CHAPTER- I

General Introduction

Chapter 1: General introduction

Introduction

1.1 General

The coordination compounds are important to the chemist and material scientist since from their identification in the nineteenth century. During that period the coordination compounds appeared unusual as they do not maintain the usual valence rules and for this reason they are called “complex” compounds. Modern study on coordination compounds starts with the work of Sophus Jφrgensen and Prof. Alfred Werner. Jφrgensen first tried to explain the bonding in coordination compounds, but he was failed. Prof. Werner proposed the theory in 1893 to explain the molecular structure and types of bonding in metal complexes. In 1913, Prof. Alfred Werner won Nobel Prize for this theory and for his hard work on coordination compounds. Prof. Werner discovered four complexes of cobalt (III) chloride with ammonia and named according to their color [1.1].

Complex	**Color**	**Early name**
$CoCl_3{\cdot}6NH_3$	Yellow	*Luteo* complex
$CoCl_3{\cdot}5NH_3$	Purple	*Purpureo* complex
$CoCl_3{\cdot}4NH_3$	Green	*Praseo* complex
$CoCl_3{\cdot}4NH_3$	Violet	*Vialeo* complex

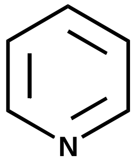
In modern chemistry, geometry and property of coordination compound depend on both the metal center and on the nature of coordinating ligand. The geometry of the coordination compound depends on the coordination number and nature of the central metal ion. Coordination number can vary from 2 to 7. Depending on the coordination number of the central metal ion various geometries are possible for example linear, triangular planer, tetrahedral, square planer, square pyramidal, trigonal bipyramidal, trigonal prismatic, octahedral, pentagonal bipyramidal and their distorted forms [1.2]. The coordination number and the geometry of a metal ion with a particular oxidation state largely depend on the reaction conditions, for instance temperature, solvents, counter anions and ligands etc.[1.3].

On the basis of donor sites the ligands are of two types, monodentate ligands and polydentate ligands. Monodentate ligands (Scheme 1.1) have one electron pair donor site, and $[Cu(NH_3)_4]^{2+}$, $[CoCl_4]^{2-}$, *cis*-diaminedichloroplatinum(II), *trans*-diaminedichloroplatinum(II), etc. are some examples of coordination compounds with monodentate ligands.

X^- (X= F, Cl, Br, I, OH) **NH_3**

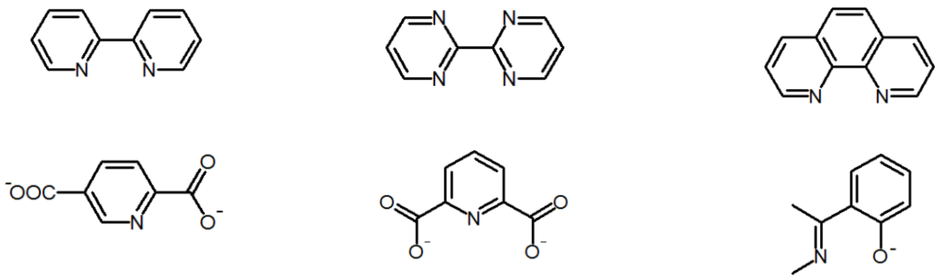
R-OH (R= aliphatic chain, aromatic ring)

$R-NH_2$ (R= aliphatic chain, aromatic ring)

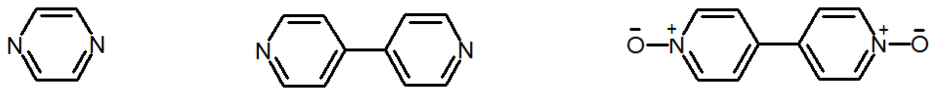


Scheme 1.1 Examples of some monodentate ligands

Polydentate ligands have more than one electron pair donor sites and depending upon the mode of coordination these are classified as (i) chelating ligands (Scheme 1.2) and (ii) bridging ligands (Scheme 1.3) [1.4]. Nitrogen and oxygen donor ligands can potentially coordinate with the 3d metal ions.



Scheme 1.2 Examples of some chelating ligands



pyrazine 4,4´-bipyridine 4,4´-bipyridyl-N,N´-dioxide

Scheme 1.3 Examples of some bridging ligands

Among the other transition metal ions, copper is mandatory for all living systems as it play a vital role in various enzymetic reactions, which are crucial for biological functions [1.5]. Copper is extensively dispersed in nature as carbonates, chlorides, sulphides etc [1.6]. In terms of abundance of the metals in biological system, copper is the third most abundant metal following iron and zinc. In an adult human body, approximately there is 200-300 mg of copper. Copper containing enzymes and proteins represent the vital class of biologically active complexes and show a variety of biological functions in oxygenation, electron transfer, disproportionation, dioxygen transfer and reduction-oxidation reaction [1.7]. In recent time copper complexes are the best promising substitutes to platinum drugs [1.8] due to following reasons

(i) Toxic side effects (such as ototoxicity, nephrotoxicity and allergy) and inherited or acquired drug resistance of platinum-based agents [1.9].

(ii) Copper is found in all living organism and also an important micro element in the human body, participate in many crucial biological mechanism [1.10].

(iii) Copper complexes are less toxic, show a variety of coordination number and as well as various possible geometries with oxidation states +1 and +2 [1.11].

(iv) Due to the better solubility and stronger affinity to the purine and pyrimidine bases copper complexes are presently use as efficient anticancer drugs [1.12]

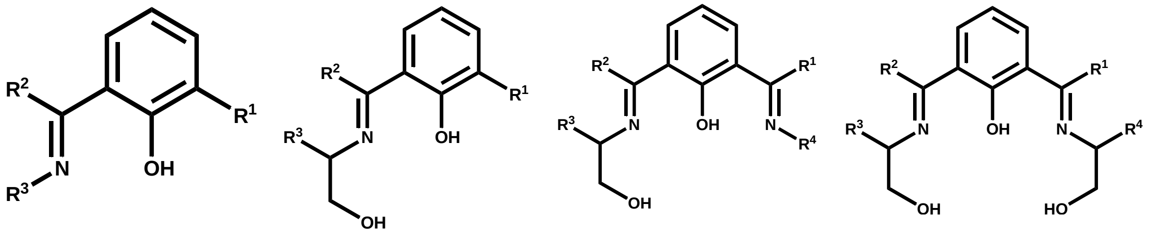
Lots of Cu(II) compounds have been widely investigated in virtue of their strong binding affinities with DNA and their cytotoxic activities.

Sigman et al. first revealed that 1,10-phenanthroline coordinated copper ion can cleave DNA [1.13]. J. A. Cowan et al. designed a copper-acridine-ATCUN complex that could inhibit propagation of the cancer cell significantly and also reduce the telomere length [1.14]. Two copper(II) complexes having considerable anticancer and antiangiogenic potential were synthesized by Bojja Sreedhar et al. in 2015 [1.15]. K. Suntharalingam synthesized a series of Cu(II) compounds capable of discriminatingly killing breast CSC-like cells over bulk breast cancer cells [1.16]. In 2016, F. Liang et al synthesized two new Cu(II) compounds that revealed high cytotoxicity [1.17]. Many studies have also confirmed that the copper compounds as prospective anticancer agents are particularly promising and represent good substitutes to platinum-based drugs [1.18].

Besides biological application of Cu(II) complexes, a rising interest in magnetochemistry is observed in the last few years, particularly owing to the practical application of the magnetic materials. Copper(II) is found in many reported compounds of different nuclearity (mononuclear, dinuclear, polynuclear) with a variety of coordination polyhedra having different geometries such as tetragonal, square planer, tetrahedral, trigonal bipyramidal etc. [1.19]. The interaction between the unpaired electrons in d^9 system can be paramagnetic, but antiferromagnetic and ferromagnetic interactions are often observed [1.20]. The absence of inter-metal magnetic interaction (paramagnetism) and its presence (antiferromagnetism, ferromagnetism) is depend on the coordination geometry of the compounds and on the magnetic path among the adjacent copper(II) centres. The distance between the metal centres and the type of bridging plays important role on the magnetic interaction. The bridges are most often monoatomic or triatomic, e.g. O-C-O in carboxylates and -O- in phenoxo or alkoxo Schiff base ligands, but other types are also found [1.21].

In 1864 Hugo Schiff, an Italian chemist, described the condensation reaction between an amine and an aldehyde in organic solvent results the formation of N-substituted imine, known as Schiff base [1.22]. The Schiff base ligands have been intensively utilized for the synthesis of 3d, 3d/4f and 4f transition metal coordination compounds [1.23]. The Schiff bases are widely used as ligand due to their multitudinous synthesis, remarkable versatility and good solubility in common organic solvents.

Schiff base containing coordination compounds have important applications in various fields e.g., magnetic [1.24], catalytic [1.25], fluorescence sensing [1.26] and biology [1.27].



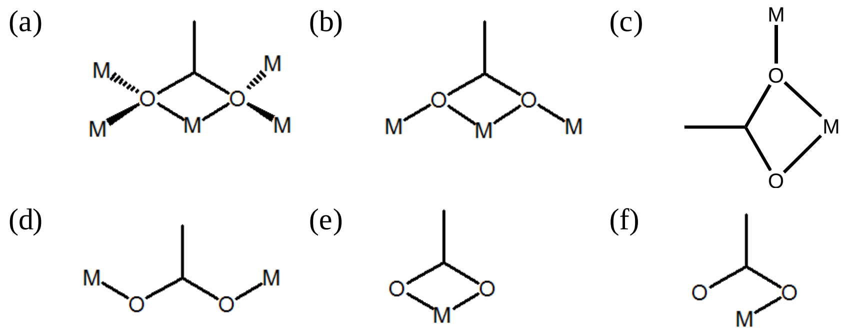
Bidentate Tridentate Tetradentate Pentadentate

Scheme 1.4 Denticity of Schiff base ligands

Mono, di-, and polycarboxylates are also widely used in combination with Schiff bases for synthesis of polynuclear complexes [1.28]. Coordination modes of carboxylate are shown in Scheme 1.5. Among these five coordination modes, (a), (b) and (c) are interesting, where oxygen atom bridges two metal centers. Most commonly observed coordination modes are (d), (e) and (f). Some examples of carboxylate coordinating compounds are, [Co{1,2-bis(4-pyridyl)ethane}(tp)] [1.29], $[Co(tp)(phen)(H_2O)]_n$, $[Cu(tp)(phen)]_n$, $[Zn(tp)(phen)(H_2O)]_n$, $[Mn(tp)(phen)]_n$,$[Cd(tp)^{1/2}(phen)Cl]_n$ [1.30], $Cu(tp)(OH_2)_2.H_2O$, $Cu(tp)(OH_2)_2$ [1.31], $Ni_3(tp)_3(2,2´\text{-bipy})_2$ [1.32] , catena-((m6-but-2-endioato)-(m2-but-2-endioato)-diaqua-di-lead tetrahydrate) [1.33].

In compound [Co{1,2-bis(4-pyridyl)ethane}(tp)], terephthalate exhibit coordination mode (e). In compound $Cu(tp)(OH_2)_2.H_2O$, terephthalate exhibits both coordination modes (e) and (f). The chelating mode (f) also present in compounds $[Co(tp)(phen)(H_2O)]_n$, $[Cu(tp)(phen)]_n$,

$[Zn(tp)(phen)(H_2O)]_n$, and $Cu(tp)(OH_2)_2$. In compounds $[Mn(tp)(phen)]_n$ and $[Cd(tp)^{1/2}(phen)Cl]_n$ terephthalate coordinate with two metal centres through motif (d). Carboxylate coordination mode (c) is present in catena-((μ_6-but-2-endioato)-(μ_2-but-2-endioato)-diaqua-di-lead tetrahydrate). On the other hand both c and e modes presents in complex $Ni_3(tp)_3(2,2'\text{-bipy})_2$.



Scheme 1.5 Various coordination modes of carboxylate ion.

In addition to coordination, carboxylate oxygen atoms are also involved in H-bonding interaction which favors the formation of supramolecular architecture of coordination compounds.

The chemistry of polynuclear Cu(II) clusters has received increasing interest because of their structural diversity and important applications in molecular magnetism [1.34], catalysis [1.35] and bioinorganic chemistry [1.36]. When multinuclear compounds extended “infinitely” into 1D, 2D or 3D through covalent linkage /covalent linkage cum weak interactions these are called metal-organic frameworks (MOFs) / coordination networks [1.37]. Depending on the functionality and flexibility of the ligands, polynuclear copper(II) compounds have various structure e.g. diamondoid [1.38], honeycomb [1.39], grid [1.40], T-shaped [1.41], ladder [1.42], brick wall [1.43], octahedral [1.44], etc. The synthesis of multinuclear copper complexes is controlled by different factors, such as ligands, metal salts, counter ions, temperature, solvents,

P^H of reaction medium etc. [1.45]. The multi-dentate ligands containing several N and O donor centers are suitable for designing polynuclear architectures due to their versatile coordination patterns [1.46]. Schiff bases are good candidates in this respect and have been widely utilized in the synthesis of multinuclear copper complexes [1.47]. The use of a Schiff base in combination with a linear dicarboxylate is also an important strategy for the synthesis of polynuclear complexes, and in this combination the Schiff bases function as chelating ligands and the linear dicarboxylate ligand behaves as a spacer.

Among the polynuclear Cu(II) complexes, tetrameric copper clusters exhibiting a variety of structures like butterfly, roof-shaped, face-to-face, cyclic, pin-wheel, Cu_4O_4 cubanes and rings have drawn particular interest [1.48]. The Cu_4O_4 cubanes are important owing to their interesting magnetic properties [1.49] and their potential application in the field of bioinorganic chemistry as biomimetic models for metalloenzymes, and also due to their nuclease activities [1.50]. Mainly two types of ligands are used for the synthesis of cubane clusters: i) Schiff bases containing two or more hydroxyl groups and ii) hydroxyl incorporated benzimidazole, imidazole, pyridyl or pyrazole ligands. These ligands aggregate the metal ions and form cubane type clusters as they possess both bridging and chelating capacities. Copper cubane geometries are of various types such as regular cubane [1.51], single-open cubane [1.52], double open cubane [1.53], and face-sharing dicubane etc. [1.54].

Bonding interactions present in the structure of the coordination compounds may be a) coordinate covalent bond (CB), b) CB and hydrogen bond (HB), c) CB and other interactions for instance π-π, metal-metal, CH-π, [1.46], and d) CB + combination of interactions (e.g., HB+ π-π, HB+MB, MB+ π-π) [1.55]. The stability of the higher dimensional structure of coordination compound increases with increasing the coordinate bond contribution. The non-covalent interactions (hydrogen bonding, C-H…π and π…π) play important role for stabilizing the crystal packing of the coordination complexes. The building blocks of supra-molecular networks are held together via non-covalent interactions. Many biological processes in living system also depend on non-covalent interactions, with the most important ones being the proteins' structure and functionality. Hydrogen bonding [1.56] interaction is relatively strong non-covalent interaction and sometimes it control metal coordination geometry [1.57]. The OH···O and NH···N hydrogen bonding interaction contribute generally higher energy (20-40 kJ/mol), whereas C-H...O interaction contributes lower energy (2-20 kJ/mol). Generally N-H…O bond distance is in between 1.80 - 2.00Å, whereas O-H…O bonds are usually shorter (1.60 - 1.80 Å) [1.58]. Depending upon the arrangement of aromatic rings the π-π interactions may be face-to-face or edge-to-face and can contribute up to 10 kJ/mole [1.59].

Molecular properties of Cu(II) coordination compounds

Cu(II) coordination compounds are potentially useful for their important properties, such as magnetic, photoluminescence, catalytic and biological activity, etc.

Magnetic properties

Magnetic materials based on 3d metal coordination compounds have potential applications in various fields such as molecular spinotronics, quantum computing, information storage etc. [1.60].

Most of the 3d metal ions contain unpaired electron in their common oxidation state and form paramagnetic coordination compounds. The spin only magnetic moment for a discrete mononuclear compound of 3d metal is calculated using the equation: (magnetic moment)$_{\text{spin only}}$= $\sqrt{n(n+2)}$ B.M., where n is the number of unpaired electron of the metal centre. When paramagnetic centers are close sufficient for direct or indirect orbital overlap, the cooperative phenomenon of ferromagnetic / antiferromagnetism / ferrimagnetism are observed. Magnetic interactions in 3d metal coordination compound occur generally in two ways: (a) *superexchange mechanism*, where indirect interaction between metal centers having magnetic orbital (orbital having unpaired electrons) takes place through the orbitals of bridging ligands, and (b) *direct metal-metal interaction*, where metal magnetic orbital directly overlap each other. Magnetic moment of $[Cu_2(CH_3COO)_4(2H_2O)]$ (Figure 1.1) is less than 1.732 B.M., this is due to the direct overlap of $d_{x^2-y^2}$ orbital containing unpaired electron.

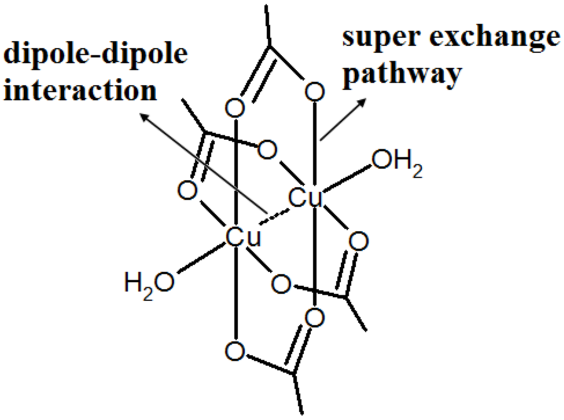


Figure **17**,
Fig. 1.1 Structure of $[Cu_2(CH_3COO)_4(2H_2O)]$.

Magnetic properties of polynuclear compounds of copper(II) are widely investigation due to their potential applications as single chain magnets (SCMs), single molecule magnets (SMMs) and in magnetic refrigeration, etc. [1.61]. It is well known that the coupling constant of alkokxido / phenoxido-bridged Cu(II) compounds depends on different structural features, for example geometry of copper ions, copper-oxygen bond lengths, Cu-O-Cu bond angles, torsion angles and Cu···Cu distances [1.62]. Among these, the Cu-O-Cu bond angle is the most significant. Usually, copper complexes which have Cu-O-Cu bond angle greater than 97° shows antiferromagnetism, whereas ferromagnetic character is found for lesser values of Cu-O-Cu bond angle [1.62].

During the last few years tetranuclear copper cubanes have paying great attention owing to their interesting magnetic properties [1.63]. A number of tetranuclear copper(II) cubanes containing alkoxo- / hydroxo-bridging have been widely studied [1.64]. Literature survey reveals that tetranuclear Cu(II) compounds having cubane like core framework showed both antiferromagnetic and ferromagnetic interactions because of the flexible nature of the coordination geometry as well as due to the diverse distortions in cubane core structure [1.65]. In the present time, the most important target is to enlarge a meaningful perceptive of the magneto-structural relationship of copper cubanes having versatile coordination geometry of copper ions.

Interactions with serum albumins

Serum albumins (SAs) are the most plentiful proteins in the circulatory system and they are involved in several physiological purposes [1.66]. Transportation of various exogenous and endogenous compounds is the most important function of serum albumins [1.67]. Serum albumins have tremendous binding ability and they bind with metal complexes, Schiff bases and various transition metal ions for instance Mn(II), Cu(II), Co(II), Ni(II), Hg(II), Zn(II). There are two major serum proteins, human serum albumin (HSA) and bovine serum albumin (BSA). In 1999, Sugia et al. and in 2012, Majorek et al. reported the crystal structure of HSA and BSA, respectively [1.68]. BSA and HSA are structurally homologous to each other and composed of 583 and 585 amino acid residues, respectively. Both the serum albumins BSA and HSA consist of three major domains, i.e. domain I (1-195), domain II (196-383) and domain III (384-585) according to their crystal structures [1.68]. These each domain further classified as sub-domain A and sub-domain B, and stabilized by 17 disulphide bridges [1.69]. The X-ray diffraction studies of different ligand-albumin compounds confirmed the existence of two binding sites in the domain II and domain III, which have cavities formed mostly of positively charged residues and hydrophobic and in which a very large number of complexes may be accommodated [1.68-1.69]. The main binding areas of serum albumin are located in sub-domain IIA and IIIA [1.68-1.69]. Serum albumin may bind the neutral, basic and acidic molecules of drugs. The sub-domain IIIA of serum albumin shows the major binding activity, while IIA looks to be more specialized. Most complexes bind with the amino acid residues of binding site in a reversible way by means of weak chemical bonds. The several types of intermolecular bonding interactions are involved to make the binding relationship such as hydrophobic, ionic and hydrogen bonding [1.70]. Since SAs play a vital role in drug transport, the study of the binding affinity of metal complexes towards serum proteins and understanding the mechanistic pathway of interaction is vital. The interactions of metal complexes with SAs depend on the geometry of the complexes, metal ions and ligands [1.71]. Therefore, an appropriate combination of metal ion and ligands is a vital requirement for the synthesis of a proficient serum albumin targeted metallo-drug. Interactions of metal complexes with serum proteins have been studied by employing different techniques including equilibrium dialysis, chromatographic, electrophoretic and different spectroscopic methods. Amongst them most commonly used techniques are electronic absorption and fluorescence spectroscopy.

Serum albumin molecule consists of three aromatic amino acids, namely tryptophan, tyrosine and phenyl alanine. These are responsible for protein fluorescence. We can apply this experiment to get the nature of the binding behavior of metal complex with SA when interaction between the complex and albumin can quenched the emission intensity of SA. Quenching of emission categorized as static quenching and dynamic quenching [1.72]. The static quenching is caused by the ground state association of complex with serum albumin, whereas the dynamic quenching is the result of the collision between excited serum albumin molecules and the complexes [1.73]. The number of albumin molecules reduces in both the process and caused fluorescence quenching [1.74].

Using UV-vis spectroscopic technique we can easily differentiate this two type of fluorescence quenching [1.75]. Any changes in absorption spectra of albumins with incremental addition complex concentrations confirms the static quenching, whereas for dynamic quenching there will be no such change. In contrast for dynamic quenching with rising temperature the quenching constant will increase and the opposing effect can be detected in static quenching [1.76].

Interactions with DNA

The interaction between metal complexes with DNA has gained much interest in current times because of their potential applications in molecular biology and cancer therapy [1.77]. Copper complexes are attractive in this respect not only for exhibiting diverse geometries but they also have exciting photophysical and electrochemical properties. The primary target of anticancer drugs is DNA and the interaction metal complexes with DNA were employed to understand the nature of the interaction between them [1.78].

The DNA can interact with transition metal complexes by the non-covalent way (groove binding), by intercalation or electrostatic binding and through oxidative, photolytic and hydrolytic mechanisms they can cleave the DNA [1.79]. Although platinum based drugs are extensively used as anti cancer drug but it possesses toxic side effects (such as ototoxicity, nephrotoxicity and allergy) [1.9]. Literature survey reveals that many Cu(II) complexes act as efficient anti cancer and anti tumour agents [1.12]. Because of these limitations of platinum based drugs and applicability of Cu(II) complexes as efficient anti cancer and anti tumour agents, the centre of attention of modern chemists has been transferred to the copper(II) complexes in recent times [1.8-1.12].

The interaction between the metal complexes and DNA can be measured by various methods such as (i) electronic absorption spectral technique (ii) electronic emission spectral technique (iii) circular dichroism spectral technique (iv) viscosity measurement methods (v) cyclic voltametric study etc.

Hypochromism in the electronic spectra of complex with or without red/blue shift upon gradual increasing concentration of DNA confirms the presence of intercalation between them [1.80]. On the contrary non-intercalative interaction between the complex and DNA [1.81] supported by the hyperchromism in the absorption spectra of a compound with increasing concentration of CT-DNA.

To examine the mode of interaction between the complex and DNA, fluorometric titration was performed. Ethidium bromide (EB) shows emission with an orange colour upon exposed to ultra violet radiation. The intensity of EB fluorescence increases around 20 fold in presence of DNA due to strong intercalation of the planar ethidium bromide phenanthridium ring between adjacent base pair of the double helix [1.82]. DNA bounded EB shows emission at around 600 nm on excitation at 500 nm. Addition of metal complex, which is capable to interact with DNA, to the solution of a mixture of EB and DNA results in the quenching of fluorescence intensity of DNA-EB system. The decrease in fluorescence intensity occurs due to decrease in the availability of the number of binding sites for EB on the DNA [1.83]. The decrease in fluorescence intensity in presence of complex solution may be employed to study the non-intercalation between DNA and the complex.

1.2. Scope.

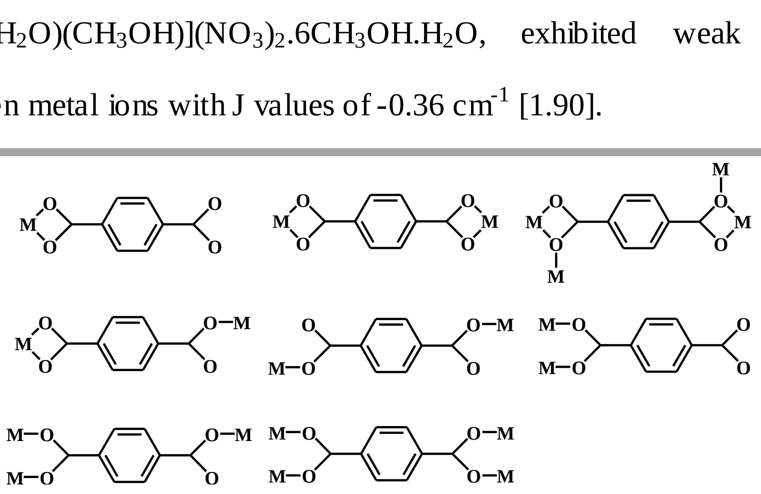
Structure and molecular properties of coordination compounds strongly depend on several factors e.g. metal ion, ligand(s) and weak interactions.

Polydentate Schiff bases are often used to build polynuclear complexes, since they have versatile coordination modes and Schiff base coordinated polynuclear copper compounds are significant because of their interesting structure and molecular properties such as in the area of catalysis, magnetism, chemical sensor, and bioinorganic chemistry [1.84]. Schiff base ligands having phenoxo, hydroxo, and alkoxo donors centre are crucial for the synthesis of multi-nuclear copper compounds [1.65]. (E)-2-((1-hydroxybutan-2-ylimino)methyl)phenol, (E)-2-((1-hydroxybutan-2-ylimino)methyl)-6-methoxyphenol, and 2-Ethoxy-6-[(1-hydroxymethyl-propylimino)-methyl]-phenol are potential polydentate ligands for the synthesis of 3d metal coordination compounds.

Using these ligands some di /tetra nuclear nickel(II), tetranuclear Mn(III), heterometallic Mn(III)/Ni(II), Mononuclear /dinuclear Sn(II), dinuclear copper(II), hexanuclear heterometallic (Cu/Na), mononuclear Mo(VI), mononuclear Pd(II) and one Dy_9 cluster have been reported in the literature [1.85]. But till date there is no report on the polynuclear compounds of Cu(II) using these Schiff bases only and in combination with these Schiff bases and carboxylate ligand. Therefore to explore the chemistry of polynuclear Cu(II) compounds of these ligands more work needed in this area. To synthesize Cu(II) coordination polymer, we have adopted a synthetic strategy where linear dicarboxylate is used in combination with Sciff base. In this combination the Schiff bases function as chelating ligands and the linear dicarboxylate ligand behave as spacer.

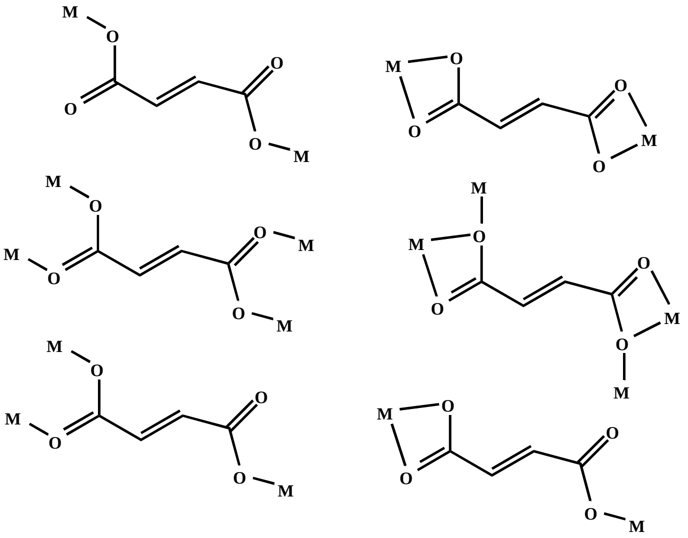
Fumarate (fum) and terepthalate (tp) are two commonly used linear dicarboxylate in coordination chemistry [1.86]. They both possess versatile coordination modes (Scheme 1.6 and 1.7) and have a special conformation with a 180° angle between the carboxylic acid groups. As they possess versatile coordination modes, the complexes of these carboxylates are very important owing to their interesting structure and molecular properties such as magnetic, photoluminescence, bioactivity, etc. [1.86]. Sun et al. [1.87] reported two one dimensional chain structures of $[Co(tp)(phen)(H2O)]_n$, $[Cu(tp)(phen)]_n$ and one three dimensional network structure of $[Mn(tp)(phen)]_n$. Variable temperature magnetic measurements for all the three complexes were consistent with the presence of weak antiferromagnetic interaction through the terephthalate bridge [1.87].

N. Behera et al. [1.88] reported compounds $\{[Co(L)_2(fum)(H_2O)_2]\cdot 2H_2O\}_n$ and $\{[Mn(L)_2(fum)]\}_n$ [L = 1-(4-acetylphenyl)imidazole]. $\{[Co(L)_2(fum)(H_2O)_2]\cdot 2H_2O\}_n$ is 1D coordination polymer, where fumarate coordinate to metal center in μ-η^1:η^1 bidentate fashion. On the other hand $\{[Mn(L)_2(fum)]\}_n$ is a 2D coordination polymer, where fumarate coordinate to metal center in μ_4-η^1:η^1: η^1:η^1 tetradentate fashion [1.88]. L. Croitor et al. [1.89] reported three one dimensional coordination polymer $[Mn(fum)(2\text{-}pyao)_2]_n$, $[Zn(fum)(2\text{-}pyao)_2]_n$ and $[Cd(fum)(2\text{-}pyao)_2]_n$, where 2-pyao = pyridine-2-aldoxime [1.89]. F.-M. Nie et al. [1.90] reported dinuclear nickel(II) complex $[Ni_2(ntb)_2(\mu\text{-}fum)(H_2O)(CH_3OH)](NO_3)_2.6CH_3OH.H_2O$ [ntb = tris(2-benzimidazolylmethyl)amine)]. The magnetic susceptibility measurements of $[Ni_2(ntb)_2(\mu\text{-}fum)(H_2O)(CH_3OH)](NO_3)_2.6CH_3OH.H_2O$, exhibited weak antiferromagnetic interactions between metal ions with J values of -0.36 cm^{-1} [1.90].



Scheme 1.6 Coordination modes of terephthalate.

Using these two carboxylate a lots of transition metal complexes are reported in the literature [1.86] but till date there is no report on the fumarate containing 3d metal complexes in combination with Schiff base ligand [1.86], and polynuclear complexes of terephthalate in combination with Schiff bases are limited [1.86]. As the main focus of my research work is to construct polynuclear copper complexes using Schiff base and linear dicarboxylate, therefore I have enough scope to enrich the chemistry of these two carboxylates through the synthesis of polynuclear complexes using these two carboxylates in combination with Schiff base and investigation of their potential applications in different fields for instance in molecular magnetism, in molecular biology, etc.



Scheme 1.7 Coordination modes of fumarate.

High nuclear Cu(II) complexes have paying much interest owing to their attractive molecular structures and important applications in different field for instance molecular magnetism [1.91], bioinorganic chemistry [1.92], coordination polymers and catalysis [1.93]. Among them, tetranuclear (Cu_4O_4) cubane-type Cu(II) complexes draw particular interest owing to their magnetic properties [1.94], along with as a model system for metallo-enzymes [1.95]. Binding of polynuclear copper complexes with serum proteins is fundamental step to realize the prospective of these complexes as drugs, because therapeutic efficiency, drug delivery and drug absorption are closely depends on the nature and magnitude of this binding [1.96]. Cambridge Database (CCDC) search exposes that until now a small number of Schiff base coordinated polynuclear Cu(II) complexes were reported using Schiff base ligands, and they mainly focused on magneto-structural relationship but interactions with biomolecules (Serum albumins /DNA) are quite rare [1.97]. So in order to enrich the family of Schiff base coordinated polynuclear copper(II) complexes we were studied the variable temperature magnetic measurements of these complexes as well as the interactions with CT-DNA and Serum albumins (BSA/HSA) using electronic absorption and emission spectral techniques.