Copper(II) complexes with halides and pseudohalides:

A brief introduction

Chapter 1

Copper(II) complexes with halides and pseudohalides:

A brief introduction

1.1. Introduction

Copper is widely distributed in nature as metal, in sulphides, arsenides, chlorides, carbonates and so on [1]. Copper is one of the transition elements frequently found at the active site of proteins. The copper containing enzymes and proteins constitute an important class of biologically active compounds [2]. The biological functions of copper proteins/enzymes include electron transfer, dioxygen transport, oxygenation, oxidation, reduction, and disproportionation [3,4]. The common oxidation states of copper are I \((d^{10})\), II \((d^{9})\), and III \((d^{8})\). Cu(I) forms mononuclear and polynuclear complexes having linear, planar, tetrahedral and distorted planar geometries. The most common oxidation state of Cu is +2, and Cu(II) complexes have been extensively studied. These complexes have trigonal planar, tetrahedral, octahedral, distorted octahedral, square planar and pentagonal bipyramidal geometries. Thiosemicarbazones and semicarbazones are molecules of great interest due to their potential pharmacological properties and a wide variation in their modes of bonding and stereochemistry. Semicarbazones are also reported to possess versatile structural features [5] and have very good antifungal and antibacterial properties [6,7]. A variety of semicarbazones and their metal complexes possess anti/protozoa and anti-convulsant activity also [8]. Copper(II) complexes are interesting due to their biological applications and interesting stereochemistries. Recently there has been considerable amount of interest in the studies of semicarbazones due to their unusual coordination modes when bound to metals, high pharmacological potentiality and good chelating property [9].

Copper is a bioelement and is an active site in several metalloenzymes and proteins [10,11]. Among all the transition metal complexes, copper(II) Schiff base
complexes with pseudohalogens are well known for their preparational accessibilities, exhibiting the flexibility of the coordination geometry around the metal center. Azide-copper(II) complexes are also of great interest for bioinorganic chemists to explore the structure and role of active sites in copper proteins such as metalazido hemocyanins and tyrosinases [12,13]. The chemistry of copper(II)-azido complexes has also received great deal of attention to enhance the fundamental knowledge about the magnetic interactions between the paramagnetic centers and for developing new functional molecule-based materials [14]. Examples of Cu(II)-azide systems with bidentate coligands are numerous and their structures are much diverse and more sensitive to the coligands used. Hence a variety of mononuclear, binuclear and polymeric complexes have been obtained, not only due to the coordination diversity of the azide ion, but also due to the coordination flexibility of the Cu(II) ion.

Even though thiocyanate is not as good a mediator of magnetic exchange between metal centers as the azide ion, still many copper complexes have been reported with thiocyanate and Schiff bases with ferromagnetic as well as antiferromagnetic interactions. Also the thiocyanate-bridged metal-coordination complexes have deserved special attention because they exhibit interesting electrochemical, zeolitic, magnetic, and photomagnetic properties [15]. The tetranuclear copper(II) chain complexes designed using the dipyridylmethanediol ligand has been found to promote ferromagnetic couplings between the copper(II) centers, thus opening a new avenue for the synthesis of molecular magnets [16].

1.2. Stereochemistry

The Cu(II) ion with $3d^9$ outer electron configuration lacks cubic symmetry and hence yields distorted forms of the basic stereochemistries such as tetrahedral, square planar, square pyramidal and octahedral [17]. Coordination numbers four, five and six predominate, but variations of each structure occur through bond length or bond angle distortions. The four coordinate complexes may be tetrahedral, square planar or a distorted mixture thereof, and the five coordinate complexes, square pyramidal, trigonal bipyramidal or a mixed version thereof. Jahn Teller effect plays a major role in deciding the distortion effect on stereochemistries of Cu(II) complexes. The typical distortion involved in octahedral geometry is elongated structures with the odd electron residing in the $d_{x^2-y^2}$ orbital resulting in four short Cu–L bonds and two trans long bonds, which are
usually more energetically favorable than the compressed structures, consistent with their more frequent occurrence. In the six coordinate species, the structures vary from compressed tetragonal through regular octahedral to elongated tetragonal but also include examples where the bond angles are clearly not 90°.

### 1.3. Outline of proligands used in the present study

#### 1.3.1. Semicarbazones

Semicarbazones are usually obtained by the condensation of semicarbazides with suitable aldehydes and ketones. An interesting fact is that the semicarbazones exist predominantly in the amido form in the solid state, whereas due to the interaction of the solvent molecules they can exhibit a amido-iminol tautomerism in solution state. Amido form acts as a neutral ligand and the iminol form can deprotonate and serve as anionic ligand in metal complexes. Thus semicarbazones are versatile ligands in both neutral and anionic forms. Both tautomeric forms have an efficient electron delocalization along the semicarbazone moiety. Aromatic substituents on the semicarbazone skeleton can further enhance the delocalization of electron charge density. These classes of compounds usually react with metallic cations giving complexes in which the semicarbazones behave as chelating ligands. Upon coordination to a metal center, the delocalization is further increased through the metal chelate rings. The coordination possibilities are further increased if the substituent has additional donor atoms. The following three semicarbazone ligands were synthesized by varying the carbonyl compounds.

![Fig. 1.1. Structures of the three semicarbazone ligands.](image)

#### 1.3.2. Thiosemicarbazones

Thiosemicarbazones are compounds obtained by the reaction of thiosemicarbazides or substituted thiosemicarbazides with aldehydes and ketones. The –C=S group provides the
possibility for the electron delocalization within the thiosemicarbazone moiety and also, increases the denticity of these compounds. The thioamide sulfur and azomethine nitrogen are the available donor sites present in the thiosemicarbazone compounds. Further, the number of coordination sites can be increased by the suitable substitution on the thiosemicarbazone framework. If heterocyclic rings are attached to the thiosemicarbazone moiety, the hetero atoms can act as the donor sites. An interesting attribute of the thiosemicarbazones is that in the solid state, they predominantly exist in the thioamido form, whereas in solution they exist both in thioamido and in thioiminol forms. The thioiminol form predominates in the solution state and can effectively coordinate to a metal atom. The following two thiosemicarbazone ligands were prepared by varying the ketones.

![Fig. 1.2. Structures of the two thiosemicarbazone ligands.](image)

1.3.3. Schiff bases

The condensation of primary amines with carbonyl compounds yields Schiff bases that are regarded as one of the most potential groups of chelators for the facile preparations of metallo-organic hybrid materials [18]. The exceptional qualities of Schiff bases such as facile syntheses, easily tunable steric, electronic properties and good solubility in common solvents have led to their extensive study [19]. In the past two decades, the synthesis, structure and properties of Schiff base complexes have stimulated much interest for their noteworthy contributions in the development of single molecule magnets, material science [20,21], catalysis of many reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation, hydrolysis etc [22]. This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning the metal centered electronic factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts. The flexibility of disposition of different donor sites is the secret behind their successful performance in mimicking peculiar geometries.
around the metal centers, leading to very interesting spectroscopic properties with varied magnetic activities [23]. Schiff bases also display biological activity and play an important role in biological systems [24]. Additionally the Schiff bases are found to have wide applications in field such as antibacterial, antiviral, antifungal agents [25].

In view of the above observation, the following five Schiff base ligands were synthesized by varying the aldehyde/ketone and the amine/hydrazide.

![bpap](image)

![Hdbsap](image)

![Hbsde](image)

![Hcsde](image)

![Hdbsde](image)

Fig. 1.3. Structures of the five Schiff base ligands.

Copper complexes containing pseudohalogens like azide or thiocyanate ions have been extensively investigated due to their excellent magnetic properties [26]. The use of Schiff bases as coligands in such metal-pseudohalogen complexes lead to interesting results [27]. This is because even a very small change in the coligands can lead to astonishing variation in the structure and magnetism of the resulting complexes. The stereochemical properties of the coligands certainly influence the structural diversity of the metal complexes [28]. The metal-pseudohalogeno systems containing Schiff base coligands are not as investigated as the systems without Schiff bases.
1.4. Classification of copper(II) complexes based on nuclearity

1.4.1. Mononuclear complexes: These are divided into three types. (i) Four coordinated complexes in which the copper ion has square planar geometry. (ii) Five coordinated complexes in which the copper ion has square pyramidal geometry. The tridentate Schiff base ligand coordinates the Cu(II) atom in equatorial mode and the axial position is occupied by an anionic ligand. (iii) Six coordinated complexes have distorted octahedral geometry and the tridentate ligand binds the Cu(II) atom in the equatorial mode and axial positions are occupied by anionic ligands.

1.4.2. Dinuclear complexes: The coordination mode flexibility of the coligands enabled the bridging of the entities leading to dinuclear complexes.

1.4.3. Polymers: Depending upon the crystallization conditions, the [Cu(L)X] complexes may sometimes build trans-μ_{1,3} bridged 1D-polymeric chains along the Jahn-Teller axis. In these complexes the tridentate ligand coordinates in the equatorial mode, and the axial positions are occupied by X.

1.4.4. Weak interactions: Aggregation of mononuclear complexes into dimers and networks via H-bonding involving coordinated or lattice solvent molecules have been reported.

1.5. Objectives of the present work:

1. To synthesize mononuclear to multinuclear copper coordination complexes with pseudohalides and halides as coligands and their molecular structural determination.
2. To explore the various intermolecular interactions present in them.
3. To study the packing modes, in the context of these interactions.
4. To study the versatility in coordination modes of Cu(II) complexes with halides and pseudohalides as coligands.
5. Magnetostructural correlation of copper complexes based on its stereochemistry and the coordination mode of coligands.
Copper(II) complexes with halides and pseudohalides: A brief introduction

REFERENCES