METAL COMPLEXES OF MULTIDENTATE HYBRID ORGANOTELLURIUM LIGANDS

BY

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14/7

Ligands
Formation chemistry

.... To

My Parents

Sivapriya and Karuna

CERTIFICATE

This is to certify that the thesis entitled **"METAL COMPLEXES OF MULTIDENTATE HYBRID ORGANOTELLURIUM LIGANDS"**, being submitted by **Mr. J. SOORIYAKUMAR**, 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. J. Sooriyakumar has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

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

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J. Sooriyakumar

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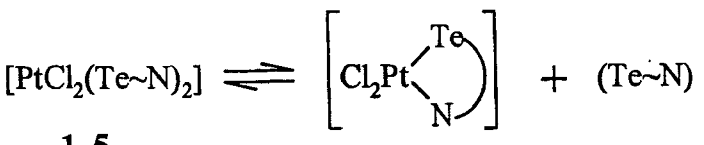
ABSTRACT

N-{2-(4-methoxyphenyltelluro)ethyl} morpholine (L^1) and bis{2-(morpholin-N-yl)ethyl}telluride (L^2) are synthesized by reacting $ArTe^-$ (generated by borohydride reduction of Ar_2Te_2) and Na_2Te with N-(2-chloroethyl)morpholine hydrochloride under N_2 atmosphere, respectively. **L^2 is an unstable yellow coloured oily liquid whereas, L^1** a white colored solid (molecular ion peak (m/z) at 351 in mass spectrum). The ^1H NMR spectra of L^1 and L^2 are as expected. L^1 and L^2 are characterized structurally (Te-C 2.15(4)/ 2.129(3) Å; C(1B)-Te(1B)-C(8B) 97.5(1)°). The morpholine ring in L^1 has the chair conformation and tellurium has distorted pseudo tetrahedral geometry. The complexes $[PtCl_2(L^1)_2].2C_6H_6$ (1), $[PdCl_2(L^1)_2]$ (2), $[HgBr_2(L^1)]_2$ (3), [Ru(*p*-cymene)$Cl_2(L^1)$] (4), $[PtCl_2(L^2)_2]$ (5), $[PdCl_2(L^2)_2]$ (6) and $[HgBr_2(L^2)]_2$ (7) are synthesized and characterized by the ^1H and $^{13}C\{^1H\}$ NMR spectroscopy along with elemental analyses, conductance and molecular weight measurements. The CH_2-Te signals in ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes generally appear downfield with respect to free L^1 and L^2 where as, the shift in CH_2-N signals is insignificant. This indicates that the coordination of L^1 with metal ions is through tellurium and not through nitrogen. In ^1H NMR spectra of **1** and **5**, the appearance of additional signals may be due to equilibrium given in equation 1which is supported by HETCOR spectra of **1** and **5**.



1, 5

...1

(Te~N) = L^1, L^2

^1H NMR spectrum of **4** has two CH_2Te signals (both deshielded) due to magnetic nonequivalence of two protons, supported again by its HETCOR spectrum. The single crystal structures of *trans*-$[PtCl_2(L^1)_2].2C_6H_6$ (1) and *trans*-$[PdCl_2(L^1/L^2)_2]$ (2, 6)

corroborate these inferences (Pt-Te : 2.582(15) Å; Pd-Te: 2.586(2) - 2.605(2)Å) about the ligation of **L^2**. The Pd/Pt in **1-2** and **6** has nearly square planar geometry. **3** and **7** are formulated as dimeric species having bromo bridges as shown below. **4** is a half sandwich compound of *p*-cymene. The three other sites are occupied by two Cl atoms and one Te atom.

N-[2-(4-Methoxyphenyltelluro)ethyl]benzamide [**L^3**] is synthesized by the reaction of ArTeNa with N-(2-chloroethyl)benzamide in ethanol under N_2 atmosphere. The ^{1}H NMR spectrum of **L^3** is as expected. The bands at 1641 and 3383 cm^{-1} observed in the IR spectrum of **L^3** may be assigned to ν(C=O) and ν(NH), respectively. In mass spectrum of **L^3** the molecular ion peak (m/z) is observed at 382. **L^3** is characterized structurally and Te-C(1) was found to be 2.107(8)/2.140(13) Å. The complexes $[PdCl_2(L^3)]$ (**8**), $[PtCl_2(L^3)]$ (**9**), $[(phen)Pd(L^3)](ClO_4)_2$ (**10**), $[(DPPE)Pd(L^3)](ClO_4)_2$ (**11**), $[RuCl_2(L^3)_2]$ (**12**) and $[HgBr_2(L^3)_2]$ (**13**) are synthesized. The downfield shifts are observed in CH_2Te and CH_2N signals of **L^3** on the formation of all the complexes (except **13**), indicating that **L^3** coordinates through Te and N in them. **L^3** ligates in **13** through tellurium only.

2-(2-{4-Ethoxyphenyl}-telluroethyl)-1,3-dioxane [**L^4**] and Bis(2-{1,3-dioxan-2-yl}ethyl)telluride [**L^5**] are prepared by reacting $ArTe^-$ and Na_2Te with 2-(2-bromoethyl)-1,3-dioxane, respectively. Their ^{1}H and $^{13}C\{^1H\}$ NMR spectra are characteristic. $[RuCl_2(p\text{-cymene})(L^4 / L^5)]$ (**14 / 15**) and $[PdCl_2(L^5)_2]$ (**16**) have been synthesized and characterized by ^{1}H NMR, conductance measurement and elemental analyses. In ^{1}H NMR spectra of the complexes **14 –16**, there are two CH_2-Te signals due to magnetic non-equivalence of two protons, as supported by their HETCOR spectra. Both show a downfield shift with respect to the free ligand **L^4/L^5**. The CH_2O signal in the spectra of **14-16** is unaffected. This indicates that the ligation of **L^4/L^5** is only through Te. The single crystal structures of **14-16** are consistent with these observations The Ru-Te in **14** and **15** is 2.6559(9)- 2.642(1) Å and Ru-Cl 2.404(3) - 2.417(3) Å). In **16** Pd-Te is ~ 2.587(6) Å and Pd(1)-Cl(1): 2.999(2) - 2.299(2) Å.

Attempts were made to synthesize a cyclic (Te_3, N_3) (**L^6**) type ligand and a potential (Te, S_2) (**L^7**) type donor by treating Na_2Te (generated *in situ* by borohydride reduction of elemental tellurium) with equimolar amount of bis(2-chloroethyl)amine and two moles of $ClCH_2CH_2SPh$, respectively. The products obtained were found to be highly unstable and therefore attempts were made to stabilize them as their metal complexes. The ligand **L^6** was reacted *in situ* with $PdCl_4^{2-}$ and similarly, ligand **L^7** with $(DPPE)PdCl_2$ in the presence of $AgClO_4$. However, from the reaction mixture we could crystallize *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ **(17)** and $[(Ph_2PCH_2CH_2PPh_2)Pd(\mu\text{-}Cl)]_2(ClO_4)_2.2CHCl_3$ **(18)** only. Both of them are characterized structurally. The compounds **17** and **18** were prepared by independent methods also. The **17** is formed in good yield when Na_2PdCl_4 reacts with bis(2-chloroethyl)amine hydrochloride in methanol. The compound **18** can be prepared by the reaction of 1,2-bis(diphenylphosphino)ethanedichloro palladium(II) dissolved in chloroform with $AgClO_4$ taken in methanol.

Table of contents

Chapter I: Introduction

Chapter II: Materials and Methods

Chapter III: N-{2-(4-Methoxyphenyltelluro)ethyl} morpholine (L^1), Bis{2-(morpholin-N-yl) ethyl}telluride (L^2) and Their Metal Complexes

Chapter IV: N-[2-(4-Methoxyphenyltelluro)ethyl]benzamide and Its Metal Complexes

Chapter V: (Te, O) and (Te, O_2) Type Hybrid Organotellurium Ligands and Their Metal Complexes

Chapter VI: (Te_3, N_3) and (Te, S_2) Type of Hybrid Organotellurium Ligands - Attempted Synthesis