ABSTRACT

The thesis entitled **Synthesis, structural assessment and biological studies of some mixedligand complexes of copper(II), zinc(II) and cadmium (II)** embodies an account of aqueous medium synthesis of mixedligand complexes of the chosen metal ion and biological studies involving the cadmium complexes for antimicrobial activity and influence of some Cu and Zn complexes in the enhancement of silk production by eri silkworm. The content of the thesis is spread over seven chapters – the first chapter deals with introduction, chapter 2 is concerned with details of chemical, analytical methods and equipment used, and the chapters 3-7 are the work chapters that describe the syntheses and biological studies. The chapters 3-7 are self-contained ones with a short introduction, experimental and results and discussion followed by references. Wherever necessary, figures and tables were provided in the respective chapters for clarity. A list of figures and tables are appended in the beginning for ready references.

Chapter 1:

The **Chapter 1** deals with an introductory overview of the research work focusing on background and underlying motives of the work chosen for the present Ph.D. program. The importance and significance of the coordination chemistry of copper(II), zinc(II) and cadmium(II) has been reflected in this chapter drawing citations from relevant literature. Diversity of structure, challenges in synthesis and biological property of copper(II), zinc(II) and cadmium(II) complexes of halide and organic ligands has found particular attention in this chapter. Fluoride, being unique among the halogens, study of its interaction with these metal ions with bio relevant organic coligands has been one of the

primary goals of the present research. Accessing mixed ligand complexes of chloro, bromo, and iodo ligand remained a recurring theme of the research. Cadmium being a toxic element, study of antimicrobial property of its compounds is also set as an objective of this research. Both copper and zinc being essential elements for the biological system, study of the enhancement of production of silk by eri silk worm (*Samia cynthia ricini*) has been set as one of the goal for the present Ph.D. research.

Chapter 2:

Description of experimental works, chemicals, materials and details of the equipment used for the analytical and characterization methods, DFT computation using DMol3/B3LYP, and antimicrobial and biological study protocol are the subject matter of **Chapter 2**.

Chapter 3:

In **Chapter 3** synthesis, characterization, assessment of structure of mixedligand complex of copper(II) incorporating biorelevant ligands, amino acids and oxine has been described. The complexes whose synthesis are reported herein are $[CuF_2(oxin)_2]$ **(1)**, $[CuCl_2(oxin)_2]$**(2)**, $[CuBr_2(oxin)_2]$ **(3)**, $[CuF_2(Hleu)(H_2O)]$ **(4)**, $[CuBr_2(Hleu)(H_2O)]$ **(5)**, [CuF2(Hmet)(H2O)] **(6)**, $[CuF_2(Hphe)(H_2O)]$ **(7)**, $[CuBr_2(Hphe)(H_2O)]$ **(8)**, $[CuF_2(Hcys)(H_2O)]$ **(9)** and $[Cu(val)_2(H_2O)]$ **(10)**. Except the serendipitous synthesis of the compound $[Cu(val)_2(H_2O)]$ **(10)**, which is known, all compounds are hitherto unreported. The formation of the compounds was found to be dependent upon the pH of the reaction solution as well as the concentration of the ligands. The synthesis strategy offers useful clues to the synthesis of newer mixed ligand halo complexes. The structure

of the compound $[Cu(val)_2(H_2O)]$ **(10)** has also been established by X-ray diffraction analysis while for the rest nine compounds **(1-9)**, the structures were assessed by a combination of analytical and spectral studies. The structure of cis-$[Cu(val)_2(H2O)]$ **(10)** has been found to possess a distorted square-pyramidal geometry. For the compounds **1-9** which did not afford quality crystal - DFT method was resorted to. The Density Functional Theory (DFT) calculation on two representative compound suggested the energy optimized structure to be a distorted tetrahedral.

Chapter 4:

The **Chapter 4** portrays an account of the synthesis, characterization and assessment of mixedligand halo complexes of Zn(II). The principal ligands were either fluoride or bromide and the coligands selected were biorelevant ligands such as amino acid and benzimidazole. The complexes described in this chapter are characterized as: $[ZnF_2(Hleu)(H_2O)].2H_2O$ **(11)**, $[ZnBr(leu)(H_2O)]$ **(12)**, $[ZnF_2(Hser)(H_2O)].3H_2O$ **(13)**, $NH_4[ZnF(ser)_2(H_2O)].5H_2O$ **(14)**, $[ZnBr(ser)(H_2O)]$ **(15)**, $[ZnF_2(Hphe)(H_2O)]$ **(16)**, $[ZnF_2(Hhis)(H_2O)].2H_2O$ **(17)** and $[ZnF_2(bim)(H_2O)]$ **(18)**. The pH of the reaction solution played an important role affecting the composition of the synthesized complexes. A four-coordinated complex $[ZnF_2(Hser)(H_2O)].3H_2O$ **(13)** formed at a pH ~ 6 transforms to six coordinate complex, $NH_4[ZnF(ser)_2(H_2O)].5H_2O$ **(14)**, at pH ~3. The compounds, **(13)**, **(14)** and **(17)** are water soluble while the rest are sparingly soluble. The newly synthesized complexes are characterized and structure assessed by elemental analysis and spectral studies. The DFT optimized structure of a representative complex, $[ZnF_2(Hleu)(H_2O)]$ **(11)** indicated a distorted tetrahedral structure .

Chapter 5:

Chapter 5 of the thesis contains an account of synthesis and characterization of a series of mixed ligand halo complexes of cadmium(II) incorporating natural amino acids, imidazole and benzimidazole. Complexes formed with amino acid and imidazole as coligands are soluble in water. Those with benzimidazole as coligand are insoluble in water. All the synthesized compounds are non-ionic in nature and are of the type $[CdX_2(L)(H_2O)]$ (X = F, Cl, Br or I ; L= l-luecine, l-serine, l-methionine, l-cysteine, imidazole, benzimidazole).

The DFT optimized structure of representative complexes, $[CdF_2(Hser)(H_2O)]$ **(20)** and $[CdF_2(Bim)(H_2O)]$ **(25)** are also presented herein. The HOMO-LUMO energy gap and other bond parameters are in conformity with the proposed structure of the compounds. Occurrence of coordinated water molecule in each of the complexes is quite characteristic. The choice of simple starting materials, aqueous medium, pH-based strategy has been the hallmark of the syntheses.

Chapter 6:

Chapter 6 incorporates biological study of some selected synthesized compounds reported in chapter 3-5. Cadmium and fluoride being toxic and environmentally relevant element, three water soluble and one sparingly soluble mixedligand fluoro-cadmium compounds were screened for antimicrobial activity against two gram positive strains, *Staphylococcus aureus* **[A]** and *Bacillus subtilis* **[B]**, and two gram negative strains,

Klebsiella pneumoniae **[C]** and *Escherichi coli* (*E.coli*)**[D]** and the results have been discussed in this chapter.

This chapter also describe a study on the influence of certain water soluble copper Cu (II) and Zn(II) compounds in the production of silk of eri silkworm (*Samia cynthia ricini*). Harvesting silk from eri silkworm is an important culture of North East India especially among the socio-economically backward and tribal people. Though traditionally silk culture is quite an old practice yet research on the development and production of silk has not been adequately addressed. Accordingly, this chapter presents an account of the work carried out on the influence of certain Cu(II) and Zn(II) complexes on the production of silk by eri silkworm . Experiment shows that the water soluble copper compound, $[Cu(val)_2(H_2O)]$ **(10)**, can reduce the mortality rate of eri silkworm. The water soluble zinc compound, $NH_4[ZnF(ser)_2(H_2O)].5H_2O$ **(14)** has been found to be very effective in enhancing the production of silk by eri silkworm (*Samia cynthia ricini*). The present research therefore clearly demonstrates that the treated larva survives 12 hours more in their 5th instars compared to the control larva which led to the production of 200% more silk.

Chapter 7:

An overall conclusion in terms of research highlights reflecting the findings of the works is included at the end. The synthesis strategy leading to the formation of mixed ligand halo complexes in aqueous medium is believed to be the redeeming feature of the present research. The results of investigations on biological activity of some selected complexes with regard to antimicrobial activity and enhancement of silk production by eri silkworm

holds immense potential for practical applications. A brief idea about the future scope of studies has also been projected in this chapter.

A list of publications and copies of published papers has been attached at the end.