CHAPTER I

Introduction

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- Review of metallatriangle complexes having copper(II) at the corners

“The extent of a man is incomplete until he does not include the reflection of his past in it”

Gulzar
This chapter reports a brief review on the following:

- Copper containing enzymes and their active sites
- Review of multidentate ligating systems containing benzimidazolyl, imidazolyl and pyridyl group bound to copper(II)
- Review of multidentate ligating systems containing benzimidazolyl amide and pyridyl amide bound to copper(II)
- Review of metallatriangle complexes having copper(II) at the corners

1.1 Copper containing enzymes and their active sites

Copper is an important transition metal in biological systems and is known to play a significant role in transport and activation of molecular oxygen. Copper proteins work in biological electron transport and oxygen transportation, by utilizing the easy interconversion of Cu(I) to Cu(II) and vice versa. Enzymes containing copper are capable of activating the C–H bond in an efficient and controlled way. Tyrosinase is a copper containing metalloenzymes and is structurally similar to the oxygen carrying protein hemocyanin. Both have been the subject of intensive modeling with low molecular weight coordination compounds.

Tyrosinase use molecular oxygen to catalyze two different enzymatic reactions: (i) the ortho-hydroxylation of monophenols to ortho-diphenols (monophenolase, cresolase acticity) and (ii) the oxidation of ortho-diphenols to ortho-quinones (diphenolase, catecholase activity) (Scheme 1). The reactive quinones polymerize non-enzymatically to the macromolecular melanins. Because of their overlapping substrate specificities, a positive test for catecholase activity does not necessarily mean that the enzymes exhibit cresolase activity. The copper binding sites of tyrosinase share a high sequence homology with the haemocyanin, the oxygen carrier proteins of the mollusks and arthropods. During evolution, a functional change of this protein family has been proposed: from enzymatic oxygen detoxification towards oxygen transport.
The common feature between tyrosinase and hemocyanin is a ‘type 3 copper center’ with a diamagnetic spin-coupled copper pair. Each of the two metal atoms, CuA and CuB of the active site are coordinated by three conserved histidine molecules. During the catalytic cycle the ‘type 3 copper center’ can adopt different functional forms: the oxy-state \([\text{Cu(II)}–\text{O}_2^{2–}\text{–Cu(II)}]\), deoxy-state \([\text{Cu(I)}–\text{Cu(I)}]\), half-met state \([\text{Cu(I)}–\text{Cu(II)}]\) and met state \([\text{Cu(II)}–\text{OH}–\text{Cu(II)}]\). In latter case, the two copper atoms are bridged by hydroxo ions. The valences of two copper atoms change from Cu(I) to Cu(II), which can be followed spectroscopically. In oxy-state, the molecular oxygen is reversibly bound as peroxide between two copper atoms in a ‘side-on’ conformation. According to current conceptions, both the met- and the oxy-state of tyrosinases enable the diphenol oxidase activity, whereas the monohydroxylase reaction requires the oxy-state.\(^4\)

Cu-Zn-SOD is an antioxidant enzyme that protects cells from the toxic effects of superoxide ion by its dismutation into dioxygen and hydrogen peroxide in biological systems. The biological function of SOD is known to play a very important role in preventing oxidative damage by the anticancer and anti-aging mechanisms\(^5\)-\(^10\) and it has been found that cancer cells have less superoxide dismutase activity than normal cells.

Galactose oxidase (GOase) is also an important mononuclear ‘type 2’ copper fungal enzyme that effectively carries out conversion of primary alcohols to aldehydes under ambient aerobic conditions (Scheme 2).\(^11\) The active-site of the GOase consists of a distorted square-pyramidal copper(II) center coordinated to two histidine (496 and 581) and two tyrosine (272 and 495) residues of the protein backbone along with an exogenous water (at pH = 7) or an acetate (pH = 4.5) moiety and is located in a
hydrophobic region rich with aromatic residues.\textsuperscript{12,13} The enzyme uses molecular oxygen in achieving a two electron oxidation of a wide variety of primary alcohol substrates to aldehydes\textsuperscript{14} via a redox cooperativity pathway existing between a neighboring radical cofactor, a tyrosine (272) residue, and the redox active copper(II/I) metal center in the enzyme active-site.\textsuperscript{15-17} Interestingly, the active form of the enzyme is an anti-ferromagnetically coupled diamagnetic species that is EPR silent and which results from the coupling of the radical cofactor, the tyrosine (272) residue, with the unpaired electron of the copper(II) center in the active-site.\textsuperscript{18}

\[
\text{RCH}_2\text{OH} + \text{O}_2 \xrightarrow{\text{GOase}} \text{RCHO} + \text{H}_2\text{O}_2
\]

\textbf{Scheme 2}

Among copper-containing monooxygenases, dopamine β-hydroxylase (DBH) and peptidylglycine α-amidating monooxygenase (PAM) are very interesting enzymatic systems.\textsuperscript{19} DBH catalyzes the benzylic hydroxylation of dopamine (DM) into noradrenaline (NE) whereas PAM catalyses the biosynthesis of peptidic hormones, which contain an amide linkage at their C-terminus. Both enzymes catalyze the stereospecific insertion of an O-atom into a C–H bond.\textsuperscript{20-22} While DBH has been the subject of extensive structural investigations, there is no crystallographic data available to date on this enzyme. On the other hand, the X-ray structure of the PHM domain of PAM has been recently resolved\textsuperscript{23} which confirms that PHM contains two ‘type 2’ copper atoms per active site.\textsuperscript{24}

Phenoxazinone synthase catalyzes the oxidative coupling of two molecules of an aminophenol to form the phenoxazinone chromophore.\textsuperscript{25} The reaction constitutes the final step in the biosynthesis of actinomycin \textsuperscript{226} and is a complex six-electron oxidative condensation (Scheme 3). The enzyme phenoxazinone synthase, a ‘type 2’ copper-containing oxidase (subunit molecular mass 88,000, 3.7 Cu per subunit), is naturally found in the bacterium \textit{Streptomyces antibioticus}.\textsuperscript{27} In its active form the enzyme consists primarily of a mixture of dimers and hexamer.\textsuperscript{28} The structure of hexameric PHS has been determined using X-ray diffraction to a resolution limit of 2.30 Å. The structure forms a hexameric ring that is centered on a pseudo 6-fold axis and has an outer diameter of 185 Å with a large central cavity that has a diameter of 50 Å. This hexameric structure is stabilized by a long loop connecting two domains;
bound to this long loop is a fifth copper atom that is present as a ‘type 2’ copper. This copper atom is not present in any other multicopper oxidase, and its presence appears to stabilize the hexameric structure. The enzyme is a copper containing protein and catalyzes the oxidation of a wide variety of aminophenols to phenoxazinones.

Scheme 3

1.2 Review of multidentate ligating systems containing benzimidazolyl, imidazolyl and pyridyl group bound to copper(II)

Benzimidazole is an important heterocyclic aromatic organic compound. Benzimidazoles and their derivatives exhibit remarkable biological activities. The most prominent benzimidazole compound in nature is N-ribosyl-dimethyl benzimidazole, which serves as an axial ligand for cobalt in vitamin B₁₂.

A large number of benzimidazole containing ligands have been reported in literature and these types of multidentate ligands are utilized for the complexation reactions with copper metal ion. Dey et al. reported penta-coordinated mononuclear copper(II) complex of tridentate 2,6-bis-(benzimidazolyl)pyridine (L) formulated as [Cu(L)(H₂O)₂](NO₃)₂ (I). The complex was characterized by single crystal X-ray diffraction analysis. The structural study shows the metal in a highly distorted square pyramidal geometry (τ = 0.1425) that comprises two aqua molecules in the first coordination sphere. The crystal packing of (I) shows a 3–D polymer formed through H–bonds involving aquo ligands, NH benzimidazole groups and nitrate anions. On reaction with pseudohalides in acetonitrile at ambient temperature complex (I) changed to mono cationic copper(II) derivatives [Cu(L)(X)(H₂O)]NO₃ [X = SCN⁻ and N₃⁻]. These copper(II) complexes have been isolated from the reaction mixtures and characterized by physico-chemical and spectroscopic tools.
A mononuclear copper(II) complex based on ligand, 2,6-bis-(2-benzimidazolyl)pyridine (L), has been synthesized and characterized by elemental analysis, molecular conductivity, $^1$H NMR, IR, UV-Vis spectra and X-ray single crystal diffraction. The crystal structure of [Cu(2,6-BIPY)$_2$(pic)$_2$·2DMF (pic = picrate) shows copper is six-coordinated forming a distorted octahedron. The crystal structure of the complex is stabilized by hydrogen bonds, due to the picrate and DMF. The ligand shows a well-defined band at 3185 cm$^{-1}$ due to N–H stretching in the benzimidazole group, which can be found at 3086 cm$^{-1}$ in the complex, indicating hydrogen bonds between N–H bonds and other atoms. Free ligand shows two strong absorptions at 300 and 345 nm attributed to π–π* transitions. By comparison, the Cu(II) complex shows three strong absorption bands at 302, 362 and 402 nm attributed to π–π* and n–π* transitions and a weak absorption band at 702 nm attributed to d-d transition ($^2$E$_{2g}$$-^{2}T_{2g}$).

Nie et al. have reported mononuclear copper(II) complexes, [CuL(2-fca)(CH$_3$OH)]ClO$_4$·CH$_3$OH (1), [CuL(m-nba)(CH$_3$OH)]ClO$_4$ (2), and [CuL(pic)(ClO$_4$)]CH$_3$OH (3), where L is 2,6-bis-(benzimidazol-2-yl)pyridine, while 2-fca, m-nba, and pic are the anions of 2-furoic acid, meta-nitrobenzoic acid and picolinic acid, respectively. In complex (1) and (2), the Cu(II) resides within a distorted square-pyramidal N$_3$O$_2$ coordination sphere with three nitrogens of L, one carboxylate oxygen, and one methanol. In complex (3), Cu(II) is coordinated with three nitrogens of L, one nitrogen and one oxygen of picolinate, and one oxygen of perchlorate in a distorted octahedral geometry. Two molecule of (1), (2) and (3) interact by intermolecular hydrogen bonding and strong π–π stacking interactions to form a dinuclear structural unit. The dinuclear units are further connected by H–bonds via perchlorate or lattice methanol to form a 1–D chain for (1) and 2–D network structures for (2) and (3). Hydrogen bonding and π–π stacking interactions are important for the stabilization of the final supramolecular structures of the three complexes.

A series of Cu(II) coordination compounds with benzimidazole derived bidentate chelating ligands have been prepared and characterized by X-ray crystallography. The 2-(4,5-dihydro-1H-imidazol-2-yl)-1H-benzimidazole CuCl$_2$ complex showed very potent superoxide dismutase (Cu-Zn-SOD) activity in vitro with IC$_{50}$ of 0.09 lM,
comparable to those described in the literature for best low molecular weight Cu-Zn-SOD mimics. Cytotoxicity studies with seven different human tumor cell lines in vitro showed that the most active 2-(4,5-dihydro-1H-imidazol-2-yl)-5-nitro-1H-benzimidazole CuCl₂ complex 10 inhibited the growth of cancer cells with IC₅₀ between 4.76 and 10.84 μM.

A copper(I) dimer [Cu(L)(CH₃CN)]₂(BF₄)₂·2CH₃OH with a chelating and bridging tridentate ligand 1-(2-pyridylmethyl)-2-(2-pyridyl)benzimidazole (L) has been reported. The ligand L acts as a tridentate ligand, effecting dimerization of two chelate rings through the imine nitrogen centers of the imidazole groups. This dimerization gives rise to a ten-membered dimetalla ring. Tetra-coordination at copper(I) is complemented by acetonitrile. The two co-crystallized methanol molecules are connected with each other via hydrogen bonds. The crystal structure analysis demonstrates that the system prefers to form a partially saturated eight-membered chelate ring \([\{[\text{Cu}(L)(\text{CH}_3\text{CN})]\}_2]\)^{2+} involving both pyridyl groups of one molecule of L. This arrangement not only precludes π conjugation of the chelating part of the acceptor ligand, it also produces a twist angle of 61.8° between the benzimidazole and 2-(2-pyridyl) ring systems which further diminishes the potential for π conjugation which leads to approximately boat-shaped chelate ring, which involves two tetrahedral centers, the d¹⁰ configurated metal (111.3(3)°) and the methylene carbon center C13 (115.0(7)°), and six sp² centers (115.5(7)°–128.2(7)°, intra-ring bond angles). Two such chelate rings then dimerize through the remaining donor atom of L, the imine nitrogen center of the imidazole ring, which results in a ten-membered dimetalla ring system (Cu₁–N₁–C₇–C₈–N₃–Cu₁a–N₁a–C₇a–C₈a–N₃a). Complex [Cu(L)(CH₃CN)]₂(BF₄)₂ displays only a poorly defined metal-to-ligand charge transfer (MLCT) absorption shoulder at 330 nm in CH₂Cl₂ extending into the visible region. Both oxidation and reduction of the complex occur irreversibly; the corresponding peak potentials from cyclic voltammetry in THF/0.1 M Bu₄NPF₆ are 0.54 and 1.90 V vs. (C₅H₅)₂Fe²⁺/Fe, respectively.³⁶

A mixed ligand polymeric [Cu(bbhi)(L1)] complex (1), where bbhi = 1,1-(1,4-butanediyl)-bis-1H-benzimidazole, L1 = deprotonated 5-nitroisophthalic acid has been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction. Complex (1) can be described as CsCl-type net utilizing bimetal cores
as eight-connected nodes, the bridging bbbi ligands and L1 serve as spacers to yield a unique eight-connected net topology. The Cu(II) cation in (1) is five coordinated by two nitrogen atoms from two bbbi ligands and three oxygen atoms from three L1 anions. The Cu–N distances are 2.0057(17) and 2.0170(17) Å, the Cu–O bond lengths are in the range of 1.9739(14)–2.2779(15) Å. Owing to the Jahn–Teller effect, the uncoordinated carboxylic oxygen atom O2 also has weak interactions with Cu atom (Cu1–O2 = 2.867 Å).37

The reaction of copper chloride dihydrate with a tripodal N4 ligand tris{(1H-benzo[d]imidazol-2-yl)methyl}amine (ntb) under mild conditions affords [Cu(ntb)Cl]2[CuCl4]2H2O (1). The unit cell consists of eight [Cu(ntb)Cl]+ cations, four CuCl42– anions and eight water molecules as solvent of crystallization. Copper atoms in the cation and the anion differ in their geometry. In cation, the geometry of the central copper atom is intermediate between square-pyramidal and trigonal bipyramidal (τ = 0.28) in which two N atoms of the benzimidazole and the amine N atom occupy the equatorial positions and one of the nitrogen atoms from benzimidazole occupies the axial position. The remaining site of the equatorial plane is occupied by a Cl– ion. The geometry of the central metal ion in the anionic part is a distorted tetrahedron occupied by four Cl– atoms. The Cu–Namine distance in the cation is 2.2440(15) Å and the average distance of equatorial Cu–Nbenzimidazole is 1.966 Å. The distance between the copper and axial nitrogen is 2.1264(15) Å. In the CuCl42– moiety, the average Cu–Cl bond length is 2.2433 Å and this unit along with two water molecules, participates in hydrogen bonding interactions with the benzimidazole nitrogens generating a 3–D architecture. The four chloride ions of the CuCl42– unit provide two different types of H-bonding interactions. Two chloride ions form H bonds with benzimidazole N–H, while the other two are involved in bifurcated H–bonding with a water molecule and benzimidazole N–H to form a 3–D framework. The distance between the two Cu centers of the [Cu(ntb)Cl]+ units is 9.643 Å while the Cu atoms of [Cu(ntb)Cl]+ and CuCl42– units are 7.0393 Å apart. The complex (1) exhibits two reversible one-electron redox couples with E1/2 at +0.530 and -0.031 V versus Fc/Fc+. It is also evident that the CuCl42– unit does not undergo electron transfer in the available potential range. The irreversible couple observed at +1.0 V could be assigned to the oxidation of the ntb ligand. The reaction of (1) with 3,5-di-
tert-butylcatechol in presence of molecular oxygen has been studied in dimethylformamide. The reaction of complex (1) with 3,5-di-tert-butylcatechol yields a solution whose spectra is significantly different from that of the complex. In the solution the peak at 366 nm, which is due to the $\pi$(benzimidazole) $\rightarrow$ Cu(II) LMCT transition, vanishes. Simultaneously, a band at exactly 400 nm appears that is indicative of the oxidation from 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-ortho-quinone. The course of the reaction was followed at 400 nm at regular time intervals. 

The spectroscopic and magnetic measurements of three mononuclear copper(II) bromide compounds with the ligands bis-(2-benzimidazolyl)ethane (abbreviated as dbz), bis-(2-benzimidazolyl)propane (abbreviated as tbz) and bis-(2-benzimidazolyl)butane (abbreviated as qbz) and the general formula [Cu(L)Br$_2$] (in which L = dbz, tbz or qbz) have been determined together with the X-ray structure of two of the three compounds. Each compound has a tetrahedral Cu$_2$Br$_2$ chromophore with Cu–N distances from 1.976(3) to 1.993(11) Å and Cu–Br distances from 2.356(2) to 2.3982(7) Å. Angles N–Cu–N and Br–Cu–Br vary from 94.44(13) to 105.5(4)$^\circ$ and from 97.88(2) to 98.94(8)$^\circ$, respectively. The dihedral angles are 52.6(3) and 67.8(4)$^\circ$ for compounds [CuBr$_2$(dbz)] and [CuBr$_2$(tbz)], respectively. The length of the alkane chain determines the degree of tetragonality and the EPR measurements at 77 K as a frozen solution reveal a $d_{x^2-y^2}$ for the copper compounds with the ligands dbz and qbz and a $dz^2$ ground state with the copper tbz compound. X-band EPR spectra of polycrystalline powders of the complexes were recorded at room temperature and 77 K. The compounds show an axial S = 1/2 signal with a $g_{\text{iso}}$ of 2.16 for CuBr$_2$(dbz) (1). Axially split signals with $g_\perp$ of 2.14 and 2.05 and with a $g_\parallel$ value of 2.33 and 2.19, were observed for compounds CuBr$_2$(tbz) (2) and CuBr$_2$(qbz) (3), respectively. Frozen-solution EPR spectra of the three complexes recorded at 77 K in DMSO:MeOH or in DMF (with or without MeOH) did show interesting differences. The compounds show a significant difference in frozen solution. Compounds (1) and (3) reveal a typical $d_{x^2-y^2}$ ground state spectrum with $g_\perp$ at approximately 2.06, $g_\parallel$ at approximately 2.32 and an $A_\parallel$ of approximately 15 mT in agreement with a CuN$_2$X$_2$(Y) chromophore, i.e. with a fifth ligand added to the coordination sphere, probably a solvent molecule. Compound (1) also shows a nitrogen hyperfine splitting.
at \( g_\perp \) of 1.5 mT, consisting of five lines, in agreement with two nitrogen donors from the ligand. In the frozen-solution spectrum of compound (2) in DMSO:MeOH, however, the values of \( g_\parallel = 2.00, \ g_\perp = 2.25 \) (\( A_\parallel \) and \( A_\perp \) at 6.9 and 8.4 mT, respectively) strongly suggest that the \( dz^2 \) ground state has resulted and that a solvent ligand has been added in a different way. So the major species in solution might have trigonal bipyramidal geometry. A minor species appears to be formed directly when the solution of DMSO:MeOH is prepared and appears to have a common \( dz^2 \) ground state spectrum; this species may involve DMSO, DMF or MeOH complexes with a distorted tetragonal based geometry. When the solution is allowed to stand for 1 day at r.t. this minor compound becomes the major species and a \( g_\parallel \) of 2.36 and a \( A_\parallel \) of 12.11 mT is visible, which confirms the conclusion of a CuN\(_2\)X\(_2\)(Y)X species in solution. The freshly prepared frozen solution spectrum of compound (2) (\( dz^2 \) ground state) is comparable with compounds from the literature, which have in solution both the same structure and also a \( dz^2 \) ground state.

The structure of a mononuclear copper(II) compound with the ligand bis-(2-benzimidazolyl)propane ( abbreviated as tbz) has been reported. The compound [Cu(tbz)\(_2\)][(CF\(_3\))SO\(_4\)]\(_2\)(H\(_2\)O) crystallizes in the triclinic space group P\( \bar{1} \), with \( a = 12.363(6), b = 13.218(9), c = 15.365(8) \) Å, \( \alpha = 82.74(5), \beta = 68.04(4), \gamma = 65.30(5), \) and \( Z = 2. \) The Cu(II) atom has a geometry intermediate between tetrahedral and square planar consisting of four nitrogen atoms of two tbz ligands. The Cu–N–Cu angle is \( \sim135^\circ \), while the dihedral angle between them amounts to 62° (0° for square planar and 90° for a tetrahedron). Ligand field bands are observed at 10.2 \( \times 10^3 \), 13.8 \( \times 10^3 \), and 20.3 \( \times 10^3 \) cm\(^{-1} \), while the most characteristic infrared vibrations of the triflate anion are observed at 1273, 1260, 1238, 1221, 1171 and 1157 cm\(^{-1} \). The EPR measured as a powdered solid at room temperature resulted for the title compound in a \( g_\perp \) value of 2.08, a \( g_\parallel \) value of 2.35 with an \( A_\parallel \) value of only 10.0 mT.

Four novel nicotinato-copper(II) complexes containing polybenzimidazole and polyamine ligands were synthesized with formula [Cu\(_2\)(bbma)\(_2\)(nic)\(_2\)][ClO\(_4\)]\(_2\)CH\(_3\)OH.H\(_2\)O \( (1), \) [Cu\(_2\)(dien)\(_2\)(nic)\(_2\)][ClO\(_4\)]\(_2\)2CH\(_3\)OH \( (2), \) [Cu(ntb)(nic)]ClO\(_4\)H\(_2\)O \( (3) \) and [Cu(tren)(nic)]BPh\(_4\)CH\(_3\)OH.H\(_2\)O \( (4), \) in which bbma is \( bis\)- (benzimidazol-2-yl-methyl)amine, dien is diethylenetriamine, ntb is \( tris\) - (2-benzimidazolylmethyl)-amine, tren is \( tris\)-(2-aminoethyl)amine and nic is
nicotinate anion. Complexes (1) and (2) contain centrosymmetric dinuclear entity with the two Cu(II) atoms bridged by two nicotinate anions in an anti-parallel mode. The Cu–Cu separation is 7.109 Å for (1) and 6.979 Å for (2). Complexes (3) and (4) are mononuclear with nicotinate coordinated to Cu(II) ion by the carboxylate O atom in (3) and the pyridine N atom in (4). All of the complexes exhibit abundant hydrogen bonds to form 1–D chain for (1), (3), (4) and 2–D network for (2). Magnetic susceptibility measurements over the 2–300 K range reveal very weak ferromagnetic interaction between the two Cu(II) ions in (1) and antiferromagnetic interaction in (2) mediated by nicotinate ligand, with $J$ value to be 0.15 and $-0.19$ cm$^{-1}$, respectively. 

A library of multicationic ntb-Cu(II) complexes, 2–9, have been reported by replacing the labile water in the complex [Cu(ntb)(H$_2$O)]$^{2+}$, 1, (ntb = tris-[(benzimidazol-2-yl)methyl]amine) with multifunctional carboxylates acting as a bridge linker between two or four ntb-Cu(II) units under slightly acidic or alkaline conditions. Their X-ray crystal structures reveal that these complexes contain one, two or four [Cu(ntb)]$^{2+}$ units. The pH media used in preparation can control the coordination patterns of the carboxylates and the overall architecture of the complexes, although the Cu(II) centers in the complexes always maintain a five-coordinated structure regardless of the preparation conditions used. Both intra and intermolecular π–π interactions involved in the benzimidazoles, as well as extensive hydrogen bonding networks in the complexes were observed to occur in the crystal packing.

The reaction of copper(II) nitrate trihydrate and 2-(2-pyridyl)benzimidazole (pybzim) leads to [Cu(pybzim)$_2$(NO$_3$)]$(NO$_3$)$. The asymmetric unit of the title complex consists of the [Cu(pybzim)$_2$(NO$_3$)]$^+$ cation and nitrate ion, the nitrate binding mode in the complex is classified as monodentate. The Cu(II) centre of [Cu(pybzim)$_2$(NO$_3$)]$^+$ is five-coordinated by four N donors from two 2-(2-pyridyl)benzimidazole ligands and oxygen atom of nitrate anion. The angular structural addison parameter $\tau$ has a value of 0.16. Compared with the ideal values of 1 for an equilateral bipyramid and 0 for a square pyramid, the $\tau$ descriptor of the examined structure indicates a square-pyramidal stereochemistry.

Four copper(I) cyanide coordination polymers containing 2-(n-pyridyl)benzimidazole ligands, namely [Cu$_2$(CN)(2-PyBIm)]$_n$ (1), [Cu$_2$(CN)$_2$(3-PyHBIm)]$_n$ (2), {[Cu$_3$(CN)$_3$(4-[10]
PyHBIm)₄.2H₂O (3) and [Cu₅(CN)₃(4-PyIm)₂]₄ (4), have been synthesized and characterized by X-ray crystallography. Complex (1) is a one-dimension coordination polymer in which 2-(2-pyridyl)benzimidazole is deprotonated and adopts a bridging tridentate coordination mode. Complex (2) has ladder like structure in which 2-(3-pyridyl)benzimidazole does not deprotonate and acts as a bidentate bridge. Complex (3) displays a saddle shaped helical chain constructed through 12-cyanide group and the outstretched neutral 2-(4-pyridyl)benzimidazole monodentate ligand. Complex (4) shows two-dimension layer polymeric structure in which deprotonated 2-(4-pyridyl)benzimidazole acts as a tridentate bridging ligand. The cyanide groups in four complexes all act as bidentate bridging ligands.

A series of simple Cu(II) carboxylate complexes \{carboxylate = acetate (CH₃COO), salicylate (salH) or benzoate (BZA)\}, some containing either one chelating \{1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy)\} or two monodentate \{benzimidazole (BZDH) or 5,6- dimethylbenzimidazole (5,6-DMBZDH)\} nitrogen donor ligands, have been prepared and characterised. X-ray crystal structures have been determined for the square pyramidal complex \([Cu(BZA)₂(bipy)(H₂O)]\) and the two square planar complexes \([Cu(CH₃COO)₂(5,6-DMBZDH)]\) and \([Cu(salH)₂(BZDH)]\). All of the complexes are poor catalase mimics in the presence of imidazole and totally inactive in its absence. The complexes all exhibit excellent superoxide dismutase (SOD) mimetic activity.

Cu(BZA)₂(EtOH)₀.₅ (1) was generated by the reaction of copper(II) hydroxide with benzoic acid (BZAH). \([Cu(TBZH)₂(BZA)](BZA).0.5TBZH. H₂O (2) and [Cu(2-PyBZIMH)(2-PyBZIM)](BZA).1.66EtOH (3) were obtained when (1) reacted with thia bendazole (TBZH) and 2-(2-pyridyl)benzimidazole (2-PyBZIMH), respectively. \([Cu(BZA)₂(phen)(H₂O)]\) (4) was isolated from the reaction of benzoic acid and 1,10-phenanthroline (phen) with copper(II)acetate dihydrate. Molecular structures of (2), (3) and (4) were determined crystallographically. (2) and (3) are hydrogen bonded dimers and trimers, respectively. The copper centres in complexes (2) and (3) are bis-chelate derivatives that have N₄O ligation and their geometry is very similar being approximately square pyramidal. However in complex (2) both TBZH ligands are neutral in (3) one of the 2-PyBZIMH chelators is deprotonated on each copper. The structural results for (4) represent a re-examination of this crystallographically known
compound for which no hydrogen atom coordinates have been previously reported. It crystallizes as hydrogen bonded dimer and is a mono-chelate of phen with each copper centre possessing $\text{N}_2\text{O}_3$ ligation and square pyramidal geometry.\textsuperscript{46}

A new benzimidazole based copper (II) complex, $\text{bis}-(\text{meta})$-hydroxybenzoato$(1\text{-bis}$(benzimidazole))copper(II) dihydrate has been characterized by using single crystal X-ray diffraction methods. The unit cell contains two independent molecules, A and B. B is a mononuclear Cu(II) complex with square-planar coordination geometry formed by two benzimidazole molecules and two hydroxybenzoate anions. A is a dimer of B consisting of hydroxybenzoate anions that bridge the copper atoms, each of which assumes square pyramidal geometry. Aromatic $\pi$–$\pi$ stacking is observed between parallel benzimidazole rings of neighboring A-molecules. The IR spectrum of the compound is consistent with the crystal structure.\textsuperscript{47}

1.3 Review of multidentate ligating systems containing benzimidazolyl amide and pyridyl amide bound to copper(II)

Mohamadou \textit{et al.}\textsuperscript{48} describes the synthesis, crystal structures, and electronic and magnetic properties of three new Cu(II) compounds containing the tridentate pzpy ligand (where pzpy is an amide deprotonated ligand, 2-(N,2-pyridylmethyl)pyrazinecarboxamide) with the general formula $[\text{Cu(pzpy)}(\text{L})(\text{OH}_2)_x]$ (where $x = 1$ for $\text{L} = \text{CH}_3\text{CO}_2^-$ and $x = 0$ for $\text{L} = \text{N}_3^-$ or NC–N–CN$^-$). The geometries of the Cu(II) ions are described as a five-coordinate slightly distorted square pyramidal monomeric compound $[\text{Cu(pzpy)}(\text{OH}_2)(\text{CH}_3\text{CO}_2)]$ (1) and polymeric complexes, $[\text{Cu(pzpy)}(\text{N}_3)]_n$ (2) and $[\text{Cu(pzpy)}(\text{N(CN)}_2)]_n$ (3). Polymerization for complex (2) comes from equatorial–apical bridges of the pyrazine nitrogen atoms, while in compound (3), the copper centers are bridged by NC–N–CN$^-$ anions.

Singh \textit{et al.}\textsuperscript{49} have reported a distorted square planar copper(II) complex $[\text{Cu(L}^4\text{)]0.5\text{EtOH}0.5\text{MeOH}$ (1) of a deprotonated tetradeutate pyridine amide ligand $[\text{H}_2\text{L}^4 = N,N'$-bis-(2-pyridinecarboxamide)-2,2'$'$-biphenyl]. The asymmetric unit contains two crystallographically independent molecules. The copper(II) center is supported by two types of nitrogen donor atoms, pyridine [N(1a) and N(4a)] and deprotonated amide [N(2a) and N(3a)]. Average Cu(II)–N$\text{amide}$ and Cu(II)–N$\text{py}$ bond lengths are 1.929 Å and 1.981 Å, respectively. Thus average Cu–N$\text{amide}$ bond length is
shorter by about 0.05 Å than that of Cu–N_{py} bond length. The N–Cu–N angles span the ranges 83.30(12)^°–104.42(12)^° and 150.31(12)^°–153.37(12)^°, substantially deviating from ideal square planar and tetrahedral geometry. The dihedral angle between the planes N(1a)–Cu(1a)–N(2a) and N(3a)–Cu(1a)–N(4a) is 43.02(25)^°, deviating significantly from 0^° (ideal square planar) and 90^° (ideal tetrahedral). Thus the nonplanar biphenyl ligand backbone provides a distorted CuN_{4} coordination geometry, intermediate between square planar and tetrahedral. In MeOH the dark green complex shows a crystal field transition at 615 nm with a shoulder at 770 nm. This spectral feature indicates that MeOH is coordinated to the copper(II) center in (1), giving rise to a distorted square pyramidal geometry. Thus the stereochemistry of the copper(II) center in (1) changes from distorted square planar in the solid state to distorted square pyramidal in MeOH solution. The μ_{eff} values (at 298 K) in the solid state and in MeOH solution are 1.88 and 1.90 BM, respectively. Thus the copper(II) center in (1) has S = 1/2 state. The EPR spectra for powdered samples of (1) at 300 K as well as at 77 K are isotropic with a g value 2.10. However, in MeOH–toluene glass (1:1.2 v/v) at 120 K, it shows a well resolved axial spectrum (g_{∥} = 2.221 and g_{⊥} = 2.037, A_{∥} = 162 \times 10^{-4} \text{ cm}^{-1}), characteristic of d_{x^{2}-y^{2}} ground state. To investigate the extent of stabilization of Cu(II) state towards reduction and to identify the effect of Cu(II)N_{4} geometry on Cu(II)/Cu(I) redox thermodynamics, cyclic voltammetric study of (1) was done. In DMF at a glassy-carbon working electrode the complex shows a reversible reductive response at E_{1/2} = −0.80 V versus SCE.

Lebon et al.\textsuperscript{50} reported two Cu(II) complexes (dimethanol)-\textit{bis}-[N-(4-methyl-2-pyridyl)-2,3,6-trimethoxybenzamide]copper(II) dimethanol diperchlorate (1) and \textit{bis}-[N-(2-methoxybenzyl)quinoline-2-carboxamide]copper(II) diperchlorate (2) derived from pyridine and quinolone based amide ligands. The complex (1) contains tetragonally elongated octahedral (dimethanol)\textit{bis}-[N-(4-methyl-2-pyridyl)-2,3,6-trimethoxybenzamide]copper(II) cations counterbalanced with ClO_{4}^{-} anions. The Cu(II) ion is located on an inversion center and is bonded to the ligand by the pyridine N(2) [2.011(2) Å] and the carbonyl O(11) [1.955(1) Å] atoms, with a bite angle of 89.17(6)^°. The two ligands forms a pseudoequatorial square plane of the complex while the methanol molecules are located in the axial positions and form long bonds with copper [2.423(2) Å]. The deviation of the Cu(II) ion from the mean plane N(2)–
C(7)–N(9)–C(10)–O(11) is 20.613 Å. The coordinated methanol molecules are hydrogen bridged to adjacent ClO₄⁻ anions. The amide NH(9) forms a hydrogen bond with the oxygen atom of a free solvent methanol molecule. A single parallel intermolecular π–π interaction is formed between the methoxybenzyl rings [distance between mean planes (dmp) = 3.410 Å]. In complex (2), two ligands chelate Cu(II) with a bite angle of 80.85(7)°, via the amide O(13) atom and the N(2) atom in the pyridine moiety, forming short bonds of respectively, 2.096(2) and 1.924(2) Å with Cu(II). The apex perchlorate O(25) atom forms a longer bond of 2.464(8) Å with Cu(II). The Cu(II) ion is located on an inversion center. The significant deviation of the angles O(13)–Cu–O(25) [78.03(19)°] and O(13)–Cu–N(2) [80.87(7)°] from the ideal value of 90° is due to the small bite size of the five membered planar chelate ring. The deviation of the Cu(II) atom from the plane N(2)–C(11)–C(12)–O(13) is 0.274 Å. The molecules are organized in a 3–D network in which van der Waals π–π interactions between the aromatic cycles contribute most of the crystallographic cohesion. The quinoline rings (dmp = 3.543 Å) as well as the methoxybenzyl rings (dmp = 3.545 Å) are not strictly superposed, but slightly shifted by 0.88 and 1.29 Å, probably in order to optimize the electrostatic contribution to the interaction. A T-shaped π–π intermolecular interaction is also formed between the quinoline and methoxybenzyl rings. Moreover, a single hydrogen bond is obtained between the amide NH(14) and a perchlorate oxygen atom of a neighboring molecule.

Mononuclear bis-(2-benzoylimino-benzimidazolinato)copper(II) (1) as the first neutral chelate of an acylimino-benzimidazoline contains guanidine and amide moieties directly coordinated to a metal atom. The ligands are arranged in trans position. The molecular structure of the complex was determined by X-ray crystal structure analysis. (1) crystallizes in monoclinic P21/c space group with cell parameters a = 9.875(1), b = 23.956(3), c = 12.190(1) Å, β = 106.721(2), Z = 4. The complex is a chelate with two bidentate ligands bonding through N and O. The coordination geometry is tetrahedrally distorted square planar (Cu1O1N1/Cu1O2N4 25.8(3)°) with trans arrangement of the ligands. The central N atoms N2 and N5 in the ligands are deprotonated. The angles between the phenyl rings and the chelate rings are 39.8(3)° and 3.0(5)°. The crystal structure contains molecules of the solvent.
dimethylformamide. Between all chelate molecules, two hydrogen bonds exist which lead to infinite chains of molecules.

Pandey et al.\textsuperscript{52} utilized an acyclic hexadentate pyridine amide ligand, containing a –OCH\textsubscript{2}CH\textsubscript{2}– spacer between two pyridine-2-carboxamide units (1,4-\textit{bis-[\textit{o}-(pyridine-2-carboxamidophenyl)]}-1,4-dioxabutane (H\textsubscript{2}L\textsubscript{9}), in its deprotonated form) to synthesize a Copper(II) complex [Cu\textsuperscript{II}(L\textsubscript{9})] in which the Cu(II) adopts a trigonal bipyramidal geometry by two amide nitrogen, two pyridine nitrogen and one ether oxygen of (L\textsubscript{9})\textsuperscript{2–}. The trigonal plane comprises N1, O3 and N4 and the axial coordination are provided by two amide nitrogen N2 and N3. The crystal structure reveals that the two axial bonds are considerably shorter than the three equatorial bonds, leading to axial compression. The \(\mu_{\text{eff}}\) values at 298 K correspond to \(S = 1/2\). The EPR spectra for powdered samples of [Cu\textsuperscript{II}(L\textsubscript{9})], both at room temperature and at 77 K display a rhombic pattern with three distinct \(g\) values 2.22, 2.12 and 2.02. The EPR spectrum of [Cu\textsuperscript{II}(L\textsubscript{9})] in CH\textsubscript{2}Cl\textsubscript{2}-C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3} glass (77 K) shows high rhombicity of the spectrum suggests a severe distortion of the copper(II) site. Spectral parameters \(g_1 = 2.281, g_2 = 2.170, g_3 = 2.050, A_1 = 100\) G, \(A_2 = 21\) G, \(A_3 = 92\) G, \(W_x = 49.5\) G, \(W_y = 28.5\) G and \(W_z = 45.5\) G (\(S = 1/2\)) were obtained by spectral simulation. The axially compressed, rhombically distorted trigonal bipyramidal geometry observed in the crystal structure point towards a \(d_\text{z}^{2}\) ground state for the CuII ion, which allows the assignment of \(g_1, g_2\) and \(g_3\) to \(g_x, g_y\) and \(g_z\), respectively \([g_x, g_y > g_z ~ 2; R [(g_3 – g_2)/(g_2 – g_1)] > 1]\). Cyclic Voltammetric experiments in CH\textsubscript{2}Cl\textsubscript{2} reveal a quasireversible Cu\textsuperscript{II}–Cu\textsuperscript{I} redox process at \(E_{1/2} = –0.88\) V. indicates that O (ether) is stabilizing the copper(II) state.

Jain \textit{et al.}\textsuperscript{53} reported a series of seven new pyridine dicarboxamide ligands H\textsubscript{2}L\textsubscript{1–7} and their mono, di, tri and tetra nuclear copper(II) complexes where the ligands were obtained by condensation reactions involving pyridine-2,6-dicarboxylic acid (H\textsubscript{2}dipic), pyridine-2,6-dicarboxyl dichloride or 2,6-diaminopyridine with heterocyclic amine or carboxylic acid precursors. Crystallographic analyses of \(N,N’-\text{bis-(2-pyridyl)pyridine-2,6 dicarboxamide monohydrate (H}_2\text{L}_8\cdot\text{H}_2\text{O)}\), \(N,N’-\text{bis-[2-(2-pyridyl) methyl]pyridine-2,6 dicarboxamide}\) and \(N,N’-\text{bis-[2-(2-pyridyl)ethyl]pyridine-2,6 dicarboxamide monohydrate}\) revealed extensive intramolecular hydrogen bonding interactions. 2,6-\textit{bis-(pyrazine-2-carboxamido)pyridine (H}_2\text{L}_6\) and
2,6-bis-(pyridine-2-carboxamido)pyridine (H$_2$L$^7$) reacted with copper(II) acetate monohydrate to give tri-copper(II) complexes [Cu$_3$(L)$_2$(μ$_2$-OAc)$_2$]. X-Ray crystallography confirmed deprotonation of the amidic nitrogen atoms and that the (L$^{6,7}$)$_2^-$ ligands and acetate anions hold three copper(II) ions in approximately linear fashion. X-Ray crystallography of [Cu$_3$(L)$_2$(μ$_2$-OAc)$_2$] reveals that two (H$_2$L$^7$) ligands are doubly deprotonated at the amidic nitrogen and span three copper atoms. The internal copper centre Cu(3) is bound by the nitrogen atoms N(10) and N(40) from the central pyridyl rings of each (L$^7$)$_2^-$ anion, while Cu(1) and Cu(2) are chelated by the carboxamide and pyridyl nitrogen atoms of each ligand arm to give two CuC$_2$N$_2$ rings per terminal metal centre. Two μ$_2$-acetato groups bridging adjacent copper centres [Cu(1)...Cu(3) and Cu(3)...Cu(2)] complete the molecular structure. H$_2$L$^8$ reacted with copper(II) tetakis-(pyridine) perchlorate to give [Cu(L$^8$(OH)$_2$)]$_2$.2H$_2$O, in which (L$^8$)$_2^-$ was tridentate through the nitrogen atoms of the central pyridine ring and the deprotonated carboxamide groups at one copper centre, with one of the terminal pyridyl rings coordinating to the other copper atom in the dimer. The corresponding reaction using H$_2$L$^7$ gave [Cu$_3$(L$^7$(py)$_2$)[ClO$_4$]$_2$, which transformed during an attempted recrystallization from ethanol under aerobic conditions to a tetracopper(II) complex [Cu$_4$(L$^7$)$_2$(L$^7$–O)$_2$]. X-Ray crystallographic analysis revealed that the complex [Cu$_4$(L$^7$)$_2$(L$^7$–O)$_2$].C$_2$H$_5$OH.2H$_2$O has two (L$^7$)$_2^-$ and two (L$^7$–O)$_2^-$ ligands in the molecule, in the latter oxidation of the nitrogen atom of the central pyridyl ring generates an N-oxide. Each copper atom is bound by the nitrogen atoms of the terminal pyridyl rings and deprotonated carboxamide group from one (L$^7$)$_2^-$ ligand and by the same donor atoms plus the N-oxo atom from an (L$^7$–O)$_2^-$ ligand, giving a square pyramidal [N$_4$O] coordination sphere at the metal centre. Each N-oxygen atom bridges two adjacent copper centres. The central pyridyl ring of (L$^7$)$_2^-$ is too distant from any copper center to enable it to bind, hence these ligands are tetra-dentate whereas (L$^7$–O)$_2^-$ is penta-dentate. While coordination of pyridine N-oxide ligands to copper(II) is common. Complex has a [2 × 2] grid structure with the (L$^7$)$_2^-$ ligands being face-on to one another and perpendicular to the (L$^7$–O)$_2^-$ ligands, which are themselves face-to-face.

Rowland et al.$^{54}$ reported mono and di nuclear copper(II) complexes [Cu(APPy)] and [Cu$_2$(AEPy)$_2$] where APPyH$_2$ = bis-[3-(2-pyridinecarboxamido)propyl]-methylamine and AEPyH$_2$ = bis-[3-(2-
pyridinecarboxamido)ethyl]methylamine. In the deprotonated form, APPy$^{2-}$ binds copper(II) to afford the penta-coordinate complex $[\text{Cu(APPy)}]$ with distorted square pyramidal geometry while, AEPy$^{2-}$ affords the dimeric copper(II) complex $[\text{Cu}_2(\text{AEPy})_2]$. Crystallographic study reveals that the crystals are composed of monomeric units of $[\text{Cu(APPy)}]$. The APPy$^{2-}$ ligand employs five nitrogen donors (two pyridine nitrogen, two carboxamide nitrogen, and one tertiary amine nitrogen) to bind the copper(II) center and the geometry around copper is distorted square pyramidal. The base of the square pyramid comprise of one pyridine-2-carboxamido moiety, the tertiary amine nitrogen and the carboxamido nitrogen of the second pyridine-2-carboxamide group which lies perpendicular to the basal plane. The pyridine ring nitrogen of this second pyridine-2-carboxamide group occupies the apical position to complete the square pyramid geometry. In this configuration, the two carboxamido nitrogen are *trans* to each other and are nearly collinear ($\text{N}_{\text{amido}}-\text{Cu}-\text{N}_{\text{amido}}$ angle is around 173°). In $[\text{Cu}_2(\text{AEPy})_2]$, each copper(II) center resides in a distorted square pyramidal geometry generated by the $\text{N}_{\text{py}}-\text{N}_{\text{amido}}-\text{N}_{\text{amine}}$ portion of one ligand and one pyridine-2-carboxamido end of the other. The base of the square pyramid around each copper is completed by the $\text{N}_{\text{py}}-\text{N}_{\text{amido}}-\text{N}_{\text{amine}}$ portion of one ligand and $\text{N}_{\text{amido}}$ donor center of the sharing ligand while the apical position is occupied by the second $\text{N}_{\text{py}}$ of the shared ligand. The carboxamido nitrogen donors occupy *trans* positions in the basal plane of each copper center. The two copper(II) centers, connected by the pendant ethylene linkages, are 5.3433(14) Å apart. The X-band EPR spectrum of $[\text{Cu(APPy)}]$ in CH$_3$OH glass (80 K) is typical for monomeric copper(II) complexes in tetragonal geometry ($g_\perp = 2.05$, $g_\parallel = 2.21$, $A_\parallel = 138$ G) with $d_{x^2-y^2}$ ground state. In $[\text{Cu}_2(\text{AEPy})_2]$, the two Cu(II) centers are too far apart to interact with each other. Susceptibility measurement at room temperature shows that polycrystalline $[\text{Cu}_2(\text{AEPy})_2]$, has a magnetic moment of 1.78 BM per copper. Also in solid state, $[\text{Cu}_2(\text{AEPy})_2]$, exhibits a broad EPR signal around $g = 2$ with no visible hyperfine interaction in the temperature range 80-300 K. Since the EPR spectrum of $[\text{Cu}_2(\text{AEPy})_2]$ in methanol or DMF glass at 80 K resembles monomeric Cu(II) EPR spectrum ($g_\perp = 2.06$, $g_\parallel = 2.20$, $A_\parallel = 135$ G), it appears that the dimer dissociates in solution.
Gupta et al.\textsuperscript{55} reported a new benzimidazole based diamide ligand \(N,N'-\text{bis-}(\text{glycine-2-benzimidazolyl})\text{hexanediamide}\) (GBHA) and its Cu(II) complexes of general composition \([\text{Cu}(\text{GBHA})X]X\), where \(X\) is an exogenous anionic ligand (\(X = \text{Cl}^-, \text{NO}_3^-, \text{SCN}^-\)). The X-ray structure of one of the complexes, \([\text{Cu}(\text{GBHA})\text{Cl}]\text{Cl}.\text{H}_2\text{O}.\text{CH}_3\text{OH}\), has been determined by X-ray single crystallography. The compound crystallizes in the monoclinic space group \(C2/c\) with unit cell dimensions \(a = 26.464(3) \, \text{Å}, b = 10.2210(8) \, \text{Å}, c = 20.444(2) \, \text{Å}, \beta = 106.554(7)^\circ\) and \(Z = 8\). The \([\text{Cu}(\text{GBHA})\text{Cl}]\text{Cl}.\text{H}_2\text{O}.\text{CH}_3\text{OH}\) complex is the first structurally characterized mononuclear trigonal bipyramidal copper(II) \(\text{bis-}\)benzimidazole diamide complex having coordinated amide carbonyl oxygen. The coordination geometry around the Cu(II) ion is distorted trigonal bipyramidal (\(\tau = 0.59\)). Two carbonyl oxygen atoms and a chlorine atom form the equatorial plane, while the two benzimidazole imine nitrogen atoms occupy the axial positions. The geometry of the Cu(II) center in the solid state is not preserved in DMSO solution, changing to square pyramidal, as suggested by the low temperature EPR data \(g_\parallel > g_\perp > 2.0023\). All the complexes display a quasi-reversible redox wave due to the Cu(II)/Cu(I) reduction process. \(E_{1/2}\) values shift anodically from \(\text{Cl}^- < \text{NO}_3^- < \text{SCN}^-\), indicating that the bound \(\text{Cl}^-\) ion stabilizes the Cu(II) ion while the N–bonded \(\text{SCN}^-\) ion destabilizes the Cu(II) state in the complex. When calculated against NHE, the redox potentials turn out to be quite positive as compared to other copper(II) benzimidazole bound complexes. It is therefore concluded that binding of amide carbonyl oxygen destabilizes the Cu(II) state. The complex \([\text{Cu}^{II}(\text{GBHA})(\text{NO}_3)](\text{NO}_3)\) could be successfully reduced by the addition of dihydroxybenzenes to the corresponding \([\text{Cu}^{II}(\text{GBHA})](\text{NO}_3)\). \(^1\text{H}\) NMR of the reduced complex shows slightly broadened and shifted \(^1\text{H}\) signals. The reduction of the Cu(II) complex presumably occurs with the corresponding \(2\text{e}^-\) oxidation of the quinol to quinone. Such a conversion is reminiscent of the functioning of a copper containing catechol oxidase from sweet potatoes and the \textit{met} form of the enzyme tyrosinase.

New \(N\)-octylated benzimidazole based diamide ligands \(N,N'-\text{bis-}(N\text{-octylbenzimidazolyl-2-ethyl})\text{hexanediamide}\) (O-ABHA), possessing a chiral center, and \(N,N'-\text{bis-}(N\text{-octylbenzimidazolyl-2-methyl})\text{hexanediamide}\) (O-GBHA) have been synthesized and utilized to prepare Cu(II) complexes of general composition...
[Cu(L)X]X, where L = O-ABHA or O-GBHA and X = Cl\(^-\) or NO\(_3\)\(^-\). The X-ray structure of one of the complexes, [Cu(O-GBHA)NO\(_3\)]NO\(_3\) has been obtained. The Cu(II) ion is found to possess a distorted octahedral geometry with a highly unsymmetrical bidentate nitrate group. The N\(_2\)O\(_2\) equatorial plane comprises an amide carbonyl O, a nitrate O and the two benzimidazole imine N-atoms while another amide carbonyl O and nitrate O take up the axial positions. The complexes carry out the oxidation of aromatic alcohols to aldehydes in the presence of cumenyl hydroperoxide at 40–45 °C and act as catalyst with turnovers varying between 13- and 27-fold. The percentage yields of the respective products have been obtained which vary from 32% to 65% with respect to the catalyst turnover.\(^5\)\(^6\)

A dimeric copper(II) complex bridged via a new tetradentate bis-benzimidazole diamide ligand \([N,N'-bis-(benzimidazolyl-2-yl) (methyl)pentane diamide](GBGA)\) with the composition \([Cu_2(GBGA)_2(NO_3)_2](NO_3)_2\) has been isolated and characterized. The X-ray structure of the above complex reveals that the unit cell consists of two centrosymmetric, crystallographically independent molecules, but differing in the coordination mode of NO\(_3\) ion. In one case NO\(_3\) ion is symmetric bidentate while in the other case it is monodentate. The coordination around Cu(II) is either a trigonally distorted octahedron (where the N\(_2\)–O\(_2\) equatorial plane is formed by two benzimidazole N atoms and two carbonyl O atoms) or a distorted square pyramidal. The copper(II) complex carries out the selective oxidation of cinnamyl alcohol (allylic), geraniol (aliphatic-allylic) and 3-pyridyl carbinol (hetero aryl alcohol) to their respective aldehydes in the presence of tertiary butyl hydroperoxide as an alternative source of oxygen. The catalytic efficiency has been found to be much higher for the analogous copper(II) complex formed with the corresponding N-octylated ligand (O-GBGA). The percentage yield of the products viz geranial, cinnamyl aldehyde and 3-pyridyl carbinal varies between 34% and 57%. While the respective turnovers are 13-, 19- and 32-fold with respect to the copper(II) catalyst. A higher turnover in the case of 3-pyridyl carbinol is due to the transformation of the parent Cu(II) catalyst (having a N\(_2\)–O\(_2\) type equatorial plane) to a more active Cu(II) species which have been shown to have a 4N donor equatorial plane as identified by low temperature EPR spectroscopy. Such a switch from a carbonyl O donor to an
amine N donor of the peptidic link in the ligand may be important for the redox functioning of copper(II) bound to small peptides.$^{57}$

Copper(II) complexes of a bis-benzimidazole diamide ligand N-picoly N,N′-bis-(2-methylbenzimidazolyl)hexanedi amide [Pic-GBHA = L2] have been synthesized and characterized. One of the compound [Cu(L2)(NO$_3$)$_2$] has been structurally characterized. The copper atom is bound to two benzimidazolyl nitrogen atoms, two amide carbonyl oxygen atoms and a bidentate nitrate ion, resulting in a distorted octahedral geometry. EPR spectra obtained at low temperature indicate a tetragonal geometry in the solution state. Complexes display a quasi-reversible redox wave due to the Cu(II)/Cu(I) reduction process having fairly cathodic $E_{1/2}$. These Cu(II) complexes were utilized to carry out oxidation of ditertbutylcatechol (DTBC) in methanol using molecular oxygen as the oxidant in. Low temperature EPR study of the oxidation reaction implicates the formation of an active copper species with fairly low $A_{∥}$ value. The presence of picolyl groups on the ligand also serve as a proton sponge giving 2–3 times higher rates of reaction in comparison to the non-picolylated ligand, implying a role of free basic groups in the pH control of enzymatic oxidation of catechols by catechol oxidase and tyrosinase.$^{58}$

Lumb et al.$^{59}$ reported the X-ray crystal structure of a dinuclear Cu(II) complex (I) of a pyridine dicarboxamide ligand, N,N′-bis-(2-methylbenzimidazolyl)-pyridine-1,3-dicarboxamide (GBPA) having benzimidazole moieties appended to the amide arms and coordinating through the deprotonated amide nitrogen atoms instead of the carbonyl oxygen. The coordination sphere around each metal ion in (I) is square planar due to coordination by the pyridine and amide nitrogen with the fourth position being occupied by N of the benzimidazole moiety of the symmetry related molecule in the dimer. Because of the molecular symmetry, both metal centres have identical square planar geometry. In each mononuclear unit, the ligand molecule (GBPA) coordinates to one of the two Cu(II) centres using the pyridine nitrogen atom N1 and two amide nitrogen atoms N2 and N7 in a tridentate fashion. The Cu1–N1 distance is 1.928(4) Å while Cu1–N2 and Cu1–N7 distances are 1.982(5) and 2.002(5) Å, respectively. In addition to this, the nitrogen atom N6 of the benzimidazole moiety in one of the side arms of neighbouring ligand molecule coordinates to this metal center thus completing four coordinated square planar arrangement around the metal center.
The Cu1–N6 distance stands at 1.949(5) Å. Therefore, each ligand molecule coordinates in a tetra-dentate fashion involving both the Cu(II) centres, with one of the benzimidazole arms of the ligand (containing nitrogen atom N6) acting as a bridge between these two metal centres. The non-bonding Cu⋯Cu distance in the dimer is 3.07 Å. Two water molecules in the asymmetric unit self-assemble to form a water dimer through H–bonding interactions between them. These water dimers are in turn, involved in hydrogen bonding interactions with the complex molecules thereby linking the successive dinuclear entities to form a 1–D tape extending along the c–axis. Solid-state, variable-temperature (2.0–300.0 K) dc magnetic susceptibility data using 0.05 T (2–30 K) and 1.0 T (30–300 K) fields were collected on polycrystalline sample of complex (I). The data for (I) shows a behaviour characteristic of very weak, antiferromagnetic coupled Cu(II) ions due to super exchange through N–C–C–N group. The χMT value for this complex at 300.0 K is 0.82 cm³mol⁻¹K, higher than that expected for two uncoupled S = 1/2 spins assuming g = 2 (0.75 cm³mol⁻¹K) and it does not vary upon cooling until approximately 50.0 K, dropping faster then and arriving finally to 0.33 cm³mol⁻¹K at 2.0 K. The experimental magnetic data were fitted using the equation for dinuclear copper(II) complexes with the Hamiltonian in the form \( H = -JS_1S_2 \) with \( S_1 = S_2 = 1/2 \). The best fit parameters were found for \( J = -2.68 \pm 0.05 \text{ cm}^{-1} \), \( g = 2.08 \pm 0.01 \), TIP = \( 30 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \) and \( R = 5.2 \times 10^{-6} \). The Cu(II) complex (I) displays a quasi-reversible redox wave due to Cu(II)/Cu(I) with large peak to peak (\( \Delta E_P \)) separation of ca. 0.4 V. \( E_{1/2} \) was observed at ca. −0.2 V versus Fe⁴⁺/Fe. The \( E_{PC} \) has been observed at a fairly negative potential, implying that the Cu(II) centers are highly stabilized due to involvement of deprotonated Namide in the copper(II) complex. A shift of \( E_{1/2} \) value towards cathodic reduction potential ratifies that deprotonated Namide stabilizes the higher oxidation (+2) state. The reason that the deprotonated ligand is not well suited for the stabilization of soft Cu(I) species may be due to two considerably hard deprotonated Namide donor atoms per copper ion.

1.4 Review of metallatriangle complexes having copper(II) at the corners

The self-assembly is one of the most efficient way to afford the complex metal organic polygons. These assemblies can be obtained by designing proper building blocks. The smallest and simplest of the metal mediated molecular polygons, the
trinuclear metallacycles requires the minimum number of building blocks. The use of metal ions in the assembly of complex structures has become a well-established field of supramolecular chemistry. The basis of the synthetic strategy is the linking of more or less rigid organic ligands with suitably disposed coordination sites via metal ions whose stereo chemical preferences may be used to guide the self-assembly reaction.

Considerable effort is currently directed toward the self-assembly of supramolecular macrocyclic architectures using Copper(II) containing subunits because of the metal center’s adopting a variety of coordination geometry and kinetic stability. The prevailing strategy focuses on cyclic structures in which linker groups is used to extend edge units and to create vertices.

The metal-mediated rational construction of discrete molecular assemblies is one of the thriving areas of supramolecular chemistry. Many examples of structurally fascinating compounds have been designed and prepared according to this synthetic paradigm, and some of them are finding applications as receptors and molecular vessels for trapping reactive intermediate, DNA cleavage and for catalytic reactions.

A trinuclear metallacycle is a metallacycle that contains three metal centers, or M–M bonded dimetal entities, with structural functions and three linkers (i.e., di or polytopic bridging ligands). The degree of metal-metal bonding interactions between the structural metal ions should be negligible; otherwise the compound is defined as a cluster. The three structural metal atoms are most often ca. equidistant and define the vertexes of a ca. equilateral triangle: nevertheless, not all the trinuclear metallacycles can be defined as molecular triangles (metallatriangles).

Chaudhuri and co-workers structurally characterized an imidazole bridged \([\{\text{Cu}(\text{Me}_3\text{tcn})(\mu-\text{im})\}_3\text{ClO}_4\}_3\) (Me₃tcn = 1,4,7-trimethyl-1,4,7-triazacyclonane), and later its EPR in which the Cu(II) metal corners have a distorted square pyramidal geometry with two adjacent coordination sites bound to the imidazole linkers (Cu…Cu = 5.92Å).
Clodt et al. recently reported and structurally characterized a trinuclear copper(II) complex \( \text{cis-[Cu\{L–(2H)-N.O\}]_3} \) (I) derived from \( \text{bis-(N-acylamidines)} \) type ligand \( N^4,N^4'-\text{bis-(amino(phenyl)methylene)}-\text{[1,1'-biphenyl]-4,4'-dicarboxamide} \) (L) having a linear biphenyl spacer. Crystals of (I) suitable for X-ray analysis were obtained from \([\text{Cu(CH_3CN)_4}]PF_6\) and L. The slightly yellow solution slowly turned blue on formation of copper(II). Slow diffusion of diethyl ether into the solution led to red crystals of (I). It crystallized in the triclinic space group \( \text{P}–1 \), \( \text{C}_{84}\text{H}_{60}\text{Cu}_{3}\text{N}_{12}\text{O}_{6} \cdot 3\text{C}_3\text{H}_7\text{NO} \), MW = 1743.35, red crystal, having cell parameters \( a = 13.3524(2) \), \( b = 13.4896(3) \), \( c = 25.5935(6) \) Å, \( \alpha = 79.232(1) \), \( \beta = 76.486(1) \), \( \gamma = 79.531(1) \)°, \( V = 4357.08(16) \) Å³, \( Z = 2 \), \( \lambda = 0.71073 \) Å, \( T = 223(2) \) K with two metallatriangles in the unit cell together with a minimum of six molecules of DMF. The three copper atoms are interconnected by three deprotonated \( N \)-acylamidine ligands in a square-planar \( \text{cis-N,O} \) coordination. Small deviations from the ideal square-planar geometry is reported, as the Cu(II) ion is located 0.047 Å below the plane of the complex. The internal distances of the metallomacrocycle are 6.2 and 7.8 Å, measured between the aromatic protons of the spacer unit biphenyl. The biphenyl spacer units are almost coplanar with the coordination sphere of the copper atoms but are tilted by about 25° within the biphenyl system. The average O–Cu and N–Cu bond lengths are 1.918(3) and 1.919(3) Å, respectively. The average Cu–Cu distance is 14.863 Å. The bond lengths of the \( N \)-acylamidine moieties reveal the expected electron delocalization within the chelate rings.

A chiral trinuclear metallacycle \( \{\text{Cu(DMF)(μ–(S,S)L13)}\}_3 \) was obtained by Jeong and co-workers by self-assembly of the chiral flexible linker \( (S,S)-1,2\)-dimethoxydi-4-(2'-carboxyl-5'-pyridyl)phenyl ethane, \( (S,S)\text{H}_2\text{L13} \), with Cu(II) ions. The X-ray structure showed that each copper ion has a square-pyramidal geometry, with the basal plane defined by two chelating 2'-carboxylic pyridine moieties and a dimethylformamide (DMF) molecule in apical position.

Examples of two assembly types incorporating the \( \text{bis-β-diketonato} \) bridging ligands, 1,1-(1,4-phenylene)-\( \text{bis-(butane-1,3-dione)} \) \( (\text{H}_2\text{L}^2) \), 1,1-(1,4-phenylene)-\( \text{bis-(pentane-1,3-dione)} \) \( (\text{H}_2\text{L}^3) \) and 1,1-(1,4-
phenylene)-bis-(4,4-dimethylpentane-1,3-dione) (H$_2$L$_4$) have been demonstrated to react with selected heterocyclic nitrogen donor bases to generate extended supramolecular architectures of type {[Cu$_3$(L$^2$)$_3$(bipy)(THF)]·2.75THF}$n$ and 
{[Cu$_3$(L$^2$)$_3$(bipy)(THF)]·bipy·0.75THF}$n$ while with pyrazine (pyz),
{[Cu$_3$(L$^2$)$_3$(pyz)]·0.5THF}$n$ whose structures have been confirmed by X-ray
diffraction have been reported.$^{71}$

A ligand bridged trinuclear Cu(II) complex [Cu$_2$(μ–L)$_2$CuCl$_2$] has been synthesized
and characterized by elemental analysis, IR, UV–Vis and X-ray spectroscopy, where
L is a dianionic tetradentate Schiff base ligand with N$_2$O donor atoms synthesized by
condensation between 1 equivalent of 1,3-diaminopropane and salicylaldehyde
(salpn). The molecular structure of [Cu$_2$(μ–L)$_2$CuCl$_2$] was determined by X-ray
crystallography. In the complex, the most remarkable aspect of the trinuclear complex
is that it adopts a bent structure for the three copper atoms, with a Cu1–Cu3–Cu2
intramolecular angle of approximately 90.62(2)$^\circ$. All three copper atoms are five
coordinate, with a slightly distorted square pyramidal geometry. In the two terminals
moieties, the basal plane of the square pyramidal is formed by two oxygen atoms and
two nitrogen atoms of the Schiff base ligand, and the apical position at the copper
atom is occupied by the bridging Cl1 anion. The Cu1–Cl1–Cu2 angle is 110.51(5)$^\circ$.
The central copper atom also has a five-coordinate, slightly distorted square pyramidal geometry, with four phenolato oxygens belonging to the Schiff base
ligands from Cu(salpn) units describing the square planar base and the Cl anions
being apical.$^{72}$

Kopel et al.$^{73}$ structurally characterized a mixed ligand trinuclear copper(II) complex
[Cu$_3$(mdpta)$_3$(btc)](ClO$_4$)$_3$·4H$_2$O, where btc = 1,3,5-benzenetricarboxylic acid and
mdpta= N,N-bis-(3-aminopropyl)methylamine in monoclinic space group P21/n, $a =
18.5892(3)$ Å, $b = 9.7725(3)$ Å, $c = 26.5520(3)$ Å, $\beta = 92.315(4)^\circ$. The Cu–Cu
distance was found to be 9.351 Å. The complex is trinuclear with btc$^{3–}$ bridged. The
coordination polyhedron around each copper atom can be described as a distorted
square with a CuON$_3$ chromophore formed by one oxygen atom of carboxylate and
three nitrogen atoms of mdpta. The perchlorate anions and water molecules are out of
the coordination sphere. The magnetic properties have been studied in the 1.8–300 K
temperature range revealing a very weak antiferromagnetic exchange interaction with
\[ J = -0.56 \text{ cm}^{-1} \text{ for } g = 2.13(9) \]. The Curie-Weiss behavior indicates a linear relation of the reciprocal magnetic susceptibility curve at higher temperatures (100–300 K) with a Curie constant \( C = 0.426 \text{ cm}^3 \text{ mol}^{-1} \text{ K} \) and Weiss-constant, \( \theta = -1.74 \text{ K} \) and a small anomaly is observed only at the lowest temperatures. The compound reveals a magnetic behavior which is characteristic of antiferromagnetic spin coupling. The \( \chi_{\text{Cur}}T \) values decreases gradually with lowering of the temperature, from 0.425 cm\(^3\) mol\(^{-1}\) K at 300 K to 0.256 cm\(^3\) mol\(^{-1}\) K at 1.8 K, and the effective magnetic moment from 1.85 B.M. at 300 K to 1.43 B.M. at 1.8 K. The powdered sample of the complex indicates a rhombic deformed square pyramidal EPR spectrum in the higher temperature region with spectroscopic splitting factors \( g_1 = 2.178, g_2 = 2.118, g_3 = 2.070 \) at 293 K and \( g_1 = 2.174, g_2 = 2.119, g_3 = 2.068 \) at 77 K. At liquid helium temperature (4.2 K), an isotropic EPR signal with a single symmetric line only at \( g = 2.06(1) \) with \( \delta H_{pp} = 180 \text{ G} \) is observed.

A trinuclear Copper(I) complex \([\text{Cu}_3(\text{L2})_3][\text{PF}_6]_3\] has been reported and structurally characterized in space group P–1 with cell parameters \( a = 12.3610 \text{ Å}, b = 12.6347 \text{ Å}, c = 21.7155 \text{ Å}, \alpha = 97.193(10)^\circ, \beta = 102.657(11)^\circ, \gamma = 110.031(11)^\circ \). The X-ray crystal structure of compound reveals the complex to be a trimer and possess a trinuclear circular helical type architecture containing a triangle inside. Each copper(II) ion is coordinated to four nitrogen atoms, provided by the pyridylimine groups of two distinct ligands. The pyridylimine units are essentially planar (dihedral angles in the range 1.8–6.2\(^\circ\)) however there is substantial twisting about the central N–N bonds (dihedral angles 81–101\(^\circ\)). Consistent with this intra-ligand twisting, the inter-metallic separation of the copper(II) ions (4.45–4.53 Å). Cu–N bond lengths (1.98 – 2.05 Å) and bond angles (79.9 – 80.3\(^\circ\)). The pyridyl rings define cavities, above and below the plane of the metal centres. One cavity of each trimer contains a hexafluorophosphate anion, while the other cavity contains part of a diethyl ether solvent molecule. The anion in the cavity forms short contacts to the pyridyl and methyl protons. Anion encapsulation by cationic supramolecular arrays has been noted in a number of systems. The trinuclear circular helicate is chiral and the structure contains equal amounts of the two enantiomers. The remaining anions and a non-coordinated acetonitrile molecule are packed around the trimeric arrays and again form short contacts to the pyridyl and methyl protons.
References


Chapter I

Introduction


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