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Tellurated heterocycles, 2-[(2-thienyltelluro)methyl]tetrahydrofuran (L^1) and [(2-thienyltelluro)methyl]tetrahydro-2H-pyran (L^2): Synthesis and complexation reactions with Pd(II), Pt(II), Hg(II), Ru(II) and Cu(I) Single crystal structures of [Ru(*p*-cymene)Cl_2(L^1)] and *cis*-[$PdCl_2$(L^2)$_2$]

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Dedicated to (Late) Professor W. R. McWhinnie.

Abstract

2-Thienyllithium (ThLi) reacts with elemental Te to give ThTeLi which on reaction with tetrahydrofurfurylchloride and 2-(bromomethyl)tetrahydro-2H-pyran at −78 °C results in L^1 and L^2. Their complexes [$PdCl_2$(L^1)$_2$] (**1**), [$PtCl_2$(L^1)$_2$] (**2**), [$HgBr_2$(L^1)$_2$] (**3**), [Ru(*p*-cymene)Cl_2(L^1)] (**4**), [CuBr(L^1)] (**5**), [$PdCl_2$(L^2)$_2$] (**6**), [$PtCl_2$(L^2)$_2$] (**7**), [$HgBr_2$(L^2)$_2$] (**8**) and [Ru(*p*-cymene)Cl_2(L^2)] (**9**). Both the ligands and all nine complexes have characteristic ^{1}H and ^{13}C NMR spectra which reveal that in most of the complexes the two ligands L^1 and L^2 coordinate through Te only. This is corroborated by single crystal structures of **4** and **6**. The **4** is a half sandwich compound, in which co-ligands of *p*-cymene are Cl and L^1 (monodentate coordinated through Te). The Ru–Te bond length is 2.6340(7) Å. In the **6** Pd has nearly square planar geometry and molecules of ligand L^2 are *cis* to each other, which is something rare with the monodentate telluride ligands. The Pd–Te bond lengths are 2.538(2) and 2.517(2) Å. The crystal structure of **6** also shows presence of secondary Te···Cl interactions in the crystal lattice. The Pd–Pd distance in **6** becomes 3.188(3) Å, less than 3.26 Å (sum of vander Waal's radii). The ligation of L^1 and L^2 is compared with those of related ligands.

Keywords: 2-[(2-Thienyltelluro)methyl]tetrahydrofuran; [(2-Thienyltelluro)methyl] tetrahydro-2H-pyran; Metal complexes; Synthesis; Single crystal structure; X-ray diffraction

1. Introduction

The tellurium ligands, including hybrid ones [1–6] have received considerable attention in the last decade. Tellurium containing derivatives of heterocycles have been designed and used as ligands but in most of the asymmetric telluride ligands [RR′Te], having heterocyclic group [7–16] the other group is phenyl (or its substituted derivative). Some symmetric telluride ligands [R_2Te] are also known in which two heterocyclic groups (R) are identical [13–16]. No telluride in which both heterocyclic groups are different, has been explored as a ligand so far. It was therefore thought worthwhile to design such ligands with thienyl and furfuryl or pyranyl groups viz. 2-[(2-thienyltelluro)methyl]tetrahydrofuran (L^1) and [(2-thienyltelluro)methyl]tetrahydro-2H-pyran (L^2) and explore their complexation with metal ions (Ag(I), Cu(I), Hg(II), Pd(II), Pt(II) and Ru(II)). 2-[2-(4-Methoxyphenyltelluro)ethyl]thiophene (L^3) [15], bis[2-(2-thienyl)-ethyl] telluride (L^4) [15], 2-(phenyltelluromethyl)tetra hydro–2*H*-pyran (L^5) [8], 2-(phenyltelluromethyl)tetra

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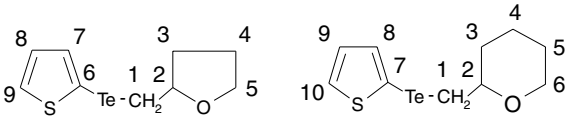
hydrofuran ($\mathbf{L}^6$) [8] 2-(4-ethoxyphenyltelluromethyl) tetra hydro–2*H*-pyran ($\mathbf{L}^7$) [11] and 2-(methytelluro)thiophene ($\mathbf{L}^8$) [24,25] are the tellurated heterocycle ligands studied earlier and have one heterocyclic ring common with $\mathbf{L}^1$ or $\mathbf{L}^2$. However, crystal structure of none of the complexes of $\mathbf{L}^5$ and $\mathbf{L}^6$ is known so far. In case of $\mathbf{L}^4$ and $\mathbf{L}^7$ known crystal structures are that of Ru-complex only. Therefore, crystal structure of no Pd-complex having oxygen containing heterocyclic group is known so far and *cis*-$[PdCl_2(\mathbf{L}^2)_2]$ is the first example of this kind. The $\mathbf{L}^2$ is more sterically demanding than $\mathbf{L}^8$ and still formation of a *cis* isomer predominantly on complexation with Pd(II) is very interesting. In fact *cis*-$[PdCl_2(\mathbf{L}^2)_2]$ is among the rare examples of this kind. These results are reported in the present paper. The $\mathbf{L}^1$ and $\mathbf{L}^2$ are the also the first examples of potentially (S, Te, O) type ligands, which can also act as a hemilabile ligands using oxygen.



$\mathbf{L}^1$ $\mathbf{L}^2$

2. Experimental

The C and H analyses were carried out with a Perkin Elmer elemental analyzer 240 C. Tellurium was estimated by atomic absorption spectrometer. The ^1H and $^{13}C\{^1H\}$ 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 FT-IR spectrometer as KBr and CsI pellets. The conductance measurements were made in acetonitrile (concentration ~1 mM) using an ORION conductivity meter model 162. The molecular weights (concentration ~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-Thienyl lithium (1 M solution in THF) was obtained from Aldrich (USA) and used as such. The [Ru(*p*-cymene)Cl_2] was prepared by the literature method [17].

2.1. X-ray crystallography

The crystal structures of **4** and **6** have been solved. The X-ray data for **4** and **6** both were collected on an Enraf Nonius Kappa CCD area detector diffractometer, with ϕ and ω scans chosen to give a complete asymmetric unit. Cell refinement [18] gave cell constants corresponding to a monoclinic cell in both the cases. An absorption correction was applied [18] in both the cases. The structure was solved by direct methods [19a] and was refined using the WINGX version [19b] of SHELX-97 [20]. 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 cycle of full-matrix least-squares refinement of **4** was based on 4505 observed reflections (3209 for $F^2 > 4\sigma(F^2)$) and 229 variable parameters and converged (largest parameter shift was 0.001 times its esd). In the case of **6** the final cycle of full-matrix least-squares refinement was based on 4558 observed reflections and 262 variable parameters and converged. The crystal data and structure refinement data for **4** and **6** are given in Table 1 whereas the selected bond lengths and bond angles for **4** and **6** are given in Table 2. Figs. 1 and 2 show the molecular structures of **4** and **6**. The secondary interactions for **6** are shown in Fig. 3. CCDC numbers 600506 and 600907 contain the supplementary crystallographic data for **4** and **6**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, fax: (int.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

2.2. 2-[(2-Thienyltelluro)methyl]tetrahydrofuran ($\mathbf{L}^1$)

2-Thienyllithium solution (5.0 cm^3 of 1.0 M solution in THF) was added to elemental tellurium (0.63 g, 5.0 mmol) taken in dry THF (25 cm^3) at 0 °C in a Schlenk tube. The mixture was stirred at this temperature for 1.5 h (Te was dissolved) and thereafter cooled to −78 °C. Tetrahydrofurfuryl chloride (0.60 g, 5.0 mmol) was added with constant stirring at −78 °C. The mixture was allowed to attain room temperature in ~12 h, after which it was poured into 100 cm^3 of ice cold water. The ligand $\mathbf{L}^1$ was extracted into chloroform (3×50 cm^3) from the aqueous layer. The combined chloroform extract was washed with brine (saturated solution of NaCl) (2×10 cm^3) and dried over Na_2SO_4 and evaporated under reduced pressure on a rotary evaporator to give $\mathbf{L}^1$ as a red brown oil. Yield: ~75%; ^1H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.53–1.64 (m, 1H, H_4), 1.77–1.71 (m, 2H, H_4 and H_3), 1.99–2.1.16 (m, 1H, H_3), 3.00–3.06 (m, 2H, CH_2-Te), 3.70–3.78 (m, 1H, H_5), 3.81–3.94 (m, 1H, H_5), 4.06–4.12 (m, 1H, H_2), 6.90–6.92 (m, 1H, H_7), 7.37–7.41 (m, 2H, H_8 and H_9) $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 17.1 (C_1), 26.1 (C_4), 32.4 (C_3), 68.2 (C_5), 78.9 (C_2), 128.7 (C_9), 135.9 (C_8), 140.5 (C_7), 142.4 (C_6).

2.3. [(2-Thienyltelluro)methyl]tetrahydro-2H-pyran ($\mathbf{L}^2$)

2-Thienyllithium solution (5.0 cm^3 of 1.0 M solution in THF) was added to elemental tellurium (0.63 g, 5.0 mmol) taken in dry THF (25 cm^3) at 0 °C in a Schlenk tube. The mixture was stirred at this temperature for ~1.5 h (till almost all of tellurium dissolved to give a brown solution of ThTeLi), cooled to −78 °C and 2-(bromomethyl)tetrahydro-2H-pyran (0.89 g, 5.0 mmol) was added with constant stirring. The reaction mixture was allowed to come

Table 1
Crystal data and structure refinement for $[RuCl_2(p\text{-cymene})(\mathbf{L}^1)]$ (**4**) and $[PdCl_2(\mathbf{L}^2)_2]$ (**6**))

Empirical formula	$C_{19}\ H_{26}\ O\ S\ Cl_2\ Ru\ Te$	$C_{20}\ H_{28}\ O_2\ Cl_2\ Pd\ S_2\ PdTe_2$
Formula weight	602.03	797.04
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	10.590(2)	14.509(4)
b (Å)	12.458(2)	11.097(5)
c (Å)	16.286(3)	16.359(8)
β (°)	106.04(2)	101.54(3)
Volume (Å^3)	2065.0(6)	2581(2)
Z	4	4
D_{calc} (g/cm^3)	1.936	2.052
Absorption coefficient (mm^{-1})	2.509	3.319
$F(000)$	1176	1520
Crystal size (mm^3)	$0.36 \times 0.24 \times 0.16$	$0.10 \times 0.08 \times 0.05$
θ Range for data collection (°)	3.07–27.40	3.14–25.03
Index ranges	$-13 \leqslant h \leqslant 11,\ -13 \leqslant k \leqslant 15,\ -21 \leqslant l \leqslant 20$	$-17 \leqslant h \leqslant 17,\ -13 \leqslant k \leqslant 13,\ -19 \leqslant l \leqslant 19$
Reflections collected	13 113	8859
Independent reflections [R_{int}]	4505 [0.0671]	4558 [0.0873]
Maximum and minimum transmission	0.6896 and 0.4653	0.8516 and 0.7325
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4505/0/229	4558/3/262
Goodness-of-fit on F^2	1.035	1.033
Final R indices [$F^2 > 4\sigma(F^2)$]	$R_1 = 0.0497,\ wR_2 = 0.1127$	$R_1 = 0.0786,\ wR_2 = 0.1792$
R indices (all data)	$R_1 = 0.0830,\ wR_2 = 0.1279$	$R_1 = 0.1813,\ wR_2 = 0.2201$
Largest difference peak and hole (e$^-$ Å^3)	1.408 and −1.422	2.426 and −2.105

to room temperature slowly (∼ in overnight) after which it was poured into 100 cm^3 of ice cold water. The ligand $\mathbf{L}^2$ was extracted into chloroform (3×50 cm^3) from the aqueous solution. The combined chloroform extract was washed with brine (saturated solution of NaCl) (2×10 cm^3), dried over Na_2SO_4 and evaporated under reduced pressure on a rotary evaporator to give $\mathbf{L}^2$ as a golden yellow oil. Yield: ∼75%; ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.18–1.49 (m, 4H, H_4 and H_5), 1.64–1.75 (m, 2H, H_3), 2.73–2.78 (m, 1H, CH_2Te), 2.95–2.99 (m, 1H, CH_2Te), 3.34–3.42 (m, 2H, H_6), 3.87–3.98 (m, 1H, H_2), 6.82–6.85 (m, 1H, H_8), 7.28–7.34 (m, 2H, H_9 and H_{10}) ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 15.4 (C_1), 19.0 (C_4), 25.4 (C_5), 35.8 (C_3), 68.5 (C_6), 77.4 (C_2), 125.2 (C_{10}), 134.7 (C_9), 140.8 (C_8), 141.9 (C_7).

2.4. Synthesis of $[PdCl_2(\mathbf{L}^1)_2]$ (**1**)

To a solution of $\mathbf{L}^1$(0.14 g, 0.50 mmol) made in 10 cm^3 of acetone was added $Na_2[PdCl_4]$ (0.07 g, 0.25 mmol) dissolved in 10 cm^3 of water. The resulting mixture was stirred for 2 h at room temperature and poured into 100 cm^3 of water. The complex was extracted into chloroform (4×25 cm^3). The extract was dried over anhydrous sodium sulphate, concentrated to ∼10 cm^{3}on a rotary evaporator and mixed with hexane (20 cm^3). The resulting orange solid (**1**) was filtered, washed with hexane and dried in vacuo. It was recrystallized from chloroform–hexane mixture (1:1). Yield: 73%; m.p. 121 °C; Λ_M (Ω^{-1} cm^2 mol^{-1}) 2.8. Anal. Calc. for $C_{18}H_{24}O_2S_2Te_2Pd_2Cl_4$ C, 28.10; H, 3.12; Te, 33.20. Found: C, 28.07; H, 3.09; Te, 33.12%. Mol. wt.: 757.8 (Calc. 768.6). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.93–1.95 (bm, 4H, $H_3 + H_4$), 3.57–4.28 (m, 5H, H_2, H_5 and CH_2–Te), 6.91 (bt, 1H, H_7), 7.57–7.58 (bd, 1H, H_8), 7.66 (bs, 1H, H_9) ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 26.1 (C_4), 29.2 (C_1), 32.6 (C_3), 68.1 (C_5), 76.5 (C_2), 128.2 (C_9), 133.5 (C_8), 140.0 (C_7), 142.0 (C_6).

2.5. Synthesis of $[PtCl_2(\mathbf{L}^1)_2]$ (**2**)

The $K_2[PtCl_4]$ (0.10 g, 0.25 mmol) was dissolved in 10 cm^3 of water and mixed with $\mathbf{L}^1$(0.14 g, 0.50 mmol) dissolved in 10 cm^{3}of acetone. The resulting mixture was stirred for 3 h at room temperature and poured into 100 cm^3 of water. The complex was extracted into chloroform (4×25 cm^3). The extract was dried over anhydrous sodium sulphate, concentrated to ∼10 cm^3 on a rotary evaporator, and mixed with hexane (20 cm^3). The resulting red colored compound (**2**) was filtered, washed with hexane and recrystallized from chloroform–hexane (2:1) mixture. Yield: 75%; m.p. 125 °C (d); Λ_M (Ω^{-1} cm^2 mol^{-1}) 1.90. Anal. Calc. for $C_{18}H_{24}O_2S_2Te_2Pt_2Cl_4$ C, 25.19; H, 2.79; Te, 29.76. Found: C, 25.12; H, 2.76; Te, 29.12%. Mol. wt.: 854.1 (Calc. 857.2). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.32 (bs, 2H, H_4), 1.48–1.66 (bs, 2H, H_3), 2.23–2.27 (m, 2H, CH_2–Te), 3.75 (bs, 3H, H_2 and H_5), 7.08 (bs, 1H, H_7), 7.32–7.36 (bm, 1H, $H_8 + CHCl_3$ of $CDCl_3$), 7.55 (bs, 1H, H_9) ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 26.1 (C_4), 29.5 (C_1), 32.6 (C_3), 68.2 (C_5), 75.4 (C_2), 128.4 (C_9), 134.0 (C_8), 139.6 (C_7), 141 (C_6).

Table 2
Selected bond lengths (Å) and angles (°)

*[RuCl$_2$(p-cymene)(**L**^{1})] (**4**)*			
Te(1)–Ru(1)	2.6340(7)	Ru(1)–Cl(2)	2.417(2)
Ru(1)–Cl(1)	2.436(2)	Ru(1)–C(11)	2.163(6)
Ru(1)–C(10)	2.195(6)	Ru(1)–C(13)	2.194(7)
Ru(1)–C(12)	2.155(7)	Ru(1)–C(15)	2.201(6)
Ru(1)–C(14)	2.207(6)	Te(1)–C(5)	2.163(7)
Te(1)–C(1)	2.110(7)	O(1)–C(6)	1.480(9)
S(1)–C(1)	1.710(7)	O(1)–C(7)	1.42(1)
S(1)–C(2)	1.666(9)		
Cl(1)–Ru(1)–Cl(2)	86.55(6)	C(1)–Te(1)–C(5)	91.7(3)
Cl(1)–Ru(1)–Te(1)	82.84(4)	Cl(2)–Ru(1)–Te(1)	79.09(4)
C(1)–Te(1)–Ru(1)	101.5(2)	C(5)–Te(1)–Ru(1)	110.6(2)
Te(1)–C(1)–S(1)	119.4(4)	Te(1)–C(1)–C(4)	126.3(5)
S(1)–C(2)–C(3)	114.0(7)	C(6)–O(1)–C(7)	106.1(7)
Te(1)–C(5)–C(6)	111.0(5)	O(1)–C(7)–C(8)	112.2(8)
*[PdCl$_2$(**L**^{2})$_2$] (**6**)*[a]			
Pd(1)–Cl(1)	2.370(4)	Pd(1)–Cl(2)	2.327(6)
Pd(1)–Te(1)	2.538(2)	Pd(1)–Te(2)	2.517(2)
Te(1)–C(1)	2.15(2)	Te(2)–C(11)	2.15(2)
Te(1)–C(7)	2.09(2)	Te(2)–C(17)	2.08(2)
C(2)–O(1)	1.18(2)	C(12)–O(2)	1.30(2)
O(1)–C(3)	1.31(2)	O(2)–C(13)	1.27(2)
C(7)–S(1)	1.68(2)	C(17)–S(2)	1.69(2)
S(1)–C(8)	1.69(2)	S(2)–C(18)	1.66(2)
Pd(1)–Pd(1)	3.188(3)		
Cl(1)–Pd(1)–Cl(2)	92.5(2)	Te(1)–Pd(1)–Te(2)	93.72(7)
Cl(1)–Pd(1)–Te(1)	172.9(2)	Cl(2)–Pd(1)–Te(2)	170.8(1)
Cl(2)–Pd(1)–Te(1)	94.5(1)	Cl(1)–Pd(1)–Te(2)	79.2(2)
C(1)–Te(1)–Pd(1)	104.6(4)	C(11)–Te(2)–Pd(1)	95.9(8)
C(7)–Te(1)–Pd(1)	95.7(4)	C(17)–Te(2)–Pd(1)	109.1(6)
C(1)–Te(1)–C(7)	95.2(6)	C(11)–Te(2)–C(17)	97(1)
Te(1)–C(1)–C(2)	108(1)	Te(2)–C(11)–C(12)	115(2)
C(1)–C(2)–O(1)	128(2)	C(11)–C(12)–O(2)	121(2)
C(2)–O(1)–C(3)	133(2)	C(12)–O(2)–C(13)	128(2)
O(1)–C(3)–C(4)	115(2)	O(2)–C(13)–C(14)	118(2)
Te(1)–C(7)–S(1)	121.4(9)	Te(2)–C(17)–S(2)	121(1)
C(7)–S(1)–C(8)	93(1)	C(17)–S(2)–C(18)	86(2)
S(1)–C(8)–C(9)	109(2)	S(2)–C(18)–C(19)	116(3)
C(10)–C(7)–S(1)	111(1)	C(20)–C(17)–S(2)	114(2)
C(10)–C(7)–Te(1)	127(1)	C(20)–C(17)–Te(2)	125(2)
Cl(1)–Pd(1)–Pd(1)	96.3(1)	Cl(2)–Pd(1)–Pd(1)	89.5(1)
Te(1)–Pd(1)–Pd(1)	85.11(5)	Te(2)–Pd(1)–Pd(1)	95.35(7)

[a] Symmetry equivalent position ($-x+1$, $-y+1$, $-z$) given by a prime.

2.6. Synthesis of [HgBr$_2$(**L**^{1})$_2$] (**3**)

$HgBr_2$ (0.20 g, 0.55 mmol) taken in acetone (20 cm^3) was mixed with a solution of $\mathbf{L}^1$ (0.32 g, 1.1 mmol) made in chloroform (20 cm^3) and the resulting mixture was stirred at room temperature until the ligand $\mathbf{L}^1$ 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 chloroform and filtered through celite. The filtrate was concentrated to 10 cm^3 on a rotary evaporator and mixed with 20 cm^3 of hexane. A white complex (**3**) was separated, filtered, dried in vacuo and recrystallized from chloroform–hexane (1:1) mixture. Yield: 60%; m.p. 95 °C (d); Λ_M (Ω^{-1} cm^2 mol^{-1}) 9.2. Anal. Calc. for $C_{18}H_{24}O_2S_2Te_2HgBr_2$ C, 22.69; H, 2.52; Te, 26.81. Found: C, 22.15; H, 2.50; Te, 26.77%. Mol. wt.: 949.2 (Calc. 951.5). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 2.28–2.32 (m, 4H, $H_3 + H_4$), 3.53 (m, 2H, CH_2–Te), 3.80–4.16 (m, 3H, $H_2 + H_5$), 6.90 (m, 1H, H_7), 7.36 (m, 1H, H_8), 7.84–7.86 (m, 1H, H_9).

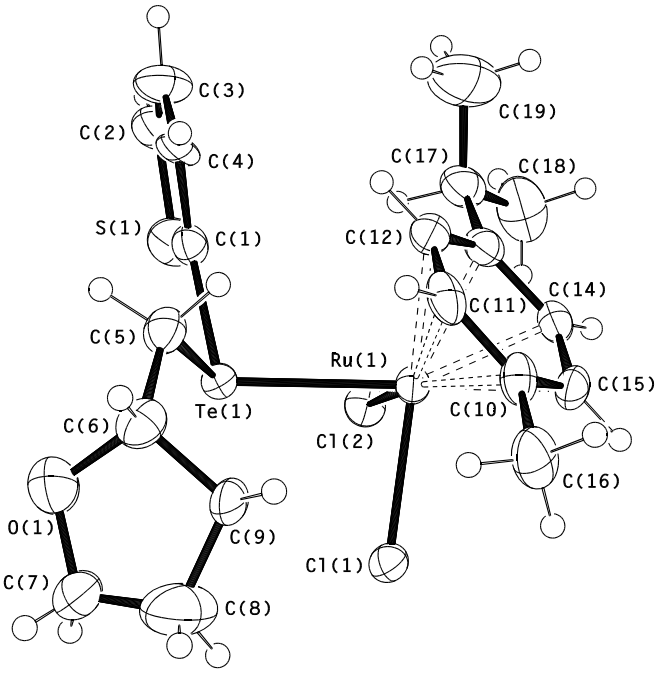


Fig. 1. Molecular structure of [Ru(*p*-cymene)Cl$_2$(**L**^{1})] (**4**).

2.7. Synthesis of [Ru(p-cymene)Cl$_2$(**L**^{1})] (**4**)

The [RuCl$_2$(*p*-cymene)]$_2$ (0.61 g, 1.0 mmol) was dissolved in 20 cm^3 of dichloromethane. A solution of $\mathbf{L}^1$ (0.59 g, 2.0 mmol) also made in 10 cm^3 of dichloromethane was added to it. The mixture was stirred for 2 h at room temperature. The solvent was completely removed on a rotary evaporator under reduced pressure. The residue obtained was dissolved in dichloromethane (5 cm^3) and mixed with hexane (20 cm^3). The resulting red precipitate of **4** was filtered, washed with hexane and dried in vacuo. The single crystals of complex **4** suitable for X-ray diffraction were grown from chloroform–hexane 1:1 mixture. Yield: 78%; m.p. 105 °C (d); Λ_M (Ω^{-1} cm^2 mol^{-1}) 11.6. Anal. Calc. for $C_{19}H_{26}OSTeRuCl_2$ C, 37.89; H, 4.32; Te, 21.20. Found: C, 37.52; H, 4.31; Te, 20.91%. Mol. wt.: 595.3 (Calc. 601.6). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.22–1.28 (m, 6H, CH_3 of *i*-Pr), 1.88–2.04 (m, 4H, $H_3 + H_4$), 2.14 (s, 3H, CH_3 of *p*-cymene), 2.83–3.16 (m, 3H, CH of *p*-cymene + CH_2–Te), 3.63–3.71 (m, 2H, H_5), 3.88–3.90 (m, 1H, H_2), 5.04–5.06 (m, 1H, Ar–H of *p*-cymene), 5.30–5.41 (m, 3H, Ar–H of *p*-cymene), 6.91–6.93 (m, 1H, H_7), 7.58–7.66 (m, d, 1H, H_8), 7.67–7.70 (bd, 1H, H_9). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 18.4 (CH_3 of *i*-Pr), 22.0 (CH_3 of *p*-cymene), 26.0 (C_4), 30.7 (CH of *i*-Pr), 30.7 (C_1), 32.2 (C_3), 67.9 (C_5), 75.2 (C_2), 80.1, 81.2, 85.3 (Ar–C of *p*-cymene), 128.5 (C_9), 133.2 (C_8), 138.5 (C_7), 140.0 (C_6).

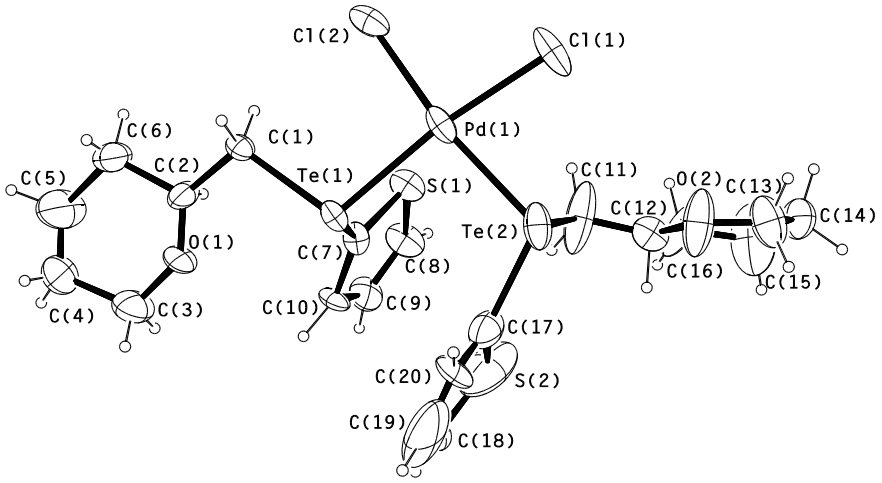


Fig. 2. Molecular structure of $[PdCl_2(\mathbf{L}^2)_2]$ (**6**).

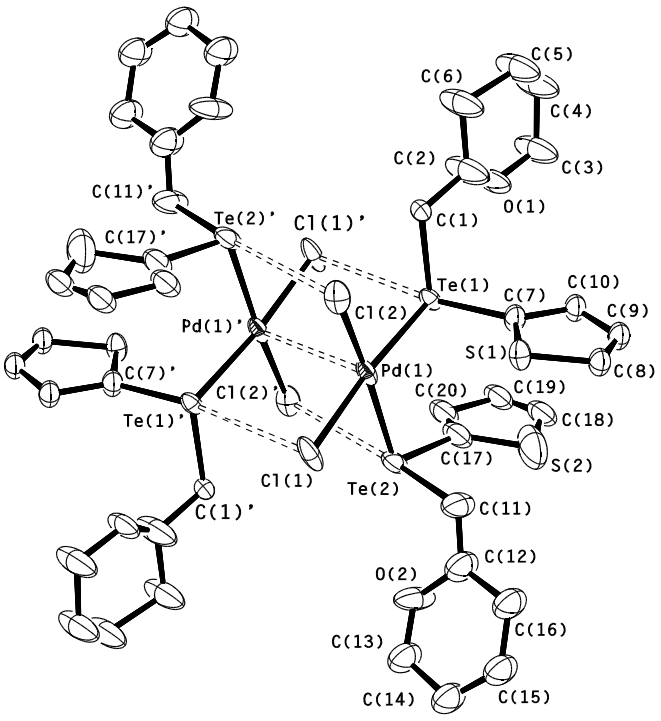


Fig. 3. Secondary interactions in **6**.

2.8. Synthesis of $[CuBr(\mathbf{L}^1)]$ (**5**)

A solution of $\mathbf{L}^1$(0.14 g, 0.50 mmol) made in 10 cm^3 of chloroform was mixed with Cu_2Br_2 (0.07 g, 0.50 mmol) dissolved in 10 cm^3 of nitromethane. The resulting mixture was stirred under inert atmosphere for 2 h at room temperature, after which the solution was filtered through celite. The clear filtrate was concentrated to ~10 cm^3 on a rotary evaporator and mixed with hexane (20 cm^3). The resulting white solid **5** was filtered, washed with hexane and dried in vacuo and stored under dry nitrogen atmosphere. It was recrystallized from chloroform–hexane mixture (1:1). Yield: 76%; m.p. 135–137 °C (d); Λ_M (Ω^{-1} cm^2 mol^{-1}) 10.1. Anal. Calc. for $C_9H_{12}OSTeCuBr$ C, 24.59; H, 2.73; Te, 29.06. Found: C, 24.31; H, 2.71; Te, 29.03%. Mol. wt.: 432.4 (Calc. 439.1). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.90–2.09 (m, 4H, H_3 and H_4), 3.01–3.03 (d, 2H, CH_2–Te), 3.72–3.79 (m, 1H, H_5), 3.88–3.95 (m, 1H, H_5), 4.09–4.13 (m, 1H, H_2), 6.91–6.94 (bt, 1H, H_7), 7.33–7.45 (m, 2H, $H_8 + H_9$).

2.9. Synthesis of $[PdCl_2(\mathbf{L}^2)_2]$ (**6**)

A solution of $\mathbf{L}^2$ (0.15 g 0.50 mmol) was made in 10 cm^3 of acetone and added to $Na_2[PdCl_4]$ (0.07 g, 0.25 mmol) dissolved in 10 cm^3 of water. The resulting mixture was stirred for 2 h at room temperature and poured into 100 cm^3 of water. The complex was extracted into chloroform (4×25 cm^3). The extract was dried over anhydrous sodium sulphate, concentrated to ~10 cm^3 on a rotary evaporator and mixed with hexane (20 cm^3). The resulting orange solid **6** was filtered, washed with hexane and dried in vacuo. It was recrystallized from chloroform–hexane mixture (1:1) to obtain single crystals suitable for X-ray diffraction. Yield: 77%; m.p. 125–127 °C; Λ_M (Ω^{-1} cm^2 mol^{-1}) 4.9. Anal. Calc. for $C_{20}H_{28}O_2S_2Te_2Pd_2Cl_4$ C, 30.12; H, 3.51; Te, 32.03. Found: C, 30.10; H, 3.49; Te, 32.01%. Mol. wt.: 791.1 (Calc. 796.6). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.88 (m, 6H, H_3, H_4 and H_5), 3.32 (m, 2H, CH_2–Te), 3.80–3.96 (m, 3H, H_2 and H_6), 7.10 – 7.14 (m, 1H, H_8), 7.17–7.20 (m, 1H, H_9), 7.86–7.96 (m, 1H, H_{10}) $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 23.0 (C_4), 25.4 (C_5), 29.6 (C_1), 32.8 (C_3), 68.8 (C_6), 75.1 (C_2), 128.8 (C_{10}), 134.5 (C_9), 139.0 (C_8), 142.1 (C_7).

2.10. Synthesis of $[PtCl_2(\mathbf{L}^2)_2]$ (**7**)

The solution of $\mathbf{L}^2$ (0.15 g, 0.50 mmol) made in 10 cm^3 of acetone was mixed with $K_2[PtCl_4]$ (0.10 g, 0.25 mmol) dissolved in 10 cm^3 of water. The resulting mixture was stirred for 3 h at room temperature and poured into 100 cm^3 of water. The complex was extracted into chloroform (4×25 cm^3). The extract was dried over anhydrous

sodium sulphate, concentrated to ~10 cm^3 on a rotary evaporator and mixed with hexane (20 cm^3). The resulting red colored compound (**7**) was filtered, washed with hexane and recrystallized from chloroform–hexane (2:1) mixture. Yield: 74%; m.p. 149–150 °C; Λ_M (Ω^{-1} cm^2 mol^{-1}) 12.1. Anal. Calc. for $C_{20}H_{28}O_2S_2Te_2Pt_2Cl_4$ C, 27.11; H, 3.16; Te, 28.82. Found: C, 27.09, H, 3.14, Te, 28.78%. Mol. wt.: 879.2 (Calc. 885.2). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.47–1.78 (m, 6H, H_3, H_4 and H_5), 3.34–3.58 (m, 2H, CH_2–Te), 3.84–3.95 (m, 3H, H_2 and H_6), 7.03 (m, 1H, H_8), 7.49 (m, 2H, H_9 and H_{10}) ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 23.1 (C_4), 25.5 (C_5), 29.5 (C_1), 32.7 (C_3), 68.5 (C_6), 76.5 (C_2), 128.1 (C_{10}), 133.6 (C_9), 139.1 (C_8), 142.5 (C_7).

2.11. Synthesis of [$HgBr_2(\mathbf{L}^2)_2$] (**8**)

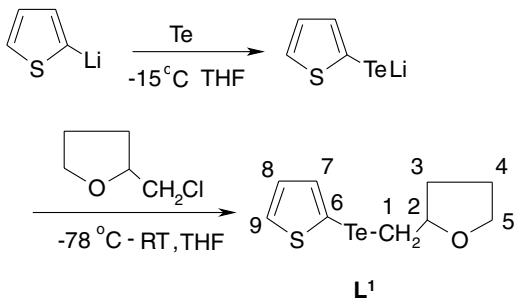
$HgBr_2$ (0.20 g, 0.55 mmol) dissolved in acetone (20 cm^3) was mixed with a solution of $\mathbf{L}^2$ (0.34 g, 1.1 mmol) made in chloroform (20 cm^3). The resulting mixture was stirred at room temperature until the ligand $\mathbf{L}^2$ was consumed (as monitored by TLC). The solvent was removed from the mixture on a rotary evaporator. The resulting residue was dissolved in 20 cm^3 of chloroform and filtered through celite. The filtrate was concentrated to 10 cm^3 on a rotary evaporator and mixed with 20 cm^3 of hexane. A white complex (**8**) was filtered, dried in vacuo and recrystallized from chloroform–hexane (1:1) mixture. Yield: 71%; m.p. 103 °C (d); Λ_M (Ω^{-1} cm^2 mol^{-1}) 44.2. Anal. Calc. for $C_{20}H_{28}O_2S_2Te_2HgBr_2$ C, 24.50; H, 2.85; Te, 26.05. Found: C, 24.35; H, 2.82; Te, 25.91%. Mol. wt.: 971.9 (Calc. 979.5). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.18–1.52 (m, 4H, H_4 and H_5), 1.79–1.82 (m, 2H, H_3), 3.51–3.53 (m, 1H, CH_2Te), 3.73–3.80 (m, 1H, CH_2–Te), 3.94–3.99 (m, 2H, H_6), 4.08–4.11 (m, 1H, H_2), 7.10–7.14 (m, 1H, H_8), 7.17–7.20 (m, 1H, H_9), 7.65–7.67, m, H_{10}) ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 22.4 (C_4), 24.98 (C_5), 27.0 (C_1), 32.5 (C_3), 69.6 (C_6), 72.4 (C_2), 128.8 (C_{10}), 134.9 (C_9), 139.0 (C_8), 140.4 (C_7).

2.12. Synthesis of [Ru(p-cymene)$Cl_2(\mathbf{L}^2)$] (**9**)

The $[RuCl_2(p\text{-cymene})]_2$ (0.61 g, 1.0 mmol) was taken in 20 cm^3 of dichloromethane and a solution of $\mathbf{L}^2$ (0.61 g, 2.0 mmol) made in 10 cm^3 of dichloromethane was added to it. The mixture was stirred for 2 h at room temperature. The solvent was completely removed on a rotary evaporator under reduced pressure. The residue obtained was dissolved in dichloromethane (5 cm^3) and mixed with hexane. The resulting red precipitate (**9**) was filtered, washed with hexane and dried in vacuo. It was recrystallized from dichloromethane–hexane (1:1) mixture. Yield: 79%; m.p. 162 °C (d); Λ_M (Ω^{-1} cm^2 mol^{-1}) 20.5 *Anal* Calc. for $C_{20}H_{28}OSTeRuCl_2$: C, 39.02; H, 4.55; Te, 20.72. Found: C, 39.38; H, 4.23; Te, 21.59%. Mol. wt.: 611.4 (Calc.615.6). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 1.26–1.29 (m, 6H, CH_3 of *i*-Pr), 1.43–1.72 (m, 6H, H_3, H_4 and H_5), 2.12–2.15 (m, 3H, $CH_3$of *p*-cymene), 2.80–2.90 (m, 3H, CH of *i*-Pr + CH_2Te), 3.41–3.52 (m, 1H, H_6), 3.70–3.74 (m, 1H, H_6), 3.92 (m, 1H, H_2), 5.0–5.04 (m, 1H, Ar–H of *p*-cymene), 5.31–5.35 (m, 3H, Ar–H *p*-cymene), 7.11 (m, 1H, H_8), 7.57 (m, 2H, H_9 and H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) (δ vs. TMS) 18.5 (CH_3 of *i*-Pr), 22.1 (CH_3 of *p*-cymene and C_4), 23.0 (C_1), 25.4 (C_5), 30.8 (CH of *i*-Pr), 32.3 (C_3), 68.4 (C_6), 76.5 (C_2), 80.5, 81.4, 85.2 (Ar–C of *p*-cymene), 128.4 (C_{10}), 133.2 (C_9), 140.0 (C_8), 141.2 (C_7).

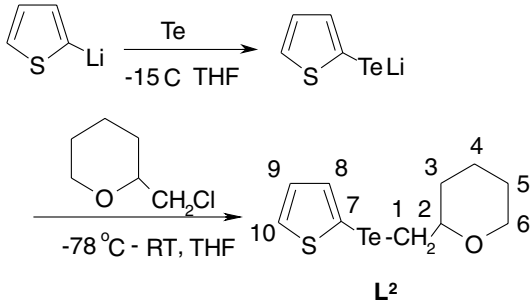
3. Results and discussion

Ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ have been synthesized according to Eqs. (1) and (2) given below. $\mathbf{L}^1$ is obtained as red brown oil, which is stable under ambient conditions but starts decomposing after three weeks with precipitation of white insoluble powder of tellurium dioxide. $\mathbf{L}^2$ has been obtained as golden yellow oil, which is stable under ambient conditions but also starts decomposing after a month, again with the precipitation of white insoluble powder of tellurium dioxide. Both $\mathbf{L}^1$ and $\mathbf{L}^2$ are soluble in common organic solvents such as chloroform, dichloromethane and acetone but insoluble in hexane. The stabilities and solubilities of $\mathbf{L}^1$ and $\mathbf{L}^2$ are nearly similar to those of other tellurated heterocylcles [8,11,15,24,25]. The complexes **1**–**9** are soluble in common organic solvents such as chloroform and dichloromethane and are stable under ambient conditions. The stochiometries of the complexes have been authenticated by their elemental analyses.



L¹

(1)



L²

(2)

The molar conductance values (Λ_M) in acetonitrile of complexes **1**–**9** at ~1 mM concentration level have been found to be much lower than the values expected for a 1:1 electrolyte. Molecular weights determined in chloroform by vapor pressure osmometric methods were found

to be very close to the values calculated from their molecular formulae. The IR bands between 460– 470 cm^{-1} are observed due to ν(Te–C (aliphatic)). In the IR spectra of **1** and **2** the bands observed at 349 and 340 cm^{-1} may be assigned to the stretching of *trans* Cl–Pd–Cl and *trans* Cl–Pt–Cl systems respectively. The ν_{sym} (Ru–Cl) and ν_{asym} (Ru–Cl) bands in IR spectra of **4** and **9** appear in the ranges 362–365 and 327–334 cm^{-1} respectively. The IR spectra of **6** and **7** do not have bands corresponding to stretching of *trans* Cl–Pd–Cl and Cl–Pt–Cl, indicating that molecules of ligand $\mathbf{L}^2$ are present in *cis* conformation around Pd/Pt as supported by the single crystal structure of Pd-complex **6**. The formation of *cis* complex is rare [24,25].

In the ^{1}H NMR spectrum of $\mathbf{L}^1$, the CH_2 protons of the furfuryl group viz. H_3, H_4, H_5 become non-equivalent and appear as multiplets. On comparing ^{1}H NMR spectrum of $\mathbf{L}^1$ with that of 2-(phenyltelluromethyl)tetra hydrofuran [8] it appears that most of signals of tetrahydrofuran ring protons occur at similar positions except those of H_3 and H_4 which give more complex signals in case of $\mathbf{L}^1$, and are shielded also in comparison to those of 2-(phenyltelluromethyl)tetra hydrofuran. The protons of thienyl group viz. H_8 and H_9 merge together and appear as a multiplet. Its H_7 also appears as a multiplet but is upfield as compared to H_8 and H_9. In general theinyl protons appear somewhat deshielded in proton NMR spectrum of $\mathbf{L}^1$ in comparison to those of 2-[2-(4-methoxyphenyltelluro) ethyl]thiophene [15]. In the ^{1}H NMR spectra of **1** and **2** the signals of H_1 ($TeCH_2$) appear as a multiplet and are deshielded by ~0.59–0.72 ppm as compared to free ligand, indicating that $\mathbf{L}^1$ binds to the metals through tellurium only. The signals due to H_2 and H_5 also merge with that of H_1 in the spectrum of **1** and H_4protons also appear deshielded by ~0.3–0.4 ppm as compared to free ligand. All the protons of thienyl group viz. H_7, H_8 and H_9 appear separately as broad triplet, broad doublet and a broad singlet respectively in the spectrum of **1**. The shift observed in the proton signals of the thienyl group is virtually insignificant in the spectra of **1** and **2**. The Te–CH_2 signal in ^{1}H NMR spectra of **3** and **4** shows a downfield and an upfield shift respectively (~0.5 and 0.03 ppm) suggesting that the binding with metal takes place through Te in case of complex **3** also. For **4** coordination of $\mathbf{L}^1$ through Te alone is supported by its crystal structure. In the ^{1}H NMR spectrum of **5**, the deshielding of Te–CH_2 signal is virtually insignificant which is common for a $3d^{10}$ system. In the ^{1}H NMR spectrum of $\mathbf{L}^2$ also the CH_2–Te protons become non equivalent and appear as multiplets and are shielded by ~0.9–1.0 ppm, as compared to 2-(bromomethyl)tetrahydro-2H-pyran due to the replacement of Br atom by Te moiety. The pyran signals of $\mathbf{L}^2$ are shielded in comparison to those of 2-(phenyltelluromethyl)tetra hydro-2*H*-pyran (except H_3 which is deshielded) and 2-(4-ethoxyphenyltelluromethyl) tetra hydro-2*H*-pyran [8,11]. However, thienyl protons of $\mathbf{L}^2$ are some what deshielded in comparison to those of 2-[2-(4-methoxyphenyltelluro) ethyl]thiophene [15]. The ^{1}H NMR spectrum of **6** has thienyl ring protons that are deshielded by ~0.2 ppm and CH_2–Te protons by ~0.35 ppm, indicating the ligation of $\mathbf{L}^2$ also through Te only, which is evident from the single crystal structure of **6**. The deshielding of thienyl protons may be a secondary effect of coordination of $\mathbf{L}^2$ via Te atom. In the proton spectra of **7** and **8** the CH_2–Te signals are deshielded by ~0.5 and 0.8 ppm, respectively. The CH_2–Te signal in the proton NMR of **9** merges with CH_3 signal of isopropyl group of *p*-cymene and appears shielded by ~0.12 ppm as compared to free $\mathbf{L}^2$. However, as in the case of $\mathbf{L}^1$ the coordination of $\mathbf{L}^2$ with Ru through Te alone may not be ruled out in **9** by this observation.

The ^{13}C {^{1}H} NMR spectra of **3** and **5** could not be recorded because of their poor solubility in $CDCl_3$ as well as other organic solvents. In ^{13}C {^{1}H} NMR spectra of $\mathbf{L}^1$ and $\mathbf{L}^2$ thienyl signals are not much different than those of 2-[2-(4-methoxyphenyltelluro)ethyl]thiophene [15]. In the carbon-13 NMR spectrum of **1** and **2**, the CH_2–Te signal undergoes a deshielding of ~12 ppm in comparison to that of free ligand $\mathbf{L}^1$, corroborating the ligation of $\mathbf{L}^1$ through Te alone as suggested by ^{1}H NMR data. The shifts observed in the signals for thienyl ring carbon atoms are virtually insignificant. In the carbon-13 NMR spectrum of **4**, the CH_2–Te signal exhibits a deshielding of ~13 ppm as compared to that of free $\mathbf{L}^1$. The shifts in the signals for all other carbon atoms are insignificant, thereby indicating the ligation of $\mathbf{L}^1$ through Te alone which is supported by ^{1}H NMR data and also evident from the single crystal structure of **4**. The ^{13}C {^{1}H} NMR spectra of **6** and **7** show deshielding of CH_2–Te signal (~14 ppm) as compared to that of free $\mathbf{L}^2$. The other signals do not undergo any significant change on complex formation, indicating that the ligation of $\mathbf{L}^2$ is also through Te alone. This is also apparent from the single crystal structure of **6**. The carbon-13 NMR spectra of **8**, and **9** exhibit CH_2–Te signals deshielded by ~12 and 8 ppm respectively [compared to free $\mathbf{L}^2$], indicating that this ligand also coordinates the Ru and Hg via Te.

3.1. Crystal structures of complexes *4* and *6*

The single crystal structures of complexes **4** and **6** have been solved. The complex **4** is a half sandwich compound (Fig. 1). The metal coordination sphere is composed of two chlorine ligands, η^6 bonded *p*-cymene ring and ligand $\mathbf{L}^1$ coordinated through Te. The Ru–Te bond length of 2.6340(7) Å is consistent with the literature value of 2.6528(9) Å [15]. The Ru–Cl bond distances of 2.436(2) Å and 2.417(2) Å are normal and consistent with the literature values of 2.4173 (8) Å [21]. The Cl–Ru–Cl bond angle is 86.55(6)° while the Cl–Ru–Te bond angles are 82.84(4)° and 79.09(4)°. The aromatic ring of *p*-cymene ligand is almost planar as C–C–C bond angles vary from 116.8(6)° to 122.3(6)°. In the crystal structure of **6**, the ligand $\mathbf{L}^2$ coordinates through Te only. The $\mathbf{L}^2$ molecules are in *cis* configuration (Fig. 2) around Pd(II) which is not common for monodentate Te ligands. The Pd–Te bond lengths of

2.538(2) and 2.517(2) Å can be compared to sum of respective covalent radii, 2.63 Å (1.31 Å for square planar Pd(II) and 1.32 Å for tetrahedral Te) and are consistent with the reported value (2.52 Å) of Pd–Te bond *trans* to a Pd–Cl bond [9,13,14,22]. The Pd–Cl bond lengths of 2.370(4) Å and 2.327(6) Å are comparable to the standard statistical value of 2.326(46) Å found in four coordinate Pd complexes containing terminal Cl ligands [23] and are consistent with the reported values of 2.351(1)/2.352(1) Å [24] for *cis*-Pd–Cl bonds. The Cl–Pd–Cl bond angle is 92.5(2)° while the Te–Pd–Te bond angle is found to be 93.72(7)°. The crystal structure of **6** shows presence of weak secondary Te···Cl interactions (Te(1)′···Cl(1)/Te(1)···Cl(1)′ = 3.249 Å; Te(2)′···Cl(2)/Te(2)···Cl(2)′ = 3.423 Å; sum of van der Waal's radii = 3.81 Å) in its crystal lattice (Fig. 3). The Pd–Pd distance in the crystal of **6** is 3.188(3) Å which is less than the sum of vander Waal's radii 3.26 Å. However, Pd(1)–S(1) distance is 3.4433(48) Å, which is greater than the sum of van der Waal's radii 3.43 Å. The bond angles at Te, 95.7(4)° and 109.1(6)° are consistent with its nearly trigonal pyramidal (93.6(3)–107.6(18)°) geometry and are comparable with the reported values for *cis*-$[PdCl_2(L)_2]$ system ($L = (C_4H_3S)TeCH_3$) [24]. In both **4** and **6**, the C–C bond lengths and bond angles of all rings were found to be normal.

3.2. Comparison of ligation of L^1 and L^2 with other tellurated hetrocycles

2-[2-(4-Methoxyphenyltelluro) ethyl]thiophene (L^3) [15], bis[2-(2-thienyl) ethyl] telluride (L^4) [15], 2-(phenyltelluromethyl)tetra hydro-2*H*-pyran (L^5) [8], 2-(phenyltelluromethyl)tetra hydrofuran (L^6) [8] and 2-(4-ethoxyphenyltelluromethyl) tetra hydro-2*H*-pyran (L^7) [11] are the tellurated heterocycle ligands studied by us earlier and have one heterocyclic ring common with L^1 or L^2. 2-(Methytelluro)thiophene (L^8) is another such ligand reported by Raija et al. [24,25]. All ligands L^1 to L^8 are found to coordinate in their metal complexes reported so far through Te only. There is a CH_2Te group in L^1 to L^7 which in ^1H and $^{13}C\{^1H\}$ NMR spectra shows coordination shifts (generally deshielding) on the formation of metal complexes. In Table 3 the reported positions of signals of CH_2Te in ligands and metal complexes are compiled and coordination shift values are also given. In proton NMR spectra the coordination shift varies from 0.2 to 0.8 ppm and in carbon-13 NMR from 7.6 to 14.2 ppm. These coordination shift values do not offer any conclusive trend. However, in the case of Hg and Pt complexes of L^1 and L^2 the values of coordination shifts are some what higher than those

Table 3
CH_2Te signal in ^1H and $^{13}C\{^1H\}$ NMR spectra of L^1, L^2, other related ligands and their metal complexes

Ligand/complex	^1H NMR[a]		$^{13}C\{^1H\}$ NMR[a]	
	CH_2Te signal (ppm)	Deshielding	CH_2Te signal (ppm)	Deshielding
2-[(2-Thienyltelluro) methyl] tetrahydrofuran (L^1)	3.03		17.1	
Pd(II)	3.62	0.59	29.2	12.1
Pt(II)	3.75	0.72	29.5	12.4
Ru(II)	3.00	−0.03	30.7	13.6
Hg(II)	3.53	0.50	–	–
[(2-Thienyltelluro)methyl] tetrahydro-2H-pyran (L^2)	2.97		15.4	
Pd(II)	3.32	0.35	29.6	14.2
Pt(II)	3.46	0.49	29.5	14.1
Ru(II)	2.85	−0.12	23.0	7.6
Hg(II)	3.76	0.79	27.0	12.6
2-[2-(4-Methoxyphenyltelluro) ethyl]thiophene (L^3) [15]	3.05		8.6	
Pd(II)	3.30	0.25		
Pt(II)	3.38	0.33		
Ru(II)	3.37	0.32		
Hg(II)	3.70	0.40		
Bis[2-(2-thienyl) ethyl] telluride (L^4) [15]	2.90			3.31
Pd(II)	3.36	0.46		
Pt(II)	–	–		
Ru(II)	3.27	0.37		
Hg(II)	–	–		
2-(Phenyltelluromethyl)tetra hydro–2*H*-pyran (L^5) [8]	3.01/3.16			
Pd(II)	3.24/3.45	0.23/0.29		
Pt(II)	3.24/3.45	0.23/0.29		
2-(Phenyltelluromethyl)tetra hydrofuran (L^6) [8]	3.10/3.51			
Pd(II)	3.47/3.71	0.37/0.20		
Pt(II)	3.47/3.71	0.37/0.20		
2-(4-Ethoxyphenyltelluromethyl) tetra hydro–2*H*-pyran (L^7) [11]	2.90/3.06		16.3	
Ru(II)	3.46/3.69	0.56/0.63	27.1	
Hg(II)	3.31/ 3.42	0.41/0.36	32.7	

[a] Recorded in $CDCl_3$.

Table 4
Bond lengths in Ru(II) and Pd(II) complexes of $\mathbf{L}^1$, $\mathbf{L}^2$, and other related ligands

Ligand	Metal	M–Te	M–Cl	Te···Cl/M···M
2-[(2-Thienyltelluro) methyl] tetrahydrofuran ($\mathbf{L}^1$)	Ru	2.6340(7)	2.417(2)/2.436(2)	
[(2-Thienyltelluro)methyl] tetrahydro-2H-pyran ($\mathbf{L}^2$)	Pd	2.538(2)/2.517(2)	2.370 (4)/2.327(6)	3.249, 3.423/3.188(3)
2-[2-(4-Methoxyphenyltelluro) ethyl]thiophene ($\mathbf{L}^3$) [15]	Pd	2.5951(7) 2.5872(7)	2.300(2)/2.299(2)	3.449–3.450/3.214
Bis[2-(2-thienyl) ethyl] telluride ($\mathbf{L}^4$) [15]	Ru	2.6528(9)	2.415(2)/2.4222(2)	–
2-(4-Ethoxyphenyltelluromethyl) tetra hydro–2*H*-pyran ($\mathbf{L}^7$) [11]	Ru	2.6197(8)	2.4205(12)/2.4136 (12)	–
2-(Methytelluro)thiophene ($\mathbf{L}^8$) [24,25]	Pd	2.538(1)/2.546(1)	2.351(1)/2.352(1)	

observed when these metals make complexes with other ligands viz. $\mathbf{L}^3$ to $\mathbf{L}^7$. Thus ligation capabilities of $\mathbf{L}^1$ and $\mathbf{L}^2$ on the basis of values of coordination shifts can not be rated lower than those of $\mathbf{L}^3$ to $\mathbf{L}^7$. In Table 4 the bond lengths of Ru and Pd complexes of $\mathbf{L}^1$ to $\mathbf{L}^4$, $\mathbf{L}^7$ and $\mathbf{L}^8$ are compared. The Ru–Te bond length is longest in the case of $\mathbf{L}^4$, probably due to steric reasons as the Te is attached to two organic groups, which are more flexible due to long chain lengths. The steric effect of $\mathbf{L}^1$ appears to be next to $\mathbf{L}^4$. In Pd-complex of $\mathbf{L}^3$ the two Te atoms are *trans* to each other, therefore Pd–Te bond lengths are long. On contrary in Pd-complexes of $\mathbf{L}^2$ and $\mathbf{L}^8$, the two Te atoms are *cis* and therefore Pd–Te distances are shorter than the values obtained in the case of Pd-$\mathbf{L}^3$ complex. Similar trends are shown in Pd–Cl bond lengths also.

4. Conclusion

The ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ are synthesized which are probably first organotellurium ligands where Te is directly attached to two different heterocyclic groups. The complexes [Ru(*p*-cymene)Cl_2($\mathbf{L}^1$)] and *cis*-[$PdCl_2$($\mathbf{L}^2$)$_2$] are first structurally characterized complex of such organotellurium ligands. Both the ligands coordinate through Te only. The formation of *cis*-Pd-complex by a telluroether ligand behaving in a monodentate mode is something very rare, particularly in view of reasonably bulky nature of groups attached to Te. The secondary interactions in the crystal of **6** reduces the Pd–Pd distance to 3.188(3) Å, which is less than the sum of van der Waal's radii 3.26 Å.

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