

2-[2-(4-Methoxyphenyltelluro)ethyl]thiophene (L^1) bis[2-(2-thienyl)ethyl] telluride (L^2) and their metal complexes; crystal structure of *trans*-dichlorobis{2-(2-(4-methoxyphenyltelluro)ethyl) thiophene-Te}palladium(II) and {bis[2-(2-thienyl)ethyl] telluride} dichloro(*p*-cymene)ruthenium(II)

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Abstract

The reaction of $ArTe^-$ ($Ar = 4-MeOC_6H_4$) and Te^{2-} generated in situ by borohydride reduction of Ar_2Te_2 and Te , respectively, with 2-(2-thienyl)ethyl chloride has resulted in 2-[2-(4-methoxyphenyltelluro)ethyl]thiophene (L^1) and bis[2-(2-thienyl)ethyl] telluride (L^2), respectively. Their complexes $[AgNO_3(L^1)]$ (1) $[PdCl_2(L^1)_2]$ (2) $[PtCl_2(L^1)_2]$ (3) $[HgBr_2(L^1)_2]$ (4) $[Ru(p\text{-cymene})Cl_2(L^1)]$ (5) $[Ru(p\text{-cymene})Cl_2(L^2)]$ (6) and $[PdCl_2(L^2)_2]$ have been synthesized. The ligands and complexes exhibit characteristic 1H and $^{13}C\{^1H\}$ NMR spectra. Both the ligands coordinate only through Te in all the complexes. The single crystals of **2** and **6** are characterized by X-ray diffraction. Compound **2** has square planar geometry around Pd and *trans* arrangement of ligands. The Pd–Te bond distances 2.5951(7) and 2.5872(7) Å are longer than the values expected due to strong *trans* influence. The unique intermolecular secondary $Te \cdots Cl$ interaction (distance = 3.450/3.449 Å) between neighbouring molecules has been observed in the crystal structure of **2**. The distance between Pd atoms of two neighbouring molecules 3.2143(10) Å has also been found less than the sum of van der Waal's radii 3.26 Å. These secondary interactions in **2** result in the formation of a dimeric species, which remains intact even in the solution. Compound **6** is a half sandwich having three coordination sites occupied by two Cl atoms and the Te atom of L^2 with Ru–Te bond distance of 2.6528(9) Å and Ru–Cl, 2.415(2)/2.422(2) Å.

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1. Introduction

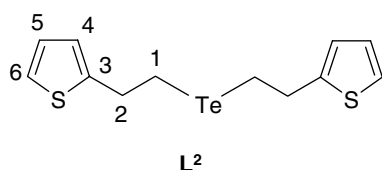
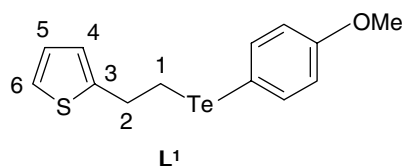
The interest in tellurium ligands [1–6] has grown in the last decade. The important reasons for it are the increasing evidence of enhanced ligating properties of

telluroether ligands compared to thioethers [1–4], the availability of standardized routes for synthesis of such ligands, the possibility of using metal complexes of Te-ligands as precursor for II–VI semiconductors, and the improved availability of FT NMR for studying behaviour in solution. Hybrid organotellurium ligands have also received attention in the last decade [2]. They are organotellurium compounds of $RR'Te$ type, where R or R' has a coordinating group. The R and R' groups explored are alkyl, aryl and heterocyclic groups derived

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from pyridine [7] and pyrrolidine [8a]. However complexes of such tellurides having thienyl group have not been investigated so far, except one report on *cis*-[PdCl₂{(C₄H₃S)TeCH₃}₂] [8b]. It was therefore thought worthwhile to design 2-[2-(4-methoxyphenyltelluro)ethyl]thiophene (**L**¹) and bis[2-(2-thienyl)ethyl] telluride (**L**²) by reacting ArTe⁻ and Te²⁻ with 2-(2-thienyl)ethyl chloride respectively. Their complexation with Ag(I), Hg(II), Pd(II), Pt(II) and Ru(II) has been studied.



The complexes, *trans*-dichlorobis{2-(2-(4-methoxyphenyltelluro)ethyl)thiophene-Te}palladium(II) (**2**) and {bis[2-(2-thienyl)ethyl] telluride}dichloro(*p*-cymene)ruthenium(II) (**6**) have been characterized by X-ray diffraction studies on its single crystals. In both the complexes the ligands **L**¹ and **L**² coordinate through

tellurium only. The results of these investigations are reported in the present 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 spectrometer. The ¹H and ¹³C{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 Protégé 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.

2.1. X-ray diffraction analysis

X-ray diffraction data for **2** and **6** were collected on a Bruker Smart APEX CCD diffractometer and Enraf Nonius Kappa CCD area detector diffractometer with ϕ and ω scans chosen to give a complete asymmetric unit, using a graphite monochromatized Mo-K α radiation

Table 1

Crystal data and structure refinement of *trans*-dichloro-bis{2-(2-(4-methoxyphenyl-telluro)ethyl)thiophene-Te}palladium(II)(**2**) and {bis[2-(2-thienyl)ethyl] telluride}dichloro (*p*-cymene)ruthenium(II) (**6**)

Compound	2	6
Empirical formula	C ₂₆ H ₂₈ Cl ₂ O ₂ Pd S ₂ Te ₂	C ₂₂ H ₂₈ S ₂ Cl ₂ RuTe
Formula weight	869.10	656.13
Temperature	293(2) K	120(2)
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	Cc
Unit cell dimensions	$a = 28.262(1) \text{ \AA}$ $b = 7.7048(3) \text{ \AA}$ $c = 27.770(1) \text{ \AA}$ $\alpha = 90^\circ$ $\beta = 97.857(1)^\circ$ $\gamma = 90^\circ$	$a = 5.9522(3) \text{ \AA}$ $b = 35.531(3) \text{ \AA}$ $c = 11.516(1) \text{ \AA}$ $\alpha = 90^\circ$ $\beta = 101.948(5)^\circ$ $\gamma = 90^\circ$
Volume (Å ³)	5990.3(4)	2382.7(3)
Z	8	4
Density (calculated) (Mg/m ³)	1.927	1.829
$F(000)$	3328	1288
Crystal size/colour/shape	0.250 × 0.104 × 0.030 mm/red/parallel-piped	0.10 × 0.07 × 0.02/red/slab
θ range for data collection (°)	–1.93 to 25.04	3.55 to 27.47
Index ranges	–33 ≤ h ≤ 33, –9 ≤ k ≤ 9, –33 ≤ l ≤ 33	–7 ≤ h ≤ 7, –42 ≤ k ≤ 46, –14 ≤ l ≤ 14
Reflections collected	23811	11515
Independent reflections	5300 [$R_{\text{int}} = 0.0585$]	4972 [$R_{\text{int}} = 0.0809$]
Max. and min. transmission	0.9440 and 0.6932	0.9561 and 0.8052
Data/restraints/parameters	5300/0/318	4972/47/244
Goodness-of-fit on F^2	1.004	0.962
Final R indices	$R_1 = 0.0413$, $wR_2 = 0.0750$ [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0499$, $wR_2 = 0.0812$ [$F^2 > 4\sigma(F^2)$]
R indices (all data)	$R_1 = 0.0645$, $wR_2 = 0.0792$	$R_1 = 0.0945$, $wR_2 = 0.0936$
Largest difference peak and hole (e Å ⁻³)	0.980 and –0.870	1.334 and –1.115

($\lambda = 0.71073 \text{ \AA}$) at 293(2) and 120(2) K, respectively. An analytical face indexed absorption correction was applied in case of **2**. SMART software (data collection and data reduction) and SHELXTL were used for solution and refinement of its structure [9]. Table 1 summarizes the crystal data along with other experimental parameters for **2** and Fig. 1 depicts the its ORTEP diagram. Cell refinement [10] of **6** gave cell constants corresponding to a monoclinic cell whose dimensions are also given in Table 1 along with other experimental parameters. The molecule is displayed in the ORTEP diagram in Fig. 2. An absorption correction was applied in this case also [10]. The structure was solved by direct methods [11] and was refined using the WinGX version [12] of SHELX-97 [13]. 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. In **6** the disorder in the second ($\text{CH}_2\text{CH}_2\text{C}_4\text{H}_3\text{S}$) group was modelled by setting the bond distances and angles to be essentially the same as

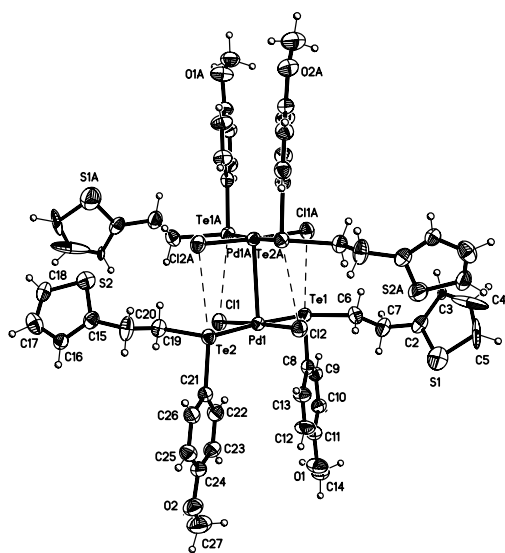


Fig. 1. ORTEP plot of the molecule **2**.

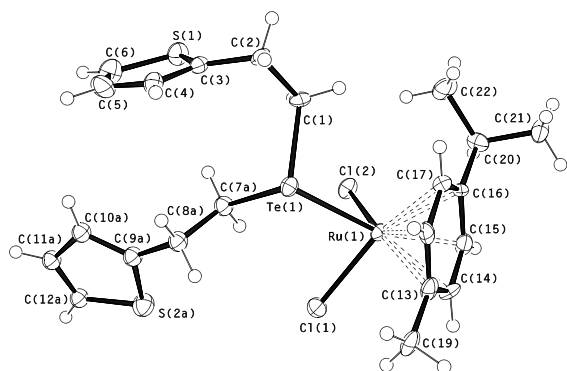


Fig. 2. ORTEP plot of the molecule **6**.

in the first. The selected bond lengths and angles of **2** and **6** are given in Tables 2 and 3, respectively. Additional material for both the structures available from the Cambridge Crystallographic Data Center [CCDC Nos. 235562 and 235563 for palladium (**2**) and ruthenium (**6**) complexes] comprises the final atomic coordinates and thermal parameters for all atoms and a complete listing of bond distances and angles.

2.2. Synthesis of 2-(2-thienyl)ethyl chloride

A solution of 3.28 g (28 mmol) of thionyl chloride made in 50 cm³ of chloroform was added drop wise in nearly 30 min with vigorous stirring to 3.28 g (26 mmol) of 2-(2-thienyl)ethanol (Aldrich, USA) and 2.17 g (21 mmol) of triethylamine, both dissolved in 50 cm³ of chloroform and cooled in ice bath. The mixture was further stirred in ice bath for 10 min and thereafter heated on steam bath until hydrogen chloride evolution ceased. After cooling, the deep red coloured solution was poured in 100 cm³ of ice-cold 1 N hydrochloric acid and the mixture was extracted 3–4 times with chloroform. The chloroform extracts were combined, washed successively with 1 N hydrochloric acid, 2 N sodium bicarbonate and water and dried over anhydrous sodium sulfate. The chloroform was evaporated off on a rotary evaporator to give dark red coloured liquid. Yield: ~70%. NMR: ¹H (CDCl₃, 25 °C): δ (vs TMS): 3.28–3.32 (t, 2H, H₂), 3.72–3.77 (t, 2H, H₁), 6.91–6.92 (t, 1H, H₄), 6.97–7.00 (m, 1H, H₅), 7.20–7.22 (d, 1H, H₆).

2.3. Synthesis of 2-[2-(4-methoxyphenyltelluro)ethyl]-thiophene (**L**¹)

Bis(4-methoxyphenyl)ditelluride (0.50 g, 1.0 mmol) was dissolved in 30 cm³ of ethanol 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

Table 2

Selected bond lengths (Å) and bond angles (°) of **2**

Bond length		Bond angle	
Pd(1)–Te(1)	2.5951(7)	Cl(1)–Pd–Cl(1)	177.06(7)
Pd(1)–Te(2)	2.5872(7)	Te(1)–Pd(1)–Te(2)	176.55(3)
Pd(1)–Cl(1)	2.300(2)	Cl(1)–Pd(1)–Te(1)	85.18(5)
Pd(1)–Cl(2)	2.299(2)	Cl(1)–Pd(1)–Te(2)	94.08(5)
Pd(1)–Pd(1A)	3.214(1)	Cl(2)–Pd(1)–Te(1)	94.64(5)
Te(1)–C(6)	2.143(7)	Cl(2)–Pd(1)–Te(2)	85.93(5)
Te(1)–C(8)	2.117(7)	C(6)–Te(1)–C(8)	93.6(3)
Te(2)–C(19)	2.133(6)	C(19)–Te(2)–C(21)	94.2(3)
Te(2)–C(21)	2.114(7)	C(19)–Te(2)–Pd(1)	106.3(2)
Te1...Cl1A/Te1A...Cl1	3.450	C(21)–Te(2)–Pd(1)	100.9(2)
Te2...Cl2A/Te2A...Cl2	3.449		
Pd–Pd	3.214(1)	C(8)–Te(1)–Pd(1)	96.6(2)

Table 3
Selected bond lengths (Å) and angles (°) of **6**^a

<i>Bond lengths</i>					
Ru(1)–Te(1)	2.6528(9)	Ru(1)–Cl(1)	2.415(2)	Ru(1)–Cl(2)	2.422(2)
Ru(1)–C(13)	2.202(9)	Ru(1)–C(14)	2.184(9)	Ru(1)–C(15)	2.204(9)
Ru(1)–C(16)	2.209(8)	Ru(1)–C(17)	2.174(8)	Ru(1)–C(18)	2.161(8)
Te(1)–C(1)	2.155(8)	S(1)–C(6)	1.720(8)	Te(1)–C(7a)	2.167(7)
S(1)–C(3)	1.734(7)	C(1)–C(2)	1.528(8)	C(9a)–S(2a)	1.734(7)
C(2)–C(3)	1.494(8)	C(12a)–S(2a)	1.721(8)	C(7a)–C(8a)	1.528(8)
		C(8a)–C(9a)	1.493(8)		
<i>Bond angles</i>					
Cl(1)–Ru(1)–Cl(2)	88.53(8)	Cl(1)–Ru(1)–Te(1)	84.47(6)	Cl(2)–Ru(1)–Te(1)	86.90(6)
C(1)–Te(1)–Ru(1)	100.5(2)	C(7a)–Te(1)–Ru(1)	103.8(2)	C(1)–Te(1)–C(7a)	96.2(3)
C(6)–S(1)–C(3)	92.2(4)	C(12a)–S(2a)–C(9a)	92.2(4)	C(8a)–C(7a)–Te(1)	108.2(5)
C(2)–C(1)–Te(1)	113.2(5)	C(3)–C(2)–C(1)	113.9(5)	C(9a)–C(8a)–C(7a)	113.9(5)

^a The disorder in the second (CH₂CH₂C₄H₃S) group was modelled by setting the bond distances and angles to be essentially the same as in the first.

atmosphere until it became colourless due to the formation of ArTe[−] Na⁺. 2-(2-Thienyl)ethyl chloride dissolved in 5 cm³ of ethanol was added to this solution with constant stirring. The reaction mixture was refluxed further for 2–3 h, cooled to room temperature and poured into ice cold water (20 cm³) in which 0.1 g of NaOH was dissolved. The ligand was extracted into chloroform (200 cm³) 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 red oil, which was extracted with hexane. On removing hexane from the extract under reduced pressure on a rotary evaporator ligand **L**¹ was obtained as clear yellow oil. Yield: 80%. Anal. Calc. for C₁₃H₁₄OSTe: Te, 36.92. Found: Te, 36.74%. NMR: ¹H (CDCl₃, 25 °C): δ (vs TMS): 3.03–3.08 (m, 2H, H₁), 3.23–3.28 (m, 2H, H₂), 3.77 (s, 3H, OCH₃), 6.71–6.77 (m, 3H, H₄ and ArH *m* to Te), 6.87–6.89 (t, 1H, H₅), 7.09 (d, *J* = 1.2 Hz, 1H, H₆), 7.66–7.69 (m, 2H, ArH *o* to Te); ¹³C{¹H} (CDCl₃, 25 °C): (vs TMS): 8.57 (C₁), 29.65 (C₂), 54.76 (OCH₃), 100.19 (ArC–Te), 114.02 (ArC *m* to Te), 124.01 (C₄), 124.63 (C₆), 126.45 (C₅), 140.32 (ArC *o* to Te), 145.37 (C₃), 159.44 (ArC *p* to Te).

2.4. Synthesis of [AgNO₃(L¹)] (**1**)

A solution of AgNO₃ (0.1 g, 0.58 mmol) made in 15 cm³ of dry acetonitrile was stirred under dry nitrogen atmosphere in absence of light with a solution of **L**¹ made in 10 cm³ of chloroform. The mixture was stirred at room temperature for 1 h. The pink coloured complex precipitated, which was filtered, washed well with acetone followed by cold chloroform and dried in vacuo. It was recrystallized using acetonitrile. Yield: 70%; m.p., 130 °C (d). Mol. wt.: Found, 511; Calc. 515.5. *A*_M, 28.15 ohm^{−1} cm² mol^{−1}. Anal. Calc. for C₁₃H₁₄NO₄STeAg: C, 30.26; H, 2.71; N, 2.51; Te, 24.80. Found: C, 30.31; H, 2.68; N, 2.36 Te, 24.10%. NMR: ¹H (CH₃CN, 25 °C): (vs TMS): 3.06–3.09 (2t, 4H, H₁ + H₂), 3.69 (s, 3H,

OCH₃), 6.72–6.75 (bt, 3H, H₄ + ArH *m* to Te), 6.81–6.84 (m, 1H, H₅), 7.12 (d, *J* = 5.0 Hz, 1H, H₆), 7.54 (d, *J* = 9 Hz, 2H, ArH *o* to Te).

2.5. Synthesis of [PdCl₂(L¹)₂] (**2**)

To a solution of **L**¹ (0.17 g, 0.50 mmol) made in 10 cm³ of acetone was added Na₂[PdCl₄] (0.08 g, 0.25 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 sodium sulphate, concentrated to ~10 cm³ and mixed with hexane (20 cm³). The resulting reddish solid was filtered, washed with hexane and dried in vacuo. The single crystals of the complex **2** were grown from chloroform hexane mixture (1:1). Yield: 75%; m.p., 110 °C. Mol. wt.: Found, 1726; Calc. 869.1. *A*_M, 5.26 ohm^{−1} cm² mol^{−1}. Anal. Calc. for C₂₆H₂₈Cl₂O₂PdS₂Te₂: C, 35.90; H, 3.22; Te, 29.37. Found: C, 35.41; H, 3.01; Te, 28.98%. NMR: ¹H (CDCl₃, 25 °C): δ (vs TMS): 3.10–3.40 (bd, 3H, 2H₂ + 1H₁), 3.50 (bs, 1H, H₁), 3.83 (s, 3H, OCH₃), 6.81–6.82 (m, 1H, H₄), 6.88–6.91 (bm, 2H, H₅ + ArH *m* to Te), 7.13–7.15 (t, 1H, H₆), 7.20–7.60 (bd, 2H, ArH *o* to Te).

2.6. Synthesis of PtCl₂(L¹)₂ (**3**)

A solution of **L**¹ (0.17g, 0.50 mmol) made in 10 cm³ of acetone was added to K₂[PtCl₄] (0.08 g, 0.25 mmol) dissolved in 10 cm³ of water. The resulting mixture was stirred for 3 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 sodium sulphate, concentrated to ~10 cm³, and mixed with hexane (20 cm³). The resulting orange colored compound was filtered, washed with hexane and recrystallized from chloroform: hexane (2:1) mixture. Yield: 78%; m.p., 91–94 °C. Mol. wt.: Found, 955; Calc.

957.3. M_M , 8.67 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calc. for $\text{C}_{26}\text{H}_{28}\text{Cl}_2\text{O}_2\text{PtS}_2\text{Te}_2$: C, 32.59; H, 2.92; Te, 26.65. Found: C, 32.08; H, 2.85; Te, 26.09. NMR: ^1H (CDCl_3 , 25 °C): δ (vs TMS): 2.87–2.95 (m, 1H, H_2), 3.18–3.26 (m, 1H, H_2), 3.33–3.43 (m, 1H, H_1), 3.59–3.65 (m, 1H, H_1), 3.74–3.87 (s, 3H, OCH_3), 6.69–6.81 (m, 3H, H_4 and Ar–H *m* to Te), 6.84–6.89 (m, 1H, H_5), 7.06–7.15 (m, 1H, H_6), 7.26–7.37 (m, 1H, ArH *o* to Te), 7.46–7.49 (d, $J = 8.5$ Hz, 1H, ArH *o* to Te).

2.7. Synthesis of $[\text{HgBr}_2(\text{L}^1)]_2$ (4)

The HgBr_2 (0.20g, 0.55 mmol) dissolved in acetone (20 cm^3) was mixed with a solution of L^1 (0.17g, 0.55 mmol) made in chloroform (20 cm^3). The resulting mixture was stirred at room temperature 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 chloroform and filtered through celite. The filtrate was concentrated to 10 cm^3 and mixed with 20 cm^3 of hexane. A white complex was separated, filtered, dried in vacuo. and recrystallized from chloroform–hexane (1:1) mixture. Yield: 70%; m.p. 65 °C; Mol. wt.: Found, 1403; Calc. 1412. M_M , 9.38 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calc. for $\text{C}_{13}\text{H}_{14}\text{OSTeHgBr}_2$: C, 22.09; H, 1.98; Te, 18.00. Found: C, 21.77; H, 1.91; Te, 17.72%. NMR: ^1H (CDCl_3 , 25 °C): δ (vs TMS): ^1H (CDCl_3 , 25 °C): δ (vs TMS): 3.37–3.41 (t, 2H, H_2), 3.69–3.72 (t, 2H, H_1), 3.76 (s, 3H, OCH_3), 6.87–6.94 (m, 4H, ArH *m* to Te + H_4 + H_5) 7.14–7.16 (m, 1H, H_6), 7.65 – 7.67 (m, 2H, ArH *o* to Te).

2.8. Synthesis of $[\text{Ru}(p\text{-cymene})\text{Cl}_2(\text{L}^1)]$ (5)

The $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.61g, 1 mmol) was dissolved in 20 cm^3 of dichloromethane. A solution of L^1 (0.69g, 2 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 was filtered, washed with hexane and dried in vacuo. The complex was crystallized using chloroform hexane 1:1 mixture. Yield: 76%; 160 °C (d). Mol. wt.: Found, 646; Calc. 651.7. M_M , 9.48 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calc. for $\text{C}_{23}\text{H}_{24}\text{OSRuTe}$: C, 42.35; H, 3.68; Te, 19.50. Found: C, 42.01; H, 3.66; Te, 19.02%. NMR: ^1H (CDCl_3 , 25 °C): δ (vs TMS): 1.23 (d, $J = 3$ Hz, 6H, CH_3 of *i*-Pr), 2.15 (s, 3H, CH_3 of *p*-cymene), 2.84 (t, 2H, H_2), 3.04–3.07 (m, 1H, CH of *i*-Pr), 3.32 – 3.41 (bd, 2H, H_1), 3.84 (s, 3H, OCH_3), 4.86–5.39 (m, 4H, Ar–H *p*-cymene), 6.72 – 6.83 (m, 1H, H_4), 6.85–6.89 (m, 3H, ArH *m* to Te + H_5), 7.05–7.07 (m, 1H, H_6), 7.66–7.83 (2d, 2H, ArH *o* to Te).

2.9. Synthesis of L^2

Tellurium powder (0.65 g, 5 mmol) and sodium borohydride (0.38 g, 10 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. To the resulting colourless thin slurry of Na_2Te kept under reflux, a solution of 2-(2-thienyl)ethyl chloride (1.47 g, 10 mmol) made in 5 cm^3 of ethanol was added drop wise with constant stirring under nitrogen atmosphere. The mixture was cooled to room temperature and poured into 100 cm^3 of water. The ligand L^2 was extracted into diethyl ether 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 a reddish yellow viscous liquid that is unstable as it shows the sign of decay within few days. Yield: 79%. Anal. Calc. for $\text{C}_{12}\text{H}_{14}\text{S}_2\text{Te}$: Te, 36.49, Found: Te, 36.36%. ^1H NMR (CDCl_3 , 25 °C): δ (vs TMS): 2.88–2.93 (t, 2H, H_1), 3.26–3.31 (t, 2H, H_2), 6.83–6.84 (d, $J = 3$ Hz, 1H, H_4), 6.92–6.95 (m, 1H, H_5), 7.14–7.16 (d, $J = 6$ Hz, 1H, H_6). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 25 °C): δ (vs TMS): 3.96, 4.73 (C_1), 31.74, 34.21 (C_2), 124.25 (C_4), 125.61 (C_6), 126.68 (C_5), 145.34 (C_3).

2.10. Synthesis of $\{\text{Ru}(p\text{-cymene})\text{Cl}_2(\text{L}^2)\}$ (6)

To a solution of $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.61g, 1 mmol) made in 20 cm^3 of dichloromethane was added a solution of L^2 (0.68 g, 2 mmol) made in 10 cm^3 of dichloromethane. 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 (10 cm^3). The resulting red precipitate was filtered, washed with hexane and dried in vacuo. The single crystals suitable for diffraction were grown from chloroform hexane 1:1 mixture. Yield: 74%; m.p., 99 °C. Mol. wt.: Found, 652; Calc. 655.7. M_M , 10.47 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calc. for $\text{C}_{22}\text{H}_{28}\text{Cl}_2\text{RuS}_2\text{Te}$: C, 40.26; H, 4.27; Te, 19.46. Found: C, 40.01; H, 4.23; Te, 19.09%. NMR: ^1H (CDCl_3 , 25 °C): δ (vs TMS): 1.24–1.26 (d, $J = 6$ Hz, 6H, CH_3 *p*-cymene), 2.16 (s, 3H, Ar– CH_3 *p*-cymene), 2.77–2.82 (m, 1H, CH *p*-cymene), 2.84–2.91 (m, 1H, H_2), 3.12–3.17 (t, 2H, H_1 + H_2), 3.22–3.27 (m, 1H, H_1), 5.14–5.16 (d, $J = 5.3$ Hz, 2H, Ar–H *p*-cymene), 5.26–5.28 (d, $J = 4.8$ Hz, Ar–H *p*-cymene), 6.85 (bs, 1H, H_4), 6.95 (m, 1H, H_5), 7.17–7.18 (m, 1H, H_6).

2.11. Synthesis of $[\text{PdCl}_2(\text{L}^2)]_2$ (7)

PdCl_2 (0.07g, 0.39 mmol) was stirred with 5 ml of dry benzotrile and the mixture was warmed to give a clear solution. After cooling the clear solution to room temperature it was mixed with a solution of L^2 (0.27g, 0.78

mmol) made in 10 cm³ of chloroform. The mixture was further stirred for 3 h at room temperature. The solvent was completely removed on a rotary evaporator under reduced pressure. The residue obtained was dissolved in dichloromethane (5 cm³) and mixed with hexane. The resulting red brown precipitate was filtered, washed with hexane and dried in vacuo. The complex was crystallized using chloroform hexane 1:1 mixture. Yield: 70%; m.p. 85 °C. Mol. wt.: Found, 869; Calc. 876.6. A_M , 12.41 ohm⁻¹ cm² mol⁻¹. Anal. Calc. for C₂₄H₂₈S₄Te₂PdCl₂: C, 32.85; H, 3.19; Te, 29.11. Found: C, 32.61; H, 3.16; Te, 29.08%. ¹H NMR (CDCl₃, 25 °C): δ (vs TMS): 2.87–2.97 (m, 2H, H₂), 3.35–3.37 (m, 6H, 4H₁ and 2H₂), 6.87–6.88 (d, J = 3 Hz, 1H, H₄), 6.92–6.95 (m, 1H, H₅), 7.16–7.17 (d, J = 4.4 Hz, 1H, H₆). ¹³C{¹H} (CDCl₃, 25 °C): δ (vs TMS): 16.85 (C₁), 29.83. (C₂), 124.14 (C₄), 125.38 (C₆), 127.12 (C₅), 145.75 (C₃).

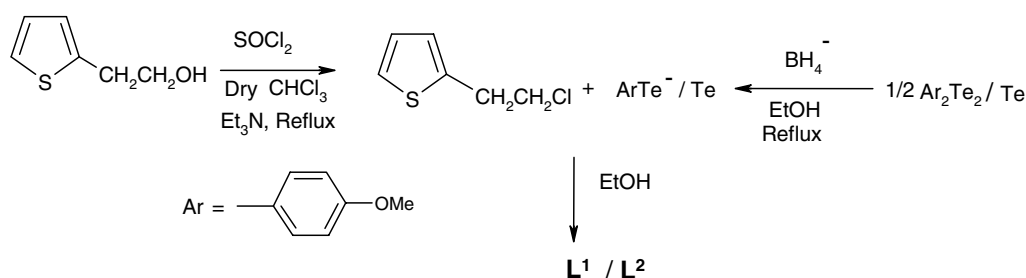
3. Results and discussion

The ligand **L**¹ synthesized by the sequence of reactions given in Scheme 1 was found stable for two months under ambient conditions. Thereafter, deposition of white solid starts in the oil **L**¹, which is most likely a tellurium dioxide formed by oxidative decomposition of **L**¹. However, **L**² begins to show the sign of decomposition after storing it for four days at room temperature but TeO₂ appears to be again formed. Generally Te-alkyl bond is considered weaker with respect to that of Te-aryl bond and this may be responsible for the difference between stability of **L**¹ and **L**² as in the later both Te–C bonds are Te-alkyl ones. All the complexes **1**–**7** of both the ligands can be stored at room temperature for two months easily. Both **L**¹ and **L**² and their complexes are highly soluble in chloroform and dichloromethane and moderately soluble in acetone. In methanol, ethanol and hexane the two ligands are sparingly soluble. The molecular weight and conductance measurements on complexes **1**–**7** suggest that **1**, **3** and **5**–**7** are monomeric in nature and complex and **4** is dimeric. All the complexes are non-electrolytes. In IR spectrum of Ag(I) complex two bands appear at 1384 and 1487 cm⁻¹ and there is no band at 1700–1800 cm⁻¹ (due to free NO₃⁻). This suggests that nitrate is in a

mondentate bonding mode in this complex. The CH₂Te signal in ¹H NMR of silver complex appears shielded with respect to that of free **L**¹. Similar observations are reported earlier also when formation of a metal-tellurium bond by a 3/4d¹⁰ metal occurs [2–4]. Thus the coordination number of Ag in its complex appears to be two (coordinated by Te and O of NO₃⁻ group). The complex **4** exhibits bands at 225, 235 and 290 cm⁻¹ indicating the presence of both bridging and terminal Br ligands. The CH₂ protons in **4** appear ~0.1–0.6 ppm deshielded with respect to those of **L**¹, indicating the ligation of the ligand **L**¹ through Te. Thus **4** appears to be dimeric having two bromo bridges and its Hg is coordinated by Te and three bromine atoms. The most plausible geometry of Hg in **4** appears to be tetrahedral. In the complexes **2** and **3** ν (M–Cl) appears at 330 and 315 cm⁻¹ indicating the presence of two *trans* M–Cl bonds of a square planar complex. However in the spectrum of **7** (also square planar most probably) the ν (M–Cl) due to two *trans* Pd–Cl appears at 348 cm⁻¹. IR spectrum of **5** has ν_{syn} (Ru–Cl) and ν_{asym} (Ru–Cl) at 350 and 330 cm⁻¹, respectively, whereas that of **6** has these band at 325 and 305 cm⁻¹, respectively. In complexes **1**, **2**, **3**, **5**, **6** and **7** H₁ protons appear deshielded (~0.25–0.5) whereas H₂ protons and aryl protons *ortho* to tellurium appear almost unaffected or shielded (up to 0.4 ppm). These observations suggest that there is weak intramolecular S···Te interaction in the ligands, which breaks down on complex formation through Te donor site resulting in the shielding of H₂ and ArH *ortho* to Te, otherwise they are expected to exhibit small deshielding. Thienyl protons are marginally affected on complex formation and sulfur of thienyl group is not involved in ligation of **L**¹ and **L**² as evidenced by single crystal structures of **2** and **6**. Therefore **L**¹ and **L**² coordinate in all seven complexes through Te alone. The presence of positive charge on sulfur probably blocks its coordination. The two signals for C₁ and C₂ in ¹³C{¹H} NMR spectrum of **L**² appear probably due to the presence of its two conformers.

3.1. Crystal structures of **2** and **6**

The molecular structure of **2** is shown in Fig. 1. Palladium has nearly square planar geometry and a



Scheme 1.

trans structure having two tellurium atoms and two chlorine atoms in its coordination sphere. Pd–Te bond distances 2.5951(7) and 2.5872(7) Å of **2** are comparable with the reported values for other *trans*-[PdCl₂(Te-ligand)₂] complexes; 2.5873(2)[14], 2.5865(2)/2.6052(2)[15] and 2.5975(6)/2.6021(6)[15] when Te-ligands are bis(2-{1,3-dioxan-2-yl}ethyl) telluride, *N*-{2-(4-methoxyphenyltelluro)ethyl}morpholine and bis{2-(*N*-morpholino)ethyl} telluride, respectively. However, for complex [PdCl₂{4-MeOC₆H₄TeCH₂CH₂SEt}]₂ [16] the reported Pd–Te bond distance 2.492(13) Å is shorter than those of **2**. It may be due to chelate effect of the bidentate ligand. The strong *trans* influence exerted in **2** by each Pd–Te bond on the other is probably responsible for this elongation. The Pd–Cl bond lengths 2.3006(18)/2.2990(18) 2.6528(9) are also comparable with the values reported for other *trans*-[PdCl₂(Te-ligand)₂] complexes (2.9990(8)–2.329(2) Å). The bond angles at Te are consistent with its nearly trigonal pyramidal (93.6(3)–107.67(18)°) geometry. The unique feature of crystal structure of **2** is the intermolecular interaction between Te coordinated to Pd and Cl (Te···Cl distances 3.449/3.450 Å are shorter than sum of van der Waal's radii 4 Å). These secondary interaction in **2** (may be supported a little bit by crystal forces) reduces Pd–Pd distance between the two molecules to 3.2143(10) Å (sum of van der Waal's radii is 3.26 Å) and result in the formation of a dimeric species, which remains intact even in the solution as molecular weight of **2** is found to be double of the value expected for a monomeric moiety. This indicates that secondary intermolecular Te···Cl interactions are significantly strong [20a] and not fully dissociated on dissolution in chloroform. However, the dimeric nature even in solution suggests that the tendency of Te and Cl to form supramolecular associations [20a] through inter/intramolecular interaction is mainly responsible for dimer formation.

The molecular structure of **6** is shown in Fig. 2. It is a half-sandwich compound in which two chlorine atoms, the tellurium atom and the *p*-cymene ring constitute the coordination sphere around ruthenium. The Ru–Te bond length of 2.6528(9) Å is consistent with the values 2.651(5) and 2.6559(9) Å reported for [Ru(*p*-cymene)Cl₂{bis(1,3-dioxan-2yl)ethyl telluride}] [14] and [Ru(*p*-cymene)Cl₂{N-[2-(4-methoxyphenyltelluro)ethyl]phthalimide}] [17] but some what longer than the values 2.619(8), 2.642(1), 2.6381(16)/2.6411(2) Å observed for [Ru(*p*-cymene)Cl₂L] type of complexes when L = 2-(4-ethoxyphenyltelluromethyl)tetrahydro-2*H*-pyran [18], 2-(2-{4-ethoxyphenyl}telluroethyl)-1,3-dioxane [18] and bis{(4-methoxyphenyltelluro)} methane [19], respectively. The Ru–Cl bond lengths of **6**, 2.415(2)/2.422(2) Å are consistent with the values observed for [Ru(*p*-cymene)Cl₂L] type of complexes (L = Te-ligand) [12,15–17] and [RuCl{η²-C₆H₃(CH₂NMe₂)₂-2,6}{η⁶-C₁₀H₁₄}] [20b].

The smaller difference between Ru–Te/Pd–Te bond lengths of **2** and **6** with respect to values reported in literature may also arise from a combination of steric and electronic effects of various organic groups/moieties present in the organotellurium ligands which due to large size of Te are more prone to these effects. However, the contribution of crystal packing to the variation of these bond lengths may also not be ruled out, particularly in view of large size of tellurium atom.

On the basis of spectroscopic evidences it appears that in **3** and **7** metal atoms also have square planar geometry as supported in case of **2** by single crystal structure determination. Similarly **5** may be described like **6** as a half sandwich compound containing *p*-cymene as π-ligand and two Cl and L² (bonded through Te) as three two electron donors.

4. Conclusion

The ligands 2-[2-(4-methoxyphenyltelluro)ethyl]thiophene (L¹) and bis[2-(2-thienyl)ethyl] telluride (L²) are the first examples of thienyl group containing tellurides studied extensively for ligation reactions. The L¹ and L² are synthesized and properly characterized for the first time. The palladium(II) complex of L¹ has an unique structure in which there are intermolecular interactions between Te coordinated to Pd and Cl atoms and two Pd atoms of neighbouring molecules are closer than the sum of van der Waal's radii. These secondary interactions in **2** result in the formation of a dimeric species, which remains intact even in the solution as supported by molecular weight values. Complex **6** is the first structurally characterized example of Ru(II) complex formed with thienyl group containing telluride.

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