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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 [$(EtS(CH_2)_2SEt)HgBr(\mu\text{-}Br)Hg(Br)(\mu\text{-}Br)_2Hg(Br)(\mu\text{-}Br)BrHg(EtS(CH_2)_2SEt)]\cdot 2HgBr_2$ (**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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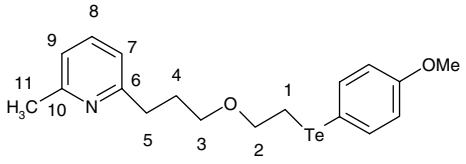
1. Introduction

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·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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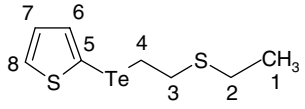

L²

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 (**L**^{1}) and 1-ethylthio-2-[2-thienyltelluro]ethane (**L**^{2}). It is observed that both these ligands first form complexes having composition [$HgBr_2$·**L**^{1}/**L**^{2}], which decompose during the attempt of growing single crystals resulting in 4-MeOC$_6$H$_4$HgBr (**2**) in the case of **L**^{1} and [(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**) in the case of **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 **L**^{1}, which remains stable under ambient conditions for 3–4 months. The **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 ^{1}H 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 ^{1}H 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 **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 ^{1}H and ^{13}C NMR spectra of **L**^{2} are characteristic. On reacting **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 ^{1}H and