

ABSTRACT

The thesis entitled “*Functional Activity of Uranyl (UO_2^{2+}) Ion in Response to Biologically Relevant Heteroatomic Organic Donor Substrates*” deals with the study on functional activity of UO_2^{2+} ion towards a series of acyclic species bearing phenolic ($-OH$), ($-HC=N-$), ($-C=O$) and ($-NH-N-$) organic donor functionalities in non-aqueous medium. The thesis is divided into six chapters including concise introduction on chemistry of uranyl ion in view of current study and further their potential application in nuclear technology, post consequences and environmental impact and remediation followed by chapter II as, materials and methods, and findings of the current research work are discussed in four chapters (III–VI).

Chapter I provides a key introductory note envisioned by inorganic chemist and further their contribution towards the study on the behavior of uranyl (VI) ion in diverse environments. The current work is one of the academic, curiosity-driven research in uranyl chemistry and have their potential in advancement of safer use of nuclear technology.

Chapter II provides the list of chemicals and reagents procured through various sources and details of the synthetic procedures followed for the preparation of starting materials which were commercially not available. It also provides information about the physicochemical, spectroscopic, and crystallographic techniques used for the characterization of newly synthesized derivatives.

Chapter III discusses interactive behavior of UO_2^{2+} with N_4O_3 -type organic species having ‘O’ (oxygen) of phenolic ($-OH$), ‘N’ of azomethine ($-HC=N-$) and imidazolidine donor functionalities derived from the reaction of triethylenetetramine and hydroxy aromatic aldehydes. The behavior of donor species was specific for UO_2^{2+} ion as donor species act as tripodal donor and have tendency to encapsulate uranyl ion in its oxidation state (VI). It was believed that they may act as suitable donor species for UO_2^{2+}

sensing but at the same time the steric constraints imposed by donor species on uranyl ion appeared to be paramount. The critical behavior of H₂O during crystallization in MeOH or CH₃CN as solvent resulted unexpected uranyl ion speciation.

Chapter IV discusses the complexation studies of UO₂²⁺ with symmetrically substituted guanidine-based donor species (with ‘O’ and ‘N’ donor functionalities) derived from the reaction of hydroxy aromatic aldehydes and triaminoguanidine chloride. In addition to the usual coordination ability of donor species, they may also act as an interesting building block in making UO₂²⁺ based supramolecular structures. The hydrolysis reaction followed by carboxamide bond formation may have its worth in studying decorporation of UO₂²⁺ ion in biological system.

Chapter V discusses to study the complexation reactions of UO₂²⁺ with organic species derived from isophthalohydrazide and benzene 1,3,5-tricarbohydrazide and aromatic aldehydes. The donor species may exhibit keto-enol, keto-enamine, *E/Z* isomerization and [-C=N-N=C(O)] tautomerization under reaction conditions. Therefore, an understanding of external influences such as solvent, pH changes, light, heat etc. may further play crucial role in explaining the chemistry of uranyl ion in natural environment.

Chapter VI discusses the complexation reactions of UO₂²⁺ with donor species, bearing ‘O’ of phenolic (-OH), ‘O’ of carboxamide (C=O), ‘N’ of azomethine (-HC=N-) and ‘N’ of pyridine donor functionalities derived from pyridine-2,6-dicarbohydrazide. The interaction of UO₂²⁺ with these donor species resulted trinuclear, tetranuclear and hexanuclear uranyl complexes. Herein, the formation of uranyl complexes of higher nuclearity were found beyond classical explanation of their coordination chemistry. The unprecedented formation of peroxo- and carbonato bridged uranyl complexes were main achievement of this chapter. Peroxo linkage formation may be supported by intrusion of O₂ or formation of -O-O- bond by photolytic manner.

