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Secondary bonding in functionalized organotellurium compounds: preparation and structural characterization of bis(acetamido)tellurium(IV) diiodide and bis(4-methylbenzoylmethyl)tellurium(II)

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Abstract

Elemental tellurium inserts, under mild conditions, between C–I bond of iodoacetamide to afford bis(acetamido)tellurium(IV) diiodide (NH_2COCH_2)$_2TeI_2$, **1**. Heating of *N*-bromomethylphthalimide with activated tellurium powder however, resulted in the formation of bis(phthalimido)methane, **2**, instead of the expected product bis(phthalimidomethyl)tellurium(IV) dibromide. The IR spectrum of **1** is indicative of intramolecular Te···O=C interaction which is also substantiated by its single-crystal structure. The compound with planar small-bite chelating organic ligands acquires butterfly shape that imparts almost perfect C_{2v} molecular symmetry but unlike other organotellurium(IV) iodides, the solid state structure of **1** is devoid of any intermolecular Te···I or I···I secondary interactions owing to the presence of intramolecular Te···O secondary bonds as well as intermolecular N–H···O, N–H···I and C–H···I hydrogen bonds. Bis(4-methylbenzoylmethyl)telluride (4-MeC$_6$H$_4$COCH$_2$)$_2$Te, **3b**, prepared by the reduction of the corresponding dibromide, is the first structurally characterized acyclic dialkyltelluride and interestingly, does not involve intramolecular Te···O=C interaction invariably present in the parent dihalides (4-YC$_6$H$_4$COCH$_2$)$_2$TeX$_2$ (Y = H, X = I **4a**; Y = H, X = Br **5a**; Y = MeO, X = Br **5c**). Weak intermolecular Te···Te and C–H···O hydrogen bonds appear to be the non covalent intermolecular associative forces that dominate its crystal packing in the solid state of this Te(II) derivative. The dialkyltellurides (4-YC$_6$H$_4$COCH$_2$)$_2$Te, (Y = H, **3a**, Me, **3b**) undergo oxidation in presence of (SCN)$_2$ to give the corresponding bis(isothiocyanato)tellurium(IV) derivatives and form 2:1 adducts with Pt(II) and Pd(II) chlorides.
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1. Introduction

Solid state structural studies on diorganotellurium(IV) dihalides indicate that the primary geometry about Te atom in these monomeric covalent compounds is invariably pseudo trigonal bipyramidal with two Te–C bonds and the stereochemically active lone pair of electrons occupying the equatorial sites and the two halogen atoms occupying the apical sites [1]. The presence of ubiquitous intermolecular Te···X (halogen) interactions in the non functionalized diorganotellurium(IV) dihalides [2] and their significance in supramolecular association and crystal engineering have been surveyed recently [3]. However, if an organic

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ligand is functionalized to bear a nucleophillic atom A, viz. N, O, S, Cl or Br, chelation via Te···A secondary interactions affects the stability, chemical reactivity [4] and biological activity [5] significantly. Even an ionic structure $[Ph(2-Me_2NCH_2C_6H_4)TeX]^+X^-$ for [2-((dimethylamino)methyl)phenyl]phenyltellurium dibromide/iodide involving stabilization of asymmetric telluronium cation by means of intramolecular Te···N secondary interaction has been structurally characterized [6]. Among unsymmetrical diorganotellurium(IV) dichlorides with $ArRTeCl_2$ [7] or $ArAr'TeCl_2$ [8] stoichiometry (where R and Ar or Ar′ are the sp^3 and sp^2-hybridized carbon-linked organic groups respectively and only one is a small-bite O donor bidentate ligand) intramolecular 1,4-type Te···O secondary interaction is preferred to intermolecular Te···Cl secondary interactions as the latter may or may not act as molecular associative force to result in a supramolecular structure. The recently determined solid state structures of symmetrical bis(2,6-dimethoxyphenyl)tellurium dihalides [9] are however, devoid of any intermolecular Te···X secondary interaction presumably, due to the formation of intramolecular 4-membered rings by both the organic ligands making the Te atom coordinatively saturated.

In order to examine (a) the generality of the observation that the 1,4-type Te···O interactions give rise to intramolecularly stabilized telluronium cations also in the functionalized symmetrical diorganotellurium(IV) dihalides ($R_2^FTeX_2$; $R^F =$ functionalized organic ligand) and (b) if such intramolecular interactions are retained in the corresponding diorganotellurides R_2^FTe, we have attempted [10] to prepare a number of $R_2^FTeX_2$ by the insertion of tellurium across Csp^3-X (X = Br, I) bond (Eq. (1)) and study their solid state structures in comparison to their reduction products R_2^FTe.

$$2R^F\!-\!X + Te \rightarrow R_2^FTeX_2 \tag{1}$$

In this paper structural characterization of bis(acetamido)tellurium(IV) diiodide, **1** and bis(4-methylbenzoylmethyl)telluride, **3b**, is described. Also included in this communication are some observations on the ligational behaviour of **3** and their oxidative reaction with thiocyanogen.

2. Results and discussion

Elemental tellurium reacts with iodoacetamide at ~100 °C in toluene to give mustered yellow coloured crystalline bis(acetamido)tellurium(IV) diiodide, **1**, in quantitative yield. **1** is sparingly soluble in chloroform and acetone. The IR spectrum shows $v(CO)$ at 1651 cm^{-1} which is shifted downfield with respect to the acetamide (1680 cm^{-1}) indicating coordination of the CO group to Te(IV). The ^1H NMR of a saturated solution

of **1** in CDCl$_3$ shows a singlet for methylene protons at δ 4.46 and another at δ 7.74 due to NH$_2$ protons. The ^{13}C NMR spectrum of **1** consists of two singlets at δ 168 for carbonyl and δ 39 for methylene carbon atoms.

2.1. Crystal structure of bis(acetamido)tellurium(IV) diiodide 1

The ORTEP view and atom numbering of the molecular structure of compound **1** is shown in Fig. 1 and selected interatomic distances, bond angles and torsion angles are given in Table 1. (H$_2$NCOCH$_2$)$_2$TeI$_2$ crystallizes in the monoclinic crystal system and the $P2_1/n$ space group with four molecules per unit cell and is isomorphous with (PhCOCH$_2$)$_2$TeX$_2$, (X = Br, I) [10a]. The primary molecular geometry is pseudo-trigonal bipyramidal with the two I atoms occupying apical positions. The stereochemical activity of the lone pair at one of its equatorial corner is comparable to that observed in case of other dialkyltellurium(IV) dihalides [10,11] as the reduced equatorial C–Te–C and axial X–Te–X angles for all such compounds lie within the narrow ranges 93.04–96.63° and 172.47–174.50°, respectively. Interatomic distances of Te atom from the amido O atoms (2.837 and 2.854 Å) are short enough to qualify for bonafide Te···O secondary interactions of appreciable strength. The acetamido groups attached to Te atom thus behave as small-bite chelating ligands and adopt cisoidal configuration about the central atom resulting thereby in a pentagonal bipyramidal molecular geometry with one equatorial corner occupied by the lone pair. Both the secondary bonded O atoms are almost coplanar with the C–Te–C equatorial plane and subtend an angle O$_{1A}$–Te–O$_{1B}$ of 156.14°, wide enough to accommodate the Te lone pair. Of particular interest is the presence of nucleophillic atoms with lone pairs of electrons in the region also occupied by the lone pair on Te as per VSEPR theory and may be compared with the presence of halogen atoms reported to be clustered in this region in many organotellurium(IV) halides as a result of intermolecular Te···X secondary bonds [1–3]. Another significant feature of the molecular structure of **1** is the planarity of –CONH$_2$ fragments as evident from the values of bond angles around N (each 120°) and torsion angles involving H–N–C–O atoms (each
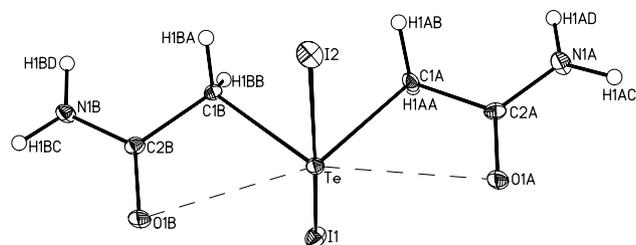

Fig. 1. ORTEP view of bis(acetamido)tellurium(IV) diiodide, **1**.

Table 1
Selected interatomic distances (Å) and angles (°) for bis(acetamido)tellurium(IV) diiodide, **1**

Te–C(1A)	2.137(7)	Te–C(1B)	2.117(7)
O(1A)–C(2A)	1.224(9)	O(1B)–C(2B)	1.228(9)
Te–I(1)	2.8714(8)	Te–I(2)	2.9146(8)
N(1A)–C(2A)	1.292(11)	N(1B)–C(2A)	1.317(10)
N(1A)–H(1N1)	0.88	N(1B)–H(2N1)	0.8800
N(1A)–H(1N2)	0.88	N(1B)–H(2N2)	0.8800
Te–O(1A)	2.839	Te–O(1B)	2.854
C(2A)–C(1A)–Te	104.7(5)	C(2B)–C(1B)–Te	105.9(5)
C(1B)–Te–C(1A)	95.9(3)	I(1)–Te–I(2)	172.72(2)
C(1B)–Te–C(1A)–C(2A)	166.3(5)	C(1A)–Te–C(1B)–C(2B)	171.2(5)
Te–C(1A)–C(2A)–O(1A)	8.3(9)	Te–C(1B)–C(2B)–O(1B)	−1.2(9)
Te–C(1A)–C(2A)–N(1A)	−171.7(7)	Te–C(1B)–C(2B)–N(1B)	−179.5(6)

Hydrogen bond parameters				
D–H–A	d(D–H) (Å)	d(H–A) (Å)	d(H–A) (Å)	⟨(DHA) (0)
N(1A)–H(1AC)...O(1B)#1	0.88	2.47	3.246(10)	148.2
N(1A)–H(1AC)...I(1)#1	0.88	3.24	3.861(8)	129.2
N(1A)–H(1AD)...O(1B)#2	0.88	2.12	2.914(9)	150.3
N(1B)–H(1BC)...I(2)#3	0.88	2.9	3.734(7)	158.7
N(1B)–H(1BD)...O(1A)#4	0.88	2.03	2.847(9)	154.9
C(1A)–H(1AB)...I(1)#4	0.99	3.02	3.977(8)	163.8

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, y + 1/2, -z + 3/2$; #2 $x + 1/2, -y + 1/2, z-1/2$; #3 $-x-1/2, y-1/2, -z + 3/2$; #4 $x-1/2, -y + 1/2, z-1/2$.

being close to 0° or 180°). This means the N atoms must be sp^2-hybridized. The C–N bond lengths 1.292(11) and 1.317(10) Å are also considerably shorter than the sum of single bond covalent radii of Csp^2 and N atoms (1.44 Å) (cf. [12]).

The crystal packing pattern of **1** is presented in Fig. 2. It depicts with dashes the contacts shorter than van der Waals' and that can be characterized as hydrogen bonds on the basis of parameters given in Table 1. The NH protons being adjacent to a C=O group in the amido fragment being sufficiently acidic form bifurcated (three-center) hydrogen bonds [13] where a given proton is held among the N donor and two acceptors, the O and I from the neighboring molecules. A given carbonyl O acceptor atom likewise, is also involved in two hydrogen bonds simultaneously. The shorter N–H bond length 0.88 Å in comparison to the sum of the covalent radii (1.02 Å) thus appears to be a manifestation of N–H···O/I hydrogen bonding. Likewise, CH groups bonded to the sufficiently electropositive Te(IV) atom being acidic enough cause C–H···I hydrogen bonds which possess the required linearity (⟨C–H···I = 163.8°) and donor–acceptor distance [interatomic d(H–I) = 3.016 Å]. The significant importance of relatively weak C–H···X hydrogen bonds (where X = F, O, N, Cl, Br, I) in the field of crystal engineering has been recognized earlier [13]. The donor–acceptor separation values in Table 1, indicate that N–H···O hydrogen bonds of moderate strength cooperated with the relatively weak N–H···I and C–H···I hydrogen bonds act as the molecular associative forces that result in the centrosymmetric supramolecular assembly in the solid state of the title compound. The crystal packing
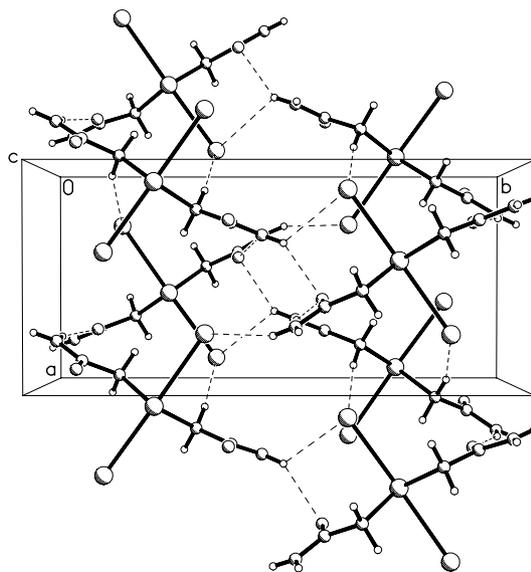

Fig. 2. Unit cell structure of bis(acetamido)tellurium(IV) diiodide, **1**.

is devoid of any intermolecular Te···I secondary bonding as the shortest distance (4.96 Å) between Te and I atoms of any neighboring pair of molecules is greater than the sum of their van der Waals radii (4.35 Å). It may thus be concluded that H-bonds are preferred to Te···X secondary interaction as the bonding motif for supramolecular self assembly in intramolecularly bonded functionalized diorganotellurium dihalides.

Halogen exchange reactions of **1** with MX (M = K or Ag; X = Cl, Br, N$_3$, SCN) did not proceed probably due to the insoluble nature of the reactants. In order to

extend the solid state studies to functionalized diorgano-tellurium(II) compounds, attempts were made to reduce **1** to $(NH_2COCH_2)_2Te$ with a variety of reducing agents. Thus, $NH_2NH_2 \cdot xH_2O$ and $Na_2S \cdot 9H_2O$ caused complete reduction of **1** to elemental tellurium. $Na_2S_2O_5$ did not react. Having failed to reduce **1** to the corresponding telluride we turned our attention to bis(4-substituted benzoylmethyl)tellurides $(4\text{-}YC_6H_4COCH_2)_2Te$, which were recently obtained in our laboratory by the reduction of $(4\text{-}YC_6H_4COCH_2)_2TeBr_2$. Since the dihalides $(4\text{-}YC_6H_4COCH_2)_2TeX_2$, are characterized by the presence of 1,4-type Te–O interactions, it appeared interesting to examine if such an interaction is retained in the $(4\text{-}YC_6H_4COCH_2)_2Te$.

2.2. Crystal structure of bis(4-methylbenzoylmethyl)telluride 3b

Among the known organotellurium(II) compounds for which solid state structures have been determined, leaving a cyclic telluride dibenzotelluraphene [14] and a few alkyl aryl tellurides with RTeAr stoichiometry [15], rest of the diaryltellurides Ar_2Te and aryltellurium(II) halide/pseudohalide ArTeX, are reported to be stabilized by the presence of intramolecular 1,5-type secondary interaction. In addition to 5-membered intramolecular ring formed by the functionalized organic ligand Ar, 1,4-type Te–O/S non bonded interactions have also been observed in ArTeY compounds where Y is a small-bite bidentate anionic group linked to Te(II) through O or S atom, viz. carboxylate $(RCOO^-)$ [16], dithioxanthate $(ROCSS^-)$ [17], dithiocarbamate (R_2NCSS^-) [18], dithiophosphate $[(RO)_2PSS^-]$ [17a,19] or dithiophosphinate $(R_2\,PSS^-)$ [19a,20]. We are not aware of any 1,4-type intramolecular Te(II)–O(carbonyl or ethereal) secondary interaction, though such an interaction involving only one of the carbonyl groups has been reported in case of $(PhCOCH_2)_2Se$ [21]. Moreover, unlike diaryltellurides which are solids, dialkyltellurides are generally malodorous liquids or low melting solids. As such only one report on the crystal structure of a cyclo-alkyltelluride [22] and none on any acyclic dialkyltelluride has so far appeared. Our earlier attempts to grow diffraction quality crystals of thermally and photo labile dialkyltellurides **3**, had failed. The yellow crystals gradually turned blackish within a couple of hours at room temperature. However, we have now observed that even after a couple of weeks if these blackish crystals are redissolved in pet. ether, filtered and allowed to crystallize at low temperature a small crop ($\sim$20% of the original) of yellow crystals can be recovered at least in case of **3b**.

The ORTEP view of the molecular structure with atom numbering is presented in Fig. 3 and selected bond parameters are given in Table 2. The Te–C distances 2.158(3) and 2.164(3) Å are longer than those
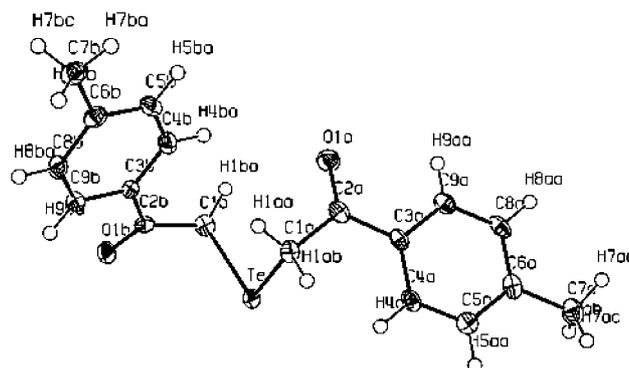

Fig. 3. ORTEP view of bis(4-methylbenzoylmethyl)telluride, **3b**.

observed in case of tellurium(IV) derivatives **1**, **5a** and **5c** (in the range 2.117–2.140 Å) and that of the sum of single bond covalent radii (2.142 Å) of Te and sp^3-hybridized C atoms, but comparable to the average value of Te–C distances (2.17 Å) reported for 1-telluracyclohexane-3,5-dione [22], the only structurally characterized compound where Te(II) is bonded to sp^3-hybridized C atoms. The 95.19(13)° value of C–Te–C angle in **3b** is reminiscent of the stereochemical activity of the lone pairs on Te atom and is typical of value observed for Ar_2Te and RArTe [92.3(2)–98.8(3)°] [4c,15,23]. The interesting feature of the structure of **3b** is the insignificant intramolecular 1, 4-type Te$\cdots$O=C secondary interaction as is evident from the interatomic distances between Te and the carbonyl oxygen atoms being 3.600 and 3.670 Å. The other consequences of the release of carbonyl O atoms from intramolecular Te$\cdots$O attractive non bonded interaction in going from the functionalized dialkyltellurium(IV) dihalides to their tellurides is (a) the attainment of almost ideal tetrahedral angle at the methylene C atoms [107.8(2)° and 108.7(2)°] and (b) the complete loss of the planarity of the cisoidal R_2Te moiety observed in the corresponding diorganotellurium(IV) derivatives, resulting therein the transoidal orientation of the benzoyl fragments so as to minimize the repulsion between lone pairs on the carbonyl O atoms in the diorganotellurium(II) compound.

It may be emphasized here that in spite of the absence of any significant intramolecular Te$\cdots$O=C interaction, at least in the solid state, the v(CO) absorptions in the infrared spectrum of **3** are observed at lower wave numbers (1656–1640 cm^{-1}) as compared to those in the parent acetophenones (1697–1689 cm^{-1}) and their 2-bromo derivatives (1693–1684 cm^{-1}). Thus, even a significant negative shift of this frequency in case of the tellurides with respect to the parent acetophenones or 2-bromoacetophenones cannot unequivocally be taken as an evidence for Te$\cdots$O=C coordination unless supported by X-ray data. It is interesting to note that vCO for (PhC-

Table 2
Selected interatomic distances (Å) and angles (°) for bis(4-methylbenzoylmethyl)telluride, **3b**

Te–C(1A)	2.164(3)	Te–C(1B)	2.158(3)		
O(1A)–C(2A)	1.220(4)	O(1B)–C(2B)	1.233(4)		
C(1A)–C(2A)	1.514(5)	C(1B)–C(2B)	1.501(5)		
C(2A)–C(3A)	1.500(5)	C(2B)–C(3B)	1.493(5)		
C(2A)–C(1A)–Te	107.8(2)	C(2B)–C(1B)–Te	108.7(2)		
C(1B)–Te–C(1A)	95.19(13)				
C(1A)–Te–C(1B)–C(2B)	−90.4(2)	C(1B)–Te–C(1A)–C(2A)	−75.5(2)		
Te–C(1A)–C(2A)–O(1A)	94.8(3)	Te–C(1B)–C(2B)–O(1B)	−87.0(3)		
O(1A)–C(2A)–C(3A)–C(4A)	−175.2(3)	O(1B)–C(2B)–C(3B)–C(4B)	−162.5(3)		
O(1A)–C(2A)–C(3A)–C(9A)	6.3(5)	O(1B)–C(2B)–C(3B)–C(9B)	16.1(5)		
Hydrogen bond parameters					
D–H–A	*d*(D–H) (Å)	*d*(H–A) (Å)			⟨(DHA) (°)
C(1A)–H(1AB)...O(1B)#1	0.99	2.46		3.401(4)	158.6
C(1A)–H(1AB)...O(1B)#1	0.98	2.56		3.495(5)	158.8

Symmetry transformations used to generate equivalent atoms: #1 −*x* + 1/2, *y*−1/2, −*z* + 1/2.

OCH$_2$)$_2$S (1690 cm^{-1}), (PhCOCH$_2$)$_2$Se (1670 cm^{-1}) [24] and (PhCOCH$_2$)$_2$Te (1642 cm^{-1}) [10b] decrease with increasing mass of the chalcogen.

The crystal packing pattern of **3b** is shown in Fig. 4. The Te–Te interatomic distance 4.147 Å between a pair of molecules is shorter than the sum of their van der Waals radii (4.40 Å). At the same time H-bond parameters given in Table 2, clearly indicate the presence of C–H–O hydrogen bonds formed by the carbonyl O atoms (as H-bond acceptors) and C of methylene or methyl groups (as H-bond donors). The shortest distance between tellurium and the centroid of any aromatic ring that has been observed in the crystal packing is 4.057 Å. The distance is too long to account for the presence of any significant Te–π (aryl) secondary interaction as a bonding motif for supramolecular assembly [25]. The solid state structure of compound **3b** thus appears to consist of dimeric units formed by means of a Te···Te secondary interaction and a (methylene)C–H···O (carbonyl) H-bond which in turn are linked into chains via (methyl)C–H···O (carbonyl) H-bonds that give rise to centrosymmetric supramolecular structure.
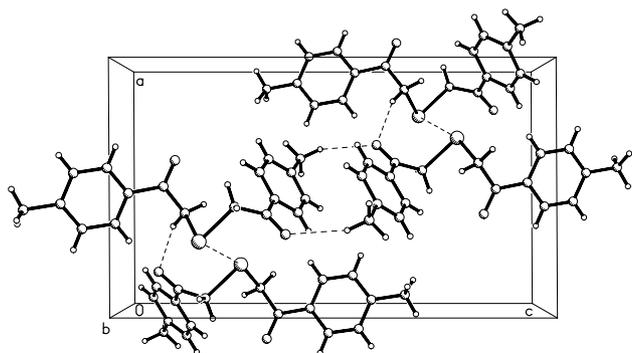

Fig. 4. Unit cell structure of bis(4-methylbenzoylmethyl)telluride, **3b**.

2.3. Reactions of bis(4-substituted benzoylmethyl)tellurides 3

2.3.1. Reactions of 3 with pseudohalogen (SCN)$_2$

Oxidative addition of dihalogens to **3** has been reported earlier [10b]. Thiocyanogen reacts with **3a** and **3b** at 0 °C to afford yellowish oxidative addition products (4-YC$_6$H$_4$COCH$_2$)$_2$Te(SCN)$_2$, which are sparingly soluble in common organic solvents. The *v*(CN) absorption appears below 2100 cm^{-1} in their IR spectra which indicates these to be N-bonded [26] isothiocyanto derivatives. The broader shape of *v*(CN) absorption with a shoulder, insolubility and colour of the compounds probably hint at some molecular association via weak Te–S bonds formed by the bridging thiocyanate groups in the solid state of these functionalized dialkyltellurium(IV) diisothiocyantes.

2.3.2. Reactions of 3 with Pt(II) and Pd(II) chlorides

Non-functionalized cyclic and acyclic diorganotelluroethers (R$_2$Te) behave as monodentate ligands and form 1:2 complexes with d^8 and d^{10} metal centers. (Te, N) or (Te, O) hybrid telluroethers often form 1:1 complexes with d^8 metal centers in which both the ligating atoms coordinate the central metal atom [27]. As the dialkyltellurides **3**, possess both hard and soft donor centers and the carbonyl oxygen atoms are not involved in intramolecular coordination, their ligational behavior towards Pt(II) and Pd(II) chlorides has been examined. Brown/yellow adducts MCl$_2$·2R$_2$Te, as evident from elemental analyses, are obtained when a solution of diketonic telluroethers **3**, in dichloromethane is added to a solution of MCl$_2$(PhCN)$_2$ (M = Pt, Pd). The adducts are only sparingly soluble in chloroform, acetone and alcohol. The IR spectra of the adducts show *v*(CO) at 1645–1668 cm^{-1} which is ∼8 cm^{-1} higher than for the corresponding free telluroether ligand **3**. The deshielding of the methylene protons in the ^{1}H NMR

spectra of the adducts (wherever meaningful spectra of saturated solutions could be obtained) indicate the monodentate behavior of **3** with only Pt/Pd–Te interaction in the adducts.

2.4. Reactions of elemental Te with other functionalized halomethyl organic substrates

N-Bromomethylphthalimide in refluxing toluene does not react with Te powder but when heated (∼150 °C) together in absence of a solvent afforded crystalline bis(phthalimido)methane **2** and other unidentified non-tellurium containing product(s) (see Section 3). A plausible mechanism for the formation of **2** is given in Scheme 1 and is based on the observation that the parent phthalimide remains unaffected when heated in absence of Te and the general lability of RTeX species and Te–N bonds. The colourless crystals of compound **2** melt at 230 °C and are soluble in common organic solvent. The IR spectrum shows $v(CO)$ at 1732 cm^{-1} which is very close to that observed in case of *N*-bromomethylphthalimide 1728 cm^{-1}. The ^{1}H NMR spectrum consists of a singlet at δ 5.46 for methylene protons and two multiplets at δ 7.73 and δ 7.86 for the aryl protons.

Both, *N*-bromoethylphthalimide and 2-bromoethanol failed to react with Te in the sense of Eq. (1) up to 100 °C even in presence of NaI which shows that it is imperative for a functional group to be present at the α-carbon atom for the insertion of Te (Eq. (1)) to take place. Iodoacetic acid also failed to react as it sublimes out (∼50 °C) before it could react with Te powder.

3. Experimental

3.1. General

The commercial tellurium powder (Fluka) was activated by washing with conc. HCl and water and drying at 120 °C. It was grinded for 15 min just before use. Iodoacetamide, *N*-(2-bromoethyl)phthalimide, *N*-bromomethylphthalimide, 2-bromoethanol and iodoacetic acid were used as received. PtCl$_2$(PhCN)$_2$ and PdCl$_2$(PhCN)$_2$ were prepared by standard methods. Whenever required the reactions were carried out under dry N$_2$ atmosphere. The ^{1}H and ^{13}C NMR spectra were
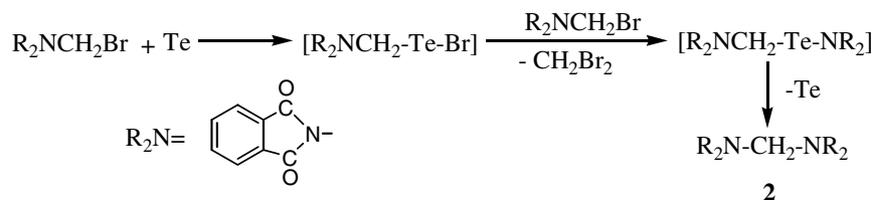
recorded at 300.13 and 50.32 MHz, respectively, in CDCl$_3$ on a Varian DRX 300 spectrometer using TMS as internal standard. IR spectra were examined as KBr pellets using a Perkin–Elmer RX1 spectrometer. Fast atom bombardment (FAB) mass spectrum of **1** was recorded on a JEOL SX 102/DA-6000 Mass Spectrometer/Data System using Argon/Xenon (6 kV, 10 mA) as the bombarding gas. The accelerating voltage was 10 kV and *m*-nitrobenzyl alcohol was used as the matrix. Elemental carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba 1108 make analyzer. Tellurium was estimated volumetrically and the halogen content gravimetrically as silver halide. The preparation of bis(*p*-substituted benzoyl methyl)tellurides has been reported elsewhere [10b].

3.1.1. Synthesis of bis(acetamido)tellurium(IV) diiodide 1

A mixture of activated tellurium powder (0.65 g, 5 mmol) and iodoacetamide (1.85 g, 10 mmol) in 3 ml toluene was heated (∼100 °C) with stirring till all the tellurium was consumed. The resulting yellow paste was freed from toluene by decantation and washing with ether. The residue was extracted with hot acetone. The solvent was removed under reduced pressure and the residue was recrystallized from acetone to give yellow needles of **1**. Yield (2.3 g, 92%); m.p. 152 °C; Anal. Found: C, 9.62; H, 1.58; N, 5.53; I, 50.50; Te, 24.90. Calc. for C$_4$H$_8$N$_2$O$_2$I$_2$Te: C, 9.65; H, 1.66; N, 5.63; I, 51.01; Te, 25.64%. IR (v/cm^{-1}), 1650 (CO), 3259 (N–H); ^{1}H NMR (δ ppm), 7.74 (4H, s, 2NH$_2$), 4.46 (4H, s, 2CH$_2$); ^{13}C NMR, (δ ppm), 167.97 (CO), 38.92 (CH$_2$); FAB mass, *m/z* 373 (M$^+$ − I for ^{130}Te with characteristic isotopomeric pattern).

3.1.2. Oxidative addition of (SCN)$_2$ to (4-YC$_6$H$_4$CO-CH$_2$)$_2$ Te (Y = H **3a**, Me **3b**)

(C$_6$H$_5$COCH$_2$)$_2$Te(NCS)$_2$. A freshly prepared solution of (SCN)$_2$ [obtained by the reaction of Pb(SCN)$_2$ with Br$_2$ in CCl$_4$] (0.145 g, 1.25 mmol) in CCl$_4$ (20 ml) was slowly added to the solution of (C$_6$H$_5$COCH$_2$)$_2$Te (0.35 g, 1 mmol) in the same solvent under stirring at 0 °C. White product separated during addition. It was stirred for ∼1 h and filtered and washed 4 times with CCl$_4$. Light yellow colored product was recrystallized from CH$_2$Cl$_2$ to give (C$_6$H$_5$COCH$_2$)$_2$Te(NCS)$_2$. Yield (0.33 g, 64%); m.p. 120 °C; Anal. Found: C, 44.39; H,

$$R_2NCH_2Br + Te \longrightarrow [R_2NCH_2\text{-Te-Br}] \xrightarrow[- CH_2Br_2]{R_2NCH_2Br} [R_2NCH_2\text{-Te-NR}_2]$$

$$\downarrow -Te$$

$$R_2N\text{-CH}_2\text{-NR}_2$$

2

Scheme 1.

2.64; N, 5.90; Te, 27.30. Calc. for $C_{18}H_{14}O_2S_2N_2Te$: C, 44.85; H, 2.93; N, 5.81; Te, 26.47%. IR (v/cm^{-1}), 1683.2 (CO), 2001.0 (NCS); ^{1}H NMR (δ ppm), 7.99–7.44 (10H, m, 2 Ar), 4.77 (4H, s, 2CH$_2$).

$(4\text{-}MeC_6H_4COCH_2)_2Te(NCS)_2$ was prepared similarly from $(4\text{-}MeC_6H_4COCH_2)_2Te$ and $(SCN)_2$. Yield (60%); m.p. 98 °C; Anal. Found: C, 47.67; H, 3.14; N, 5.32; Te, 24.67. Calc. for $C_{20}H_{18}O_2S_2N_2Te$: C, 47.09; H, 3.56; N, 5.49; Te, 25.01%. IR (v/cm^{-1}), 1650.7 (CO), 2067.9 (NCS); ^{1}H NMR (δ ppm), 7.93-7.31 (8H, m, 2 Ar), 4.73 (4H, s, 2CH$_2$), 2.45 (6H, s, 2CH$_3$).

3.1.3. Reaction of $(4\text{-}YC_6H_4COCH_2)_2Te$ $(Y = H, Me, MeO)$ 3 with $MCl_2 \cdot (PhCN)_2$ $(M = Pt$ and $Pd)$

$PtCl_2[(C_6H_5COCH_2)_2Te]_2$. To a solution of $[PtCl_2(PhCN)_2]$ (0.47 g, 1.0 mmol) in CH_2Cl_2 (20 ml) was added to a solution of $(C_6H_5COCH_2)_2Te$ (0.73 g, 2.0 mmol) in the same solvent slowly. On the basis of TLC monitoring the reaction was completed in 14 h. The reaction mixture was concentrated and addition of pet-ether afforded the 1:2 complex, Yield (0.60 g, 60%); m.p. 164 °C; Anal. Found: C, 38.28; H, 2.68; Te, 24.60. Calc. for $C_{32}H_{28}O_4Cl_2Te_2$ Pt: C, 38.52; H, 2.82; Te, 25.57%. IR (v/cm^{-1}), 1657.7 (CO); ^{1}H NMR (δ ppm), 7.7 (20H, m, 4 Ar), 2.60 (8H, s, 4CH$_2$).

The following adducts were prepared similarly.

$PtCl_2[(4\text{-}MeC_6H_4COCH_2)_2Te]_2$, Yield (81%); m.p. 186 °C; Anal. Found: C, 41.30; H, 3.54; Te, 24.81. Calc. for $C_{36}H_{36}O_4Cl_2Te_2Pt$: C, 41.03; H, 3.44; Te, 24.21%. IR (v/cm^{-1}), 1663.4 (CO); ^{1}H NMR (δ ppm), 7.93–7.33 (16H, m, 4 Ar, 5.29 (8H, s, 4CH$_2$), 2.46 (12H, s, 4CH$_3$).

$PtCl_2[(4\text{-}MeOC_6H_4COCH_2)_2Te]_2$, Yield (55%); m.p. 190 °C; Anal. Found: C, 38.50; H, 3.02; Te, 22.21. Calc. for $C_{36}H_{36}O_8Cl_2Te_2Pt$: C, 38.68; H, 3.24; Te, 22.81%. IR (v/cm^{-1}), 1668.7 (CO).

$PdCl_2[(C_6H_5COCH_2)_2Te]_2$, Yield (70%); m.p. 178 °C; Anal. Found: C, 42.55 ; H, 2.86; Te, 27.40. Calc. for $C_{32}H_{28}O_4Cl_2Te_2Pd$: C, 42.28; H, 3.10; Te, 28.07%. IR (v/cm^{-1}), 1658.0 (CO); ^{1}H NMR (δ ppm), 7.97–7.45 (20H, m, 4 Ar), 4.65 (8H, s, 4CH$_2$).

$PdCl_2[(4\text{-}MeC_6H_4COCH_2)_2Te]_2$, Yield (72%); m.p. 186–189 °C; Anal. Found: C, 44.60; H, 3.56; Te, 25.60. Calc. for $C_{36}H_{36}O_4Cl_2Te_2Pd$: C, 44.80; H, 3.76; Te, 26.43%. IR (v/cm^{-1}), 1653.2 (CO).

$PdCl_2[(4\text{-}MeOC_6H_4COCH_2)_2Te]_2$, Yield (48%); m.p. 188-195 °C; Anal. Found: C, 41.86; H, 3.70; Te, 23.48. Calc. for $C_{36}H_{36}O_8Cl_2Te_2Pd$: C, 42.01; H, 3.52; Te, 24.78%. IR (v/cm^{-1}), 1645.2 (CO); ^{1}H NMR (δ ppm), 8.02–6.90 (16H, m, 4 Ar), 4.68 (8H, s, 4CH$_2$), 3.90 (12H, s, 4CH$_3$).

3.1.4. Reaction of Te with N-bromomethylphthalimide

N-Bromomethylphthalimide (1.0 g, 3.9 mmol) and activated Te powder (0.25 g, 2.0 mmol) were heated together at 150 °C in absence of a solvent. Brownish vapors were deposited at the wall of the flask and the reaction mixture became dark solid. It was cooled and 5 ml toluene was added. After refluxing for 15 min the solid dissolved to give yellowish transparent solution and a little black solid indicating consumption of most of the Te powder. Workup of the reaction mixture by distilling off the solvent and washing the residue with chloroform, however, gave Te powder (0.21 g). The filtrate, after concentration and addition of pet-ether, was cooled to 0 °C. Colourless crystals of bis(phthalimido)methane, **2**, were separated. Yield, (0.20 g); m.p. 230 °C; Anal. Found: C, 67.01; H, 3.21; N, 9.50. Calc. for $C_{17}H_{10}N_2O_4$: C, 66.70; H, 3.26; N, 9.15%. IR(v/cm^{-1}), 1732.1 (CO); ^{1}H NMR (δ ppm), 7.88–7.70 (8H, m, 2Ar), 5.64 (2H, s, CH$_2$). Concentration of the mother liquor afforded yellow solid (0.25 g) of variable composition and melting point.

The parent *N*-bromomethylphthalimide remained unaffected when heated in absence of Te powder under similar conditions.

3.2. X-ray crystallography

The conditions to grow suitable crystals of **1** and **3b** for crystallographic studies are given at appropriate places in the result and discussion section. The X-ray diffraction measurements were performed at 103(2) K using a Bruker PS4 diffractometer employing graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Details of the crystallographic parameters for compounds **1** and **3b** are given in Table 3. The structures were solved by direct methods (SIR92) [28] and expanded using

Table 3
Crystallographic data for compounds **1** and **3b**

	1	**3b**
Empirical formula	$C_4H_8I_2N_2O_2Te$	$C_{18}H_{18}O_2Te$
Formula weight	497.52	393.92
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/n$
Unit cell dimensions		
a (Å)	7.3936(13)	11.2075(13)
b (Å)	16.073(3)	7.3963(8)
c (Å)	9.0676(16)	19.167(2)
α (°)	90	90
β (°)	91.430(3)	90.288(2)
γ (°)	90	90
U (Å^3)	1077.3(3)	1588.8(3)
Temperature (K)	103(2)	103(2)
Wavelength	0.71073	0.71073
Z	4	4
μ(Mo Kα) (mm^{-1})	8.457	1.874
Reflections collected	7067	11295
Independent reflections	2497 [$R_{int} = 0.0642$]	3798 [$R_{int} = 0.0530$]
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0425$, $wR_2 = 0.1158$	$R_1 = 0.0339$, $wR_2 = 0.0579$
R indices (all data)	$R_1 = 0.0564$, $wR_2 = 0.1275$	$R_1 = 0.0654$, $wR_2 = 0.0650$

Fourier techniques (DIRDIF 94) [29]. Data reduction and refinement were generally routine [30].

4. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC numbers are 241611 for bis(acetamido)tellurium diiodide **1** and 224723 for bis(4-methylbenzoylmethyl)telluride **3b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44-1223-336-033; or e-mail: deposite@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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