

CHEMISTRY OF ORGANTHIOETHERS WITH METAL IONS OF d^{10} ELECTRONIC CONFIGURATION

By

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Dedicated to my parents

Whose love and support has helped me throughout...

Certificate

This is to certify that the thesis entitled, “Chemistry of Organothioethers With Metal Ions of d^{10} Electronic Configuration” being submitted by Ms. Geeta Tiwari, 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. Geeta Tiwari 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 award of any degree or diploma.

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ABSTRACT

The thesis entitled “**Chemistry of Organothioethers with Metal Ions of d^{10} Electronic Configuration**” deals with the design and synthesis of new polyfunctional organosulfur compounds 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 as donors in various fields including organic-conductors, supramolecular, coordination chemistry, cation sensors, catalysis and biological chemistry.

Chapter II describes the synthetic strategies and experimental details involved in the preparation of starting materials. This chapter also details the sources for procuring various chemicals and the physicochemical techniques used for the characterization. These studies include elemental analysis, IR, ^1H NMR, ^{13}C NMR, ^{19}F NMR, ES-MS, UV-visible, and fluorescence spectroscopy, thermal analysis (TG/DSC) and single crystal X-ray diffraction studies.

Chapter III deals with the synthesis of ditopic organosulfur species with nitrogen as a subsidiary heteroatom donor in the ligand core with a view to examine their reactivity patterns towards Ag(I) and Hg(II) ions. Influence of anion in non-aqueous aprotic solvent, acetonitrile was also studied.

Chapter IV describes the synthetic methodology and applications of sterically influenced ditopic organosulfur derivatives. The isolation of 1,2,4,5-tetramethyl-3,6-bis(methylnitrate) benzene using $\text{Hg}(\text{NO}_3)_2$ was unexpected. Reactivity of these ligands with other d^{10} metal ions such as Ag(I), Zn(II), Cd(II), and Hg(II) ion were studied. The structure of ditopic thio-donors along with their various complexes were also established by the use of single crystals X-ray

crystallography. Formation of a Cd(II) based polymer having seven and eight coordination environment was the notable feature achieved by these systems.

Chapter V deals with the synthesis of conformationally flexible hexa-thiosubstituted benzenes and their potential reactivity pattern toward Ag(I) was examined. The two stable coordination polymers were obtained with AgNO₃ and AgBF₄ despite the poor reactivity mode. Two different behaviors for these systems, i.e. both ligand and metal-directed coordination polymer formation can be related to their valuable conformational behavior

Chapter VI deals with the development of synthetic methodology for the synthesis of conformationally rigid di-, tetra-, and hexa-thiosubstituted benzenes *via* C-F bond activation process under non-catalytic condition has been developed. The structural aspects of the synthesized di-, tetra- and hexa-thiosubstituted benzenes were further established by X- ray crystallography. Solution behavior of these species was also studied with a view to examine their photoresponsive behavior and their conversion into an extended conjugated system under photochemical conditions.

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