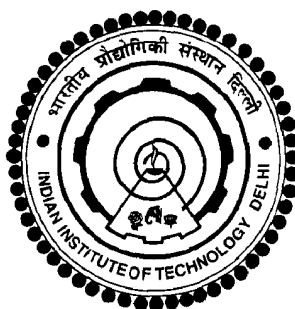


**DESIGN AND SYNTHESIS OF POLYORGANOSULFUR
SPECIES AND THEIR EXCEPTIONAL
COORDINATION BEHAVIOR WITH d^{10} METAL IONS**

NEERU



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2012**

**DESIGN AND SYNTHESIS OF POLYORGANOSULFUR
SPECIES AND THEIR EXCEPTIONAL
COORDINATION BEHAVIOR WITH d^{10} METAL IONS**

By

**NEERU
DEPARTMENT OF CHEMISTRY**

Submitted

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



INDIAN INSTITUTE OF TECHNOLOGY DELHI

JULY 2012

Dedicated to my family and teachers,

Whose love, support and guidance has helped me throughout...

Certificate

This is to certify that the thesis entitled, “Design and synthesis of polyorganosulfur species and their exceptional coordination behavior with d^{10} metal ions”, being submitted by Ms. Neeru, 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. Neeru has worked under my 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 award of any degree or diploma

Date:

Dr. Jai Deo Singh

Professor

Department of Chemistry

Indian Institute of Technology, Delhi

New Delhi- 110016

Acknowledgements

*First I would like to express my deepest gratitude to my research supervisor **professor Jai Deo Singh**, for his innovative ideas, scientific knowledge and intellectual debates, that have inspired me profoundly during my work.*

*I would like to thank **Prof. A. K. Singh**, Head, Department of Chemistry and **Prof. B. Jayaram** and **Late Prof. U. K. Nadir**, former Heads, Department of Chemistry, IIT Delhi, India for providing departmental facility to carry out research work.*

*I would like to take this opportunity to thank **Prof. R. J. Butcher**, Department of Chemistry, Howard University, Washington, D. C., USA; **Prof. A. R. Ramanan**, Department of Chemistry, IT Delhi, DST-FIST, India and IIT Delhi for providing X-ray facilities. I am highly indebted to **Prof. V. K. Yadav**, Indian Institute of Technology Kanpur for Mass spectroscopic studies. Personally, I am highly indebted to **Mr. Sumant kumar Gupta**, University of Rajasthan, Jaipur for screening of ^1H NMR spectra for present research work with great enthusiasm.*

*My special thanks are due to **instrumentation staff** of Chemistry Department, IIT Delhi for recording analytical and spectral data. I am also grateful to supporting staff of the department for their timely help and assistance.*

*I am thankful to my seniors, **Dr. Shabana Khan** and **Dr. Sarika Singh** for their research suggestions. I am especially indebted to **Abhishek Kumar**, for helping me in thesis writing and proof reading and my lab colleagues **Geeta Tiwari, Prabhu, Dolly, Mantesh, Anuj, Suman, Suman yadav, Gaurav, Nirmal, Samirul, Khokan, Dashrath** and **Maddiletti** for their full heartedly cooperation and providing friendly atmosphere during my research work. I am*

thankful to Council of Scientific and Industrial research, Government of India for financial assistance in the form of Junior and Senior Research Fellowship for this research work.

I am grateful to the Department of Chemistry, IIT Delhi, for giving me this opportunity. I am very much thankful to my family for their Love and affection and, finally I sincerely thanks 'Almighty God' for providing me tremendous strength during my tough times and for everything I do have in my life.

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

Neeru

ABSTRACT

The thesis entitled “**Design and synthesis of polyorganosulfur species and their exceptional coordination behavior with d^{10} metal ions**” focus on the design and synthesis of new polyfunctional organosulfur species and their potential applications in supramolecular coordination polymer chemistry.

Chapter I presents a brief overview on recent developments in the field of organosulfur chemistry and describes their applications in various fields including supramolecular, conducting polymers, cation sensors, catalysis, biology, organic and coordination chemistry.

Chapter II describes the synthetic strategies and experimental details involved in the preparation of starting materials. This chapter also details the procurement source for various chemicals and the physicochemical techniques used for characterization. These include elemental analysis, IR, $^1\text{H}/^{13}\text{C}$ NMR, ES-MS, UV-visible, fluorescence spectroscopy, TG analysis and single crystal X-ray diffraction studies.

Chapter III focus on the synthesis of flexible tetrasubstituted organosulfur species with nitrogen as a subsidiary heteroatom donor in the ligand core with a view to examine their reactivity and coordination behavior towards d^{10} metal ions of group 12 (Zn(II), Cd(II) and Hg(II) ions) with nitrate as counter anion in non-aqueous aprotic solvent, acetonitrile. Formation of 2-D coordination polymer and coordination saturation was achieved in Cd(II) and Hg(II) complexes via bridging nitrate. Solution state study indicated that light is an important factor in deriving the metal-ligand coordination assembly from low dimensionality to higher.

Chapter IV focus on reactivity and coordination behavior of tetrasubstituted organosulfur species towards d^{10} metal ions of group 11, specifically Ag(I) with nitrate as counter anion. The influence of light and solvent on coordination polymer was studied and it was found that

light and solvent play a profound role in extension of assembly through anionic part, nitrate, either by nitrate- nitrate interactions or through bridging mode of nitrate. Generation and stabilization of nitrate dimer (N_2O_6) between the layers of Ag(I) coordination polymer in one case and extension of Ag(I) coordination polymer from 1-D to 2-D in light in other case are two important results and supports the anion activation that has been rarely mentioned in literature.

Chapter V focus on the synthesis of two types of tetrasubstituted organosulfur species, one with extended flexibility and second with, limited flexibility. The aim of this chapter was to study similar type of reactions as in chapter III and IV, however systems with extended flexibility proved labile in nature and system with limited flexibility had solubility problem associated with them. Thus both restricted us to study the parallel anion chemistry as in chapter III and IV with group 11 and 12 metal ions. Whatsoever, the system with extended flexibility proved their worth in metal ion sensing in non aqueous medium as ‘turn- off’ fluorescence based chemical sensor for Cu(II) or Hg(II) ions.

Chapter VI focus on the synthesis, reactivity and structural aspects of flexible hexasubstituted organosulfur derivatives and their coordination behavior toward Ag(I) in non-aqueous aprotic medium. Despite known passivity of such systems toward metal ions due to ‘steric buttressing effect’ disposed by aliphatic protons around donor and prominent intermolecular S...S interactions, stable coordination polymers, with Ag(I), were achieved. Limited solubility of hexasubstituted organosulfur derivatives with N in the molecular core confined our study to selected systems having only sulfur as donor atom in the molecular core. The prominent influence of anions (NO_3^- , CH_3SO_3^- , ClO_4^- , BF_4^-) on structural organization has been evaluated. All the anions coordinate to Ag(I) in unidentate manner, while nitrate coordinates to Ag(I) in unidentate as well as bridging manner and supported

the coordination assembly. Stabilization of water dimer (smallest water cluster) in case of Ag(I) complex with CH_3SO_3^- as counter anion was notable finding of this chapter.

TABLE OF CONTENTS

Certificate

Acknowledgements

Abstract i

List of figures ix

List of tables xvii

Abbreviations used xviii

Chapter I GENERAL INTRODUCTION

Introduction 1

References 26

Chapter II MATERIALS AND METHODS

Chemicals used 37

Synthesis of precursors 38

Physicochemical studies 40

References 43

Chapter III DESIGN, SYNTHESIS AND STRUCTURAL ASPECTS OF 1,2,4,5-TETRASUBSTITUTED (ARYLTHIOMETHYL) BENZENES AND THEIR CHEMISTRY WITH Zn(II), Cd(II) and Hg(II) IONS.

Introduction 44

Results and discussion 45

- Synthesis of Species L_1 - L_6 45

- Synthesis of metal complexes 1-4 46

• Characterization of species (L₁ - L₆) and metal complexes (1-4)	47
➤ IR	47
➤ Mass spectrometric studies	49
➤ ¹ H NMR studies	50
➤ ¹³ C{ ¹ H} NMR studies	53
➤ Single crystal X-ray diffraction studies	54
➤ Solution state studies	62
➤ UV-visible studies of L₁ with Zn(II), Cd(II) and Hg(II)	63
➤ Fluorescence studies of L₁ with Zn(II), Cd(II) and Hg(II)	64
Conclusion	66
Experimental section	67
Tables	72
References	75

Chapter IV CHEMISTRY OF 1,2,4,5 TETRASUBSTITUTED (ARYLTHIOMETHYL) BENZENES WITH Ag (I) ION

Introduction	77
Results and discussion	78
• Synthesis of metal complexes (1a-1c) of species L₁	78
• Characterization of metal complexes (1a-1c)	79
➤ Mass spectrometric studies	79
➤ ¹ H NMR studies	80
➤ Thermal studies	81

➤ Single crystal X- ray diffraction studies	83
• Synthesis of metal complex of species L₂	88
• Characterization of Ag(I) complex 2	89
➤ Mass spectrometric studies	89
➤ Single crystal X- ray diffraction studies	89
• Synthesis of metal complexes of species L₃	93
• Characterization of metal complexes (3a-3b)	94
➤ IR	94
➤ ¹ H NMR studies	95
➤ Single crystal X- ray diffraction studies of L₃, 3a and 3b	97
• Solution state studies	102
❖ UV-visible studies of species L₁ with Ag(I)	103
❖ Fluorescence studies	104
Conclusion	109
Experimental section	110
Tables	113
References	115

Chapter V SYNTHESIS AND CHARACTERIZATION OF 1,2,4,5-TETRASUBSTITUTED (ARYLTHIOMETHYL) BENZENES AND THEIR APPLICATION AS CHEMICAL SENSORS

Introduction	117
Results and discussion	117

• Synthesis of species 1-12	117
• Characterization of species 1-12	120
➤ Mass spectrometric studies	120
➤ ¹ H NMR studies	121
➤ ¹³ C { ¹ H} NMR studies	123
➤ Single crystal X-ray diffraction studies	124
➤ Solution state studies	127
Conclusion	130
Experimental section	131
Tables	137
References	138
 Chapter VI DESIGN, SYNTHESIS AND STRUCTURAL ASPECTS OF HEXASUBSTITUTED (ARYLTHIOMETHYL) BENZENES AND THEIR CHEMISTRY WITH Ag(I) ION.	
Introduction	139
Results and discussion	140
• Synthesis of species 1-8	140
• Synthesis of complexes (9-13)	141
• Synthesis of species 14-15	143
• Characterization of species 1-15	144
➤ Mass spectrometric studies	144
➤ ¹ H NMR studies	145
➤ ¹³ C { ¹ H} NMR studies	145
➤ Single crystal X-ray diffraction studies	146

Conclusion	160
Experimental section	161
Tables	167
References	169