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Synthesis and structure of new aryltellurenyl halides derived from $(dmpTe)_2$ (dmp = 2,6-dimethoxyphenyl)

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ABSTRACT

[RTeTeR] (R = dmp = 2,6-dimethoxyphenyl) (**1**) reacts with bromine to give $[RTeTe(Br)_2R]$ (**2**) and $[RTeBr_3]$ (**3**), and with $SOCl_2$ to yield $[RTeTe(Cl)_2R]$ (**5**) and $[RTeCl_3]$ (**6**). The recrystallization of compound **3** in acetone produces $[RTeBr_2(CH_2{-}C(O){-}CH_3)]$ (**4**). The hydrolysis of **2** in aqueous ammonia and methanol containing media affords the methoxy/oxo-derivative $[RTe(\mu\text{-}O)(OCH_3)]_2$ (**7**). All the title compounds were obtained with good yields, and strong $Te\cdots O_{(methoxy)}$, as well as Te···X (X = Br, Cl) secondary interactions, support the distorted octahedral configurations shown mostly in the polymeric compounds **3**, **4**, **5** and **6**. Complexes **2** and **5** close the series of compounds with the structure $[RTeTe(X)_2R]$ (X = Cl, Br, I), started earlier with $[RTeTe(I)_2R]$.

1. Introduction

The reactions of diarylditellurides $(RTe)_2$ 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 [3–5]. 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 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. 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. After working also with PhTeI (Ph = phenyl), mesTeI (mes = 2,4,6-trimethylphenyl) and (dmeph)TeI (dmeph = 2,6-dimetylphenyl) as part of our research on the effects of the ligand R on the stabilization and structure of aryltellurenyl iodides, we have recently described the intermediary $[tmpTeI]_2$ (tmp = 2,3,5,6-tetramethylphenyl), as well as seven new iodide complexes derived from it [8]. 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. It is well known that the chemistry of organyltellurenyl iodides cannot be carefulness generalized to the lighter halogens chlorine and bromine (van der Waals radii: 1.75 and 1.85 Å, respectively) [9]. The smaller reactivity of iodine seems to be equalized by its bulk (1.98 Å) and, consequently, by its tendency to achieve complexes structurally unique, also regarding secondary I···I and I···H interactions. These effects and trends have not been noticeable in organyltellurenyl bromides and chlorides. Therefore, attempts to reproduce organyltellurenyl iodides compounds or reactions with bromine and chlorine can be, in most cases, a very frustrating and disappointing experience. Moreover, some unexpected results may prove to be quite rewarding, as we shall see below. We report the synthesis and the structural characterization of the start complex $(RTe)_2$ (R = dmp = 2,6-dimethoxyphenyl) (**1**), and of its derivatives $[RTeTe(Br)_2R]$ (**2**), $[dmpTeBr_3]$ (**3**), $[dmpTeBr_2(CH_2{-}C(O){-}CH_3)]$ (**4**), $[RTeTe(Cl)_2R]$ (**5**), $[dmpTeCl_3]$ (**6**) and $[dmpTe(\mu\text{-}O)(OCH_3)]_2$ (**7**). Compounds **2** and **5** reproduce the same result obtained with I_2 [6],

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where the methoxy groups of the intermediary RTeI (R = 2,6-dimethoxiphenyl) are also able to stabilize tellurium iodides in mixed-valent, unusual compositions.

2. Experimental

All manipulations were conducted under dried nitrogen and with anhydrous solvents by use of standard Schlenk techniques. The synthetic procedures for all complexes are resumed in the Scheme 1.

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

6.02 g (22.8 mmol) of 1-iodine-2,6-dimethoxybenzene, 2.91 g (22.8 mmol) of tellurium and 0.32 g (45.6 mmol) of lithium powder were dissolved in 100 mL of tetrahydrofuran (THF). The mixture was stirred until complete lithium dissolution, ca. 18 h. Thereafter the reaction vessel was opened to the air, and 5 mL of a dilute aqueous solution of ammonium chloride was added slowly. The product was extracted with diethyl ether and the solvent was evaporated. Recrystallization of the remained red solid from a 3:1 mixture of diethyl ether/CH_2Cl_2 yielded pure crystals of **1**. Yield: 85%. *Properties*: red, crystalline solid. $C_{16}H_{18}O_4Te_2$ (529.50). Melting point: 131.7–132.9 °C. Anal. Calc.: C, 36.29; H, 3.43. Found: C, 36.27; H, 3.44%. IR (KBr): 3008.6 [ν(C–H)$_{Ar}$], 2932.2 [ν_{as}(C–H)$_{Me}$], 2831.2 [ν_s(C–H)$_{Me}$], 1587.5 [ν(C=C)], 1472.9 [δ_s(C=C–H)], 1255.3 [ν_{as}(C–O)], 1105.5 [δ_{as}(C–O–C)], 766.8, 731.2 [$\delta_{out\ pl}$(C–C–H)].

2.2. Preparation of [RTeTe(Br)$_2$R] (**2**)

To 5 mL of a solution of 0.212 g (0.4 mmol) of **1** in CH_2Cl_2, 0.021 mL (0.4 mmol) of bromine was added. After 2 h stirring the mixture was filtered. Crystals of **2** were obtained from the solution cooled at −18 °C. Yield: 95% based on [dmpTe]$_2$. *Properties*: red, crystalline substance. $C_{16}H_{18}Br_2O_4Te_2$ (689.32). Melting point: 143.5–145.1 °C. Anal. Calc.: C, 27.88; H, 2.63. Found: C, 27.79; H, 2.65%. IR (KBr): 3003.2 [ν(C–H)$_{Ar}$], 2931.1 [ν_{as}(C–H)$_{Me}$], 2825.2 [ν_s(C–H)$_{Me}$], 1587.0 [ν(C=C)], 1472.0 [δ_s(C=C–H)], 1255.0 [ν_{as}(C–O)], 1104.6 [δ_{as}(C–O–C)], 766.5, 740.8 [$\delta_{out\ pl}$(C=C–H)].

2.3. Preparation of [dmpTeBr$_3$] (**3**)

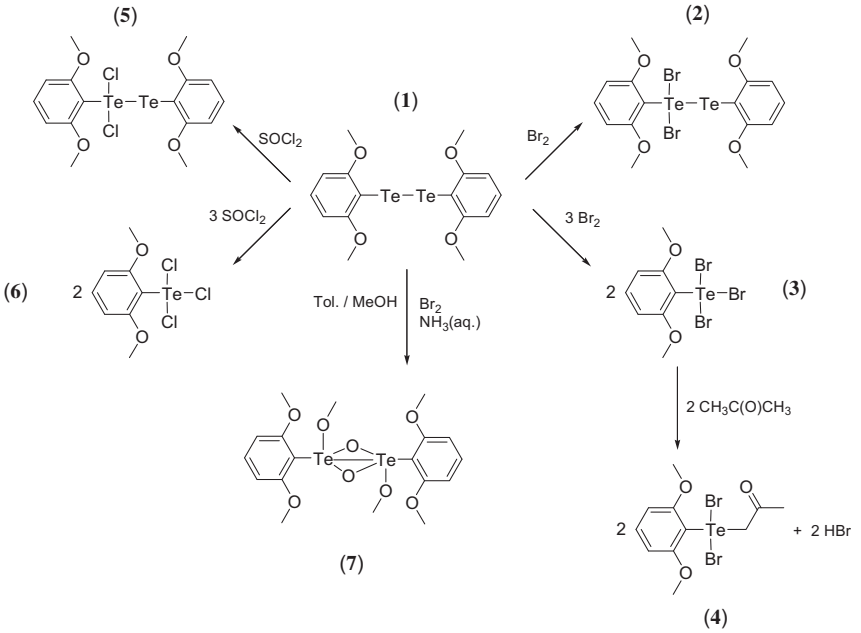
To 5 mL of a solution of 0.212 g (0.4 mmol) of **1** in CH_2Cl_2, 0.063 mL (1.2 mmol) of bromine was added. After 1 h stirring the red mixture turned colorless and was filtered. Crystals of **3** were obtained from the solution cooled at −18 °C. Yield: 90% based on [dmpTe]$_2$. *Properties*: yellow, crystalline solid. $C_8H_9Br_{2.50}O_2Te$ (464.53). Melting point: 114.0–115.2 °C. Anal. Calc.: C, 20.69; H, 1.95. Found: C, 20.73; H, 1.91%. IR (KBr): 3004.7 [ν(C–H)$_{Ar}$], 2931.3 [ν_{as}(C–H)$_{Me}$], 2828.4 [ν_s(C–H)$_{Me}$], 1586.8 [ν(C=C)], 1472.5 [δ_s(C=C–H)], 1256.2 [ν_{as}(C–O)], 1102.5 [δ_{as}(C–O–C)], 766.3, 739.6 [$\delta_{out\ pl}$(C=C–H)].

2.4. Preparation of [dmpTeBr$_2$(CH$_2$–C(O)–CH$_3$)] (**4**)

Compound **4** was obtained by dissolution of [dmpTeBr$_3$] (**3**) in acetone and further recrystallization. Yield: 86% based on **3**. *Properties*: light yellow crystalline substance. $C_{11}H_{14}Br_2O_3Te$ (481.64). Melting point: 193.4–194.7 °C. Anal. Calc. C, 27.43; H, 2.93. Found: C, 27.11; H, 2.88%. IR (KBr): 3004.3 [ν(C–H)$_{Ar}$], 2931.2 [ν_{as}(C–H)$_{Me}$], 2836.2 [ν_s(C–H)$_{Me}$], 1585.4, [ν(C=O)], 1683.1, [ν(C=C)], 1471.9 [δ_s(C=C–H)], 1257.2 [ν_{as}(C–O)], 1106.5 [δ_{as}(C–O–C)], 765.8, 730.3 [$\delta_{out\ pl}$(C–C–H)].

2.5. Preparation of [RTeTe(Cl)$_2$R] (**5**)

To 5 mL of a solution of 0.212 g (0.4 mmol) of **1** in CH_2Cl_2, 0.030 mL (0.4 mmol) of $SOCl_2$ was added. After 1 h stirring the mixture was filtered. Cooling of the solution at −18 °C led to the formation of crystals of **5**. Yield: 96% based on [dmpTe]$_2$. *Properties*: light red crystalline solid. $C_{16}H_{18}Cl_2O_4Te_2$ (600.40). Melting point: 142.3–143.9 °C. Anal. Calc.: C, 30.01; H, 3.02. Found: C, 29.91; H, 3.12%. IR (KBr): 3004.3 [ν(C–H)$_{Ar}$], 2931.4 [ν_{as}(C–H)$_{Me}$], 2826.5 [ν_s(C–H)$_{Me}$], 1585.9 [ν(C=C)], 1471.5 [δ_s(C=C–H)], 1256.6 [ν_{as}(C–O)], 1103.5 [δ_{as}(C–O–C)], 766.5, 739.0 [$\delta_{out\ pl}$(C=C–H)].



Scheme 1. Reactions of (RTe)$_2$ (R = 2,6-dimethoxiphenyl) and of [RTeBr$_3$] discussed in this work.

2.6. Preparation of [dmpTeCl$_3$] (**6**)

To 5 mL of a solution of 0.212 g (0.4 mmol) of **1** in CH_2Cl_2, 0.090 mL (1.2 mmol) of $SOCl_2$ was added. After ½ h stirring the red mixture turned colorless and was filtered. Yellow crystals of **6** were formed by cooling the filtrate to −18 °C. Yield: 82% based on [dmpTe]$_2$. *Properties*: light yellow crystalline substance. $C_8H_9Cl_3O_2Te$ (371.10). Melting point: 109.2–110.5 °C. Anal. Calc.: C, 25.89; H, 2.44. Found: C, 25.38; H, 2.51%. IR (KBr): 3003.3 [ν(C–H)$_{Ar}$], 2931.6 [ν_{as}(C–H)$_{Me}$], 2826.2 [ν_s(C–H)$_{Me}$], 1587.3 [ν(C=C)], 1471.9 [δ_s(C=C–H)], 1255.2 [ν_{as}(C–O)], 1103.6 [δ_{as}(C–O–C)], 767.2, 741.1 [$\delta_{out\ pl}$(C=C–H)].

2.7. Preparation of [dmpTe(μ-O)(OCH$_3$)]$_2$ (**7**)

In 10 mL of a 1:1 mixture of methanol/toluene, 0.212 g (0.4 mmol) of **1** were dissolved, followed by the addition of 0.021 mL (0.04 mmol) of Br_2 (the substitution of Br_2 by I_2 does not change the final product). After ½ h stirring the addition of a few milliliters of dilute aqueous ammonia to the red brown mixture turned it colorless. After filtration and cooling of the solution to −18 °C, crystals of **7** were formed. Yield: 72% based on [dmpTe]$_2$. *Properties*: colorless, crystalline substance. $C_{18}H_{24}O_8Te_2$ (623.58). Melting point: 179.5–180.7 °C. Anal. Calc.: C, 34.67; H, 3.88. Found: C, 34.09; H, 3.95%. IR (KBr): 3005.1 [ν(C–H)$_{Ar}$], 2930.2 [ν_{as}(C–H)$_{Me}$], 2826.1 [ν_s(C–H)$_{Me}$], 1588.4 [ν(C=C)], 1471.1 [δ_s(C=C–H)], 1256.4 [ν_{as}(C–O)], 1103.5 [δ_{as}(C–O–C)], 765.4, 739.2 [$\delta_{out\ pl}$(C=C–H)].

2.8. X-ray structure determinations

Data were collected with a Bruker APEX II CCD area-detector diffractometer. The structure was solved by direct methods using SHELXS [10]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package [10]. 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.

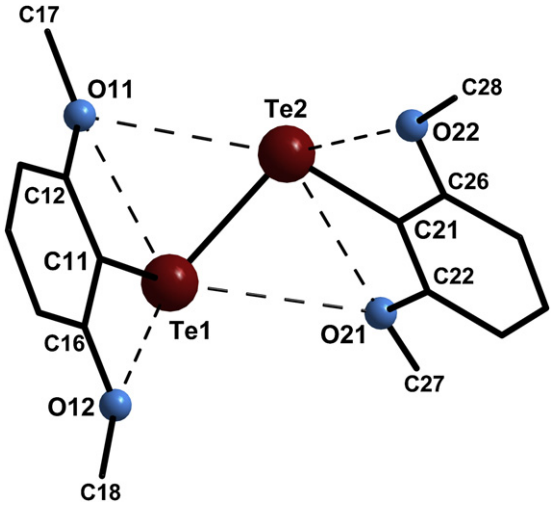


Fig. 1. Molecular structure of [dmpTe]$_2$ (**1**). Hydrogen atoms have been omitted for clarity. Dashed lines represent secondary interactions. Selected bond lengths [Å] and angles [deg]: Te1–C11 2.130(5), Te1–Te2 2.7055(5), Te2–C21 2.120(6), Te1···O11 3.1638 (2), Te1···O12 3.0938(2), Te1···O21 3.5022(2), Te2···O11 3.4251(2), Te2···O21 3.1363(2), Te2···O22 3.0751(1), C22–O21 1.352(7), C26–O22 1.362(7), C16–O12 1.367(6), C12–O11 1.355(6); C11–Te1–Te2 99.90(14), C21–Te2–Te1 101.44(15), C26–C21–C22 120.0(6), C26–C21–Te2 119.4(4), C22–C21–Te2 120.6(4).

3. Results and discussion

Crystal data and experimental conditions for [RTe]$_2$ (R = dmp = 2,6-dimethoxyphenyl) (**1**), [RTeTe(Br)$_2$R] (**2**), [dmpTeBr$_3$] (**3**), [dmpTeBr$_2$(CH$_2$–C(O)–CH$_3$)] (**4**), [RTeTe(Cl)$_2$R] (**5**), [dmpTeCl$_3$] (**6**) and [dmpTe(μ-O)(OCH$_3$)]$_2$ (**7**) are given in Table 1. Figs. 1–7 show the molecular structures/polymeric associations of the title compounds. All complexes obtained in this work were achieved starting from compound **1**, [RTeTeR], with initial cleavage of the Te–Te bond and formation of the intermediary dmpTeX (X = Cl, Br). 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 [11,12]. It is also known that these species present a relative stability in solution, although in the literature few reports describe their characteristics in

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	$C_{16}H_{18}O_4Te_2$	$C_{16}H_{18}Br_2O_4Te_2$	$C_{16}H_{18}Br_5O_4Te_2$	$C_{11}H_{14}Br_2O_3Te$	$C_{16}H_{18}Cl_2O_4Te_2$	$C_8H_9Cl_3O_2Te$	$C_{18}H_{24}O_8Te_2$
Fw	529.50	689.32	929.06	481.64	600.40	371.10	623.58
T (K)	296(2)	293(2)	293(2)	293(2) K	293(2)	293(2)	293(2)
Crystal system	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	C_2/c	$P2_1/c$	*Pbca*	$P2_1/c$
a/Å	8.3428(5)	7.9624(3)	8.1971(9)	26.288(3)	13.2640(2)	8.0339(3)	10.6486(7)
b/Å	10.0205(6)	10.2422(4)	14.1122(16)	12.1942(17)	7.50700(10)	13.8130(6)	7.1299(4)
c/Å	10.8135(6)	13.4832(5)	21.281(2)	9.2198(10)	20.3157(3)	20.8987(9)	13.9056(8)
α/deg	98.480(3)	95.939(2)	90	90	90	90	90
β/deg	96.874(4)	101.336(2)	90	90.858(7)	104.7490(10)	90	107.8210(10)
γ/deg	96.394(4)	109.883(2)	90	90	90	90	90
V/Å^3	879.99(9)	996.42(7)	2461.8(5)	2955.2(6)	1956.24(5)	2319.18(17)	1005.10(10)
Z	2	2	4	8	4	8	4
ρ_{calcd}(g cm^{-3})	1.998	2.298	2.507	2.165	2.039	2.126	2.060
μ (Mo Kα)(mm^{-1})	3.328	6.954	10.504	7.415	3.272	3.228	2.945
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
F (000)	500	640	1700	1808	1136	1408	600
Collected reflns.	18059	18013	20117	13571	20371	11599	5196
Unique reflns.	4996	4777	2520	3620	5655	2729	2739
GOF (F^2)	0.944	1.031	1.233	0.994	1.028	0.969	1.031
R_1[a]	0.0436	0.0175	0.0508	0.0375	0.0187	0.0377	0.0271
wR_2[b]	0.0933	0.0413	0.1581	0.0886	0.0374	0.0716	0.0652

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

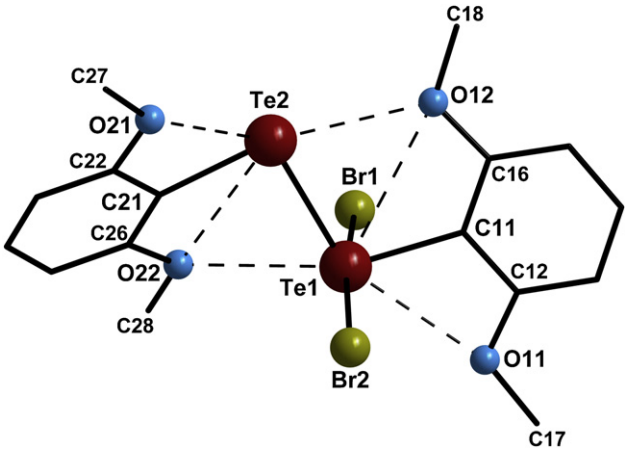


Fig. 2. Molecular structure of [RTeTeBr$_2$R] (**2**). Hydrogen atoms have been omitted for clarity. Dashed lines represent secondary interactions. Selected bond lengths [Å] and angles [deg]: Te1–Br1 2.6878(3), Te1–Br2 2.7424(3), Te2–Te1 2.7401(2), Te1–C11 2.103(2), Te2–C21 2.103(2), C26–O22 1.368(3), C22–O21 1.363(3), C18–O12 1.433(3), O11–C12 1.362(3), O11–C17 1.437(3), O12–C16 1.355(3), O22–C28 1.430(3), O21–C27 1.425(3), Te1···O11 2.880(2), Te1···O22 2.937(2), Te2···O12 2.854(0), Te2···O21 2.929 (3); C11–Te1–Br1 88.82(6), C11–Te1–Te2 99.41(6), Br1–Te1–Te2 97.548(8), C11–Te1–Br2 89.32(6), C21–Te2–Te1 95.70(6), Br1–Te1–Br2 169.747(9), Te2–Te1–Br2 92.703(8),O22–C26–C21 115.44(19), O21–C22–C21 114.5(2).

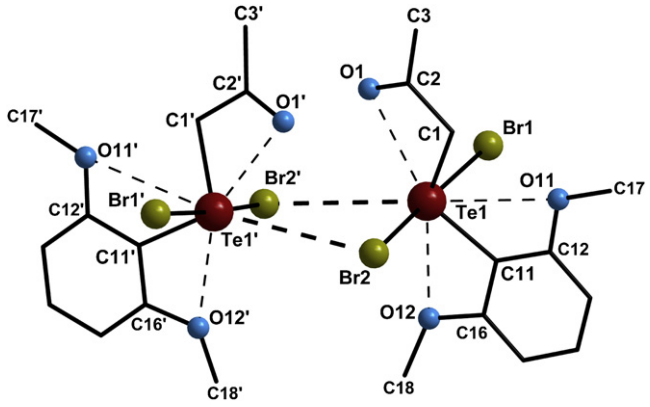


Fig. 4. Pseudo-dimeric assembling of [dmpTeBr$_2$(CH$_2$–C(O)–CH$_3$)] (**4**), Hydrogen atoms have been omitted for clarity. Dashed lines represent secondary interactions. Symmetry code: (′) = 1 − *x*, *y*, 1.5 − *z*. Selected bond lengths [Å] and angles [deg]: Te1–Br1 2.7202(6), Te1–Br2 2.6468(6), Te1–C11 2.101(4), Te1–C1 2.135(5), C1–C2 1.510(6), O1–C2 1.212(5), C2–C3 1.474(7), O12–C16 1.368(5), O12–C18 1.431(6), O11–C12 1.350(6), O11–C17 1.427(5), Te1···O1 2.8990(3), Te1···O11 3.3459(3), Te1···O12 2.8224(4), Te1··· Br2′ 3.8086(4); C11–Te1–C1 101.94(17), C11–Te1–Br2 88.31(11), C1–Te1–Br2 89.42(13),C11–Te1–Br1 89.50(11), C1–Te1–Br1 87.07(14), Br2–Te1–Br1 175.393(18), C2–C1–Te1 106.5(3), O1–C2–C3 123.5(4), O1–C2–C1 119.9 (4), C3–C2–C1 116.6(4), C11–Te1··· Br2′ 138.68(0), C1–Te1···O12 153.42(1).

the solid state. As examples of the influence of the size of the substituent on the stabilization of such intermediary, we have reported the tetrameric structure of PhTeI [13], while the use of a very bulky R allowed the isolation of Mes*TeI (Mes* = 2,4,6-tri-*tert*-butylphenyl), which exhibits discrete molecules, although in the solid state also presents Te···I (3.727) and I···I (3.818 Å) intermolecular contacts [14]. As expected, in the course of the reactions described in this work, the stabilization of dmpTeX (X = Cl, Br) has occurred through different routes, driven by the substituent dmp, the stoichiometry and the reactivity of Cl and Br. With exception of the starting reagent **1**, in all the title complexes the tellurium centers interact in a relatively strong manner with the oxygen atoms of the two methoxyphenyl groups. Wada et al. [15,16] have discussed this kind of interactions, including the dependence of the rotational barrier of the Ar-group. In (RTe)$_2$ (**1**) the Te···O distances are 3.1638(2) (Te1···O11), 3.0938(2) (Te1···O12) and 3.5022(2) Å (Te1···O21). The sum of the Te/O van der Waals radii is 3.58 Å [9], and in the mixed-valent {Te^{II}/Te^{IV}} complex [RTeTe(Br)$_2$R] (**2**) these interactions are comparatively stronger, measuring 2.880(2) (Te1···O11), 2.854(0) (Te2···O12) and 2.937(2) Å (Te1···O22) (see Fig. 2). Complex **2** represents the first compound of this series which reproduces partially the organyltellurenyl iodide chemistry: the mixed-valent complex [RTeTe(I)$_2$R] (R = dmp) was first obtained by stirring (dmpTe)$_2$ with iodine (1:1) in CH_2Cl_2 for 2 h at −10 °C with further crystallization at −18 °C [6]. The Te···O$_{(methoxy)}$ contacts present in the title compounds are also able to support a given structure, as in the case of complex **3**, [dmpTeBr$_3$]: Fig. 3 shows that the pseudo octahedral configuration of **3** is only possible because of the shortening of the Te1···O11 contact (2.812(0)), simultaneously with the elongation of the (in the same plane lying) Te1···O12 distance (3.2983(3) Å). This effort, to keep O11 in the same plane that Br1, Br2 and Br3 in as much as possible, is also visible in the distortion of the

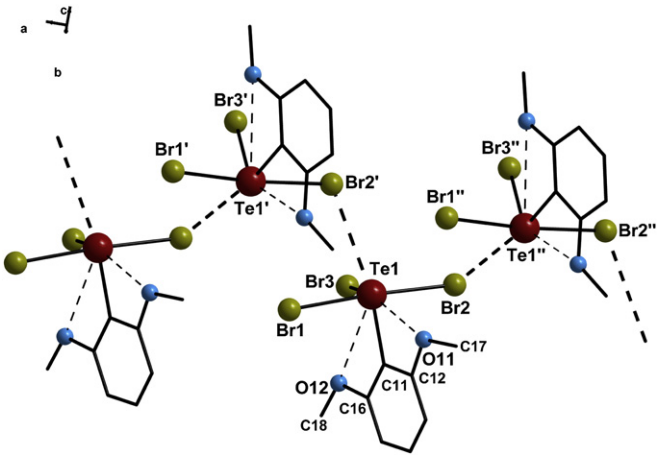


Fig. 3. Polymeric assembling of [dmpTeBr$_3$]$_n$ (**3**). Hydrogen atoms have been omitted for clarity. Dashed lines represent secondary interactions. Symmetry code: (′) 0.5 + *x*, *y*, 1.5 − *z*; (″) = −0.5 + *x*, *y*, 1.5 − *z*. Selected bond lengths [Å] and angles [deg]: Br2–Te1 2.6896(13), Br1–Te1 2.6322(13), Br3–Te1 2.429(2), C11–Te1 2.109(9), O11–C12 1.362 (11), O12–C16 1.380(13), Te1···O11 2.812(0), Te1···O12 3.2983(3), Te1··· Br2′ 3.473(0), Br2··· Te1″ 3.473(0); Br3–Te1–Br1 94.20(7), Br3–Te1–Br2 83.09(6), Br1–Te1–Br2 175.18(4), C11–Te1–Br1 88.3(3), C11–Te1–Br2 88.3(3), C11–Te1–Br3 100.9(3), C16–C11–Te1 128.1(8), C12–C11–Te1 111.0(7), C12–O11–C17 119.2(8), C16–O12–C18 118.3(8), C11–Te1··· Br2′ 169.53(0), Br3–Te1···O11 149.95(0).

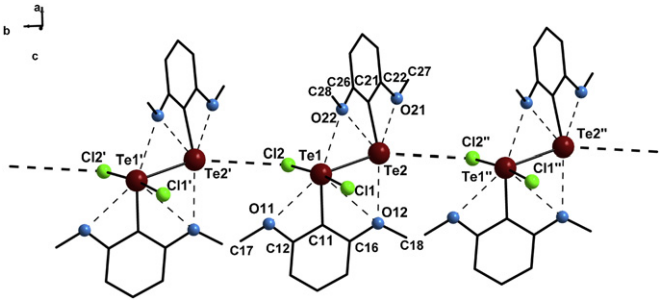


Fig. 5. Polymeric association of the molecules [RTeTeCl$_2$R] (**5**). Dashed lines represent secondary bonds. Hydrogen atoms have been omitted for clarity. Symmetry code: (′) = *x*, 1 + *y*, *z*; (″) = *x*, −1 + *y*, *z*. Selected bond lengths [Å] and angles [deg]: Te1–C11 2.1064(17), Te1–Cl1 2.4914(5), Te1–Cl2 2.5889(5), Te1–Te2 2.74208(17), Te2–C21 2.1089(18), O21–C22 1.361(2), O22–C26 1.367(2), Te1···O11 2.9271(15), Te1···O12 3.2451(12), Te1···O22 2.9266(13), Te2···O12 2.8201(14), Te2···O21 2.9882(16), Te2···O22 3.1834(12), Cl2··· Te2′ 3.7837(5); C11–Te1–Cl1 88.63(5), C11–Te1–Cl2 87.45 (5), Cl1–Te1–Cl2 173.356(18), C11–Te1–Te2 99.83(5), Cl1–Te1–Te2 94.338(14), Cl2–Te1–Te2 91.616(12),C21–Te2–Te1 95.65(5), C22–O21–C27 118.03(16), C12–O11–C17 118.30(15), Te1–Cl2··· Te2′ 121.01(2), Te2–Te1···O11 150.59(3), C11–Te1···O22 159.90(6), Te1–Te2···O21 134.39(3), C21–Te2···O12 166.90(6).

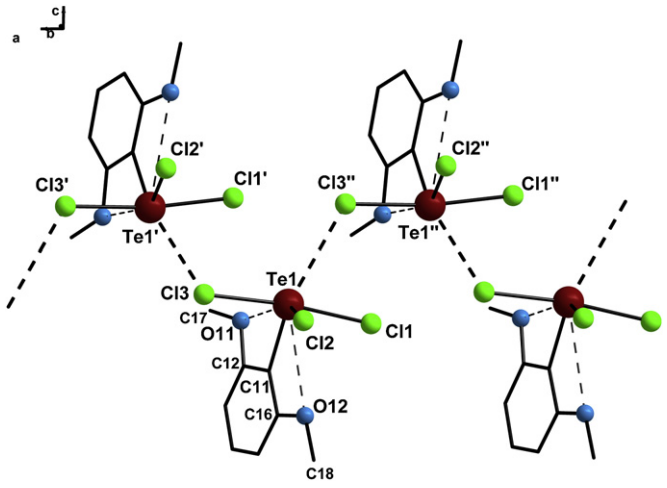


Fig. 6. Polymeric assembly of [dmpTeCl$_3$] (**6**). Dashed lines represent secondary bonds. Hydrogen atoms have been omitted for clarity. Symmetry code: (′) = 0.5 + *x*, *y*, 1.5 − *z*; (″) = −0.5 + *x*, *y*, 1.5 − *z*. Selected bond lengths [Å] and angles [deg]: Te1−C11 2.102(5), Te1−Cl1 2.4660(13), Te1−Cl2 2.3014(14), Te1−Cl3 2.5185(12), O11−C12 1.360(6), O12−C16 1.353(6), Te1···O11 2.773(4), Te1···O12 3.323(4), Te1··· Cl3″ 3.387(1), Cl3··· Te1′ 3.387(1); C11−Te1−Cl2 102.32(15), C11−Te1−Cl1 88.36(14), Cl2−Te1−Cl1 89.57 (5), C11−Te1−Cl3 87.48(14), Cl2−Te1−Cl3 85.38(5), Cl1−Te1−Cl3 172.63(5), C12−O11−C17 118.6(4), C16−O12−C18 118.6(4), C11−Te1···Cl3″ 166.36(16), Cl1−Te1···O11 103.69(8).

phenyl ring between the two methoxy bonds (see Fig. 3). The axial bonds C11−Te1$^{n\prime}$···Br2$^{n\prime}$ of the distorted polymeric octahedra in **3** are mainly linear, with 169.53(0)°. The dissolution of complex **3** in acetone and further recrystallization leads to the substitution of Br3 by one $CH_3COCH_2^-$ anion, with HBr elimination and formation of [dmpTeBr$_2$(CH$_2$−C(O)−CH$_3$)] (**4**). Although in **3** the distance Br3−Te1 is the shorter one, with 2.429(2) Å {Br2−Te1 = 2.6896(13); Br1−Te1 = 2.6322(13)}, a nucleophilic attack to Te1 in this position is not suprising, since the bond Te1−Br3 seems to be the more vulnerable, on the contrary of the bonds Te1−Br1/Te1−Br2, both stereochemically and simetrically favoured. The eletrophilic substitution of methyl ketones with aryltellurium trichlorides with formation of acylmethyl(aryl)tellurium dichlorides has been already fully discussed by Chauhan and co-workers [17]. Complex **4** attains two secondary Te···Br interactions with 3.8086(4) Å; these Te···Br contacts allow **4** to configure a twisted dimeric assembly, in which the two "monomeric" units present a distorted octahedral geometry, with the Br ligands in the axial position. Although the Te···Br contacts are only a litle bit shorter than the sum of the Te/Br van der Waals radii, 3.91 Å [9], it is reasonable to assume that they play a significant role in the structural stabilization of the compound. [DmpTeTe(Cl)$_2$Dmp] (**5**) replicates the main structure and the Te···O$_{(methoxy)}$ interactions of complex **2**, achieving a polymeric association extended through Cl2$^{n\prime}$···Te2$^{n\prime}$ secondary contacts, with a distance of 3.7837(5) Å, in the border of the sum of the van der Waals radii of both atoms (tellurium and chlorine), 3.81 Å [9]. Complex **5** closes the series of mixed-valent aryltellurenyl halides with the structure [RTeTe(X)$_2$R] (R = dmp; X = Cl, Br, I), started with [RTeTe(I)$_2$R] [6]. Beckmann and co-workers [18] have obtained the analogue series [PhTeTe(Br)$_2$Ph] and [RTeTe(X)$_2$R] (R = 2,6-Mes$_2$C$_6$H$_3$; X = Cl, I). Complex [dmpTeCl$_3$] (**6**) is structurally equivalent to complex **3** – according to the unit cell parameters of **3** and **6** shown in Table 1, their crystals are virtually isomorphic – with a similar polymeric, zigzag type configuration, attained through Te1$^{n\prime}$···Cl3$^{n\prime}$ secondary bonds, with a distance of 3.387(1) Å. The pseudo octahedral structure of the compound is also achieved with support of the equatorial Te1···O11 bond (2.773(4)), while the opposite Te1···O12 contact measures 3.323(4) Å. The axial bonds C11−Te1··· Cl3″ are (as in **3**), predominantly linear, with 166.36(16)°. The reported similar compound 2,4,6-*t*-Bu$_3$C$_6$H$_2$TeCl$_3$ [19] appears as dimer, through secondary Te···Cl bonds,unlike **6**, which shows a polymeric assembly. Complex [dmpTe(μ-O)(OCH$_3$)]$_2$ (**7**) results from the insertion of μ-oxo and further methoxy ligands to the tellurium centers of the starting reagent **1**. A similar binuclear μ-O structure of tellurium has been already described, although no references have been made about the occurrence of a Te−Te bond [20]. Tellurium atoms – van der Waals radium of 2.06 Å [9] – belonging to the same molecule do not use to stay too far from each other. As examples of Te−Te distances in different halogen compounds of 2,6-dimethoxyphenyl, we can cite 2.7055(5) Å in compound **1**, 2.7401(2) in **2**, 2.74208(17) in **5**, and 2.757 (4)/2.855(16) Å in the iodides [RTeTe(I)$_2$R] and [R$_2$TeTeR$_2$][Te$_4$I$_{14}$], respectively [6]. In the case of compound **7** the Te−Te distance is quite longer, 3.1585(2) Å, but even so, it seems more plausible to assume that the μ-oxo bridges occur as a consequence of the proximity of the tellurium atoms, instead attributing the proximity of the Te centers to the occurrence of the oxo bridges. Finally, the concepts of supramolecular chemistry are very appropriate to most of the complexes presented in this work, as is routine in the chemistry of aryltellurenyl halides, principally because of the halogen···H secondary interactions. Complexes **2**, **5** and **6** attain one-dimensional chains along the *a* (**2**, **6**) and *b* axes, and compound **3** grows as bi-dimensional layers in the plane *ab*.

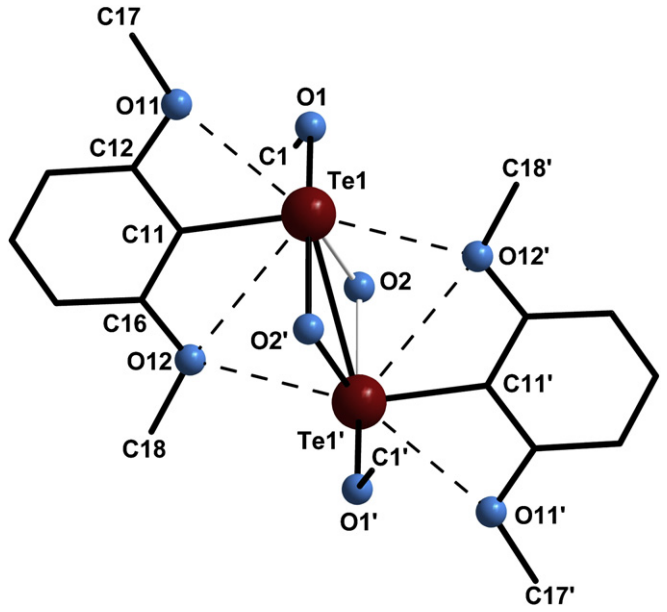


Fig. 7. Molecular structure of [dmpTe(μ-O)(OCH$_3$)]$_2$ (**7**). Hydrogen atoms have been omitted for clarity. Dashed lines represent secondary bonds. Symmetry code: (′) = 1 − *x*, −*y*, 2 − *z*. Selected bond lengths [Å] and angles [deg]: Te1−O2 1.895(2), Te1−O1 1.996(2), Te1−C11 2.123(3), Te1−O2′ 2.142(2), O11−C12 1.361(4), O2−Te1′ 2.142(2), O1−C1 1.422(4), O12−C16 1.351(4), Te1···O11 2.930(1), Te1···O12′ 3.061(2); O2−Te1−O1 88.78(10), O2−Te1−C11 106.39(11), O1−Te1−C11 91.63(11), O2−Te1−O2′ 77.23(10), O1−Te1−O2′ 164.80(9), C11−Te1−O2′ 86.73(10), O2−Te1−Te1′ 41.42(7), O1−Te1−Te1′ 129.92(7), C11−Te1−Te1′ 97.50(9), O2′−Te1−Te1′ 35.82(6), C12−O11−C17 118.0(3), Te1−O2−Te1′ 102.77(10), C1−O1−Te1 121.8(2), C16−O12−C18 117.6(3), O2−Te1···O11 153.27(0),C11−Te1···O12′ 154.41(0).

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Appendix A. Supplementary material

CCDC 790695–790701 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5**, **6** and **7**, respectively. 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.

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