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α-Telluration of 2-acetylthiophene: Electronic influence of the heteroaromatic moiety on solid state structures

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ABSTRACT

Room temperature oxidative addition of α-bromo-2-acetylthiophene to elemental tellurium and aryltellurium(II) bromide provides direct routes to (2-thiophenoylmethyl)tellurium(IV) dibromides, (2-$(C_4H_3S)COCH_2)_2TeBr_2$ (**1b**) and 2-$(C_4H_3S)COCH_2ArTeBr_2$ (Ar = 1-$C_{10}H_7$, Npl, **2b**; 2,4,6-$Me_3C_6H_2$, Mes, **3b**). The chloro analogues, 2-$(C_4H_3S)COCH_2ArTeCl_2$ (Ar = Npl, **2a**; Mes, **3a**) were prepared by the condensation reaction of the parent methyl ketone with $NplTeCl_3$ or $MesTeCl_3$. Metathesis of these products with an alkali iodide affords the iodo analogues **1c**, **2c** and **3c**. These diorganotellurium dihalides are reduced with aqueous bisulfite to diorganotellurides **1**–**3**, which can be oxidized readily with dihalogens to the desired diorganotellurium(IV) dihalides. Compound **1** is a rare example of a symmetrical telluroether with C_{sp3}–Te–C_{sp3} grouping that has been characterized by single-crystal diffraction techniques. Preference of the 2-thiophenoylmethyl ligand for small-bite (C, O) chelation over less strained (C, S) coordination is evident in the crystal structures of the Te(IV) compounds **1b**, **2a**, **2b** and **3a**. The unexpected transoidal orientation of the two acylmethyl ligands in the solid state molecular configuration of symmetrical diorganotellurium(IV) dibromide **1b** appears to be a combined effect of electronic repulsion due to the thiophene moieties and steric repulsion of bromo ligands.

1. Introduction

Functional group promoted metallation of organic substrates makes available organolithiums that readily undergo the insertion of elemental tellurium into the carbon-metal bond to afford lithium arenetellurolates. This synthetic protocol is especially effective in the *ortho* telluration of heteroaromatic substrates [1]. Lithium or sodium arenetellurolates are very good nucleophilic species and can be easily alkylated by alkyl halides to obtain alkylaryltellurides [2]. However, the reaction of lithium 2-thiophenetellurolates with acylmethyl halides results in reductive dehalogenation to give parent ketones [3] instead of the expected acylmethyl(2-thiophenyl)tellurides. Another strategy of α-telluration of acylmethanes is their electrophilic substitution reaction with $TeCl_4$ or $ArTeCl_3$ [4–8]. The condensation reaction of $TeCl_4$ with simple arylmethyl ketones such as acetophenone, its ring substituted derivatives [3,9–11] and substituted acetylacetones [12,13] eliminates 2 mol of HCl to produce organotellurium(IV) dichlorides. However, organotellurium(IV) trichlorides were isolated in the reaction of $TeCl_4$ with 2,6-diacetylpyridine, 2-acetylcyclohexanone or 3-acetyl-7-methoxycoumarin where dehydrochlorination was limited to only 1 mol [14]. Although the condensation product of $TeCl_4$ with 2-acetylthiophene, the bis(2-thiophenoylmethyl)tellurium dichloride has been obtained in poor yields [3,10,14] the reaction product of $TeCl_4$ with 2-acetylpyridine still remains uncharacterized [14]. These observations highlight the substantial role heteroaromatic moiety electronic factors play in the electrophilic reactions of their acetyl derivatives.

A simple and direct route to bis(acylmethyl)tellurium(IV) dibromides, practiced in our laboratory, involves oxidative insertion of elemental tellurium into the C–Br bond of $RCOCH_2Br$. In continuation, we now describe the isolation and structural characterization of (2-thiophenoylmethyl)tellurium(II and IV) derivatives which have been obtained at ambient conditions by (i) oxidative addition of α-bromo/iodo-2-acetylthiophenes to elemental tellurium and (ii) electrophilic substitution of 2-acetylthiophene with the aryltellurium trichlorides that bear a sterically cumbersome aryl ligand bound to tellurium atom.

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2. Results and discussion

2.1. Synthesis

Thermally labile α-bromo-2-acetylthiophene adds to elemental tellurium at room temperature to afford $(2\text{-}(C_4H_3S)COCH_2)_2TeBr_2$ and to ArTeBr (prepared *in situ* from Ar_2Te_2 and Br_2; Ar = Npl, Mes), to give $2\text{-}(C_4H_3S)COCH_2ArTeBr_2$. The chloro analogues, $(2\text{-}(C_4H_3S)COCH_2)_2TeCl_2$ and $2\text{-}(C_4H_3S)COCH_2ArTeCl_2$, are obtained by electrophilic substitution of the parent ketone with $TeCl_4$ and $ArTeCl_3$, respectively. Iodo analogues are prepared either by oxidative addition of α-iodo-2-acetylthiophene to tellurium powder to afford **1c** or by metathesis of the bromo/chloro compounds (**1b**, **2a**, **3a**) with alkali metal iodides. Reduction of these dihalides with $Na_2S_2O_5$ affords the corresponding tellurides, (**1**, **2**, **3**) which are readily oxidized with dihalogens to afford the corresponding diorganotellurium(IV) dihalides (Scheme 1).

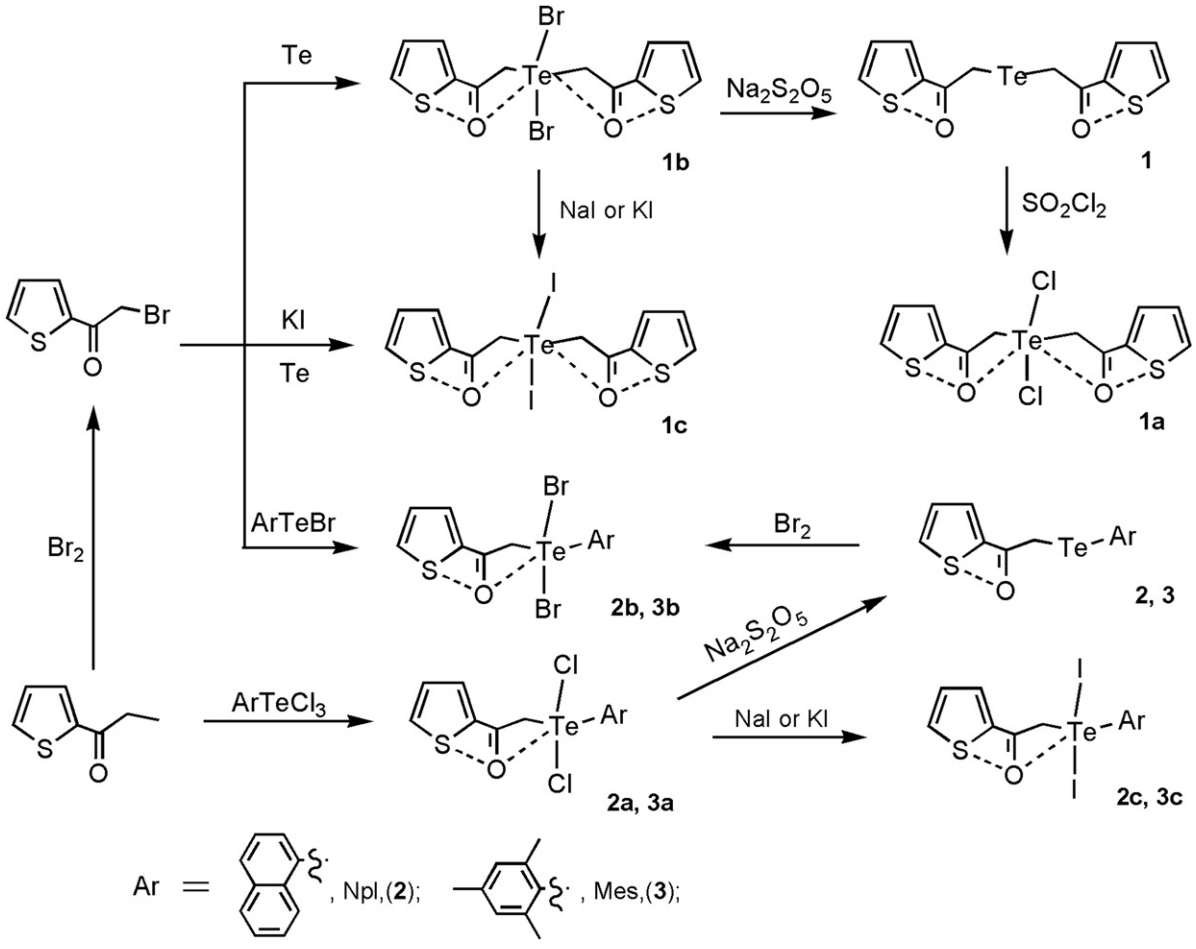
2.2. Spectroscopic studies

All dihalides (**1a**–**1c**, **2a**–**2c** and **3a**–**3c**) and tellurides **1** and **3** are sharp melting colorless to orange solids, soluble in chloroform and dichloromethane. Dialkyltelluride **1** and the Te(IV) diiodides (**1c**, **2c** and **3c**) are stable for weeks only when stored at low temperature (−10 °C), while the other new organotellurium derivatives are fairly stable at ambient conditions. The ν(CO) absorptions appearing at ~1630 cm^{-1} in the infrared spectra of **1a** and **1b** are at lower wave number than that for the parent ketone, 2-acetylthiophene.

Table 1
Important chemical shifts (in ppm) for thiophenoylmethyltellurium derivatives.

	^1H		^{13}C			^{125}Te
	CH_2	CH_3	CH_2	CH_3	CO	
1a	5.19		56.9		184.2	751
1b	5.32		54.8		184.4	686
1c	4.30		51.2		186.0	602
2a	5.60		65.6		183.9	764
2b	5.75		64.0		184.0	697
2c	5.77					606, 984
3a	5.54	2.34 (*p*-Me) 2.79, 2.82 (*o*-Me)	62.2	21.0 (*p*-Me) 23.5, 24.1 (*o*-Me)	184.4	784
3b	5.70	2.34 (*p*-Me) 2.75, 2.79 (*o*-Me)	61.2	21.0 (*p*-Me) 23.3, 24.6 (*o*-Me)	184.5	704
3c	5.73	2.32 (*p*-Me) 2.64 (*o*-Me)	58.9	21.0 (*p*-Me) 23.2, 25.7 (*o*-Me)		590, 885
1	4.18		10.1		190.8	559
2	4.17					
3	3.94	2.29 (*p*-Me) 2.51(*o*-Me)				

Important NMR chemical shifts are listed in Table 1 for critical comparison. Methylene protons, appearing at ~4.1 ppm in the ^1H NMR spectra of Te(II) derivatives **1**–**3**, are appreciably shielded when compared to their Te(IV) analogues (δ 4.3–5.8 ppm). Protons of the thiophene moiety appear in the aromatic region, along with



Scheme 1.

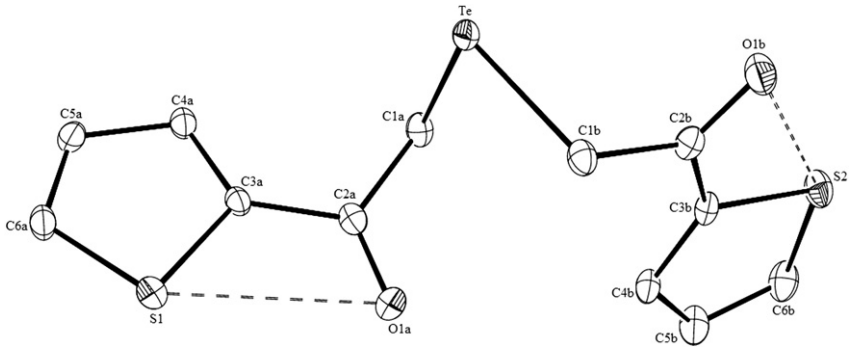


Fig. 1. Molecular structure of **1**. Selected interatomic distances (Å) and angles (°): Te–C1a 2.170(2), Te–C1b 2.164(2), Te···O1a 3.588(2), Te···O1b 3.609(2), O1a···S1 3.000(2), O1b···S2 2.93(2), C1a–Te–C1b 94.66(8), O1a···Te–C1b 66.96(6), O1b···Te–C1a 108.06(6), O1a···S1–C6a 142.60(9), O1b···S2–C6b 144.29(9).

the ring protons of the naphthyl and the mesityl groups. Appearance of separate signals (1:1) for the *ortho* methyls of the mesityl group in the ^{1}H NMR spectra of **3a**–**3c** is indicative of restricted rotation of the benzene ring about the Te–C(Mes) bond. The ^{13}C NMR chemical shifts for the carbonyl carbon appear in the range 184–191 ppm and the methylene carbon between 56 and 66 ppm for Te(IV) derivatives and at 10.1 ppm in case of **1**. All the symmetrical diorgantellurium derivatives (**1**, **1a**, **1b**, **1c**) give rise to a single ^{125}Te NMR resonance indicating the presence of only one Te containing species in their solutions. While the chemical shift for telluride **1** (δ 559 ppm) is towards high field, those for the Te(IV) derivatives are consistent with the electronegativity of the halo ligands (δ 751 (**1a**), 686 (**1b**), 602 ppm (**1c**)). Two ^{125}Te chemical shifts are observed for asymmetric diorganotellurium(IV) diiodides **2c** and **3c**, indicating that they are not as stable to dispropotionation, at least in solution, as their chloro or bromo analogues.

2.3. Crystal structures

The molecular structures of **1**, **1b**, **2a**, **2b** and **3a** are shown in Figs. 1–5 with selected bond parameters collected in the caption to each figure. Asymmetric units in each case consist of one molecule. Interestingly, 2-thiophenoylmethyl, the functionalized organic ligand, adopts planar *cis* geometry (see Scheme 1) invariably among the molecular structures of all the organotelluriums crystallographically characterized in the present study. The near linearity attained by the O···S—C_{trans} triad ($\angle$ O—S—C_{trans} ranges from 141.9 (1)° in **3a** to 144.3(1)° in **1**) makes the overlap of vacant σ^{*}(S—C_{trans}) molecular orbital with filled *p*-orbital on the O atom feasible. The observed shorter d(S, O) compared to Σ r_{vdw}(S, O), 3.32 Å, appears to be a manifestation of intramolecular secondary bonding interaction that stabilizes the observed *cis* conformation of the bifunctional organic ligand.

The central Te(IV) atom among **1b**, **2a**, **2b** and **3a**, imparts trigonal bipyramidal primary geometry with expected X—Te—X and C—Te—C angular distortions due to its lone pair. However, the sterically demanding 1-naphthyl and mesityl ligands in **2a**, **2b** and **3a**, appreciably widen the C—Te—C angle in comparison to **1b** (see Table 2). Among the molecular structures of unsymmetrical diorganotellurium(IV) dihalides **2a**, **2b** and **3a**, the carbonyl O atom of the sole functionalized ligand is involved simultaneously in the intramolecular secondary bonding interaction to either of its heavier congeners. The observed internuclear distance between O and Te atoms, which is shorter than the sum of their van der Waals radii [d(Te, O) = 2.983(3) (**2a**), 2.982(4) (**2b**), 2.862(2) Å (**3a**); Σ r_{vdw}(Te, O) = 3.58 Å] and near linearity of the O···Te—C_{trans} triad ($\angle$ O—Te—C_{trans} measures 150.3(1)°, 149.6(2)° and 162.3(1)° in **2a**,

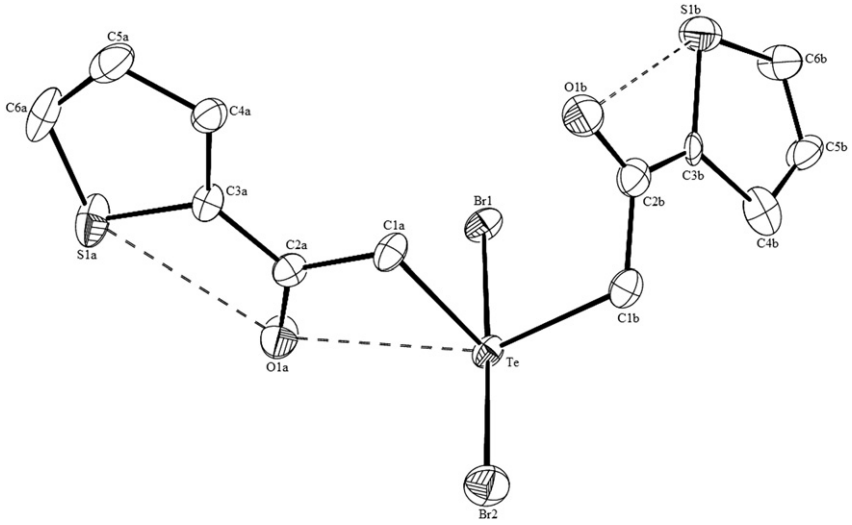


Fig. 2. Molecular structure of **1b**. Selected interatomic distances (Å) and angles (°): Te–C1a 2.133(4), Te–C1b 2.157(5), Te–Br1 2.7143(6), Te–Br2 2.6196(8), Te···O1a 2.880(4), Te···O1b 3.553(4), O1a···S1a 3.001(3), O1b···S1ba 2.938(6), C1a–Te–C1b 94.9(2), Br1–Te–Br2 177.50(2), O1a···Te–C1b 148.1(2), O1b···Te–C1a 60.1(1), O1a···S1a–C6a 142.1(2), O1b···S1ba–C6ba 143.5(3).

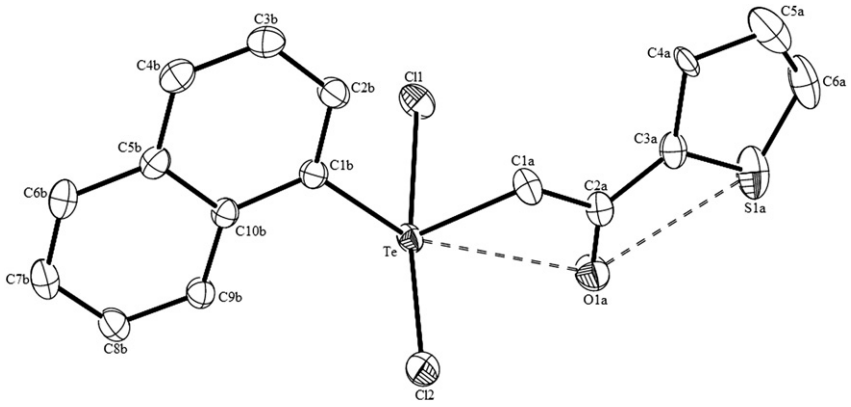


Fig. 3. Molecular structure of **2a**. Selected interatomic distances (Å) and angles (˚): Te–C1a 2.126(3), Te–C1b 2.124(3), Te–Cl1 2.545(1), Te–Cl2 2.477(1), Te···O1a 2.984(3), O1a···S1a 2.995(3), C1a–Te–C1b 98.1(1), Cl1–Te–Cl2 169.93(4), O1a···Te–C1b 150.2(1), O1a···S1a–C6a 143.9(2).

2b and **3a** respectively) substantiate the presence of attractive 1,4-Te···O interaction. This interaction brings the O atom in to the equatorial C1A—Te—C1B plane, reduces the tetrahedral angle Te—C1A—C2A to 106.3°, 106.5° and 105.1° in **2a**, **2b** and **3a** respectively and marginally the *trans* Te—C(aryl) bond length [d (Te—C(aryl)) = 2.124(3) (**2a**), 2.129(5) (**2b**), 2.131(2) Å (**3a**); *cf.* 2.103 Å in NpI_2TeCl_2 [15] and 2.100(2) Å in $(2,6\text{-}(MeO)_2C_6H_3)_2TeCl_2$ [16]. The functionalized ligand thus prefers (C, O), rather than (C, S), mode of chelation, though the latter, involving its *trans* conformation, would have resulted in the formation of a less strained five-member intramolecular ring.

In the crystal structure of symmetrically functionalized diorganotellurium(IV) **1b** (Fig. 2), one of the thiophene rings is two-fold disordered with 70:30 occupancies. Interestingly, the observed molecular configuration is unique. Among the molecular structures of bis(acylmethyl/amidomethyl)tellurium(IV) dihalides $[(RCOCH_2)_2TeX_2$, R = Me, Et, *t*-Bu, 4-YC_6H_4, NH_2, NEt_2, NMePh and X = Cl, Br, I] described earlier by us [7,8,17–20], both the carbonyl functionalized organic ligands exhibit (C, O) chelating behavior and impart six-coordination to the central Te atom. The skeletal frameworks of the organic ligands, Te—C—C(O)—C/N, in these compounds are invariably almost coplanar, with the equatorial C–Te–C plane and the cisoidal orientation of the ligands imparting a butterfly shape C_{2v} molecular symmetry. In the anticipated molecular structure of **1b** (see Scheme 1), by analogy to the structure of its chloro analogue, $(2\text{-}(C_4H_3S)COCH_2)_2TeCl_2$ [21], the cisoidal 2-thiophenoyl moieties would bring five electron-rich chalcogen atoms in the domain of the lone pair of the central atom. However, the steric and electronic repulsions appear to predominate the subtle 1,4-Te···O secondary bonding interactions. As a consequence, while one of the organic ligands retains its (C, O) chelating mode of coordination in the observed structure of **1b**, the free rotation about the Te—C bond allows the other to move its carbonyl O atom out of the equatorial plane (to an almost transoidal conformation) and close to the van der Waals distance from the Te(IV) [d(Te, O1B) = 3.55 Å]. The intraligand S···O secondary bonding interaction and hence planar *cis* conformation of this monodentate organic ligand is, however, retained in the molecule of **1b** and the five-coordinate central Te atom becomes accessible for intermolecular Te···X secondary bonding interactions. The centrosymmetric zero-dimensional dimeric units that are realized via reciprocatory Te···Br1 interactions self-assemble, in the crystal lattice of **1b**, by means of C—H1BA···O1A H-bonding interactions into one-dimensional supramolecular arrays (Figure S1).

Among the diorganotellurides, **1** and **3** were obtained in the crystalline state and single-crystal data for the symmetric telluroether (**1**) were collected. Absence of axial halo ligands in it seems to provide steric freedom to the 2-thiophenyl moieties. Free rotation about the Te—C bonds allows the organic ligands to adopt transoidal orientation with minimum electronic repulsion, at least in the solid state. The interplanar angles between the equatorial C–Te–C plane and the mean planes comprising of skeletal atoms of the organic ligands are 82.42(5)° and 72.46(6)° and the internuclear distances between the Te(II) and carbonyl O atoms [d(Te, O) = 3.588(2)Å and

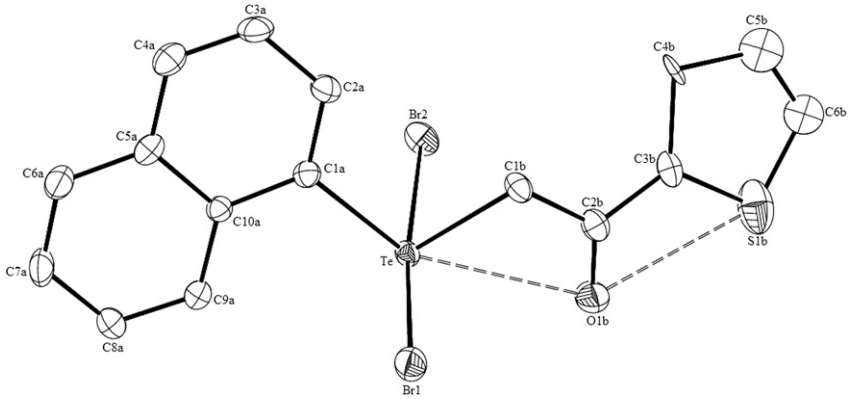


Fig. 4. Molecular structure of **2b**. Selected interatomic distances (Å) and angles (◦): Te–C1a 2.129(5), Te–C1b 2.133(4), Te–Br1 2.6361(5), Te–Br2 2.7071(6), Te···O1b 2.982(4), O1b···S1b 2.984(5), C1a–Te–C1b 98.0(2), Br1–Te–Br2 171.14(2), O1b···Te–C1a 149.6(2), O1b···S1b–C6b 144.0(3).

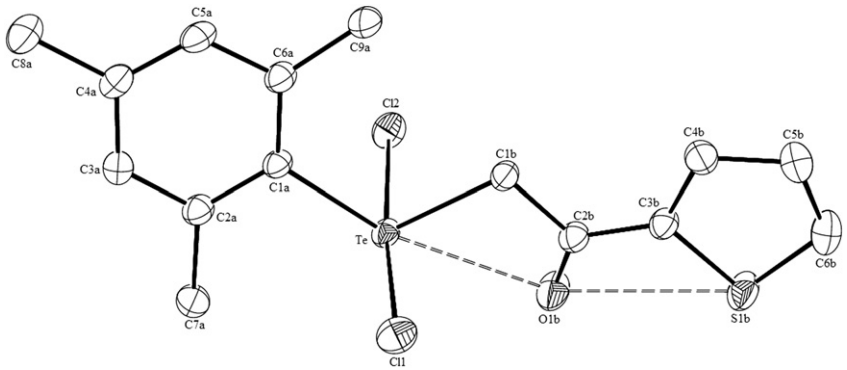


Fig. 5. Molecular structure of **3a**. Selected interatomic distances (Å) and angles (°): Te–C1a 2.131(2), Te–C1b 2.131(2), Te–Cl1 2.4919(6), Te–Cl2 2.5127(6), Te···O1b 2.862(2), O1b···S1b 3.000(2), C1a–Te–C1b 108.49(8), Cl1–Te–Cl2 173.32(2), O1b···Te–C1a 162.29(6), O1b···S1b–C6b 141.9(1).

3.609(2) Å] are comparable to Σ r_{vdw}(Te, O). Thus, the molecular structure of **1** is devoid of intramolecular Te···O attractive interactions that are reported to be present in analogous compounds, (4-$MeC_6H_4COCH_2)_2$Te and (2,4,6-$Me_3C_6H_2COCH_2)_2$Te [19,22]. Instead, reciprocatory intermolecular Te···O secondary bonding interactions that give rise to centrosymmetric zero-dimensional supramolecular units in its crystal packing (Figure S2) may be substantiated from the d(Te, O1B) of 3.485(2) Å and ∠ O1B—Te—C_{trans} of 151.87°(7).

2.4. Conclusion

Oxidative addition of the aroylmethyl bromide to Te(0) and Te (II) provides a direct route to (2-thiophenoylmethyl)tellurium(IV) dibromides, which are readily reduced to the corresponding telluroethers. As a consequence of secondary bonding interaction between the lighter chalcogen atoms, the planar functionalized organic ligand invariably adopts *cis*–S, O configuration among all the Te(IV) and Te(II) derivatives. The (C, O) mode of chelation of the ligand caused by 1,4-Te···O secondary bonding interaction is preferred to the (C, S) mode. Among (2-thiophenoylmethyl)aryltellurium(IV) dihalides, the central Te atom is five-coordinate even in the presence of a bulky aryl ligand. Interestingly, the anticipated six-coordination of Te atom in bis(2-thiophenoylmethyl)tellurium (IV) dibromide is not realized, possibly as a combined effect of electronic repulsion due to the thiophene moieties and steric hinderance of bromo ligands.

3. Experimental

3.1. General procedures

Preparative work was performed under dry nitrogen. Melting points were recorded in capillary tubes and are uncorrected. All solvents were purified and dried before use, with α-bromoacetylthiophene being obtained as pale yellow lachrymatory oil by bromination of 2-acetylthiophene (Merck, Germany) in glacial acetic acid. 1-Naphthyltellurium trichloride and mesityltellurium trichloride were prepared by the chlorination of their corresponding ditellurides with SO_2Cl_2. IR spectra were recorded as KBr pellets using a Perkin–Elmer RX1 spectrometer. ^{1}H NMR spectra were recorded at 300.13 MHz in $CDCl_3$ on a Bruker DRX300 spectrometer using Me_4Si as the internal standard. $^{13}C\{^1H\}$ (100.54 MHz) and $^{125}Te\{^1H\}$ (126.19 MHz) NMR spectra were recorded in $CDCl_3$ on a JEOL Eclipse Plus 400 NMR spectrometer, using Me_4Si and Me_2Te as internal standards. Microanalyses were carried out using a Carlo Erba 1108 analyzer. Tellurium was estimated volumetrically.

Table 2
Important bond angles and distances (°, Å) in compounds **1**, **1b**, **2a**, **2b** & **3a**.

	C–Te–C	Te–C–C	O···Te–C_{trans}	Te···O	Te–C(Ar)
1	94.7(1)	110.5(2)	151.9(1)	3.485(2)	
1b	94.9(2)	105.9(3)	148.1(2)	2.880(4)	
2a	98.2(1)	106.3(2)	150.3(1)	2.983(3)	2.124(3)
2b	98.0(2)	106.5(3)	149.6(2)	2.982(4)	2.129(5)
3a	108.5(1)	105.1(1)	162.3(1)	2.862(2)	2.131(2)

3.2. Syntheses

3.2.1. Syntheses of symmetrical diorganotellurium derivatives

Compound ***1b***: Freshly ground tellurium powder (0.50 g, 3.94 mmol) and α-bromoacetylthiophene (1.0 mL, 7.87 mmol) were stirred together at room temperature for 24 h. A thick paste was formed that was washed with diethyl ether and extracted with dichloromethane (200 mL). The extract was passed through a small silica column and the solvent reduced to about 5 mL by distillation. Addition of hexane precipitated a colorless solid that was recrystallized from dichloromethane to give **1b** as pale yellow rectangular crystals. Yield: 1.1 g (52%). M.p.: 185 °C. Anal. Calc. for $C_{12}H_{10}O_2S_2TeBr_2$ (537.74): C, 26.80; H, 1.87; Te, 23.73. Found: C, 26.80; H, 2.00; Te, 23.85. IR (cm^{-1}): 1630.8 (νC = O). ^{1}H NMR: δ 5.32 (s, 2H, CH_2), 7.21–7.24 (t, 1H, ring proton), 7.83–7.85 (d, 2H, ring protons) ppm. $^{13}C\{^1H\}$ NMR: δ 54.8 (CH_2), 128.8, 135.1, 137.0 (ring carbons), 184.4 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 686 ppm.

Compound ***1c***: A solution of **1b** (0.27 g, 0.50 mmol) in dichloromethane (50 mL) was stirred with KI (0.33 g, 2.0 mmol) for 5 h. Potassium halides were removed by filtration and excess solvent was removed by distillation. An orange solid settled on cooling and was recrystallized from chloroform/hexane. Yield: 0.22 g (69% with respect to **1b**). M.p.: 168 °C. Anal. Calc. for $C_{12}H_{10}O_2S_2TeI_2$ (631.75): C, 22.81; H, 1.60; Te, 20.20. Found: C, 22.62; H, 1.59; Te, 20.10; ^{1}H NMR: δ 4.30 (s, 2H, CH_2), 7.15–7.18 (t, 1H, ring proton), 7.69–7.70 (d, 1H, ring proton), 7.79–7.81 (d, 1H, ring proton) ppm. $^{13}C\{^1H\}$ NMR: δ 51.2 (CH_2), 128.4, 133.4, 135.1, 140.4 (ring carbons), 186.0 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 602 ppm.

Alternatively, **1c** was also obtained when tellurium powder (0.13, 1.0 mmol) and α-iodoacetylthiophene [prepared by stirring α-bromoacetylthiophene (0.26 mL, 2.0 mmol) with KI (0.35 g, 2.1 mmol) in 1 mL acetone for 1 h were stirred together at room temperature for 2 h. An orange paste formed and was extracted with dichloromethane (20 mL), passed through a small silica column and the solvent reduced to 2 mL by distillation. Addition of petroleum ether (40–60) and cooling afforded **1c** as an orange solid. Yield: 0.35 g (56% with respect to Te). M.p.: 168 °C.

Compound ***1***: A solution of **1b** (0.27 g, 0.50 mmol) in dichloromethane (10 mL) and diethyl ether (50 mL) was stirred with an aqueous solution of $Na_2S_2O_5$ (0.10 g, 0.53 mmol) for 1 h at 0 °C. The yellow organic layer was separated, washed with water (4 × 20 mL), and passed through anhydrous Na_2SO_4. The solvent was reduced under vacuum at room temperature to about 2 mL, 3–4 drops of dichloromethane were added and the solution was kept in a deep freezer, affording yellow hexagonal crystals of **1**. Yield: 0.13 g (66%). M.p.: 85 °C (Ref. [3] 93–94 °C). Anal. Calc. for $C_{12}H_{10}O_2S_2Te$ (377.94): C, 38.14; H, 2.67; Te, 33.76. Found: C, 38.24; H, 2.70; Te, 33.85. ^{1}H NMR: δ 4.18 (s, 2H, CH_2), 7.15 (s, 1H, ring proton), 7.65–7.67 (d, 1H, ring proton), 7.80 (s, 1H, ring proton) ppm. $^{13}C\{^1H\}$ NMR: δ 10.1 (CH_2), 128.3, 132.9, 134.4, 142.2 (ring carbons), 190.8 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 559 ppm.

Compound ***1a***: Addition of a solution of SO_2Cl_2 (0.12 mL, 1.5 mmol) in dichloromethane (5 mL) to a cooled light yellow solution of **1** (0.19 g, 0.50 mmol) in the same solvent (20 mL) resulted in the precipitation of **1a** as a white solid that was collected by filtration. Recrystallization from dichloromethane gave **1a** as white needles. Yield: 0.16 g (73% with respect to **1**). M.p.: 180 °C dec (Ref. [3] 180–182 °C dec). IR (cm^{-1}): 1629.1 (νC = O). ^{1}H NMR: δ 5.19 (s, 2H, CH_2), 7.23 (s, 1H, ring proton), 7.83–7.84 (d, 2H, ring protons) ppm. $^{13}C\{^1H\}$ NMR: δ 56.9 (CH_2), 128.8, 135.1, 136.9, 140.9 (ring carbons), 184.2 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 751 ppm.

Compound **1a** was also prepared by condensation of $TeCl_4$ (0.54 g, 2.0 mmol) with 2-acetylthiophene (0.54 mL, 5.0 mmol) in refluxing chloroform (10 mL) for 4 h. The color of the solution changed from yellow to black as HCl evolved. Chloroform (20 mL) was added and the solution passed through a small silica column. Removal of excess solvent followed by cooling gave **1a** as colorless solid which was recrystallized from dichloromethane. Yield: 0.28 g (32%). M.p.: 180 °C dec.

3.2.2. Synthesis of unsymmetrical diorganotellurium dichlorides

Compound ***2a***: A mixture of 1-naphthyltellurium trichloride (0.18 g, 0.50 mmol) and two-fold excess of 2-acetylthiophene (0.11 mL, 1.0 mmol) was stirred together at room temperature under a flow of dry nitrogen for 12 h. The resulting paste was washed with cold diethyl ether (5 × 10 mL), dissolved in dichloromethane (20 mL) and passed through a short silica column. The solvent was reduced to 10 mL and petroleum ether (40–60) added to afford **2a** as a cream colored solid that was recrystallized from dichloromethane. Yield: 0.16 g (69%). M.p.: 168 °C. Anal. Calc. for $C_{16}H_{12}OSTeCl_2$ (450.84): C, 42.63; H, 2.68; Te, 28.30. Found: C, 42.67; H, 3.00; Te, 28.40. ^{1}H NMR: δ 5.60 (s, 2H, CH_2), 7.24 (t, 1H, thiophene ring), 7.62–8.28 (m, 9H, aromatic protons) ppm. $^{13}C\{^1H\}$ NMR: δ 65.6 (CH_2), 126.4, 126.8, 127.3, 128.2, 128.8, 129.5, 131.9, 132.7, 132.8, 133.4, 134.3, 135.2, 137.0, 140.3 (aromatic carbons), 183.9 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 764 ppm.

Compound **3a** was prepared similarly from mesityltellurium trichloride (0.18 g, 0.50 mmol) and 2-acetylthiophene (0.11 mL, 1.0 mmol). Yield: 0.15 g (68%). M.p.: 152 °C. Anal. Calc. for $C_{15}H_{16}OSTeCl_2$ (442.86): C, 40.68; H, 3.64; Te, 28.81. Found: C, 40.57; H, 3.77; Te, 28.60. ^{1}H NMR: δ 2.34 (s, 3H, *p*-Me), 2.79, 2.82 (2s, 6H, *o*-Me), 5.54 (s, 2H, CH_2), 7.00 (s, 1H, *m*-H mesityl ring), 7.07 (s, 1H, *m*-H mesityl ring), 7.22 (t, 1H, thiophene ring), 7. 83–7.87 (m, 2H, thiophene ring) ppm. $^{13}C\{^1H\}$ NMR: δ 21.0 (*p*-Me), 23.5 (*o*-Me), 24.1 (*o*-Me), 62.2 (CH_2), 128.8, 130.4, 131.6, 134.8, 134.9, 136.8, 140.0, 140.6, 141.0, 142.3 (aromatic carbons), 184.4 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 784 ppm.

3.2.3. Reduction of *2a*, *3a* to *2*, *3*

Compound ***2***: A solution of **2a** (0.23 g, 0.50 mmol) in dichloromethane (20 mL) was shaken with an aqueous solution of $Na_2S_2O_5$ (0.09 g, 0.47 mmol) for 20 min. The yellow organic layer was separated, washed with water (4 × 20 mL) and passed through anhydrous Na_2SO_4. The solvent was removed completely under vacuum to afford **2** as red oil. Yield: 0.09 g (47%). ^{1}H NMR: δ 4.17 (s, 2H, CH_2), 7.08–8.29 (m, 10H, aromatic protons) ppm.

Compound ***3***: A solution of **3a** (0.22 g, 0.50 mmol) in dichloromethane (5 mL) and diethyl ether ~50 mL was shaken with an aqueous solution of $Na_2S_2O_5$ (0.09 g, 0.47 mmol) for 30 min. The yellow organic layer was separated, washed with water (4 × 20 mL) and passed through anhydrous Na_2SO_4. The resulting solution was reduced to about 2 mL, diluted with hexane (5 mL) and the solution kept in a deep freezer. The resulting yellow crystalline solid was recrystallized from diethyl ether to give **3** as yellow rectangular crystals. Yield: 0.08 g (43%). M.p.: 72 °C. Anal. Calc. for $C_{15}H_{16}OSTe$ (371.95): C, 48.44; H, 4.34; Te, 34.31. Found: C, 48.24; H, 4.30; Te, 34.65. ^{1}H NMR: δ 2.29 (s, 3H, *p*-Me), 2.51 (s, 6H, *o*-Me), 3.94 (s, 2H, CH_2), 6.88–7.56 (m, 5H, aromatic protons) ppm.

3.2.4. Oxidative addition reactions of *2*, *3* with dihalogens

Compound ***2b***: Bromine (0.03 mL, 0.50 mmol) in hexane was added dropwise at room temperature to a stirred solution of **2** (0.19 g, 0.50 mmol) in the same solvent (~10 mL). A yellow solid began to separate instantly and the mixture was stirred for another 15 min to complete the reaction. The separated solid was dissolved in dichloromethane and the solution passed through a short silica column. Addition of petroleum ether (60–80) to the concentrated solution afforded **2b** as yellow crystals. Yield: 0.25 g (94%). M.p.: 165 °C. Anal. Calc. for $C_{16}H_{12}OSTeBr_2$ (539.74): C, 35.60; H, 2.24; Te, 23.64. Found: C, 34.90; H, 2.20; Te, 23.80. ^{1}H NMR: δ 5.75 (s, 2H, CH_2), 7.63–8.27 (m, 10H, aromatic protons) ppm. $^{13}C\{^1H\}$ NMR: δ 64.0 (CH_2), 126.6, 126.8, 127.4, 128.2, 128.8, 129.5, 131.8, 132.7, 133.0, 133.4, 134.3, 135.3, 137.1, 140.2 (aromatic carbons), 184.0 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 697 ppm.

Likewise, **3b** was obtained as yellow crystals from **3** (0.19 g, 0.50 mmol) and Br_2 (0.03 mL, 0.50 mmol). Yield: 0.23 g (87%). M.p.: 165 °C. Anal. Calc. for $C_{15}H_{16}OSTeBr_2$ (531.76): C, 33.88; H, 3.03; Te, 24.00. Found: C, 33.80; H, 3.12; Te, 24.10. ^{1}H NMR: δ 2.34 (s, 3H, *p*-Me), 2.75 (s, 3H, *o*-Me), 2.79 (s, 3H, *o*-Me), 5.70 (s, 2H, CH_2), 6.98 (s, 1H, *m*-H mesityl ring), 7.06 (s, 1H, *m*-H mesityl ring), 7.22 (t, 1H, thiophene ring), 7. 83, 7.85 (d, 1H, thiophene ring), 7.86, 7.87 (d, 1H, thiophene ring) ppm. $^{13}C\{^1H\}$ NMR: δ 21.0 (*p*-Me), 23.3 (*o*-Me), 24.6 (*o*-Me), 61.2 (CH_2), 128.8, 130.5, 131.5, 131.6, 135.0, 136.9, 139.6, 140.4, 141.2, 142.3 (aromatic carbons), 184.5 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 704 ppm.

3.2.5. Metathetical reactions of *2a*, *3a* to *2c*, *3c*

Compound ***2c***: A solution of **2a** (0.23 g, 0.50 mmol) in dichloromethane (30 mL) was stirred with KI (0.17 g, 1.0 mmol) for 3 h. The potassium halides were removed by filtration. Concentration of the filtrate and addition of petroleum ether (40–60) afforded orange **2c**. Use of NaI gave **2c** in comparable yield. Yield: 0.23 g (71%). M.p.: 156 °C. Anal. Calc. for $C_{16}H_{12}OSTeI_2$ (633.74): C, 30.32; H, 1.91; Te, 20.13. Found: C, 30.10; H, 1.98; Te, 20.18. ^{1}H NMR: δ 5.77 (s, 2H, CH_2), 7.1–8.5 (m, 10H, aromatic protons) ppm. $^{125}Te\{^1H\}$ NMR: δ 606, 984 (0.75:0.25) ppm.

Compound **3c** was prepared in a way similar by metathesis of **3a** (0.22 g, 0.50 mmol) with NaI or KI (1.0 mmol) as orange crystals. Yield: 0.19 g (64%). M.p.: 98 °C. Anal. Calc. for $C_{15}H_{16}OSTeI_2$ (625.76): C, 28.79; H, 2.58; Te, 20.39. Found: C, 28.78; H, 2.60; Te, 20.38; ^{1}H NMR: δ 2.32 (s, 3H, *p*-Me), 2.64 (s, 6H, *o*-Me), 5.73 (s, 2H, CH_2), 6.93(s, 1H, *m*-H mesityl ring), 7.02 (s, 1H, *m*-H mesityl ring), 7.22 (s, 1H, thiophene ring), 7.82 (s, 2H, thiophene ring) ppm. $^{13}C\{^1H\}$ NMR: δ 21.0 (*p*-Me), 23.2 (*o*-Me), 25.7 (*o*-Me), 58.9 (CH_2), 127.2, 128.4, 130.7, 133.7, 133.4, 135.0, 136.9, 140.3, 142.1, 147.10 (aromatic carbons) ppm. $^{125}Te\{^1H\}$ NMR: δ 590, 885(1:1) ppm.

Table 3
Crystal data and structure refinement details of **1**, **1b**, **2a**, **2b** and **3a**.

	1	**1b**	**2a**	**2b**	**3a**
empirical formula	$C_{12}H_{10}O_2S_2Te$	$C_{12}H_{10}Br_2O_2S_2Te$	$C_{16}H_{12}Cl_2OSTe$	$C_{16}H_{12}Br_2OSTe$	$C_{15}H_{16}Cl_2OSTe$
formula mass ($g\ mol^{-1}$)	377.92	537.74	450.82	539.74	442.84
temp (K)	110(2)	295(2)	295(2)	295(2)	295(2)
wavelength, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
cryst size (mm^3)	0.48 × 0.43 × 0.18	0.88 × 0.57 × 0.31	0.51 × 0.47 × 0.36	0.51 × 0.42 × 0.35	0.56 × 0.21 × 0.18
space group	*P* 1 21/*c* 1	*P* −1	*P* 1 21/*n* 1	*P* 1 21/*n* 1	*P* 1 21/*c* 1
a (Å)	11.4870(3)	7.1593(4)	9.5437(2)	9.6524(4)	8.8076(2)
b (Å)	7.8833(3)	9.7490(5)	13.5609(3)	13.5973(8)	13.1440(3)
c (Å)	14.7573(4)	12.0975(6)	13.0199(3)	13.3312(6)	15.0915(4)
α (deg)	90	109.268(4)	90	90	90
β (deg)	106.206(3)	96.401(4)	107.763(3)	108.220(4)	101.641(2)
Γ (deg)	90	94.559(4)	90	90	90
V ($Å^3$)	1283.26(7)	785.98(7)	1604.72(6)	1661.95(14)	1711.17(7)
Z	4	2	4	4	4
ρ_{calcd} ($Mg\ m^{-3}$)	1.956	2.272	1.866	2.157	1.719
abs coeff (mm^{-1})	2.629	7.235	2.311	6.719	2.165
F(000)	728	504	872	1016	864
index ranges	$-17 \le h \le 15$ $-9 \le k \le 11$ $-16 \le l \le 22$	$-10 \le h \le 10$ $-14 \le k \le 10$ $-17 \le l \le 18$	$-14 \le h \le 14$ $-20 \le k \le 19$ $-19 \le l \le 19$	$-14 \le h \le 14$ $-12 \le k \le 19$ $-20 \le l \le 16$	$-12 \le h \le 7$ $-18 \le k \le 19$ $-18 \le l \le 22$
no. of rflns collected	8934	9461	16172	13556	14373
no. of indep rflns	4234 (R(int) = 0.0279)	5040 (R(int) = 0.0519)	5418 (R(int) = 0.0265)	5469 (R(int) = 0.0416)	5678 (R(int) = 0.0238)
completeness to θ_{max} (%)	99.3	98.4	99.3	99.0	99.1
abs cor	Semi-empirical from equivalents	Analytical	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
max, min transmission	1.00000, 0.38285	0.174, 0.047	1.00000, 0.82083	1.00000, 0.12410	1.00000, 0.42309
refinement method	Full-matrix least-squares on F2				
no. of data/restraints/params	4234/0/154	5040/0/188	5418/0/190	5469/0/180	5678/0/185
goodness of fit on F^2	0.976	0.942	1.076	0.951	1.017
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0267, wR2 = 0.0577	R1 = 0.0485, wR2 = 0.1051	R1 = 0.0353, wR2 = 0.0966	R1 = 0.0448, wR2 = 0.1057	R1 = 0.0313, wR2 = 0.0652
R indices (all data)	R1 = 0.0410 wR2 = 0.0605	R1 = 0.0908 wR2 = 0.1164	R1 = 0.0570 wR2 = 0.1021	R1 = 0.0833 wR2 = 0.1138	R1 = 0.0524 wR2 = 0.0700
largest diff peak/hole ($e\ Å^{-3}$)	0.658/−0.776	1.361/−0.974	1.122/−1.048	1.376/−1.260	0.595/−0.504
extinction coefficient		0.0072(9)			0.0034(4)

3.2.6. Alternative Procedures for synthesis of *2b* and *3b*

To a solution of ArTeBr [prepared *in situ* by mixing dichloromethane solutions of NpI_2Te_2 (0.51 g, 1.0 mmol) or Mes_2Te_2 (0.49 g, 1.0 mmol) and Br_2 (0.05 mL, 1.0 mmol) at room temperature], α-bromoacetylthiophene (0.25 mL, 2.0 mmol) was added at room temperature under stirring. The reaction mixture was stirred for 24 h at room temperature and filtered to remove a black residue. The dark brown filtrate was passed through a small silica column, concentrated and an equal volume of petroleum ether (60–80) added. Yellow crystals separated on overnight cooling in a refrigerator. Yield: **2b**, 0.67 g (60%); **3b** 0.53 g (50%).

3.2.7. Crystallography

Single crystals suitable for X-ray crystallography were grown by slow evaporation of dichloromethane solutions of **1b**, **2a**, **2b** and **3a**. In case of the telluride **1**, cooling (−10 °C) of its solution in a mixture of dichloromethane/diethylether (1:10) resulted in the desired crystals. Intensity data were collected on an Oxford Diffraction Gemini CCD diffractometer with graphite-monochromated Mo-Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.34d program. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 and ORTEP figures generated using the program WinGX 2002 [23,24]. Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to non-hydrogen atoms. Hydrogen atoms attached to carbon were included in geometrically calculated positions using a riding model and were refined isotropically. Crystal data and structure refinement details are given in Table 3. ORTEP views of the molecular structures are depicted in Figs. 1–5, showing 30% (**1b**, **2a**, **2b**, **3a**) and 50% (**1**) probability displacement ellipsoids, omitting H atoms for clarity, and captioned with the geometrical parameters relevant to the primary geometry.

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Appendix A. Supplementary material

CCDC 780935, 780936, 780937, 780938, and 780939, contain the supplementary crystallographic data for **1**, **1b**, **2a**, **2b**, and **3a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

The centrosymmetric dimeric supramolecular units identified in the crystal lattice of **1b** and **1** (Figures S1 and S2) and parametric details of weak H-bonding C–H···O and C–H···Cl/Br in tabular form (Table S1) are given as supplementary information, can be found in the online version, at doi:10.1016/j.jorganchem.2010.07.025.

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