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

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By

NEERU

DEPARTMENT OF CHEMISTRY

Submitted

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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*

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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}H/ ^{13}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.

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