SYNTHESIS AND COMPLEXATION BEHAVIOUR OF HYBRID ORGANOTELLURIUM (Te,O) LIGANDS

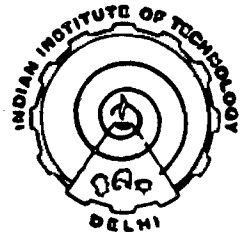
By

SEBASTIAN THOMAS

Department of Chemistry

THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY



to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI
NEW DELHI-110016, INDIA
OCTOBER, 1991

C E R T I F I C A T E

This is to certify that the thesis entitled "SYNTHESIS AND COMPLEXATION BEHAVIOUR OF SOME HYBRID ORGANOTELLURIUM (Te,O) LIGANDS "being submitted by Mr.Sebastian Thomas 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. Sebastian Thomas has worked under our guidance and supervision and has fulfilled the requirements of this thesis which, to our 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 the award of any degree or diploma.

29/10/91

Prof. B.L. Khandelwal
Department of Chemistry
Indian Institute of Technology
New Delhi-110 016

29.10.91

Dr. A.K. Singh
Department of Chemistry
Indian Institute of Technology
New Delhi-110016

ACKNOWLEDGEMENT

I wish to express my sincere thanks to Prof. B. L. Khandelwal and Dr. A. K. Singh for their astute guidance and keen interest in this work. In fact but for their painstaking supervision and inspiring discussions this work would have never attained this stage.

I am thankful to CSIR (New Delhi) and I.I.T Delhi for financial assistance and Prof. N. K. Jha (former Head of the Department) and Prof. A. S. N. Murthy, Head of the Department for providing me the necessary facilities to carry out the research work.

The cooperation and help extended by Drs. Vinod Srivastava, J. K. Basumatary, N. S. Bhandari, N. Homendra, A. K. Mitra, S. K. Gupta, Soami Satsangi, P.C. Subramanium, R. Ramkumar, Alexander.J, A. Jyothi, Kamini Uppal, Veena Singh, Ms. Anju Khanna, and Messrs. Ajay Arora, Abu Khalid, Raman Batheja, S. K. Dhingra, Joby, Francis, Roy and Johnson is greatefully acknowledged.

I am also thankful to Mr. Narayan Singh (SLA) for his cooperation and help in the laboratory. The help rendered by the technical staff of the Department is duly appreciated.

Last but not the least, I would like to record my deep sense of gratitude to my parents and all family members for their moral support in achieving the present objective.

Sebastian Thomas

October 29, 1991

(SEBASTIAN THOMAS)

I.I.T. Delhi

ABSTRACT

In the thesis entitled "SYNTHESIS AND COMPLEXATION BEHAVIOUR OF SOME HYBRID ORGANOTELLURIUM (Te, O) LIGANDS", the synthesis of ligands, aryltelluroacetic acids, 2-aryltelluroethanols, aryl(2-hydroxy-5-methylphenyl)-tellurides, bis(2-hydroxy-5-methylphenyl)telluride and ditelluride and their reactions (mostly complexation) with Hg(II), Pd(II), Pt(II) and Cu(II) have been reported. The ligands and complexes were characterised by elemental analysis and electronic, IR, ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra in conjunction with their molecular weight and conductance measurements.

The aryltelluro acetic acids, $ArTeCH_2COOH$ (L_1) and 2-aryltelluro-ethanols, $ArTeCH_2CH_2OH$ (L_2) where Ar = C_6H_5, 4-$MeOC_6H_4$ and 4-$EtOC_6H_4$ have been synthesised by the reactions of sodium aryltellurolates ($ArTe^-Na^+$) with monochloro acetic acid and 2-chloroethanol respectively. The hydrogen bonding in phenyltelluroacetic acid is greater in comparison to that of acetic acid which has been evidenced by its IR, ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra. This is consistent with the polarity of Te-C bond where Te becomes positively charged. In 2-aryltelluroethanols hydrogen bonding does not seem to be different from that of ethanol. L_1 and L_2 both ligate with Hg(II), Pd(II) and Pt(II) to form complexes of composition $[(L-H).MCl]_2$. The ligands coordinate in a uninegative bidentate mode of bonding through O and Te which has been supported by ^{1}H NMR and IR spectra of the complexes.

Electronic spectra of Pd(II) and Pt(II) complexes of L_1 and L_2 suggest square planar geometry around these metal ions. Molecular weights of the complexes support dimeric structure formed through bridging chlorines.

Aryl(2-hydroxy-5-methylphenyl)tellurides (L_3) (Ar = C_6H_5, 4-$MeOC_6H_4$ or 4-$EtOC_6H_4$) were synthesised by hydrazine reduction of the corresponding dichlorides obtained from p-cresol by ortho-mercuration followed by transmetallation reaction with $ArTeCl_3$. Its complexes with Hg(II), Pd(II) and Pt(II) having stoichiometries [(L_3-H).MCl] seem to be dimeric with bridging chlorines on the basis of their ^1H NMR and IR spectra, conductance and molecular weight measurements. Moreover coordination through both Te and O has to be invoked to explain the formation of these complexes and their spectral and physical properties.

Bis(2-hydroxy-5-methylphenyl)telluride (L_4) was prepared by hydrazine reduction of the corresponding diaryltellurium (IV) chloride synthesised by the direct reaction of p-cresol with $TeCl_4$. Hg(II) complex of L_4 having stoichiometry HgCl(L_4-H) seems to be polymeric which on reaction with PPh_3 gives a soluble complex of composition PPh_3HgCl(L_4-H). The uninegative bidentate mode of coordination for L_4 in this complex may be inferred from ^1H NMR and IR spectral data. Bis(2-hydroxy-5-methylphenyl)ditelluride (L_5) was prepared by metabisulphite reduction of $ArTeCl_3$ (Ar = 5-CH_3-2-OH-C_6H_3) obtained by o-mercuration of p-cresol followed by transmetallation with $TeCl_4$. With Hg(II) the ditelluride forms a compound of composition

$RTe.HgCl_2$ in which Te-Te bond appears to be affected. However the compound is insoluble and amorphous. Therefore its structural characterisation is extremely difficult. Reaction of ditelluride (L_5) with $CuCl_2$ results in the formation of a tellurenyl compound ArTeCl. Its unusual stability is attributed to the existence of a Te····O secondary interaction which is supported by its IR, ^1H, $^{13}C\{^1H\}$ NMR spectra.

CONTENTS