

# $N-\{2-(4-Methoxyphenyltelluro)ethyl\}$ morpholine (L<sup>1</sup>) and bis $\{2-(N-morpholino)ethyl\}$ telluride (L<sup>2</sup>): synthesis and complexation with palladium(II) and mercury(II). Crystal structures of *trans*-[PdCl<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>] and *trans*-[PdCl<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>]

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Received 19 April 2000; received in revised form 10 June 2000

#### Abstract

The reactions of 4-(2-chloroethyl)morpholine hydrochloride with  $ArTe^-$  and  $Te^{2-}$ , generated in situ (under N<sub>2</sub> atmosphere) have resulted in *N*-{2-(4-methoxyphenyltelluro)ethyl}morpholine (L<sup>1</sup>) and bis{2-(*N*-morpholino)ethyl}telluride (L<sup>2</sup>), respectively, which are first tellurated derivatives of morpholine. <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectra of L<sup>1</sup> are as expected but HETCOR experiments are used to assign the overlapping signals of CH<sub>2</sub>Te and CH<sub>2</sub>N in <sup>1</sup>H-NMR spectrum of L<sup>2</sup>. The complexes of stoichiometries [PdCl<sub>2</sub>(L<sup>1</sup>/L<sup>2</sup>)<sub>2</sub>] (1/3) and [HgBr<sub>2</sub>(L<sup>1</sup>/L<sup>2</sup>)]<sub>2</sub> (2/4) are synthesized. The NMR (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) spectra of all the four complexes have CH<sub>2</sub>Te and ArC–Te signals deshielded with respect to those of free L<sup>1</sup>/L<sup>2</sup>, indicating that the two ligands coordinate through Te only. The *trans* Pd-complexes 1 and 3 are characterized structurally and their Pd–Te bond lengths (average) are 2.596 and 2.600 Å, respectively. The Pd-Cl bonds in 1 are marginally shorter (average 2.312 Å) in comparison to those of 3 (average 2.325 Å). The geometry of palladium is square planar. The Te–C(aryl) is shorter than Te–C(alkyl). The dimeric mercury complexes 2 and 4 appear to be formed through the formation two bromo bridges between Hg atoms. © 2000 Elsevier Science B.V. All rights reserved.

 $\label{eq:keywords: N-{2-(4-Methoxyphenyltelluro)ethyl}morpholine; Bis {2-(N-morpholino)-ethyl}telluride; Palladium(II); Mercury(II); Complexes; Crystal structures$ 

## 1. Introduction

The ligand chemistry of tellurium has received much more attention in the late 1980s and 1990s than it had previously [1]. Tellurium ligands of current interest are monodentate telluroethers [1b,c], alkyl- and aryl-tellurolates [2,3], telluride [4], polytellurides [5] and halotellurium ligands [6]. Tellurium-containing species have also been used as building blocks for clusters [7,8]. Recently ditelluroethers [9] have got some attention and complexation of a tritelluroether [11] and cyclic telluroethers [12] has been also been reported. The telluroethers functionalized with the groups having other donor atoms (commonly known as hybrid telluroethers [10]) are not

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extensively studied and very important in the context of understanding the ligation of Te vis-à-vis other donor atoms. However, the ligand chemistry of some  $(Te_x, N_y)$ type of donors is explored. The nitrogen in most of these ligands is that of an alkyl/aryl amine [13–15] or pyridine [11b]. To compare the coordination behavior of different types of nitrogen donors in conjunction with tellurium, it was thought worthwhile to design tellurium ligands of  $(Te_x, N_y)$  type in which nitrogen donor site belongs to a saturated cyclic amine, morpholine. The ligands



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 $L^1$  and  $L^2$  are therefore synthesized and their complexation with Hg(II) and Pd(II) is investigated. It has been noticed that the morpholine nitrogen has weaker ligating properties in comparison to other nitrogen donor sites mentioned above. The complexes of  $L^2$  are synthesized by the reactions of its freshly prepared sample with metal-containing species, as it can not be stored for more than 2 days. The trans- $[PdCl_2(L^1)_2]$  and trans- $[PdCl_2(L^2)_2]$  are characterized structurally. The results of these investigations are reported in the present paper.  $L^1$  and  $L^2$  are the first examples of tellurated morpholine derivatives.

## 2. Experimental

The C and H analyses were carried out with a Perkin-Elmer elemental analyzer 240 C. Tellurium was estimated volumetrically [16]. The <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz, respectively. The conductance measurements were made in acetonitrile, using an ORION conductivity meter model 162. The melting points determined in open capillary are reported as such. Bis(4methoxyphenyl)ditelluride was prepared by the pubmethod [17]. 4-(2-Chloroethyl)morpholine lished hydrochloride was obtained from Aldrich (USA) and used as received.

# 2.1. Synthesis of $L^1$

Bis(4-methoxyphenyl)ditelluride (0.46 g, 1 mmol) was dissolved in 30 cm<sup>3</sup> of ethanol and the solution set to reflux under nitrogen atmosphere. The 5% solution of sodium borohydride made in NaOH (5%) was added to it dropwise, until it became colorless due to the formation of ArTe-Na+. 4-(2-Chloroethyl)morpholine hydrochloride (0.37 g, 2 mmol) dissolved in 5 cm<sup>3</sup> of ethanol was added with constant stirring. The reaction mixture was refluxed further for 2-3 h, cooled to 25°C and poured into ice cooled water (200 cm<sup>3</sup>). The resulting white-colored compound was filtered, dissolved in diethyl ether and the solution dried over sodium sulfate. The diethyl ether was evaporated off from the solution under reduced pressure. The resulting viscous liquid was dissolved in hexane and the solution was kept at  $0-5^{\circ}C$  for 24 h. The L<sup>1</sup> was separated as white crystalline solid and dried in vacuo. Yield, 60%; m.p. 49–50°C.  $\Lambda_{\rm m}$ , 8.4 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>13</sub>H<sub>19</sub>O<sub>2</sub>NTe: C, 44.69; H, 5.44; N, 4.01; Te, 36.67. Found: C, 44.92; H, 5.74; N, 4.66; Te, 36.44. <sup>1</sup>H-NMR  $(CDCl_3, 25^{\circ}C)$ :  $\delta$  (vs TMS): 2.47 (t, 4H, H<sub>3</sub>), 2.78 (t, 2H, H<sub>1</sub>) 3.04 (t, 2H, H<sub>2</sub>), 3.68 (t, 4H, H<sub>4</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 6.73–6.76 (d, 2H, ArH m to Te), 7.65–7.68 (d, 2H, ArH *o* to Te);  ${}^{13}C{}^{1}H$ -NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs

TMS): 7.6 (C<sub>1</sub>), 52.3 (C<sub>3</sub>), 55.0 (OCH<sub>3</sub>), 59.2 (C<sub>2</sub>), 66.7 (C<sub>4</sub>), 101.2 (ArC-Te), 114.7 (ArC *m* to Te), 140.5 (ArC o to Te), 160.9 (ArC p to Te). FABMS (m/z): 351  $(M^+)$ , 320  $(M^+ - OCH_3)$ , 265  $(M^+ - OCH_3OC_4H_8N)$ 237 (M<sup>+</sup> – OCH<sub>3</sub>OC<sub>4</sub>H<sub>8</sub>NCH<sub>2</sub>CH<sub>2</sub>) 114 (OC<sub>4</sub>H<sub>8</sub>NCH<sub>2</sub>- $CH_2$ ), 100 ( $OC_4H_8NCH_2$ ), 86 ( $OC_4H_8N$ ).

# 2.2. Synthesis of $L^2$

Tellurium powder (0.65 g, 5 mmol) was added to sodium borohydride (0.38 g, 10 mmol) dissolved in an mixture made of 10 cm<sup>3</sup> of 2.0 M NaOH and 50 cm<sup>3</sup> of water. The resulting slurry was refluxed for 2 h under nitrogen atmosphere. When it became colorless a solution of 4-(2-chloroethyl)morpholine hydrochloride (1.86 g, 10 mmol) made in 5 cm<sup>3</sup> of ethanol was added dropwise, keeping the reaction under reflux and constant stirring under nitrogen atmosphere. The mixture was cooled to 25°C and poured into 100 cm<sup>3</sup> of ice cooled water. The ligand L<sup>2</sup> was extracted into diethyl ether from the aqueous phase. The ether extract was washed with distilled water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. On evaporating off ether under reduced pressure on a rotary evaporator, L<sup>2</sup> was obtained as a yellow viscous liquid, which is unstable as it shows the sign of decay within a few days. Yield: 50%;  $\Lambda_{\rm m}$ , 17.3 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs TMS): 2.47 (t, 8H,  $H_3$ ), 2.69–2.76 (m, 8H,  $H_1 + H_2$ ), 3.68 (t, 8H, H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs TMS): 0.4 (C<sub>1</sub>), 52.8 (C<sub>3</sub>), 59.9 (C<sub>2</sub>), 66.5 (C<sub>4</sub>).

# 2.3. Synthesis of $[PdCl_2(L^1)_2]$ (1)

The solution of  $L^1$  (0.14 g, 0.4 mmol) was made in 10 cm<sup>3</sup> of acetone. The Na<sub>2</sub>[PdCl<sub>4</sub>] (0.08 g, 0.2 mmol) dissolved in 10 cm<sup>3</sup> of water was added to it. The resulting mixture was stirred for 2 h at room temperature and poured into  $100 \text{ cm}^3$  of water. The complex 1 was extracted into chloroform (100 cm<sup>3</sup>). The extract was dried over anhydrous sodium sulfate, concentrated to  $\sim 10 \text{ cm}^3$  with a rotary evaporator, layered with hexane and kept at 0-5°C for overnight. The reddish brown crystals were separated and dried in vacuo. The single crystals of 1 were grown from its chloroform solution layered with hexane. Yield 70%; m.p. 134°C;  $\Lambda_{\rm m}$  30.5 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>26</sub>H<sub>38</sub>O<sub>4</sub>N<sub>2</sub>Te<sub>2</sub>PdCl<sub>2</sub>: C, 35.61; H, 4.34; N, 3.31; Te, 29.22. Found: C, 35.94; H, 4.66; N, 3.43; Te, 29.68. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs TMS): 2.56 (t, 8H, H<sub>3</sub>), 2.84 (t, 4H, H<sub>2</sub>) 3.42 (t, 4H, H<sub>1</sub>), 3.66 (t, 8H, H<sub>4</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 6.80-6.83 (d, 2H, ArH m to Te), 7.75–7.78 (d, 2H, ArH *o* to Te).  ${}^{13}C{}^{1}H$ -NMR  $(CDCl_3, 25^{\circ}C)$ :  $\delta$  (vs TMS): 22.2 (C<sub>1</sub>), 53.3 (C<sub>3</sub>), 54.9 (OCH<sub>3</sub>), 55.2 (C<sub>2</sub>), 66.5 (C<sub>4</sub>), 106.2 (ArC-Te), 114.7 (ArC m to Te), 140 (ArC o to Te),160 (ArC p to Te).

# 2.4. Synthesis of $[HgBr_2(L^1)]_2$ (2)

The HgBr<sub>2</sub> (0.2 g, 0.55 mmol) dissolved in acetone (15 cm<sup>3</sup>) was added to a solution of  $L^1$  (0.19 g, 0.55 mmol) made in chloroform (20 cm<sup>3</sup>). The resulting reaction mixture was stirred at room temperature until all  $L^1$  complexed (as monitored by TLC). Its solvent was evaporated off under reduced pressure on a rotary evaporator. The resulting residue was dissolved in 20 cm<sup>3</sup> of chloroform and filtered through celite. The filtrate was concentrated to 10 cm<sup>3</sup> with a rotary evaporator and mixed with 20 cm<sup>3</sup> of hexane. The resulting white colored complex 2 was filtered, washed with hexane and dried in vacuo. The 2 was further crystallized from chloroform: hexane (1:1) mixture. Yield, 60%; m.p. 120°C(d);  $\Lambda_{\rm m}$ , 10.4 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>13</sub>H<sub>19</sub>O<sub>2</sub>NTeHgBr<sub>2</sub>: C, 22.00; H, 2.67; N, 1.97; Te, 18.05. Found: C, 22.51; H, 2.59; N, 2.11; Te, 17.78. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs TMS): 2.65 (t, 2H, H<sub>2</sub>), 2.78 (bs 4H, H<sub>3</sub>), 3.13 (t, 2H, H<sub>1</sub>), 4.01 (t, 4H,  $H_4$ ), 3.83 (s, 3H, OCH<sub>3</sub>), 6.91–6.94 (d, 2H, ArH m to Te), 7.81–7.84 (d, 2H, ArH o to Te).  ${}^{13}C{}^{1}H$ -NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs TMS): 17.6 (C<sub>1</sub>), 54.08 (C<sub>3</sub>), 55.4 (OCH<sub>3</sub>), 56.9 (C<sub>2</sub>), 66.1 (C<sub>4</sub>), 105.0 (ArC-Te), 116.6 (ArC m to Te), 139.8 (ArC o to Te), 160.2 (ArC p to Te).

# 2.5. Synthesis of $[PdCl_2(L^2)_2]$ (3)

The freshly prepared  $L^2$  (0.23 g, 0.6 mmol) was dissolved in 10 cm<sup>3</sup> of acetone. The solution of Na<sub>2</sub>[PdCl<sub>4</sub>] (0.1 g, 0.3 mmol) made in 10 cm<sup>3</sup> of water was added to it. The resulting mixture was stirred for 1 h at room temperature and poured into 100 cm<sup>3</sup> of water. The resulting complex 3 was extracted into chloroform (100 cm<sup>3</sup>). The extract was dried over anhydrous sodium sulfate, concentrated to  $\sim 10 \text{ cm}^3$  with a rotary evaporator and mixed with hexane (15 cm<sup>3</sup>). The resulting reddish brown compound was separated, filtered, washed with diethylether and dried in vacuo. The single crystals of 3 were grown by keeping over night (at  $0-5^{\circ}$ C) its solution made in dichloromethane and layered with diethylether. Yield, 80%; m.p. 142°C.  $\Lambda_{\rm m}$ , 37.4 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>24</sub>H<sub>48</sub>O<sub>4</sub>N<sub>4</sub>Te<sub>2</sub>PdCl<sub>2</sub>: C, 32.36; H, 5.40; N, 6.30; Te, 28.76. Found: C, 32.09; H, 6. 01; N, 6.28; Te, 28.50. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs TMS): 2.56 (bs, 8H,  $H_3$ ), 2.80–2.84 (t, 4H,  $H_3$ ), 3.03 (bs, 4H,  $H_1$ ), 3.70–3.76 (t, 4H, H<sub>4</sub>).  ${}^{13}C{}^{1}H$ -NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs TMS): 15.0 (C<sub>1</sub>), 53.2 (C<sub>3</sub>), 56.2 (C<sub>2</sub>), 66.8 (C<sub>4</sub>).

## 2.6. Synthesis of $[HgBr_2(L^2)]_2$ (4)

To a solution of  $HgBr_2$  (0.2 g, 0.55 mmol) made in acetone (15 cm<sup>3</sup>) was added freshly prepared  $L^2$  (0.19 g, 0.55 mmol) dissolved in chloroform (20 cm<sup>3</sup>). The

mixture was stirred at room temperature until the ligand  $L^2$  reacted completely (as monitored by TLC). The solvent from the reaction mixture was removed on a rotary evaporator. The resulting residue was dissolved in 20 cm<sup>3</sup> of chloroform and filtered through celite. The filtrate was concentrated to 10 cm<sup>3</sup> and mixed with 20 cm<sup>3</sup> of hexane. The resulting white-colored compound 4 was filtered. It was recrystallized from chloroform: hexane (1:1) mixture and dried in vacuo. Yield, 50%; m. p. 128°C(d).  $\Lambda_{\rm m}$ , 11.9 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>TeHgBr<sub>2</sub>: C, 20.11; H, 3.35; N, 3.91; Te, 17.50. Found: C, 19.91; H, 3.62; N, 3.69; Te, 17.21. <sup>1</sup>H-NMR (CDCl<sub>3</sub> 25°C): δ (vs TMS): 2.70 (bs, 8H, H<sub>3</sub>), 2.76 (t, 4H, H<sub>2</sub>), 3.16 (bs, 4H, H<sub>1</sub>), 3.87 (t, 8H, H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  (vs TMS): 15.4 (C<sub>1</sub>), 53.0 (C<sub>3</sub>), 55.2 (C<sub>2</sub>), 65.8 (C<sub>4</sub>).

## 2.7. X-ray diffraction analysis

Bruker-AXS SMART2K CCD diffractometer was used to collect X-ray diffraction data. The reflections were collected for both the complexes 1 and 3 in excess of a full sphere. The data were reduced and the structures solved using the programs SMART, SAINT and SHELXTL [18]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were given an isotropic displacement factor equal to 1.5 times the equivalent isotropic displacement factor of the parent carbon atom. The final difference Fourier map for 3 shows a large maximum of ca. 3 e Å<sup>-3</sup> close to the Pd position (too close for a bond). This is about twice as much as usual for heavy metal complexes and may in part be due to the relatively poor crystal quality of 3.

## 3. Results and discussion

The ligands  $L^1$  and  $L^2$  are synthesized by the reactions given in Eqs. (1) and (2). The  $L^2$  is an unstable viscous liquid and shows the visible signs of decay within a few days

$$\begin{bmatrix} 4-\text{MeOC}_{6}\text{H}_{4}\text{Te}\end{bmatrix}_{2} \xrightarrow{\text{BH}_{4}} 4-\text{MeOC}_{6}\text{H}_{4}\text{Te} + 0 \xrightarrow{\text{N}} CI$$

$$= C\Gamma \qquad L^{1} \qquad 1$$
(1)
$$\begin{bmatrix} e & \text{NaBH}_{4} \\ \text{Na}_{2}\text{Te} + 2 & 0 \xrightarrow{\text{N}} CI \\ \text{NaCH} & \text{Na}_{2}\text{Te} + 2 & 0 \xrightarrow{\text{N}} CI \\ \text{Scheme in the set of t$$

$$\begin{array}{c} \text{Te} \quad \underbrace{\text{NaOH}}_{N_2} \text{Na}_2 \text{Te} + 2 \\ N_2 \end{array} \qquad \underbrace{\begin{array}{c} -2 \text{NaCH}}_{L^2} \\ L^2 \end{array} 2$$
(2)

of synthesis. Consequently its satisfactory elemental analyses could not be obtained. The reaction of freshly prepared  $L^2$  with Pd(II) and Hg(II) in a 1:2 (metal:ligand) ratio stabilizes the ligand. The reactions of  $L^1$  and  $L^2$  with palladium(II) in a 1:1 molar ratio have resulted in insoluble materials which defied all



Fig. 1. HETCOR spectrum of L<sup>2</sup>.

attempts of their characterization, probably due to their polymeric nature. Both the ligands and all four complexes (1–4) are soluble in common organic solvents and non-ionic in nature. <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectra of L<sup>1</sup> are characteristic. In its mass spectrum the molecular ion peak appears at m/z 351. The CH<sub>2</sub>N and CH<sub>2</sub>Te signals in <sup>1</sup>H-NMR spectrum of L<sup>2</sup> merge together, as supported by its HETCOR spectrum (Fig. 1).

In <sup>1</sup>H-NMR spectra of complexes 1 and 2 the  $CH_2Te$ signal appears down field (  $\sim 0.6$  and 0.4 ppm , respectively) in comparison to that of free  $L^1$ . Similarly in  $^{13}C{^{1}H}$ -NMR spectra of complexes 1 and 2, C<sub>1</sub> and ArC-Te signals depict a down field shift (  $\sim 10-15$  ppm and 3.5–4.5 ppm, respectively, with respect to that of  $L^{1}$ ). The CH<sub>2</sub>N signals exhibit insignificant shift in the spectra of both the complexes. These observations suggest that  $L^1$  in both the complexes 1 and 2, is coordinated through Te only. The structural characterization of 1 (Fig. 2) supports such an inference. In <sup>1</sup>H-NMR spectra of complexes 3 and 4 CH<sub>2</sub>Te and CH<sub>2</sub>N signals appear separately but only first exhibit deshielding (~0.45 to 0.70 ppm) with respect to that of free  $L^2$ . Similarly in <sup>13</sup>C{<sup>1</sup>H}-NMR spectra of the two complexes,  $C_1$  signal undergoes a down field shift of ~15 ppm. On the basis of these observations it may be inferred that  $L^2$  also ligates through Te only. The crystal structure of 3 (Fig. 3) corroborates this conclusion. The most plausible geometry of mercury in complexes 2 and 4 appears to be tetrahedral. The two bromide ions bridge the Hg atoms. However, all attempts to grow single crystals of 2 and 4 have failed.

### 3.1. Crystal structures of 1 and 3

The molecular structures of 1 and 3 are shown in Figs. 2 and 3 and crystal structures in Table 1. Their selected bond lengths and angles are given in Table 2. There are many similarities in the two structures. Both



Fig. 2. Molecular structure of trans-[PtCl<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>] (1).



Fig. 3. Molecular structure of trans-[PtCl<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>] (3).

of them are *trans* square planar co-ordination compounds of the type  $[PdCl_2(RTeR')_2]$  (R = R' for 3). There is no exact symmetry in either of them, however in the latter, co-ordination plane is a pseudo mirror plane and there is a pseudo center of symmetry at the position of palladium. The tellurium atoms in both the complexes have distorted pyramidal geometry, which may also be described as distorted tetrahedral, if a lone pair presumably occupies one corner. The lone pairs on two Te atoms of 1 or 3 have a *trans* orientation with respect to the linear Te–Pd–Te system. The organic groups present on the two tellurium atoms in each complex are in an orientation of least steric interaction. In 1 the two 4-MeOC<sub>6</sub>H<sub>5</sub> groups present on different Te atoms are also *trans* to Te–Pd–Te system.

The average values of Pd(II)-Te bond lengths in 1 and 3 are very similar (2.596 and 2.600 Å, respectively). The sum of covalent radii of square planar Pd(II) (1.31 Å) and pyramidal Te(II) (1.32 Å) [19] is 2.63 Å and comparable with the present averages. In square planar Pd complexes having two trans Pd-Te bonds viz., trans-dichlorobis(tellurapentane-Te)palladium(II) [20], trans - bis(thiocyanato)bis[di(3 - trimethylsilylpropyl)telluride]palladium(II) [21], bis(tetraphenylphosphonium) bis(tetratellurido) palladate(II) dimethylformamide solvate [22] and its unsolvated version [23], the PdVTe bond lengths are in the range from 2.584 to 2.606 Å (average 2.593Å). These values are consistent with the Pd-Te bond lengths of 1 and 3. The trans influence of other ligands relative to that of Te donor site affects the Pd-Te bond lengths, when they are trans to Te. A Te-Pd bond trans to a Pd-Cl bond is close to 2.52 Å [9a,10b], and on the other hand trans to Pd-P it is closer to 2.63 Å [9a,24]. The Pd-Cl bonds in 1 are marginally shorter (average 2.312 Å) in comparison to those of **3** (average 2.325 Å). They are also comparable to the standard statistical value (2.326(43) Å) found in four-coordinate Pd compounds with terminal  $Cl^-$  ligands [25a].

The Te–C bond lengths vary from 2.152 to 2.160 Å (ave. 2.154 Å) for the alkyl groups in the two ligands. In **1**, average value of Te–C(phenyl) bond lengths is 2.130 Å. The standard statistical values of 2.158(30) Å for a Te–C( $sp^3$ ) bond and 2.116(20) Å for a Te–C(aryl) bond [25b], are very close to those observed for Te–C(alkyl/aryl) bonds of **1** and **3**. The C–C, C–N and C–O bond lengths have normal values. The morpholine rings in **1** and **3** have the usual chair conformation.

Table 1 Crystal and structure refinement data

	1	3
Empirical formula	$C_{26}H_{38}N_2O_4Te_2PdCl_2$	C <sub>24</sub> H <sub>48</sub> N <sub>4</sub> O <sub>4</sub> Te <sub>2</sub> PdCl <sub>2</sub>
Formula weight	875.08	889.16
Temperature (K)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$
Unit cell dimensions		
a (Å)	12.9165(5)	12.5813(12)
b (Å)	10.7030(3)	12.1953(12)
<i>c</i> (Å)	22.5642(8)	22.3070(2)
α (°)	90	90
β (°)	99.32(5)	106.09(9)
γ (°)	90	90
V (Å <sup>3</sup> )	3078.1(8)	3288.4(6)
Ζ	4	4
$D_{\text{calc}} (\text{g m}^{-3})$	1.888	1.796
Absorption coefficient (mm <sup>-1</sup> )	2.668	2.500
F(000)	1696	1744
Crystal size (mm <sup>3</sup> )	$0.40 \times 0.19 \times 0.09$	$0.48 \times 0.38 \times 0.18$
$\theta$ range for data collection (°)	1.60-33.19	1.68-31.00
Absorption	Numerical	Numerical
corrections	integration	integration
Refinement method	Full matrix least	Full matrix least
	squares on $F^2$	squares on $F^2$
Reflections collected	55 352	55 056
Independent reflections	11 291	10 487
	$(R_{\rm int} = 0.0425)$	$(R_{\rm int} = 0.0307)$
Data/restraints/ parameters	11 291/0/337	0487/0/334
Goodness of fit on $F^2$ Final <i>R</i> indices	1.065	1.479
$[I > 2\sigma(I)]$		
$R_1$	0.0237	0.0577
$wR_2$	0.0478	0.1279
R indices all data		
$R_1$	0.0344	0.0609
$wR_2$	0.0496	0.1286
Largest differential	0.658	3.288
peak and hole		
(e Å <sup>-3</sup> )	-0.590	-3.453

Table 2 Selected bond lengths (Å) and bond angles (°) of  $1 \mbox{ and } 3$ 

Bond length		Bond angle	
Complex 1			
Pd-Te(1)	2.5865(2)	Te(1)-Pd-Te(2)	177.282(6)
Pd-Te(2)	2.6052(2)	Te(1)-Pd-Cl(1)	96.069(12)
Pd–Cl(1)	2.3110(4)	Te(1)-Pd-Cl(2)	84.853(12)
Pd–Cl(2)	3.3120(4)	Te(2)-Pd-Cl(1)	87.125(12)
Te(1)-C(1A)	2.129(2)	Te(2)-Pd-Cl(2)	97.974(12)
Te(1)-C(8A)	2.156(2)	Cl(1)-Pd-Cl(2)	179.24(2)
Te(2)-C(1B)	2.130(2)	Pd-Te(1)-C(1A)	99.68(5)
Te(2)-C(8B)	2.152(2)	Pd-Te(1)-C(8A)	107.64(5)
		C(1A)-Te(1)-C(8A)	94.40(7)
		Pd-Te(2)-C(1B)	97.74(4)
		Pd-Te(2)-C(8B)	105.00(5)
		C(1B)-Te(1)-C(8B)	95.65(7)
Complex 3			
Pd-Te(1)	2.5975(6)	Te(1)-Pd-Te(2)	179.31(2)
Pd-Te(2)	2.6021(6)	Te(1)-Pd-Cl(1)	87.78(5)
Pd–Cl(1)	2.3215(2)	Te(1)-Pd-Cl(2)	92.24(4)
Pd-Cl(2)	2.329(2)	Te(2)-Pd-Cl(2)	88.07(4)
Te(1)-C(6A)	2.160(6)	Te(2)-Pd-Cl(1)	91.90(5)
Te(1)-C(6B)	2.160(6)	Pd-Te(1)-C(6A)	102.2(2)
Te(2)-C(6C)	2.152(6)	Pd-Te(1)-C(6B)	101.5(2)
Te(2)-C(6D)	2.155(6)	Cl(1)-Pd-Cl(2)	179.39(7)
		C(6A)-Te(1)-C(6B)	89.6(2)
		Pd-Te(2)-C(6C)	99.8(2)
		Pd-Te(2)-C(6D)	102.8(2)
		C(6C)-Te(2)-C(6D)	89.8(2)

#### 4. Conclusion

The first tellurated derivatives of morpholine, N-{2-(4-methoxyphenyltelluro) ethylmorpholine (L<sup>1</sup>) and bis{2-(N-morpholino)ethyl}telluride ( $L^2$ ) are synthesized, which have a suitable bite for bi-/tri-dentate (Te, N)/(N, Te, N) ligation, but their 1:1 complexes with Pd(II) are insoluble, most probably due to some kind of polymerization. The donor capability of morpholine nitrogen seems to be weaker in comparison to those of other nitrogen donors studied in conjunction with Te.  $L^1$  and  $L^2$  coordinate through Te only, in all the four complexes. The Pd-Te bonds in the complexes 1 and 3 are longer in comparison to those which are *trans* to Pd-Cl. Thus trans influence of Te has a very significant effect on the Pd-Te bond lengths of a trans Te-Pd-Te system. The Te–C(alkyl) is longer than Te-C(aryl) even in the complexes. The Hg-complexes 2 and 4 are bromo bridged dimeric species in which  $L^1$  and  $L^2$  coordinate through Te only.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 150157 for complex **1** and 150158

#### Acknowledgements

A.K.S. and J.S. thank Department of Science and Technology (India) for financial assistance.

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