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# Hybrid (Te, N) and (N, Te, N) ligands having pyrrolidine ring and their palladium(II) and mercury(II) complexes: synthesis and crystal structures

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## Abstract

Reactions of (2-choroethyl)pyrrolidine hydrochloride with $ArTe^-$ or $Te^{2-}$ generated in situ by borohydride reduction of $Ar_2Te_2$ or elemental tellurium give $N$-{2-(4-methoxyphenyltelluro)ethyl}pyrrolidine ($L^1$) or bis{2-(pyrrolidine-$N$-yl)ethyl}telluride ($L^2$), respectively, as viscous liquids, which are characterized by $^1H$- and $^{13}C\{^1H\}$-NMR spectroscopy. The potentially bidentate hybrid organotellurium ligand ($L^1$) reacts with $HgBr_2$ and $Na_2PdCl_4$ to give complexes $[HgBr_2 \cdot L^1]$ (1) and $[PdCl_2 \cdot L^1]$ (2) respectively. The potentially tridentate ligand ($L^2$) also forms a complex $[HgBr_2 \cdot L^2]$ (3). All three complexes give characteristic $^1H$- and $^{13}C\{^1H\}$-NMR spectra, although the deshielding of carbon atoms linked to Te/N as well as protons attached to them is small in the case of both Hg complexes. The single crystal structures of 1–3 have been solved. In 1 and 2 the ligand $L^1$ coordinates via Te and N both with metal indicating that the pyrrolidine N has good ligating strength. The Pd–Te and Hg–Te bond lengths are 2.4781(3) and 2.747(1) Å, respectively. The Pd–Cl *trans* to Te (2.3915(7) Å) is longer than other Pd–Cl bond length. There are two independent molecules in the asymmetric unit of 3 that have essentially the same bidentate molecular structures. There is no evidence of significant intermolecular Hg–Br bonding. The Hg–Te bond in 3 (ave. 2.686(2) Å) is shorter than in 1. The potentially tridentate ligand $L^2$ in complex 3 coordinates only as a bidentate donor. The molecular weights of 1 and 2 are close to double the formula weight indicating strong molecular association in solution. Te–C(alkyl) is somewhat longer than Te–C(aryl) for complexes 1 and 2.
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## 1. Introduction

There are several reasons for the growing interest in tellurium ligands [1–4] over the last decade. Among those of importance are the increasing evidence of enhanced ligating properties of telluroether ligands compared to thioethers [1b], the availability of standardized synthetic routes to the ligands, the possibility of using metal complexes of Te-ligands as a precursor for II–VI semiconductors, and the improved availability of

FT-NMR for studies of behaviour in solution. Hybrid organotellurium ligands have also received attention in the last decade. They generally have oxygen, sulfur and nitrogen as the donor sites along with tellurium [1–3]. There are two types of hybrid organotellurium ligands [1–3] containing tellurium and nitrogen as donor sites: (i) the $-NR_2$ group is attached to an alkyl or aryl group based skeleton and (ii) nitrogen is a part of a heterocyclic ring. In the latter case it has been observed that coordination via nitrogen is not realized when nitrogen is a part of morpholine or phthalimide systems [5–8] but the nitrogen readily coordinates [9] when a pyridine ring provides the nitrogen of the hybrid ligand. It was therefore thought worthwhile to design suitable hybrid

organotellurium ligands having other nitrogen heterocyclic ring systems, to improve the understanding of such ligands containing nitrogen as a co-donor site. Therefore, $N$-{2-(4-methoxyphenyltelluro)ethyl}pyrrolidine ($L^1$) and bis{2-(pyrrolidine-$N$-yl)ethyl}telluride ($L^2$) were synthesized by reaction of the nucleophiles 4-MeC$_6$H$_4$Te$^-$ and Te$^{2-}$ with the appropriate organic halide.



$L^1$                                                    $L^2$
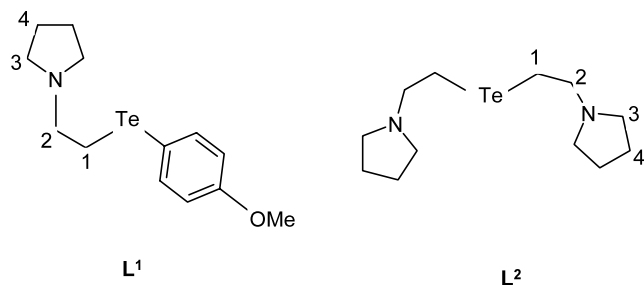
The complexation of $L^1$ and $L^2$ with Pd(II) and Hg(II) has been investigated. The characterization of the complexes [HgBr$_2$($L^1$)] (1), [PdCl$_2$($L^1$)] (2) and [HgBr$_2$($L^2$)] (3) by single crystal X-ray diffraction reveals that the nitrogen donor site of these ligands coordinates readily, even with Hg(II). The results of these investigations are reported in this paper.

## 2. Experimental

The C and H analyses were carried out with a Perkin–Elmer elemental analyzer 240 C. Tellurium was estimated by atomic absorption spectrometry. The $^1$H- and $^{13}$C{$^1$H}-NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz respectively. IR spectra in the range 4000–250 cm$^{-1}$ were recorded on a Nicolet Protége 460 FTIR spectrometer as KBr and CsI pellets. The conductance measurements were made in MeCN (concentration $\sim 1$ mM) using an ORION conductivity meter model 162. The molecular weights (concentration $\sim 5$ mM) in chloroform were determined with a Knauer vapour pressure osmometer model A0280. The melting points determined in open capillary are reported as such.

### 2.1. X-ray diffraction analysis

The crystals were mounted on a glass fibre. Data were collected on an Enraf Nonius Kappa CCD area detector diffractometer, with $\varphi$ and $\omega$ scans chosen to give a complete asymmetric unit. For [PdCl$_2$·$L^1$] (2) and [HgBr$_2$·$L^2$] (3) cell refinement [10] gave cell constants corresponding to a monoclinic cells whose dimensions are given in Table 1 along with other experimental parameters. Cell refinement [10] for [HgBr$_2$·$L^1$] (1) gave cell constants corresponding to a triclinic cell whose dimensions are also given in Table 1 along with other

experimental parameters. An absorption correction was applied [11] but in the case of [HgBr$_2$·$L^2$] the weak quality of the data was such that an effective absorption correction was difficult.

The structures of all three complexes were solved by direct methods [12] and were refined (by full-matrix least-squares on $F^2$) using the WinGX version [13] of SHELX-97 [14]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycles of full-matrix least-squares refinement converged (largest parameter shift was 0.001 times its esd). They were based on 3543 observed reflections (3261 for $F^2 > 4\sigma(F^2)$) and 174 variable parameters for [PdCl$_2$·$L^1$], 4002 observed reflections (3313 for $F^2 > 4\sigma(F^2)$) and 174 variable parameters for [HgBr$_2$·$L^1$] and 8080 observed reflections (5116 for $F^2 > 4\sigma(F^2)$) and 326 variable parameters for [HgBr$_2$·$L^2$]. Selected distances and bond angles of the three complexes are given in Tables 1 and 2 and the molecules are displayed in the ORTEP diagrams given in Figs. 1–3.

### 2.2. Synthesis of N-{2-(4-methoxyphenyltelluro)ethyl}pyrrolidine ($L^1$)

Bis(4-methoxyphenyl)ditelluride (0.50 g,1.0 mmol) was dissolved in 30 cm$^3$ of EtOH and the solution set to reflux under nitrogen atmosphere. A solution of sodium borohydride in NaOH (5%) was added dropwise to the refluxing solution of the ditelluride under nitrogen atmosphere until it became colourless due to the formation of ArTe$^-$ Na$^+$. (2-Choroethyl)pyrrolidine hydrochloride (0.362 g, 2.0 mmol) dissolved in 5 cm$^3$ of EtOH was added to this solution with constant stirring. The reaction mixture was refluxed further for 2–3 h, cooled to room temperature (r.t.) and poured into ice cold water (20 cm$^3$) in which 0.1 g of NaOH was dissolved. The ligand was extracted into chloroform (200 cm$^3$) from this aqueous mixture. The extract was washed with water and dried over anhydrous sodium sulphate. The solvent was evaporated off under reduced pressure on a rotary evaporator, resulting in a red oil, which was extracted into hexane. Further hexane was removed under reduced pressure to get ligand $L^1$ as clear yellow oil. Yield 70%. $\Lambda_M$, 14.4 ohm$^{-1}$ cm$^2$ mol$^{-1}$. Anal. Found: Te, 38.01. Calc. for C$_{13}$H$_{19}$ONTe: Te, 38.36%. NMR: $^1$H (CDCl$_3$, 25 °C): $\delta$ (vs Me$_4$Si): 1.68 (s, 4H, H$_4$), 2.45 (s, 4H, H$_3$), 2.81 (t, 2H, H$_1$), 2.94 (t, 2H, H$_2$), 3.78 (s, 3H, OCH$_3$), 6.66 (d, 2H, ArH $m$ to Te), 7.61 (d, 2H, ArH $o$ to Te); $^{13}$C{$^1$H}-NMR (CDCl$_3$, 25 °C): $\delta$ (vs Me$_4$Si): 8.80 (C$_1$), 23.33 (C$_4$), 54.38 (C$_3$), 57.44 (C$_2$), 58.50 (OCH$_3$), 101.93 (ArC-Te), 114.92 (ArC $m$ to Te), 140.53 (ArC $o$ to Te),161.36 (ArC $p$ to Te).

Table 1
Crystal data and structure refinement for **1**, **2** and **3**

|  | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{13}H_{19}NOBr_2TeHg$ | $C_{13}H_{19}Cl_2NOPdTe$ | $C_{24}H_{48}N_4Br_4Hg_2Te_2$ |
| Colour | Colourless | Red | White |
| Formula weight | 693.30 | 510.19 | 1368.68 |
| Temperature (K) | 120(2) | 120(2) | 120(2) |
| Wavelength (Å) | 0.71069 | 0.71073 | 0.71069 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $C2/c$ | $P2(1)/c$ |
| $a$ (Å) | 8.887(5) | 24.9350(4) | 11.745(5) |
| $b$ (Å) | 9.563(5) | 8.5322(2) | 13.054(5) |
| $c$ (Å) | 11.695(5) | 16.1710(3) | 23.787(5) |
| $\alpha$ (°) | 99.585(5) | – | – |
| $\beta$ (°) | 109.038(5) | 115.019(1) | – |
| $\gamma$ (°) | 108.705(5) | – | – |
| $V$ (Å$^3$) | 848.1(7) | 3117.6(1) | 3647(2) |
| $Z$ | 2 | 8 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 2.715 | 2.174 | 2.493 |
| Absorption coefficient (mm$^{-1}$) | 15.463 | 3.359 | 14.380 |
| $F(000)$ | 628 | 1952 | 2496 |
| Crystal size (mm) | $0.20 \times 0.20 \times 0.04$ | $0.40 \times 0.15 \times 0.06$ | $0.10 \times 0.07 \times 0.07$ |
| $\theta$ range for data collection (°) | 4.94–28.13 | 3.08–27.47 | 3.01–27.49 |
| Index ranges | $-11 \leq h \leq 10$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$ | $-29 \leq h \leq 32$, $-11 \leq k \leq 10$, $-20 \leq l \leq 20$ | $-15 \leq h \leq 15$, $-14 \leq k \leq 16$, $-30 \leq l \leq 30$ |
| Reflections collected | 13 037 | 14 093 | 14 271 |
| Independent reflections | 4002 [$R_{int} = 0.0492$] | 3543 [$R_{int} = 0.0482$] | 8080 [$R_{int} = 0.0651$] |
| Max. and min. transmission | 0.5767 and 0.1480 | 0.8239 and 0.3468 | 0.4326 and 0.3273 |
| Goodness-of-fit on $F^2$ | 1.000 | 1.050 | 0.986 |
| Final $R$ indices [$F^2 > 4\sigma(F^2)$] | $R_1 = 0.0321$, $wR_2 = 0.0708$ | $R_1 = 0.0274$, $wR_2 = 0.0678$ | $R_1 = 0.0681$, $wR_2 = 0.1501$ |
| $R$ indices (all data) | $R_1 = 0.0476$, $wR_2 = 0.0769$ | $R_1 = 0.0308$, $wR_2 = 0.0697$ | $R_1 = 0.1180$, $wR_2 = 0.1736$ |
| Extinction coefficient | 0.0011(3) | 0.00040(6) | 0.00038(7) |
| Largest difference peak and hole (e Å$^{-3}$) | 1.982 and $-2.777$ | 1.408 and $-1.478$ | 3.196 and $-4.555$ |

### 2.3. Synthesis of bis{2-(pyrrolidine-N-yl)ethyl}telluride ($L^2$)

Tellurium powder (0.65 g, 5.0 mmol) and sodium borohydride (0.38 g, 10.0 mmol) solution (made in 10 cm$^3$ of 2.0 M NaOH) were mixed in 50 cm$^3$ of water. The mixture was refluxed for 2 h under nitrogen atmosphere. The resulting colourless thin slurry of $Na_2Te$ was kept under reflux, and a solution of (2-chloroethyl)pyrrolidine hydrochloride (1.70 g,10.0 mmol) made in 5 cm$^3$ of EtOH was added dropwise, with constant stirring under nitrogen. The mixture was cooled to r.t. and poured into 100 cm$^3$ of water. The ligand $L^2$ was extracted into $Et_2O$ from the aqueous phase. The ether extract was washed with distilled water and dried over anhydrous $Na_2SO_4$. On evaporating off ether under reduced pressure on a rotary evaporator $L^2$ was obtained as an orange yellow viscous liquid, which was found to be unstable as it showed signs of decay within few days. Yield 60%. $\Lambda_M$, 5.22 ohm$^{-1}$ cm$^2$ mol$^{-1}$. Anal. Found: Te, 38.66. Calc. for $C_{13}H_{24}N_2Te$: Te, 39.43%. NMR: $^1H$ (CDCl$_3$, 25 °C): $\delta$ (vs Me$_4$Si): 1.68–1.76 (m, 8H, H$_4$), 2.45–2.52 (m, 8H, H$_3$), 2.70–2.85 (m, 8H, H$_2$ and H$_1$); $^{13}C\{^1H\}$: $\delta$ (vs TMS) (CDCl$_3$,

25 °C): $\delta$ (vs Me$_4$Si): 0.14 (C$_1$), 22.66 (C$_4$), 53.01 (C$_3$), 59.91(C$_2$).

### 2.4. Synthesis of [HgBr$_2$($L^1$)] (1)

HgBr$_2$ (0.20 g, 0.55 mmol) dissolved in acetone (15 cm$^3$) was added to the solution of $L^1$ (0.18 g, 0.55 mmol) made in chloroform (20 cm$^3$). The resulting mixture was stirred at r.t. until all of the $L^1$ complexed (monitored by TLC). Thereafter, the solvent from the mixture was evaporated off under reduced pressure on a rotary evaporator. The resulting residue was dissolved in 20 cm$^3$ of chloroform and filtered through celite. The filtrate was concentrated to 10 cm$^3$ and mixed with 20 cm$^3$ of hexane. A colourless complex separated out which was filtered and dried in vacuo. The single crystals of the complex were grown from chloroform over layered with hexane. Yield; 70%; m.p. 110 °C. Mol. wt.: Found, 1310; calc. 1368.7. $\Lambda_M$, 17.88 ohm$^{-1}$ cm$^2$ mol$^{-1}$. Anal. Found: C, 22.16; H, 2.56; N, 2.40; Te, 18.41. Calc. for $C_{13}H_{19}Br_2HgNOTe$: C, 22.51; H, 2.74; N, 2.02; Te,18.60%. NMR: $^1H$ (CDCl$_3$, 25 °C): $\delta$ (vs Me$_4$Si): 1.25 (m, 4H, H$_4$), 2.03 (t, 4H, H$_3$), 2.66 (m, 2H, H$_1$), 3.04 (m, 2H, H$_2$), 3.83 (s, 3H, OCH$_3$), 6.92 (d, 2H, ArH $m$ to Te), 7.86 (d, 2H, ArH $o$ to Te); $^{13}C\{^1H\}$

Table 2
Bond lengths (Å) and angles (°) for $HgBr_2L^1$ (1) and $PdCl_2L^1$ (2)

| Bond lengths | | | |
|---|---|---|---|
| **1** | | **2** | |
| Hg(1)–Br(1) | 2.578(1) | Pd(1)–Cl(1) | 2.3160(7) |
| Hg(1)–Br(2) | 2.537(1) | Pd(1)–Cl(2) | 2.3915(7) |
| Hg(1)–Te(1) | 2.747(1) | Pd(1)–Te(1) | 2.4781(3) |
| Hg(1)–N(1) | 2.457(4) | Pd(1)–N(1) | 2.086(2) |
| Te(1)–C(1) | 2.122(6) | Te(1)–C(1) | 2.117(3) |
| Te(1)–C(8) | 2.172(5) | Te(1)–C(8) | 2.144(3) |
| N(1)–C(9) | 1.467(7) | N(1)–C(9) | 1.504(3) |
| N(1)–C(10) | 1.482(7) | N(1)–C(10) | 1.496(4) |
| N(1)–C(13) | 1.476(7) | N(1)–C(13) | 1.498(4) |
| C(8)–C(9) | 1.515(9) | C(8)–C(9) | 1.497(4) |
| C(10)–C(11) | 1.523(9) | C(10)–C(11) | 1.527(4) |
| C(11)–C(12) | 1.538(9) | C(11)–C(12) | 1.535(4) |
| C(12)–C(13) | 1.526(8) | C(12)–C(13) | 1.535(4) |
| Bond angles | | | |
| **1** | | **2** | |
| Br(1)–Hg(1)–Te(1) | 114.17(3) | Cl(1)–Pd(1)–Te(1) | 83.80(2) |
| Br(2)–Hg(1)–Te(1) | 125.84(3) | Cl(2)–Pd(1)–Te(1) | 166.41(2) |
| Br(1)–Hg(1)–N(1) | 98.1(1) | Cl(1)–Pd(1)–N(1) | 170.93(7) |
| Br(2)–Hg(1)–N(1) | 108.8(1) | Cl(2)–Pd(1)–N(1) | 93.61(7) |
| Te(1)–Hg(1)–N(1) | 85.4(1) | Te(1)–Pd(1)–N(1) | 89.78(7) |
| Br(1)–Hg(1)–Br(2) | 114.81(3) | Cl(1)–Pd(1)–Cl(2) | 94.12(2) |
| Hg(1)–Te(1)–C(1) | 101.1(2) | Pd(1)–Te(1)–C(1) | 102.83(8) |
| Hg(1)–Te(1)–C(8) | 88.6(2) | Pd(1)–Te(1)–C(8) | 91.01(8) |
| C(1)–Te(1)–C(8) | 93.8(2) | C(1)–Te(1)–C(8) | 96.2(1) |
| Hg(1)–N(1)–C(9) | 105.9(3) | Pd(1)–N(1)–C(9) | 112.6(2) |
| Hg(1)–N(1)–C(10) | 109.2(4) | Pd(1)–N(1)–C(10) | 112.3(2) |
| Hg(1)–N(1)–C(13) | 112.8(3) | Pd(1)–N(1)–C(13) | 112.2(2) |
| C(9)–N(1)–C(10) | 110.8(5) | C(9)–N(1)–C(10) | 110.5(2) |
| C(9)–N(1)–C(13) | 114.5(5) | C(9)–N(1)–C(13) | 106.8(2) |
| C(10)–N(1)–C(13) | 103.7(4) | C(10)–N(1)–C(13) | 101.9(2) |
| Te(1)–C(8)–C(9) | 116.0(4) | Te(1)–C(8)–C(9) | 107.6(2) |
| C(8)–C(9)–N(1) | 115.4(5) | C(8)–C(9)–N(1) | 113.7(2) |

(CDCl₃, 25 °C): $\delta$ (vs Me₄Si): 20.26 (C₁), 23.11 (C₄), 53.88 (C₃), 59.43 (C₂), 55.69 (OCH₃), 107.00 (ArC-Te), 116.44 (ArC *m* to Te) 139.99 (ArC *o* to Te), 157.80 (ArC *p* to Te).

## 2.5. Synthesis of $[PdCl_2(L^1)]$ (2)

To a solution of $L^1$ (0.16 g, 0.50 mmol) made in 10 cm³ of acetone was added Na₂[PdCl₄] (0.08 g, 0.27 mmol) dissolved in 10 cm³ of water. The resulting mixture was stirred for 2 h at room temperature and poured into 100 cm³ of water. The complex was extracted into chloroform (100 cm³). The extract was dried over anhydrous Na₂SO₄, concentrated to ∼10 cm³, and mixed with hexane (20 cm³). The resulting red–yellow compound was separated, filtered, washed with hexane and dried in vacuo. The single crystals of the complex were grown by keeping overnight its solution made in MeCN and layered with hexane at 0–5 °C. Yield, 70%; m.p. 124 °C. Mol. wt.: Found, 953; calc. 510.2. $\Lambda_M$, 6.88 ohm⁻¹ cm² mol⁻¹. Anal. Found: C, 30.41; H, 3.91; N, 2.57; Te, 25.08; Calc. for
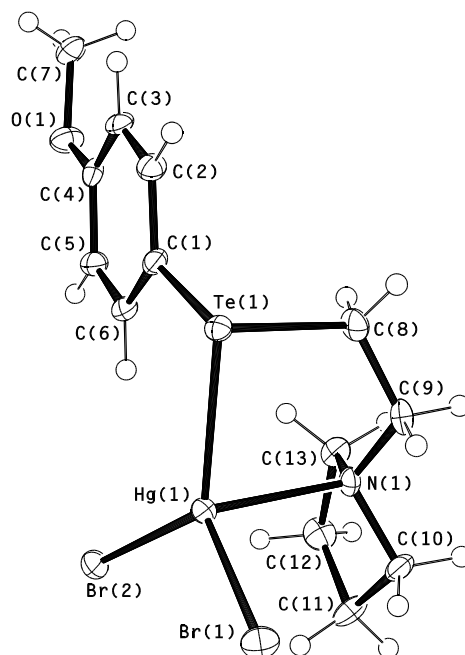


Fig. 1. ORTEP plot of the molecule **1**. The atoms are drawn with 50% probability ellipsoids.
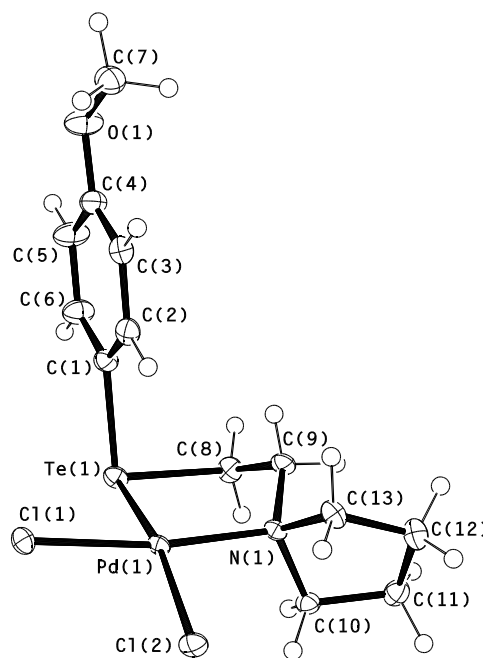


Fig. 2. ORTEP plot of the molecule **2**. The atoms are drawn with 50% probability ellipsoids.

C₁₃H₁₉Cl₂NOPdTe: C, 30.58; H, 3.72; N, 2.74; Te, 25.98%. NMR: ¹H (CDCl₃, 25 °C): $\delta$ (vs Me₄Si):, 1.60 (m, 4H, H₄), 2.49–2.85 (m, 4H, H₃), 3.37 (m, 1H, H₁), 3.60 (m, 1H, H₁), 3.84 (s, 3H, OCH₃), 4.15 (m, 1H, H₂), 4.21(m, 1H, H₂), 7.05–7.08 (d, 2H, ArH *m* to Te), 8.09–8.12 (d, 2H, ArH *o* to Te); ¹³C {¹H} (CDCl₃, 25 °C): $\delta$ (vs Me₄Si): 15.33 (C₁), 21.85, 22.01 (C₄), 55.43 (OCH₃), 59.93, 60.50, 60.9, (C₃), 65.00 (C₂), 106.80 (ArC-Te),
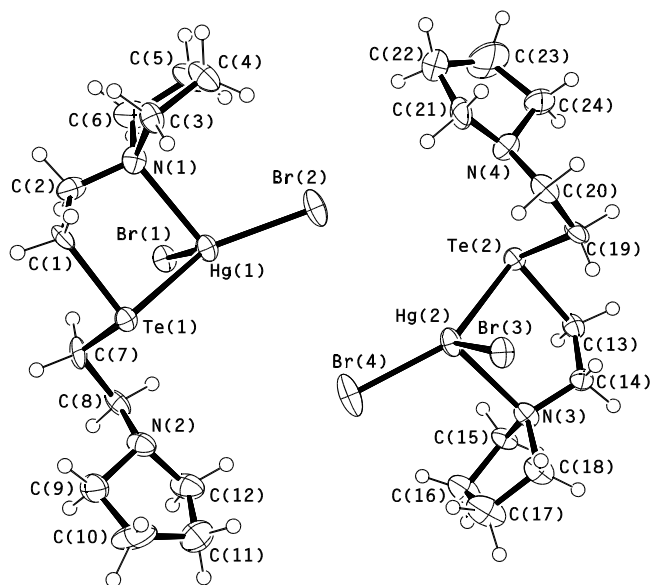
Fig. 3. ORTEP plot of the two molecules in the asymmetric unit of **3** The atoms are drawn with 50% probability ellipsoids.
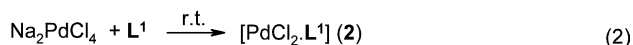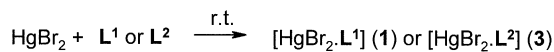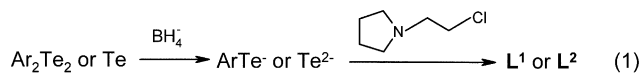
116.19 (ArC $m$ to Te) 138.27 (ArC $o$ to Te), 161.50 (ArC $p$ to Te).

## 2.6. Synthesis of [HgBr$_2$(L$^2$)] (3)

To a solution of HgBr$_2$ (0.20g, 0.55 mmol) in acetone (20 cm$^3$) was added a freshly prepared solution of **L$^2$** (0.17g, 0.55 mmol) in CHCl$_3$ (20 cm$^3$). The resulting mixture was stirred at r.t. until the ligand **L$^2$** was consumed (as monitored by TLC). The solvent was removed from the mixture on a rotary evaporator. The resulting residue was dissolved in 20 cm$^3$ of CHCl$_3$ and filtered through celite. The filtrate was concentrated to 10 cm$^3$ and mixed with 20 cm$^3$ of hexane. A colourless complex was separated, filtered, dried in vacuo. and recrystallized from CHCl$_3$–hexane (1:1) mixture. Yield, 70%; m.p. 91–92 °C; Mol. wt.: Found, 1310; calc. 683.6. $\Lambda_M$, 20.1 ohm$^{-1}$ cm$^2$ mol$^{-1}$. Anal. Found: C, 20.77; H, 3.21; N, 4.64, Te, 18.02; Calc. for C$_{12}$H$_{24}$Br$_2$HgN$_2$Te: C, 21.04; H, 3.50; N, 4.09; Te, 18.64%. NMR: $^1$H (CDCl$_3$, 25 °C): $\delta$ (vs Me$_4$Si): 1.88–1.89 (m, 4H, H$_4$), 2.74 (bm, 4H, H$_3$), 2.81 (bs, 2H, H$_1$), 3.07 (bs, 2H, H$_2$); $^{13}$C{$^1$H} (CDCl$_3$, 25 °C): $\delta$ (vs Me$_4$Si): 16.83 (C$_1$), 23.38 (C$_4$), 53.38 (C$_2$), 54.53 (C$_3$).

## 3. Results and discussion

The reactions given in equation 1 result in the formation of the two ligands **L$^1$** and **L$^2$** which are oily liquids highly soluble in chloroform and dichloromethane. **L$^2$** is also soluble in methanol but **L$^1$** only moderately.

$$Ar_2Te_2 \text{ or } Te \xrightarrow{BH_4^-} ArTe^- \text{ or } Te^{2-} \xrightarrow{\quad} L^1 \text{ or } L^2 \quad (1)$$

$$HgBr_2 + \textbf{L}^1 \text{ or } \textbf{L}^2 \xrightarrow{r.t.} [HgBr_2 \cdot L^1] \textbf{ (1) } \text{ or } [HgBr_2 \cdot L^2] \textbf{ (3)}$$

$$Na_2PdCl_4 + L^1 \xrightarrow{r.t.} [PdCl_2 \cdot L^1] \textbf{ (2)} \quad (2)$$

The **L$^1$** is moderately stable and can be stored under ambient conditions for ca. 1 month after which it solidifies as it decomposes. **L$^2$** is much less stable than **L$^1$** and has to be stored at 0–5 °C. Elemental tellurium starts to precipitate when **L$^2$** is kept in organic solvents for more than 3–4 h. The reactions of **L$^1$** and **L$^2$** with HgBr$_2$ and Na$_2$PdCl$_4$ result in complexes **1** to **3**, as shown in equation 2.

The conductance measurements on the ligands and complexes indicate that they are all non-electrolytes. In the IR spectra of **1** and **3** $v$(Hg–Br) appears at 213 and 217 cm$^{-1}$, respectively, while in that of **2**, $v$(Te–C(alkyl)) appears at 449 cm$^{-1}$ and $v$(Pd–Cl) at 295 cm$^{-1}$. The molecular weight measurements suggest that in solution no association occurs for **1**, whereas for **2** and **3** the molecular weights are close to double the expected formula weights, indicating some molecular association. The $^1$H- and $^{13}$C{$^1$H}-NMR spectra of both the ligands are characteristic. On the formation of **1**, the $^1$H-NMR spectrum shows deshielding of the order of 0.20–0.25 ppm for the aromatic protons of **L$^1$** and H$_1$ while, H$_2$, H$_3$, and H$_4$ all show shielding as expected for a d$^{10}$ metal. In the $^{13}$C{$^1$H}-NMR spectrum of **1**, C$_1$ is deshielded by ca 11.5 ppm in comparison to that of ligand **L$^1$**. The signals corresponding to ArC $o$ to Te, C$_2$ and ArC-Te are also deshielded by ca 1.5, 2.0 and 5.0 ppm, respectively. These observations concur with the ligation of **L$^1$** through Te and N. The $^1$H-NMR spectrum of the palladium complex **2** is somewhat complicated as signals of H$_1$ and H$_2$ protons give four groups of signals, because of strong chelation. In comparison to free **L$^1$**, the H$_2$ protons show deshielding of ca 1.2 ppm. For H$_1$, H$_3$ and aromatic protons the deshielding has been found to be ca 0.5–0.8, 0.2 and 0.4 to 0.5 ppm, respectively. Similarly in the $^{13}$C{$^1$H}-NMR spectrum of **2** the signals of C$_1$, C$_2$, C$_3$ and ArC-Te have been found to be deshielded (ca 5.6–7.0 ppm) with respect to those of free **L$^1$**. Thus in **2**, **L$^1$** is also coordinated through both Te and N. In the $^1$H-NMR spectrum of crystals of **3** H$_1$, H$_2$, H$_3$ and H$_4$ all appear to be somewhat deshielded (0.17–0.30) ppm. The signals of the pendent arm (Fig. 3) protons do not appear with significant intensity. It is thus very likely that a fast exchange on the NMR time scale occurs between coordinated and pendent arm, which is supported by the absence of separate signals for the pendent arm in the $^{13}$C spectrum of **3**. The C$_1$ carbon signal of **L$^2$** on

formation of **3** shows deshielding of ca 16.7 ppm whereas the $C_2$ signal is shielded by 6.53 ppm on complexation with Hg. The $C_3$ and $C_4$ signals on formation of **3** are deshielded by $\sim 0.7$ and 1.52 ppm, respectively. These observations indicate that Hg–N bonding is not very strong, which is consistent with the exchange of pendent and coordinated wings of $L^2$. The attempts to study the molecular associations of **2** and **3** and exchange of pendent arm with the coordinated one in the case of **3** using variable temperature NMR did not succeed as both the complexes have inadequate solubility below 0 °C for recording reasonable NMR.

### 3.1. The molecular structures of [HgBr₂(L¹)] (1) and [PdCl₂(L¹)] (2)

HgBr₂(L¹)] (**1**) is the first example of a Hg-complex in which a (Te, N) type hybrid organotellurium ligand acts as a chelating ligand, in that the metal is also coordinated via nitrogen as is demonstrated in Fig. 1. The selected bond lengths and angles are given in Table 2. The Hg–Te bond length of 2.747(1) Å is consistent with the earlier report of 2.728(1) Å for [HgBr(1-(NMe₂)-2-(TeC₆H₄-4-OEt)-4-MeC₆H₅)]₂ [15]. The Hg–N bond length of 2.457(4) Å is within the range of values reported in literature [16,17] for complexes of Hg with various nitrogen donors [2.226(9)–2.505(7) Å]. In this case it is longer than the sum of the covalent radii of mercury and nitrogen (ca 2.23 Å) suggesting relatively weak coordination which is consistent with the conclusions reached from the NMR spectra. The Hg–Br bond lengths of 2.578(1) and 2.537(1) Å are only marginally longer than the value of 2.500(1) Å reported earlier for the Hg-complex of a (Te, N) ligand coordinating only through Te [15]. The bond angles around Hg are in the range 85.4(1) to 125.84(3)°, with the Br(1)–Hg(1)–Br(2) at 114.81(3)°. It seems unlikely that the difference in the Hg–Br bond lengths arises from intermolecular association involving the bromine atoms because the two closest Hg···Br- contacts, Hg(1)···Br(1)- and Hg(1)···Br(2)- of 4.629(2) and 5.864(2) Å are clearly larger than the sum of the van der Waals radii of Hg and Br of ca 3.39 Å. Thus the geometry around Hg can best be described as distorted tetrahedral, with the coordination sphere being made up of Te, N and the two Br atoms. The bond angles at Te and N are consistent with their nearly trigonal pyramidal (88.6(2)–101.1(2)°) and tetrahedral geometry (105.9(3)–112.8(3) °), respectively.

The molecular structure of [PdCl₂(L¹)] (**2**) also shows (Fig. 2) the ligand $L^1$ chelating through Te and N. The selected bond lengths and angles are given in Table 2. Again, the bond angles at Te and N are consistent with their nearly trigonal pyramidal (91.01(8)–102.83(8) °) and tetrahedral geometry (101.9(2)–112.6(2) °), respectively. The Pd–N bond length of 2.086(2) Å is consistent with the literature reports [9]. This is close to the sum of the covalent radii of palladium and nitrogen.(ca 2.02 Å) suggesting relatively strong coordination, which is again consistent with the conclusions reached from the NMR spectra. The Pd–Te bond length of 2.4781(3) Å is also consistent with the earlier report of 2.517 (1) Å for [PdCl₂(4-MeC₆H₄TeCH₂CH₂-2-(C₅H₄N))][9]. The Pd(1)–Cl(1) bond (2.3160(7) Å) is shorter than Pd(1)–Cl(2) (2.3915(7) Å) as is to be expected for the *trans* influence of Te but both are somewhat longer than the values of 2.287(3) and 2.352(3) Å reported for another Pd-complex of a (Te, N) ligand (4-MeC₆H₄TeCH₂CH₂-2-(C₅H₄N)) [9]. The geometry around palladium is distorted square planar with the *cis* Cl(1)–Pd(1)–Cl(2) angle 94.12(2)° and the *trans* N(1)–Pd(1)–Cl(1) and Te(1)–Pd(1)–Cl(2) angles 170.93(7) and 166.41(2)°, respectively.

### 3.2. The molecular structure of [HgBr₂(L²)] (3)

In the crystal of **3**, there are two independent molecules in the asymmetric unit that have molecular structures that are essentially the same (Fig. 3). Although the ligand $L^2$ has three potential coordination sites, coordination is via Te and only one nitrogen donor atom. The second ring containing N forms a pendent arm. The selected bond lengths and angles are given in Table 3. As with **1** and **2**, the bond angles at Te and the

Table 3
Selected bond lengths (Å) and angles (°) for HgBr₂L² (**3**)

| *Bond lengths* | | | |
|---|---|---|---|
| Hg(1)–Br(1) | 2.700(2) | Hg(2)–Br(3) | 2.685(2) |
| Hg(1)–Br(2) | 2.505(2) | Hg(2)–Br(4) | 2.509(2) |
| Hg(1)–Te(1) | 2.684(1) | Hg(2)–Te(2) | 2.688(1) |
| Hg(1)–N(1) | 2.48(1) | Hg(2)–N(3) | 2.52(1) |
| Te(1)–C(1) | 2.16(1) | Te(2)–C(13) | 2.15(1) |
| N(1)–C(2) | 1.48(2) | N(3)–C(14) | 1.46(2) |
| N(1)–C(3) | 1.47(2) | N(3)–C(15) | 1.49(2) |
| N(1)–C(6) | 1.48(2) | N(3)–C(18) | 1.50(2) |
| C(1)–C(2) | 1.49(2) | C(13)–C(14) | 1.53(2) |
| Te(1)–C(7) | 2.14(1) | Te(2)–C(19) | 2.11(1) |
| *Bond angles* | | | |
| Br(1)–Hg(1)–Te(1) | 103.57(4) | Br(3)–Hg(2)–Te(2) | 106.83(4) |
| Br(2)–Hg(1)–Te(1) | 143.85(5) | Br(4)–Hg(2)–Te(2) | 145.29(5) |
| Br(1)–Hg(1)–N(1) | 91.1(3) | Br(3)–Hg(2)–N(3) | 92.3(2) |
| Br(2)–Hg(1)–N(1) | 109.3(3) | Br(4)–Hg(2)–N(3) | 108.3(2) |
| N(1)–Hg(1)–Te(1) | 85.8(3) | N(3)–Hg(2)–Te(2) | 84.8(2) |
| Br(1)–Hg(1)–Br(2) | 108.62(5) | Br(3)–Hg(2)–Br(4) | 104.61(6) |
| Hg(1)–Te(1)–C(1) | 90.1(3) | Hg(2)–Te(2)–C(13) | 90.2(3) |
| Hg(1)–Te(1)–C(7) | 95.4(4) | Hg(2)–Te(2)–C(19) | 98.1(4) |
| C(1)–Te(1)–C(7) | 94.5(5) | C(13)–Te(2)–C(19) | 92.0(5) |
| Hg(1)–N(1)–C(2) | 105.4(7) | Hg(2)–N(3)–C(14) | 104.1(7) |
| Hg(1)–N(1)–C(3) | 113.8(8) | Hg(2)–N(3)–C(15) | 112.5(8) |
| Hg(1)–N(1)–C(6) | 114.8(8) | Hg(2)–N(3)–C(18) | 113.2(8) |
| C(2)–N(1)–C(3) | 113(1) | C(14)–N(3)–C(15) | 114(1) |
| C(2)–N(1)–C(6) | 110(1) | C(14)–N(3)–C(18) | 109(1) |
| C(3)–N(1)–C(6) | 101(1) | C(15)–N(3)–C(18) | 104(1) |
| Te(1)–C(1)–C(2) | 114.8(9) | Te(2)–C(13)–C(14) | 113.4(9) |
| N(1)–C(2)–C(1) | 117(1) | N(3)–C(14)–C(13) | 113(1) |

coordinating N atom are consistent with their nearly trigonal pyramidal (91.1(3)–98.1(4)°) and tetrahedral geometry (104.1(7)–114.8(8)°), respectively. In both **1** and **2**, the Te–C(alkyl) bond is somewhat longer than the Te–C(aryl), as expected. The Hg–Te bond length in **3** (ave 2.686(2) Å) is some what shorter than that in **1** or [HgBr(1-(NMe$_2$)-2-(TeC$_6$H$_4$-4-OEt)-4-MeC$_6$H$_5$)]$_2$ [15]. As in **1**, the Hg–N bond length (ave 2.50(2) Å) is longer than the sum of the covalent radii of mercury and nitrogen again consistent with the relatively weak coordination suggested by the NMR spectra. The geometry around Hg in **3** is more distorted from tetrahedral than in **1** with the angles subtended at Hg ranging from 84.8(2)° for N(3)–Hg(2)–Te(2) to 145.29(5)° for Br(4)–Hg(2)–Te(2); the latter value being particularly high for tetrahedral geometry. The Hg–Br bond lengths cover a wider range (2.505(2)–2.700(2) Å) than in **1**, but bracket the average value in **1** of 2.56(3) Å. Given that two of the longer Hg–Br bonds at ca 2.70 Å are close to the values found for bridging Br atoms in related species such as [HgBr$_2$L]$_2$, where L = As(C$_6$H$_5$)$_2$(C$_8$H$_7$O$_2$) [18]. However as with **1**, there is no evidence of significant intermolecular Hg$\cdots$Br bonding because the shortest such distances are Hg(1)$\cdots$Br(4) 4.541(3), Hg(1)$\cdots$Br(3) 4.445(3), Hg(2)$\cdots$Br(2) 4.236(3), Hg(2)$\cdots$Br(1) 4.335 (3) Å; values that are greater than the sum of the van der Waals radii of Hg and Br of ca 3.39 Å but much shorter than found in **1**. Thus all of the Br atoms have similar Hg$\cdots$Br non-bonding distances, whether or not they are forming shorter or longer Hg–Br bonds. Interestingly, but perhaps just coincidentally, the inclusion of the two additional positions in a very large coordination sphere results in a pseudo octahedral arrangement around the Hg atoms, with for example the *trans* angles Br(1)–Hg(1)$\cdots$Br(3), Te(1)–Hg(1)$\cdots$Br(2) and N(1)–Hg(1)$\cdots$Br(4) being 153.48(7), 143.85(6), and 174.9(4)1 respectively. The presence of the pendent arm of the ligand **L$^2$** as a potentially tridentate ligand coordinates in a bidentate mode may be a more important factor in the packing although the Hg(1)$\cdots$N(2) and Hg(2)$\cdots$N(4) distances are 4.45(2) and 4.44(2) Å, respectively.

## 4. Supplementary material

Crystallographic data for the structural analysis of compounds **1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 213574, 213575, and 213576. Copies of this information may be obtained free of charge from The Director,

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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