

**ORGANOCHALCOGEN (SELENIUM & TELLURIUM) BASED
NOVEL DESIGNER LIGANDS – SYNTHESIS,
CHARACTERIZATION AND REACTIVITIES TOWARDS
d⁸ AND d¹⁰ METAL (II) ION SPECIES**

by

MARILYN DAISY MILTON

Department of Chemistry

Submitted

In fulfillment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology, Delhi

November, 2001

Jaundis

I. I. T. DELHI.
LIBRARY
Acc. No. JH-2817

JH
541.5
ML-0

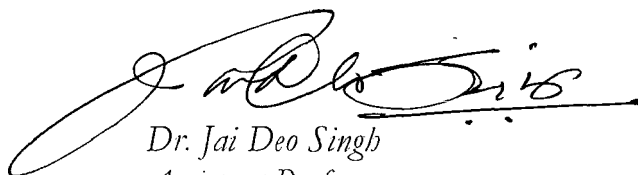
I. I. T. DELHI
LIBRARY
RECEIVED

*Dedicated to my
Mother*

Certificate

This is to certify that the thesis entitled, "Organochalcogen (Selenium & Tellurium) Based Novel Designer Ligands – Synthesis, Characterization and Reactivities towards d^8 and d^{10} Metal (II) Ion Species", being submitted by Ms. Marilyn Daisy Milton, to the Indian Institute of Technology, Delhi, for the award of degree of 'Doctor of Philosophy in Chemistry', is a bonafide research work carried out by her. Ms. Marilyn Daisy Milton has worked under my guidance and supervision and has fulfilled the requirements for the submission of 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 the award of any degree or diploma.

Date 29/11/2001



Dr. Jai Deo Singh
Assistant Professor
Department of Chemistry
Indian Institute of Technology, Delhi
New Delhi-110016

Acknowledgements

I extend my deep sense of gratitude to my Research Supervisor, Dr. Jai Deo Singh for his excellent guidance, untiring efforts, constant support and constructive criticism during the course of this investigation. I wish to acknowledge my indebtedness to Dr. Jai Deo Singh, for instilling in me the spirit of scientific inquiry. Thank you Sir.

I would like to thank Professor H. M. Chawla, Head, Department of Chemistry, for providing the necessary facilities.

A special word of thanks is due to Prof R. J. Butcher, Dept. of Chemistry, Howard University, Washington, D.C, USA; Prof T. P. Singh and Mr. Pravindra Kumar, Dept. of Biophysics, All India Institute of Medical Sciences (AIIMS), New Delhi, for carrying out X-ray studies.

I also wish to thank Prof. C. P. Morley, Department of Chemistry, University of Wales Swansea, U.K. and RSIC, Lucknow for Mass Spectroscopic Studies. Thanks are due to Dr. Raja Roy and Mr. Rajesh Grover, Central Drug Research Institute (CDRI), Lucknow, for carrying out NMR studies. I also express my gratitude to Prof. I. K. Verma, Dept. of Polymer Science and Engineering, for providing TG analysis facilities. I am grateful to Dr. A. Ramanan for XRD studies. I am also thankful to Prof. B. L. Khandelwal, Prof. A. S. Brar, Dr. Ravi Shankar and Dr. Ashok Sharma for constant encouragement and valuable advice.

I am also thankful to the supporting staff for their assistance and cooperation during my research.

My sincere thanks to all my laboratory colleagues and friends for their help and moral support. Especially, I would like to thank my friends, Ms. Shashikala Singh and Mr. Gaurav Bhalla for their help in literature survey. I thank Mr. Naveen Kumar and Ms. Padmavathy for reviewing the entire manuscript with painstaking attention for details.

A special thanks to my family for sacrificing their personal priorities to cope up with my studies and for their constant support and encouragement.

A thank to all those who helped me and because of my forgetfulness remain unnamed, thank you.

Marilyn

Marilyn Daisy Milton

ABSTRACT

The present work entitled “**Organochalcogen (Selenium & Tellurium) Based Novel Designer Ligands – Synthesis, Characterization and Reactivities towards d^8 and d^{10} Metal (II) Ion Species**” deals with design and synthesis of different types of organochalcogen (Se and Te) ligands with variable donor abilities and their reactivities towards d^8 and d^{10} metal (II) ions. A comparative study of these donors has also been accomplished (wherever it was possible) and their behavior towards Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II) metal ions have been examined.

Chapter 1 gives an overview of the recent advances made in the field of organoselenium and tellurium chemistry with special reference to ‘designed’ ligands and their applications. This chapter also discusses the aims of the present work.

Chapter 2 deals with the synthetic strategies and experimental details involved in the synthesis of the precursor compounds. It also gives a brief account of the characterization techniques used in this work.

Chapter 3 deals with the synthesis of a series of relatively stable bis(2-aminoalkyl)chalcogenide, $[\text{NH}_2(\text{CH}_2)_n\text{E}(\text{CH}_2)_n\text{NH}_2]$ ($n = 2$ or 3 ; $\text{E} = \text{Se}$ or Te), ligand systems. The ligands on reaction with Group 12 metal (II) ions give dimeric complexes of the type $[\text{M}_2\{\text{NH}_2(\text{CH}_2)_n\text{E}(\text{CH}_2)_n\text{NH}_2\}_2\text{Cl}_4]$, where $\text{M} = \text{Zn}$, Cd and Hg . The effect of varying the halide ion on the structure of the resulting metal complexes has also been studied by complexation reaction of CdI_2 with $\text{NH}_2(\text{CH}_2)_2\text{Se}(\text{CH}_2)_2\text{NH}_2$ in 1:1 molar ratio. The various ligands and their metal complexes have been analyzed by physicochemical methods like elemental analysis, ES-MS, IR and NMR spectroscopy and single crystal X-ray crystallography. Thermal decomposition of these complexes at

elevated temperature has been studied by TGA and the residual material being analyzed by powder pattern X-ray diffraction studies.

Chapter 4 discusses the synthesis of carefully designed tridentate ligands $[\text{PhE}(\text{CH}_2)_n\text{N}(\text{H})\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)(=\text{O})]$ ($n = 2$ or 3 ; $\text{E} = \text{Se}$ or Te), incorporating O, N and Se/Te donor atoms in their structural framework and their coordination complexes with Pd(II) and Pt(II) metal ions. The ligands and their metal complexes have been analyzed by various physicochemical techniques like elemental analysis, IR, $^1\text{H-NMR}$, $^1\text{H-}^1\text{H COSY}$, $^{13}\text{C-NMR}$ and $^1\text{H-}^{13}\text{C}$ heteronuclear single bond correlation and $^{77}\text{Se-NMR}$ spectroscopy, FAB mass spectrometry, TGA and single crystal X-ray crystallography. The $^1\text{H-NMR}$ for the metal complexes reveals a complex splitting pattern for the methylene protons. Single crystal X-ray structure of $[\text{PhE}(\text{CH}_2)_2\text{N-C}(\text{CH}_3)\text{CHC}(\text{CH}_3)(=\text{O})\text{PtCl}]$ shows that the central platinum center is coordinated to (Se/Te, N, O and Cl) in an approximately square-planar environment and form loose dimers through intermolecular Pt...Pt and Pt...E contacts.

Chapter 5 deals with the synthesis of potentially pentadentate acyclic ligands, 2,6-bis(phenylchalcogenoalkylimino)pyridine, $[\{\text{PhE}(\text{CH}_2)_n\text{N}=\text{CH-}\}_2\text{C}_5\text{H}_3\text{N}]$ ($\text{E} = \text{Se}$ or Te , $n = 2, 3$), incorporating nitrogen and selenium or tellurium donor atoms. The complexes of these ligands with MCl_2 ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$) have been synthesized and analyzed by various physicochemical methods like elemental analysis, FAB mass, IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and $^{77}\text{Se-NMR}$ spectroscopy, TGA and single crystal X-ray crystallography. The coordination sphere approximates to trigonal bipyramidal geometry around the central metal (Zn, Cd or Hg) atom, with the (N, N, N) nitrogen donor sets of

the ligands being involved in coordination while the two pendant arms bearing chalcogen remaining uncoordinated.

Chapter 6 discusses the synthesis of polydentate ligands containing terdentate (N_2E ; $E = Se$ or Te) binding units connected to C_3 -symmetric spacers such as 2,4,6-trimethylbenzene and 1,3,5-triazine through nitrogen linkages. These ligands have been characterized by elemental analysis, IR, 1H , ^{13}C and ^{77}Se NMR and FAB mass studies. The tri-substituted ligands of the present study are symmetrical and have well-defined spatial arrangement of N_2E , ($E = Se$ or Te) sub-units at 1,3,5- or 2,4,6- positions of the central spacer. The di-substituted ligands are unsymmetrical in nature. Attempts to examine their coordination behavior towards M^{2+} ions yielded highly insoluble materials. Therefore, further characterization of these materials could not become possible. Nevertheless, this chapter provides some useful insights into design concept.

CONTENTS

	<i>Certificate</i>	
	<i>Acknowledgements</i>	
	<i>Abstract</i>	i
	<i>List of Figures</i>	vii
CHAPTER 1	GENERAL INTRODUCTION	1
	Introduction	1
	References	19
CHAPTER 2	MATERIALS AND METHODS	28
	2.1 Chemicals	28
	2.2 Synthesis of Precursors	29
	2.3 Physicochemical Studies	35
	2.3.1 Elemental Analysis	35
	2.3.2 Melting Point	35
	2.3.3 Conductance Measurements	36
	2.3.4 Infrared (IR) Spectroscopy	36
	2.3.5 Nuclear Magnetic Resonance (NMR) Spectroscopy	36
	2.3.6 Mass Spectrometry	37
	2.3.7 Thermogravimetric (TG) Analysis	37
	2.3.8 Powder Pattern X-ray Diffraction Studies	37
	2.3.9 Single Crystal X-ray Diffraction Studies	37
	References	39
CHAPTER 3	DESIGN AND SYNTHESIS OF BIS(2-AMINO ALKYL)CHALCOGENIDES $\text{NH}_2(\text{CH}_2)_n\text{E}(\text{CH}_2)_n\text{NH}_2$ ($n = 2$ or 3; $\text{E} = \text{Se}$ or Te) AND THEIR REACTIONS WITH GROUP 12 METAL IONS	40
	3.1 Introduction	40
	3.2 Results and Discussion	41
	3.2.1 Syntheses of Ligands ($\text{L}^1\text{-L}^4$)	41
	3.2.2 Complexation Reactions with Zn(II), Cd(II) and Hg(II) metal ions	42
	3.2.3 Electrospray Mass Spectra	43
	3.2.4 Infrared Spectra	43
	3.2.5 ^1H NMR Spectra	46

3.2.6	¹³ C NMR Spectra	46
3.2.7	Crystal Structure	52
3.2.8	Thermal Studies	59
3.3	Conclusion	63
3.4	Experimental	64
	Tables	71
	References	75

CHAPTER 4

DESIGN AND SYNTHESIS OF ORGANO- CHALCOGEN BEARING HETEROFUNCTIONAL TRIDENTATE DONORS AND THEIR Pd(II) AND Pt(II) METAL IONS COMPLEXES 77

4.1	Introduction	77
4.2	Results and Discussion	78
4.2.1	Syntheses of Ligands (L ⁵ -L ⁸)	78
4.2.2	Complexation Reactions with Pt(II) and Pd(II) metal ions	80
4.2.3	Characterization	82
4.2.4	FAB mass Spectra	83
4.2.5	IR Spectra	83
4.2.6	NMR Spectroscopy	85
4.2.7	Crystal Structure	95
4.2.8	Reactivity of Metal Complexes	115
4.2.9	Thermogravimetric (TG) Analysis	116
4.3	Conclusion	118
4.4	Experimental	119
	Tables	122
	References	138

CHAPTER 5

DESIGN, SYNTHESIS AND STRUCTURAL ASPECTS OF ACYCLIC N₃E₂ TYPE DONORS AND THEIR COMPLEXES WITH GROUP 12 METALS IONS 141

5.1	Introduction	141
5.2	Results and Discussion	143
5.2.1	Syntheses of Ligands (L ⁹ -L ¹²)	143
5.2.2	Complexation Reactions with Zn(II), Cd(II) and Hg(II) metal ions	144
5.2.3	FAB mass Spectra	145
5.2.4	IR Spectra	145
5.2.5	¹ H NMR Spectra	147
5.2.6	¹³ C NMR Spectra	147

	5.2.7	^{77}Se NMR Spectra	156
	5.2.8	Crystal Structure	156
	5.2.9	Thermogravimetric (TG) Analysis	168
5.3		Conclusion	170
5.4		Experimental	171
		Tables	172
		References	186
CHAPTER 6		DESIGN AND SYNTHESIS OF ORGANO- CHALCOGEN BASED TRIPODAL DONORS	189
6.1		Introduction	189
6.2		Results and Discussion	189
	6.2.1	Mass Spectra	193
	6.2.2	IR Spectra	196
	6.2.3	^1H NMR Spectra	200
	6.2.4	^{13}C NMR Spectra	204
	6.2.5	^{77}Se NMR Spectra	208
6.3		Conclusion	208
6.4		Experimental	210
		Tables	212
		References	220