

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

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*THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSOPHY*

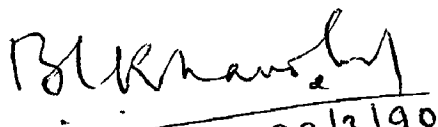


to the
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
NEW DELHI-1 10016, INDIA
MARCH, 1990

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.


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A C K N O W L E D G E M E N T

With the culmination of the proposed work and compilation in this form, I have an opportunity to accord my sincere thanks to Prof. B.L. Khandelwal and Dr. A.K. Singh for their astute guidance and keen interest in this work. They provided me with necessary manoeuvrability and freedom to work, albeit keeping a watchful eye on the progress without which 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.

I would also like to thank Dr. D.C. Povey, University of Surrey (U.K.) for determining the single crystal X-ray structure of a mercury complex.

The cooperation and help extended by Drs. K.M.M.S. Prakash, G.K. Mehrotra, Bandana Khandelwal, Safia Begum, N.S. Bhandari, S.K. Gupta, Kamini Uppal, Veena Singh, Vinay Shukla, S.K. Jain, Ms. Anju Khanna and Messrs Ajai Arora, S. Thomas, J.K. Basumatary, Abu Khalid, N. Homendra, G.S. Kapoor, A. Gupta, K. Varsha, Manisha Gupta, I.K. Pandey, A. Mitra, A.K. Sinha, Girijesh Kumar, B.N.P. Chaurasia and S.K. Garg is gratefully acknowledged.

I am also thankful to Mr. Narayan Singh (SLA) for his cooperation and help in the laboratory work and Mr. J.K. Lohia and Samsheer S. Dagar for executing prompt and excellent typing of the manuscript of the thesis. 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, brother and sisters for their moral support in achieving the present objective.

March 22, 1990
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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-(NMe₂)-2-(TeAr)-4-Me-C₆H₃ (L¹) and RN(C₂H₄TeAr)₂ (L²) (where R = H or Me and Ar = C₆H₅; 4-MeOC₆H₄ or 4-EtOC₆H₄), 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, ¹³C and ¹²⁵Te NMR spectra in conjunction with their molecular weight and conductance measurements. Molecular structure of a HgBr₂ complex with L¹ was also determined by single crystal X-ray diffraction.

The 1-(NMe₂)-2-(TeAr)-4-MeC₆H₃ was synthesized by metabisulphite reduction of 1-(NMe₂)-2-(Cl₂TeAr)-4-MeC₆H₃ obtained from 1-(NMe₂)-4-MeC₆H₄ by ortho mercuration followed by transmetallation reaction with ArTeCl₃. Methyl iodide reacts with L¹ resulting in ArAr'Te(Me)I type of compounds.

Potentially tridentate (Te, N, Te) ligands (L²), RN(C₂H₄TeAr)₂ were synthesized by the nucleophilic attack of sodium aryl tellurolate (NaTeAr) on RN(C₂H₄Cl)₂ in aqueous-alcoholic medium in an inert atmosphere.

A weak Te $\cdots$ N secondary interaction in the (Te, N) ligands (L¹) has been inferred because $\nu(\text{N}-\text{C}(\text{Me}))$ vibrations undergo blue shift on the formation of Hg complexes. In the Hg(II) complexes the ligand (L¹) coordinates only through Te, resulting in halo-bridged dimers. This

has been supported by single crystal X-ray diffraction studies on $\text{HgBr}_2 \cdot \text{L}^1$. 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 $^3\text{J}(^{195}\text{Pt-H})$ 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 $[\text{RhCl} \cdot \text{L}^1]$ complex. Rhodium(III) complexes, $[\text{RhCl}_3 \cdot 2\text{L}^1]$ dissociate into $[\text{RhCl}_2 \cdot 2\text{L}^1]^+$ and Cl^- and/or $\text{RhCl}_3 \cdot \text{L}^1$ and L^1 , exist as cis and trans isomers and exhibit ligand exchange reaction among them.

$\text{Te} \cdots \text{N}$ secondary interaction has been exhibited in L^2 by the resolution of $(\text{N})\text{CH}_2\text{CH}_2(\text{Te})$ singlet in CF_3COOD and shielding of $\text{CH}_2(\text{N})$ carbons in ^{13}C NMR spectra when it does not coordinate along with tellurium. Mercury(II) forms with L^2 type of ligands monomeric and non-ionic complexes $[\text{HgCl}_2 \cdot \text{L}^2]$ 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 platinum(II) complexes are five coordinate having square pyramidal geometry. The appearance of one $\nu(\text{M-Cl})$ 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 $[\text{MCl} \cdot \text{L}^2 \cdot \text{S}]^+$ and Cl^- ions ($\text{M} = \text{Pt}$ or Pd and $\text{S} = \text{solvent}$), In Rh(I) complexes $[\text{RhCl} \cdot \text{L}^2]_2$, 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 ^1H NMR signals of Rh(I) complexes. Rh(III) complexes $[\text{RhCl}_3.\text{L}^2]$ 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 ^1H NMR signals of $[\text{RhCl}_3.\text{L}^2]$ exhibit broadening.

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