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Reactions of hybrid organotellurium ligands 1-(4-methoxyphenyl telluro)-2-[3-(6-methyl-2-pyridyl) propoxy]ethane (L^1) and 1-ethylthio-2-[2-thienyltelluro]ethane (L^2) with mercury (II) bromide: formation of complexes and their decomposition

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Abstract

Two tellurium ligands 1-(4-methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl)propoxy]ethane ($\mathbf{L}^1$) and 1-ethylthio-2-[2-thienyltelluro]ethane ($\mathbf{L}^2$) have been synthesized by reacting nucleophiles [4-MeO–$C_6H_4Te^-$] and [C_4H_3S-2-Te^-] with 2-[3-(6-methyl-2-pyridyl)propoxy]ethylchloride and chloroethyl ethyl sulfide, respectively. Both the ligands react with $HgBr_2$ resulting in complexes of stoichiometry [$HgBr_2 \cdot \mathbf{L}^1/\mathbf{L}^2$] (**1**/**4**), which show characteristic NMR (^1H and $^{13}C\{^1H\}$). On crystallization of **1** from acetone–hexane (2:1) mixture, the cleavage of $\mathbf{L}^1$ occurs resulting in 4-$MeOC_6H_4HgBr$ (**2**) and [$RTe^+ \rightarrow HgBr_2$]Br^- (**3**) (where R = –$CH_2CH_2OCH_2CH_2CH_2$-(2-(6-CH_3–C_5H_3N))). The **2** is characterized by X-ray diffraction on its single crystal. It is a linear molecule and is the first such system which is fully characterized structurally. The Hg–C and Hg–Br bond lengths are 2.085(6) and 2.4700(7) Å. The distance of four bromine atoms (3.4041(7)–3.546(7) Å) around Hg (*cis* to C) is greater than the sum of van der Waal's radii 3.30 Å. This mercury promoted cleavage is observed for an acyclic ligand of RArTe type for the first time and is unique, as there appears to be no strong intramolecular interaction to stabilize the cleavage products. The **4** on crystallization shows the cleavage of organotellurium ligand $\mathbf{L}^2$ and formation of a unique complex [(EtS(CH_2)$_2$SEt)HgBr(μ-Br)Hg(Br)(μ-Br)$_2$Hg(Br)(μ-Br)BrHg(EtS(CH_2)$_2$SEt)]·2$HgBr_2$ (**5**), which has been characterized by single crystal structure determination and ^1H and $^{13}C\{^1H\}$ NMR spectra. The elemental tellurium and [$C_4H_3SCH_2$]$_2$ are the other products of dissociation as identified by NMR (proton and carbon-13). The cleavage appears to be without any transmetalation and probably first of its kind. The centrosymmetric structure of **5** is unique as it has [$HgBr_3$]$^-$ unit, one Hg in distorted tetrahedral geometry and one in pseudo-trigonal bipyramidal one. The molecule of **5** may also be described as having [(EtSCH_2CH_2SEt)HgBr]$^+$ [$HgBr_3$]$^-$ units, which dimerize and co-crystallize with two $HgBr_2$ moieties. There are very weak Hg···Br interactions between co-crystallized $HgBr_2$ units and rest of the molecule. [Hg(3)–Br(1)/Hg(3)–Br(4) = 3.148(1)/3.216(1) Å]. The bridging Hg···Br distances, Hg(2)–Br(4)′, Hg(2)′–Br(4) and Hg(1)–Br(2), are from 2.914(1) to 3.008(1) Å.

Keywords: Tellurium ligands; 1-(4-Methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl)propoxy]ethane; 1-Ethylthio-2-[2-thienyltelluro]ethane; Mercury complexes; Decomposition; Crystal structures

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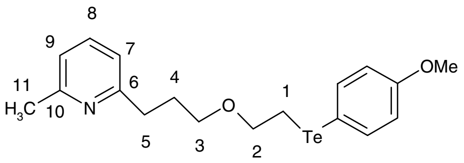
1. Introduction

In recent years, there has been growing interest in tellurium ligands [1,2]. This is because there are increasing evidences of enhanced ligating properties of telluroether compared to thioethers, 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. Mercury(II) is among the Lewis acids with which Te-donor sites easily ligate. However, the cleavage of neutral organotellurium ligands, viz. diorganyl tellurides has been reported several times. The reaction of (2-(2-pyridyl)phenyl)(3-ethoxyphenyl) tellurium (RR′Te) with $HgCl_2$ has resulted in $[R'HgCl \cdot 2RTeCl_2]$ [3,4]. Bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] telluride undergoes C–Te bond cleavage on reaction with mercury (II) bromide and it is attributed to the stabilizing effect of intramolecular N→Te interactions in the resulting products [5]. $[Pt(COD)_2]Cl_2$ has also been found promoting cleavage of macrocyclic organotellurium ligands [6]. Recently, for a palladium catalyzed Fujiwara-Heck cross coupling reaction between organic tellurides and alkenes, migration of an organic moiety to Pd is proposed as a key step [7,8].



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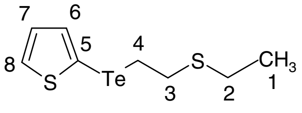

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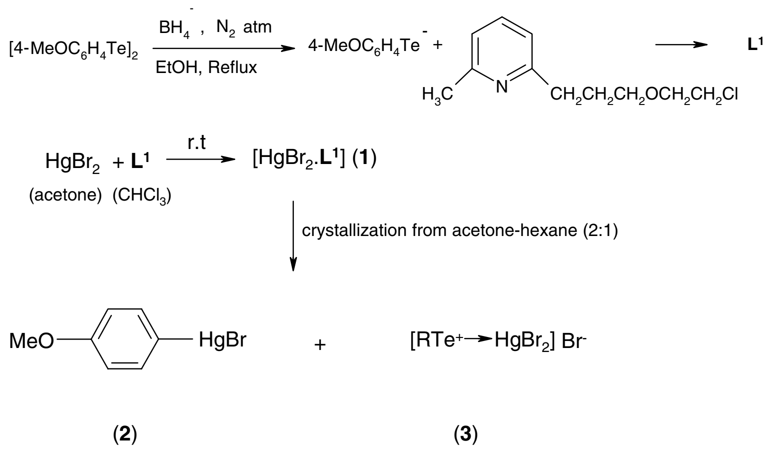
In view of these observations, we have carried out reactions of $HgBr_2$ with newly synthesized 1-(4-methoxyphenyl telluro)-2-[3-(6-methyl-2-pyridyl) propoxy]ethane ($\mathbf{L}^1$) and 1-ethylthio-2-[2-thienyltelluro]ethane ($\mathbf{L}^2$). It is observed that both these ligands first form complexes having composition $[HgBr_2 \cdot \mathbf{L}^1/\mathbf{L}^2]$, which decompose during the attempt of growing single crystals resulting in $4\text{-}MeOC_6H_4HgBr$ (**2**) in the case of $\mathbf{L}^1$ and $[(EtS(CH_2)_2SEt)HgBr(\mu\text{-}Br)Hg(Br)(\mu\text{-}Br)_2Hg(Br)(\mu\text{-}Br)BrHg(EtS(CH_2)_2SEt)] \cdot 2HgBr_2$ (**5**) in the case of $\mathbf{L}^2$. Both **2** and **5** have been characterized by X-ray diffraction on their single crystals. The structure of **5** is unique and most probably is the first example of this type. Other products of these decompositions have also been identified. However, the single crystals of both mercury complexes and other decomposition products could not be grown. The results of these investigations are reported in the present paper.

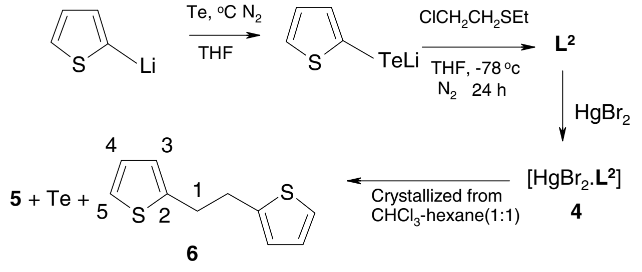
2. Results and discussion

The reactions given in Scheme 1 result in $\mathbf{L}^1$, which remains stable under ambient conditions for 3–4 months. The $\mathbf{L}^1$ has good solubility in chloroform and dichloromethane but in methanol and hexane the solubility was only moderate. Its reaction with $HgBr_2$ and decomposition of the mercury complex formed is also shown in Scheme 1. The **1** is characterized by elemental analyses and proton and carbon-13 NMR. In d^{10} systems, coordination shifts in NMR are not found to be significant and this is true for **1** and **4** also. The ^1H NMR of **3** is also characteristic. The elemental analyses support its stoichiometry. Such compounds are among the expected ones in the tellurium chemistry [14]. The **2** shows characteristic ^1H NMR and gives satisfactory elemental analyses. The ν(HgBr) in IR spectra of **2** and **3** has been observed at 294 cm^{-1}, as expected for a terminal Hg–Br. The **3** is insoluble in organic solvents non-polar in nature or having low polarity.Its single crystals could not be grown.The compounds **1**–**3** are stable under ambient conditions and may be stored for 2–3 months easily. The **2** (Fig. 1) is the first example of linear ArC–Hg–Br system (angle C–Hg–Br = 175.0(1)°) which is fully characterized structurally [15]. The Hg atom is surrounded by four more Br atoms in the crystal (making nearly octahedral geometry), which are *cis* to aryl carbon but the distances of all such atoms (3.4041(7)–3.546(7) Å) are greater than the sum of van der Waal's radii (3.30 Å). The Hg–C distances of **2** (Table 2) are consistent with the literature report of 2.08 Å for almost linear Me–HgX [16]. Similarly, Hg–Br distance of **2** (Table 2) is consistent with the value of 2.480(3) Å reported for MeHgBr [16]. This mercury promoted cleavage is observed for an acyclic ligand of RArTe type for the first time and is unique, as there appears to be no strong intramolecular interaction to stabilize the cleavage products.

The ligand $\mathbf{L}^2$ was synthesized by reactions given in Scheme 2. It is stable for 2 weeks only under ambient conditions and is soluble in organic solvents such as chloroform, dichloromethane and benzene but is very poor in methanol solubility. The ^1H and ^{13}C NMR spectra of $\mathbf{L}^2$ are characteristic. On reacting $\mathbf{L}^2$ with $HgBr_2$, a yellowish substance (small amount) is precipitated, which is insoluble and defied all attempts of its characterization. After filtering off this substance the mother liquor was concentrated and mixed with hexane to obtain **4**, which on crystallization gives elemental tellurium and single crystals of **5**. The **6** was obtained from the mother liquor. **4**–**6** show characteristic ^1H and



Scheme 1.

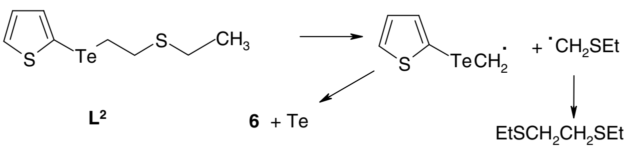


Scheme 2.

$^{13}C\{^{1}H\}$ NMR. Single crystal structure of **5** has been determined and Fig. 2 shows ORTEP diagram. In the structure of **5**, bond angles reveal that Hg(1) has distorted tetrahedral geometry and Hg(3) pseudo-trigonal bipyramidal geometry. The Hg(2)—Br (1) distance 3.451(1) Å is greater than the sum of van der Waal's radii 3.30.Å. The Hg—S distances (2.612(3) and 2.523(3) Å) in **5** are longer than the values reported in the literature 2.340 (2)–2.40(1) Å [17–19]. There are three types of Hg—Br distances in **5**. Among the long ones, Hg(2)–Br(4)′ = 3.008(1); Hg(2)′–Br(4) = 3.008(1) and Hg(1)–Br(2), = 2.914(1) Å represent the weak bridging interactions (or secondary), whereas Hg(3)–Br(1) = 3.148(1) and Hg(3)–Br(4) = 3.216(1) Å show further weak secondary interactions. Hg(1)–Br(1), Hg(2)–Br(3), Hg(2)–Br(2), Hg(2)–Br(4), Hg(3)–Br(5) and Hg(3)–Br(6) bond distances are between 2.417(1) and 2.573(1) Å and consistent with the values reported for single covalent bond 2.480(3) Å [16]. The closeness of Hg(2)–Br(3), Hg(2)–Br(2) and Hg(2)–Br(4) distances indicates that Hg(2) is a part of $[HgBr_3]^-$ ion, which is also supported by bond angles Br(2)–Hg(2)–Br(3), Br(2)–Hg(2)–Br(4) and Br(3)–Hg(2)–Br(4) (115.19(5)–122.20(5)°) which are very close to 120° expected for $[HgBr_3]^-$ anion [19–21]. Thus, **5** can be described as having $[(EtSCH_2CH_2SEt)\ HgBr]^+[HgBr_3]^-$ units which dimerize and co-crystallize with two $HgBr_2$ moieties resulting in the structure shown in Fig. 2. The cleavage of $\mathbf{L}^2$ in its Hg(II) complex resulting in **5** most probably occurs as shown in Scheme 3. So far, this kind of cleavage has never been reported for diorganyl tellurides. Generally, reverse transmetalation or transmetalation has been made responsible for cleavage of organotellurium ligands in their complexes. Therefore, the present one is the first example of the type where cleavage occurs without any kind of transmetalation.

3. 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 ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz, respectively. IR spectra in the range 4000–250 cm^{-1} were recorded on a Nicolet Protége 460



Scheme 3.

FT-IR spectrometer as KBr and CsI pellets. Far IR spectra in the range 500–100 cm^{-1} were recorded in polyethylene on Perkin–Elmer spectrometer 1700X. The melting points determined in open capillary are reported as such.

3.1. X-ray diffraction analysis

A colourless block crystal of $CH_3OC_6H_4HgBr$, **2**, was mounted on a glass fibre, covered in Paratone–N, and placed rapidly into the cold N_2 stream of the Kryo-Flex low temperature device. A hemisphere of data was collected on a Bruker APEX CCD diffractometer using a counting time of 20 s per frame. Data reduction was performed using the SAINT software [9] and the data were corrected for Lorentz, polarization and absorption effects using the SAINT and SADABS programs. Cell refinement gave cell constants corresponding to an orthorhombic cell, whose dimensions are given in Table 1 along with other experimental parameters. A colourless, slab crystal of $[(EtS(CH_2)_2SEt)HgBr_2Hg(Br)Br_2Hg(Br)Br_2Hg(EtS(CH_2)_2SEt)]\cdot 2HgBr_2$ (**5**) was mounted on a glass fibre. Data 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 [10] gave cell constants corresponding to a triclinic cell whose dimensions are given in Table 1 along with other experimental parameters. An absorption correction was applied [10]. The structures of **2** and **5** were solved by direct methods [11] and were 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. The final cycle of full-matrix least-squares refinement for **2** was based on 1913 observed reflections (1537 for $F^2 > 4\sigma(F^2)$) and 93 variable parameters and converged (largest parameter shift was 0.001 times its esd). The final cycle of full-matrix least-squares refinement for **5** was based on 4372 observed reflections (3744 for $F^2 > 4\sigma(F^2)$) and 156 variable parameters and converged (largest parameter shift was 0.001 times its esd). The relatively high residual peaks are not unusual in view of the slab-like shape of the small crystal of **5** combined with the presence of so many heavy atoms. Selected distances and bond angles for **2** and **5** are given in Tables 2 and 3, respectively. The molecules **2** and **5** are displayed as an ORTEP diagram in Figs. 1 and 2, respectively. Additional material available from the Cambridge Crystallographic Data Centre comprises the final atomic coordinates and thermal parameters for all atoms, and a complete listing of bond distances and angles.

3.2. Synthesis of 2-[3-(6-methyl-2 pyridyl)propoxy] ethylchloride

A solution of 2-[3-(6 methyl-2 pyridyl)propoxy] ethanol (3.15 g, 16 mmol) in dry chloroform was cooled in

Table 1
Crystal data and structure refinement for **2** and **5**

Empirical formula	C_7H_7OBrHg	$C_{12}H_{28}Br_{12}Hg_6S_4$
Formula weight	387.63	2463.04
Temperature (K)	173(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	$P\bar{1}$
$a/b/c$ (Å)	6.7989(3)/6.9342(3)/35.456(2)	9.3682(4)/10.6672(5)/11.1783(4)
$\alpha/\beta/\gamma$ (°)	90 (all)	62.414(2)/79.026(3)/84.561(2)
Volume (Å^3)	1671.6(1)	971.95(7)
Z	8	1
D_{calc} (g/cm^3)	3.081	4.208
Absorption coefficient (mm^{-1})	23.124	36.163
$F(000)$	1376	1064
Crystal size (mm^3)	0.40 × 0.30 × 0.30	0.20 × 0.10 × 0.02
θ range for data collection (°)	2.30–27.52	3.08–27.52
Index ranges	$-8 \leqslant h \leqslant 8$, $-9 \leqslant k \leqslant 9$, $-46 \leqslant l \leqslant 46$	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-14 \leqslant l \leqslant 13$
Reflections collected	14707	19675
Independent reflections (R_{int})	1913 (0.0471)	4372 (0.1153)
Maximum and minimum transmission	0.0547 and 0.0389	0.5316 and 0.0520
Refinement method	full-matrix least squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	1913/0/93	4372/0/156
Goodness-of-fit on F^2	1.147	1.062
Final R indices [$F^2 > 4\sigma(F^2)$]	$R_1 = 0.0278$, $wR_2 = 0.0637$	$R_1 = 0.0588$, $wR_2 = 0.1640$
R indices (all data)	$R_1 = 0.0345$, $wR_2 = 0.0662$	$R_1 = 0.0711$, $wR_2 = 0.1732$
Largest difference peak and hole (e Å^3)	1.145 and −2.388	3.962 and −4.840

Table 2
Selected bond lengths (Å) and angles (°) for **2**[a]

Hg(1)–Br(1)	2.4700(7)	Hg(1)–C(1)	2.085(6)
Hg(1)–Br(1)′	3.4041(7)	Hg(1)–Br(1)″	3.4133(7)
Hg(1)–Br(1)‴	3.4214(7)	Hg(1)–Br(1)⁗	3.546(7)
Br(1)–Hg(1)–C(1)	175.0(1)		
Br(1)–Hg(1)–Br(1)′	86.08(2)	Br(1)–Hg(1)–Br(1)″	85.88(2)
Br(1)–Hg(1)–Br(1)‴	82.84(2)	Br(1)–Hg(1)–Br(1)⁗	89.16(2)

[a] Symmetry equivalent position $(-1/2 + x, 3/2 - y, -z)$ given by a prime, $(1/2 + x, 3/2 - y, -z)$ by a double prime, $(1 - x, 2 - y, -z)$ by a triple prime, and $(1 - x, 1 - y, -z)$ by a quadruple prime.

Table 3
Selected bond lengths (Å) and angles (°) of **5**

Hg(1)–Br(1)	2.492(1)	Hg(1)–Br(2)	2.914(1)
Hg(2)–Br(3)	2.537(1)	Hg(2)–Br(2)	2.573(1)
Hg(2)–Br(4)	2.551(1)	Hg(2)–Br(4)′	3.008(1)
Hg(2)′–Br(4)	3.008(1)	Hg(2)–Br(1)	3.451(1)
Hg(1)–S(1)	2.612(3)	Hg(1)–S(2)	2.525(3)
Hg(3)–Br(5)	2.417(1)	Hg(3)–Br(6),	2.425(1),
Hg(3)–Br(1)	3.148(1)	Hg(3)–Br(4)	3.216(1)
Br(1)–Hg(1)–S(1)	125.20(8)	Br(1)–Hg(1)–S(2)	146.55(8)
S(1)–Hg(1)–S(2)	86.57(10)	Br(1)–Hg(1)–Br(2)	92.03(4)
S(1)–Hg(1)–Br(2)	91.86(8)	S(2)–Hg(1)–Br(2)	97.61(8)
Br(3)–Hg(2)–Br(2)	115.19(5)	Br(3)–Hg(2)–Br(4)	122.20(5)
Br(2)–Hg(2)–Br(4)	121.51(5)	Br(2)–Hg(2)–Br(4)′	96.99(4)
Br(3)–Hg(2)–Br(4)′	98.87(4)	Br(4)–Hg(2)–Br(4)′	85.07(4)
Br(2)–Hg(2)–Br(1)	79.26(4)	Br(3)–Hg(2)–Br(1)	97.44(4)
Br(4)–Hg(2)–Br(1)	83.16(4)	Br(4)′–Hg(2)–Br(1)	163.28(4)
Br(5)–Hg(3)–Br(6)	179.07(5)	Br(5)–Hg(3)–Br(1)	87.70(4)
Br(6)–Hg(3)–Br(1)	92.86(4)	Br(5)–Hg(3)–Br(4)	92.14(4)
Br(6)–Hg(3)–Br(4)	88.70(4)	Br(1)–Hg(3)–Br(4)	78.80(3)

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

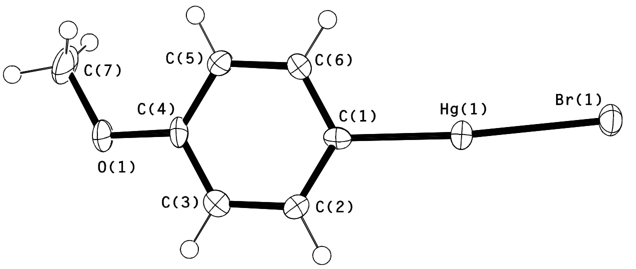


Fig. 1. ORTEP plot of the molecule $CH_3OC_6H_4HgBr$ (**2**). The atoms are drawn with 50% probability ellipsoids.

an ice bath. Thionyl chloride (2.80 g, 23.5 mmol) dissolved in dry chloroform was added to it dropwise over a period of 0.5 h. The mixture was stirred in ice bath for 20 min and heated thereafter over steam bath for 2 h. The deep red coloured solution was washed with saturated bicarbonate solution and water successively. The organic layer separated, dried over $MgSO_4$ and evaporated on a rotary evaporator to give 2-[3-(6-methyl-2 pyridyl)propoxy]ethylchloride as a deep red oil. Yield: 76%. ^{I}H NMR ($CDCl_3$, 25 °C): δ (vs TMS): 1.97–2.06 (p, 2H, H_4), 2.53 (s, 3H, H_{11}), 2.82–2.87 (t, 2H, H_5), 3.51–3.53 (t, 2H, H_3), 3.59–3.63 (t, 2H, H_2), 3.63–3.68 (t, 2H, H_1), 6.96–6.99(2s, 2H, H_7 and H_9), 7.46–7.51 (t, 1H, H_8).

*3.3. Synthesis of 1-(4-methoxyphenyl telluro)-2-[3-(6-methyl-2-pyridyl)propoxy]ethane (**L**^{1})*

Bis(4-methoxyphenyl)ditelluride (1 g, 2.13 mmol) was refluxed in ethanol (50 ml) under dry nitrogen atmosphere. Sodium borohydride (0.20 g) dissolved in 2 ml of 1 M NaOH was added dropwise until the solution became colourless. A solution of 2-[3-(6-methyl-2 pyridyl)propoxy]ethylchloride made in 10 cm^3 of ethanol was added and the mixture was refluxed for 2–3 h. It was cooled to room temperature and poured into 100 cm^3 of water. Ligand **L**^{1} from aqueous phase was extracted into 100 cm^3 of chloroform. The extract was dried over anhydrous sodium sulfate. The chloroform was evaporated under reduced pressure to give ligand **L**^{1} as yellow viscous oil. Yield: 70%. ^{I}H NMR ($CDCl_3$, 25 °C): δ (vs TMS): 1.91–2.01 (m, 2H, H_4), 2.52 (s, 3H, H_{11}), 2.71–2.82 (t, 2H, H_1), 2.95–3.0 (t, 2H, H_5), 3.43–3.47 (t, 2H, H_3), 3.66–3.70 (t, 2H, H_2), 3.78 (s, 3H, OCH_3), 6.73–6.76 (d, 2H, *m* to Te), 6.93–6.96 (2s, 2H, H_7 and H_9), 7.43–7.48 (t, 1H, H_8), 7.65–7.70 (d, 2H, *o* to Te); ^{13}C{^{1}H}NMR ($CDCl_3$, 25 °C): δ (vs TMS): 8.16 (C_1), 24.14 (C_{11}), 28.91 (C_4), 54.78 (OCH_3), 69.48 (C_2), 71.85 (C_3), 99.81 (ArTe–C), 114.83 (C_9), 119.37 (ArC *m* to Te), 120.19 (C_7), 136.44 (C_8), 140.62 (ArC *o* to Te), 157.35 (C_{10}), 160.52 (ArC *p* to Te), 161.15 (C_6)

*3.4. Synthesis of [$HgBr_2$·**L**^{1}] (**1**)*

To a solution of $HgBr_2$ (0.20 g, 0.55 mmol) made in acetone (20 ml) was added a freshly prepared solution of **L**^{1} (0.22 g, 0.55 mmol) in chloroform (20 ml). The resulting mixture was stirred at room temperature until the ligand **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 ml of chloroform and filtered through Celite. The filtrate was concentrated to 10 ml and mixed with 20 ml of hexane. A white complex was filtered, dried in vacuo and recrystallized from chloroform–hexane (1:1) mixture. Yield: 80%. M.p., 130 °C (d). *Anal.* Calc. for $C_{18}H_{23}NO_2TeHgBr_2$: C, 27.97; H, 2.97; N, 1.81; Te, 16.50. Found: C, 27.12; H, 2.91; N, 1.76. Te, 16.31%. ^{I}H NMR ($CDCl_3$, 25 °C): δ (vs TMS): 1.86–1.89 (m, 2H, H_4), 2.46 (s, 3H, H_{11}), 2.71–2.75 (t, 2H, H_1), 3.37 (t, 2H, H_5), 3.46-(bs, 2H, H_3), 3.65–3.68 (m, 5H, H_2 and OCH_3), 6.74–6.77 (d, 2H, *m* to Te), 6.93–6.97 (m, 2H, H_7 and H_9), 7.47–7.52 (t, 1H, H_8), 7.68–7.71 (d,2H, *o* to Te); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ (vs TMS): 24.81 (C_{11}), 28.91 (C_4), 34.86 (C_1), 55.29 (OCH_3), 66.91 (C_2), 70.44 (C_3), 99.81 (ArTe–C), 114.78 (C_9), 116.22 (ArC *m* to Te), 120.98 (C_7), 137.12

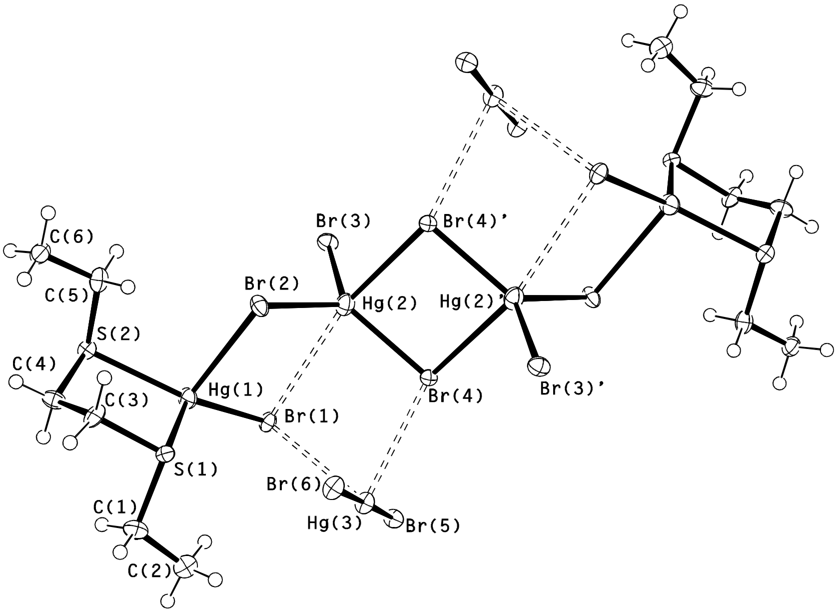


Fig. 2. ORTEP plot of **5**, the non-hydrogen atoms are drawn with 50% probability ellipsoids.

(C_8), 139.31(ArC *o* to Te), 157.35 (C_{10}), 160.52 (ArC *p* to Te), 161.15 (C_6).

3.5. Synthesis of **2** and **3**

The [$HgBr_2 \cdot$ **L**^{1}] (**1**) (0.07 g) was dissolved in acetone–hexane (2:1) mixture and kept for slow evaporation at 25 °C. After 7 days, crystals of **2** were obtained. The mother liquor was mixed with 20 ml of $CHCl_3$ and refluxed for 3 h. The **3** was obtained as solid. It was filtered, washed with $CHCl_3$ and dried in vacuo.

2: Yield: ~18%. *Anal.* Calc. for C_7H_7OHgBr: C, 27.70; H, 1.80. Found: C, 27.71; H, 1.82%. NMR (^{1}H CDCl$_3$, 25 °C): δ (vs TMS): 3.71 (s, 3H, OCH_3), 6.89–6.91 (d, 2H, ArH *m* to Hg), 7.34–7.37 (d, 2H, ArH *o* to Hg).

3: Yield: ~18%. M.p. 143–144 °C (d). *Anal.* Calc. for $C_{11}H_{16}OTeNHgBr_3$: C, 17.70; H, 2.10; N, 1.87. Found: C, 17.30; H, 2.01; N, 1.82%. NMR (^{1}H, DMSO-d$_6$, 25 °C): δ (vs TMS):1.82–1.84 (t, 2H, H_4), 2.35 (s, 3H, H_{11}), 2.66–2.81 (m, 2H, H_5), 3.63–3.68 (m, 2H, H_2), 3.75–3.81(m, 2H, H_1), 7.02–7.11 (m, 2H, $H_7 + H_9$), 7.68–7.78 (m, 1H, H_9); H_3 merged with signal of water in DMSO.

3.6. Synthesis of 1-ethylthio-2-[2-thienyltelluro]ethane (**L**^{2})

Tellurium powder (0.65 g, 5 mmol) suspended in 20 ml of THF was mixed with 5 ml of 1 mM solution of thienyl lithium (5 mmol) in THF at 0 °C. The mixture was stirred for 2 h under nitrogen atmosphere and a solution of chloroethyl ethyl sulfide (5 mmol) made in 5 ml of THF was added to it dropwise at −78 °C with constant stirring under nitrogen atmosphere. The mixture was stirred overnight at room temperature and poured into 100 ml of cold water. The ligand was extracted into 100 ml chloroform from the aqueous phase. The extract was washed with distilled water and dried over anhydrous Na_2SO_4. On evaporating off solvent under reduced pressure on a rotary evaporator, **L**^{2} was obtained as a red viscous liquid. Yield: 80%. *Anal.* Calc. for $C_8H_{12}S_2Te$: Te, 42.59. Found: Te, 42.36%. ^{1}H NMR(CDCl$_3$, 25 °C): δ (vs TMS): 1.17–1.22 (t, 3H, H_1), 2.48–2.55 (m, 2H, H_4), 2.92–2.99 (m, 4H, H_2 and H_3), 6.90–6.93 (dd, 1H, H_7), 7.37–7.38 (d, 1H, H_6) 7.42–7.44 (d, 1H, H_8). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ (vs TMS): 10.4 (C_4), 14.5 (C_1), 25.2 (C_2), 33.1 (C_3), 119.3 (C_6), 134.2 (C_8), 141.8 (C_7), 142.7 (C_5).

3.7. Synthesis [$HgBr_2 \cdot$ **L**^{2}] (4)

A freshly prepared solution of **L**^{2} (0.19 g, 0.55 mmol) in chloroform (20 ml) was added to a solution of $HgBr_2$ (0.20 g, 0.55 mmol) made in acetone (20 ml). The yellow coloured precipitate (small amount) formed instantaneously was filtered off and the resulting filtrate 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 resulting in the complex **4**, which was washed with hexane and dried in vacuo. Yield: ~30%. ^{1}H NMR (CDCl$_3$, 25 °C,): δ (vs TMS): 1.26–1.30 (m, 3H, H_1), 2.56–2.68 (m, 2H, H_4), 2.78–2.85 (m, 4H, H_2 and H_3), 7.14–7.16 (bm, 1H, H_7), 7.40–7.42 (m, 1H, H_6) 7.73 (bs, 1H, H_8). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ (vs TMS): 10.0 (C_4), 14.0 (C_1), 26.8 (C_2), 30.95 (C_3), 128.8 (C_6), 134.4 (C_8), 139.2 (C_5), 140.6 (C_7).

3.8. Synthesis of $[(EtS(CH_2)_2SEt)HgBr(\mu\text{-}Br)Hg(Br)(\mu\text{-}Br)_2Hg(Br)(\mu\text{-}Br)BrHg(EtS(CH_2)_2SEt)]\cdot 2HgBr_2$ (**5**) and (**6**)

The $[HgBr_2\cdot \mathbf{L}^2]$ (0.1 g) was dissolved in 20 ml of chloroform and filtered through Celite. The filtrate was concentrated to 10 ml and mixed with 20 ml of hexane. With the evaporation of hexane, white crystals of **5** were obtained. They were dried in vacuo. The mother liquor of this crystallizing solution was concentrated to 10 ml on a rotary evaporator and mixed with hexane (20 ml), which resulted in **6** which was washed with hexane and dried in vacuo.

5: Yield: 20%. *Anal.* Calc. for $C_6H_{14}Hg_3S_2Br_6$: C, 5.84, H, 1.13. Found: C, 5.80, H, 1.04%. ^1H NMR ($CDCl_3$, 25 °C): δ (vsTMS): 1.32–1.36 (t, 3H, H_1), 2.76–2.84 (q, 2H, H_2), 2.93 –3.03 (m, 2H, H_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ (vs TMS): 14.6 (C_1), 26.15 (C_2), 31.00.(C_3).

6: Yield: ~20%. *Anal.* Calc. for $C_{10}H_{10}S_2C$, 61.85, H, 5.15, Found: C, 60.31, H, 5.01. ^1H NMR ($CDCl_3$, 25 °C): δ (vs TMS): 2. 38– 2.44 (d, 4H, H_1), 7.24–7.31 (m, 2H, H_4), 7.41–7.51 (m, 4H, H_3 and H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ (vs TMS): 21.04 (C_1), 127.25 (C_3), 129.92 (C_4), 136. 12 (C_5), 142.23 (C_2).

4. Conclusions

1-(4-Methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl) propoxy]ethane ($\mathbf{L}^1$) and 1-ethylthio-2-[2-thienyltelluro]ethane ($\mathbf{L}^2$) have been synthesized. Only very few ligands having thienyl group linked to tellurium are known and therefore the synthesis of $\mathbf{L}^2$ is significant. The decomposition of mercury complexes of both the ligands during crystallization indicates the intricate behaviour of mercury when associated with tellurium ligands. The $4\text{-}MeOC_6H_4HgBr$ (**2**) is fully characterized by X-ray diffraction. The $[(EtS(CH_2)_2SEt)HgBr(\mu\text{-}Br)Hg(Br)(\mu\text{-}Br)_2Hg(Br)(\mu\text{-}Br)BrHg(EtS(CH_2)_2SEt)].2HgBr_2$ (**5**) is also characterized by X-ray diffraction and is a unique complex, which is probably first example of this type.

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