Ligation of Di- and Hybrid- Telluroethers with Metallic and Organometallic Moieties

by

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Submitted
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To the

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Dedicated to my
brothers and sister

CERTIFICATE

This is to certify that the thesis entitled "**Ligation of Di- and Hybrid-Telluroethers with Metallic and Organometallic Moieties**" being submitted by **Mr. M. Kadarkaraisamy** to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. M. Kadarkaraisamy has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached requisite standard.

The results contained in the dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree of diploma.

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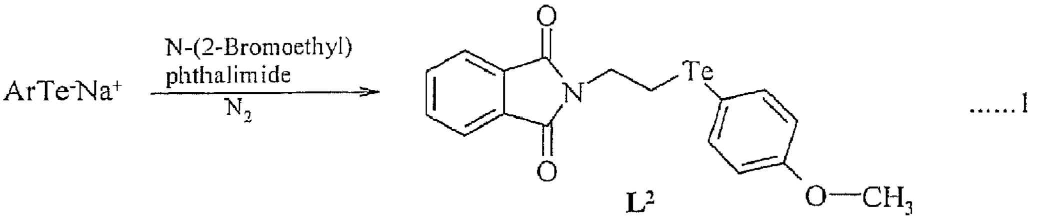
ABSTRACT

The present thesis is focussed on bis(4-methoxyphenyltelluro)methane (**L^1**), N-[2-{4-methoxyphenyltelluro}ethyl]phthalimide (**L^2**), 2-{(4-ethoxyphenyltelluro)methyl} tetrahydro-*2H*-pyran (**L^3**) and 1, 4-oxatellurane (**L^4**) and their ligation. Their complexes with Pd(II), Pt(II), Ru(II), Ru(III), Cu(I), Hg(II) and Co(II) are explored. Elemental analyses, IR, ^1H and $^{13}C\{^1H\}$ NMR spectra, mass spectra, molecular weight, conductance measurements and X-ray diffraction studies on single crystals are used to characterize ligands and their metal complexes. The **L^1** was synthesized by reacting $ArTe^-Na^+$ ($Ar = 4\text{-}MeOC_6H_4$) with chloroform in nitrogen atmosphere. The oxidative addition of I_2 with **L^1** results in $[ArTeI_2]_2CH_2$ (**1**). The crystal structure of **L^1** is the first report of structural characterization of $(Ar/RTe)_2CH_2$ (Te–C bond length 2.13-2.15(2) Å; Te-C-Te bond angle 117.0(2) °). In the compound **1**, both tellurium atoms are in a typical saw-horse structure associated with Te(IV) (Te-C bond length 2.14-2.18 Å; Te-C-Te bond angle115.5(6) °; I-Te-I angle ~ 180 °). Two of the Te-I bonds are longer than the other two. Inter molecular Te-I contacts [3.735(1) and 3.879(1) Å] in **1** lead to polymeric links of essentially Te-I-Te'-I' rectangular bridges. The ruthenium complexes $[RuCl_2(DMSO)_2($**L^1**$)]$ (**2**) , $[RuCl_2($*p*-cymene$)(\mu$-**L^1**$)($*p*-cymene$)RuCl_2]$ (**3**), $[\{Cl_2(CO)_3Ru(\mu$-**L^1**$)\}_2Ru(CO)_2Cl_2]$ (**4**), $[Ru(CO)_3Cl.($**L^1**$)]ClO_4$ (**5**) and $[RuCl_3($**L^1**$)_3]$ (**6**) were synthesized by reacting *cis*-$[Ru(DMSO)_4Cl_2]$, $[RuCl_2($*p*-cymene$)]_2$, $[RuCl_2(CO)_3]_2$ and $RuCl_3.xH_2O$ with **L^1**. The $[Ag($**L^1**$)_2]ClO_4$ (**7**), $[CoBr_2($**L^1**$)_2]$ (**8**) and $[CuBr($**L^1**$)]_2$ (**9**) are synthesized by the reaction of $AgClO_4$, $CoBr_2$ and CuBr with **L^1** in CH_3NO_2 and CH_3CN in N_2 atmosphere. **2** and **3** were characterized structurally. **2** is a *cis*-isomer and ruthenium has distorted octahedral geometry (Ru-Te 2.5988(5)/2.6727(5)) Å). The ligand **L^1** forms four membered non-planar chelate ring. The Te-Ru-Te bite angle is 78.2(0)°. In **3**, the ligand **L^1** exhibits

bridging mode of coordination (Ru-Te: 2.638(1) / 2.641(2) Å). The Te-C-Te bond angle (119.3(9) °) in **3** is close to that of free ligand. The two aryl groups are in *meso*-conformation. In the complex **6**, ligand **L**^{1} seems to coordinate in a monodentate mode. It is most probably a *mer* isomer. In the ^{1}H and ^{13}C{^{1}H} NMR spectra of **4**, **5**, **7**, **8**, and **9** the CH_2-Te signal appears deshielded (~0.3 ppm) with respect to that of free ligand. In the aromatic region no splitting of doublets occurs, supporting the bidentate mode of ligation for **L^1**.

N-[2{4-methoxyphenyltelluro}ethyl]phthalimide (**L**^{2}) (equation 1) was characterized structurally



The reaction of **L**^{2} with $RuCl_3.xH_2O$ in methanol results in a novel tellurium heterocycle *Te*-chloro, *Te*-anisyl-1a-aza-4oxa-3-tellura-*1H*, *2H*, *4αH*-9-fluorenone (**10**) characterized structurally. The signal at 5.54 ppm in ^{1}H NMR spectrum of **10** and at 83.8 ppm in its ^{13}C{^{1}H} NMR spectrum may be attributed to C-H group generated on the formation of tellurium heterocycle. The complexes [$RuCl_2$(*p*-cymene)(**L**^{2})] (**11**), [$RuCl_2(DMSO)_2$(**L**^{2})] (**12**) and [{$L^2Cl_2(CO)_2Ru(\mu$-$L^2)\}_2Ru(CO)_2Cl_2$] (**17**) were prepared by the reaction of **L**^{2} with [$RuCl_2$(*p*-cymene)]$_2$, [$RuCl_2(DMSO)_4$] and [$RuCl_2(CO)_3]_2$ respectively. The [$HgBr_2(L^2)]_2$ (**13**), [$(PPh_3)_2Hg(L^2)][ClO_4]_2$ (**14**), [$PtCl_2(L^2)$] (**15**) and [(DPPE)Pt(L^2)] $[ClO_4]_2$ (**16**) are synthesized by reacting **L**^{2} with $HgBr_2$, [$(PPh_3)_2HgBr_2$] (with silver perchlorate), K_2PtCl_4 and [Pt(DPPE)Cl_2](with silver perchlorate) respectively . **11** is characterized structurally (Ru-Te: 2.6515(3) Å). The IR band appearing at ~1686 cm^{-1} in the spectrum of **L**^{2} due to carbonyl group, is not affected on complexation. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **10-17** are as expected.

The CH_2-Te signal of **11**, **12** and **13**, was found deshielded ~0.4 ppm [with respect to that of free **L^2**] in case of ^1H NMR and ~18 ppm in $^{13}C\{^1H\}$ NMR whereas CH_2-N signal remains unaffected. This indicates that **L^2** coordinates in them through tellurium only. In the ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **14-17** both CH_2-Te and CH_2-N signals were noticed deshielded, (~0.3, ~0.2 ppm in ^1H NMR and ~15, ~2 ppm in $^{13}C\{^1H\}$ NMR) suggesting bidentate mode of coordination of the ligand.

L^3 synthesized by the reaction of $ArTe^-Na^+$ with 2-(bromomethyl)tetrahydro-*2H*-pyran in N_2 atmosphere reacts with iodine in THF resulting in its diiodo derivative (**24**). The H_{1a} and H_{1b} protons in **L^3** are not magnetically equivalent, as supported by its HETCOR spectra. In ^1H and $^{13}C\{^1H\}$ NMR spectra of **24** the CH_2-Te signal appears deshielded (~0.6 ppm and 40 ppm respectively) with respect to that of free **L^3**. The complexes of stoichiometry $[RuCl_2(\mathbf{L^3})_2]$ (**18**), $[CuBr(\mathbf{L^3})]_2$ (**19**), $[RuCl_2(p\text{-cymene})(\mathbf{L^3})]$ (**20**), $[RuCl_2(DMSO)_2(\mathbf{L^3})_2]$ (**21**), $[Ru(CO)_2Cl_2.(\mathbf{L^3})]_4$ (**22**) and $[HgBr_2(\mathbf{L^3})]_2$ (**23**) are synthesized by reacting **L^3** with $RuCl_3.xH_2O$, CuBr, $[RuCl_2(p\text{-cymene})]_2$, *cis*-$[Ru(DMSO)_4Cl_2]$, $[RuCl_2(CO)_3]_2$ and $HgBr_2$ respectively. In ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes **20**, **21** and **23** only CH_2-Te signal was found deshielded (~ 0.6 ppm and ~20-30 ppm respectively). This indicates that the ligand is coordinated to metal through tellurium alone. In **18**, **19** and **22** both CH_2-Te and CH_2-O signals were found deshielded suggesting bidentate ligation mode of **L^3** in them.

The ligand **L^4** synthesized by the reaction of Te^{2-} with 2-chloroethyl ether is orange yellow colored malodorous oil. The $[PdCl_2(\mathbf{L^4})_2]$ (**25**), $[PtCl_2(\mathbf{L^4})_2]$ (**26**), $[HgBr_2(\mathbf{L^4})_2]$ (**27**) and $[(PPh_3)_2Hg(\mathbf{L^4})_2][ClO_4]_2$ (**28**) were synthesized by reacting **L^4** with Na_2PdCl_4, K_2PtCl_4, $HgBr_2$ and $[(PPh_3)_2HgBr_2]$ (with silver perchlorate) respectively. The **25** and **26** are structurally characterized. The geometry is square planar. The two **L^4** coordinate through Te (Pd-Te: 2.6024(3); Pt-Te: 2.5945(3) Å) and are *trans* to each other.

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