Chapter I

General Introduction

1.1. General

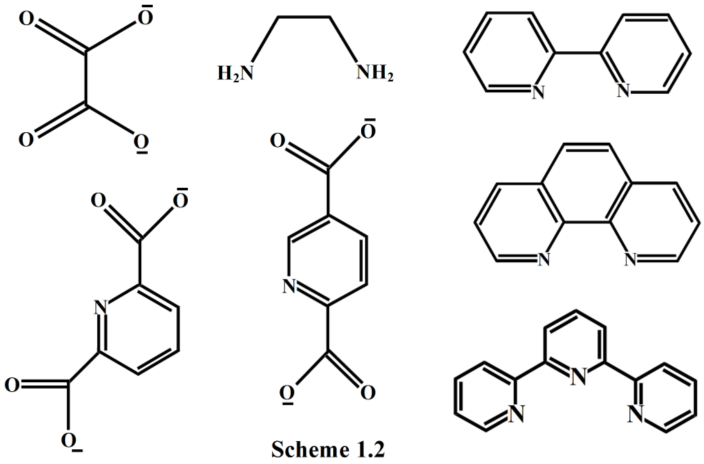
Coordination compounds often popularly known as "complexes" came to light from the first journey of modern chemistry. In the beginning well-known coordination compounds include dyes such as "Prussian blue" used as an artist’s pigment was discovered in 1704. In 1798, Tassaert noticed that the solutions containing cobalt(II) in aqueous ammonia changed to brown when it was exposed to air and the colour changed to wine red when it was boiled. After Tassaert, Fremy observed that cobalt(III) had associated with upto six NH_3 molecules. But formulations like $CoCl_3{\cdot}6NH_3$ could not explain how the NH_3 molecules were attached to the neutral $CoCl_3$ molecule. First we understood well the characteristics of these compounds in the late 18th century, pursuing the work of Alfred Werner. Werner could discover the spatial arrangements of the ligands (ammonia) which were involved in the formation of hexacoordinated cobalt complexes[1.1] and Werner won Nobel Prize for his “Coordination Theory” in 1913.

Coordination compounds have mainly two parts: (i) the coordination centre which is usually a metal atom or ion and (ii) a number of bonded molecules or ions called ligands.[1.2,1.3] Ligands can be classified as (A) monodentate and (B) polydentate ligands (e.g. bidentate, tridentate, tetradentate, pentadentate, hexadentate, ambidentate, chelating and bridging ligands), depending on the number of donor atoms of ligands that attach to the metal ion or atom. Ligands which share electron pair of a single donor atom with a metal atom or ion are called monodentate ligands (**Scheme 1.1**).

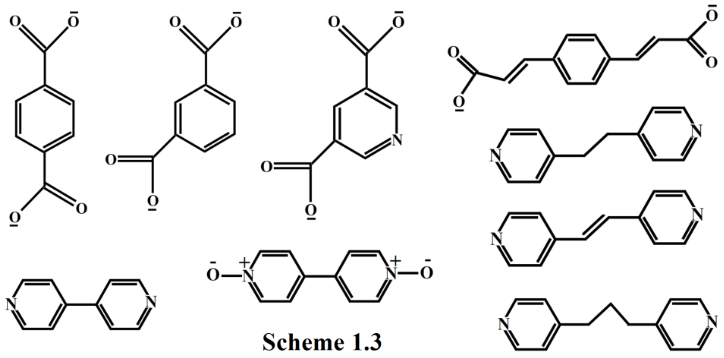
Neutral monodentate ligands	**H_2O, NH_3, Pyridine, R-NH_2 (R=aliphatic chain/aromatic ring), R-OH (R=aliphatic chain/aromatic ring)**
Negative monodentate ligands	**F^-, Cl^-, Br^-, I^-, OH^-, R-COO^- (R=aliphatic chain/aromatic ring)**
Positive monodentate ligands	**NO^+, NH_2-NH_3^+**

Scheme 1.1

The ligands that form bond with metal atom or cation through electron pairs present on more than one donor atoms are called multidentate or polydentate ligands. Among multidentate ligands chelating (**Scheme 1.2**) and bridging ligands (**Scheme 1.3**) are very much important for the formation of coordination compounds.

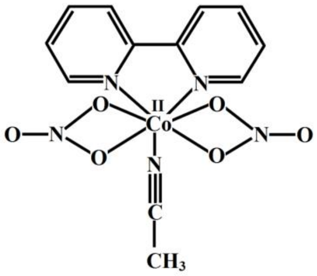


Scheme 1.2

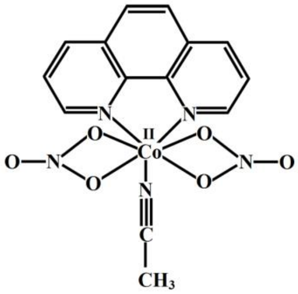


Scheme 1.3

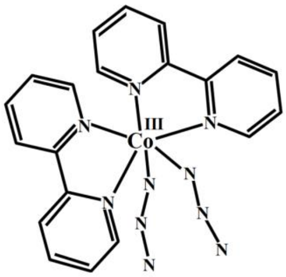
Chelating ligands are used to form coordination compounds with transition metal ions. Some examples of complexes of this category are [Co(bipy)(NO_3)$_2$(CH_3CN)] (bipy = 2,2'-bipyridine) (Figure 1.1),[1.4a] [Co(phen)(NO_3)$_2$(CH_3CN)] (phen = 1,10-phenanthroline) (Figure 1.2),[1.4a] [Co(III)(bipy)$_2$(N_3)$_2$]Cl (Figure 1.3),[1.4b] [Cu(bipy)$_2$(NO_3)]ClO_4 (Figure 1.4),[1.4c] [Cu(phen)$_2$(H_2O)](ClO_4)$_2$ (Figure 1.5),[1.4c] [Cu_2(ox)(phen)$_2$(H_2O)$_2$](NO_3)$_2$ (ox = oxalate) (Figure 1.6).[1.4d]



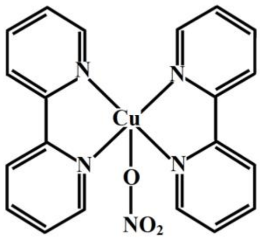
$[Co(bipy)(NO_3)_2(CH_3CN)]$
Figure 1.1



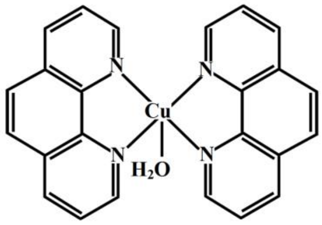
$[Co(phen)(NO_3)_2(CH_3CN)]$
Figure 1.2



$[Co(III)(bipy)_2(N_3)_2]\ Cl$
Figure 1.3

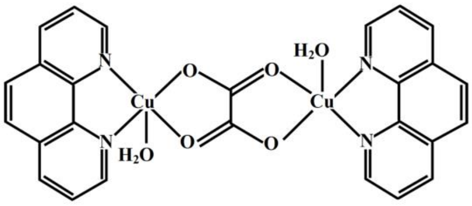


$[Cu(bipy)_2(NO_3)]ClO_4$
Figure 1.4



$[Cu(phen)_2(H_2O)](ClO_4)_2$

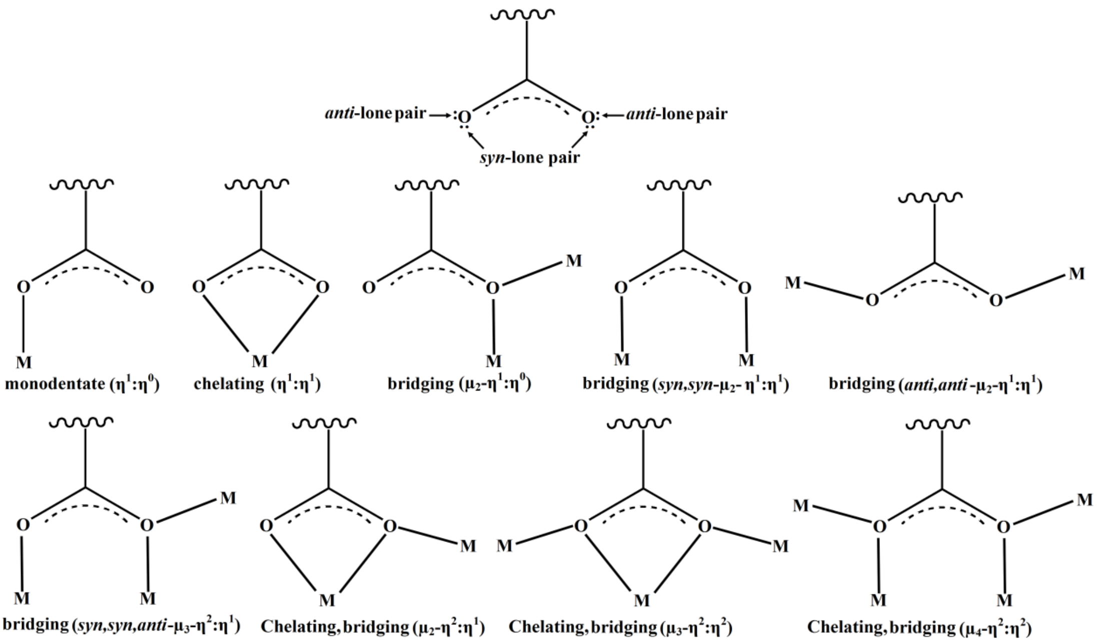
Figure 1.5



$[Cu_2(ox)(phen)_2(H_2O)_2](NO_3)_2$

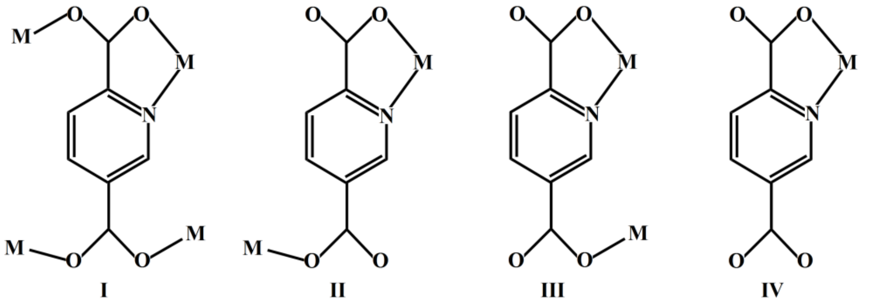
Figure 1.6

In the last few decades, great efforts have been devoted for the preparation of 3d metal complexes not only for their attractive structures and topologies but also owing to their interesting physical and chemical properties, such as photoluminescence,[1.5] magnetism,[1.6] gas storage,[1.7] separation,[1.8] catalysis,[1.9] drug delivery[1.10] etc. These coordination compounds are formed by the metal centres bonded with multifunctional organic or inorganic linkers (N- and/or O- donor) acting as chelating and bridging ligands. The examples of such types of ligands are benzene dicarboxylate, pyridine dicarboxylate, oxalate, neutral pyridyl based co-ligands etc. Generally these linkers are used to construct the coordination compound with desirable framework due to their versatile coordination modes (**Scheme 1.4** shows the various coordination modes of carboxylate).



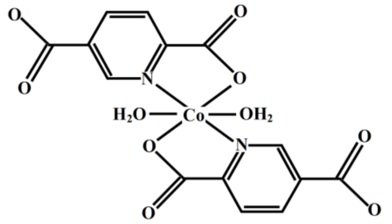
Scheme 1.4

Pyridine 2,5-dicarboxylate (2,5-pdc) with a 180° angle between the carboxylate groups has been used as an efficient ‘‘coordinating agent’’ in designing novel inorganic supramolecular systems for its flexible coordination modes (**Scheme 1.5**) as well as for its hydrogen bonding capability.

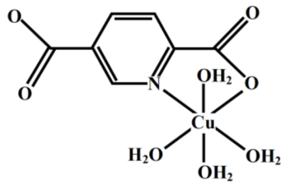


Scheme 1.5

Çolak *et al.* reported a complex trans-(H_2ben)[Co(2,5-pdc)$_2$(H_2O)$_2$]·4H_2O [ben = 1,4-butanediamine] (Figure 1.7)[1.11a] and Manna *et al.* reported another complex {[Cu(2,5-pdc)(H_2O)$_4$]·H_2O} (Figure 1.8),[1.11b] both of these two compounds achieved 3D supramolecular network through H-bonding and forms $R_4^2(8)$ and $R_6^4(24)$ synthons respectively.

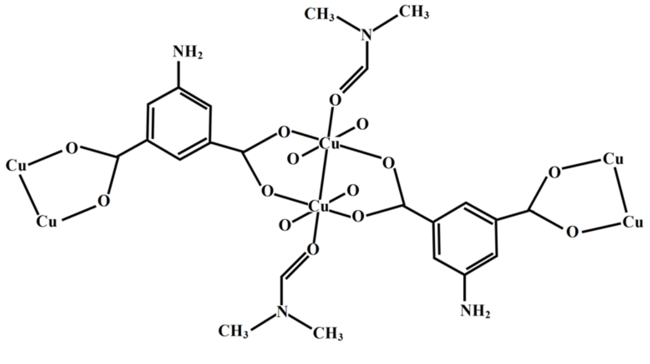


trans-$(H_2ben)[Co(2,5\text{-}pdc)_2(H_2O)_2]\cdot 4H_2O$
Figure 1.7

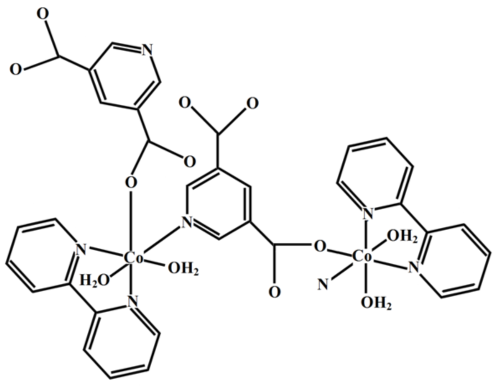


$\{[Cu(2,5\text{-}pdc)(H_2O)_4]\cdot H_2O\}$
Figure 1.8

Over the last few years scientists in all over the world are concentrating their research in the field of design and synthesis of coordination compounds containing metal-carboxylate.[1.12] Aromatic polycarboxylates are well-known bridging ligands for the syntheses of polynuclear metal complexes. Some of the examples where aromatic polycarboxylates acts as bridging ligands are $[Co_{24}(OH)_{12}(SO_4)_{12}(m\text{-phth})_6(DMSO)_{18}(H_2O)_6]\cdot(DMSO)_6\text{-}(EtOH)_6(H_2O)_{36}$ (*m*-phth = isophthalate),[1.13a] and $[Cu(\mu_4\text{-abdc})\ (DMF)]_n$ (abdc = 5-aminobenzene-1,3-dicarboxylic acid) (Figure 1.9).[1.13b] Another notable example of a cobalt complex containing pyridine 3,5-dicarboxylate (3,5-pdc) and neutral ligand is $[Co_2(3,5\text{-pdc})_2(2,2'\text{-bpy})_2(H_2O)_4]\cdot 4H_2O$ (Figure 1.10). In this complex each 3,5-pdc ligand acts as a bridge between Co(II) centers through one carboxyl O atom and the pyridyl N atom.[1.14]



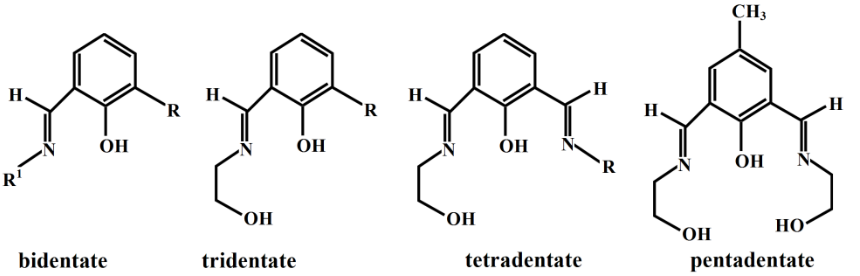
$[Cu(\mu_4\text{-abdc})\ (DMF)]_n$
Figure 1.9



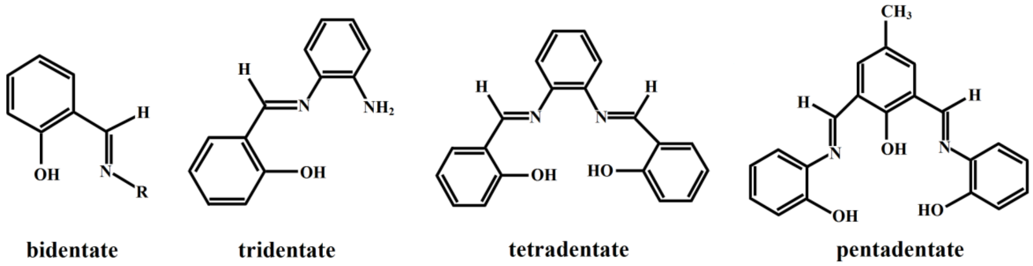
$[Co_2(3,5\text{-pdc})_2(bpy)_2(H_2O)_4]\cdot 4H_2O$
Figure 1.10

Schiff bases are flexible polydentate ligands and used to form coordination compounds with interesting topologies and different dimensionalities showing diverse functionalities. The Schiff base ligands are formed by the condensation reaction of a primary amine and an aldehyde or ketone. Schiff bases that contain aryl substituent bonded with nitrogen or the carbon atom of the imines are considerably more stable and used widely.[1.15] The Schiff base acts as an excellent ligand to form mono/di/tri/tetra/penta/hexanuclear etc. compounds with various 3d metal ions. Schiff base ligands are generally bidentate N, O-; tridentate N, O, O-/N, O, N-; tetradentate N, N, O, O-etc.[1.16]

When the imine (-C=N) is ortho to the hydroxyl functional group, the Schiff base ligands will be acts as an excellent multidentate ligands. This orientation favours complexation process by forming six-member chelate ring with metal ion, and hence increases the stability of the metal complexes. Schematic representation of some such Schiff bases are shown in **Scheme 1.6** and **1.7**.



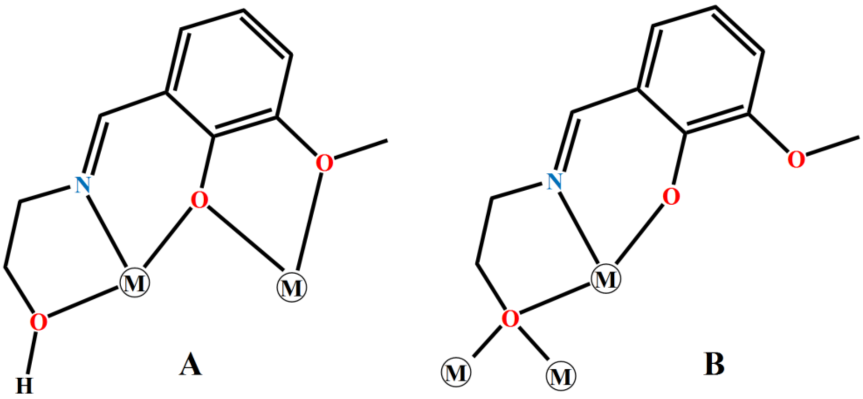
Scheme 1.6



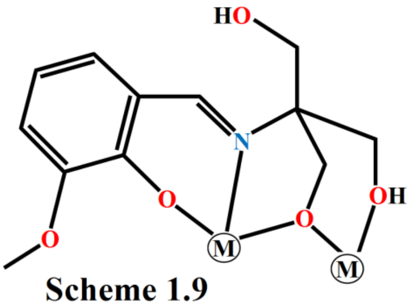
Scheme 1.7

Transition metal complexes of Schiff base ligands have attracted interest in the last few decades, not only for their intriguing structures, but also for their application in the fields of magnetism,[1.17] catalysis,[1.18] fluorescence,[1.19] medicinal chemistry (antimicrobial, antifungal, antidiabetic and antitumor activities),[1.20] etc. Among the 3d metal coordination compounds, polynuclear copper(II) and cobalt(II/III) complexes are considered for their potential applications in the above mentioned area of chemistry.

Multidentate N, O donor Schiff base ligands are potential for the formation of coordination compounds of Cu(II) and Co(II/III) metal ions and in these compounds the ligands show versatile coordination modes (**Scheme 1.8** and **1.9**).



Scheme 1.8

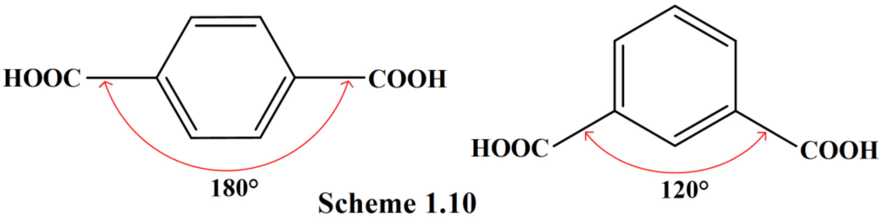


Scheme 1.9

Combined use of Schiff bases and bridging ligands (e.g. benzene mono/dicarboxylate, pyridine mono/dicarboxylate etc.) is a potential approach for the synthesis of coordination compounds. The factors which control the structure and composition of Schiff base containing metal complexes are: the coordination behaviour of the metal ions, denticities of the organic ligands, nature of bridging units, solvents used and the counter ions present etc.[1.21] Beside metal-ligand covalent bonds[1.22] the non-covalent interactions such as H-bonding,[1.23] π···π [1.24] and C-H···π [1.25] etc. play important role for controlling the structure of the compounds.

Multidentate carboxylate anions are widely used as auxiliary organic ligands for the synthesis of coordination compounds. Polycarboxylates are generally used to form tightly bound metal clusters as they exhibit a variety of coordination modes. Benzene dicarboxylates (terepthalate, isophthalate etc.) are well-known examples of this category. The most common type coordination mode of terepthalate in Schiff base metal complexes is bis-monodentate and such type of coordination mode is found in $\{[CuL(\mu_2\text{-tp})](CH_3OH)\}_n$ (L = N,N-dimethyl-N'-(pyrid-2-ylmethyl)-ethylene-diamine, tp = terephthalate)[1.26a] and $[Cu_2(L)_2(\mu\text{-tp})](ClO_4)_2$ [L = N,N'-(bis-(pyridin-2-yl)benzylidene)-1,3-propanediamine].[1.26b]

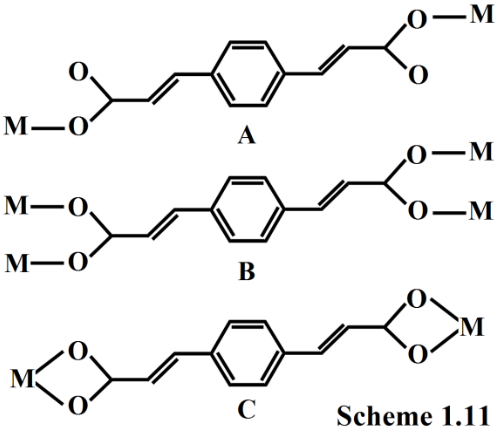
1,3-benzenedicarboxylate (isophthalate) is also a superior candidate for the construction of coordination compounds due to its various coordination modes as well as unique bent angle of 120° (**Scheme 1.10**). The example of Schiff base and isophthalate containing metal complex is $\{[(CuL)_2Mn(m\text{-phth})][(CuL)_2]\}_n$ [where H_2L = N,N'-bis(α-methylsalicylidene)-1,3-propanediamine) and *m*-phth = 1,3-benzenedicarboxylate].[1.26c]



Scheme 1.10

p-Phenylenediacrylate ($ppda^{-2}$) is an another multidentate ligand acts as an important bridging ligand and it shows a variety of coordination modes (**Scheme 1.11**). The possible coordination modes of *p*-Phenylenediacrylate are: (A) Bis-monodentate (η^2 μ), (B) Bridging Tetra monodentate (η^4 μ^2:μ^2) and (C) Chelating Bis-bidentate (η^4 μ). Another significant feature of *p*-phenylenediacrylate is that it has two additional C=C bonds in the side chain. This situation offer expanded space between carboxylate groups and hence reduced steric hindrance. *p*-phenylenediacrylate (1,4-ppda) coordinated Schiff base complex is

$\{[Ni_2(HL)_2(ppda)(H_2O)_2]\cdot DMF\cdot H_2O\}_n$ (H_2L = (E)-2-((1-hydroxybutan-2-ylimino)methyl)phenol), where two Ni(II) centres are connected through ppda ligands.[1.27]



Scheme 1.11

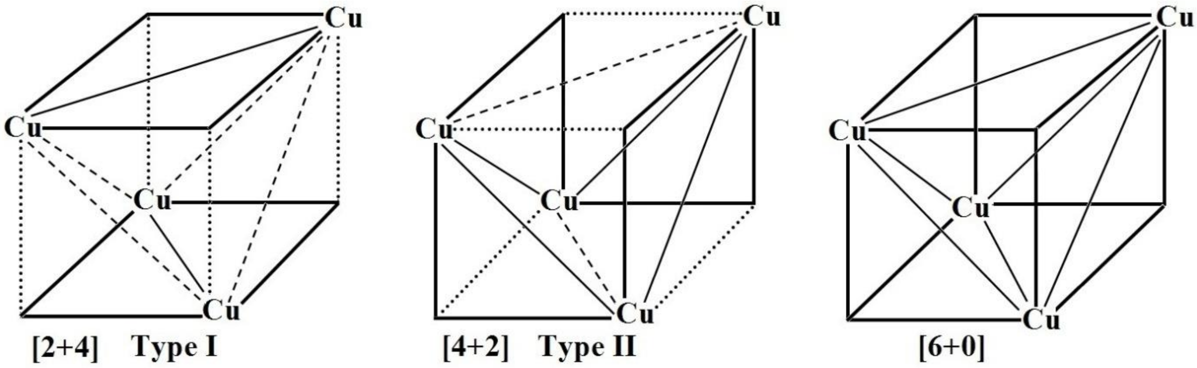
In the last few decades, polynuclear cobalt(II/III) and copper(II) complexes of Schiff base ligands are widely studied for their potential molecular properties such as single-molecule magnetism,[1.28] catalysis[1.29] and application in biology.[1.30] Cobalt is relatively less common element than other first row transition elements and its abundance among the elements is thirtieth (29 ppm). As a broad range of cobalt complexes can bind with oxygen, therefore Co(II) complexes are commonly used as model compounds for the study of natural oxygen carriers and storage.[1.31] Cobalt (II), a $3d^7$ system, be a potential candidate for the formation of single-molecule magnets (SMMs) because of the strong Ising-type anisotropic contribution of Co(II).[1.32,1.33] It is to note that sometimes in reaction medium cobalt(II) centre oxidises to cobalt(III) and form mixed valence Co(III)-Co(II) complexes.

Copper being an essential trace element is present in biological systems and play important role in bioinorganic chemistry.[1.34] Various processes occurs in living systems[1.35] are controlled by copper containing proteins (hemocyanin, tyrosinase, catecol oxidase etc.) followed by biological oxidation-reduction reactions.[1.36] Among the transition metal ions, copper is the 3rd most abundant element with an electronic configuration of $[Ar]3d^{10}4S^1$.[1.37] In complexes, copper ion generally presents in its two relevant oxidation states +1 and

+2.[1.38] In +2 oxidation state, copper possesses d^9 configuration and show Jahn-Teller distortion when the Cu(II) ion in an octahedral or tetrahedral environment. Depending upon the Schiff base ligand used, copper(II) can adopt various coordination numbers and geometries, e.g. as square planar, square pyramidal and trigonal bipyramidal.[1.39]

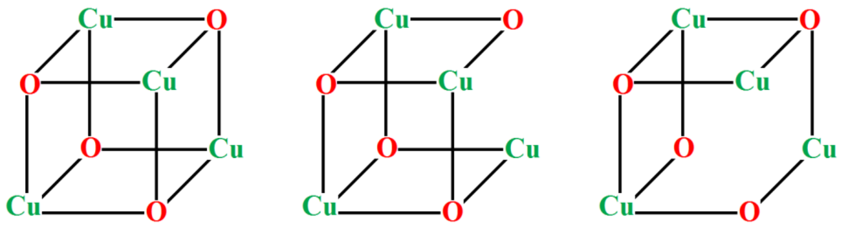
Multidentate Schiff bases derived from amino alcohols are often used for the synthesis of polynuclear copper(II) and cobalt(II/III) complexes as they can simultaneously act as chelating and bridging species towards the metal centres.[1.40] Since alcoholic hydroxyl groups can be easily deprotonated in presence of 3d metal ions, these Schiff bases can form coordination compounds of various nuclearity, such as dinuclear $[\{[Cu_2(bdhe)_2]\cdot(ClO_4)_2\}$, bdheH = N,N-bis(2-(diethylamino)ethyl)-2-hydroxyethylamine and $[Co^{II}Co^{III}(H_2L)_2(OAc)]\cdot 2CH_3OH\cdot H_2O$ [H_4L = 3,5-di-tert-butyl-2-ydroxybenzylideneamino)-2-(hydroxymethyl)propane-1,3-diol)]],[1.41a,c] trinuclear $\{[Cu_3(dmap)_2Cl_4$ (dmap-H = l,3-bis(dimethylamino)-2-propanol) and $[Co^{III}Co_2^{II}(H_2L)_2(L)Cl_2].3H_2O$ (H_3L = 3-[(2-Hydroxy-3-methoxy-benzylidene)-amino]-propane-1,2-diol]]},[1.42c,d] tetranuclear, $[\{[Cu_4(hpda)_4][ClO_4]_4\cdot H_2O\}$ (Hhpda = *N*-(2-hydroxyethyl)-1,3-propanediamine) and $[Co_4L_4\cdot 0.5H_2O]$ (H_2L = *N*,*N′*-di[1-(2-hydroxyphenyl)ethlidene]hydrazone)],[1.43c,g] and hexanuclear, $\{[Cu_6(C_4H_{10}NO)_8]\cdot(ClO_4)_4$ and $[Co^{III}_2Co^{II}_4(Piv)_8(HPiv)_2(L)_2(OH)_2]$ Hpiv = pivalic acid, H_2L = 2-[(2-Hydroxy-ethylimino)-methyl]-phenol]}.[1.44c,d] Besides various nuclearity, copper(II) and cobalt(II/III) metal ions also form coordination polymers $[\{[Cu(\mu\text{-}L)(H_2O)](ClO_4)\cdot 2H_2O\}_n$ {L = 3-[(Pyridine-2-ylmethylene)-amino]-propionic acid} and $[Co_8(H_2O)_2(OAc)_7(ampd)_6]_n$ ($ampdH_2$ = 2-amino-2-methyl-1,3-propanediol)].[1.45a,b] Tetranuclear Cu(II) and di/tetranuclear Co(II/III) clusters are particularly important in the area of magnetostructural research and in biology. Tetranuclear copper complexes have a large variety of structural motifs, such as: cubane type,[1.46] face-to-face,[1.47a] square planar,[1.47b] cyclic,[1.47c] pin-wheel,[1.47d] dimeric,[1.47e] roof-shaped[1.47f] etc. Among these structures, cubane-like tetranuclear Cu(II) complexes having Cu_4O_4 core are of particular interest from magnetostructural point of view and catalytic activity.

Depending on Cu-O bond distances distribution in the cube, Mergehenn and Haase classified cubane of type I and type II.[1.48a] Cu_4O_4 cubane complexes having four long Cu-O distances between two dinuclear subunits are designated as type I, whereas if the long Cu-O distances are within each dinuclear subunit, cubanes are classified as type II.[1.48b] Alternatively, taking into account the Cu···Cu distances within the Cu_4O_4 cubane unit, Alvarez *et al.* described [1.48c-1.48d] three types (**Scheme 1.12**) the compounds: (i) (2+4) having two short and four long Cu···Cu distances, which is equivalent to type I (defined above); (ii) (4+2) with four short and two long Cu···Cu distances, an equivalent description to type II and (iii) (6+0), where all six Cu···Cu bonds have comparable distances.

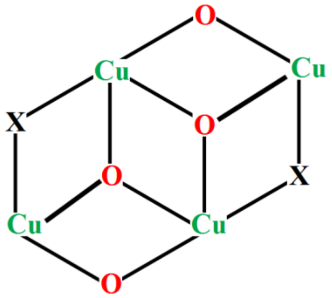


Scheme 1.12. Classification of Cu_4O_4 core (schematic figure) according to the Cu···Cu distances. Short Cu···Cu distances, long Cu···Cu distances, short Cu···O bond lengths and long Cu···O bond lengths are shown in solid lines, dashed lines, bold lines and square dots respectively.

Based on the arrangement and connectivity of the copper and oxygen atom in the tetranuclear Cu_4O_4 core containing hydroxo, alkoxo or phenoxo bridges, the cubane geometries may be of various types (**Scheme 1.13**) e.g; regular cubane,[1.49a-1.49c] pseudo-cubane,[1.49d] single-open cubane,[1.49e] double-open cubane[1.49f-1.49h] and face sharing dicubane.[1.49i-1.49j]



Close cubane **Single-open cubane** **Double-open cubane**



Face sharing cubane

Scheme 1.13.

Thakurata *et al.* reported a tetranuclear Cu(II) complex $[Cu_4L_4]\cdot 2H_2O$ [H_2L = 4-chloro-2-[(*E*)-(2-hydroxyethylimino)methyl]phenol], Yan *et al.* reported another tetranuclear complex $[Cu_4L_4]\cdot 5CH_3OH\cdot H_2O$ (L = 2-(5-fluorosalicylideneamino)ethanol) and another complex $[Cu_4(mphp)_4](ClO_4)_4$ [Hmphp = 2-methoxy-6-(pyridine-2-ylhydrazonomethyl)phenol] reported by Tang *et al.*, all of these complexes formed regular cubane-like structure.[1.49a-1.49c] Tetranuclear Cu(II) complex $[Cu_4(NSI)_4]\cdot 2C_2H_5OH\cdot 2H_2O$ (NSI = hydroxethylsalicydeneimine), reported by Gu *et al.* which possesses pseudo-cubane core structure.[1.49d] Dias *et al.* reported a tetranuclar single-open cubane-like compound $[Cu_4(\mu_4\text{-}H_2edte)(\mu_5\text{-}H_2edte)(sal)_2]_n\cdot 10nH_2O$ [H_4edte = N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine, H_2sal = salicylic acid].[1.49e] Jammi *et al.* reported a tetranuclaer Cu(II) complexes $[Cu_4L_4]$ [H_4L = 2,4-Bis(1,1-dimethylethyl)-6-{[(2-hydroxyethyl)imino]methyl}phenol] and Bhowmik *et al.* reported another complex $[Cu_4(L)_2(HL)_2(H_2O)](ClO_4)_2\cdot 2H_2O$ [H_2L = 2-[(2-hydroxy-ethylimino)-methyl]-6-methoxy-phenol] having double-open cubane-like cage structure.[1.49f-1.49g] Gungor *et al.* reported two alkoxo-bridged Cu(II) complexes of Schiff base ligands $[\{Cu(H_2L)\}_4]$[H_2L = *N*-(2-hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine] and $\{Cu(H_2L)\}_4$ [H_2L = *N*-(2-hydroxyethyl)-

4-methoxysalicylaldimine], these compounds also have double-open cubane-like structure.[1.49h] Liu *et al.* reported a tetranuclear Cu(II) complex $[Cu_4(L)_4]\cdot(NMP)$ [H_2L = salicylidene-2-aminobenzoic alcohol, NMP = N-methylpyrrole] and Dey *et al.* reported another copper complex $[C_4L_4]$ [H_2L = 2-[(2-Hydroxy-1,1-dimethyl-ethylimino)-methyl]-phenol] having pseudo-double cubane core.[1.49i-1.49j]

1.2. Molecular properties of Co(II/III) and Cu(II) coordination compounds

1.2.1. Magnetic properties

Polynuclear Cu(II) and Co(II) complexes of Schiff base ligands are important category of compounds for studying magnetic phenomenon. In mixed-valence cobalt(II/III) polynuclear complexes, the magnetic phenomenon come up from paramagnetic cobalt(II) centre alone, and not from low-spin d^6 cobalt(III) which is a diamagnetic centre.[1.44d]

$\mu_{Spin\text{-}only}$ value for an ion with 'n' unpaired electrons may be calculated by using the equation:

$$\mu_{Spin\text{-}only}=\sqrt{n[(n+2)]}\ \mu_B \cdots\cdots\cdots\cdots (1)$$

The observed magnetic moment may be more than (ferromagnetic) or less than (antiferromagnetic) that of calculated values if the exchange interaction involve. In a complex the magnetic exchange interaction occurs when adjacent magnetic centres are close enough for direct or indirect orbital overlap. There are enormous ranges of polynuclear complexes of transition metal ion with paramagnetic centres exhibiting ferromagnetic and antiferromagnetic spin exchange interactions. Generally exchange interaction occurs through O-donor bridging ligands such as oxide, alkoxide, phenoxide, hydroxide and/or carboxylate ligands.[1.50, 1.49g-1.49h]

The magnetic exchange interaction takes place via two processes: (1) direct metal-metal interaction through overlap of the suitable orbitals and (2) superexchange between neighbouring paramagnetic centres through the orbital overlap of the bridging atom. Copper(II) acetate monohydrate exist as dimer $[Cu_2(CH_3COO)_4(2H_2O)]$ (Figure 1.11) both in solid and solution state, is an unique example to understand the direct metal-metal interaction mechanism. Here a weak antiferromagnetic coupling occurs through delta-bonding and reduce the magnetic moment from spin only value 1.73 B.M to 1.4 B.M per Cu^{+2} ion.

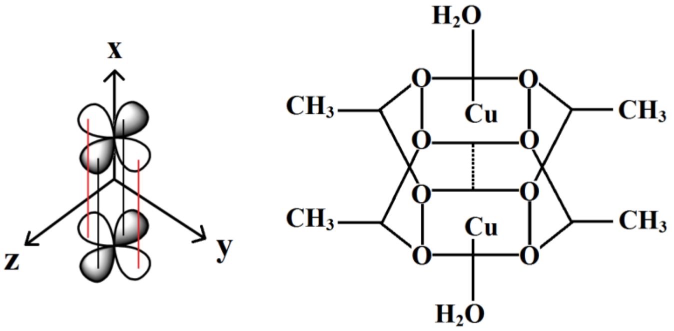


Figure 1.11. δ bond formation and dimeric structure of copper(II)acetate monohydrate.

Superexchange generally follows three atom exchange mechanism i.e. overlap of suitable partially filled orbitals of two paramagnetic centres via filled orbital of bridging donor oxygen atom with an angle of 180° (Figure 1.12) and 90° (Figure 1.13). When superexchange pathway is linear (180°), the interaction affords a suitable pathway for antiferromagnetic interaction and ferromagnetism interaction takes place when exchange interaction occurs through the overlap of the $p\sigma$ orbital of the bridging atom and two orthogonal d_z^2 orbital from each of the two interacting metal centres.

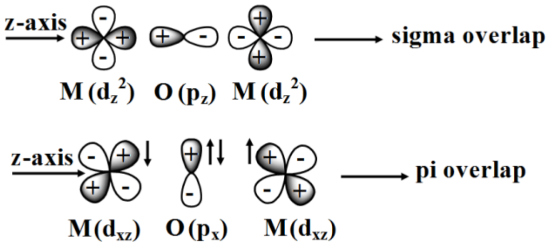


Figure 1.12. linear superexchange pathway

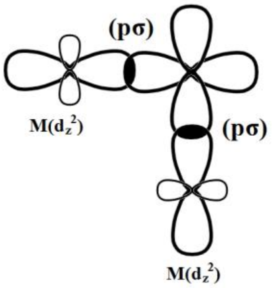


Figure 1.13. 90° superexchange pathway

Bhowmik *et al.* reported a tetranuclear Cu(II) complex $[Cu_4(L^1)_2(HL^1)_2(H_2O)](ClO_4)_2{\cdot}2H_2O$ [H_2L^1 = 2-[(2-hydroxy-ethylimino)-methyl]-6-methoxy-phenol], which shows antiferromagnetic coupling (J_{av} = -99.0 cm^{-1}).[1.49g] Gungor *et al.* reported two tetranuclear (4+2) type cubane-like complexes $[\{Cu(H_2L^1)\}_4]$ [H_2L^1 = *N*-(2-hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine] and $\{Cu(H_2L^2)\}_4$ [H_2L^2 = *N*-(2-hydroxyethyl)-4-methoxysalicylaldimine] having Cu_4O_4 core exhibit ferromagnetic coupling and the magnetic exchange coupling constant are J' = +28.7 cm^{-1}, J'' = +7.8 cm^{-1} for former complex and J' = +39.8 cm^{-1}, J'' = +10.2 cm^{-1} for later complex.[1.49h]

Paramagnetic compounds in which the individual molecules exhibit slow magnetic relaxation and magnetic hysteresis are known as single-molecule magnets (SMMs).[1.51] The essential requirement for a compound to be a SMM is the presence of a spin-reversal energy barrier between the states with the spin magnetic moments of opposite directions.[1.51a] Plenk *et al.* reported a six-coordinate [Co(oda)(aterpy)][1.52] (oda^{2-} = oxodiacetate, aterpy = 4'-azido-2,2':6',2''-terpyridine) complex, which behaves as a SMM with an effective energy barrier of 4.2 cm^{-1}. Two mixed-valence dinuclear complexes $[Co^{III}Co^{II}(LH_2)_2(X)(H_2O)](H_2O)_m$[1.53] (**1**, X = Cl and m = 4; **2**, X = Br and m = 4) reported by Chandrasekhar *et al.* shows SMM behaviour with the energy barrier of 7.9 cm^{-1} and 14.5 cm^{-1} respectively for complex **1** and **2**. The values for the magnetic relaxation energy barrier are 5.45–7.74 cm^{-1} for $[Co(dca)_2(bim)_4]$,[1.54] 4.53–9.24 cm^{-1} for $[Co(dca)_2(bim)_2]_n$[1.54] and 11.48–15.44 cm^{-1} for $[Co(dca)_2(bmim)_2]_n$[1.54] [dca = dicyanamide, bim = 1-benzylimidazole and bmim = 1-benzyl-

2-methylimidazole] reported by Świtlicka-Olszewska *et al.* Since the first example of SMMs was $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ discovered in the 1990s,[1.51b] and majority of Mn compounds shows SMM behaviour containing some Mn^{III} centres. When magnetism arises from a single paramagnetic ion then those molecules are referred to as Single-Ion Magnets (SIMs). Other than manganese, cobalt complex was the first to show SMM and SIM behaviour among the transition metal ions.[1.55,1.56] SIM behaviour is found in cobalt(II) complexes with diverse geometries such as trigonal planar,[1.57] tetrahedral,[1.58] square-pyramidal,[1.59] trigonal bipyramidal,[1.60] and octahedral.[1.61]

1.2.2. Catecholase activity

In an adult human body about 60-100 mg of copper is distributed in different organism and the element present in living system as trace amount.[1.62,1.63] Copper is necessary constituent of active sites of several proteins and enzymes[1.63a] *viz.* plastocyanin (Figure 1.14a), galactose oxidase (Figure 1.14b), hemocyanin (Figure 1.14c), catechol oxidase etc. and involved in a number of metabolic functions such as cellular respiration, electron transfer, catalysis, dioxygen uptake and transport.[1.63b] The active sites of copper containing proteins based on their spectroscopic characteristics were divided into three types namely type-1, type-2 and type-3.[1.64a-f]

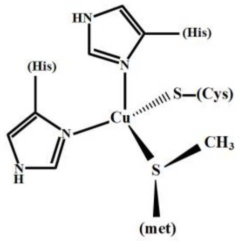


Figure 1.14a. plastocyanin

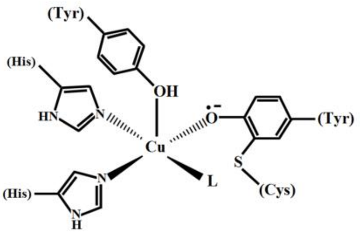


Figure 1.14b. galactose oxidase

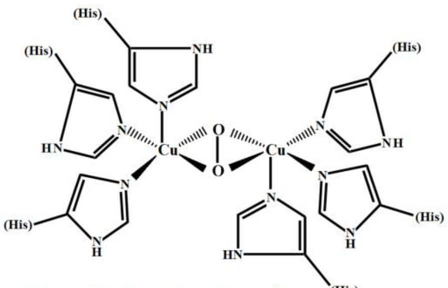
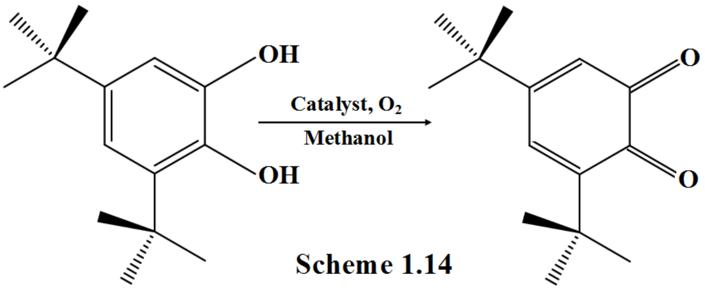


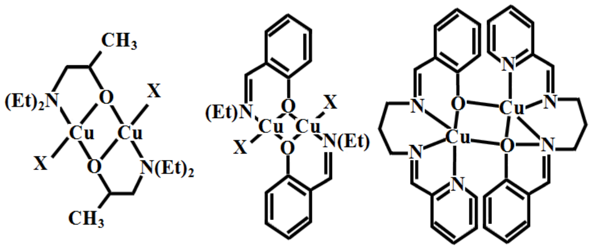
Figure 1.14c. oxyhemocyanine

Type-3 is represented by copper containing proteins, namely hemocyanine[1.64f] (transport of O_2), tyrosinase (oxidation of phenolic substrates to catechols and consequently to o-quinones) and catechol oxidase (oxidation of catechols to o-quinones, **Scheme 1.14**).



Scheme 1.14

The active site in type-3 contains a dicopper unit, where every copper ion is surrounded by three nitrogen atoms from three histidine residue. Since catechol oxidase, a type-3 enzyme[1.65a-1.65c] contains the dicopper(II) centres, therefore many copper(II) complexes mimic the enzymatic process followed by the production of quinone with H_2O_2. The catecholase activity of copper metal based model complexes depends on many factors such as coordination environment around the metal centres, metal-metal distance, type of bridging ligand etc.[1.66a] The rate versus concentration of the substrate (catechols) is analyzed on the basis of the Michaelis–Menten approach of enzymatic kinetics to get a Lineweaver–Burk plot, as well as the parameter values of the maximum initial rate (V_{max}), Michaelis–Menten constant (K_M) and turnover number (K_{cat}). Kao *et al.* reported seven dinuclear Cu(II) complexes (**1-7**) (Figure 1.15)[1.66b] with catecholase activity order 3≥4>5>2>1>6>7.



X= N_3^-(1), NCO^-(2), NO_2^-(3)

X= NO_3^-(4), Cl^-(5), NCS^-(6)

(7)

Figure 1.15

Table 1.1

Complex	**Cu…Cu(Å)**
1	**2.8067(7)**
2	**2.8690(22)**
3	**2.9279(10)**
4	**3.008 (1)**
5	**3.051 (1)**
6	**3.0575(8)**
7	**3.3784(12)**

This order of catecholase activity correlates to the Cu···Cu distances (Table 1.1) and size of ligand (X^-). Literature survey reveals that several mononuclear, dinuclear and trinuclear copper(II) and Co(II/III) complexes[1.66a-f,1.42f] are reported showing catecholase-like activity with different efficiency. But only a few number of higher nuclear copper(II) complexes are reported in the literature showing catecholase-like activity. Mitra *et al.* reported catecholase activity of a tetranuclear Cu(II) complex $[Cu^{II}_4(L)_4]$[1.66g] [H_2L = N-(2-hydroxyethyl)-3-methoxysalicylaldimine] with turnover number (K_{cat}) 6.99×10^3 h^{-1} in methanol and 1.85×10^3 h^{-1} in dichloromethane. Majumder *et al.* reported another tetranuclear complex $[\{Cu^{II}_2L(\mu_{1,1}\text{-}N_3)(ClO_4)\}_2(\mu_{1,3}\text{-}N_3)_2]$[1.66h] [L = 2,6-bis[N-(2-pyridylethyl)formidoyl]-4-ethylphenol] with turnover number 40 h^{-1} in acetonitrile. Table 1.2 shows turnover number (K_{cat}) of the catechol oxidation reaction of some reported cobalt(II/III) and copper(II) complexes.

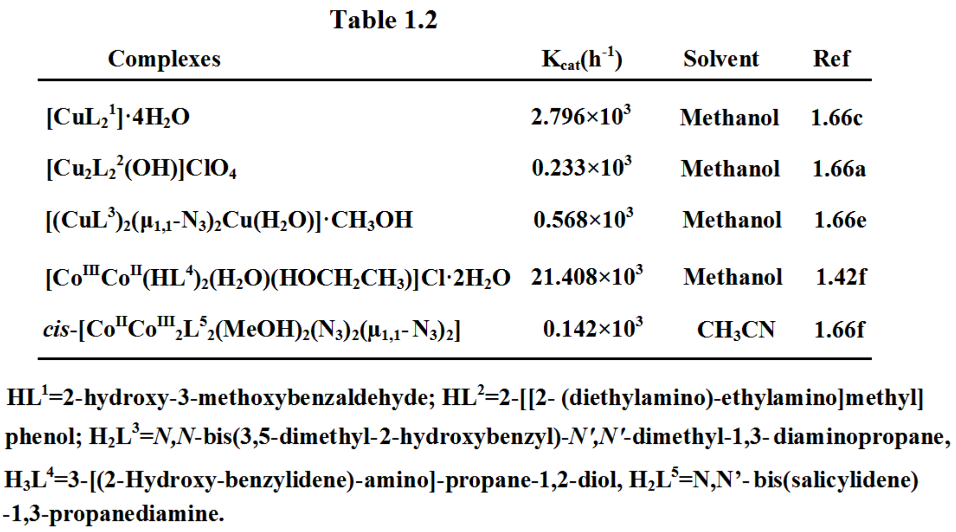


Table 1.2

Complexes	$K_{cat}(h^{-1})$	Solvent	Ref
$[CuL_2^1]\cdot 4H_2O$	2.796×10^3	Methanol	1.66c
$[Cu_2L_2^2(OH)]ClO_4$	0.233×10^3	Methanol	1.66a
$[(CuL^3)_2(\mu_{1,1}\text{-}N_3)_2Cu(H_2O)]\cdot CH_3OH$	0.568×10^3	Methanol	1.66e
$[Co^{III}Co^{II}(HL^4)_2(H_2O)(HOCH_2CH_3)]Cl\cdot 2H_2O$	21.408×10^3	Methanol	1.42f
cis-$[Co^{II}Co^{III}{}_2L^5{}_2(MeOH)_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2]$	0.142×10^3	CH_3CN	1.66f

HL^1=2-hydroxy-3-methoxybenzaldehyde; HL^2=2-[[2- (diethylamino)-ethylamino]methyl] phenol; H_2L^3=*N,N*-bis(3,5-dimethyl-2-hydroxybenzyl)-*N',N'*-dimethyl-1,3- diaminopropane, H_3L^4=3-[(2-Hydroxy-benzylidene)-amino]-propane-1,2-diol, H_2L^5=N,N'- bis(salicylidene) -1,3-propanediamine.

1.2.3. DNA/Protein binding studies

DNA and proteins (serum albumins) are regarded as the prime cellular targets for the action of drugs and several metal complexes (metallodrugs) exercise their drug activity through the binding with DNA and proteins. Therefore it is important to study the interaction of 3d metal complexes (metallodrugs) with DNA and proteins for design and syntheses of new and competent drug.[1.67] For the designing and finding of metal-based drugs attention should be focused on less-toxic, target-specific and these should bind with the DNA through non-covalent binding mode.[1.68] Copper, among the bio-essential metals, is important for many physiological processes and for their less toxic nature copper complexes are considered as better alternatives than platinum as anticancer drugs.[1.69] Several copper(II) based anticancer and cancer inhibiting agents have been reported in the literature which are able to overcome drug resistance phenomenon and active in both in *vivo* and *vitro*.[1.70a-1.70c] Zheng *et al.* reported two dinuclear Cu(II) complexes $[Cu_2(pdmaeox)Cl(CH_3OH)(dabt)]\cdot CH_3OH$ and $[Cu_2(pdmaeox)(bpy)(H_2O)](pic)\cdot H_2O$ {$H_3pdmaeox$ = N-phenolato-N'-[2-(dimethylamino)ethyl]oxamide, dabt = 2,2'-diamino-4,4'-bithiazole, pic = picrate anion and bpy = 2,2'-bipyridine} shows in *vitro* anticancer activities against selected tumor cell.[1.70d]

Non-covalent interactions occurs between DNA and metal complexes are of three types; electrostatic interactions, groove binding and intercalation.[1.71a] The intercalation attracts significant interest than other non-covalent interaction because it has strong binding ability and a wide range of application in molecular biology.[1.71b] The intercalating ability depends on two factors: (i) the type of metal used, and (ii) the structure of the ligand.[1.71c] Lian *et al.*[1.71d] reported four Schiff base coordinated copper(II) complexes, $[Cu(L)(OAc)]\cdot H_2O$, $[Cu(HL)(C_2O_4)(EtOH)]\cdot EtOH$, [Cu(L)(Bza)], [Cu(L)(Sal)] {HL = 1-(((2-((2-hydroxypropyl)amino)ethyl)imino)methyl)naphthalene-2-ol), Bza = benzoic acid, Sal = salicylic acid} and Jeyalakshmi *et al.*[1.71e] reported five copper(II) complexes $[Cu\{C_6H_5CONC(NR)NHCH_2C_6H_5\}_2]$ {where R = phenyl, 4-methylphenyl, 4-ethoxyphenyl, 2-methoxyphenyl or 1-naphthyl}, all of these copper complexes shows intrinsic binding constant (K_b) in the order of 10^4 M^{-1} via intercalative binding mode.

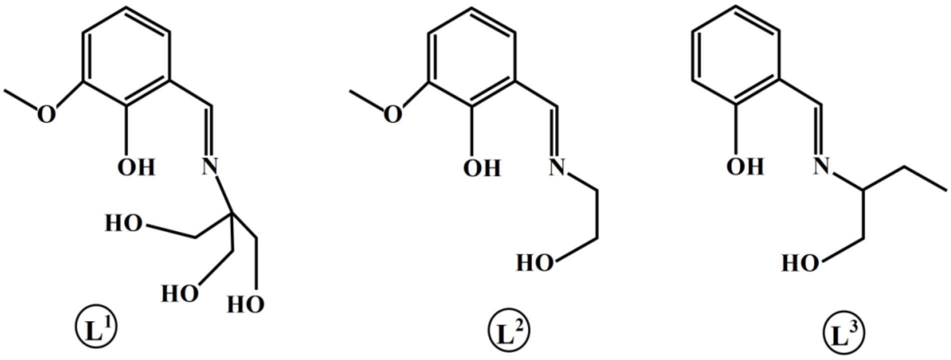
Bovine serum albumin (BSA) and human serum albumin (HSA) are two important plasma proteins in the circulatory system of cow and human respectively. These serum albumins can transport and dispose many exogenous and endogenous compounds.[1.72a,b] Serum albumins also bind with many drugs and act crucial role for drug carrier and delivery. As most of the drugs generally transported as drug-protein complex,[1.72c] it is important to understand drug–protein interactions in blood plasma and the factors that drive and control cell cycle.[1.72d] The bindings of drugs to serum albumins (BSA and HSA) in *vitro* may be considered as a model for studies of binding of drugs and protein.[1.72e] Hence detailed study of the interaction of metallodrugs with BSA and HSA grow to be very significant for the improvement of drugs.

The interactions of metal complexes (metallodrugs) with serum albumin (BSA/HSA) are studied fluorometrically. Kathiresan *et al.* reported two Cu(II) complexes $[Cu(L)(ClO_4)]$ and $[Cu(L)(phen)]ClO_4$ [L = 4-chloro-2-((2-(phenylthio)phenylimino)methyl)phenol and phen = 1,10-phenanthroline] and the complexes show a strong interaction with BSA.[1.73a] Hu *et al.*

reported three copper(II) complexes $[Cu(L^1)(NO_3)_2]$, $[Cu(L^2)Cl_2]$ and $[Cu(L^2)SO_4]_2 \cdot H_2O$ {L^1 = (E)-methyl 4-((quinolin-8-ylmethylene)amino) benzoate, L^2 = (E)-ethyl 4-((quinolin-8-ylmethylene)amino) benzoate)}. These compounds also show interaction with HSA.[1.73b] The interaction of BSA and HSA with these copper complexes followed static quenching mechanism.

1.3.Scope

A detailed literature survey regarding structures and molecular properties of Schiff base coordinated polynuclear cobalt(II/III) and copper(II) complexes have been presented in the general introduction section. Although many research group used numerous multidentate N, O, O-; N, O, N-; and N, N, O, O- donor Schiff base ligand[1.16] for the synthesis of polynuclear metal complexes, there are only a limited number of cobalt(II/III) and copper(II) complexes of high nuclearity are reported in the literature showing interesting magnetic properties, catalysis and biological activities. Use of multidentate N, O- donor Schiff bases 2-[(2-Hydroxy-3-methoxybenzylidene)amino]-2-(hydroxymethyl)propane-1,3-diol (L^1), 2-[(2-hydroxy-ethylimino)-methyl]-6-methoxy-phenol (L^2) and (E)-2-((1-hydroxybutan-2-ylimino)methyl)phenol (L^3) (**Scheme 1.15)** may generate new Cu(II) and Co(II/III) compounds with aim of study of their magnetic, catalytic and biological activities.



Scheme 1.15

Complexes formed by 1,4-phenylenediacrylate (ppda) as ligand shows interesting magnetic behaviour as conjugation present in the dicarboxylate ligand transmitted the exchange interaction from one paramagnetic centre to another via its M-O-C-O-M coordination mode. But in literature 1,4-phenylenediacrylate (ppda) containing compounds where both the carboxylate binds with two metal centres is still limited. Therefore there is a scope to synthesize new complexes of Cu(II) and Co(II/III) showing interesting magnetic behavior, where both Schiff base and 1,4-phenylenediacrylate (ppda) are present.

A number of Co(II/III) and Cu(II) compounds reported in the literature showing fascinating magnetic properties. Design and syntheses of new compounds of Schiff base ligands is important to develop Co(II/III) and Cu(II) metal based new magnetic materials.

Studies of the interaction of copper(II) complexes with calf-thymus DNA and serum albumins using spectroscopic techniques (electronic and emission spectra) represent a key point to develop possible copper metal based drugs. Therefore for the syntheses of new Cu(II) metal based drugs with better efficiency further work is required.

A literature study reveals that several mononuclear and dinuclear copper complexes have been reported in the literature showing catecholase-like activity, but there are only a few number of copper(II) complexes of high nuclearity showing catecholase-like activity. Hence there is a scope to increase the number of Cu(II) complexes of high nuclearity showing catecholase-like activity.