SYNTHESIS AND LIGAND CHEMISTRY OF SOME (Te, N) AND (Te, N, Te) DONORS

By

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C E R T I F I C A T E

This is to certify that the thesis entitled "SYNTHESIS AND LIGAND CHEMISTRY OF SOME (Te, N) AND (Te, N, Te) DONORS" being submitted by Mr. Vinod Srivastava 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. Srivastava has worked under our guidance and supervision and has fulfilled the requirements for the submission 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.

22/3/90

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ABSTRACT

In the thesis entitled "SYNTHESIS AND LIGAND CHEMISTRY OF SOME (Te, N) and (Te, N, Te) DONORS", the synthesis of ligands, $1\text{-}(NMe_2)\text{-}2\text{-}(TeAr)\text{-}4\text{-}Me\text{-}C_6H_3$ (L^1) and $RN(C_2H_4TeAr)_2$ (L^2) (where R = H or Me and Ar = C_6H_5; $4\text{-}MeOC_6H_4$ or $4\text{-}EtOC_6H_4$), and their complexation behaviour with Hg(II), Pd(II), Pt(II), Rh(I) and Rh(III) have been reported. The ligands and complexes were characterized by electronic, IR, ^1H, ^{13}C and ^{125}Te NMR spectra in conjunction with their molecular weight and conductance measurements. Molecular structure of a $HgBr_2$ complex with L^1 was also determined by single crystal X-ray diffraction.

The $1\text{-}(NMe_2)\text{-}2\text{-}(TeAr)\text{-}4\text{-}MeC_6H_3$ was synthesized by metabisulphite reduction of $1\text{-}(NMe_2)\text{-}2\text{-}(Cl_2TeAr)\text{-}4\text{-}MeC_6H_3$ obtained from $1\text{-}(NMe_2)\text{-}4\text{-}MeC_6H_4$ by ortho mercuration followed by transmetallation reaction with $ArTeCl_3$. Methyl iodide reacts with L^1 resulting in ArAr'Te(Me)I type of compounds.

Potentially tridentate (Te, N, Te) ligands (L^2), $RN(C_2H_4TeAr)_2$ were synthesized by the nucleophilic attack of sodium aryl tellurolate (NaTeAr) on $RN(C_2H_4Cl)_2$ in aqueous-alcoholic medium in an inert atmosphere.

A weak Te<---N secondary interaction in the (Te, N) ligands (L^1) has been inferred because ν(N-C(Me)) vibrations undergo blue shift on the formation of Hg complexes. In the Hg(II) complexes the ligand (L^1) coordinates only through Te, resulting in halo-bridged dimers. This

has been supported by single crystal X-ray diffraction studies on $HgBr_2.L^1$. The L^1 ligates with Pd(II) and Pt(II) through both N and Te giving a five membered chelate ring. The coordination with N is supported by the splitting of NMe_2 signal and value of $^3J(^{195}Pt-H)$ coupling constant (26-28 Hz). Rhodium(I) complexes of L^1 are dimeric in solid having four coordinated two Rh centers (square planar geometry) bridged by two Cl atoms. In chloroform solution there exists a fast rhodium exchange between these dimeric species and three coordinated $[RhCl.L^1]$ complex. Rhodium(III) complexes, $[RhCl_3.2L^1]$ dissociate into $[RhCl_2.2L^1]^+$ and Cl^- and/or $RhCl_3.L^1$ and L^1, exist as cis and trans isomers and exhibit ligand exchange reaction among them.

Te<---N secondary interaction has been exhibited in L^2 by the resolution of $(N)CH_2CH_2(Te)$ singlet in CF_3COOD and shielding of $CH_2(N)$ carbons in ^{13}C NMR spectra when it does not coordinate alongwith tellurium. Mercury(II) forms with L^2 type of ligands monomeric and non-ionic complexes $[HgCl_2.L^2]$ in which the tetrahedral geometry around Hg(II) is constituted by two Te atoms of the ligand and two Cl atoms and the N remains dormant. Palladium(II) and platinun(II) complexes are five coordinate having square pyramidal geometry. The appearance of one $\nu(M-Cl)$ suggests the trans conformation for the two Cl atoms. The two other corners of the square pyramid base are occupied by two tellurium atoms. In CH_3CN and CH_3OH the solvolysis of these complexes result in $[MCl.L^2.S]^+$ and Cl^- ions (M = Pt or Pd and S = solvent), In Rh(I) complexes $[RhCl.L^2]_2$, the ligand L^2 acts as a

tridentate ligand resulting in trigonal bipyramidal geometry around Rh(I) completed by two bridging Cl atoms. In solution of these complexes, Rh(I) appears to adopt four coordinated square planar geometry. A fast interconversion between the species having four and five coordinated Rh(I) has been speculated due to broadening of ^{1}H NMR signals of Rh(I) complexes. Rh(III) complexes $[RhCl_3.L^2]$ are octahedral. In solid state they seem to be monomeric in which the ligand (L^2) is tridentate. In solution the (Te, N, Te) ligands most probably coordinate in bidentate mode and the six coordination of Rh(III) is completed by the formation of dimeric species through two bridging Cl atoms. A fast interconversion between these monomeric and dimeric forms has been speculated because ^{1}H NMR signals of $[RhCl_3.L^2]$ exhibit broadening.

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