

## GENERAL INTRODUCTION

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Chemistry of transition metals and their complexes continue to fascinate inorganic chemists since the Werner's time. Synthesis of coordination compounds followed by structural characterization with variety of ligands and exploration of their properties has dominated the research activity in this domain. With the unfolding of their significance and recognition of potential applications in diverse fields ranging from biological to material science, the inorganic chemistry scenario in the context of transition metal complexes got hugely transformed over the last three decades or so. Biological significance apart, interesting topologies [1-7], nonlinear optics (NLO) [8,9], catalysts [10], molecular magnetic materials [11-13], electrical conductivity [14,15] molecular recognition [16,17], assembly of novel network structures [18] are some of the aspects that captivated the interest of new generation coordination chemist. Our emphasis in the present Ph.D. research has been to investigate mixedligand complexes of some late transition metals viz. copper, zinc and cadmium.

It would be appropriate to highlight the various aspects of the familiar chemistry and current interests in respect of the chosen Ph.D. research. Instead of a separate background for the three metals, we would prefer to develop the introduction through simultaneous discussion on the selected metals. The idea is to provide a holistic and comparative preamble to the research being described here.

Metals in bio-relevant coordination polyhedra can serve as attractive biomimetic models. In fact the metals, Cu, Zn and Cd selected for the present Ph.D. research programme, together are known to be present in metallothioneins in a sulfur-rich aminoacid coordination environment. Except cadmium, whose biological essentiality is not yet recognized, both copper and zinc are now known to be most important trace element essential to almost all life forms, occurring in variety of metalloproteins. Cadmium, in fact, is considered to be quite toxic next only to mercury and is designated as a human carcinogen by the International Agency for research on Cancer and the US National Toxicology program [19,20]. Again, while copper has several oxidation states (-I to +II through zero), with +II being most dominant, zinc and cadmium are congeners and are known to occur only in +II state ( $d^0$  configuration) only. Mention of occurrence of +I oxidation level for both cadmium and zinc are made in complexes produced by pulse radiolysis, however, such species are very unstable and often ill-characterized.

The bioinorganic interest in copper(II) has its origin in the redox behavior ( $+II \rightarrow +I$ ) of the metal while that for zinc(II), a redox insensitive metal, lies in structural and catalytic function. In contrast to copper(II) [ $d^9$ ], compounds of both zinc(II) and cadmium(II), [ $d^{10}$ ] are non-magnetic.

From a bioinorganic stand-point, amino-acids, imidazole and halides are of tremendous significance as ligands for simulating local coordination sites of metalloprotein [21]. Such ligands are also relevant to medicine as they are linked with the problem of scavenging toxic metals from body through chelate complex formation [22]. Complex formation for cadmium(II) with biogenic ligands are, indeed, related to this. The question of how a protein selects a specific metal ion(s), is an important issue in current bio-coordination chemistry [24,25]. Structural variations in complexes of copper(II), zinc(II), cobalt(II) and cadmium(II) with ligands derived from imidazole, pyrazole, pyridine are extensively reviewed [24]. Advent of modern physical methods about sixty years ago, triggered a renaissance of classical coordination chemistry. Synthesis and elucidating structural diversity of metal-aminoacid complexes constituted a major research agenda in coordination chemistry [26].

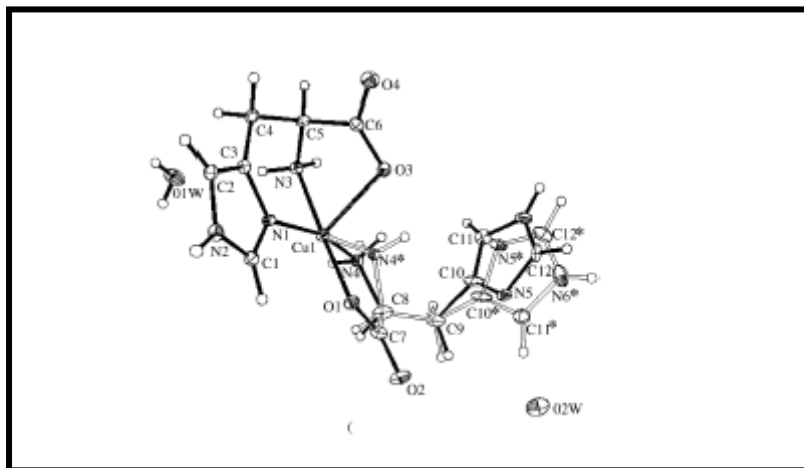
In this context, mixedligand coordination compounds are of special interest as these are implicated in storage, transport and redox functions of metal ions in biological system [26]. Structure, stability and mutual influence of two ligands bound to the same metal ion in a ternary complex have been the subject of intense investigations [27-29]. Mixedligand saccharin complexes of copper(II), zinc(II) and cadmium(II) with pyridine, o-phenanthroline and 2,2'-bipyridine of the type  $[\text{Cu}(\text{bipy})_2(\text{sac})] \cdot \text{sac} \cdot 2\text{H}_2\text{O}$ ,  $[\text{Zn}(\text{bipy})_2(\text{sac})] \cdot \text{Sac} \cdot 2\text{H}_2\text{O}$ , and  $[\text{Cd}(\text{bipy})_2(\text{sac})_2]$  have been reported rather recently [26]. Solution studies on mixedligand complexes of copper with substituted aminoacids yielded useful information [30,31].

Zinc-aquo/hydroxo linkages are important biochemical structural motifs providing an opportunity to study the inherent nucleophilicity [32] and also basicity [33]. More

recently tris-(imidazolyl) cadmium and zinc complexes,  $[(\text{TriMIm})\text{M}(\text{OH}_2)]^{2+}$  with  $\text{M-OH}_2$  ( $\text{M}=\text{Cd}, \text{Zn}$ ) motifs have been prepared and spectroscopically characterized [34]. The ligand TriMIm is pre-organized to coordinate single metal ion through trigonal planar array of imidazoles providing a four coordinate  $[3\text{N},\text{O}]$  species.

Though cadmium is known to be non-essential (rather toxic) its mixedligand complexes are important owing to the occurrence of two NMR active ( $\text{spin} = 1/2$ ) isotopes allowing  $^{113}\text{Cd}$  NMR to be utilized as ‘spin spy’ in the study of zinc containing proteins [35-48]. Copper is an essential trace element required by all living organism [49]. As central metal ion, it plays a key role in the functioning of many enzymes. Study of copper(II)-aminoacids – synthesis, structure, stability, speciation [50] stereoselectivity [51] has been the pet area for researchers. Linked to transport of copper in blood, the copper(II)-l-histidine species are important in the treatment of Menke’s disease [52], a genetic disorder. Use of similar species in curing infantile hypertrophic cardioencephalomyopathy has been report recently [53,54].

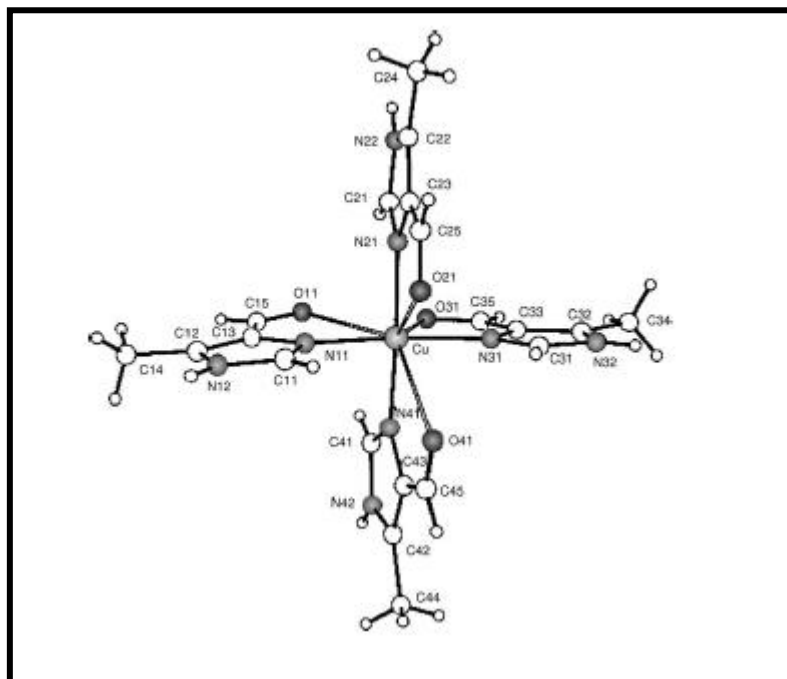
The metal exists in bound forms in the body both in high and low molecular weight complexes. The true nature of low molecular weight copper(II) binding substances were not known until very recently. For instance, despite exhaustive studies over last four decade, the structure of binary copper(II)-l-histidine complex at physiological pH remained inconclusive [49]. Deschamps et al. (2005) reported the isolation and the X-ray structure for the  $\text{CuL}_2$  complex ( $\text{L} = \text{l-histidine}$ ). Interestingly, this structure (**Fig. 1.1**) is quite different from all other structures for  $\text{Cu(II)-L-histidine}$  complex suspected from solution studies [49]. One of the l-histidine is monoanionic and bidentate  $[\text{N},\text{O}]$  while the other is monoanionic tridentate  $[\text{N},\text{N},\text{O}]$  on copper(II) completing a distorted five-coordinate square pyramidal geometry.



**Fig. 1.1 : X-ray structure for the physiological  $\text{CuL}_2$  complex. (L = l-histidine)**

As for zinc, Zn-cysteine coordination is a redeeming feature in many important DNA binding proteins [55,56]. Zinc finger proteins contains  $\text{Zn}(\text{S-cys})_2(\text{N-his})_2$  centre which play a structural role in DNA binding fingers enabling DNA transcription (TF III) [57-67]. Many other steroid based hormone receptors employ  $\text{Zn}(\text{cys})_4$  centers [62,67,68]. In fact the last decade witnessed hectic activity on retrofiral-type zinc finger protein with mixed aminoacid coordination environment of the type  $\text{Zn}(\text{cys})_3(\text{N-his})$  [68,69]. A better understanding of these nucleocapsid proteins can eventually lead to the development of a new anti-HIV strategy [70]. Otto et. al. reported [71] a series of mixedligand compounds both of Zn and Cd of the type  $[\text{M}(\text{tpdp})_2(\text{N-Melm})_2]$  (M = Zn, Cu, Cd; tpdp = N-(2-thiophenyl)-2,5-dimethylpyrrole; N-Melm = N-methylimidazole). Obtained as tetragonally compressed cores, these complexes serves a significant structural and spectroscopic models. Several mixedligand halo complexes of Zinc(II) with pyridine-2-carbaldehyde (PA) of the type,  $\text{ZnX}_2(\text{PA})_2$  (X = Cl, Br, I) with distorted six-coordinate geometry were reported in 1999 by Vahrenkemp's group [72]. An unusual example of eight-coordinate with a dodecahedral coordination polyhedra copper(II) complex with aldehyde-methylimidazole (L),  $[\text{CuL}_4]^{2+}$  bonding via pyridine like N atom of

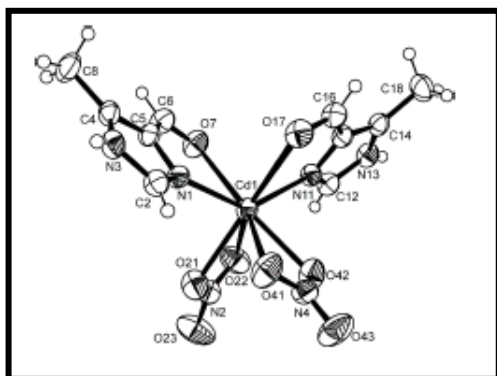
imidazole ring and O-atom of carbonyl group leading to  $\text{CuN}_4\text{O}_4$  local set-up (**Fig.1.2**) was described by Kurdziel et al. and his group in 2002 [73].



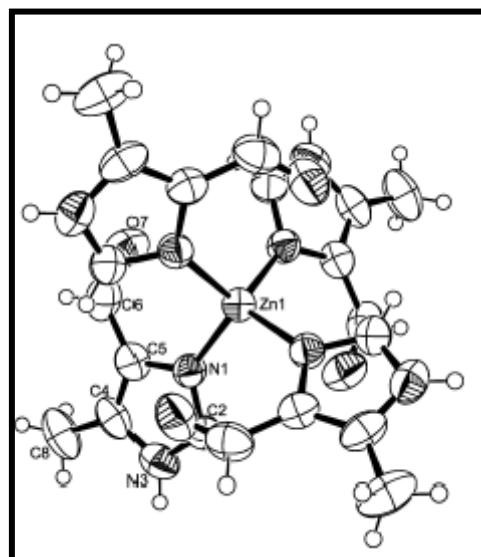
**Fig. 1.2 : X-ray structure for the physiological  $[\text{CuL}_4]^{2+}$  cation.**  
( L = 4-carbaldehyde-5-methyl imidazole )

The corresponding Cd-complex,  $[\text{CdL}_4]^{2+}$  has also eight coordinate set-up double coordination sphere of distorted dodecahedron (**Fig. 1.3**) [74]. The zinc(II) complex,  $[\text{ZnL}_4]^{2+}$  on the other hand possess a tetrahedral structure (**Fig. 1.4**) in  $\text{N}_4$  environment with the ligand being monodentate through pyridyl N of imidazole only.

The complexation in aqueous solution also occurs in a different way for each metal ion as revealed by potentiometric investigations. Crystal structures of even binary zinc-amino acid complexes are begin to be resolved only recently. A number of binary zinc-amino acid complexes,  $[\text{Zn}(\text{gly})_2]$  [75],  $[\text{Zn}(\text{leu})_2]$  [76],  $[\text{Zn}(\text{cys})_2]^{2-}$  [77],  $[\text{Zn}(\text{Me}^+)_2]$  [78],  $[\text{Zn}(\text{His})_2]$  [79],  $[\text{Zn}(\text{Ser})_2]$  [80],  $[\text{Zn}(\text{Asp})(\text{H}_2\text{O})_2]$  [81],  $[\text{Zn}(\text{Glu})(\text{H}_2\text{O})]$ ,  $[\text{Zn}(\text{Ileu})_2(\text{H}_2\text{O})_2]$  and  $[\text{Zn}(\text{Phe})_2]$  [82] have been X-ray crystallographically characterized.



**Fig. 1.3 : Structure of  $[\text{CuL}_4]^{2+}$  cation**  
(L = 4-carbaldehyde-5-methylimidazole)



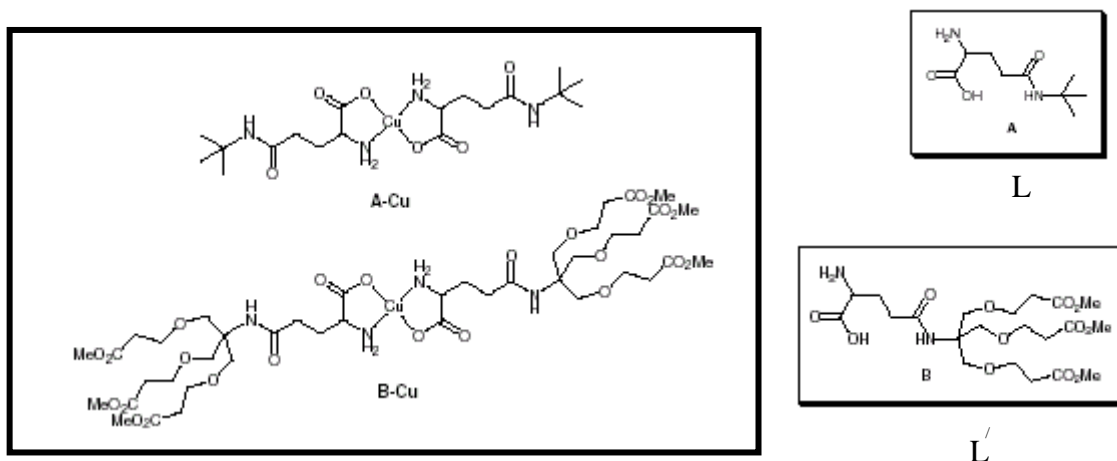
**Fig. 1.4 : The structure of  $\text{ZnL}_4$  complex.**  
(L = 4-carbaldehyde-5-methyl imidazole)

The reluctance of zinc compounds to form crystal is believed to be one of the reasons for such paucity of information. Professor Vahrenkamp's group in Freiburg, Germany, contributed immensely to coordination chemistry of zinc in relation to biological function [50]. Some recent studies on zinc(II) model complexes have focussed on the structure-activity relationship of zinc biosites [50, 83-91].

Active sites containing the metal are very often deeply embedded in protein and enzyme superstructures. Microenvironment dielectric constant and the accessibility of the metal to different substrate are profoundly influenced by such encapsulation. There has been a tremendous recent interest in encapsulated metal complexes in which a branched superstructure surrounds a central metal ion [92-97]. The effect of encapsulation on various function such as optical [98-108], redox [109-124], or catalytic [125] properties have been probed. It is now known with certainty that redox kinetics are significantly slower in encapsulated systems mimicking those in biological system [114-118]. Coordination compounds of aminoacids are a recurring

theme of research [126-133]. The side chain of a bound amino acid offers suitable points for attaching functionality capable of encapsulating metal ions.

Amino acids with bulky side chain derivatives, functionalized bipyridine and phenanthroline ligands have been effectively employed in recent times to achieve encapsulation of copper ions generating wide array of interesting molecular architectures (Fig. 1.5) [126-128, 134-139].



**Fig. 1.5:** A-Cu : Molecular structure of  $\text{CuL}_2$ ;

**:B-Cu :** Molecular structure of  $\text{CuL}'_2$

Such investigations have proved to be very significant in comprehending the role of organic superstructures to mimic the function exhibited by highly evolved metalloproteins in biological systems. Pharmacological as well as toxicological properties of amino acid and their complexes is another area that has caught the attention of researchers [140-143]. Quite a few mixedligand copper(II) complexes with salicylidene-amino acid Schiff bases (Fig. 1.6) and neutral planar chelating ligands (phenanthroline, 2,2'-bipyridyl) as coligand have been reported and their potential as anticancer therapeutic pharmaceuticals have been investigated [144].



Such study has opened up new possibility for development of chemotherapeutic arsenals, from tumor-imaging to inhibition.

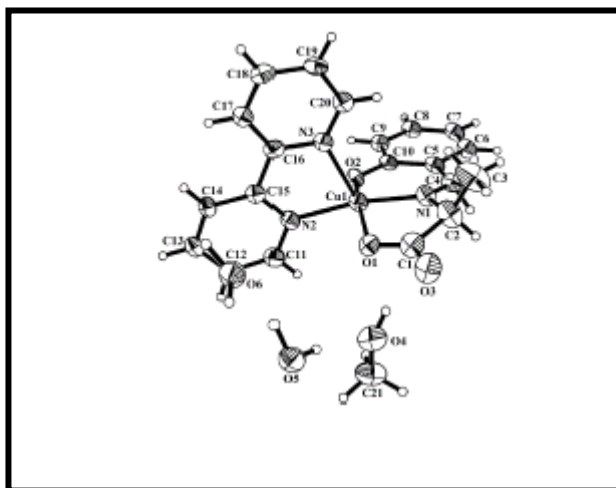
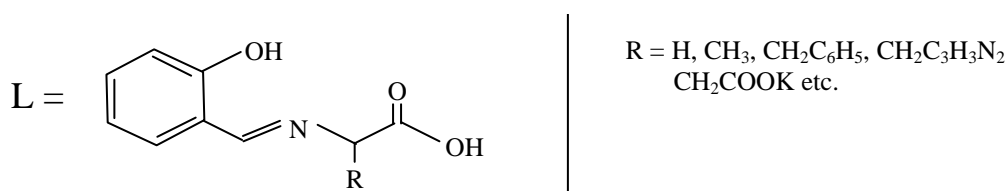


Fig. 1.6 : ORTEP representation of  $\text{CuL}_2$  where

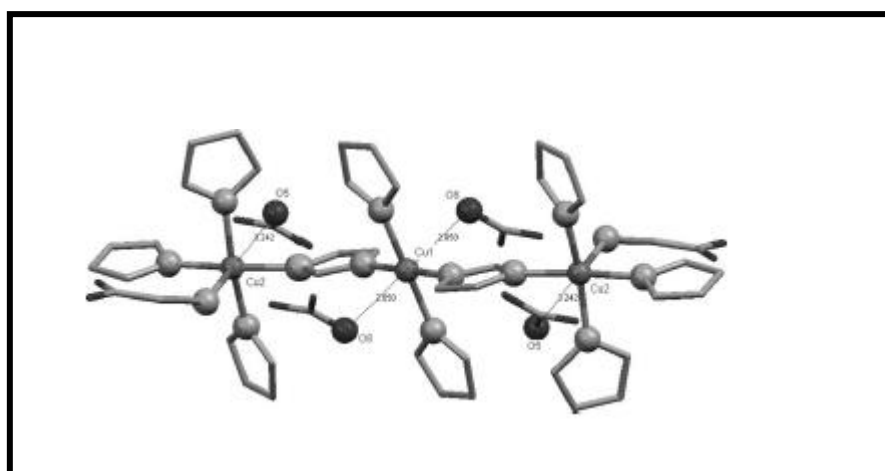


Several reports on stereoselectivity of Ni(II), Cu(II), Zn(II), Co(II) complexes of substituted 2-alanine ligands [145], biorelevant heterocyclic N donor sites (pyridyl, thiazolyl, pyrazol, thienyl) [146-148] and carboxylate groups [149] exists. Solution equilibria of some copper(II) complexes of histidine analogues has also been investigated [22]. Further, structurally characterized mononuclear mixedligand complexes of Ni(II), Cu(II) and Zn(II) with biogenic  $\alpha$ -carboxylates ligand (glycolic, lactic, mandelic, benzylic etc.) and imidazole, e.g.  $[\text{Zn}(\text{HL})_2(\text{fm})_2]$ ,  $[\text{Cu}(\text{OH})_2(\text{Im})]$  have been reported recently [150]. The coordination mode of the  $\alpha$ -carboxylic ligands varied in the complexes. Mixed aminoacid complexes of the types  $[\text{Cu}(\text{His})(\text{Ala})]$  and  $[\text{Cu}(\text{His})(\text{Val})]$  are also on record [151]. Aminoacid coordination to metals confer unusual configuration, structural lability [152]. The coordination geometry, number of

coordinated ligands, donor groups, nature of binding i.e. the microcoordination environment is the key to understanding specific physiological function [153]. Ternary complexes of metal aminoacids has also found attention due to their possible role in enzyme-inhibition [154-155].

Imidazole and functionalised imidazoles are quite ubiquitous as coordinating ligands for Cu(II) and Zn(II) and are of great interest in relation to active site mimics of multi-histidine coordination in biological system [156-164].

There exists a rich chemistry of imidazolato - copper(II) complexes embracing (i) katena - imidazolato complexes (ii) binuclear and (iii) trinuclear complexes [165-173]. A rather unusual trinuclear molecular copper complex (Fig. 1.7) that contain neutral imidazoles have been documented [165].



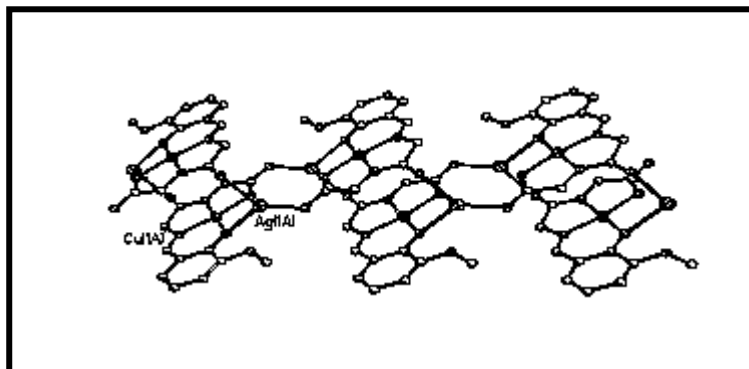
**Fig. 1.7 :** Molecular structure of trinuclear complex,  
 $[(\text{can})(\text{Im})_3\text{Cu}(\mu\text{-Im})\text{Cu}(\text{Im})_2(\text{NO}_3)_2(\mu\text{-Im})\text{Cu}(\text{Im})_3(\text{can})] \{ \text{can}^- = \text{NO}_2\text{N}(\text{CN})^- , \text{cyanamidonitrate} \}$

Zinc in  $[\text{Zn}(\text{imidazole})_4](\text{ClO}_4)_2$  has been shown to be tetrahedrally linked to imidazole nitrogen [166]. Octahedral  $[\text{Zn}(\text{HIm})_6]\text{Cl}_2$  and pseudo tetrahedral  $[\text{Zn}(\text{HIm})_2\text{X}_2]$  (X = Br, I,  $\text{NO}_3$ , NLS) are also on record [167]. The compound

[Cd(Hlm)Cl<sub>2</sub>] is polymeric with the metals being doubly bridged by Cl atoms. Coordination about Cd is octahedral [168]. Ternary complexes of zinc and cadmium of the types, [Zn(O<sub>2</sub>CMe)<sub>2</sub>(Hlm)<sub>2</sub>], [Zn(O<sub>2</sub>CEt)<sub>2</sub>(Hlm)<sub>2</sub>] (Zn in near tetrahedral N<sub>2</sub>O<sub>2</sub> environment) [169], Cd<sup>2+</sup>-Hlm-malonate [170], Cd<sup>2+</sup>-Hlm-succinate [171] have been well characterized. A mixedligand complex, [Cd(glygly)(lm)Cl], has been shown to involve dimeric units with distorted octahedral structures around each metal atom [172]. The anions, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup> has been extensively used as ancilliary ligand in such complexes while F<sup>-</sup> has remained unrepresented.

As already noted, there has been significant recent interest in hybrid inorganic-organic interface polymers owing to the prospect of rational design of molecule-based network materials with potential for application in several technologically important areas such as separations and catalysis [173,174], gas storage [175,176] and magnetism [177,178]. Polymeric coordination networks are suitable candidates for rational synthesis non-centrosymmetric solids with second order nonlinear optical (NLO) property. The metal-ligand coordination is exploited to counteract typically centrosymmetric dipole-dipole interactions [179-183]. Fascinating properties of network metal-ligand coordination polymers has generated newer synthetic challenges to construct such inorganic materials with desired architectures. Recent developments in self-assembled supramolecular chemistry has enabled rational design and synthesis of metal organic polymer based on ligand geometry and coordination propensity of metal ions [184-189]. Biogenic ligands such as aminoacids, hydroxycarboxylates, imidazoles can simultaneously bind transition metal ions and provide potential intermolecular interactions that permit supramolecular assembly formations. Selection of metal ions. Novel coordination polymers of copper based on Schiff base (derived

from glycyl glycine and o-vanillin) of the type  $\text{Ag}[\text{CuL}]_n$  has been reported recently [190](Fig. 1.8).



**Fig. 1.8 : ORTEP representation of  $[\text{CuL}]$  polymer  
(L = Schiff base derived from glycylglycine and o-vanillin)**

In view of the burgeoning diverse interests attached to the mixedligand complexes of the chosen metals viz. copper, zinc and cadmium with biogenic coligands, just highlighted, it was thought appropriate to embark on a research programme pertaining to the synthesis of coordination compounds of copper, zinc and cadmium in mixedligand polyhedra.

### **Antimicrobial activity**

In view of the growing global concern on anti-microbial resistance due to a rapid increase in multidrug-resistant bacteria and fungi, search for new antimicrobial compounds, including coordination complexes of biologically important molecules has got intensified in the past few years. Cadmium though biologically non essential, its complexes are well known for their anti-microbial activities. Cadmium(II) complexes with some acyldihydrazones show significant antifungal and antibacterial activity against various fungi and bacteria [191]. Cadmium(II) complexes of hexamethyltetraazacyclotetradecadiene act as a potential antimicrobial agent against a

number of bacterial strains (*Staphylococcus aureus*, *Bacillus cereus*, *Salmonella typhi*, *Shigella dysenteriae* and *Escherichia coli*) and against two fungi (*Candida albicans* and *Aspergillus aculeatus*)[192]. Cadmium complexes of macrocyclic tetraazacyclotetradecane ligands have also been reported to be active against *Salmonella typhi*, *Shigella dysenteriae*, *Escherichia coli* and *Bacillus cereus* [193]. Cadmium(II) chloride complexes with imidazolidine-2-thione and its derivatives also display substantial antimicrobial activity against *P. aeruginosa* [194]. Despite such progress, low molecular weight cadmium(II) complexes incorporating biogenic coligands that are soluble in aqueous medium are attractive candidate for antimicrobial studies. Accordingly exploring antimicrobial activity of some of the selected cadmium complexes prepared as part of the present Ph.D. program formed the subject matter of **Chapter 6**.

Quite apart from synthesis and antimicrobial studies our attention was drawn to the potential of zinc and copper aminoacid complexes to enhance silk production in silkworm. Silk, a natural fiber possess splendor lusture and elegance, and is an inseparable part of Indian culture and tradition since thousands of years. Sericulture in India is a commercially attractive and sustainable farm based economic enterprise especially for the rural poor in the unorganized sector. The entire North East India including Assam is known for its sericultural products. India is unique in having all the four types of silkworms commercially exploited for production of silk: *Bombyx mori*, *Antheraea mytitta*, *Samia cynthia* and *Antheraea assama* silk worm. In North East India itself all the four types of the silk worms are cultured. *Antheraea assama* silk worm is famous for the golden silk, and has been mentioned in literature as early as 1662 B.C. It is semi-domesticated. The golden silk produced by it is prerogative of India and the pride of Assam. Similarly *Samia cynthia* commonly known as Eri

silkworm is also an important species cultivated in North East India especially among the socio-economically backward class and tribal people. Eri-culture is also performed in many other countries like Tibet, Myanmar, Japan, China etc. All the varieties of silkworm are cultured in almost the same traditional way. Silk production is dependent on the larval nutrition for production of good quality of cocoons. Nutrient supplementation is one of the strategies by which cocoon and silk productivity can be enhanced and the quality maintained. Nutritional supplements include minerals, vitamins, proteins, amino acids and sugars [195,196]. The silk fibroin in silkworm is derived mainly from four amino acids: alanine, serine, glycine and tyrosine available through dietary intake [197,198]. Silkworm draws about 80% of the required aminoacids from the leaves they feed [199]. The aminoacids play a crucial role in glucose, tryptophan and organic acid metabolism. Although some research on *Bombyx mori* known for producing the popular Mulberry silk variety has been carried out, there is virtually no report of such work on Eri silk worm. Few studies have addressed amino acid supplementation to improve silk productivity [200,201]. Recent works on *Bombyx mori* shows that the production of silk in *Bombyx mori* can be enhanced by zinc compounds like  $ZnCl_2$ ,  $ZnSO_4$  etc.[202,203]. Zinc plays an important role in augmenting the growth and antioxidant protection of the larva of *Antheraea mylitta* which may improve the larval fitness, quality and quantity of silk production of *Antheraea mylitta* [204]. Our goal has been to study the effect of some of the newly synthesized aminoacid-metal compounds for enhanced silk productivity in Eri silk worm. The compounds were applied to the insect as a supplementary food alongwith their normal food, castor leaves and significant improvement in silk production was observed.

The present Ph.D. thesis is distributed into seven chapters (1 – 7).

The first **Chapter** presently under discussion relates to general introduction to the thesis. Drawing que from the vast array of related current literature, this chapter presents an overview of the scope and significance of the present Ph.D. research. Halides ( $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$ ) has been most frequently employed as primary ligand with aminoacids or imidazoles serving as ancilliary ligand. Fluoride has been more frequently deployed as primary ligand in the work being described here.

The next one, **Chapter 2**, incorporates the details of instruments/equipments and chemical methods of analysis.

**Chapters 3 to 5** that follows portrays an account of actual work conducted as a part of the present research. Divided on the basis of metal being dealt with, (**Chapter 3: Cu, Chapter 4: Zn, Chapter 5: Cd**). The **Chapter 6** is concerned with biological study of some selected compounds. This chapter is further subdivided into part-A (antimicrobial activity study) and Part-B (study of effect of some compounds on the production of silk by eri silk worm). Each of these chapters are self-complete with a short introduction followed by experimental and results and discussion. References are included in the respective chapters. A **Conclusion** reflecting the major findings has been appended in the last chapter, **Chapter 7**. Also included herein, an internal comparison of the results of all the work chapters.

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