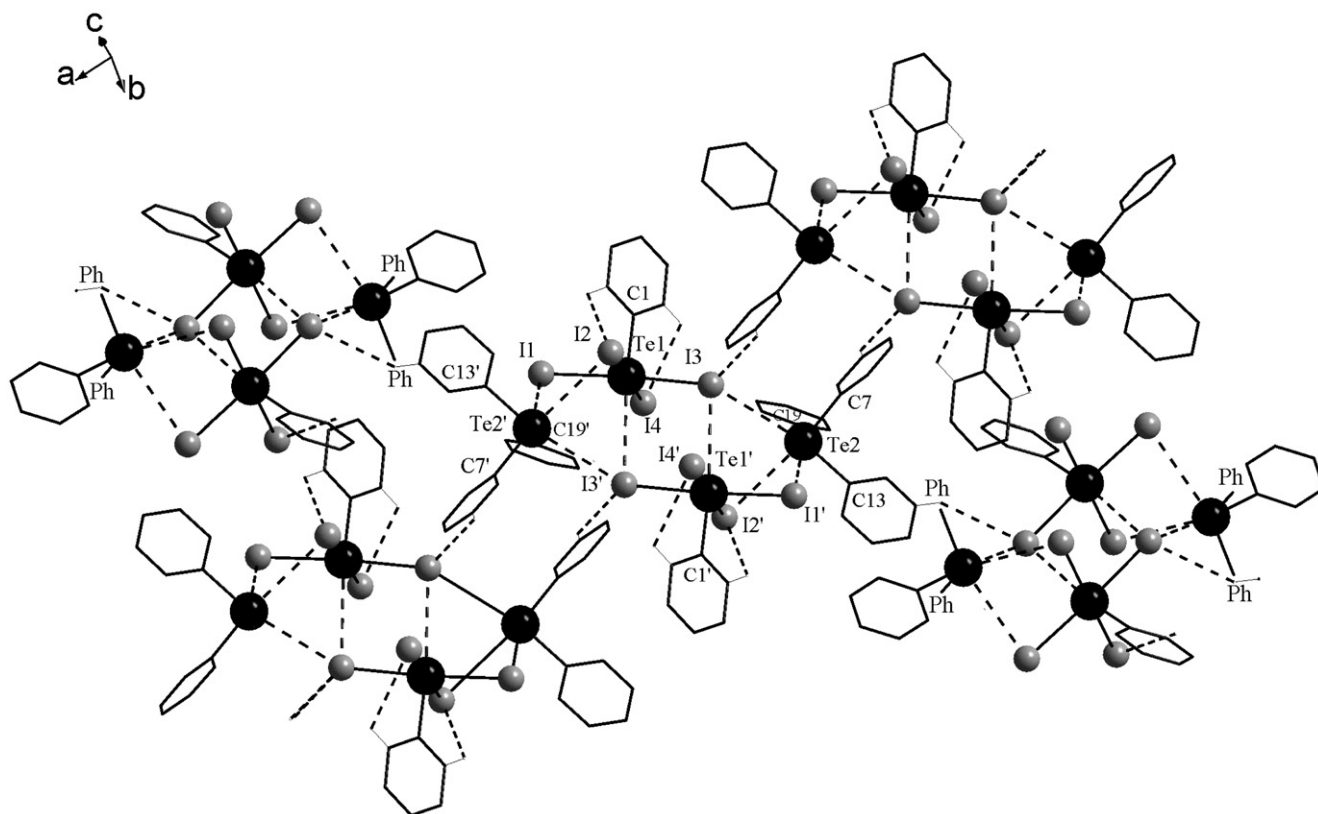
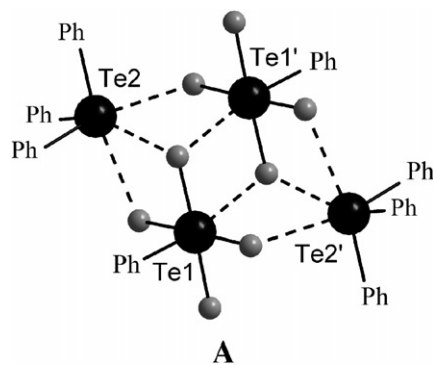


Fig. 6. Section of the lattice of  $[\text{Ph}_3\text{Te}][\text{PhTeI}_4]$  (**5**), with two layers of centrosymmetric dimers with different orientations.  $\text{H}\cdots\text{I}$  and  $\text{Te}\cdots\text{I}$  secondary bonds in dashed lines. Symmetry transformations used to generate equivalent atoms: ( $'$ )  $-x, 1-y, -z$ .

of 3.729(1)  $\{\text{Te}(22)'\cdots\text{Br}(21)\}$  and 3.719(1) Å  $\{\text{Te}(22)\cdots\text{Br}(21)\}$ . The sum of the tellurium/bromine van der Waals radii is 3.91 Å. Different from **1**, in the lattice of **2** the octahedral  $\text{TeBr}_6$  moieties are bidimensionally expanded. Along the  $a$  axis the central chain of octahedra appears quadratic and equidistant surrounded by four neighboring chains with different spatial orientations (see Fig. 3). A telluronium  $\rightarrow$  tellurolate  $\leftarrow$  telluronium sixfold (secondary) bridge model has been described by du Mont and co-workers in  $(\text{Ph}_3\text{Te})_2[\text{TeI}_6]$  [1], in which a  $\text{TeI}_6$  anionic moiety is equidistant and secondarily bonded to two  $\text{Ph}_3\text{Te}$  cations. An identical assembly was found by Oilunkaniemi and co-workers [23] for  $(\text{Ph}_3\text{Te})_2[\text{TeCl}_6]$ , in which the  $\text{Te}\cdots\text{Cl}$  secondary bonds {3.527(1) Å} between the cations and the anion expand the  $\text{TePh}_3\text{E}$  coordination of each telluronium tellurium into a distorted  $\text{TePh}_3\text{Cl}_3\text{E}$  trigonal prism (E = lone electron pair).

The complexes  $[(\text{C}_6\text{H}_5)_3\text{Te}][(\text{C}_6\text{H}_5)\text{TeCl}_4]$  (**3**),  $[(\text{C}_6\text{H}_5)_3\text{Te}][(\text{C}_6\text{H}_5)\text{TeBr}_4]$  (**4**) and  $[(\text{C}_6\text{H}_5)_3\text{Te}][(\text{C}_6\text{H}_5)\text{TeI}_4]$  (**5**) present related structures, however **3** and **4** are very similar. Both present as fundamental moiety the centrosymmetric group shown in **A**, with the tellurium atoms attaining distorted octahedral structures. In **3** and **4**, there are two kinds of  $\text{Te}\cdots\text{halogen}$  secondary interactions: the *anion–anion* interactions have distances of 3.615(2)  $\{\text{Te}(1)\cdots\text{Cl}(3)'\}$  (**3**) and 3.684(2) Å  $\{\text{Te}(1)\cdots\text{Br}(11)'\}$  (**4**), and the three *telluronium–tellurolate* interactions measure, for **3**, 3.657(2)

$\{\text{Te}(2)\cdots\text{Cl}(2)'\}$ , 3.541(3)  $\{\text{Te}(2)\cdots\text{Cl}(3)\}$  and 3.472(1) Å  $\{\text{Te}(2)\cdots\text{Cl}(4)\}$  (see Fig. 4 and Table 3). In **4**, the equivalent distances are 3.620(1)  $\{\text{Te}(2)\cdots\text{Br}(12)'\}$ , 3.662(3)  $\{\text{Te}(2)\cdots\text{Br}(11)'\}$  and 3.752(2) Å  $\{\text{Te}(2)\cdots\text{Br}(14)\}$  (see Fig. 5 and Table 3).



The complex **5** presents also the structural moiety depicted in **A**, nevertheless the octahedral configuration of the tellurium atoms is more symmetrical than **3** and **4**, since the telluronium centers are almost equidistant from the  $\text{TeI}_6$  ions. The bidimensional lattice of **5** contains, therefore, two layers of centrosymmetric “dimers” with different spatial orientations. The  $\text{Te}\cdots\text{I}$  secondary bonds have distances of 3.827(0)  $\{\text{Te}(1)\cdots\text{I}(3)'\}$ , 3.853(2)  $\{\text{Te}(2)\cdots\text{I}(3)\}$ , 3.724(1)  $\{\text{Te}(2)\cdots\text{I}(1)'\}$  and 3.673(1) Å

{Te(2)···I(2)'} (see Fig. 6 and Table 3). The sum of the tellurium/iodine van der Waals radii are 4.04 Å. Also contribute for the structural assemblage of compounds **3**, **4** and **5**, phenyl C–H···halogen secondary interactions, although they are more effective in **3** and **4**. In compound **3** the mean distance of the H···Cl contacts is 2.771 Å, in **4** the average of the H···Br secondary bonds is 2.827 Å. These values are shorter than the sum of the H/Cl and H/Br van der Waals radii, respectively, 2.95 and 3.05 Å. The H···I contacts in **5** are weaker, since their distances range from 3.086 and 3.113 (within the PhTeI<sub>4</sub><sup>−</sup> anions) to 3.172 Å (cation–anion interaction), for a sum of van der Waals radii (H/I) equal to 3.18 Å (see Fig. 6).

The strong telluronium–telluroate interactions – mainly due to Te···halogen bonding – in this chemical compounds seems to evidence that the telluronium and telluroate ions are not inert to each other, with respect to their electrophilic and nucleophilic characters. Finally, and from a supramolecular point of view, not only the tectonic ability of the anions TeX<sub>6</sub><sup>2−</sup> and RTeX<sub>4</sub><sup>−</sup> should be considered. It must be recognized that telluronium cations are also able to act as “building-blocks” in many ways, certainly with a trend more remarkable than they were expected to be.

#### Appendix A. Supplementary material

CCDC 637179, 637180, 637181, 637182 and 637183 contains the supplementary crystallographic data for **1**, **2**, **3**, **4**, and **5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.03.037](https://doi.org/10.1016/j.jorganchem.2007.03.037).

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