DESIGN AND SYNTHESIS OF HETEROATOMIC ORGANOTHIOSUBSTITUTED 1,2,3-TRIAZOLE BASED ORGANIC DONORS AND THEIR INTERACTIVE BEHAVIOUR WITH d^{10} METAL IONS

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by

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Submitted

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to the

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Dedicated to

My uncle

Lt. Nb/Sub Mr. Satyanand Yadav

Shaheed Mr. S. N. Yadav sacrificed his life with other 21 army personnel during *an avalanche tragedy in Kashmir valley* near LoC *on February 22, 2012*

And

My Beloved parents

Certificate

This is to certify that the thesis entitled, ***"Design and Synthesis of Heteroatomic Organoithisubstituted 1,2,3-triazole based Organic Donors and Their Interactive Behaviour with d^{10} Metal ions"*** *being submitted by* ***Ms. Mantesh Kumari Yadav,*** *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. Mantesh Kumari Yadav 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 "**Design and Synthesis of Heteroatomic Organothiosubstituted 1,2,3-triazole based Organic Donors and Their Interactive Behaviour with d^{10} Metal ions**" describes the design and synthesis of organothiosubstituted 1,2,3-triazole derivatives and their structural aspects with d^{10} metal ions.

Chapter I presents a brief overview on heteroatomic 1,2,3-tiazole based organic donors and their coordination chemistry with metal ions with the view of their potential applications in various fields such as supramolecular chemistry, cation and anion sensing, catalysis and biological sciences .

Chapter II describes general synthetic strategies and experimental details used for the preparation of precursors used in the current research work. The brief description of instruments and several techniques which were used for the analysis of the novel synthesized precursors and compounds is also described in this chapter.

Chapter III describes the design and synthesis of the 1,2,3-tiazole based donors, bearing organochalcogen as substituents in structural frameworks and their coordination behaviour with Ag (I) and Ni (II) metal ions. In the representative complexes, structural variations signify the influence of substituent in donor species during coordination. The chosen donor bases proved interesting examples in achieving binuclear metal complexes to a certain extent.

Chapter IV describes the design and synthesis of organothiosubstituted 1,2,3-triazole based dipodal donors and their structural aspects with Zn (II), Cd (II), Hg (II) metal ions. The donor systems of current chapter proved to be sterically restricted and conformationally flexible in their complexes and allowed us to understand the chemistry of group 12 metal halides in a comparative manner. A comparative structural study specifies that the influences of

relativistic effects in mercury complexes are viable. However, Hg (II) complexes follow structural analogy with their lighter Cd or even to Zn (II) analogues and this behavior of Hg (II) has been critically analyzed and possible suggestions were deduced for the structural analogies among Zn (II), Cd (II) and Hg (II) complexes.

Chapter V describes the design and synthesis of triazole-supported flexible tripodal systems. However, these species exhibit selectivity for metal ions at micromolar level. A successful development of a synthetic methodology for these species followed by their functional behaviour in coordination and sensing of the metal ions is elaborated. The formation of the metallosupramolecular assembly with Ag (I) species and Cu (II) ion sensing at a μM level was the major outcome of this chapter.

Chapter VI describes the design and synthesis of sterically restricted but conformationally flexible tripodal ligands of 1,3,5 vs. 2,4,6-analogy. The coordination ability of these systems was examined with d^{10} metal ions. The findings demonstrate that the combination of tripod donors with Zn (II), Cd (II) and Ag (I) ions results interesting coordination architectures of higher dimensionalities. The nature of ligands appeared to be stable as they adopt similar conformation on coordination to metal ions without any noticeable influences on coordination scenario either due to anions or metal ions.

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Abbreviation used

s	singlet
d	doublet
t	triplet
m	multiplet
br	broad
J	coupling constant
ppm	parts per million
Hz	hertz
MHz	mega hertz
r.t.	room temperature
hr	hour
min	minute
Ar	aryl
m.p.	melting point
Equiv.	Equivalent
THF	Tetrahydrofuran
DMF	N,N-Dimethylformamide
DIPEA	N,N-Diisopropylethylamine