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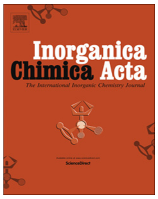

Research paper

Piperidin-1-ylamidomethyltellurium derivatives: Synthesis and solid state structures

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ABSTRACT

Oxidative insertion of low valent tellurium, Te(0) and Te(II), into the C—Br bond of α-bromoacetylpiperidine proceeds readily under mild conditions and provides a direct synthetic route to stable, crystalline piperidin-1-ylamidomethyltellurium(IV) dibromides, $(C_5H_{10}NCOCH_2)_2TeBr_2$, **1b** and $(C_5H_{10}NCOCH_2)ArTeBr_2$ (Ar = 2,4,6-$Me_3C_6H_2$, **2b**; 1-$C_{10}H_7$, **3b**; 4-MeC_6H_4, **4b**). While the bisulfite reduction of **1b** affords a yellow coloured telluroether, $(C_5H_{10}NCOCH_2)_2Te$, **1** as an oil, that of the unsymmetrical diorganotellurium dibromides, $(C_5H_{10}NCOCH_2)ArTeBr_2$ leads to the isolation of the respective diarylditellurides, ArTeTeAr. The symmetrical telluroether, **1** adds dihalogens oxidatively to give piperidin-1-ylamidomethyltellurium(IV) dihalides, $(C_5H_{10}NCOCH_2)_2TeX_2$ (X = Cl, **1a**; Br, **1b** and I, **1c**;). All the new piperidin-1-ylamidomethyltellurium derivatives have been characterized by elemental and ^1H, ^{13}C, ^{125}Te NMR spectral analyses. Single-crystal X-ray diffraction data for **1b** and **1c** indicated a butterfly molecular shape for the two halo analogues in which the six-member heterocyclic rings in the organic ligands retain the chair conformation of the independent piperidine molecule. The piperidin-1-yl appended organic ligand invariably results in the amido O atom being involved in an intramolecular Te O secondary bonding interaction and acts as a small-bite (C, O) chelating agent, at least in the solid state. Steric congestion around the six-coordinate Te(IV) atom and the partial positive charge on N owing to the resonating character of the $N\overset{\cdots}{-}C\overset{\cdots}{-}O$ amido group prevents these atoms from participating in the intermolecular associative forces. Instead, the weak C—H···O and C—H···Br interactions take centre-stage in the solid state self-assembly.

1. Introduction

The O-hydro-C-alkyl/aryl addition of Grignard reagents or organolithiums to aldehydes or ketones is an established method to prepare alcohols. Such reagents are however inaccessible in cases where the organic halide possesses a functional group. It is therefore not surprising that the C-bonded acyl, alkoxycarbonyl and amido (N-bonded as well) functionalized organometallic derivatives are known to only a limited extent. In the Reformatsky reaction, the addition of α-haloesters or α-halo N,N-disubstituted amides to an aldehyde or a ketone in the presence of zinc metal is believed to involve an organozinc compound, $O{=}C(Y)CH_2ZnBr$ (similar to RMgX) as an intermediate, albeit the alternative O-bonded structure $CH_2{=}C(Y)OZnBr$ cannot be ruled out on the basis of the X-ray diffraction data for the solid intermediate isolated in the reaction between t-$BuOCOCH_2Br$ and Zn [1].

The carbonyl activation of C_{sp3}–X bond to insert elemental Te has been studied and practiced in our laboratory to obtain functionalized diorganotellurium diiodies from the organic iodides, $YCOCH_2I$ (Y = R, RO, NH_2) [2–4]. This strategy has been successfully applied for the direct synthesis of the corresponding dibromides from α-bromo acylmethanes [5], but α-bromo alkoxycarbonylmethanes failed to react with tellurium powder when heated together up to about 100 °C [4]. Recently, the oxidative addition of α-bromo acetamides derived mainly from acyclic amines to elemental tellurium has been reported [6]. The structural diversity and broad range of pharmacological properties of natural and synthetic piperidine derivatives in general and N-acylpiperidine in particular [7,8] prompted us to prepare tellurated N-acyl piperidines by a simple method and study (i) their reactions with aldehydes and ketones (*cf.* Reformatsky reagents) and (ii) change in the conformation of the heterocyclic ring upon telluration.

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2. Experimental section

2.1. General procedures

Preparative work was performed under dry nitrogen. All solvents were purified and dried before use. α-Bromacetylpiperidine was prepared by slight modification in the literature method [9]. Bis(1-naphthyl)ditelluride, dimesitylditelluride and ditolylditelluride were prepared by reported methods [10–12]. Melting points were recorded in capillary tubes and are uncorrected. Microanalyses were carried out using a Carlo Erba 1108 analyzer. NMR spectra were recorded in $CDCl_3$ on Bruker DRX300 (^{1}H at 300.13 MHz) and JEOL Eclipse Plus 400 (^{13}C{^{1}H} at 100.54 MHz and ^{125}Te{^{1}H} at 126.19 MHz) spectrometers. Chemical shifts (δ) are reported relative to Me_4Si (^{1}H, ^{13}C) and Me_2Te (^{125}Te).

2.2. Syntheses

2.2.1. Synthesis of $(C_5H_{10}NCOCH_2)_2TeBr_2$, **1b** and $(C_5H_{10}NCOCH_2)_2TeI_2$, **1c**

Freshly ground tellurium powder (0.64 g, 5.0 mmol) and α-bromoacetylpiperidine (2.06 g, 10.0 mmol) were stirred together at ~50 °C for 24 h. The reaction mixture was washed with petroleum ether (40–60 °C) (3 × 10 mL) and the resulting grey solid extracted with dichloromethane (50 mL). The extract was passed through a short silica column and the eluent concentrated to about 10 mL. Addition of petroleum ether and cooling afforded a white solid that was recrystallized from dichloromethane to give **1b** as a colorless crystalline solid. Yield: 2.1 g, 78%. M.p.: 182 °C. Anal. Calc. for $C_{14}H_{24}O_2N_2Br_2Te$ (539.76): C, 31.2; H, 4.5. Found: C, 30.9; H, 4.4. ^{1}H NMR: δ 1.65 (m, 12H, CH_2), 3.42 (m, 4H, CH_2N), 3.64 (m, 4H, CH_2N), 4.67 (s, 4H, CH_2Te) ppm. ^{13}C{^{1}H} NMR: δ 23.90 (CH_2), 25.36 (CH_2), 26.22 (CH_2), 44.04 (NCH_2), 48.69 (NCH_2), 51.39 ($TeCH_2$), 163.95 (CO) ppm. ^{125}Te{^{1}H} NMR: δ 735.8 ppm.

When the aforementioned reaction was carried out in the presence of sodium iodide (~11.0 mmol), work up yielded an orange crystalline solid that was characterized as $(C_5H_{10}NCOCH_2)_2TeI_2$, **1c**. Yield: 2.3 g, 73%. M.p: 159 °C. Anal. Calc. for $C_{14}H_{24}O_2N_2I_2Te$ (633.76): C, 26.5; H, 3.8. Found: C, 26.7; H, 3.7. ^{1}H NMR: δ 1.68 (m, 12H, CH_2), 3.43 (m, 4H, CH_2N), 3.63 (m, 4H, CH_2N), 4.66 (s, 4H, CH_2Te) ppm. ^{13}C{^{1}H} NMR: δ 23.98 (CH_2), 25.54 (CH_2), 26.37 (CH_2), 44.14 (CH_2N), 47.82 (CH_2N), 48.75 (CH_2Te), 164.17 (CO) ppm. ^{125}Te{^{1}H} NMR: δ 643.5 ppm.

2.2.2. Reduction of $(C_5H_{10}NCOCH_2)_2TeBr_2$, **1b**

A solution of **1b** (0.54 g 1.0 mmol) in dichloromethane (20 mL) was shaken with an aqueous solution of $Na_2S_2O_5$ (0.57 g, 3.0 mmol) at room temperature for 2 h. The yellow organic layer was separated, washed (4 × 50 mL) with water, dried over anhydrous sodium sulphate, and the volatiles removed under reduced pressure. The yellow oil thus obtained was characterized as the telluride, $(C_5H_{10}NCOCH_2)_2Te$, **1**. Yield: 0.28 g, 74%. Anal. Calc. for $C_{14}H_{24}O_2N_2Te$ (379.95) C, 44.3; H, 6.4. Found: C, 43.6; H, 6.0. ^{1}H NMR: δ 1.63 (m, 12H, CH_2), 3.40 (m, 4H, CH_2N), 3.54 (m, 4H, CH_2N), 3.75 (s, 4H, CH_2Te) ppm. ^{13}C{^{1}H} NMR: δ 4.15 (CH_2Te), 24.26 (CH_2), 25.38 (CH_2), 26.01 (CH_2), 42.96 (CH_2N), 48.01 (CH_2N), 169.93 (CO) ppm. ^{125}Te{^{1}H} NMR: δ 392.1 ppm.

2.2.3. Oxidative addition of dihalogens to $(C_5H_{10}NCOCH_2)_2Te$, **1**

A dichloromethane solution of the telluride $(C_5H_{10}NCOCH_2)_2Te$ prepared by the reduction of $(C_5H_{10}NCOCH_2)_2TeBr_2$ (1.0 mmol) as described above was cooled to 0 °C and treated dropwise with a solution of SO_2Cl_2 (0.13 g, 1.0 mmol) or I_2 (0.25 g, 1.0 mmol) in dichloromethane (10 mL). Concentration of the white-orange colored solution followed by addition of hexane yielded the corresponding dihalides, $(C_5H_{10}NCOCH_2)_2TeX_2$, (X = Cl, **1a**; I, **1c**). Analytically pure samples of the new products were obtained after recrystallization from CH_2Cl_2/hexane.

1a was a colorless crystalline solid. Yield: 0.32 g, 71%. M.p.: 168 °C. Anal. Calc. for $C_{14}H_{24}O_2Cl_2N_2Te$ (450.86): C, 37.3; H, 5.4. Found: C, 37.6; H, 5.5. ^{1}H NMR: δ 1.70 (m, 12H, CH_2), 3.40 (m, 4H, CH_2N), 3.64 (m, 4H, CH_2N), 4.56 (s, 4H, CH_2Te) ppm. ^{13}C{^{1}H} NMR: δ 23.89 (CH_2), 25.28 (CH_2), 26.16 (CH_2), 43.98 (CH_2N), 48.66 (CH_2N), 53.53 (CH_2Te), 163.88 (CO) ppm. ^{125}Te{^{1}H} NMR: δ 795.4 ppm.

1c was an orange crystalline solid. M.p: 159 °C. Yield: 0.46 g, 73%. Compound **1c** was also synthesized in a better yield by metathesis when $(C_5H_{10}NCOCH_2)_2TeBr_2$ (0.54 g; 1.0 mmol) and NaI (0.36 g, 2.2 mmol) were stirred together in dichloromethane (15 mL) for 10 h. Sodium halides were removed by filtration, with addition of petroleum ether and cooling affording **1c** (0.51 g, 81%).

2.2.4. Synthesis of $(C_5H_{10}NCOCH_2)ArTeBr_2$ (Ar = 2,4,6-$Me_3C_6H_2$, Mes, **2b**; 1-$C_{10}H_7$, Nap, **3b**; 4-MeC_6H_4, Tol, **4b**)

α-Bromoacetylpiperidine (0.21 g, 1.0 mmol) was added to a suspension of ArTeBr, prepared *in situ* from the diarylditellurides, Ar_2Te_2 (0.50 mmol) and Br_2 (0.08 g, 0.50 mmol) in dichloromethane at 0 °C, at room temperature. The reaction mixture was stirred for 1–3 h, filtered and the filtrate then passed through a short silica column. Addition of petroleum ether (40-60 °C) to the concentrated solution followed by cooling afforded solid compounds.

2b, a light yellow crystalline solid; M.p 138 °C. Yield: 0.24 g, 45% with respect to Mes_2Te_2. Anal. Calc. for $C_{16}H_{23}OBr_2NTe$ (532.77): C, 36.1; H, 4.3. Found: C, 36.2; H, 4.3. ^{1}H NMR: δ 1.72 (m, 6H, CH_2), 2.31 (s, 3H, *p*-Me), 2.65 (s, 3H, *o*-Me), 2.76 (s, 3H, *o*-Me), 3.46 (s, 2H, CH_2N), 3.67(m, 2H, CH_2N), 5.23 (s, 2H, CH_2Te), 6.95 (s, ^{1}H, Aryl H), 7.01 (s, ^{1}H, Aryl H) ppm. ^{13}C{^{1}H} NMR: δ 20.97 (*p*-CH_3), 23.10 (*o*-CH_3), 23.95 (*o*-CH_3), 24.82 (CH_2), 25.35 (CH_2), 26.28 (CH_2), 44.13 (NCH_2), 48.58 (NCH_2), 59.47 ($TeCH_2$), 130.41, 131.43, 132.63, 139.87, 141.10, 141.87 (aryl C), 163.61 (CO) ppm. ^{125}Te{^{1}H} NMR: δ 742.4 ppm.

3b a pale yellow crystalline sold. M.p 190 °C. Yield: 0.26 g, 48% with respect to Np_2Te_2. Anal. Calc. for $C_{17}H_{19}OBr_2NTe$ (540.75): C, 37.8; H, 3.5. Found: C, 37.5; H, 3.4. ^{1}H NMR: δ 1.72 (m, 6H, CH_2), 3.53 (s, 2H, CH_2N), 3.71(m, 2H, CH_2N), 5.33 (s, 2H, CH_2Te), 7.55–8.17(m, 7H, Aryl H) ppm. ^{13}C{^{1}H} NMR: δ 23.92 (CH_2), 25.43 (CH_2), 26.37 (CH_2), 44.38 (NCH_2), 49.05 (NCH_2), 62.72 ($TeCH_2$) 126.56, 126.83, 127.29, 128.03, 129.38, 131.48, 132.30, 133.71, 134.28 (aryl C), 163.40 (CO) ppm. ^{125}Te{^{1}H} NMR: δ 726.9 ppm.

4b an off white solid. M.p 170 °C. Yield: 0.22 g, 44% with respect to Tol_2Te_2. Anal. Calc. for $C_{14}H_{19}OBr_2NTe$ (504.71): C, 33.3; H, 3.8. Found: C, 33.2; H, 3.8. ^{1}H NMR: δ 1.68 (m, 6H, CH_2), 2.43 (s, 3H, CH_3), 3.42 (m, 2H, CH_2N), 3.67 (m, 2H, CH_2N), 5.04 (s, 2H, CH_2Te), 7.31 (d, 2H, Aryl H), 8.04(d, 2H, Aryl H ppm. ^{13}C{^{1}H} NMR: δ 21.45 (*p*-CH_3), 23.86 (CH_2), 25.37 (CH_2), 26.27 (CH_2), 44.29 (NCH_2), 48.92 (NCH_2), 62.49 ($TeCH_2$), 130.82, 134.71, 142.11, 142.45 (aryl C), 163.33 (CO) ppm. ^{125}Te{^{1}H} NMR: δ 814.0 ppm (and an additional weaker signal at 888.9 ppm).

2.2.5. Reduction of $(C_5H_{10}NCOCH_2)ArTeBr_2$ (Ar = 2,4,6-$Me_3C_6H_2$, Mes, **2b**; 1-$C_{10}H_7$, Nap, **3b**; 4-MeC_6H_4, Tol, **4b**)

A solution of **2b** (0.53 g 1.0 mmol) in dichloromethane (20 mL) was shaken with an aqueous solution of $Na_2S_2O_5$ (0.57 g, 3.0 mmol) at room temperature for 2 h. The colorless organic layer was separated, washed (4 × 50 mL) with water, dried over anhydrous Na_2SO_4, and the volatiles removed under reduced pressure. Crystallization with hexane afforded a red crystalline solid which was characterized as dimesitylditelluride, $(Mes)_2Te_2$, **5**. Yield: 0.17 g, 69%. M.p.: 126 °C (lit. 125-127 °C [10]).

Table 1
Crystal data and structure refinement details of **1b** and **1c**.

	1b	**1c**
Empirical formula	$C_{14}H_{24}Br_2N_2O_2Te$	$C_{14}H_{24}I_2N_2O_2Te$
Formula mass (g mol^{-1})	539.77	633.75
Temperature (K)	296(2)	296(2)
Wavelength, λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Crystal size (mm^3)	0.55 × 0.21 × 0.12	0.65 × 0.58 × 0.38
Space group	P n a 2_1	P c a 2_1
a (Å)	11.6423(4)	20.088 (2)
b (Å)	11.0400(4)	6.3254(7)
c (Å)	15.1718(6)	15.4586(16)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3)	1950.05(12)	1964.3(4)
Z	4	4
ρ_{calcd} (Mg m^{-3})	1.839	2.143
μ (Mo$K\alpha$, mm^{-1})	5.629	4.663
F(000)	1040	1184
h, k, l ranges collected	$-14 \leq h \leq 18$; $-17 \leq k \leq 14$; $-17 \leq l \leq 24$	$-29 \leq h \leq 29$ $-9 \leq k \leq 9$ $-22 \leq l \leq 22$
Reflection collected	10,219	6468
Independent reflection	6584 [R(int) = 0.0618]	6407 [R(int) = 0.0528]
θ range (°)	5.09–35.02	2.32–32.06
Completeness to θ_{max}	98.9%	99.9%
Abs. correction	Semi-empirical from equivalents	
Max., min. transmisn	1.00000, 0.08175	0.3166, 01042
Refinement method	Full matrix least-squares on F2	
Data/restrns/parameters	6584/1/191	6468/1/191
GoF	1.016	1.170
R indices ($I > 2\sigma(I)$)	R1 = 0.0767, wR2 = 0.1135	R1 = 0.0232, wR2 = 0.0528
R indices (all data)	R1 = 0.1868, wR2 = 0.1507	R1 = 0.0236, wR2 = 0.0529
Largest diff peak/hole	0.756/−0.921	0.857/−1.240

Under similar reaction conditions the two-phase bisulfite reduction of **3b** and **4b** afforded Nap_2Te_2, **6** (Yield: 0.19 g, 74%. M.p.: 119–120 °C (lit. 119–122 °C) [11]) and Tol_2Te_2, **7** (Yield: 0.13 g, 59%. M.p.: 49–50 °C (lit. 52 °C) [12]) respectively.

2.3. Crystallography

Single plate like crystals suitable for X-ray diffraction measurements were grown by slow evaporation of dichloromethane solution of **1b** and **1c** at ambient temperature. Intensity data for **1b** were collected on an Xcalibur, Ruby, Gemini diffractometer and those for **1c** on a Bruker Apex 2 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 CrysAlisPro171.NET program from Oxford Diffraction Ltd. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 [13]. 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 1. The ORTEP figures (omitting H atoms for clarity and showing 30% probability displacement ellipsoids) were generated using the WinGX 2002 platform [14].

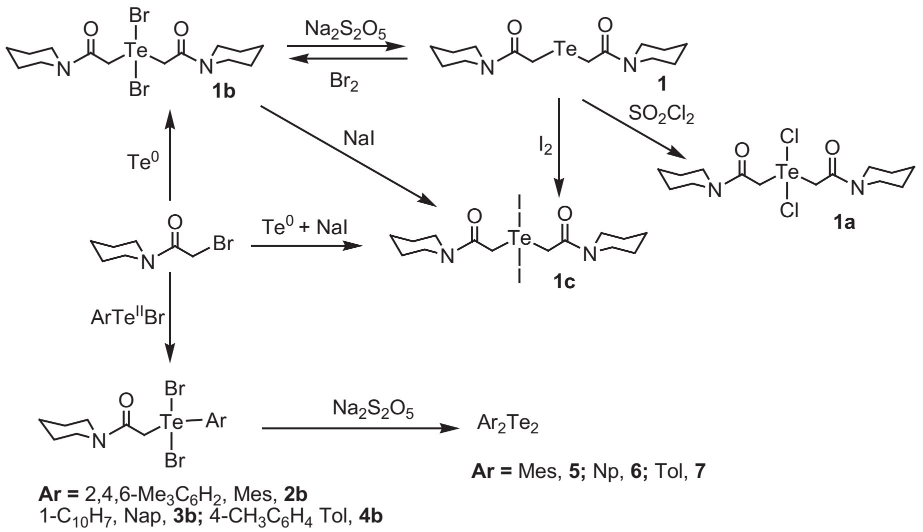
3. Results and discussion

3.1. Synthesis and spectra

α-Bromoacetylpiperidine adds oxidatively to tellurium powder under mild conditions to afford bis{(piperidin-1-yl)amidomethyl} tellurium dibromide (**1b)** and to aryltellurium(II) bromides (prepared *in situ* from the stoichiometric amounts of Br_2 and diarylditellurides, ArTeTeAr) to give alkylaryltellurium dibromides, $(C_5H_{10}NCOCH_2)ArTeBr_2$ (Ar = 2,4,6-$Me_3C_6H_2$, Mes, **2b**; 1-$C_{10}H_7$, Nap, **3b**; 4-MeC_6H_4, Tol, **4b** (Scheme 1). While partial biphasic reduction of **1b** with $Na_2S_2O_5$ yields the symmetrical telluroether, $(C_5H_{10}NCOCH_2)_2Te$, **1** as a yellow oil, preparation of the desired alkylaryltellurides by metabisulfite reduction of $(C_5H_{10}NCOCH_2)ArTeBr_2$ remains unsuccessful and instead leads to the isolation of the corresponding symmetrical diarylditellurides, Ar_2Te_2 (Ar = Mes, **5**; Nap, **6**; Tol, **7**). Compounds **5**, **6** and **7** were authenticated by comparison of their melting points and TLC with standard samples. Compound **1** adds dihalogens or its source to give **1b** and its iodo and chloro analogues, $(C_5H_{10}NCOCH_2)_2TeX_2$ (X = I, **1c**; Cl, **1a**). Compound **1c** is also obtained in the halide exchange reaction between **1b** and NaI. All the piperidin-1-yl appended amidomethyltellurium(IV) dihalides remain unaffected when warmed with acetone or acetophenone.

While the newly synthesized bis(piperidin-1-ylamidomethyl) tellurium derivatives, **1** and **1a**–**1c**, are stable at ambient conditions, the unsymmetrical diorganotellurium dihalides, $(C_5H_{10}NCOCH_2)ArTeX_2$ are unstable towards symmetrization and afford Ar_2TeX_2 on repeated recrystallizations. Telluride **1** is a liquid, whereas the tellurium(IV) dihalides are sharp melting colourless to orange solids, soluble in chloroform and dichloromethane. C and H analyses and the observed ^1H, ^{13}C and ^{125}Te chemical shifts for the new Te(IV) and Te(II) derivatives are given in the experimental section.

The chemical shifts for the methylene protons of the ring among the piperidin-1-ylamidomethyltellurium derivatives are unremarkable when compared to those of 2-bromo-1-(piperidin-1-yl) ethanone, the parent piperidine appended α-bromoamidomethane [9]. The presence of a singlet, accompanied by a pair of satellites due to ^1H-^{125}Te coupling at 3.75 ppm in the spectrum of tellurium(II) derivative, **1** suggests a small but appreciable shielding



Scheme 1.

of exo-cyclic methylene protons as a result of substitution of the Br atom of the α-bromoamidomethane (δ CH_2Br = 3.84 ppm) with the less electronegative Te(II). This signal, appearing in the range 4.56–5.33 ppm among the new Te(IV) derivatives, **1a**–**1c** and **2b**–**4b** indicates significant deshielding of the methylene protons when bonded to a dihalotellurium(IV) moiety. Interestingly, these protons among the bis(pyridine-1-ylamidomethyl)tellurium(IV) derivatives, **1a**–**1c** (δ CH_2Te range 4.56–4.67 ppm) are more shielded compared to those among the aryl(pyridine-1-ylamidomethyl)tellurium(IV) derivatives, **2b**–**4b** (δCH_2Te range 5.04–5.33 ppm). This may safely be attributed to the coordination of the carbonyl O atom(s) of the functionalized organic ligand(s), which is dual among the former Te(IV) compounds. These observations are corroborated by the high field signal at 4.1 ppm for the tellurium bonded carbons in **1** and correspondingly low field signals for such carbons among the ^{13}C NMR spectra of the Te(IV) compounds and further substantiated from the diffraction data for **1b** and **1c** (*vide infra*). The ^{125}Te NMR spectra of each bis(piperidin-1-ylamidomethyl)tellurium derivative (**1** and **1a**–**1c**) exhibits a single resonance that is consistent with their stability in solution. The spectrum of (piperidin-1-ylamidomethyl)tolyltellurium dibromide, **4b**, in addition to the strong resonance at 814.0 ppm, also exhibited a weak signal at 888.9 ppm, presumably due to $(4\text{-}MeC_6H_4)_2TeBr_2$ [15–17] produced in solution as a result of partial symmetrization. However, the spectra of **2b** and **3b** are devoid of any such additional signal indicating their kinetic stability in solution at room temperature, probably owing to the presence of sterically demanding 1-naphthyl and mesityl ligands. The separate signals for each of the methyl substituents of the mesityl ligand of **2b** in its ^1H and ^{13}C NMR spectra indicate the magnetic inequivalence of the two *ortho* methyls, which can be attributed to the restricted rotation of the mesityl ring about the Te–C_{ipso} bond owing to the steric crowding at the central five-coordinate Te(IV) atom. While the ^{125}Te chemical shift values for the Te(IV) compounds, as expected, are significantly large (643.5 ppm for **1c** to 795.4 ppm for **1a**) as compared to 392.1 ppm for the electron rich Te(II) in **1**, these appear to be insensitive to the carbonyl coordination.

3.2. Crystal structures

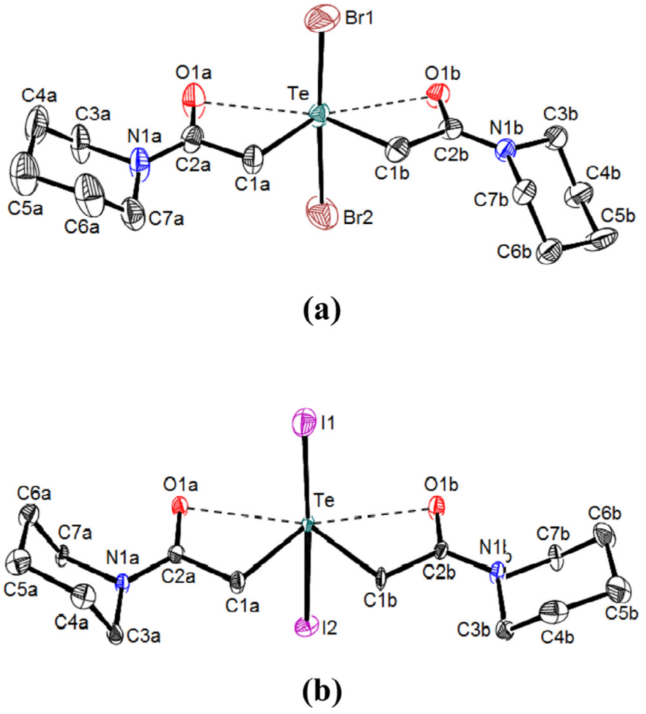


Fig. 1. Molecular structures of (a) **1b** and (b) **1c** showing 30% and 60% probability displacement ellipsoids respectively and the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) of **1b** and {**1c**}: Te–C1a 2.131(8) {2.140(4)}, Te–C1b 2.121(9) {2.140(4)}, Te–X1 2.659(2) {2.8839(5)}, Te–X2 2.652(2) {2.9241(4)}, Te···O1a 2.78(84) {2.8024(2)}, Te···O1b 2.78(64) {2.8329(2)}; C1a–Te–C1b 94.8(3) {90.06(16)}, X1–Te–X2 173.43(6) {175.881(14)}, C1A–Te–X1 89.4(3) {89.11(13)} C1a–Te–X2 88.2(3) {86.91(13)} C1b–Te–X1 86.7(3) {89.77(12)}, C1b–Te–X2 87.4(3) {89.16(12)}.

Compounds **1b** and **1c** may be said to be isomorphic as they crystallize in the space groups $Pna2_1$ and $Pca2_1$ respectively, which differ only in the glide plane in their lattices and each has one molecule in the asymmetric units. The molecular shapes of the two halo analogues, which differ only marginally, resemble a butterfly and their ORTEP views along with the relevant parametric details are given in Fig. 1. The three-coordinate piperidine N atom in the amido fragments of each of the Te bound organic ligands, has planar geometry [Σ 3(∠C—N—C) of C_3N is very close to 360°] and is characteristic of the N⋯C⋯O resonance that imparts nearly planar $C_2NC(O)C$ amidomethyl framework. Thus, all the skeletal atoms of the piperidin-1-yl appended organic ligands except the middle three ring carbons in each of the two compounds, lie in the plane perpendicular to the X–Te–X (X = Br or I) axis and are nearly coplanar with the equatorial C–Te–C plane (maximum deviation of 0.3801 Å from the mean plane for a ring carbon atom C3b in **1b** and minimum of 0.0004 Å for the methylene carbon atom C1b in **1c**). The chair conformation of the heterocyclic ring observed for the independent piperidine molecule in the solid state [18] is retained by each of the ligands in **1b** as well as in **1c**. While the values of the Cremer and Pople puckering parameters, Q, θ and φ [19] for the six-membered ring in the 'b'-labelled ligands {0.544(11)Å, 0.0(12)° and 258(51)° respectively} in the two diorganotellurium (IV) dihalides characterized crystallographically in the present investigation, are the same as that of the independent piperidine molecule, these values for the inverted chair conformation of the rings in the 'a'-labelled ligands {0.524(14)Å, 180.0(16)° and 87(70)° respectively} are comparable. As a consequence, the molecular geometry of both the compounds is reduced from C_{2v} to C_2 point group symmetry.

The primary geometry around the central Te(IV) atom in bis{(piperidin-1-yl)amidomethyl}tellurium dihalides **1b** and **1c**, with a C_2X_2 donor set, is no different from that of the Me_2TeX_2 (X = Br [20], I [21,22]) and the bond parameters are not unusual except the narrow inclination of the equatorial Te–C_{sp3} bonds which is almost equal to a right angle in case of **1c** (*cf.* 96(3)°, the average value observed for R_2TeX_2 or $RR'TeX_2$ [23]). In view of the reluctance of atoms of the heavier p-block elements to involve *s* orbital and large difference of energy between the *p* and *d* orbitals of the valence shell, the traditional description of bonding based upon sp^3d hybridization with an stereochemically active lone pair at the equatorial site to account for the butterfly shape of the C_2TeX_2 fragment, is less preferable than one based upon bonds using only *p* orbitals of its valence shell. While two of the three mutually perpendicular *p* orbitals of the Te atom, each with one unpaired electron, are involved to give two-centre two-electron (2c-2e) Te–C bonds, the formation of the linear X–Te–X triads (perpendicular to the Te–C bonds) in these compounds is a result of three-centre four-electron (3c-4e) bond as proposed in the case of the XeF_2 molecule or ICl_2^- ion [24].

The amido O atoms of both the functionalized ligands in **1b** as well as in **1c** are involved in the intramolecular secondary bonding interaction with the heavier congener. The observed internuclear distance between Te and the O atoms, though longer than sum of their covalent radii {$\Sigma\ r_{cov}$(Te,O), 2.03 Å}, are significantly shorter compared to the sum of their van der Waals radii {$\Sigma\ r_{vdw}$(Te,O), 3.58 Å} [25]. This interaction brings the O atom into the equatorial C–Te–C plane, reduces the tetrahedral ∠ Te–C_{sp3}–C to 102.4(5)°, 103.9(6)° in **1b** and 104.0(3)°, 104.8(3)° in **1c** (when compared to its putative value) due to the realization of four-membered chelate rings and imparts near linearity to the O···Te–C_{trans} triads (∠ O···Te–C_{trans} measures 150.4(1)°, 150.0(0)° and 145.4(1)°, 144.7(1)° in **1b** and **1c** respectively). The attractive 1,4-Te···O interactions with significant directionality thus appears to have appreciable covalent character and it would not be out-of-place to say that Te atom in **1b** and **1c** forms two additional 3c-4e C–Te···O bonds by involving one of the lone pairs on the amido O atoms. This results in a pseudo-octahedral geometry about the six-coordinate Te(IV) atom which resemble to that of the corresponding N-morpholino analogue, $(OC_4H_8N\text{-}COCH_2)_2TeBr_2$ [6]. The crystal packing in **1b** and **1c**, owing to the steric and electronic reasons, is devoid of the intermolecular Te···X secondary bonding interactions that are ubiquitous intermolecular associative forces to give rise to supramolecular motifs via self-assembly among the lattices of organotelluroum(IV) halides. As a consequence, the intermolecular C—H···O and C—H···X hydrogen bonds (Table S1) take centre-stage in the molecular association in the solid state of the compounds **1b** and **1c**. Diagrams depicting some supramolecular motifs identified in the crystal packings of **1b** and **1c** are given in the ESI.

4. Conclusions

The piperidin-1-yl appended amidomethyl bromide adds readily to the low valent tellurium species to provide single-step syntheses of dialkyl- and alkylaryltellurium dibromides (**1b**–**4b**). The symmetrical telluroether, bis(piperidin-1-ylamidomethyl)telluride (**1**) is obtained by the reduction of the parent Te(IV) dibromide (**1b**) with aqueous sodium sulfite solution. However, the (piperidin-1-ylamidomethyl)aryltellurium bromides (**2b**–**4b**) are unstable in solution towards symmetrization and afford Ar_2TeX_2 on repeated recrystallizations and attempts to prepare unsymmetrical (piperidin-1-ylamidomethyl)aryltellurides by the bisulfate reduction do not succeed. The small bite (C, O) chelating behavior of the amido functionalized ligand towards Te(IV) at least in the solid state is evident from the single-crystal X-ray diffraction data for bis(piperidin-1-ylamidomethyl)tellurium dibromide and –diiodide (**1b** and **1c**). The crystal lattices of these six-coordinate Te(IV) complexes are devoid of the intermolecular Te···X associative secondary bonding interactions that are common place among diorganotellurium dihalides and the weak C—H···O and C—H···X H-bonding interactions take centre-stage in the self-assembly.

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Appendix A. Supplementary data

The supramolecular arrays identified in the crystal lattices of these compounds (Figs. S15 and S17), the parametric details of weak C–H···O and C–H···X interactions in tabular form (Table S1) and 1H and 13C NMR spectra for the reported compounds are given as supplementary information. The CIFs have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033. CCDC 1402004 and 1536710 contain the supplementary crystallographic data for **1b** and **1c**. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2017.03.032.

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