ABSTRACT

The thesis entitled “Design and Synthesis of N- and S/Se- Substituted Organic Species and Their Exceptional Behavior Towards d^{10} Metal Ions, UO_2^{2+} Ion and Organic Guest Molecules” describes the synthesis of new kind of organic heteroatom donor species or architectures modified by incorporating chalcogen atoms, mainly sulfur, with controlled geometries and new arrangement of donor atoms to understand their behavior towards d^{10} metal ions, UO_2^{2+} ion and organic guest molecules.

Chapter I provides a brief overview as introductory remarks on ligand design aspects from acyclic to cyclic analogue bearing heteroatom donor combinations and their potential applications in various fields that have been realized in past two and half decades. It also explains aims and objectives of present research work.

Chapter II provides the list of chemicals and reagent used throughout the research work and details of the synthetic methodology adopted for the preparation of starting materials that are not commercially available. It also explains various physicochemical and spectroscopic studies used for the characterization of newly synthesized compounds.

Chapter III deals with the synthesis of 1,2,3-traizole based acyclic organic donors bearing heteroatomic N, S/Se donor combinations in their structural framework and three representative examples of donor species were evaluated for their interactive behavior towards Zn(II), Cd(II) and Hg(II) ions in comparable reaction conditions. The, interactive behavior of Zn(II), Cd(II) and Hg(II) ions were entirely different from each other and allow one in observing three different trends for their reactivity patterns in similar environment. These study allow one to visualize the Hg(II) when it behaves like ‘hard’ Zn(II) or its individual performances being ‘soft’ in nature and burdened with characteristic heavy metal effects. Therefore, it may be concluded that the behavior of these metal ions may be seriously influenced by the ligand architecture and position of heteroatoms in the donor species.

Chapter IV further elaborates the design and synthesis of a series of Schiff-base based acyclic organic donor species with ON_2E_2 (E = S, Se or Te) donor combinations with structurally rigid phenolic (-OH) and imine (-C=N-) linkage with appended chalcogen bearing flexible donor arms. The chemistry of UO_2^{2+} ion with these donor species was found remarkably interesting and discussed. The outcome of these results also form experimental basis in viewing the adventitious role of water and critical behavior of UO_2^{2+} ion activity (as oxidizing, reducing or catalytic) may be relevant to many chemical, biological and environmental processes.

Chapter V describes the synthesis of N and S/Se substituted organic donor functionalities assisting the preorganized bowl shaped cyclotriveratrylene (CTV) molecular architecture. These molecular species have shown ‘homomeric inclusion’ phenomenon in which inclusion of one molecule into the cavity of other molecule with exactly similar architecture. Functionalization of these CTV derivatives with chalcogen donors has shown enhancement in their interactive ability towards guest species and formation of metallosupramolecular assembly with Ag(I) salts with nitrate or perchlorate as anions.

Chapter VI describes the synthesis of chalcogen assisted pillar[5]arene derivatives considering their potential as host species. The rigid pillar shaped structure and highly rich electron density in the cavity makes them selective host species towards long chain linear aliphatic guest molecules over their branched chain or cyclic analogues. The chalcogen functionalized pillar[5]arene derivatives have also shown their selectivity for iodide ion with respect to other competitive anions.