CHAPTER I
GENERAL INTRODUCTION
1.1 INTRODUCTION

Polynuclear transition metal complexes with multidentate bridging ligands have been a wide area of interest for researchers because of their multipurpose applicability in commercial as well as in the biological fields. This leads to the design and synthesis of inorganic-organic hybrid materials of desired topologies through supramolecular synthesis.\textsuperscript{1-3} Since their identification in the nineteenth century, coordination complexes have always been a challenge to the inorganic chemists. They seemed unusual in the early days, because they appeared to disobey the usual valance rules. Today, a large part of inorganic research comprises of coordination complexes of transition metals. The field is indeed very rich and diverge.\textsuperscript{4,5}

Copper is known to mankind for thousands of years. During the Roman Empire, copper was obtained from mines in Cyprus. So, ‘Cyprus’ is the origin of the name ‘cyprium’ which was later shortened to cuprum. Copper is an essential trace element and is important for both plants and animals. It is found in the bloodstream of humans and animals, as a co-factor in various enzymes and in copper-based pigments. Copper coordination chemistry is under investigation for a long time. The common oxidation states of copper are Cu\textsuperscript{+} (d\textsuperscript{10}) and Cu\textsuperscript{2+} (d\textsuperscript{9}) and in some rare cases Cu\textsuperscript{3+} (d\textsuperscript{7}) and Cu\textsuperscript{4+} (d\textsuperscript{8}). The properties of copper in coordination chemistry are due to the almost noble metal character, the intermediate stability, the reactivity of Cu(I) in d\textsuperscript{10} electronic configuration and relatively small radius of Cu(II) ion which contributes to the high energy of hydration resulting in higher stability of Cu(II) (aq) over Cu(I) (aq).\textsuperscript{6} Cu(I) ions need to be stabilized by chelating ligands with the preferred coordination geometries being trigonal and tetrahedral. Five coordinated Cu(I) complexes are also well known adopting either square pyramidal or trigonal bipyramidal geometry. However, the most stable oxidation
state is +2 and so complexes of Cu\textsuperscript{2+} have been studied widely in many different research fields including biomedicine\textsuperscript{7,8} and catalysis\textsuperscript{9,10}. Particular interest was also given to the magnetic properties\textsuperscript{11-13} of Cu(II) complexes since Cu\textsuperscript{2+} ion carries only one unpaired electron, so it makes the interpretation of magnetic interactions in Cu(II) complexes easier compared to those with more unpaired electrons.

A large number of Cu(II) complexes are known. Numerous complexes containing aliphatic as well as aromatic carboxylic acid anions as ligands displaying the general formula \([\text{Cu}_2\text{(RCOO)}_4]\) are known in the literature. The carboxylates could be prepared either by reaction of basic copper(II) carbonate or copper(II) acetate with corresponding carboxylic acids or by reaction of a copper(II) salt (sulphate, chloride) with the sodium salt of the corresponding carboxylic acid.\textsuperscript{14-17} Generally, the resultant binuclear complexes were reported to adopt the so called ‘paddle wheel structure’ where four bidentate carboxylato ligands bridge the Cu(II) centres. As illustrated in Scheme I, on each Cu(II) centre four oxygen atoms form the basal plane, while the axial position is either occupied by solvent molecule such as methanol, ethanol, acetone, acetonitrile, dimethylformamide or by a nitrogen base acting as a monodentate ligand or sometimes by an oxygen atom of another dimeric unit forming an oligomeric chain.\textsuperscript{18-20}

![Scheme I](image-url)
In 1972, Bird and Lomer studied on the crystal structure of copper(II) carboxylate containing long chain alkyl groups, as exemplified by the structure of anhydrous copper(II) butanoate \([\text{Cu}_2(\text{CH}_3(\text{CH}_2)_2\text{COO})_4]\).\(^{21}\) They stated that the single crystals of copper(II) carboxylate complexes with longer alkyl chains would be difficult to form. But in 1974, using a gel diffusion method, Lomer together with Perera successfully obtained crystals of anhydrous copper(II) decanoate, \([\text{Cu}_2(\text{CH}_3(\text{CH}_2)_8\text{COO})_4]\) and copper(II) octanoate \([\text{Cu}_2(\text{CH}_3(\text{CH}_2)_6\text{COO})_4]\). All the three complexes crystallized in the triclinic \(P\overline{1}\) space group.\(^{22,23}\) In 2008, Ramos et al. again reported the crystal structure of anhydrous copper(II) decanoate (Figure 1.1) where they provided a better molecular representation of the structure. Two different polymorphs of the complex were obtained depending on the type of solvent used for crystallization. From \(n\)-heptane, crystals of the triclinic space with triclinic polymorphs were obtained while monoclinic polymorph was obtained from ethanol. Both polymorphs however belong to the same space group \(P\overline{1}.\)^\(^{24}\)

![Figure 1.1 Crystal structure of copper(II) decanoate, \([\text{Cu}_2(\text{CH}_3(\text{CH}_2)_8\text{COO})_4]\) (H atoms were not shown)](image)

Prior to that, investigations on the interaction of Cu(II) heptanoate, octanoate, nonanoate, decanoate and dodecanoate with pyridine adducts and the effect of addition of water to the resulting copper(II) alkanoate-pyridine complexes were carried out.\(^{25}\) They were able to crystallize only the copper(II) nonanoate-pyridine complex upon the
addition of water. Formerly the dimeric complex \([\text{Cu}_2(\text{CH}_3(\text{CH}_2)_2\text{COO})_4(\text{py})_2]\), on adding water was found to structurally rearrange into a mononuclear complex \([\text{Cu}(\text{CH}_3(\text{CH}_2)_7\text{COO})_2(\text{py})_2(\text{H}_2\text{O})]\) where the copper centre has square pyramidal environment. (Figure 1.2), with the carboxylate anions present as monodenate ligands.

![Figure 1.2](image)

Figure 1.2 The monomeric structure \([\text{Cu}(\text{CH}_3(\text{CH}_2)_7\text{COO})_2(\text{py})_2(\text{H}_2\text{O})]\)(hydrogen atoms were not drawn)\(^{26}\)

But, similar reaction of copper(II) decanoate with ammonia results in a mononuclear complex \([\text{Cu}(\text{CH}_3(\text{CH}_2)_8\text{COO})_2(\text{NH}_3)_2].\text{H}_2\text{O}\) where copper centre has an octahedral geometry with extreme tetragonal distortion (Figure 1.3).\(^{26}\)

![Figure 1.3](image)

Figure 1.3 Structure of \([\text{Cu}(\text{CH}_3(\text{CH}_2)_8\text{COO})_2(\text{NH}_3)_2]\)

Bridging carboxylate anion, \(\text{RCOO}^-\) can have versatile binding mode in its coordination towards the metal centre with \(\text{syn-syn}, \text{anti-anti}\) or \(\text{anti-syn}\) configuration (Scheme II).\(^{27}\)
The mode of carboxylate binding whether bridging, chelating or monodentate can be assigned by IR spectroscopy by calculating the magnitude of separation between the asymmetric and symmetric stretches of the carboxylate group \( \{ \Delta \nu = \nu_{\text{asym}}(\text{COO}) - \nu_{\text{sym}}(\text{COO}) \} \). The frequency value of \( \nu_{\text{asym}}(\text{COO}) \) is found in the range of \(~1541-1678\) cm\(^{-1}\), whereas that of \( \nu_{\text{sym}}(\text{COO}) \) is within \(~1202-1410\) cm\(^{-1}\).\(^{28}\) The trend of separation value is \( \Delta(\text{chelating}) < \Delta(\text{bridging}) < \Delta(\text{monodentate}) \). If \( \Delta \nu \) greater than 250 cm\(^{-1}\) shows a monodentate carboxylate coordination; if \( \Delta \nu \) value between 150 and 250 cm\(^{-1}\) indicates a bridging coordination; on the other hand a difference less than 150 cm\(^{-1}\) signifies a chelate nature.\(^{29}\)

Transition metal complexes are usually coloured because of light absorptions involving d-d and charge transfer transitions. In absence of charge transfer transitions, the values of molar extinction coefficient, \( \varepsilon \) in such complexes are normally lower than 10 M\(^{-1}\)cm\(^{-1}\) because transitions involving d-orbitals in centrosymmetric (e.g. octahedral) complexes are normally Laporte forbidden. Transition metal complexes may, however, acquire stronger colours due to the presence of Jahn-Teller distortion or vibronic coupling; d\(^3\)-copper(II) complexes are particularly prone to distortions due to Jahn-Teller effect. Complexes of lower symmetry, e.g. square pyramidal, tetrahedral etc. are
normally more intensely coloured because they are not subjected to the Laporte selection rule of electronic transitions. Such complexes may present electronic spectra wherein the spectral bands may provide useful information regarding complex species which is present in solution. The value of $\lambda_{\text{max}}$ of a $d\rightarrow d$ absorption helps in determining the geometry of a complex.\textsuperscript{30,31} Particularly for copper(II) carboxylates, where the metal centre has a square pyramidal environment, it is expected that the $\lambda_{\text{max}}$ of complexes would be found at around ~680-700 nm.\textsuperscript{32,33} Shoulders at higher wavelengths appearing in the UV-region with $\lambda_{\text{max}}$ around 350-390 nm is a typical characteristic of a binuclear copper(II) carboxylate.\textsuperscript{34} Intense absorption at $\lambda$ lower than 300 nm indicates a charge transfer from carboxylic groups to Cu(II) atom (LMCT peak).

1.2 Mesogens

By general convention, matter exist either as solid or liquid or gas. But, there is another characteristic state of matter that exists between solid and liquid with properties resembling to both the states. It has definite order like in solid but not as rigid so that it is still fluid like liquid. This intermediate state of matter is called liquid crystal. Liquid crystals has a large number of application e.g. TV screens, computer displays, clocks, telephones and calculators, car dashboards, photo-cameras etc. The discovery of liquid crystals has occurred nearly 150 years ago but its usefulness was not fully realized until over a hundred years later. The study of liquid crystals began in 1888 when Austrian botanical physiologist Friedrich Reinitzer started working the Institute of Plant Physiology at the Charles University in Prague.\textsuperscript{35} He examined the physico-chemical properties of various derivatives of cholesterol, which are now known as cholesteric liquid crystals. He reported that cholesteryl benzoate does not melt in the same manner...
as other compounds but it has two distinct melting points. At 145.5°C it melts into a hazy liquid and at 178.5°C it melts again and the hazy liquid becomes clear. He found this phenomenon to be reversible. This was the first recorded documentation of the Liquid Crystal phase. Reinitzer was the first to suggest this hazy fluid as a new phase of matter. Later, he had discovered and described three important features of cholesteric liquid crystals: the existence of two melting points, the reflection of circularly polarized light, and the ability to rotate the direction of polarized light. The cloudy liquid phase is defined as a mesophase. Melting point is the temperature at which a material changes from solid into a mesophase while the temperature at which mesophase turns into a transparent isotropic liquid is referred to as the clearing point.

The interest in liquid crystals has grown ever since due to the great variety of phenomena exhibited by liquid crystals and enormous commercial applications and importance of liquid crystal displays. Liquid crystals possess anisotropic elasticity, viscosity, dielectric and diamagnetic susceptibilities and optical and (dye) wetting properties. Because of the anisotropy, liquid crystals response to external applied electric, magnetic, and flow fields. For making LCDs and other electro-optical devices understanding of the interactions of liquid crystals with surfaces is essential. Applications based on surface modifications by chemical and biological agents are being developed to detect radiation, nerve gases, bacteria and viruses. In 1973, a series of systematic modifications of the structures of mesogens was undertaken to establish a relationship between the molecular structure and the exhibition of liquid crystalline properties. This resulted in the discovery of the most technologically and commercially important class of liquid crystals to date: the 4-alkyl-4′-cyanobiphenyl for example, 4-pentyl-4′-cyanobiphenyl (Figure 1.4).
Figure 1.4 Molecular structure of 4-pentyl-4'-cyanobiphenyl

Liquid crystals are broadly divided into two categories: thermotropic liquid crystal whose mesophase formation is dependent on temperature and lyotropic liquid crystals which is concentration and solvent dependant. The necessary requirement for a molecule to be a thermotropic liquid crystal is a structure consisting of a central rigid core and a flexible peripheral moiety (generally aliphatic groups). This structural requirement leads to two classes of thermotropic liquid crystals: calamitic (rod like) and discotic (disc like) liquid crystals.

Calamitic liquid crystals possess an elongated shape, responsible for the anisotropy of the molecular structure, as the result of the molecular length ($l$) being significantly greater than the molecular breadth ($b$), as depicted in the Scheme III.

![Scheme III](image)

Scheme III. Schematic representation of calamitic liquid crystal where length, $l$>>breadth, $b$

Calamitic liquid crystals exhibit two types of mesophases: (a) Nematic (comes from the Greek word ‘nematos’meaning thread) and (b) Smectic (comes from the Greek word ‘smectos’ meaning soap). Nematic phase is the most liquid like structure in which, one or two molecular axes are oriented parallel to one another resulting in an orientational long-range order, contrary to isotropic liquids. Schematic representation of the calamitic
nematic liquid phase is shown in Scheme IV. The nematic substance separate as spherical drops form the melt or solution which closed to form the thread like structure.

![Scheme IV](image)

Figure 1.5 (a) Schlieren texture of a nematic, (b) & (c) Nematic thread-like texture

‘Chiral nematic’ is a special class of nematic liquid crystals where Chiral refers to the unique ability to selectively reflect one component of circularly polarized light.

The smectic mesophase is viscous and terbid forming greasy droplets. Many compounds are found to show more than one type of smectic phases and as many as 12 of these variations have been identified. Only the most distinct phases are discussed here.\(^{36-39}\)

Smectic–C mesophase is a tilted form of smectic–A phase. The major difference is the tilt (inclined) of the molecular long axes with respect to the layers. Smectic–C phase is optically biaxial and so it is impossible to have homeotropic texture. It exhibits schlieren texture and can also form focal conic or broken fan shaped textures.
Smectic-A phase has higher ordered arrangement of molecules than the nematic phase. It is characterized by partial translational ordering of molecules forming layers in addition to orientational coordination. The layers are bound by weaker interlayer attractions compared to the lateral forces between the molecules and so one layer can slide over the other easily. This results in fluidity to the system with higher viscosity than nematics. It exhibits focal conic structure.

![Smectic A and Smectic C phases](image)

**Figure 1.6** Texture of (a) Smectic A and (b) Smectic C phases
The sequence of mesophase stability for a material having nematic and smectic phases with increasing temperature is shown in **Scheme V**.

*Crystalline solid ↔ Smectic ↔ Nematic ↔ Isotropic*

![Scheme V](image)

**Scheme V**

Discotic (disc-shaped) mesogenic structure was discovered in 1977. The first series of discotic compounds exhibiting mesophase belong to the hexa-substituted benzene derivatives synthesized by Chandrasekhar *et al.*\(^{40-42}\) (**Figure 1.7**)

![Figure 1.7](image)

**Figure 1.7** Hexasubstituted benzene derivative

Discotic and calamitic liquid crystals can exhibit several types of mesophases with varying degree of organisation. The two principle mesophases are nematic discotic and columnar.\(^{43-46}\)
Figure 1.8 Schematic representation of (a) Discotic nematic and (b) Discotic columnar

There is no any report on a single discotic compound exhibiting all phase structures in literature. Columnar phases are most common in discotic mesogens but it is not the unique characteristic of discotics as surfactants that aggregate into cylindrical micelles to form lyotropic columnar phases are known for a long time. Even, some rod like molecules, bent core mesogens and dendrimers also exhibit thermotropic columnar phases. The terms ‘discotic phases’ or ‘discotics’ were used to denote disc like molecules and the columnar phases formed by them. This incorrect nomenclature creates confusion about the structure of a phase and shape of its constituting molecules because it is the molecule that is discotic and not the mesophase which may be nematic, columnar or lamellar.

Lytotropic mesophases are formed of amphiphilic compounds. It has two chemically incompatible parts: one or more hydrophobic hydrocarbon tails and hydrophilic head for example salts of fatty acids and phospholipids e.g. salts of fatty acids and phospholipids. When the molecules are dissolved in polar solvent in sufficiently high concentrations above the cmc (critical micelle concentration), they self assemble such that the non-polar hydrophobic tails are protected by the polar hydrophilic heads. In a non-polar solvent, the self aggregation is of opposite type. Entropically driven hydrophobic effect helps in micelle formation. Lehman first reported ammonium oleate amphiphilic (lyotropic) compounds.47
Lyotropic liquid crystalline materials are important for biological systems e.g. membrane as well as used in display devices.\textsuperscript{48-50}

1.3 Metallomesogens

Metal complexes containing organic ligands that exhibit liquid crystalline properties are known as metallomesogens. It is relatively a new area of research in the field of liquid crystals. Research in the field of metallomesogens is rapidly developing over the past 25-30 years.\textsuperscript{51} The wide range of coordination numbers and geometries that can be accessed through the metal ion along with a large number of known organic ligands opens up opportunities for building mesogenic materials of new geometric designs.\textsuperscript{52} From literature, it is found that many thermotropic metallomesogens have been made using various metals including s-, p-, d- and even f-block elements.\textsuperscript{1,2,3,53} Both rodlike (calamitic) and disklike (discotic) thermotropic metallomesogens have been reported. Different types of ligands can be used: monodentate, bidentate or polydentate. Ligands help in determining the mesophase character. The requirement of a
metallomesogen is a rigid core, normally unstaturated, bearing long hydrocarbon chain. With the incorporation of d-block metals it acquires properties like colour, paramagnetism etc. Special characteristic of having long and polarizable concentration of electron density that every metal atom possesses imparts a profound effect since the molecular polarizability is a key factor in determining whether a molecule will form liquid crystal. In 1910, Vorlander et al. first reported metal containing thermotropic liquid crystal. They reported that the alkali metal carboxylates, R(CH$_2$)$_n$COONa formed classical lamellar phases characteristic of soap. In 1923, Vorlander reported that the diarylmercurials (Figure 5.1) form smectic phases.

![Figure 5.1 Diarylmercurials complex](image)

Giroud and Muller-Wasterhoff, for the first time carried out the systematic study on d-block metallomesogens by observing dithiolene complexes of Ni(II), Pd(II) and Pt(II) (Figure 5.2).

![Figure 5.2 Dithiolene complexes of Ni(II), Pd(II) and Pt(II)](image)
In 1976, Malthete and Billard synthesized the smectic ferrocenyl Schiff base which was the first well characterized organotransition metallomesogen (Figure 5.3).57

\[
\begin{array}{c}
\text{Fe} \\
\text{C}_{n}H_{2n+1}
\end{array}
\]

**Figure 5.3** Ferrocenyl Schiff base complex

Phthalocyanines, a class of disc like molecules, were the first type of discotic metallomesogens showing columnar mesophases.58–62 Discotic metallophthalocyanines are used as one dimensional conductors and also have other potential applications. Another mesogenic complex based on β–diketonates, bis(1-octyloxyphenyl-1,3-butanedionato)palladium(II) was first prepared by Bulkin et al. in 1977 (Figure 5.4).63

\[
\begin{array}{c}
\text{R} \\
\text{O} \\
\text{Pd} \\
\text{O} \\
\text{O} \\
\text{H}_{2n+1} \\
\text{C}_{n}
\end{array}
\]

**Figure 5.4** First mesogenic complex based on β–diketonates

Ohta et. al. reported a series of disk like β–diketonate complexes which exhibited columnar mesophases.64–67 In 2011, Bhattacharjee et. al. reported a new series of non-disk like Schiff base complexes of Zn\(^{II}\) of the type \([\text{Zn}(4-C_{n}H_{2n+1}O)_{2}\text{salophen}]\) (salophen = N,N′-phenylenebissalicylideneiminato) (Figure 5.5) that exhibited columnar mesomorphism where \(n=\)
14, 16 or 18.\textsuperscript{68} These complexes were reported to be stable down to room temperature. Zinc (II) luminescent mesomorphic complexes with ‘salen’ type asymmetric Schiff base ligands and their aggregation behavior was also detailed by them recently.\textsuperscript{69}

![Figure 5.5 Zn(4-C\textsubscript{n}H\textsubscript{2n+1}O\textsubscript{2}salophen) complex](image)

Bhattacharjee \textit{et. al.} also reported a series of non-mesomorphic and non-luminiscent tetradeutate salicylaldimine ligands which upon coordination to nickel(II) forms mesogenic complexes with columnar rectangular structures and the complexes showed intense fluorescence both in solid state and in solution (Figure 5.6).\textsuperscript{70}

![Figure 5.6 Ni(II)-salphen complex containing differently substituted salicylaldimine ligands (X= H, CH\textsubscript{3}, NO\textsubscript{2})](image)
Another prominent leap in this field was also reported by Bhattacharjee et. al with a series of lanthanide(III) complexes (lanthanidomesogen) of the type \([\text{Ln}(\text{LH})_3(\text{NO}_3)_3]\) (Ln = La, Pr, Sm, Gd, Tb, Dy; \text{LH} = (E)-5-(hexyloxy)-2-\{2-\{2-\text{hydroxyethylamino}\text{ethylimino}\text{methyl}\}\text{phenol}\} \) (Figure 5.7). The ligand and complexes were both liquid crystalline and photoluminous. These complexes exhibiting lamello-columnar mesomorphism were reported to be the first of their kind.

![Figure 5.7](image)

**Figure 5.7** \([\text{Ln}(\text{LH})_3(\text{NO}_3)_3]\) complex

**Copper complexes as catalysts in oxidative transformations**

Copper exists in various metalloprotiens specially in enzymes like galactose oxidase, laccases, hemocyanin, superoxide dismutase and cytochrome c oxidase. These enzymes are very important in different bio-oxidation reactions. So various research groups pay particular attention on copper in catalyst designing particularly with an eye on their catalytic behaviour in oxidation. Chemists found copper catalysis very much fascinating due to reasons like it is very cheap compared to metals like palladium, ruthenium etc., its wider availability, low toxicity, efficiency in cross-coupling reactions similar to palladium and also because it possesses unique chemoselectivity and reactivity. The development of highly active copper catalyst for the selective oxidation
of alcohols with air is a challenging topic in chemistry today. Mostly in homogeneous copper catalysis, ligands with nitrogen donor atoms are used but in few exceptions oxygen serves as the donor atom.

### 1.4.1 Ligand-assisted copper catalysts

In 1977, Jallabert et al. first reported a ligand assisted copper system for oxidation of alcohols. The simple Cu complex of pyridine and 1,10-phenanthroline oxidizes alcohols to aldehydes with O₂ as oxidant (Scheme VI).

\[
\begin{align*}
R_1 (\text{or } H) \quad & \quad \text{2 eq. CuCl/L, 2 eq. K₂CO₃} \quad & \quad \text{2 eq. } \text{O₂, Benzene, reflux} \quad & \quad R_1 (\text{or } H) \\
\text{R} \quad & \quad \text{OH} \quad & \quad \text{O} \quad + \quad \text{H₂O} \\
\end{align*}
\]

\[\text{R} = \text{Alkyl or ARYL} \quad \quad \text{L} = \text{pyridine or} \quad 1,10\text{-phenanthroline} \]

**Scheme VI**

Cu–phenanthroline complex is a more efficient catalyst, giving 83-86% aldehyde, than the Cu-pyridine complex which gives only 35-56% aldehyde. But disadvantage of this system was that two equivalents of the copper complex had to be used at an elevated temperature (112°C) in highly basic conditions (2 eq. of K₂CO₃). After two decades phenanthroline assisted copper system was modified by adding di–tert–butylazohydrazine (DBADH₂) (Scheme VII).²² It enhanced the rate and total turn over number (TON) of the reaction.

\[
\begin{align*}
R_1 (\text{or } H) \quad & \quad 5 \text{ mol% CuCl, 5 mol% phen, 2 eq. } \text{K₂CO₃} \quad & \quad 5 \text{ mol% DBADH₂, } \text{O₂, toluene, 70-90°C} \quad & \quad R_1 (\text{or } H) \\
\text{R} \quad & \quad \text{OH} \quad & \quad \text{O} \quad + \quad \text{H₂O} \\
\end{align*}
\]

**Scheme VII**
This method is universal for the oxidation of benzylic, allylic, primary and secondary alcohols but it also requires high amount of catalyst as well as base and additives. K$_2$CO$_3$ is insoluble in toluene and the active catalyst is absorbed on solid base. So the system is heterogeneous. Later, Cu–bipyridine (bipy) in aqueous solution has also been investigated.\textsuperscript{73} The catalytic activity of Cu with another N containing ligand like tetramethylethlenediamine (TMEDA) is also known.\textsuperscript{74} A bipy–assisted Cu system was developed in 1993 where two equivalents of base in an O$_2$ saturated MeCN solution was required to achieve efficient alcohol oxidation to the corresponding carbonyl compound.\textsuperscript{75} Although with benzyl alcohol, the reaction reached 80\% completion in 1 hour, but the oxidation reaction essentially stops after 20–80 (TON) because of the formation of a red solid, which is Cu$_2$O. In an another bipy–assisted Cu system for aerobic oxidation of alcohols in absence of a strong base better results had been found in MeCN solution at 60\(^\circ\)C.\textsuperscript{76} So, ligands affect the catalytic activity of Cu–complexes and bipy exhibits higher activity than other ligands. In most of the cases, benzylic alcohols are more easily oxidized than aliphatic alcohols and primary alcohols are more reactive than their secondary isomers.

1.4.2 TBHP mediated copper systems

There are very few reports on metal catalysed oxidation of alcohols using tert-butyl hydroperoxide (TBHP) as the primary oxidant. By using an aqueous-organic two-phase system and in the presence of quaternary ammonium phase-transfer catalysts, copper complexes become active catalyst precursors for the TBHP oxidation of alcohols. Using catalytic amounts of CuCl$_2$ and a phase transfer catalyst such as $n$-Bu$_4$N$^+$Br$^-$ (TBAB), a smooth oxidative dehydrogenation of alcohols to corresponding carbonyl compounds was observed with 70\% aqueous TBHP (Scheme VIII).\textsuperscript{77} Good conversions
and excellent selectivities were observed for various substrates. Primary and unactivated alcohols could also be oxidized but yields were lower.

![Reaction Equation]

Scheme VIII

Ferguson et al. reported\textsuperscript{78} a water soluble catalytic system composed of CuCl\textsubscript{2} and 2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt (BQC) in solvent-free conditions for the oxidation of alcohols in presence of TBHP as the oxidant. The catalytic system was found to be highly efficient for the selective oxidation of secondary benzylic, allylic and propargylic alcohols to the corresponding ketones. Furthermore, the catalytic system was stable and can be recycled and reused several times without the loss of activity. Mannam et al. also reported direct oxidation of primary alcohols to carboxylic acids with anhydrous TBHP at room temperature in the presence of a catalytic amount CuCl under ligand free condition in acetonitrile reported.\textsuperscript{79} Recently, our group has successfully developed an efficient catalytic system for oxidation of alcohols to the corresponding aldehydes and ketones using a few copper(II) tetracarboxylate dimers in combination with aqueous TBHP as the source of oxygen.\textsuperscript{9} This catalytic system requires a very small amount of the catalyst (0.5 mol\%) and no additives are needed (Scheme IX).

![Reaction Equation]

Scheme IX

\( R_1 = \text{aryl or alkyl} \)
\( R_2 = \text{H or alkyl or aryl} \)
1.4.3 TEMPO mediated copper systems

In 1966, the TEMPO(2,2,6,6-tetramethylpiperidine-N-oxyl)-Cu system for aerobic oxidation of MeOH to formaldehyde was first developed. Two decades later, ligand free TEMPO mediated Cu system for the aerobic oxidation of alcohols was reported where 10 mol% CuCl and 10 mol% TEMPO were used in DMF under an O₂ atmosphere at 25 °C to oxidize benzylic, allylic and aliphatic alcohols to their corresponding carbonyl compounds (Scheme X).

After optimizing the reaction conditions for the Cu-TEMPO system (Scheme X), secondary alcohols were oxidized with significantly lower rates compared to primary alcohols. Later, several studies on Cu and TEMPO system for aerobic oxidation of alcohols to aldehydes have been reported. In 2002, a CuCl–TEMPO catalytic system in ionic liquid rather than any traditional organic solvent was developed for aerobic oxidation of alcohols (Scheme XI).

Early reports on Cu-TEMPO catalysis for oxidation of alcohols to aldehydes assisted by bipy as a ligand and N-methylimidazole as an additive in MeCN are also
encouraging. However, in all cases, oxidation requires additives such as a base and/or co-solvent and the use of at least 5 mol% catalyst.

1.5 Aims and Objectives of the Present Thesis

From literature it is evident that the synthesis, structure and properties of many copper(II) carboxylates and their complexes especially with nitrogen donor ligands have already been widely studied and the results were published in several reports. However, only a few crystal structures with Copper(II) carboxylates containing long alkyl chains have been reported. Therefore, our aim was to prepare a few such complexes because there is a lot to explore in this field of research. Particularly, investigations on long chain carboxylates of copper as the active catalyst in various oxidation reactions are very rare. Presence of longer alkyl chains in the complexes is expected to make these compound more soluble in less polar organic solvents and thus it may be expected that such systems will be more effective as selective, molecular homogenous catalysts. We intend to expand this catalytic activity by using long chain copper(II) carboxylate complexes as the catalysts, precursors for oxidative transformations under aerobic conditions reducing the use of additives in a harmless solvent.

Presence of long chain alkyl groups in the carboxylato ligands is also expected to impart mesogenic characteristics to the copper(II) complex under study, particularly based on the identification of thermotropic columnar mesophases in several metal complexes containing long chain alkyl chains as part of the ligands. Establishing liquid crystalline behaviour through studies on a well studied class of metal complexes-Cu₂(µ-O₂CR)₄L₂ is a rather exciting option because liquid crystallinity in this system may potentially be tuned by making deliberate changes in R and L to finally produce one more
desirable advanced material, characterized by multiple properties including mesogenicity and magnetism.

1.6 References


34 Lever, A. B. P. *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, **1984**.


