Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study

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IN

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By

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Certificate

*This is to certify that the thesis entitled **"Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study"** is an authentic record of research work carried out by Ms. Manju Sebastian under my supervision, in partial fulfillment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part there of has been presented before for any other degree.*

Kochi

16-07-2010

Dr. K.K.Mohammed Yusuff

(Supervisor)

Declaration

I hereby declare that the work presented in this thesis entitled "**Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study**" is entirely original and was carried out by me independently under the supervision of Dr. K. K. Mohammed Yusuff (Former Professor of Catalysis, Department of Applied Chemistry, Cochin University of Science and Technology) and has not been included in any other thesis submitted previously for the award of any other degree.

Kochi-22   **Manju Sebastian**

16-07-2010

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Preface

Schiff base complexes of transition metal ions have played a significant role in coordination chemistry. The convenient route of synthesis and thermal stability of Schiff base complexes have contributed significantly for their possible applications in catalysis, biology, medicine and photonics. Significant variations in catalytic activity with structure and type are observed for these complexes.

The thesis deals with synthesis and characterization of transition metal complexes of quinoxaline based Schiff base ligands and their catalytic activity study. The Schiff bases synthesized in the present study are quinoxaline–2–carboxalidine–2–amino–5–methylphenol, 3–hydroxyquinoxaline–2–carboxalidine–2–amino–5–methylphenol, quinoxaline–2–carboxalidine–L–histidine and 3–hydroxyquinoxaline–2–carboxalidine–2–aminothiophenol. They provide great structural diversity during complexation. To the best of our knowledge, the transition metal complexes of quinoxaline based Schiff bases are poorly utilised in academic and industrial research.

The thesis is divided into seven chapters. Chapter 1 gives a general introduction to the topic of research carried out. Chapter 2 provides the details about experimental techniques used in the current study and the synthesis of the aldehydes. Chapters 3-6 deal with the synthesis and characterization of new quinoxaline based Schiff bases and their complexes. We could isolate single crystals of two complexes. The single crystal XRD of these complexes has been carried out. The results show that the molecules exhibit a two dimensional layer like structure and similar complexes are promising building blocks for supramolecular architectures. For all the other complexes, analytical and spectroscopic data have been used to arrive at the tentative structure of the complexes. We hope that similar type of layer like structures may exist for these complexes also. Chapter 7 deals with the studies on the application of the

synthesized complexes as catalyst towards few oxidation reactions. There is a current interest in developing catalysts with high activity and selectivity for the oxidation of organic compounds. We have studied the catalytic activity of the synthesized complexes in phenol hydroxylation, cyclohexane oxidation and benzyl alcohol oxidation using the environmentally friendly oxidant hydrogen peroxide. Benzyl alcohol oxidation was carried out in solvent free condition aiming at a greener reaction. We hope that the studies presented in the thesis would be useful to those working in the field of metal complex based catalysis in industries and academia.

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Chapter 1

Introduction

Today coordination chemistry comprises a large body of inorganic chemistry research. It is mainly the chemistry of metal complexes and has fascinated and inspired the chemists all over the world. There is an ever increasing academic, commercial and biochemical interest on the metal complexes of organic chelating ligands. This has resulted in the emergence of allied fields like organometallic chemistry, homogeneous catalysis and bioinorganic chemistry. Among the chelating ligands, Schiff bases have attracted the attention of chemists due to the ease of preparation and complexation. Schiff bases contain the azomethine group (–RC=N–) and are usually formed by the condensation of a primary amine with an active carbonyl compound. They are stable and can tune the ligational aspects by varying denticity and basicity. Metal Schiff base complexes have been known since the mid nineteenth century [1] and even before the report of general preparation of the Schiff base ligands [2]. Intensive research on the physicochemical properties and molecular structure of complexes with Schiff bases has provided interesting new results, which need to be surveyed and compared with earlier literature on these types of compounds.

1.1 CHEMISTRY OF SCHIFF BASES

In 1864, German chemist Hugo Schiff developed a new class of organic compounds [2, 3]. This group of compounds, imines, are often referred to as Schiff bases in his honour. The preparations of these compounds are simple and smart. They are prepared by condensing a carbonyl compound with an amine, generally in refluxing alcohol. The active and well-designed Schiff base ligands are considered as ''privileged ligands'' by Cozzi [4]. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Several studies [5-8] showed that the presence of a lone pair of electrons in a sp^2 hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Ligands containing sp^2 hybridized nitrogen atoms, particularly those in which the N-atom is a part of the aromatic system, show very extensive coordination chemistry [9-11]. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are considered as excellent chelating agents, [12, 13] especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered chelate ring with the metal ion. Details regarding the preparation of Schiff bases and their metal complexes are spread out in the literature. The general scheme of formation of a Schiff base is given in Figure 1.1.
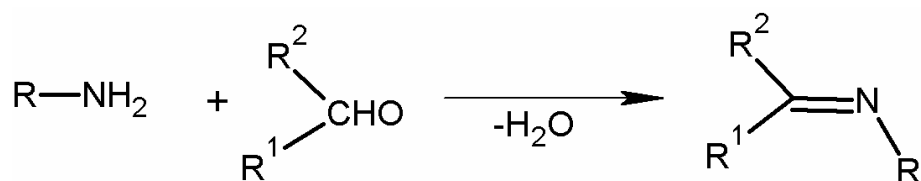
Figure 1.1: *Formation of Schiff base by condensation reaction (R groups may be variously substituted)*

Like aldehydes, the ketones are also able to form Schiff base ligands. However, Schiff base ligands with ketones are formed less readily than those with aldehydes. Schiff bases of aliphatic aldehydes are relatively unstable and readily

polymerizable [14]. In 1931, Dubsky and Sokol [15] isolated N-N'-bis (salicylidine ethylenediamino)copper(II) and nickel(II) complexes, which led to the formation of a new group of ligands called salen. The salen ligands are often the ligands of choice for several reasons. They are multidentate with four binding sites which form complexes with or without vacant sites for potential catalytic and enzymatic activity. Furthermore, substitution at the aromatic ring can modify the electronic and steric properties of the resulting complexes. In the review on metal complexes of Schiff bases by Holm *et al.*, more than half of the referred complexes are derived from salicylaldehyde [7].

1.1.1 Formation of Schiff bases

Condensation between aldehydes and amines are carried out in different reaction conditions, and in different solvents. The common solvents used for the preparation of the Schiff base are methanol or ethanol. Schiff base formation occurs either at room temperature or in refluxing conditions. The presence of dehydrating agents like magnesium sulphate normally favours the formation of Schiff bases. The water produced in the reaction can also be removed from the equilibrium mixture using a Dean Stark apparatus, if the syntheses are carried out in toluene or benzene. Degradation of the Schiff bases may occur during the purification step. Chromatography of Schiff bases on silica gel can cause some degree of decomposition of the Schiff bases through hydrolysis. In such cases, it is better to purify the Schiff bases by crystallization. In general, Schiff bases are stable solids and can be stored without precautions. A large series of Schiff bases could be easily prepared as there is enough scope for variying the amines and the aldehydes. The mono-, di-, tri- and multi- dentate chelating Schiff base ligands are designed according to the binding environments of metal ions. The preparation of Schiff bases and their complexes can be carried out by the following methods:

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a. Direct ligand synthesis followed by complexation:

In this method, the isolation and purification of Schiff bases are carried out before complexation. The complexes are then prepared by treating the metal ion and Schiff bases. One of the advantages of this method is that it is possible to perform the spectral characterization of complexes by comparing with the spectral data of the ligands.

b. Template synthesis:

In this method, the syntheses of complexes are carried out without the isolation of Schiff bases by interacting aldehyde, amine and the metal compound in a one step reaction [16-20]. The template reaction is illustrated in Figure 1.2. The metal ions catalyze the reaction by acting as a reaction template. Busch has defined template as the chemical species, which "*organizes an assembly of atoms, with respect to one or more geometric loci, in order to achieve a particular linking of atoms*" [21]. Template synthesis has been used to prepare assemblies that have unusual topologies, such as rotaxanes, helicates, macrocycles and catenanes [22]. Therefore, a templating agent can be said to contain the required information to organize a collection of building blocks so that they can be linked together in a specific manner. There are two types of templated processes: thermodynamic and kinetic. In the former, the template binds to one of the reactant and shifts the equilibrium towards the formation of the product. In the case of kinetic processes the templates operate under irreversible conditions stabilizing all the transition states leading to the formation of the wanted product. In many of the kinetically controlled reactions, the template is strongly bound to the final species. In these cases it acts not only as a kinetic template, but also as a thermodynamic one. In practice, it is often very difficult to unambiguously determine whether a template reaction is kinetically or thermodynamically controlled. Gimeno *et al.* in their review considered a template as any species that organizes an assembly of

molecular building blocks by non-covalent interactions favoring the formation of a specific product [23].
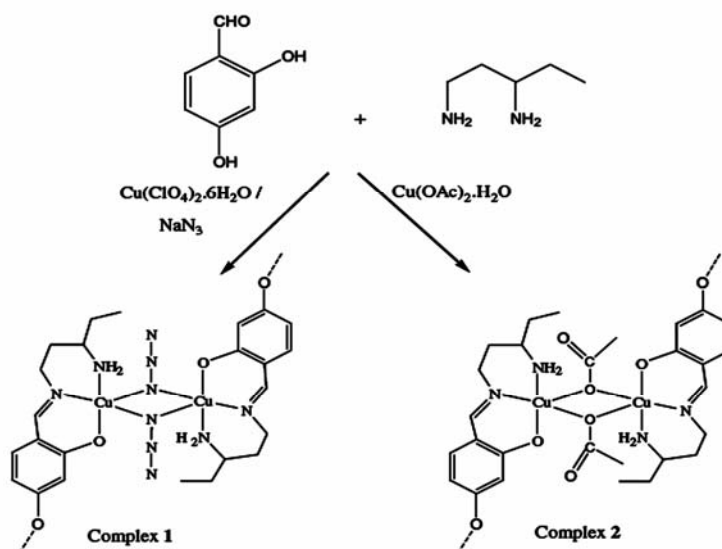
Figure 1.2: *Formation of bridged dinuclear copper(II) Schiff base complexes by template method (Adopted from Ref. 19)*

c.   Rearrangement of heterocycles (oxazoles, thiazoles etc.):

The direct approach in synthesizing a Schiff base from the condensation of an o-hydroxy-, o-amino- or o-mercaptoamine with a carbonyl compound often results in the undesirable side reaction involving ring closure with the formation of a heterocyclic compound [24, 25]. The solution to avoid this problem, which was first used by Schiff in 1869, is to prepare the Schiff base in the form of its metal chelate by reacting the metal complex of one of the starting materials (aldehyde or amine) with the other one [26]. Benzothiazoline and benzoxazole ring are reported to open in specific environments in presence of metal ions, and rearrangement of the ring leads to the formation of corresponding metal chelates of the Schiff bases. Figure 1.3 illustrates such a ring opening complexation reaction reported by Duatti *et al.* [25]

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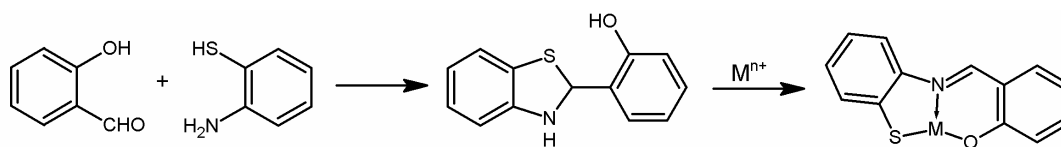
Figure 1.3: *2-(2-Hydroxyphenyl)benzothiazoline: (a) synthesis; (b) interaction with metal ion (Adopted from Ref.25)*

1.1.2 Denticity and basicity of Schiff bases

Ligands are classified according to the number of donor atoms contained and are known as uni, di, tri, or quadridentate ligands. When donor sites of a ligand occupy two or more coordination positions on the same central metal ion, a complex possessing a closed ring is formed. The phenomenon of ring formation is called chelation and ring formed is called chelate ring. The term 'chelate' was first introduced in 1920 by Morgan and Drew. Schiff bases primarily possess nitrogen donor atoms, though many can act as bi-, tri-, tetra- or polydentate mixed donor capabilities as shown in Figure 1.4. In general, the donor nature of the ligands depends both on the type of aldehyde/ketone used and the nature of primary amine/diamine.
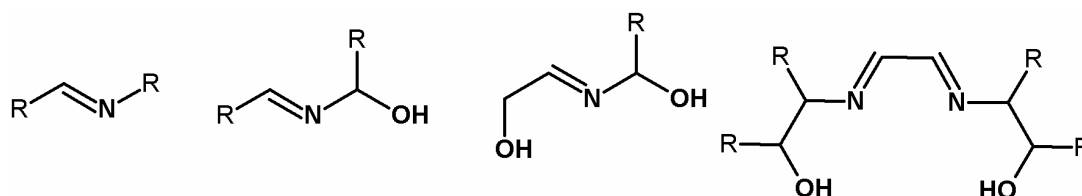
Figure 1.4: *Schiff bases of variying denticity; monodentate to tetradentate, R groups may be variously substituted*

A large number of tetradentate Schiff base ligands are reported in literature. Majority of them are derived from salicylaldehyde and 1,2-diamines (Figure 1.5). The ONNO donor Schiff bases form a family of compounds, salen or salophen, which possess a wide variety of applications [4]. Similarly there are a good number of reports on tridentate Schiff bases [27-30]. They may be of ONN, ONS, ONO, NNS or NNN donors. The tridentate ligands can tune the formation of complexes and these Schiff base complexes have found various applications in medicines such

as antibacterial agents, local anaesthetics, antiviral agents and antispasmodics [31, 32].
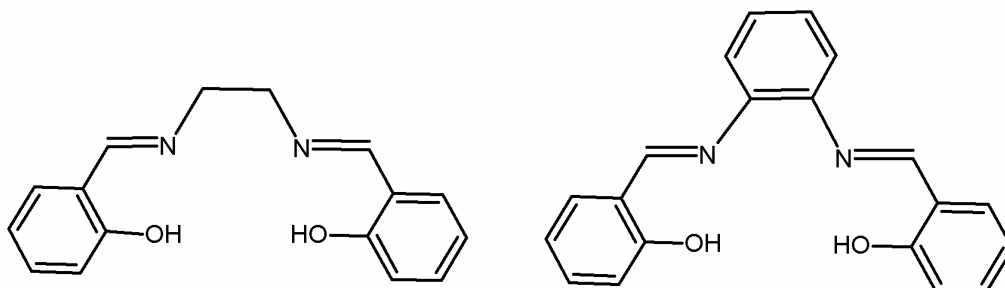
Figure 1.5: *Tetradentate Schiff base family salen and salophen*

For several reasons, Schiff bases have been found to be the most convenient and attractive ligands for forming complexes. First, steric and electronic effects around the metal core can be finely tuned by an appropriate selection of bulky and/or electron withdrawing or donating substituents incorporated into the Schiff bases. Secondly, the two donor atoms, N and O, of the chelated Schiff base exert two opposite electronic effects: the phenolate oxygen is a hard donor and stabilizes the higher oxidation state of the metal atom; whereas the imine nitrogen is a boarderline donor and stabilizes the lower oxidation state of the metal ion [33]. Thirdly, Schiff bases are currently prepared in high yield through one-step procedures via condensation of common aldehydes with amines, in practically quantitative yields. While sulphur donor ligands, being soft bases, prefer to combine with late transition elements and with metal ions in lower oxidation state, the ONS donor Schiff bases can show symbiosis [34]. The presence of soft sulphur atom softens the hardness of the oxygen atom, and this enables such ligands to form a large number of complexes with structural diversity.

The basicity of the Schiff bases also plays a key role in the formation and stabilisation of the complexes. The –OH or –SH groups present in the Schiff bases can induce tautomerism in the compound, which leads to complexes with different structures. A large number of salen complexes shows keto-enol tautomerism. Also

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the deprotonation of thiolic, alcoholic and phenolic groups are favoured due to the stabilisation of various oxidation states of the central metal ion.

1.1.3 Applications of Schiff bases and their metal complexes

Versatility of Schiff base ligands and the biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable. The applications of the Schiff bases and their complexes are discussed here briefly:

1.1.3.1 Catalytic applications

In Schiff base metal complexes, the environment at the coordination center can be modified by attaching different substituents to the ligand and a useful range of steric and electronic properties essential for the fine-tuning of structure and reactivity can thus be provided [35-37]. The Schiff bases form metal complexes with p-block and d-block metals and these complexes have been known to act as highly efficient catalysts in various syntheses and other useful reactions [38-42]. Many Schiff base complexes of ruthenium and palladium are used as catalyst in the syntheses of quality polymers. Unique asymmetric catalysis of metal complexes of salen and the related Schiff-base ligands has been reviewed by Katsuki [43]. The review summarises the generation of *cis* metallo-salen and its related complexes, their structural features, and their application to asymmetric syntheses. Wang *et al*. in 1999 reported the effective oxidation of olefins using Mn(II) amino acid Schiff base complexes [44]. Gupta and Sutar reviewed the catalytic activities of transition metal complexes-both simple and polymer anchored. They have highlighted the potential of Schiff base complex as catalyst towards oxidations, hydrogenations, polymerizations, various coupling reactions and ring closures [45, 46]. Heterogenization of homogeneous catalysts has recently attracted the attention of chemists due to better selectivity and recyclability of the catalysts. In recent years there is an exponential increase in the number of publications in catalysis by supported Schiff base complexes. However, homogeneous catalysis is more

relevant as the mechanism of the reaction can be arrived. BINAP ligands (BINAP is the abbreviation for the organophosphorus compound 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) are famous for their stereoselective transformations. Che and Huang [47] have reviewed the catalytic activity of chiral BINAP Schiff base complexes in stereoselective organic transformations. Their studies reveal that these types of chiral metal complexes are active catalysts for stereoselective organic transformations including hydroxylation of styrene, aldol reactions, alkene epoxidation, trimethylsilyl cyanation of aldehydes, desymmetrization of *meso-N*-sulfonylaziridine, Baeyer-Villiger oxidation of aryl cyclobutanone, Diels-Alder reactions of 1,2-dihydropyridine, and ring-opening polymerization of lactide. A discussion on the catalytic reactions carried out in the present investigation is given in section 1.3.

1.1.3.2 Biological and medicinal applications

Many ligands have been designed to mimic the function of natural carriers in recognizing and transporting specific metal ions, anions or neutral molecules and in understanding and reproducing the catalytic activity of metallo-enzymes and proteins [29]. Schiff bases are known to be important intermediates in many enzymatic reactions involving interaction of an enzyme with an amine or carbonyl group of the substrate [48]. One of the most prevalent types of catalytic mechanism in enzyme is usually that of a lysine residue with a carbonyl group of the substrate to form an imine or Schiff base. Similarly the biosynthesis of porphyrin, for which glycine is a precursor, which involves the intermediate formation of a Schiff base, is another important pathway. Synthetic chemists are interested in studiying the efficiency of the biosynthetic machinery by designing biomimetic reactions that approximate natural reaction pathways. Probably the most astonishing biomimetic reactions are the ones, which combine several transformations in sequence and produce complicated structures from comparably simple starting materials, in a simple laboratory operation. In such a simple method, Matsumoto *et al.* [49] used Co(II), Mn(II) and Fe(II) complexes of salen as catalyst for the synthesis of

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carpanone in good yield by the oxidation of trans-2-(1-propenyl)-4,5-methylenedioxyphenol with molecular oxygen. The Schiff bases derived from pyridoxal and amino acids are extensively studied and are considered as very important ligands from the biological point of view [50-54]. Transition metal complexes of such ligands might work as important enzyme models.

Schiff bases can accommodate different metal centres involving various coordination modes allowing successful synthesis of homo- and heterometallic complexes with varied stereochemistry. This feature is employed for modelling active sites in biological systems [55]. Morrow and Kolasa reported the cleavage of plasmid DNA by square planar nickel-salen in the presence of either magnesium monoperoxypthalic acid (MPPA) or iodosylbenzene [56]. According to cell biologists deoxyribonucleic acid (DNA) is the primary target molecule for most anticancer and antiviral therapies. Investigations on the interaction of DNA with small molecules are important in the design of new types of pharmaceutical molecules. In the 1980s the chemical nuclease activity of transition metal complexes was discovered and is recently used extensively in bioengineering. Literature search reveals that a large number of Schiff base complexes are excellent DNA cleavagers [57-61]. The metal DNA interaction is described in detail by Hadjiliadis and Sletten in their book: 'Metal complexes-DNA interaction' [62]. A number of research groups are actively engaged in developing new therapeutic reagents and DNA probes from transition metal Schiff base complexes. Silveria *et al.* used oxindazole Schiff base complexes of copper(II) for the cleavage of double stranded DNA and the potency of the complex as anti tumour agent was also explored [63].

Almost all transition metal complexes of Schiff bases show good antibacterial, antiviral, antimalarial and antitubercular activity [64-67]. The potent biological activity can be related to the presence of nitrogen atom with a lone pair of electron in it so that the nitrogen can participate in hydrogen bonding with NH or OH groups present in biomolecules like amino acids, proteins, DNA or RNA.

1.1.3.3 Applications as fluorescent and electronic materials

Zinc(II) Schiff base complexes have been shown to be effective emitters. Recently Zhou *et al.* [68] reported the Schiff base 2-(hydroxymethyl)-4-methyl-6-((quinolinyl-8-imino)methyl)phenol and its zinc(II) complex (Figure 1.6). The complex acts as a visual and fluorescent sensor. The electron transfer from the nitrogen atom of the heterocycle to the metal ion enhances the internal charge transfer (ICT) process. As a result, a red-shift in emission wavelength can be observed which is also favoured by the strong binding of the zinc. Nowadays there is an increasing interest in the development of fluorescent sensors for the enantioselective recognition of chiral organic compounds and drug molecules [69, 70].
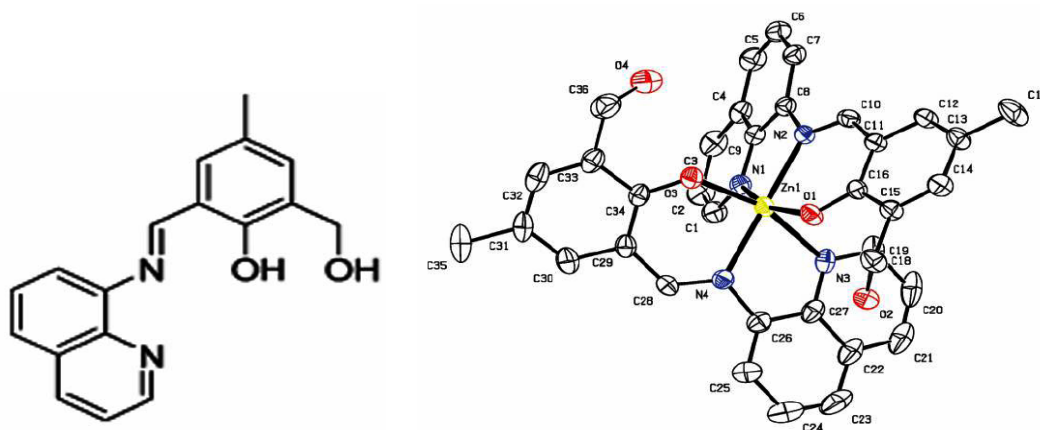
Figure 1.6: *Structure of the Schiff base, 2-(hydroxymethyl)-4-methyl-6-((quinolinyl-8-imino)methyl)phenol, and its zinc(II) complex (Adopted from ref. 68)*

Banerjee *et al.* [71] developed a highly enantioselective fluorescent sensor from the chiral Schiff base, 4-methyl-2,6-bis-[(2-hydroxy-1-phenylethylimino) methyl] phenol. It acts as highly enantioselective fluorescent agent for α-hydroxycarboxylic acid, e.g., mandelic acid. They observed that, within a certain concentration range, one enantiomer of the chiral acid increases the fluorescence intensity of the Schiff-base compound by 122-fold, while the other enantiomer

enhances the intensity only by 42-fold. Such highly enantioselective responses towards the chiral acid make the Schiff-base compound attractive as a fluorescent sensor for determining the enantiomeric composition of α-hydroxycarboxylic acids. Similarly there are a number of reports in which Schiff base complexes find application as active fluorescent sensors [72-75].

Cozzi *et al.* reviewed the photophysical properties of the Schiff base complexes with several metal ions [76]. They evaluated the photophysical properties of salen complexes for possible use in the luminescent probes. Mixed valence Schiff base complexes are considered as functional materials for optoelectronics and molecular magnets. The salicylidene Schiff base derivative, *N*-salicylidene-(*S*)-α-naphthylethylamine, has been used for making multistate/ multifunctional switches by Zhao *et al.* [77]. Wei *et al.* [78] prepared blue luminescent zinc and beryllium complexes of Schiff bases derived from calixarene. These Schiff bases complexes have good solubility in normal solvents and can easily form thin films. Some of the Schiff base complexes may find application in the development of new molecular switches. In NLO studies, transition metal complexes are of more importance than conventional organic compounds due to the intense charge transfer transition and the possible donor acceptor capabilities.

1.1.3.4 Other applications

Many Schiff base compounds are found to be good corrosion inhibitors. Emregül and Atakol [79] studied the corrosion behavior of iron in 2 M HCl solution at 298 K with three Schiff base compounds and found that these compounds have the perfect inhibition efficiency. Literature survey reveals an increased attention to Schiff base compounds as corrosion inhibitors especially in acidic environments for various metals like steel, aluminum and copper [80-85]. Organocobalt complexes with tridentate Schiff base act as inhibitor of emulsion polymerization and copolymerization of dienyl and vinyl monomers.

Chromium [86] and cobalt Schiff base complexes [87] have been used as dyes which give fast colour to leather, food packages and wools. Cobalt complexes of a salen type Schiff base have excellent light resistance and storage ability and resist degradation even in acidic gases like CO_2. Tetradentate Schiff bases like salens and salophens act as chromogenic reagent for determination of nickel in some natural food samples [88].

1.2 QUINOXALINE SCHIFF BASES

Quinoxalines, also called benzopyrazines, are heterocyclic compounds containing a fused ring made up of a benzene ring and a pyrazine ring. They along with the isomers cinnolenes, phthalazines and quinazolines belong to a class of heterocyclic compounds known as diazanaphthalenes with two heteroatoms in the same or different rings. The fusion of a benzene ring, however, causes decrease in the aromaticity due to the bond alternation (Figure 1.7). Quinoxalines have 10-π electrons that are located in five bonding molecular orbitals. There are also two non-bonding orbitals that lie in the molecular plane and are confined to the nitrogen atoms. Each of these orbitals contains an electron pair and these electrons are responsible for the basic properties of quinoxalines [89]. Quinoxaline can act as Lewis base, form metal complexes, and can participate in hydrogen bonding with hydrogen atoms present in electronegative atoms.
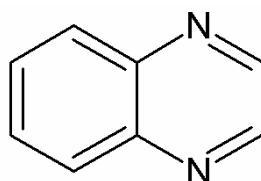
Figure 1.7: *Structure of quinoxaline*

Quinoxaline derivatives have been widely used in dyes, pharmaceuticals, and in electrical/photochemical materials. Quinoxaline ring moiety is a part of the chemical structures of various antibiotics such as echinomycin, levomycin and actinoleutin, which are known to inhibit growth of gram positive bacteria and are

active against various transplantable tumors. A number of synthetic strategies have been developed for the preparation of substituted quinoxalines. Quinoxalines are readily made from 1,2-dicarbonyl compounds and aromatic 1,2-diamines. A well-known route to quinoxalines is the reaction of o-phenylenediamine with a 1,2 – dicarbonyl compound [89]. Heravi *et al.* used Suzuki–Miyaura coupling (Figure 1.8) reaction for the synthesis of 2,3-disubstituted quinoxalines [90].
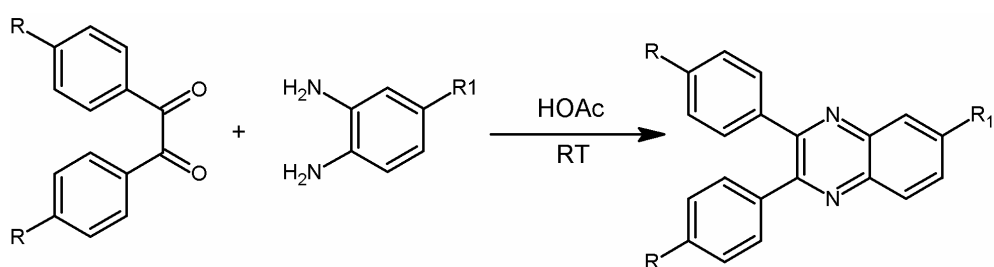
Figure 1.8: *Synthesis of quinoxaline by condensation of 1,2-dicarbonyl compound and orthophenylenediamines (Adopted from Ref. 90)*

Quinoxaline compounds show tautomerism if they have a hydroxy, thiolic or amino group at the ortho position. 2-Hydroxy- and 2-mercaptoquinoxalines exist in the quinoxalin-2-one and quinoxaline-2-thione forms, whereas 2-aminoquinoxaline exists as such rather than as an imine (Figure 1.9) in the solid state [89].
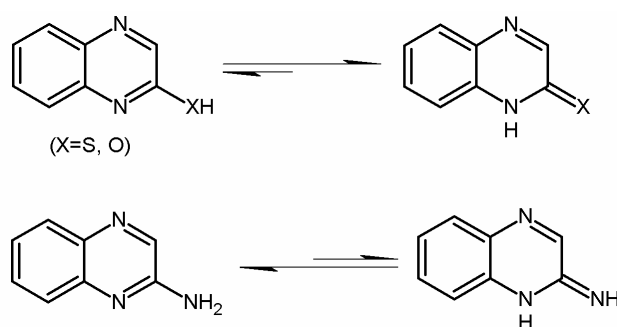
Figure 1.9: *Tautomerism in quinoxaline derivatives (Adopted from Ref. 89)*

Ovchinnikov and Muèller (1974) reported the possibility of linking of metal ions to heterocycles to form stable complexes, which permits the utilization of heterocyclic systems with pendant arms for modelling cation receptors in proteins [91, 92]. During the past several years, quinoxalines have been used effectively as building

blocks for metal-containing two dimensional networks [93]. Metal halides coordinate readily with quinoxalines to form interesting coordination polymers. Substituted quinoxalines, which have the potential to form novel three-dimensional structures upon coordination, have been synthesized. Quinoxaline heterocycles have attracted much attention owing to their natural occurrences [94] and biological activities [95]. Many quinoxaline derivatives display unusual solid-tumor selectivity against multi drug-resistant cancer cells. The synthetic utility and pharmacological importance of these compounds have prompted many scientists to synthesize and characterize novel quinoxaline derivatives [96, 97].

1.2.1 Transition metal complexes of quinoxaline Schiff bases

Complexes derived from quinoxalines have been reported in the literature [98-100]. The presence of quinoxaline ring helps in the formation of one dimensional structures and may provide potential supramolecular recognition sites for π–π aromatic stacking interactions to form high-dimensional supramolecular networks [101]. Schiff bases with an electron withdrawing heterocyclic ring system derived from quinoxaline-2-carboxaldehyde would be interesting as their ligand field strengths are expected to be weaker than the Schiff bases containing only aromatic rings, like naphthaldehyde [102-104]. Dong *et al.* in 2005 synthesized a silver(I) complex of quinoxaline diazine Schiff base and are found to form one dimensional and two dimensional network structure depending upon the counter ion [105]. Two series of transition metal complexes of Schiff bases formed by the condensation of quinoxaline-2-carboxaldehyde with semicarbazide, 2-aminophenol or furfurylamine were synthesised and characterised by Mayadevi *et al.* [104, 106] Sreekala *et al.* synthesized transition metal complexes of quinoxaline-2-carboxalidineglycene by adopting template method [107]. There are a couple of reports of formation of Schiff base complexes of diamines which contain quinoxaline moiety [104, 105, 108 and 109].

1.2.2 Applications of complexes of quinoxaline backbone

Quinoxaline is abundant in chemical and biological systems. Its derivatives appear in proteins and are extensively employed for modelling in biological applications, to electronic devices and materials. Quinoxaline derivatives are also used as analytical reagents in the determination of metal ions [110].

The quinoxaline-type ligands can act as either neutral or anionic chelators and, in addition, could possibly act as bridging ligands. This leads one to expect that these ligands will exhibit various coordination modes in metal complexes and it is even possible that they can function as controlling ligands in catalytic reaction.

The quinoxaline metal complexes are found to be more active than the free ligand and some side effects may decrease upon complexation. Numerous quinoxaline derivatives are important as biocidal agents, as these compounds have the ability to bind and cleave double stranded DNA under physiological conditions. They are used for genomic research and as diagnostic agents in medicinal applications [111-114].

Numerous quinoxalinoporphyrins have been electrochemically examined in recent years as models for the development of porphyrin-based molecular wires and devices [115]. Organic light-emitting devices (OLEDs) have received much attention because of their potential applications in flat-panel displays. Doping of a suitable dye into a host layer can improve both the efficiency and the stability significantly. Thus, there is great interest in the synthesis of dyes with desired properties, such as high emission quantum yield, high thermal and photochemical stability and good colour purity. Fluorescent molecules having quinoxaline building blocks usually display high electron affinities and good thermal stabilities, and also act as electron-transporting materials [116]. Quinoxalines have been successfully incorporated in polymers for use as electron-transport materials in multilayer OLEDs [117-120].

1.3 APPLICATIONS OF TRANSITION METAL SCHIFF BASE COMPLEXES AS CATALYST FOR ORGANIC TRANSFORMATIONS

Catalysis is an area of research which still continues to be a premier frontier area of chemistry. It plays a key role in modern chemical technology; in fact, it is the backbone of chemical industry. During the last decades, chemists shift their phenomenological approaches towards the structural and mechanistic investigation at the molecular level by a combination of instrumentation, quantum mechanical calculation and computational methods. This renovation has improved the understanding of catalysis.

There are a large number of important organic transformations such as oxidation, hydrogenation, hydroformylation, carbonylation, polymerization and various coupling reactions. The possibility of multiple oxidation states, accessibility of vacant coordination sites, tuning of the redox potentials by the ligand and the facility to undergo substitutions at the ligands, are one or more of the characteristics of transition metal complexes to behave as catalysts. But the major problems of homogeneous catalysis are the separation of the catalysts from the reaction medium. The procedure for separation of catalysts from reaction mixture generates large volumes of waste eluent and devours a lot of energy. However homogeneous catalysts are still attractive due to the very good activity and selectivity. The chemical and mechanical aspects of the homogeneous reaction can be studied. The catalyst can be easily modified for optimizing selectivity. Furthermore, these reactions need low temperatures and pressures.

There is a continuing interest in studies on the catalytic transformations by transition metal complexes. Information regarding their structure, environment of the metal atom, the number of ligands attached and the coordination changes during a reaction can be obtained proficiently. Thus design of catalysts, which lead to better selectivity, is possible. The generation of chirality on complexation is found to be worthwhile in asymmetric catalysis. Many Schiff base complexes show

excellent catalytic activity at reasonable temperatures *ie.* below 100 ºC. Similarly the activities of the complexes are varied by the changing the nature of the ligand.

Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis. Schiff bases are able to transmit chiral information to produce non racemic products through catalytic processes. For the preparation of such Schiff bases, either chiral aldehydes or chiral amines can be used. They are extensively used as oxidation catalysts. The oxidation of organic compounds has been considered as a reaction of academic and industrial interest to analyze the catalytic activity of various metal complexes.

The high atom efficiency of peroxides makes them an efficient oxidant for industrial applications. Hydrogen peroxide and TBHP are the main peroxides used as reagents for oxidation reactions. As this oxidant is often partially destroyed by catalase type activity of the complexes, the development of novel synthetic methodologies employing H_2O_2 is a major challenge. It should be noted that, unselective side reactions might occur after the homolytic cleavage of H_2O_2 leading to hydroxyl radicals. Several attempts have been successfully made to suppress the unselective side reactions by fine tuning the catalyst or optimising the reaction conditions.

1.3.1 General reactions catalyzed by Schiff base complexes

Schiff base complexes are found to catalyse a large number of organic transformations such as polymerization reaction, epoxidation, ring opening of epoxides, reductions, oxidations, alkylation, Michael addition, Heck reaction, annulation, carbonylation, benzoylation, cyclopropanation, Diels Alder reaction, aldol condensation etc.

Schiff base complexes have been used as catalysts in reduction of ketones to alcohols [121] and in the alkylation of allylic substrates [122]. Jacobsen *et al.* found that the enantioselective ring opening of large cycloalkanes are catalysed by

chiral Schiff base complexes of cobalt(II) [123] and chromium(III) [124]. The reaction is found to be difficult to take place with routine reagents. Binaphthyl ligands are considered as versatile frameworks for chiral ligands in coordination and metallosupramolecular chemistry [125]. BINAP Schiff base complexes are found to catalyse many reactions [126]. Michael addition was easily carried out in presence of chiral salen Schiff base complexes and complexes of BINAP Schiff bases. Some of the chiral binaphthyl Schiff bases used by Zhou *et al.* are given in Figure 1.10.
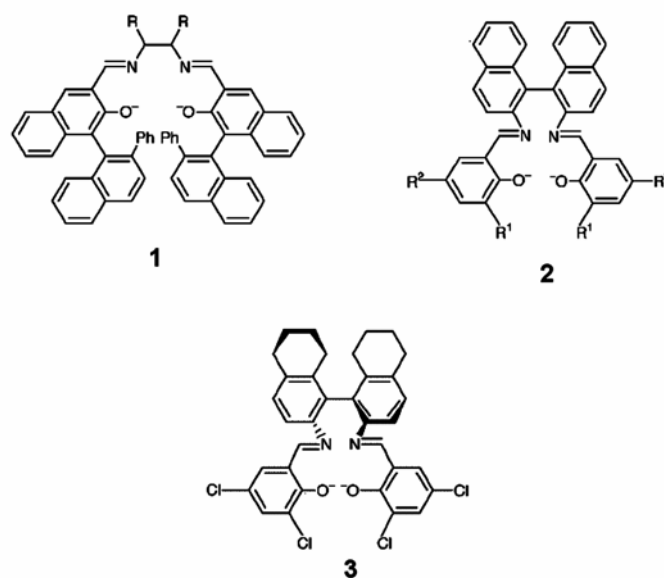
Figure 1.10: *Some commonly used binaphthyl Schiff bases (Adopted from Ref. 126)*

Schiff base complexes showed catalytic activity in carbonylation of alcohols and alkenes at low pressure to produce arylpropionic acid and their esters [127], which are used as non-steroidal anti-inflammatory drugs. In addition to monometallic, the bimetallic Schiff base complexes also show catalytic activity in carbonylation reactions. The use of salen complexes as catalyst was first carried out in 1985 by Kochi and co-workers. Chiral manganese salen complexes were first developed by Jacobsen and Katsuki and are generally known as Jacobsen's Catalyst. Jacobsen's catalyst is (R,R)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamino manganese(III) chloride which is prepared by resolving 1,2-

diamino cyclohexane as the appropriate tartrate, and reacting with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in the usual method of preparing salen-type ligands. Reaction with manganese(II) acetate in the presence of air gives the manganese(III) complex, which may be isolated as the chloro complex by addition of lithium chloride. These complexes are efficient catalyst towards epoxidation of *cis* olefins. One such complex used by them and the scheme of one of the reaction carried out using this catalyst are shown in Figure 1.11 and Scheme 1.1. It is generally agreed that the Jacobsen's catalyst (Figure 1.11) is oxidised to a reactive oxo-Mn(V)salen complex. The latter has not been isolated and characterised but related species with other metal centres are known. The Mn(salen)Cl is almost certainly planar; the oxo species has been postulated as planar, bent and twisted (folded) by different researchers.
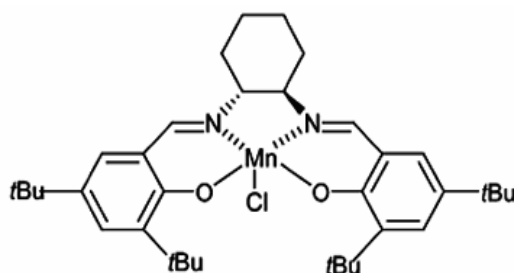
Figure 1.11: *Structure of the Jacobsen's catalyst, (R,R)-N,N'-bis(3,5-di-tert butylsalicylidene)-1,2-cyclohexanediamino manganese(III) chloride*
***(Adopted from* Ref. 4)**
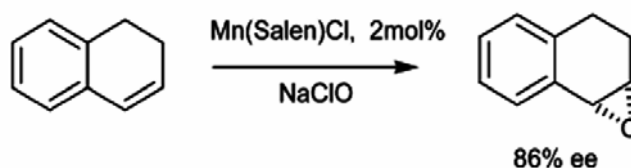
Scheme 1.1: *A stereoselective epoxidation catalysed by Jacobsen's catalyst*
(Adopted from Ref. 4)

Schiff base complexes are used as catalyst in Heck reaction [128]. Usually complexes of phosphene ligands are used to catalyse this reaction. But compared to phosphene, Schiff bases can easily be prepared. Palladium(II) complexes of salen

Schiff base ligands showed high catalytic activity in Heck reaction than the commercially used phosphene complexes [129]. Arellano *et al.* [130] used the palladium(II) Schiff base complex of 2-*tert*-butyl-4-methyl-6{(*E*)-[(2*S*)-1-(1-arylmethyl)pyrrolidinyl]imino}methylphenol as catalyst for Heck reaction. Legros and Bolm [131] reported the preparation of a tridentate Schiff base iron catalyst, prepared in situ from Fe(acac)$_3$, which is able to promote the enantioselective oxidation of sufide to sulfoxides.

The iron(III) and cobalt(II) complexes of pyridine Schiff base ligands showed significant activity in the polymerization of ethylene. These complexes were also used successfully for copolymerization of ethylene with 1-hexene [132]. They have observed that the iron(III) Schiff base complexes showed higher yield and activity than the cobalt(II) complexes.

Canali and Sherrington reviewed the utilisation of homogeneous and supported metal salen complexes in asymmetric catalysis [133]. They have focused on the chiral salen ligands, and in particular on the use of their optically pure metal complexes as asymmetric catalysts. The activity of the chiral metalloporphyrins in the enantiomeric synthesis of aziridines and amides was moderate [134, 135] but the activity was improved in the presence of manganese(III) complex of the chiral Schiff base, tetrabromo substituted salen [136]. The preparation of Schiff base ligands by condensation of readily available amines with aldehydes/ketones is much easier as compared to the lengthy steps involved in the synthesis of porphyrin ligands. The chiral complexes, *tert*-butyl glycinate-benzophenone nickel(II), diphenylmethylene imino palladium(II) and (1*R*,2*R* or 1*S*,2*S*)-[*N*,*N'*-bis(2'-hydroxybenzylidene)]-1,2-diaminocyclohexane copper(II), have increased enantioselectivity in alkylation of enolates [137-139]. The isomerization of norbornadiene to quadricyclane was significantly catalyzed using (9,10-phenanthrenequinone diimine) rhodium complexes [140, 141]. These interconversions are useful for the storage of solar energy. The asymmetric reduction of dialkyl ketones to alcohols [142, 143] is very difficult to achieve, but

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salen Schiff base complexes of transition metals have been found to be efficient catalysts in these reductions [144]. The cobalt complexes with 3-oxobutylideneaminato ligands were efficient catalysts for the enantioselective borohydride reduction of ketones, imines, and α,β-unsaturated carbonyl compounds to afford the corresponding secondary alcohols [145]. Chiral Cr(salen)Cl complexes are used as catalyst in hetero-Diels-Alder reaction [146]. The product yield and enantioselectivity were influenced by the nature of catalysts. These studies reveal that Schiff base complexes are potential catalysts to influence the yield and selectivity in chemical transformations.

1.3.2 Hydroxylation of phenol

The oxidation of phenol by hydrogen peroxide (H_2O_2) is a widely applied process in the chemical industry for the preparation of the dihydroxylated derivatives. This oxidation process is frequently reported as taking place through the decomposition of H_2O_2 with formation of an unstable electrophilic intermediate, which attacks the phenol nucleus to give a phenoxy ion. This ion can be considered as the precursor of the products usually formed in this process: hydroquinone, catechol and benzoquinone. Phenol and its derivatives are found in wastewaters including those from the oil refining, petrochemical, coke and coal gasification industries. Removal of phenol from such wastewaters is an important challenge for chemists. Diphenols, *i.e.*, catechol and hydroquinone, are considered as important chemicals in industrial chemistry. Manufacture of diphenols through phenol hydroxylation with H_2O_2 as the oxidant has become one of the promising approaches in the 21st century, as the process demands for the simple techniques and produces little environmental pollution.

Two factors should be taken into account in the hydroxylation of phenol. First, the introduction of a second hydroxyl substituent onto the aromatic nucleus tends to activate the molecule towards further reaction and this leads to the formation of a mixture of unwanted tarry by-products. Secondly, hydroquinone and catechol are generally used for different purposes. For example, hydroquinone is a

photographic developer and catechol is an intermediate in the production of industrial anti-oxidants. Consequently, one has to obtain hydroquinone or catechol selectively. A commercial catalytic process has been developed for hydroxylating phenol using hydrogen peroxide, which tends to produce mixtures containing a major fraction of catechol. A significant fraction of hydroquinone was also formed. The proportion of tarry by-products has been controlled by limiting the use of very low mole ratios of hydrogen peroxide to phenol; but, inevitably, this restricts the extent of conversion of the phenol and hence the space yield of the plant.

The catalysts reported to be used in phenol hydroxylation to date are molecular sieves, heteropoly compounds of the Dawson structural type: molybdovanadophosphate and tungstovanadophophosphate, copper–aluminum hydrotalcite-like compounds and metal complexes. The catalysts mentioned above have some catalytic activity for phenol hydroxylation, but the reaction lacks industrial value because of their relatively low yield. Therefore, catalysts with high activity and high selectivity have become an important target in this field.

Many Schiff base complexes are used for catalytic phenol hydroxylation reaction. Copper(II) salicylaldimine complexes have been successfully employed in hydroxylation of phenol [147]. Van Wyk *et al.* reported the catalytic hydroxylation of phenol in aqueous media using a cobalt(II) N-(aryl)salicylaldimine Schiff base complexes [148]. They reported catechol and hydroquinone as the products and at higher pHs benzoquinone was also obtained. In 2001, Musie *et al.* reported a new method for phenol hydroxylation. They used supercritical carbon dioxide as the medium for reaction which is inert towards oxidation [149]. Polymeric iron(III) Schiff base complexes catalyze hydroxylation of phenol. Due to the insolubility of the complex, the reaction is a heterogeneous catalytic reaction and catechol is obtained as the main product with good selectivity (78-85 %) [149]. The structure suggested for the polymeric iron(III) complex of the Schiff base, 4-(naphthalen-1-yliminomethyl)-phenol, is given in Figure 1.12.
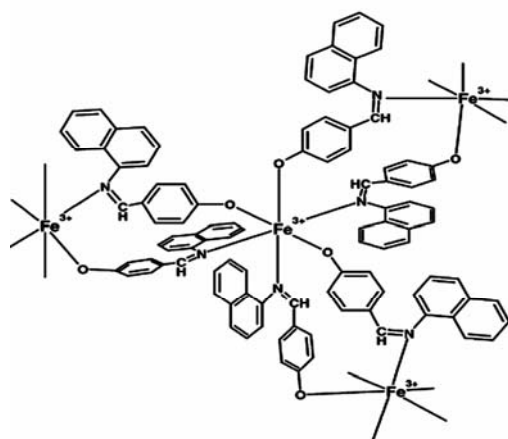
Figure 1.12: *Suggested structure of the polymeric iron(III) complex with 4-(naphthalen-1-yliminomethyl)-phenol Schiff base (Adopted from Ref. 149)*

Zhang *et al.* [150] studied the hydrogen peroxide oxidation of phenol using a manganese(II) Schiff base complex as mimetic peroxidase and the mechanism suggested by them is given in Figure 1.13. The mechanism of phenol hydroxylation may follow an ionic pathway or free radical pathway. The reaction proceeds through the formation of the active species from hydrogen peroxide, OOH^-, which initially forms an intermediate with metal ion. In the next step a new intermediate, phenol-metal-OOH, is formed. This intermediate facilitates the attack of OOH^- at the ortho and para position of the phenol to form catechol and hydroquinone.
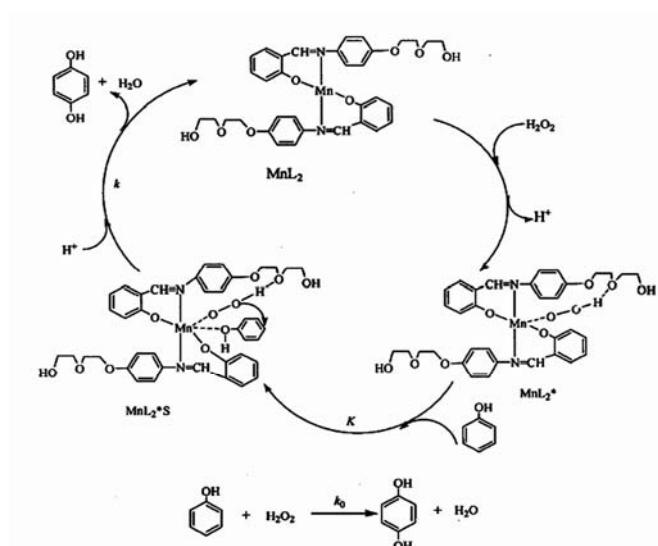
Figure 1.13: *The mechanism of the oxidation of phenol catalyzed by the Schiff base complexes (Adopted from Ref. 150)*

1.3.3 Oxidation of cyclohexane

The selective oxidation of saturated hydrocarbons is one of the most challenging and promising subjects in oxidation chemistry. Cycloalkanes are an important chemical class of hydrocarbons found in diesel, jet and gasoline fuels. The significant industrial production of cyclohexane derivatives—10^6 ton per year of cyclohexanone alone—has stimulated studies aiming to find milder, energy-saving conditions for the oxidation of cyclohexane [151]. The system currently used makes use of soluble salts of cobalt and manganese as catalysts for the oxidation of cyclohexane by oxygen to cyclohexanol and cyclohexanone. Cyclohexanol and cyclohexanone are oxidized by nitric acid to give adipic acid (Figure 1.14). The oxidation of cyclohexanone by nitric acid leads to the generation of nitrogen dioxide, nitric oxide, and nitrous oxide. The first two gases can be recycled for the synthesis of nitric acid. Nitrous oxide, however, is an ozone depleter and cannot be recycled. Indiscriminate nitrous oxide emission from this process is therefore the cause of considerable concern. Part of the cyclohexanone can also be converted to the corresponding oxime and then to caprolactam—the monomer for nylon 6. Phthalic acids are one of the monomers for the manufacture of polyesters.
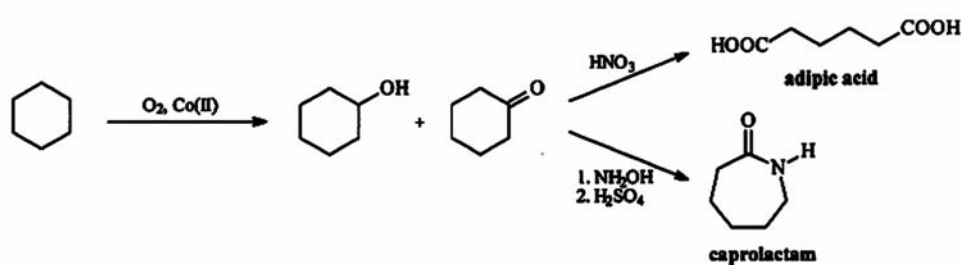
Figure 1.14: *Conversion of cyclohexane to adipic acid or ε-caprolactam.*

The functionalization of unactivated C-H bonds of cyclohexane requires high pressure and temperature, and a number of catalysts have been developed. In this reaction, various oxidizing agents having active oxygen such as hydrogen peroxide, iodosobenzene, t-butyl peroxide and ozone have been used. Solvents

(heptanol, 2-methylpropanal, acetaldehyde), and cocatalysts (such as acetic acid, chloroacetic acid, trifluoroacetic acid) have also been used for this reaction.

The oxidation of cyclohexane under mild condition is a topic of great interest. The reaction proceeds through the formation of peroxy intermediate. The cyclohexyl hydroperoxide is formed initially when hydrogen peroxide is used, which is later oxidised to cyclohexanol and cyclohexanone. Imamoto et al. used porphyrin complexes as catalyst towards oxidation of cyclohexane [152]. Zhou *et al.* used transition metal complexes of deuteroporphyrins as catalyst. They proposed the reaction mechanism involving the intermediate formation of the μ–oxo dimer. In 2002, Rathnaswamy *et al.* used cobalt and manganese cluster compounds for the oxidation of cyclohexane [153]. Supported metal complexes are also largely used for cyclohexane oxidation. The Co(II) complex of the Schiff base derived from dialdehyde starch (obtained by the periodate oxidative cleavage of the C2-C3 bond in starch) and amino alcohol has been found to be an active and reusable catalyst for cyclohexane oxidation with oxygen. The reaction takes place in the absence of solvents or reducing agents and high turnover number of catalyst and high selectivity of the product could be obtained [154].

In 2009 Comba *et al.* [155] proposed a mechanism for the catalytic cyclohexane oxidation on the basis of labelling and computational studies. They have used high valent iron complexes and have proposed both aerobic and anaerobic mechanism (Figure 1.15) for the reaction.
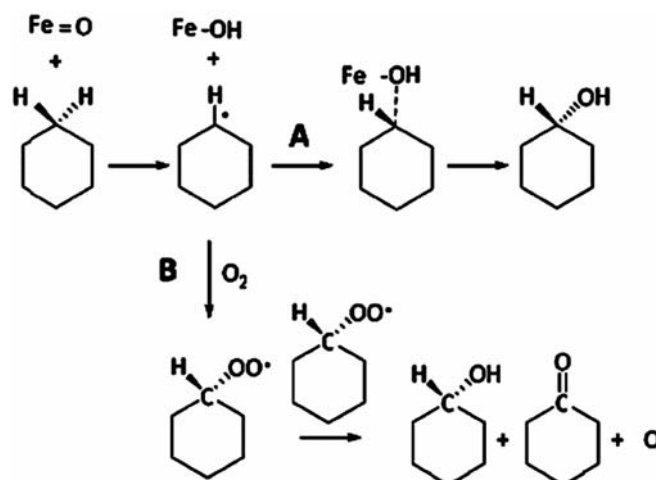
Figure 1.15: *Anaerobic (A) and Aerobic (B) Pathway for the Ferryl-Based Oxidation of Cyclohexane (Adopted from Ref. 155)*

1.3.4 Oxidation of benzyl alcohol

Traditionally, oxidation of benzyl alcohol to benzaldehyde is performed with stoichiometric amounts of chromium(VI) reagents. These oxidants are not only relatively expensive, but also they generate copious amounts of heavy-metal waste. Moreover, the reaction is often performed in environmentally undesirable solvents like chlorinated hydrocarbons. Hydrogen peroxide is a clean oxidant compared to other oxidants [156]. To reduce the harmness and cost of solvents, studies towards solvent free process have been carried out [157-160].

The copper(II) [161], manganese(II) [162] and ruthenium(II) [163] complexes are found to catalyze the selective oxidation of benzyl alcohol to benzaldehyde. Highly selective oxidation of benzylic alcohols to benzaldehydes using an active dinuclear manganese(IV) complex as catalyst and hydrogen peroxide or *tert*-butyl hydroperoxide as oxidant was reported by Feringa *et al.* [164]. From an economic and environmental perspective, catalytic aerobic alcohol oxidation represents a promising protocol. [165-167]. Wang *et al.* [168] in 2007, reported the selective oxidation of benzyl alcohol to benzaldehyde using a supported Cr(salen) complex. The supported complexes show good conversion and selectivity. Kang *et al.* [169] and Ali *et al.* [170] utilized the catalytic activity of

nanocubic zinc hexacyanoferrate for solvent-free oxidation of benzyl alcohol using H_2O_2 as oxidant. The reaction was carried under the optimum conditions of certain parameters such as benzyl alcohol to H_2O_2 molar ratio, the amount of catalyst, reaction time and temperature. Figiel *et al.* [171] reported the oxidation of benzyl alcohols to benzaldehydes by the TEMPO/O_2 system (TEMPO=*2,2,6,6-tetramethylpiperidine-1-oxyl*). They used copper(II)ethanolamine complexes and the reaction proceeds with a high efficiency (up to 99% yield of benzaldehyde with >99% selectivity) and without the need of any organic solvent, or of an ionic liquid. Thus this reaction has both environmental and economical benefits in comparison with previously reported systems for benzyl alcohol oxidation.

Scope of the present investigation

Study of the transition metal complexes with quinoxaline derivatives has gained much attention because of their potential diverse applications as catalysts, chemotherapeutic agents, insecticides, fungicides and organic light emitting diodes. Thus in the recent years there is an upsurge in synthesizing compounds suitable for such applications. Literature survey revealed that there are only scanty reports on Schiff base complexes derived from quinoxaline-2-carboxaldehyde and 3-hydroxyquinoxaline-2-carboxaldehyde. The ligational aspects of quinoxaline based Schiff bases are more attractive than those of Schiff bases derived from benzaldehyde due to the presence of two nitrogen atoms in the ring, which may affect the electronic properties of the complexes. These effects may modify the electron transfer properties involved in catalysis. Thus, it is worthwhile to carry out the structural and spectral studies of quinoxaline based Schiff bases and their metal complexes with different structural features. Hence, we have carried out detailed study on the quinoxaline based compounds with the following objectives in mind.

➢ To synthesize some novel Schiff bases derived from the heterocyclic aldehydes, quinoxaline-2-carboxaldehyde and 3-hydroxyquinoxaline-2-carboxaldehyde

➢ To tune the denticity of the Schiff bases as three by selecting amines which contain a hydroxyl/thiolic group in the ortho position.

➢ To synthesize and characterize the transition metal complexes of the above Schiff bases.

➢ To study the complexation by template reaction without isolating Schiff base.

➢ To study the catalytic activity of the synthesized complexes in some oxidation reactions.

The ligands chosen for the present study are the following:

1. Quinoxaline–2–carboxalidine–2–amino–5–methylphenol (qamp)
2. 3–Hydroxyquinoxaline–2–carboxalidine–2–aminothiophenol (hatp)
3. 3–Hydroxyquinoxaline–2–carboxalidine–2–amino–5–methylphenol (hamp)

Manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of these Schiff bases have been synthesized and characterized. The template synthesis of amino acid Schiff base complexes are successfully carried out using quinoxaline-2-carboxaldehyde, L-histidine and metal ion. The synthesized complexes were screened for their catalytic activity in the oxidation of phenol, cyclohexane and cbenzyl alcohol. The crystal structures of two of the complexes are studied through single crystal XRD.

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Chapter **2**

Experimental techniques and synthesis of aldehydes

2.1 INTRODUCTION

Details about the general reagents used, preparation of the aldehydes and various analytical and physicochemical methods employed in the characterization of ligands and complexes are discussed in this chapter. Procedural details regarding the synthesis of ligands and metal complexes and characterization of ligands and complexes are given in the appropriate chapters.

2.2 REAGENTS

The following metal salts were used:

Manganese(II) chloride tetrahydrate (Merck), manganese(II) acetate tetrahydrate (Merck), anhydrous ferric(III) chloride (Qualigens), cobalt(II) chloride hexahydrate (Merck), cobalt(II) acetate hexahydrate (Merck), nickel(II) chloride hexahydrate (Merck), nickel(II) acetate hexahydrate (Qualigens), copper(II) chloride dihydrate (Merck), copper(II) acetate dihydrate (Merck) and zinc(II) acetate dihydrate (Merck).

The amines, 2–aminothiophenol, 2–amino–5–methylphenol and L-histidine, were purchased from Sigma Aldrich Chemicals Private Limited, Bangalore. Orthophenylenediamine (Lobachemie), D–glucose (SD Fine Chem Limited), sodium sulphate (Merck), sodium metaperiodate (Merck), glacial acetic acid, hydrazine hydrate (Qualigens), soidum bicarbonate (Sisco Research Laboratories Limited), bromine (Merck) and sodium pyruvate (Sisco Research Laboratories Limited) were used in the present investigation.

Hydrogen peroxide (30 % w/v, Merck), cyclohexane (Qualigens), phenol (Merck) and benzyl alcohol (SRL) were used for the catalytic activity studies using metal complexes. Gas cylinders containing oxygen, nitrogen or hydrogen (Sterling gases, Cochin) were also used for the catalytic activity studies. All other reagents were of analytical reagent grade and the solvents employed were either of 99 % purity or purified by known procedures [1].

2.3 SYNTHESIS OF ALDEHYDES

The aldehydes selected were quinoxaline–2–carboxaldehyde and 3–hydroxyquinoxaline–2–carboxaldehyde. The synthetic steps for the preparation of aldehydes are given below:

2.3.1 Synthesis of quinoxaline – 2– carboxaldehyde

The following procedure was adopted to synthesize quinoxaline –2–carboxaldehyde [2, 3]. Refluxing D–glucose (36 g, 0.2 mol) with orthophenylenediamine (21.6 g, 0.2 mol) in the presence of hydrazine hydrate (5 mL, 0.1 mol) and glacial acetic acid (6 mL) on a boiling water bath under carbon dioxide atmosphere (provided by the addition of a pinch of sodium bicarbonate) for 5 hours gave the compound, 2(D–arabinotetrahydroxybutyl)quinoxaline. This product was purified by recrystallisation from hot water. The recrystallised 2(D–arabinotetra hydroxybutyl)quinoxaline (5 g, 0.02 mol) was dissolved in water (300 mL) containing glacial acetic acid (10 mL) and sodium metaperiodate

(13 g, 0.06 mol) and was kept at room temperature (28 ± 2 °C) with controlled stirring for 16 hours. It was then filtered and the filtrate was neutralised with sodium bicarbonate. The neutral solution was then extracted with ether. The ether extract was dried with anhydrous sodium sulphate. It was then filtered and evaporated to dryness. The resulting residue was recrystallized from petroleum ether to give pure quinoxaline- 2-carboxaldehyde (Figure 2.1) (Yield: 60%, M.P.: 107 °C).
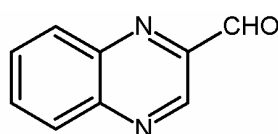

Figure 2.1: *Structure of quinoxaline-2-carboxaldehyde*

2.3.2 Synthesis of 3-hydroxyquinoxaline – 2– carboxaldehyde

A procedure different from that of Ohle [2] was used to synthesize 3-hydroxyquinoxaline–2–carboxaldehyde, as it can be used directly for preparation of Schiff base ligands without further purification. Figure 2.2 gives the structure of 3-hydroxyquinoxaline-2-carboxaldehyde.
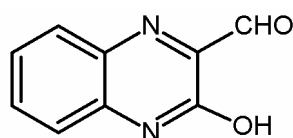
Figure 2.2: *Structure of 3-hydroxyquinoxaline-2-carboxaldehyde*

2.3.2.1 *3 –Hydroxy–2–methylquinoxaline*

O–Phenylenediamine (0.1 mol, 10.8 g) and sodium pyruvate (0.1 mol, 11 g) were dissolved in 250 mL water. A slight excess of con. HCl was needed to convert sodium pyruvate to pyruvic acid. The solutions were then mixed and stirred for 30 minutes. The precipitated yellow compound (Scheme 1) was then filtered and dried over anhydrous calcium chloride. (Yield: 90 %, m.p.: 255 °C)
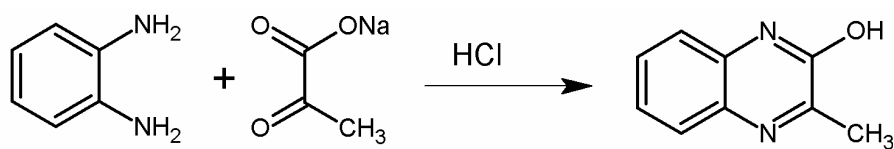
Scheme 1

2.3.2.2 *3–Hydroxy–2–dibromomethylquinoxaline*

3–Hydroxy–2–methylquinoxaline (0.1 mol, 16.2 g) was dissolved in glacial acetic acid (200 mL). To this, 10% (v/v) bromine in acetic acid (110 mL) was added and kept in sunlight for 1 ho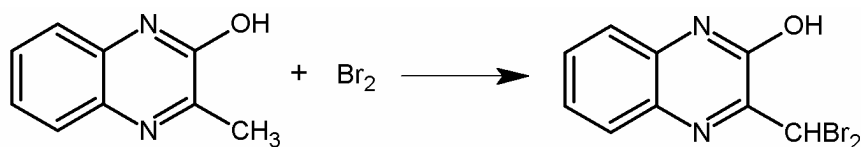ur with occasional stirring. The solution was then diluted to 1 L with water and the precipitated dibromo derivative (Scheme 2) was filtered and purified by recrystallisation from 50% alcohol (Yield: 95 %, m.p.: 246 °C).

Scheme 2

2.3.2.3 *3–Hydroxyquinoxaline–2–carboxaldehyde*

The dibromo compound (0.0157 mol, 5 g) was thoroughly mixed with 20 g of precipitated calcium carbonate. This was taken in a 3 L round bottom flask containing water (1.5 L). The solution was kept on a water bath with timely stirring for 3 hours. The aldehyde formed remains in aqueous solution (Scheme 3). This yellow solution was collected by filtration is very stable and can be used to prepare the Schiff bases.
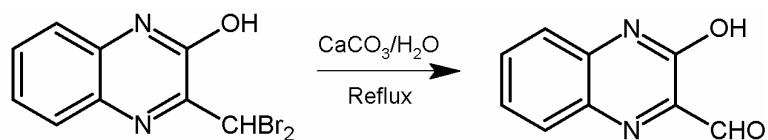
Scheme 3

The aldehyde and the compounds involved in the preparation of the aldehyde are characterized by various physicochemical and spectral studies. The details of the characterizations are given in a paper published from our group [4], and the data agrees with that for the present compounds.

2.4 PREPARATION OF SCHIFF BASES

We have synthesized three new Schiff base ligands by taking quinoxaline–2–carboxaldehyde or 3–hydroxyquinopxaline–2-carboxaldehyde. The amines chosen were 2–aminothiophenol, L–histidine and 2–amino–5–methylphenol. The ligands synthesized are:

1. quinoxaline–2–carboxalidine–2–amino–5–methylphenol (qamp)
2. 3–hydroxyquinoxaline–2–carboxalidine–2–aminothiophenol (hatp)
3. 3–hydroxyquinoxaline–2–carboxalidine–2–amino–5–methylphenol (hamp)

The ligand qamp is monoprotic. The ligands, hatp and hamp, are diprotic and exhibit tautomerism, and hence they coordinate with metal center either in keto form or in enol form in neutral condition. We could not isolate the Schiff base quinoxaline-2-carboxalidine-L-histidine (qlh), hence complexes of this ligand were prepared using template method. The formation of Schiff base complexes through the rearrangement of benzothiazoline is also studied. The details regarding synthesis of the Schiff bases are given in respective chapters.

2.5 CHARACTERIZATION TECHNIQUES

2.5.1 CHN analysis

Microanalysis for carbon, hydrogen, nitrogen and sulphur in the synthesized ligands and complexes were carried out on an Elementar model Vario EL III at Sophisticated Analytical Instrument Facility (SAIF), Sophisticated Test and

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Instrumentation Centre (STIC), Kochi. These results give an idea about the structure of the ligands and complexes.

2.5.2 Estimation of metal ions

In all the cases, the organic part of the complexes was completely eliminated before the estimation of metal ions. The following procedure was adopted for this purpose in the case of all the complexes. A known weight (0.2–0.3 g) of the metal complex was treated with concentrated sulphuric acid (5 mL) followed by concentrated nitric acid (20 mL). After the reaction has subsided, perchloric acid   (5 mL, 60 %) was added. This mixture was kept aside until the colour of the solution changes to that of the metal salt. The clear solution thus obtained was evaporated to dryness on water bath. After cooling, concentrated nitric acid (15 mL) was added and was again evaporated to dryness on a water bath. The residue was dissolved in water and this neutral solution was used for the estimation of metals. The estimation of metals was carried out on a Thermo Electron Corporation, M series Atomic Absorption Spectrophotometer.

2.5.3 Estimation of chloride

Chlorine present in the complexes was converted into soluble sodium chloride by the peroxide fusion. An intimate mixture of the complex (0.2 g) sodium carbonate (3 g) and sodium peroxide (2 g) was fused on a nickel crucible for nearly two hours. It was then treated with concentrated nitric acid. Chloride was then volumetrically estimated by Volhard's method [5]. Chloride was precipitated as silver chloride by the addition of a known volume of standard silver nitrate solution. The excess silver nitrate was titrated against standard ammonium thiocyanate solution using ferric alum as indicator.

2.5.4 Conductance Measurements

Molar conductance values of the complexes were measured using a systronic conductivity bridge type 305. The solvent used was methanol, DMF or dimethyl sulphoxide. The molarity of the solution was 10^{-3} M.

2.5.5 Electronic spectra

Electronic spectroscopy is a valuable tool for coordination chemists to draw important information about the structural aspects of the complexes. The ligands, which are organic compounds, have absorption in the ultraviolet region and in some cases these bands extend to higher wavelength region due to conjugation. Upon complexation with transition metal ions, changes will take place in the electronic properties of the system. New features or bands in the visible region due to d-d absorption and charge transfer spectra from metal to ligand (M→L) or ligand to metal (L→M) can be observed and this data can be processed to obtain information regarding the structure and geometry of the complexes. The electronic spectra of the complexes in solution phase (0.0005 molar) were recorded in the region 200-1100 nm on a Thermoelectron Nicolet evolution 300 UV−Vis spectrophotometer. In the solution phase some important d–d bands, which are important in assuming geometry, were obscured. In such cases, the spectra were also taken in the solid state using the mull technique [6].

2.5.6 IR Spectra

The vibrational states of a molecule can be probed in a variety of ways. The most direct way is infrared spectroscopy because vibrational transitions typically require an amount of energy that corresponds to the infrared region of the spectrum between 4000 and 400 cm^{-1} (wavenumbers). The IR spectra provide valuable information regarding the structure of the complex and the nature of the functional groups present. Hence it can be used as an effective tool to confirm the formation of the complexes and to determine the mode of coordination of ligands to the

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transition metals. Infrared spectra of the ligands and simple complexes were recorded using Jasco-8000 Fourier Transform Infrared Spectrophotometer.

2.5.7 NMR spectra

^{1}H NMR spectra were recorded in CDCl$_3$ or DMSO-d$_6$ on a Bruker AVAVCE III 400 MHz -NMR spectrometer using TMS as the internal standard at the SAIF, Sophisticated Test and Instrumentation Centre, Kochi. NMR spectral data provide valuable information regarding the structure of Schiff bases. The NMR spectra of the zinc(II) complexes were also recorded to know the nature of binding of metal ion.

2.5.8 EPR spectra

EPR spectroscopy is a reliable method to determine the geometry and electronic structure of the complexes. The EPR spectra of the complexes in DMF were recorded on Varian E-112 X/Q band spectrophotometer at liquid nitrogen temperature and the standard used was tetracyanoethylene (TCNE) with a g value of 2.0027. The EPR spectra of transition metal complexes contain a wealth of information about their electronic structures. The interpretation of the EPR spectra of these complexes can be done on the basis of the ligand field theory. The degeneracy of the d orbitals and the presence of the unpaired electrons give rise to orbital contributions as a result of which anisotropic g values are obtained.

2.5.9 Magnetic susceptibility measurements

The magnetic susceptibility measurements were done at room temperature (28 ± 2 °C) on a simple Gouy-type balance. The Gouy tube was standardized using Co[Hg(SCN)$_4$] as standard as recommended by Figgis and Nyholm [7]. The effective magnetic moments were calculated using the equation.

$$\mu_{eff} = 2.84 \ (\chi_m T)^{½} \ B.M.$$

Where T is the absolute temperature and χ_m is the molar susceptibility corrected for diamagnetism of all the atoms present in the complex using pascals constants [8-10]. The magnetic susceptibility measurements were done on a Magway MSB Mk 1 Magnetic Susceptibility Balance.

2.5.10 Thermogravimetric analysis

Thermogravimetric analysis is an effective tool to study the nature of decomposition of the metal complexes. The thermal stability of the synthesized complexes can be determined using this method. In this technique, the sample under consideration is heated at a controlled rate in an atmosphere of nitrogen and the mass of the substance is recorded as a function of temperature. The major advantage of this method is that it can directly give idea about the upper limit of thermal stability of a material. The thermograms obtained are characteristic for a given sample due to the unique sequence of physico-chemical reactions occurring over definite temperature ranges which in turn depends upon the structure of the molecule. The changes in weight occur as a result of the rupture or formation of various physical and chemical bonds at elevated temperatures. This may lead to the evolution of volatile products or the formation of heavier reaction products. TG analyses were carried out on a Perkin Elmer, Diamond thermogravimetric analyser at a heating rate of 10 ºC per minute in an atmosphere of nitrogen.

2.5.11 Single crystal XRD

The diffraction/scattering of X-ray radiations by array of atoms in a single crystal of a compound is exploited to establish the structure and geometry of the complexes. At present this versatile technique is valued as the final word by many chemists for establishing the accurate structure of the complex compounds. X–ray crystal structure determination was performed with a Bruker SMART APEX CCD X–ray diffractometer at University of Hyderabad and at CSMCRI Gujarat using graphite monochromated MoKα radiation (λ=0.71073 Å, φ and ω scans). The data was reduced using SAINTPLUS [11] and a multiscan absorption correction using

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SADABS was performed [12]. The structure was solved using SHELXS–97 and full matrix least squares refinement against F^2 was carried out using SHELXL–97 in anisotropic approximation for non-hydrogen atoms [13]. All hydrogen atoms were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms.

2.5.12 Gas Chromatography

The analysis of the reactants and products of the different catalytic reactions was conducted using a Chemito 8510 Gas Chromatograph. In gas chromatography, the separation is carried out in a tubular column made of metal and an adsorbent which serves as the stationary phase is filled in this column. The carrier gas serving as the mobile phase is made to flow continuously through the column. The instrumentation consists of a tank of carrier gas, an injection port for introducing the sample, the column and a detector. The various components in the reaction mixture were separated using an OV-17 or carbowax column. The peaks appearing on the recorder are characteristic of the different components. The peak area is found to be proportional to the amount of the component present in the mixture.

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Quinoxaline-2-carboxalidine-2-amino-5-methylphenol complexes of manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II)

Contents

3.1 Introduction

3.2 Experimental

3.3 Results and discussion

3.4 Conclusions

Reference

3.1 INTRODUCTION

Multidentate ligands are extensively used for the preparation of metal complexes with interesting properties. Among these ligands, Schiff bases containing nitrogen and phenolic oxygen donor atoms are of considerable interest due to their potential application in catalysis, medicine and material science [1–4]. They have proven to be effective in constructing supramolecular architectures such as coordination polymers and helical assemblies [5–8]. Transition metal complexes of these ligands exhibit varying configurations, structural lability and sensitivity to molecular environments. The central metal ions in these complexes act as active sites for catalyzing chemical reactions. This feature is employed for modeling active sites in biological systems.

Aminophenols are important to the pharmaceutical industry, since they have antibacterial and antitubercular action. Schiff bases obtained by the condensation of 2-aminophenol with some aldehydes/ketones find application as antituberculosis compounds. They also find application in the biophysical and

clinical studies as metal ligand luminescence probes [9]. Recently light-emitting devices (LEDs) based on the small molecule like aminophenols were demonstrated [10]. There are a number of reports regarding Schiff base formation between aminophenol and salicylaldehyde derivatives [11-13]. However there is only one report on the Schiff base derived from aminophenol and quinoxaline-2-carboxaldehyde. The synthesis and characterization of quinoxaline-2-carboxalidine-2-aminophenol and its transition metal complexes have been reported by our group [14].

Therefore, in view of our interest in synthesis of new Schiff base complexes, which might find application as catalysts and as luminescence probes, we have synthesized and characterized new transition metal complexes of tridentate ONN donor Schiff base formed by the condensation of quinoxaline-2-carboxaldehyde and 2-amino-5-methylphenol. The results of our studies are presented in this chapter.

3.2 EXPERIMENTAL

3.2.1 Materials and methods

Synthetic procedure of quinoxaline-2-carboxaldehyde and the techniques employed for the characterization of ligand and complexes are given in chapter II.

3.2.2 Synthesis of quinoxaline−2−carboxalidine−2−amino−5−methylphenol (qamp)

The Schiff base quinoxaline−2−carboxalidine−2−amino−5−methylphenol (qamp) was synthesized by the reaction of quinoxaline−2−carboxaldehyde (10 mmol, 1.581 g) in methanol (60 mL) and 2−amino−5−methylphenol (10 mmol, 1.231 g) in methanol (20 mL). The solution was stirred for 3 hours. The yellow precipitate obtained was filtered, and was recrystallised from alcohol (Yield: 90 %, M.P.: 225 ºC).

3.2.3 Preparation of Complexes

The complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by the following procedure:

The Schiff base qamp (0.01 mol, 2.633 g) in 1:1 chloroform–methanol (50 mL) solution was added to a solution of manganese(II) acetate tetrahydrate (0.01 mol, 2.4510 g), ferric chloride (0.01 mol, 1.622 g), cobalt(II) acetate hexahydrate (0.005 mol, 1.245 g), nickel(II) acetate hexahydrate (0.005 mol, 1.244 g), copper(II) chloride dihydrate (0.01 mol, 1.705 g) or zinc(II)acetate dihydrate (0.005 mol, 1.097 g) in methanol (15 mL). The solution was then refluxed for three hours and left to cool at room temperature (28±2 °C) overnight. The crystalline complex separated out was filtered, washed with ether and dried in vacuum over anhydrous calcium chloride.

3.3 RESULTS AND DISCUSSION

The complexes are found to be stable in air and non-hygroscopic. They are soluble in common solvents like ethanol, methanol, acetonitrile and DMF. The analytical data (Table 3.1) show that the found and calculated values of the percentage of elements are in good agreement. The Co(II), Ni(II) and Zn(II) complexes are formed with metal to ligand ratio of 1:2. Other complexes are formed in 1:1 ratio. The very low conductance values (Table 3.2) of the complexes in DMF indicate the non-electrolytic nature of the complexes [15].

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Table 3.1: *Analytical data of qamp and its complexes*

Compound	Colour	Yield (%)	Analytical data. Found (calculated)%				
			C	H	N	M	Cl
qamp	Yellow	90	72.46 (72.99)	4.21 (4.98)	15.64 (15.96)	–	–
[Mn(qamp)(OAc)].H_2O	red	65	54.78 (54.83)	3.98 (4.35)	10.69 (10.66)	13.96 (13.93)	–
[Fe(qamp)Cl_2]	black	70	49.67 (49.40)	3.15 (3.11)	10.69 (10.80)	14.31 (14.35)	18.51 (18.23)
[Co(qamp)$_2$].H_2O	Violet	85	63.73 (63.90)	4.23 (4.36)	14.24 (13.97)	9.75 (9.80)	–
[Ni(qamp)$_2$].H_2O	blue	80	63.70 (63.92)	3.99 (4.36)	13.93 (13.98)	9.76 (9.74)	–
[Cu(qamp)Cl]	Violet	70	53.19 (53.16)	3.36 (3.35)	11.67 (11.63)	17.64 (17.59)	9.86 (9.81)
[Zn(qamp)$_2$].$2H_2O$	Violet	85	61.75 (61.40)	4.12 (4.51)	13.79 (13.42)	10.42 (10.45)	–

Table 3.2: *Conductivity and magnetic moment data of complexes*

Compound	λ_m[#]	μ_{eff} (B.M)
[Mn(qamp)(OAc)].H_2O	15	5.94
[Fe(qamp)Cl_2]	9	4.01
[Co(qamp)$_2$].H_2O	4	5.08
[Ni(qamp)$_2$].H_2O	12	3.20
[Cu(qamp)Cl]	13	1.95
[Zn(qamp)$_2$].$2H_2O$	8	–

[#] Molar conductivity (in Mho cm^2 mol^{-1}), 10^{-3} Molar solution in DMF

3.3.1 ^{1}H NMR spectra of the qamp and [Zn(qamp)$_2$].2H$_2$O

The proton NMR spectrum of the Schiff base (in CDCl$_3$) and that of the Zn(II) complex (in DMSO-d$_6$) were recorded using tetramethylsilane as the internal standard. The NMR spectrum of qamp is given in Figure 3.1 and the spectral data are summarized in Table 3.3. The signal at 9.70 ppm corresponds to phenolic –OH proton. The azomethine proton appears as a singlet at 8.98 ppm and all the eight aromatic protons appear as a multiplet in the range 7.80- 8.20 ppm. Protons of the methyl group attached to the phenolic ring resonate at 2.37 ppm as a singlet.

The NMR spectrum of the zinc(II) complex is given in Figure 3.2. The phenolic OH signal at 9.70 ppm observed in the spectrum of the ligand is not seen in the spectrum of the Zn(II) complex indicating the participation of the phenolic OH group in chelation with proton displacement. The signal due to azomethine proton gets shifted upon complexation, which might probably be due to the donation of the lone pair of electrons by the nitrogen to the central metal atom, resulting in the formation of a coordinate linkage (M $\leftarrow$ N). The aromatic and quinoxaline protons resonate as a number of complex multiplets in the region δ 7.46–8.20 ppm. The signal due to methyl group attached to the phenolic ring is observed almost at the same chemical shift for that in spectrum of the ligand. A broad singlet appeared in the region 3.91– 4.26 indicates the presence of water molecules in the complex.

Table 3.3: ^{1}H NMR Spectroscopic data of qamp and [Zn(qamp)$_2$].2H$_2$O

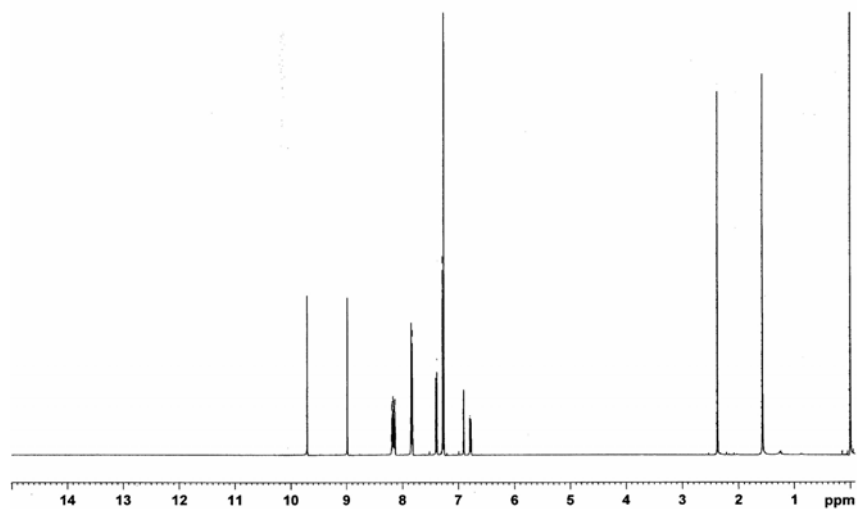| Compound	Chemical shift, δ (ppm)	Assignment
qamp	9.70	(s, 1H, OH phenolic)
	8.98	(s, 1H, CH azomethine)
	6.80-8.20	(m, 8H, Ar)
	2.37	(s, 3H, methyl)
[Zn(qamp)$_2$].2H$_2$O	9.10	(s, 2H, CH azomethine)
	7.16-8.20	(m, 14H, Ar)
	2.40	(s, 6H, methyl)
	3.91-4.26	(br s, 4H, water)

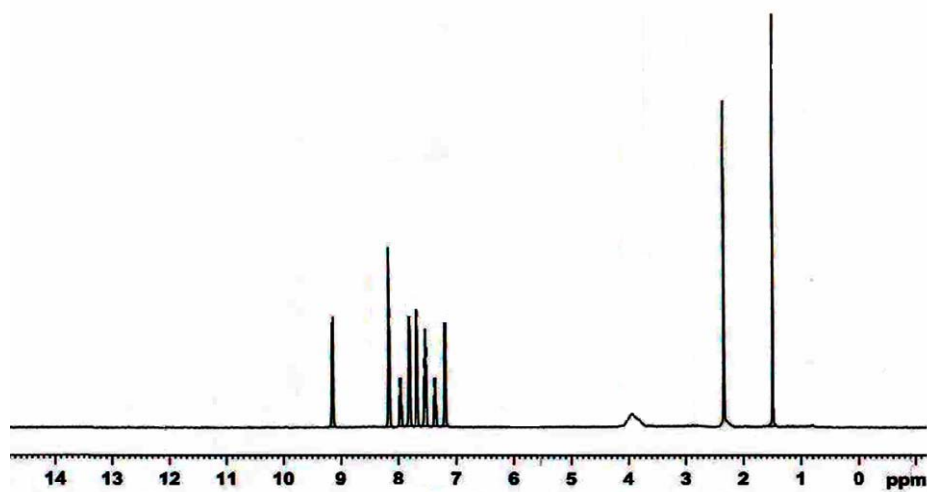**Figure 3.1:** *The ^1H NMR spectrum of qamp*

Figure 3.2: *The ^1H NMR spectrum of [Zn(qamp)$_2$].2H$_2$O*

3.3.2 Magnetic susceptibility measurements

The magnetic moment values (at 28 ± 2 °C) of the complexes are shown in Table 3.2. The μ_{eff} value of the Mn(II) complex was found to be 5.94 B.M. as expected for high spin d^5 system. Iron(III) is known to exist in three states: high spin state with S=5/2 (ground term ^6A, μ =5.92 B.M.), intermediate spin state with S= 3/2 (ground term $^4A_2$, $\mu = 4.00$ B.M) and the low spin state with S=1/2 (ground term $^2T_2$, $\mu = 2$ to 2.6 B.M). The iron(III) complex shows a magnetic moment of 4.01 B.M., which confirms that iron(III) complex is five coordinated with the

intermediate spin state of 3/2 [16, 17]. The cobalt(II) complex exhibits a magnetic moment of 5.08 B.M. and the high magnetic moment value suggests an octahedral geometry for the complex. The nickel(II) complex has a magnetic moment value of 3.10 B.M., which is in the normal range observed for octahedral Ni(II) complexes [18]. The magnetic moment of the copper(II) complex is 1.95 B.M. which suggests the lack of Cu−Cu interactions and monomeric nature of the complex.

3.3.3 Infrared spectra

The most significant IR spectral bands along with their tentative assignments are listed in Table 3.4. The IR spectrum of the ligand is compared with that of the complexes to know the changes during complex formation.

On complexation the ν(C=N) band at 1626 cm^{-1} of the Schiff base shifts to lower or higher frequencies in the spectra of all the complexes indicating coordination of the azomethine nitrogen [19]. For the Schiff base, the C=N− stretching of quinoxaline ring is observed as a strong band at 1577 cm^{-1}. This band undergoes a small shift (~5 cm^{-1}) on complexation; such small shifts have been reported when ring nitrogens are involved in coordination to the metal [20]. The ν(C−O) band for all the complexes appears at lower frequencies compared to that for the free ligand, suggesting the deprotonation and coordination of phenolic oxygen [21]. Thus the Schiff base coordinates through azomethine nitrogen, phenolic oxygen and quinoxaline oxygen and acts as a monobasic tridentate ligand (Figure 3.3).
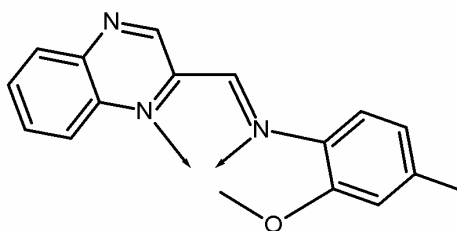

Figure 3.3: *Mode of coordination of qamp*

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The manganese(II), cobalt(II), nickel(II) and the zinc(II) complexes exhibit a broad band in the region 3300–3400 cm^{-1} due to the presence of water molecule. Appearance of new bands in the spectra of all the complexes (Figures 3.4-3.10) in the regions 490–450 and 450–400 cm^{-1} has been attributed to ν(M–O) and ν(M–N), respectively. The IR spectrum of the acetato complex, [MnL(OAc)].H$_2$O, displays ν_{asym} (COO$^-$) and ν_{sym} (COO$^-$) at 1545 and 1390 cm^{-1} suggesting monodentate acetato coordination [22].

Table 3.4: *IR spectral data of qamp and its complexes*

Assignments (in cm^{-1})	ν (OH)	ν (C=N)$^{\#}$	ν (C=N) *	ν (C–O)$^{\$}$	ν (M–O)	ν (M–N)
qamp	3330	1626	1577	1261	-	-
[Mn(qamp)(OAc)].H$_2$O	3300 b	1606	1584	1234	465	413
[Fe(qamp)Cl$_2$]	-	1583	1547	1255	490	424
[Co(qamp)$_2$].H$_2$O	3390	1664	1579	1252	567	468
[Ni(qamp)$_2$].H$_2$O	3200b	1674	1579	1254	457	432
[Cu(qamp)Cl]	-	1612	1578	1252	425	409
[Zn(qamp)$_2$].2H$_2$O	3381	1672	1587	1252	465	418

b-broad, $^{\#}$ azomethine, * quinoxaline, $^{\$}$ phenolic
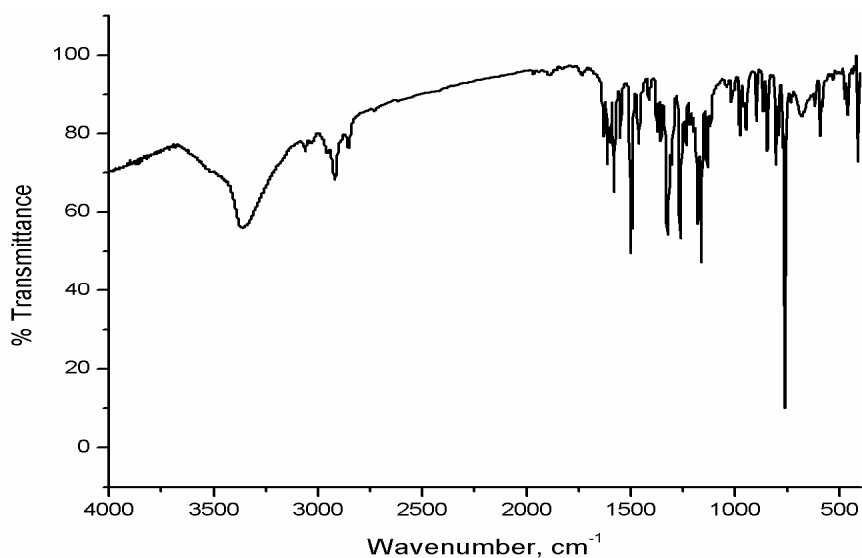
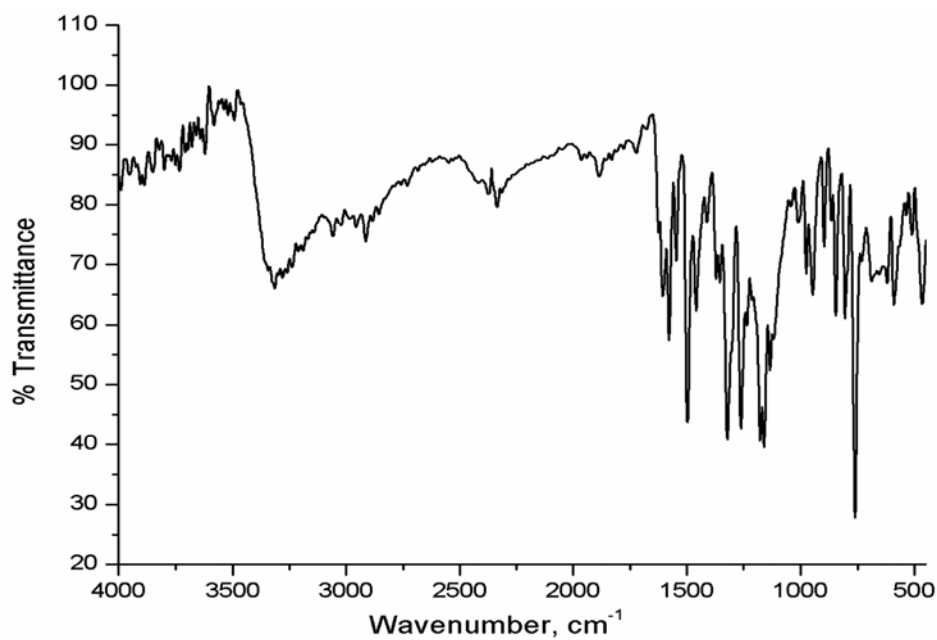**Figure 3.4:** *FTIR spectrum of the Schiff base qamp*
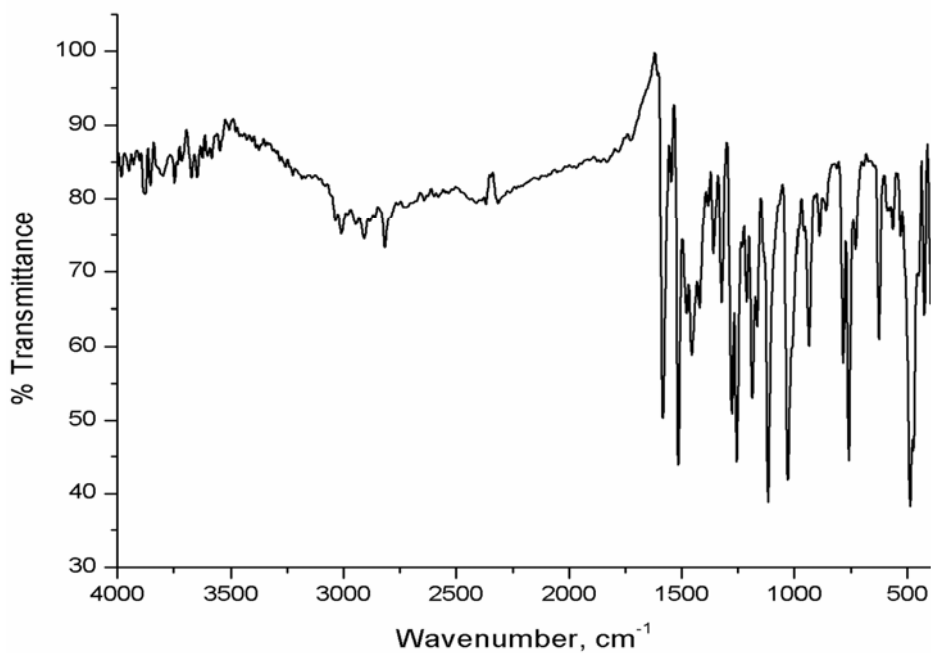
Figure 3.5: *FTIR spectrum of [Mn(qamp)(OAc)].H$_2$O*
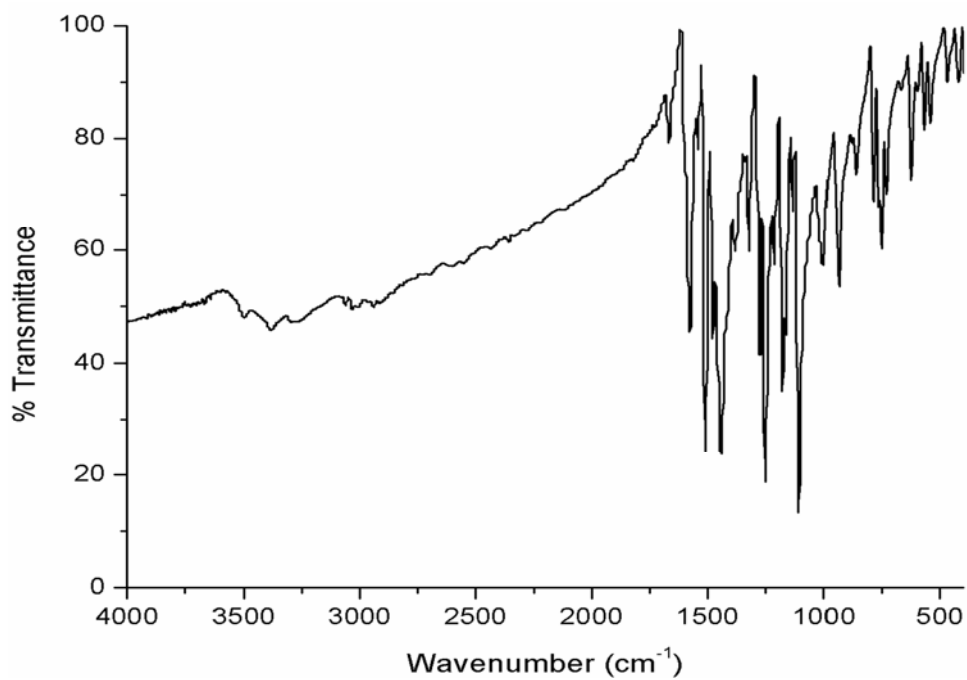

Figure 3.6: *FTIR spectrum of [Fe(qamp)Cl$_2$]*

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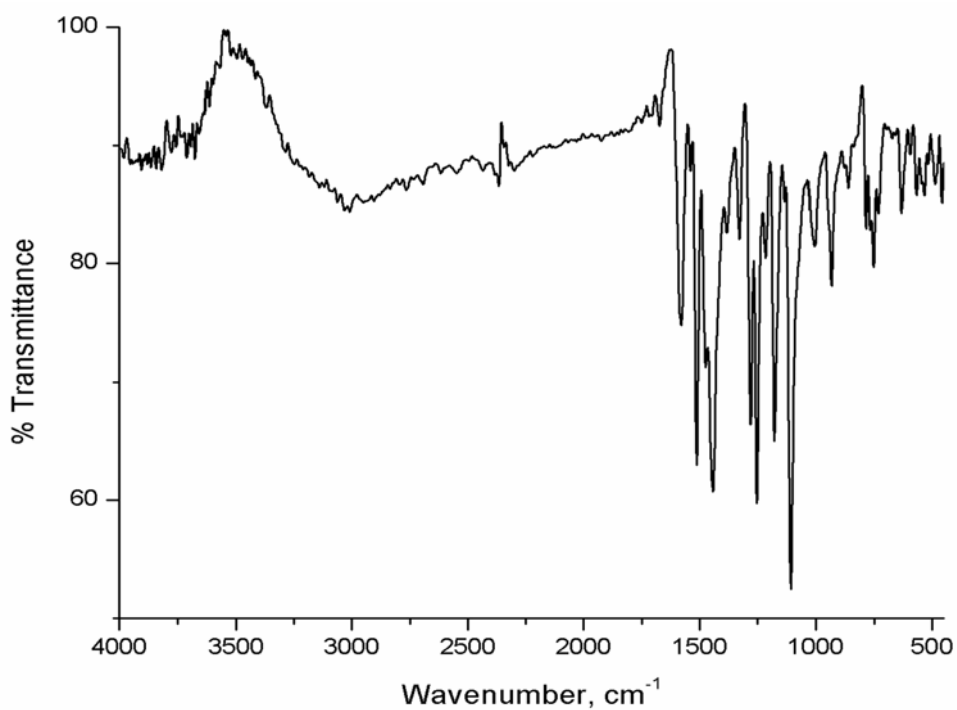**Figure 3.7:** *FTIR spectrum of [Co(qamp)$_2$].H$_2$O*

Figure 3.8: *FTIR spectrum of [Ni(qamp)$_2$].H$_2$O*
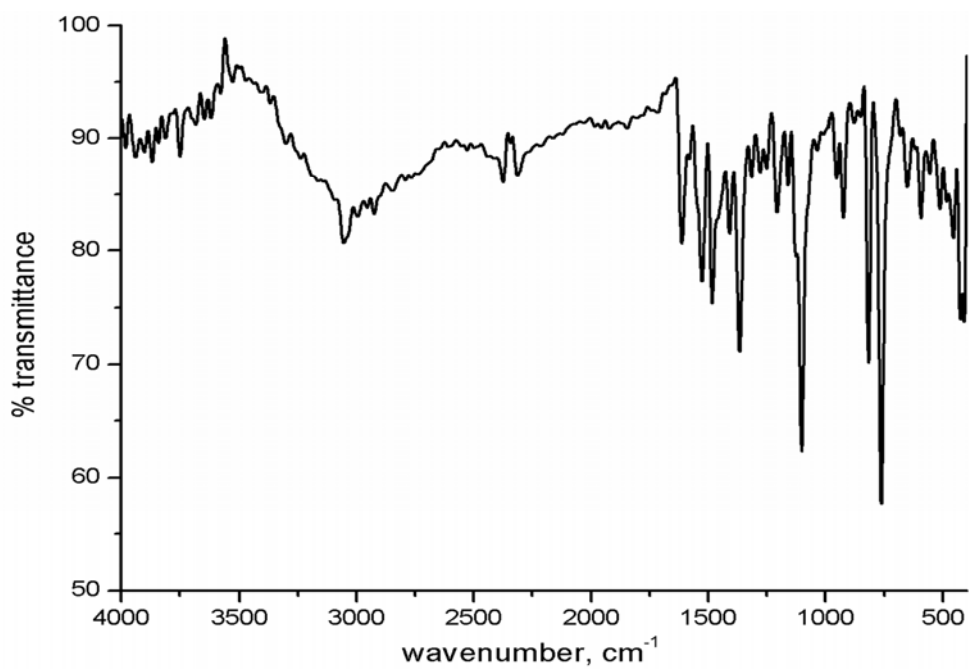
Figure 3.9: *FTIR spectrum of [Cu(qamp)Cl]*
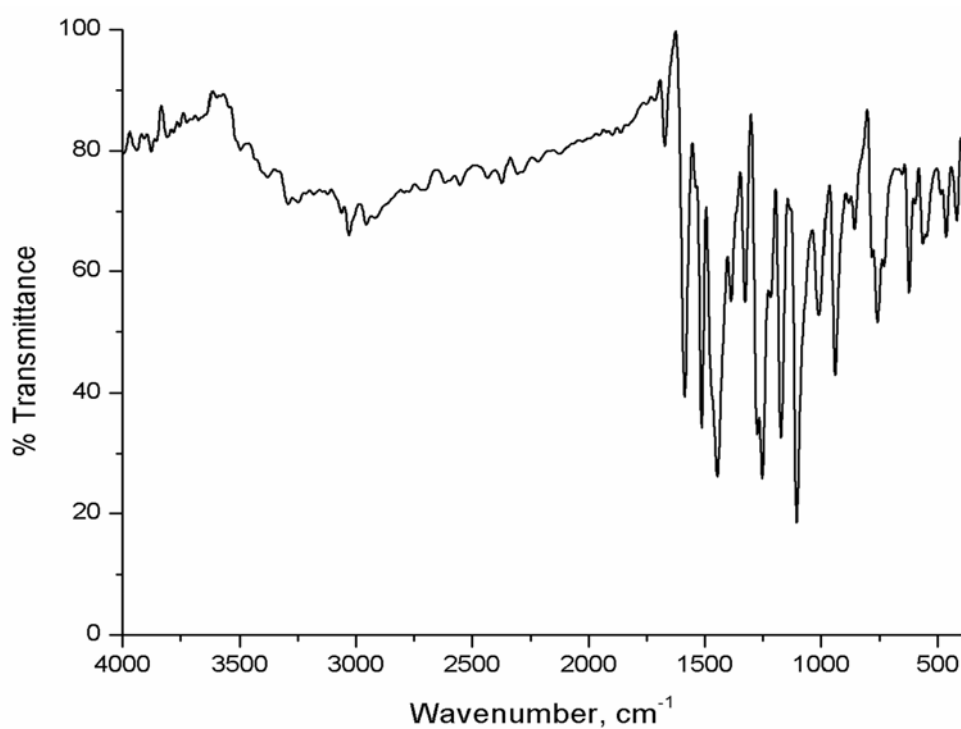
Figure 3.10: *FTIR spectrum of [Zn(qamp)₂].2H₂O*

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3.3.4 Electronic spectra

Electronic spectra of the Schiff base and its complexes were taken in methanol (~5x10^{-4} molar) in the range 50000-10000 cm^{-1}. The absorption maxima are listed in the Table 3.5 and the spectra are given in Figure 3.11-3.17. The UV–Vis spectrum of the Schiff base shows two strong bands at 42500 and 26000 cm^{-1} due to π–π* transitions [23]. These π–π* bands are not altered to a greater extent on complexation.

The spectrum of the Mn(II) complex shows two shoulders at 10810 and 9300 cm^{-1} assignable to $^6A_1$→$^4T_1$ and $^6A_1$→$^4T_2$ (G) transitions respectively [24, 18].

The solution state electronic spectrum of the iron(III) complex did not show any d-d bands. Two charge transfer bands are seen at 24000 and 18200 cm^{-1} respectively. Since the solution spectrum does not give information regarding geometry probably due to the limited solubility of the complex in methanol, we have taken the spectrum in nujol mull (Figure 3.18). The d-d bands are seen in the solid state spectra due to the high concentration of the complex in the solid state. Two bands are seen in the visible region at 11110 and 10200 cm^{-1}, and a weak broad band is observed in the near IR region at 6890 cm^{-1} indicating a square pyramidal structure. Similar observations have been made by Martin and White for the five coordinated iron(III) dithiocarbamate complex [25, 26].

For the cobalt(II) complex, a band with maxima at 18550 cm^{-1} is due to the $^4T_{1g}$(F)→$^4T_{2g}$(P) transition [25]. The intensities of the d–d band is considerably increased possibly due to the influence of nearby intense charge-transfer transitions (log ε = 3.36). The other d–d transitions are masked by the strong charge transfer band, as has been observed in the case of similar Schiff base complexes [27, 28].
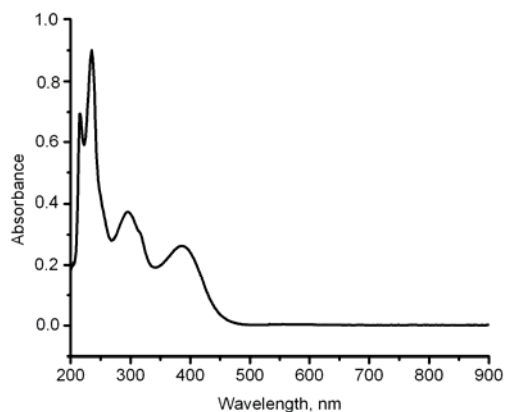
For the nickel(II) complex, the band at 17450 cm^{-1} is due to the $^3A_{2g}$→$^3T_{1g}$ transition of nickel(II) in octahedral environment. The intensity of this d–d band is

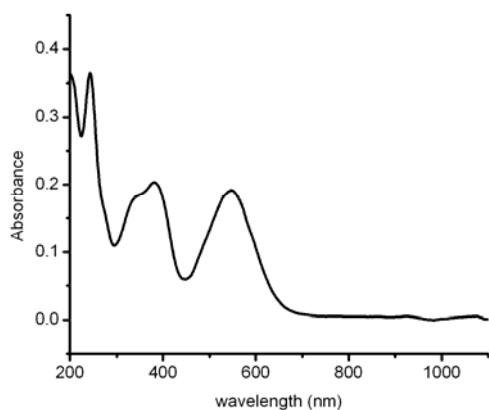also considerably increased possibly due to the influence of nearby intense charge-transfer transitions [25].

The spectrum of [Cu(qamp)Cl] shows bands at 22220 and 16000 cm^{-1} assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively [25,29] as expected for the square planar copper(II) complexes. The zinc(II) complex exhibits a charge transfer transitions at 18310 cm^{-1}.

Table 3.5: *Electronic spectral data (in methanol)*

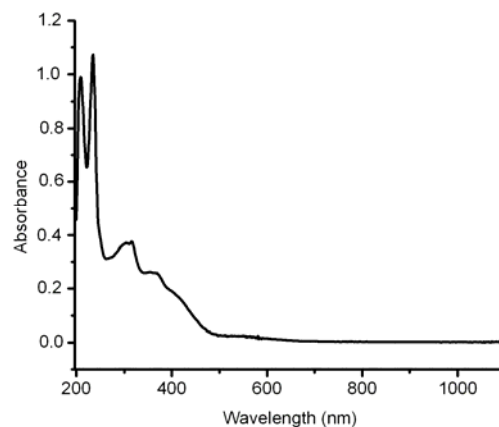| Compound	Absorption maxima (cm^{-1})	log ε (ε in L mol^{-1} cm^{-1})	Tentative assignments
qamp	42500	3.96	$\pi \rightarrow \pi^*$
	26000	3.81	$\pi \rightarrow \pi^*$
[Mn(qamp)(OAc)].H$_2$O	41320	3.56	$\pi \rightarrow \pi^*$
	29850	3.25	$\pi \rightarrow \pi^*$
	26400	3.30	CT
	18280	3.27	CT
	10800	1.67	$^6A_1 \rightarrow {}^4T_1$
	9300	1.68	$^6A_1 \rightarrow {}^4T_2(G)$
[Fe(qamp)Cl$_2$]	42920	4.12	$\pi \rightarrow \pi^*$
	24000	3.96	CT
	18200	3.70	CT
[Co(qamp)$_2$].H$_2$O	41850	3.62	$\pi \rightarrow \pi^*$
	29400	3.32	$\pi \rightarrow \pi^*$
	26450	3.35	$n \rightarrow \pi^*$
	18550	3.36	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
[Ni(qamp)$_2$].H$_2$O	41150	4.13	$\pi \rightarrow \pi^*$
	27850	3.88	$\pi \rightarrow \pi^*$
	17450	3.83	$^3A_{2g} \rightarrow {}^3T_{1g}$
[Cu(qamp)Cl]	40320	3.74	$\pi \rightarrow \pi^*$
	33900	2.44	$n \rightarrow \pi^*$
	28490	3.65	CT
	22220	2.08	$^2B_{1g} \rightarrow {}^2A_{1g}$
	16000	1.97	$^2B_{1g} \rightarrow {}^2E_g$
[Zn(qamp)$_2$].2H$_2$O	42200	3.72	$\pi \rightarrow \pi^*$
	30400	3.30	$\pi \rightarrow \pi^*$
	25840	3.31	$\pi \rightarrow \pi^*$
	18310	3.36	CT

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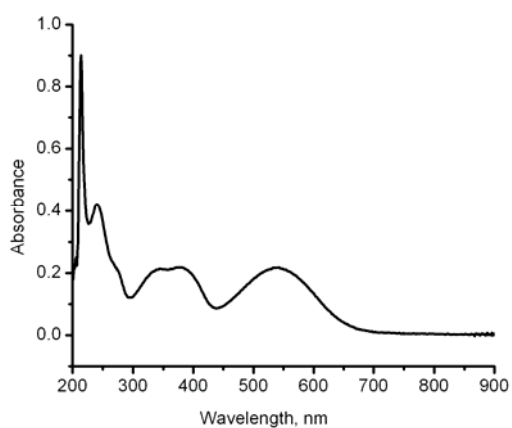
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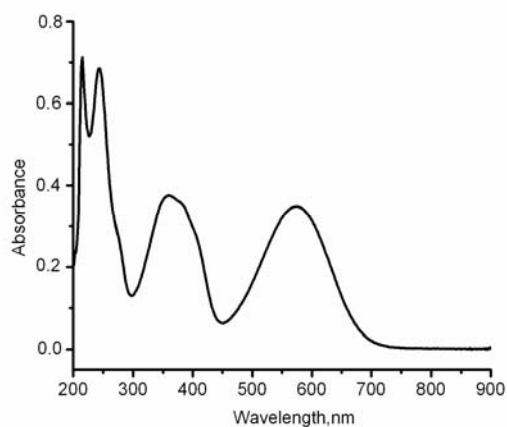**Figure 3.11:** *The UV-Vis spectrum of qamp*

Figure 3.12: *The UV-Vis spectrum of [Mn(qamp)(OAc)].H$_2$O*

Figure 3.13: *The UV-Vis spectrum of [Fe(qamp)Cl$_2$]*

Figure 3.14: *The UV-Vis spectrum of [Co(qamp)$_2$].H$_2$O*

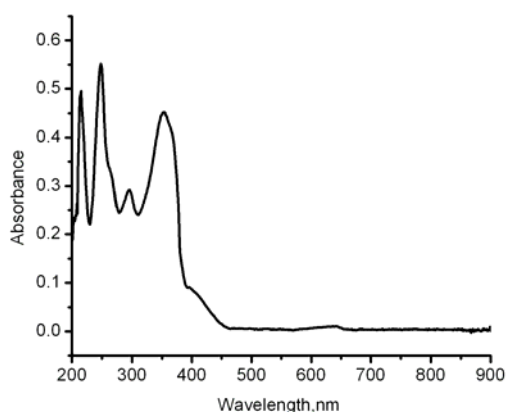

Figure 3.15: *The UV-Vis spectrum of [Ni(qamp)$_2$].H$_2$O*

Figure 3.16: *The UV-Vis spectrum of [Cu(qamp)Cl]*
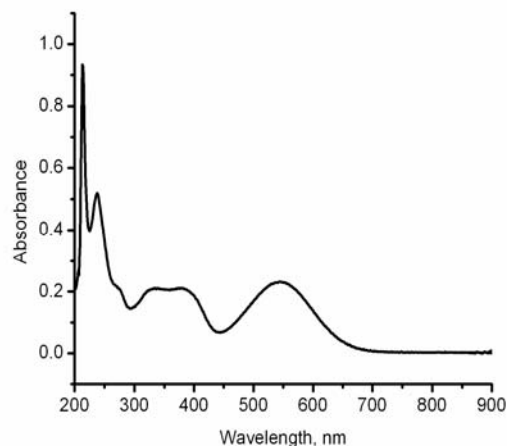
Figure 3.17: *The UV-Vis spectrum of [Zn(qamp)$_2$].2H$_2$O*
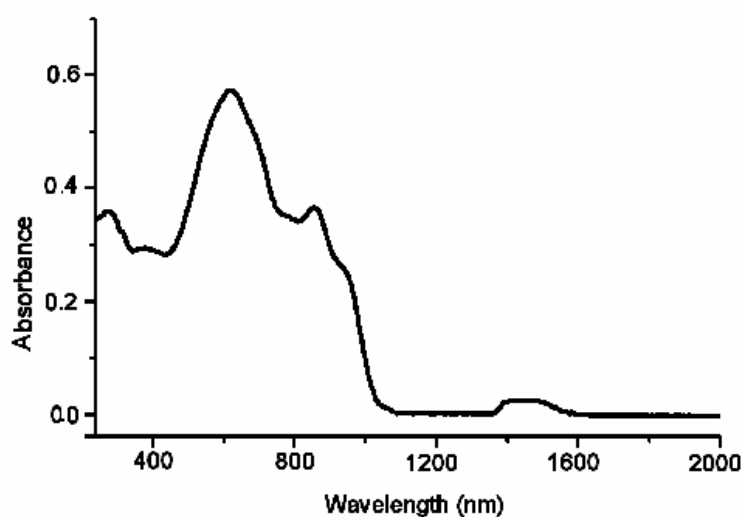
Figure 3.18: *UV-Vis-NIR spectrum of [Fe(qamp)Cl$_2$] in nujol mull*

3.3.5 Thermal analysis

The TG DTG plots of the ligand and complexes are given in Figures 3.19-3.25. The Schiff base, qamp, exhibits a one stage decomposition which begins at 160 ºC. The weight loss observed for the Mn(II), Co(II), Ni(II) and Zn(II) complexes in the range 40-140 ºC is due to the removal of lattice water (Table 3.6). The TG data indicate the presence of one hydrated water molecule in the

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manganese(II), cobalt(II) and nickel(II) complexes, and two water molecules in the zinc(II) complex. All the compounds are found to be thermally stable and exhibit multi stage decomposition pattern. TG results show good agreement with the molecular formula arrived from the analytical data.

Table 3.6: *TG data of the complexes below 200 ℃*

Complex	Temperature Range, ℃	% loss	Fragment lost	Nature of water lost
[Mn(qamp)(OAc)].H$_2$O	46–101	4.5	1 H$_2$O	Lattice water
[Co(qamp)$_2$].H$_2$O	50–120	3.0	1 H$_2$O	Lattice water
[Ni(qamp)$_2$].H$_2$O	50–130	3.1	1 H$_2$O	Lattice water
[Zn(qamp)$_2$].2H$_2$O	70–140	2.9	1 H$_2$O	Lattice water
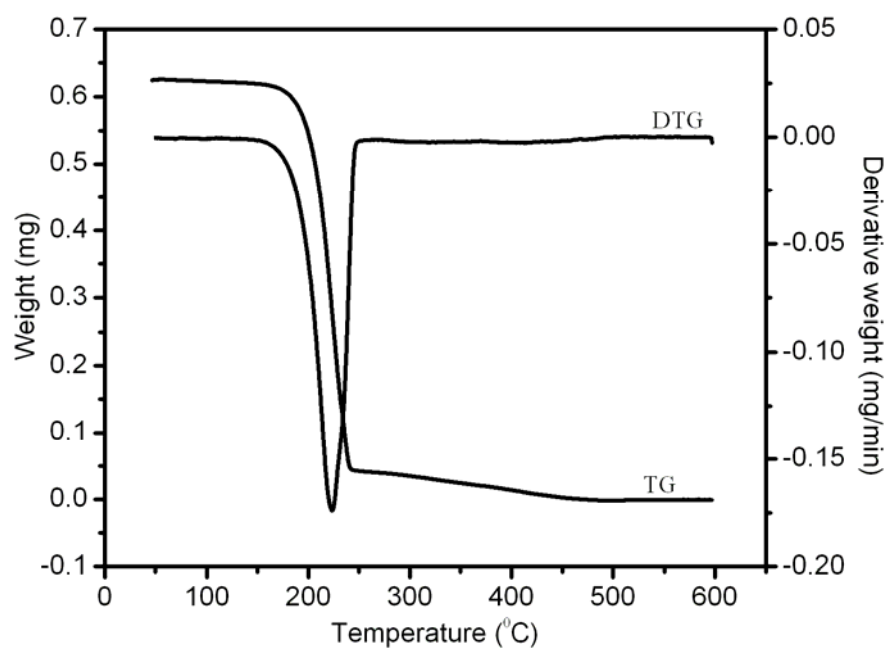
Figure 3.19: *TG DTG of qamp*
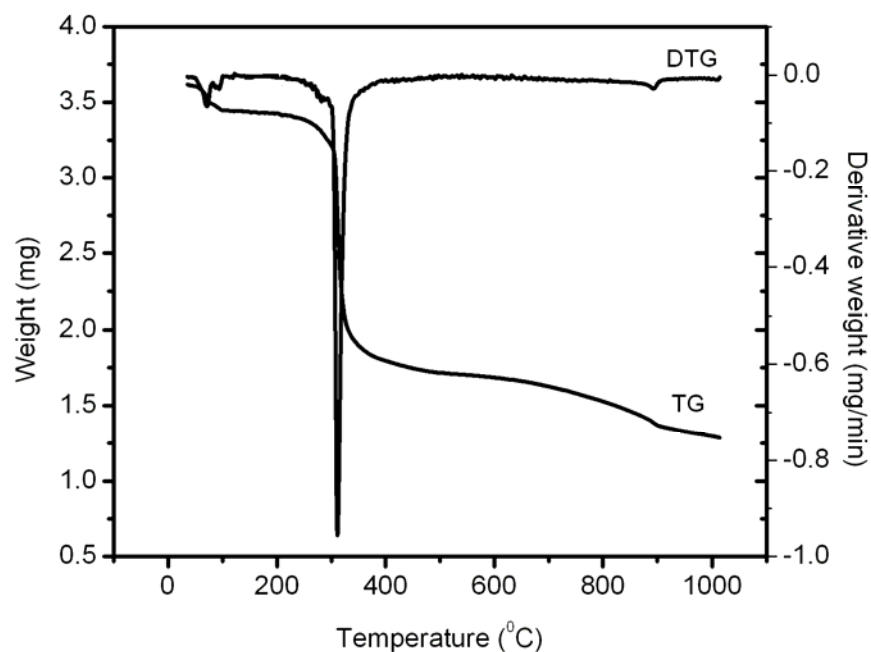
Figure 3.20: *TG DTG of [Mn(qamp)(OAc)].H₂O*
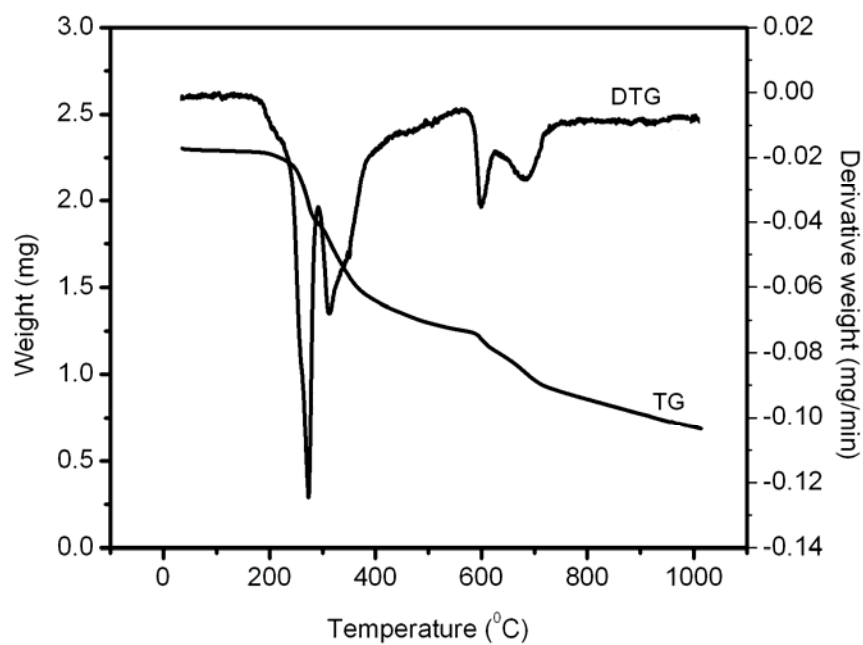
Figure 3.21: *TG DTG of [Fe(qamp)Cl₂]*

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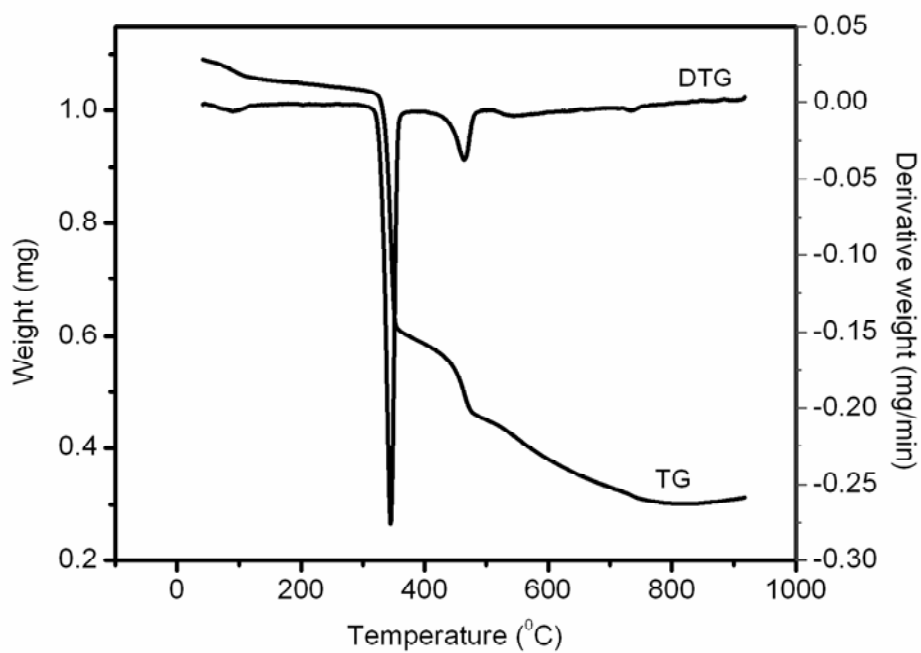
Figure 3.22: *TG-DTG of [Co(qamp)₂].H₂O*
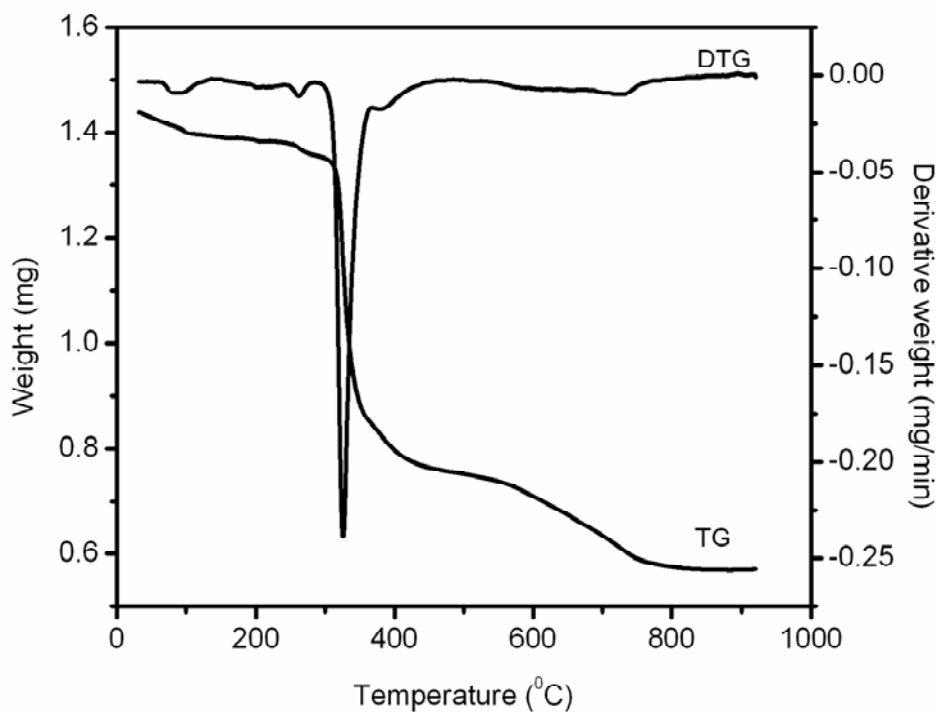
Figure 3.23: *TG-DTG of [Ni(qamp)₂].H₂O*
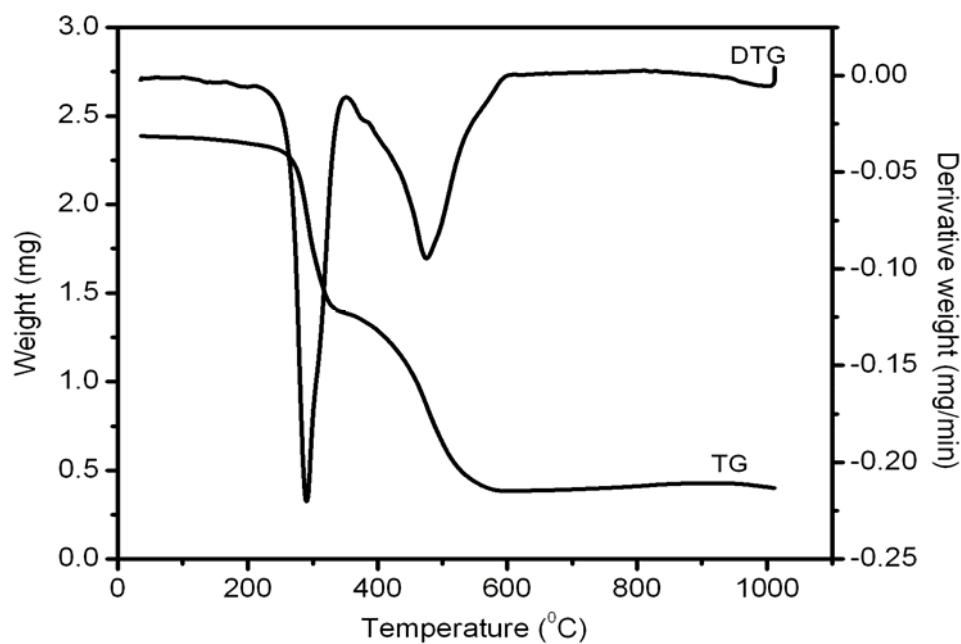
Figure 3.24: *TG-DTG of [Cu(qamp)Cl]*
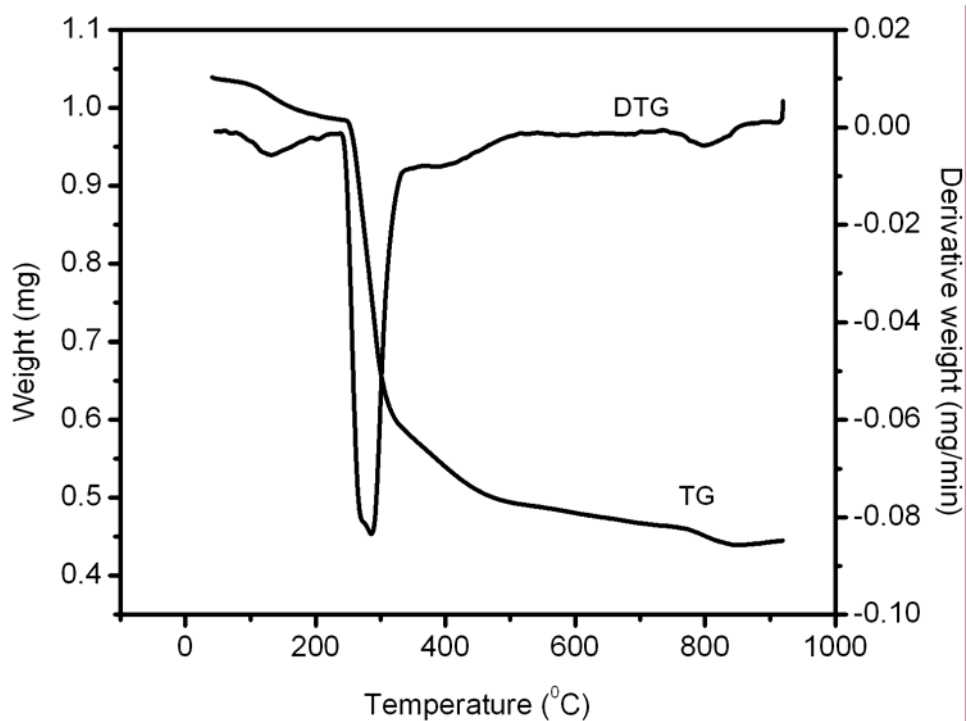
Figure 3.25: *TG-DTG of [Zn(qamp)$_2$].2H$_2$O*

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3.3.6 EPR spectra

The X band EPR spectra of the manganese(II) complex is taken in polycrystalline state at 298 K and in DMSO at 77K (Figure 3.26). The spin Hamiltonian used to represent EPR spectra of Mn(II) is given by,

$$\hat{H}=g\beta HS+D[S_z{}^2-S(S+1)/3]+E(S_x{}^2-S_y{}^2)$$

where H is the magnetic field vector, g is the spectroscopic splitting factor , β is the Bohr magneton, D is the axial zero field splitting term, E is rhombic zero field splitting parameter and S is the electron spin vector [30]. If D and E are very small compared to $g\beta HS$, six EPR transitions are expected. The solid state EPR spectrum of the Mn(II) complex is characterized by the broad isotropic spectrum with a g value of 1.98. The solution spectrum gives six hyperfine lines with the spin forbidden transitions in between the lines. The spectrum gives a g value of 1.98 with an A value of 0.011 cm^{-1}.

The copper(II) ion, with a d^9 configuration, has an effective spin of S= 3/2 and is associated with a spin angular momentum m$_s$=1/2, leading to a doubly degenerate spin state in the absence of a magnetic field. In a magnetic field, this degeneracy is lifted and the energy difference between these states is given by $E=h\nu=g\beta H$ where h is the Planck's constant, ν is the frequency, g is the Landé splitting factor, β is the electronic Bohr magneton and H is the magnetic field. For 3d^9 copper(II) ion the appropriate spin Hamiltonian assuming a B$_{1g}$ ground state is given by [31]

$$H=\beta[g_\parallel H_zS_z+g_\perp(H_xS_x+H_yS_y)]+AI_zS_z+B(I_xS_x+I_yS_y)$$

The EPR spectrum of the copper(II) complex in polycrystalline state gives an isotropic spectrum with a g value of 1.98. This spectrum exhibits a broad signal which arises from extensive exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation. This type of spectra gives no information on the electronic ground state of the Cu(II) ion present in the complexes. The EPR spectrum of the copper(II) complex gives a spectrum with $g_{\parallel}$ and $g_{\perp}$ values of 2.28 and 2.12 respectively (Figure 3.27). The trend $g_{\parallel} > g_{\perp} > g_e$ observed for copper(II) complex shows that the unpaired electron is most likely localized in $d_{x^2-y^2}$ orbital of copper(II) ion and the spectral features are characteristic of an axial symmetry [32, 33].
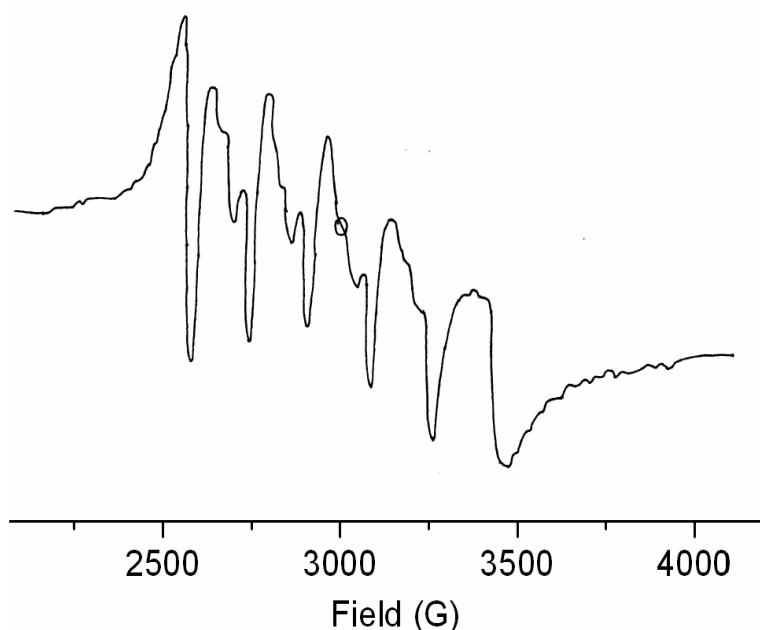
Figure 3.26: *EPR spectrum of [Mn(qamp)(OAc)].H$_2$O at 77 K*

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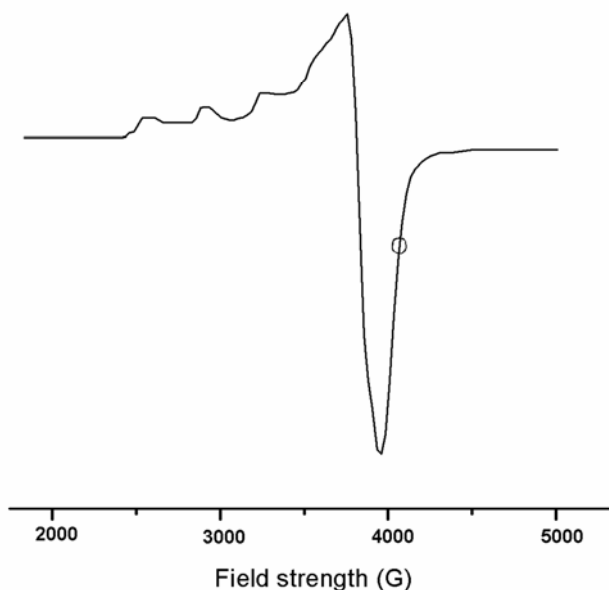
Figure 3.27: *EPR spectrum of [Cu(qamp)Cl] at 77 K*

3.3.7 Crystal structure analysis

3.3.7.1 Crystal structure of cobalt(II) complex of quinoxaline-2-carboxalidine-2-amino-5-methylphenol

The single crystals suitable for XRD were obtained by the slow evaporation of methanolic solution of the complex. The geometry of the complex is found to be distorted octahedral with one lattice water molecule. The compound crystallises in monoclinic crystal system with the space group $P2_1/n$. A summary of crystallographic data and refinement parameters are given in Table 3.7.

The molecular structure of the compound was solved at 298 K. Figure 3.28 gives the ORTEP diagram of the complex with atomic labelling scheme. The unit cell of the crystal contains four molecules of ($C_{32}H_{26}CoN_6O_3$). The important interatomic distances and angles are listed in Table 3.8. The phenolic hydroxyl group is deprotonated on complexation. Two of the monoanionic tridentate Schiff base ligands wrap the cobalt(II) center in the *cis* mode with coordination of two oxygen and four nitrogen atoms (N_4O_2) in a distorted octahedral geometry.

Table 3.7: *Crystal data summary for [Co(qamp)$_2$].H$_2$O*

Empirical formula	C$_{32}$H$_{26}$CoN$_6$O$_3$
Formula weight	601.52
Crystal size (mm^3)	0.40 x 0.36 x 0.02
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P*2$_1$/*n*
Cell constants:	
Unit cell and dimensions (Å)	
a (Å)	13.7959(15)
b (Å)	13.8622(15)
c (Å)	14.5161(16)
β(*º*)	94.684(2)
V (Å^3)	2766.8(5)
Z	4
D$_{calcd}$ (gcm^{-3})	1.444
Absorption coefficient (mm^{-1})	0.666
F(000)	1244
θ range for data collection (º)	1.96 to 26.03
Reflections collected / unique	27217 / 5445 [R(int) = 0.0841]
Max. and min. transmission	0.987 and 0.766
Data / restraints / parameters	5416 / 0 / 391
Goodness-of-fit on F^2	1.205
R$_1$, wR$_2$ [I > 2sigma(I)]	0.0975, 0.1807
R$_1$, wR$_2$ (all data)	0.1283, 0.1940

R$_1$ = $\sum$ (|Fo| − |Fc|) / $\sum$ |Fo|, wR$_2$ = [$\sum$w(Fo^2−Fc^2)^2/ $\sum$ w(Fo^2)^2]$^{0.5}$.

The azomethine (C=N) bond lengths (1.288(6) and 1.279(6) Å) are well within the range of theoretical value (~1.285 Å) [34]. The molecule has no symmetry elements other than a C2 symmetry axis and is expected to exhibit optical isomerism. However, both enantiomers coexist in the unit cell, making the space group centrosymmetric (Figure 3.29). The complex geometry can be explained by a rigid structure resulting in O(2)–Co(1)–N(5) and O(1)–Co(1)–N(2)

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bond angles that deviate significantly from linearity, i.e. 153.46(15) and 155.61(15)°. In the coordination sphere, the Co–O bond lengths are 2.031(4) and 2.045(4) Å; Co–N bond lengths are 2.049(4), 2.052(4), 2.256(4), and 2.310(4) Å. The Co–N (quinoxaline) bonds are elongated compared to Co–N (azomethine) bonds probably due to rigidity of the Schiff base. The benzene rings of the symmetry related quinoxalines are stacked via π–π interactions, having a centroid to centroid distance of 3.532 Å. Molecules are held together by O(3)–H(2)–N(3) and O(3)–H(31)–O(2) intermolecular hydrogen bonding and weak inter and intramolecular hydrogen bonding (Table 3.9) forming a 2-D polymeric structure parallel to the [010] plane as shown in Figure 3.30.

Table 3.8: *Selected bond lengths and angles for [Co(qamp)$_2$].H$_2$O*

Bond lengths (Å)			
Co(1)–O(1)	2.031(4)	Co(1)–N(2)	2.257(4)
Co(1)–O(2)	2.044(4)	Co(1)–N(5)	2.310(4)
Co(1)–N(4)	2.049(4)	N(1)–C(8)	1.288(6)
Co(1)–N(1)	2.052(4)	N(4)–C(24)	1.279(6)
Bond angles (º)			
O(1)–Co(1)–O(2)	100.56(18)	O(2)–Co(1)–N(5)	153.47(15)
O(1)–Co(1)–N(4)	96.56(15)	N(4)–Co(1)–N(5)	74.89(16)
O(2)–Co(1)–N(4)	79.73(15)	N(1)–Co(1)–N(5)	106.10(15)
O(1)–Co(1)–N(1)	80.00(16)	N(2)–Co(1)–N(5)	92.48(14)
O(2)–Co(1)–N(1)	99.71(15)	C(1)–O(1)–Co(1)	112.9(3)
N(4)–Co(1)–N(1)	176.38(17)	C(17)–O(2)–Co(1)	112.9(3)
O(1)–Co(1)–N(2)	155.63(15)	C(8)–N(1)–Co(1)	118.7(4)
O(2)–Co(1)–N(2)	87.80(15)	C(2)–N(1)–Co(1)	113.3(3)
N(4)–Co(1)–N(2)	107.49(16)	C(24)–N(4)–C(18)	126.3(4)
N(1)–Co(1)–N(2)	76.02(16)	C(24)–N(4)–Co(1)	120.3(4)
O(1)–Co(1)–N(5)	89.99(16)	C(18)–N(4)–Co(1)	113.4(3)

Table 3.9: *Selected hydrogen bond interactions in the complex*

| D-H...A | Symmetry | Distances (Å) | | Angles (∘) |
		D...A	H...A	D-H...A
O(3)-H(2)...N(3)	1/2 + x, 3/2-y, -1/2 + z	3.035(10)	2.51(8)	124(6)
O(3)−H(31)...O(2)	1−x, 1−y, 1−z	2.895(9)	2.01(8)	169(6)
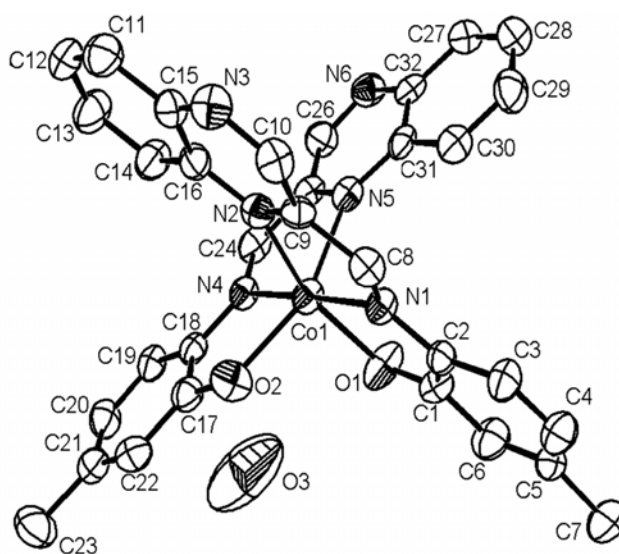
Figure 3.28: *ORTEP diagram of [Co(qamp)$_2$].H$_2$O showing the atom labeling scheme with 50% probability ellipsoids.*
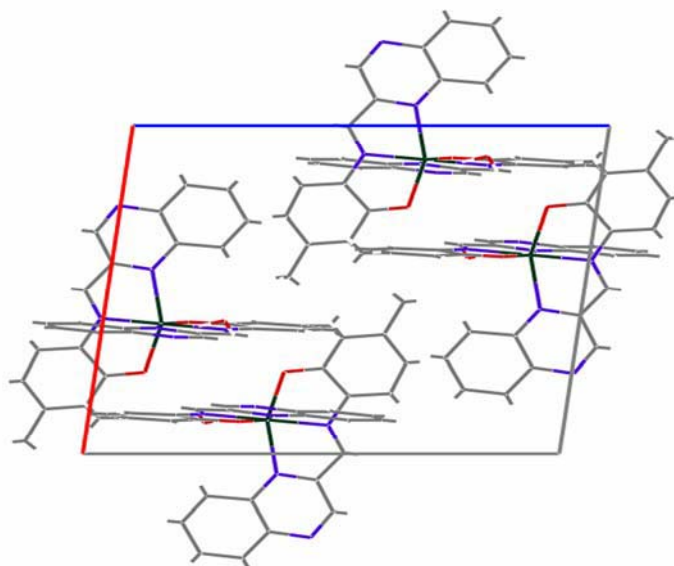
Figure 3.29: *Unit cell packing of the complex along b axis*

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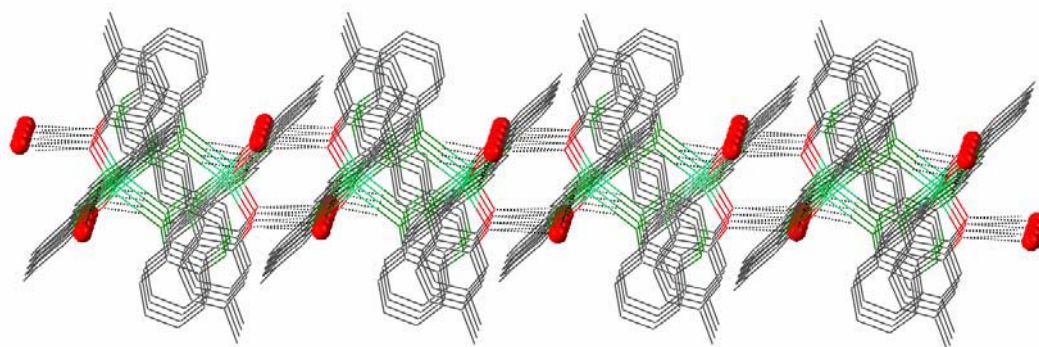**Figure 3.30:** *Two dimensional structure of [Co(qamp)$_2$].H$_2$O*

3.3.7.2 Crystal structure of nickel(II) complex of quinoxaline-2-carboxalidine-2-amino-5-methylphenol

The single crystals suitable for XRD were obtained by the slow evaporation of methanolic solution of the complex. The compound crystallises in monoclinic crystal system with the space group $P2_1/n$. A summary of crystallographic data and refinement parameters are given in Table 3.10.

Single crystal X-ray diffraction analysis reveals that the nickel(II) complex forms a two-dimensional polymeric chain due to the aggregation of the discrete monomeric entities through classical intermolecular O–H…O and O–H…N hydrogen bonds. The asymmetric unit as illustrated in the ORTEP diagram (Figure 3.31), consists of a monomeric Ni$\{(CH_3)C_6H_4(O)N=CH-C_8H_5N_2\}_2$ unit with a solvent water molecule present in the lattice. In the complex, the ligand quinoxaline −2−carboxalidine−2−amino−5−methyl phenol behaves as a monoanionic, tridentate Schiff base with its NNO donor set which coordinates to the metal center through one imine nitrogen, one quinoxaline ring nitrogen atom and a deprotonated phenolic oxygen atom in a mer arrangement. The nickel(II) center adopts a distorted octahedral geometry being chelated by two units of such tridentate Schiff base ligands.

Selected bond lengths and angles are listed in Table 3.11. The Ni–N(imine) distances are comparable to those observed for the similar kind of complexes

present in the literature [35, 36, 47]. The three trans-angles at nickel(II) are 176.00(18), 157.68(16) and 159.61(17) º for N(3)–Ni(1)–N(6), O(1)–Ni(1)–N(1) and O(2)–Ni(1)–N(4) which shows slight variation from 180 º while the cis angles differ in the range 76.64(18)–106.03(17) which also deviates from the ideal value of 90 º. These deviations in bite angles are due to the rigid structure of the Schiff base.

Table 3.10: *Crystal data summary for [Ni(qamp)$_2$].H$_2$O*

Formula	C$_{32}$ H$_{26}$ Ni N$_6$ O$_3$
Formula weight	601.30
Crystal system	Monoclinic
Space group	*P*2$_1$/*n*
a/Å	13.677(4)
b /Å	13.760(3)
c /Å	14.572(4)
β /º	96.445(5)
V /Å^3	2725.1(12)
Z	4
T(K)	298
Dc/mg m^{-3}	1.466
μ(Mo *K*α)/mm^{-1}	0.76
F(000)	1248
θ range for data collection /º	1.94 to 25.00
Reflections collected / unique	12261 / 4797
Goodness-of-fit on F2	1.194
R1 , wR2 [I > 2sigma(I)]	0.0884, 0.1529
R1 , wR2 (all data)	0.1117, 0.1630

R1 = Σ (|Fo| – |Fc|) / Σ |Fo|, wR2 = [Σw(Fo2–Fc2)2/ Σ w(Fo2)2]0.5.

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A further insight into the structure of the complex reveals the presence of a C2 symmetry axis and is expected to exhibit optical isomerism. However both the enantiomers coexist in the unit cell, being the space group centro-symmetric [38]. Both hydrogen of the uncoordinated water molecule are involved in the intermolecular hydrogen bonding with the neighbouring phenolic oxygen atom and uncoordinated quinoxaline nitrogen atom through O(3)–H1w…N(5) and O(3)–H2w …O(1) interactions. Similarly there are some weak intermolecular and intramolecular hydrogen bondings in the lattice. There is π–π stacking interaction between phenolic ring and symmetry related quinoxaline. A few significant hydrogen bonding parameters are listed in Table 3.12. It makes the monomeric unit a good template which is an important factor in establishing an ordered supramolecular structure formed by self-assembly [39-43]. All these interactions afford an infinite two dimensional chain propagating along [010] direction which is similar to that of cobalt(II) complex of qamp (Figure 3.30).

Table 3.11: *Selected bond lengths (Å) and angles (º) for [Ni(qamp)$_2$].H$_2$O*

Bond lengths			
Ni(1) –N(3)	1.988(4)	N(1) – C(1)	1.359(6)
Ni(1) – N(6)	1.992(4)	N(2) – C(7)	1.306(7)
Ni(1) – O(2)	2.033(4)	N(2) – C(6)	1.362(7)
Ni(1) – O(1)	2.044(4)	N(3) – C(9)	1.273(6)
Ni(1) – N(4)	2.226(4)	N(3) – C(10)	1.391(6)
Ni(1) – N(1)	2.290(4)	N(4) – C(24)	1.323(6)
O(1) – C(15)	1.301(6)	N(4) – C(17)	1.381(7)
O(2) – C(31)	1.284(6)	N(1) – C(8)	1.310(6)
Bond angles			
N(3) –Ni(1) –N(6)	176.00(18)	O(1) –Ni(1) –N(4)	88.84(14)
N(3) –Ni(1) –O(2)	94.36(16)	N(3) –Ni(1) –N(1)	76.64(18)
N(6) –Ni(1) –O(2)	81.68(18)	N(6) –Ni(1) –N(1)	103.82(17)
N(3) –Ni(1) –O(1)	81.25(17)	O(2) –Ni(1) –N(1)	90.77(15)
N(6) –Ni(1) –O(1)	98.45(16)	O(1) –Ni(1) –N(1)	157.68(16)
O(2) –Ni(1) –O(1)	93.90(15)	N(4) –Ni(1) –N(1)	94.33(14)
N(3) –Ni(1) –N(4)	106.03(17)	O(2) –Ni(1) –N(4)	159.61(17)
N(6) –Ni(1) –N(4)	77.93(18)		

Table 3.12: *Selected hydrogen bond interactions in the complex*

| D−H...A | Symmetry | Distances (Å) | | Angles (◦) |
		D...A	H...A	D−H...A
O(3)−H(3C)...N(5)	1/2 + x, 3/2−y, −1/2 + z	3.015(7)	2.43	127
O(3)−H(3D)...O(1)	1−x, 1−y, 1−z	2.862(7)	2.18	159
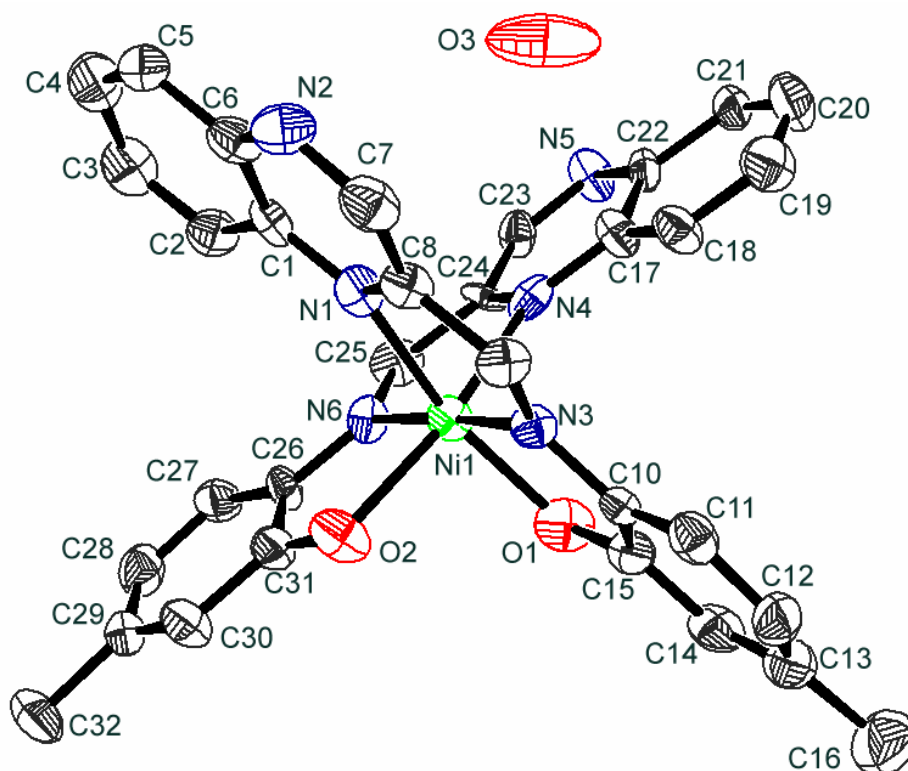
Figure 3.31: *Ortep representation of the complex [Ni(qamp)$_2$].H$_2$O, with 50 %
probability ellipsoid (Hydrogen atoms are omitted for clarity)*

3.4 CONCLUSIONS

This chapter describes the synthesis and characterizations of a new Schiff
base derived from quinoxaline-2-carboxaldehyde and 2-amino-5-methylphenol,

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and its complexes with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). Crystal structures of [Co(qamp)$_2$].H$_2$O and [Ni(qamp)$_2$].H$_2$O confirm the octahedral geometry of the complexes. In both the cases the unit cell contains a racemic mixture of two crystallographically independent enantiomers of the complex. The molecules exhibit a two dimensional polymeric structure parallel to [010] plane, formed by O–H…N and O–H…O intermolecular hydrogen bonding and π–π stacking interaction. We, therefore, conclude that the Schiff base can act as a good template in establishing an ordered polymeric structure. Based on the analytical and physicochemical data we have proposed the following structures for the other complexes (Figure 3.32).
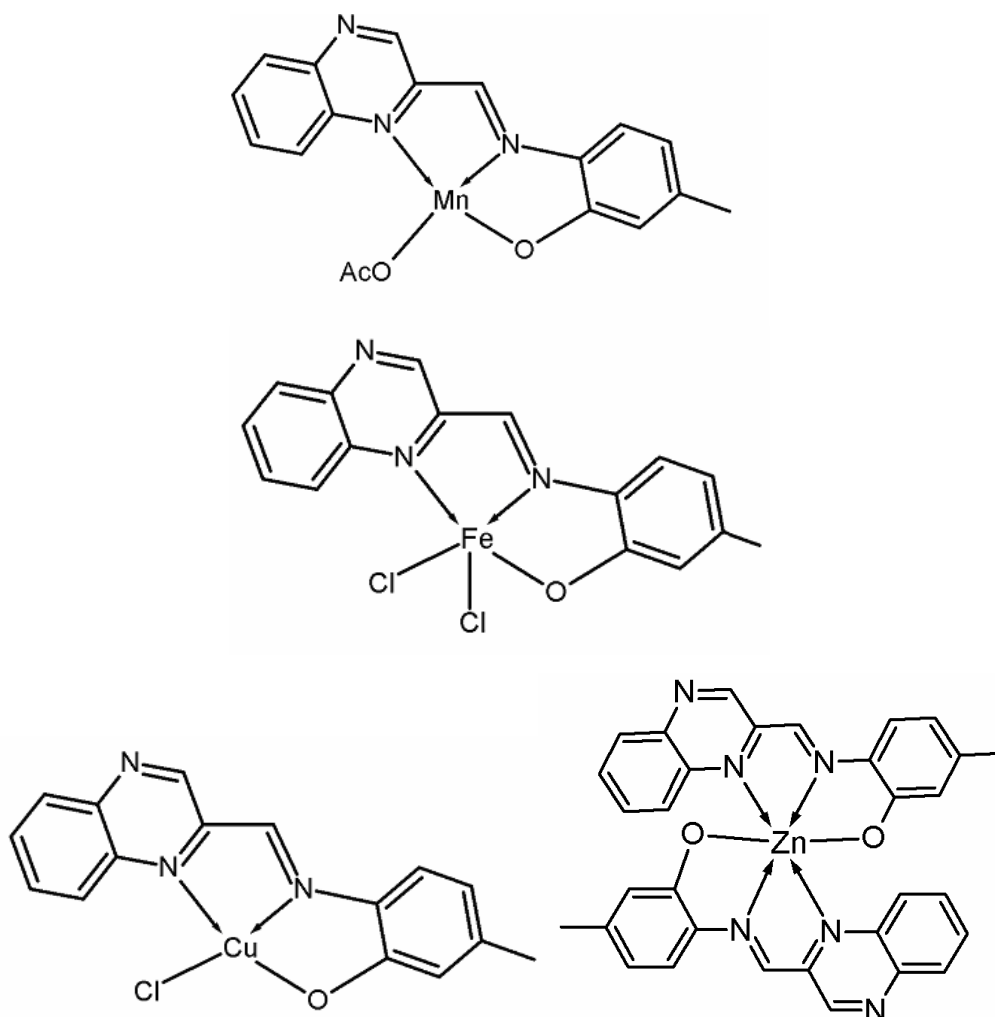

Figure 3.32: *Proposed structures of the Schiff base complexes*

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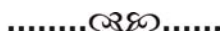
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Template synthesis and spectral characterization of quinoxaline–2–carboxalidine–L–histidine complexes of manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II)

Contents

4.1 Introduction

4.2 Experimental

4.3 Results and discussion

4.4 Conclusions

References

4.1 INTRODUCTION

Complexes of Schiff bases derived from amino acids attract chemists and biologists due to their interesting and useful pharmacological and biological properties [1-3]. They can be taken as good models to study metal-ligand interactions in metalloproteins and metalloenzymes. L-Histidine (Figure 4.1) serves as a ligand through the imidazole imido nitrogen atom in many enzymes.
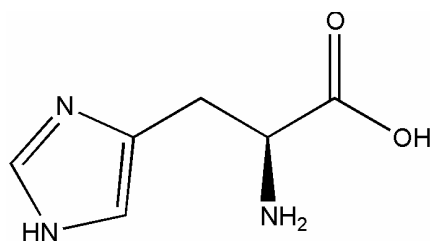
Figure 4.1: *Structure of L-histidine*

The formation of Schiff base intermediates in reactions of biological importance is well documented [4, 5]. We report here a convenient synthesis of few

Schiff base complexes via template method under mild reaction conditions. The routine use of metal template procedures for obtaining a wide range of compounds stems from 1960, when Curtis discovered a template reaction for obtaining an isomeric pair of nickel macrocyclic complexes [6]. Template effect may arise from stereochemistry imposed by metal ion coordination of some of the reactants. It promotes a series of controlled steps and characteristically provides routes to products not formed in the absence of the metal ion [7, 8]. The metal ion may sequester the cyclic product from an equilibrium mixture promoting the formation of the metal complex or it may direct the steric course of a condensation facilitating the formation of the required cyclic product [9, 10]. The template synthesis of transition metal complexes of the Schiff base derived from glycine and quinoxaline−2−carboxaldehyde was already reported from our group [11]. In continuation of this work, we have studied the synthesis and characterization of manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of a Schiff base derived from quinoxaline−2−carboxaldehyde and L−histidine.

4.2 EXPERIMENTAL

4.2.1 Materials and methods

The method of preparation of quinoxaline-2-carboxaldehyde and the techniques employed for the characterization of metal complexes are given in chapter II.

4.2.2 Preparation of Complexes

Since ligand cannot be isolated for the synthesis of complexes, template method is adopted. In this method aldehyde, amine and metal compound are refluxed in 1:1:1 molar ratio. The general scheme of the reaction (Scheme 4.1) and procedural details are given below.

4.2.2.1. Preparation of the Mn(II), Fe(III), Co(II) and Ni(II) complex

The preparation of the Mn(II) complex was carried out by taking quinoxaldehyde (1.580 g, 0.01 mol) in methanol (30 mL) and L-histidine (1.550 g, 0.01 mol) in water (20 mL). To this solution, sodium acetate in methanol (5 mL) was added to adjust the pH around 9. The mixture was then refluxed on a water bath for half an hour. The colour of the solution turns from pale yellow to dark brown. To this hot solution, manganese acetate tetrahydrate (1.979 g, 0.01 mol) in methanol (20 mL) was added. The solution was refluxed for two more hours and then was kept at room temperature (28±2 °C). The precipitate formed was filtered and washed with methanol containing water and then with acetone. Fe(III), Co(II) and Ni(II) complexes were prepared in a similar way by using ferric chloride anhydrous (1.622 g, 0.01 mol), cobalt acetate hexahydrate (2.490 g, 0.01 mol) or nickel acetate hexahydrate (2.488 g, 0.01 mol).

4.2.2.2. Preparation of the Cu(II)and Zn(II) complex

Quinoxaldehyde (1.580 g, 0.01mol) in methanol (50 mL) was added to L-histidine (1.550 g, 0.01 mol) in water (30 mL). The solution was then refluxed on a water bath for half an hour. The colour of the solution turns from pale yellow to dark brown. To this hot solution, copper chloride (1.700 g, 0.01 mol) or zinc acetate (2.190 g, 0.01 mol) in methanol (20 mL) was added. Instantaneous formation of a precipitate was observed, and the refluxing was continued for one more hour to ensure complete precipitation. The precipitate was filtered and washed with methanol containing water and then with acetone.
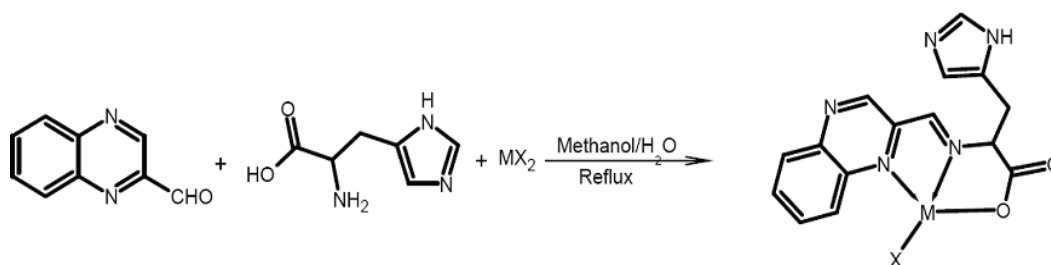
Scheme 4.1: *The general scheme showing the formation of Schiff base complex of quinoxaline-2-carboxalidine-L-histidine by template method.*

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4.3 RESULTS AND DISCUSSION

The complexes are found to be stable in air and non-hygroscopic. They are soluble in DMSO and DMF. The elemental analysis data of the complexes are given in Table 4.1. The data agree with the molecular formula of the complexes given in the Table. The molar conductivity measurements of all the complexes in DMF (10^{-3} M solution) have values in the range 5–25 $ohm^{-1}cm^2mol^{-1}$, which suggest the non-electrolytic nature of the complexes (Table 4.2). This further suggests that the anions are associated in the first coordination sphere of the complexes [12].

Table 4.1: *Analytical data of complexes of qlh*

Compound	Colour	Yield (%)	Analytical data. Found (calculated) %				
			C	H	N	M	Cl
[Mn(qlh)(OAc)]. 2H$_2$O	Black	55	46.07 (45.96)	4.25 (4.31)	15.41 (15.76)	12.86 (12.37)	–
[Fe(qlh)Cl$_2$(H$_2$O)]. H$_2$O	Black	70	40.05 (39.42)	2.98 (3.53)	15.41 (15.32)	12.11 (12.22)	15.73 (15.51)
[Co(qlh)(OAc)].2H$_2$O	Black	62	45.51 (45.55)	3.97 (4.27)	15.86 (15.62)	12.79 (13.15)	–
[Ni(qlh)(OAc)(H$_2$O)$_2$].H$_2$O	Black	65	43.42 (43.81)	4.69 (4.54)	15.19 (15.03)	12.81 (12.59)	–
[Cu(qlh)Cl]. 2H$_2$O	Black	80	41.54 (41.96)	3.32 (3.76)	16.36 (16.31)	15.09 (14.80)	8.45 (8.26)
[Zn(qlh)(OAc)].2H$_2$O	Red	80	44.87 (44.90)	4.09 (4.21)	15.48 (15.40)	14.47 (14.38)	–

Table 4.2: *Conductivity and magnetic moment data of the complexes*

Compound	μ$_{eff}$ (B.M)	λ$_m$[#]
[Mn(qlh)(OAc)]. 2H$_2$O	5.96	7
[Fe(qlh)Cl$_2$(H$_2$O)]. H$_2$O	5.30	15
[Co(qlh)(OAc)].2H$_2$O	3.96	11
[Ni(qlh)(OAc)(H$_2$O)$_2$].H$_2$O	2.97	18
[Cu(qlh)Cl]. 2H$_2$O	2.10	9
[Zn(qlh)(OAc)].2H$_2$O	–	5

[#] Molar conductivity (in Mho cm^2 mol^{-1}), 10^{-3} Molar solution in DMF

4.3.1 Magnetic susceptibility measurements

The room temperature (28 ± 2 °C) magnetic moments of the complexes are given in Table 4.2. The μ_{eff} value of the Mn(II) complex was found to be 5.96 B.M. at room temperature as expected for a high spin d^5 system. The magnetic moment of $[Fe(qlh)Cl_2(H_2O)]$ is found to be 5.83 B.M. Hence the iron(III) like manganese(II) is high spin in its complex. The room temperature magnetic moment of the cobalt(II) complex is 4.66 B.M. which indicates a tetrahedral geometry around cobalt atom. The magnetic moment of the nickel(II) complex is found to be 3.32 B.M., which is as expected for an octahedral complex. The magnetic moment of the copper(II) complex is 1.92 B.M. which suggests the lack of Cu–Cu interactions and monomeric nature of the complex. The value also indicates that the molecules are in a magnetically dilute state and therefore the possibility of spin-spin coupling could be ruled out.

4.3.2 Infrared spectra

As we were not able to isolate the free ligand, the assignments of the infrared bands of the complexes are done based on the infrared spectra of the histidine and quinoxaline–2–carboxaldehyde. The IR spectra of the complexes are given in Figures 4.2–4.7. Most of the bands due to the quinoxaline–2–carboxaldehyde and histidine are present in the spectra of the complexes. However, the C=O stretching observed in quinoxaline–2–carboxaldehyde at 1680 cm^{-1} is absent in the spectra of complexes. This confirms the formation of Schiff base. The important IR spectral bands are listed in Table 4.3. The most characteristic IR spectral bands appear at 1610–1660 cm^{-1} as a multiplet which are attributable to asymmetric stretching of $\nu(COO^-)$ and $\nu(C=N)$ stretching of the azomethine moiety [13]. The symmetric $\nu(COO^-)$ stretching is observed around 1400–1420 cm^{-1} [14]. All the complexes show a broad absorption band around 3300 cm^{-1} due to the presence of water molecule. The (N–H) stretching of imidazole ring occurs in the

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same region. However, due to overlap we could not differentiate them. The (C=N) stretching of quinoxaline ring occurs at 1550–1590 cm^{-1}. The low frequency vibrations observed around 400 cm^{-1} are due to metal–nitrogen and metal–oxygen stretching.

Table 4.3: *IR spectral data of complexes of qlh*

Assignments	$\nu(H_2O)$, $\nu(NH)$	$\nu(COO^-)$ $^\$$	$\nu(COO^-)$ @	$\nu(C=N)^\#$	$\nu(C=N)$ ##	$\nu(M-O)$	$\nu(M-N)$
[Mn(qlh)(OAc)]. 2H$_2$O	3330 b	1652	1416	1613	1571	446	409
[Fe(qlh)Cl$_2$(H$_2$O)]. H$_2$O	3300 b	1640	1412	1617	1541	440	414
[Co(qlh)(OAc)].2H$_2$O	3300 b	1645	1409	1613	1581	442	416
[Ni(qlh)(OAc)(H$_2$O)$_2$].H$_2$O	3397, 3361	1650	1407	1613	1579	440	420
[Cu(qlh)Cl]. 2H$_2$O	3505, 3421	1642	1404	1621	1556	435	413
[Zn(qlh)(OAc)].2H$_2$O	3300 b	1653	1417	1621	1586	446	415

$^\#$ azomethine , $^{\#\#}$ quinoxaline , $^@$ symmetric stretching, $^\$$ asymmetric stretching
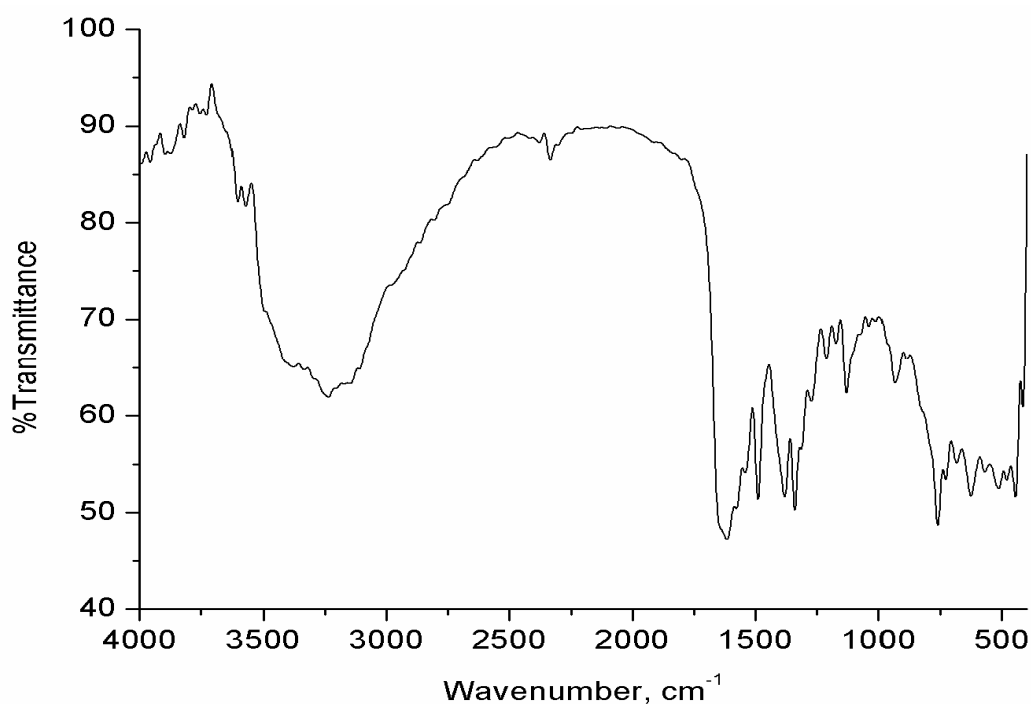
Figure 4.2: *FTIR spectrum of [Mn(qlh)(OAc)]. 2H$_2$O*
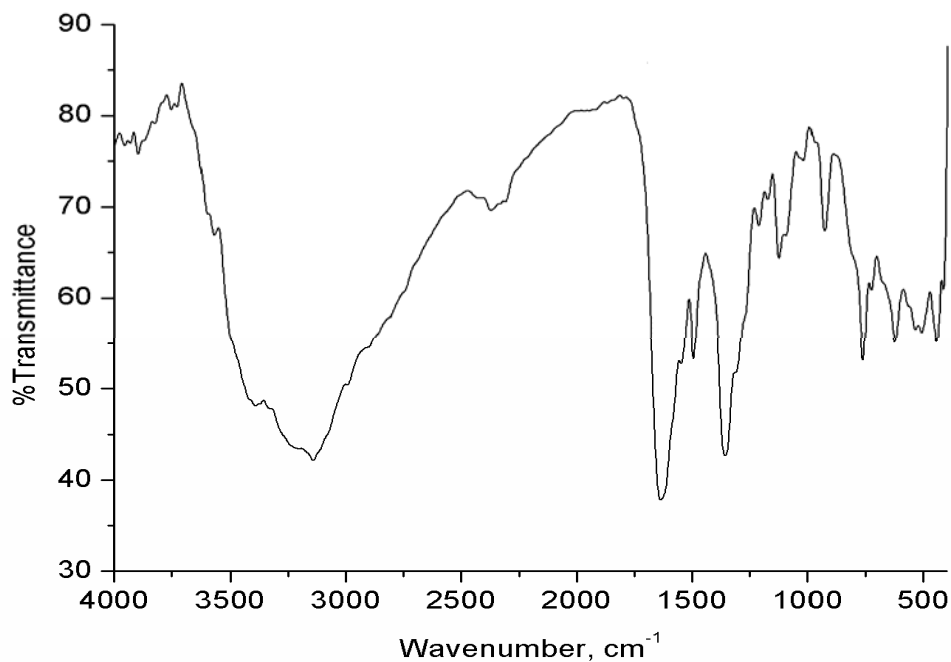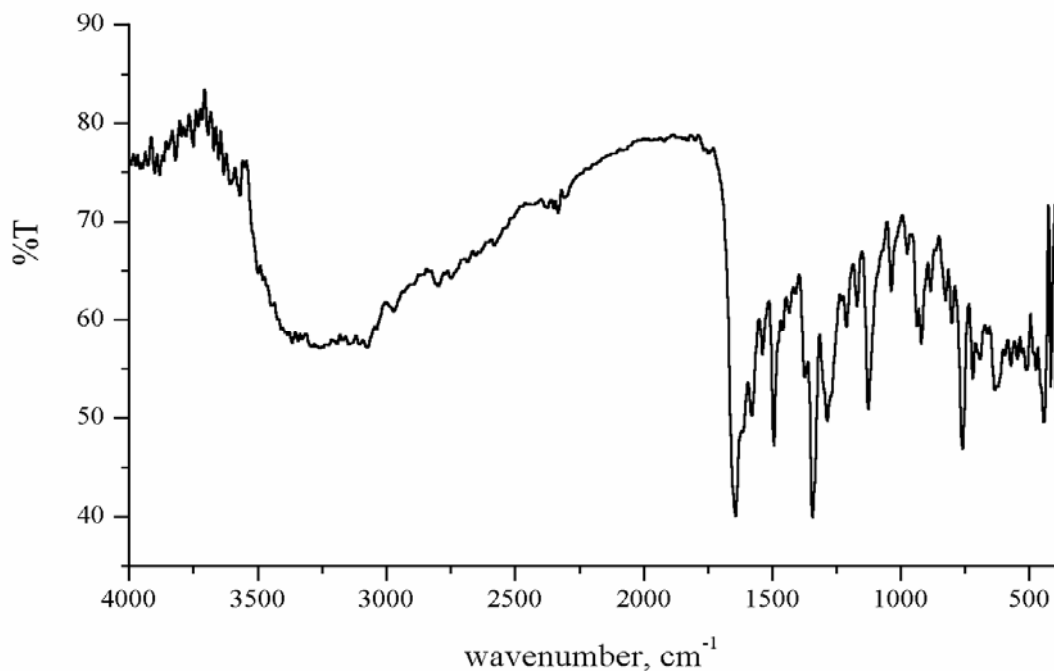
Figure 4.3: *FTIR spectrum of [Fe(qlh)Cl₂(H₂O)]. H₂O*

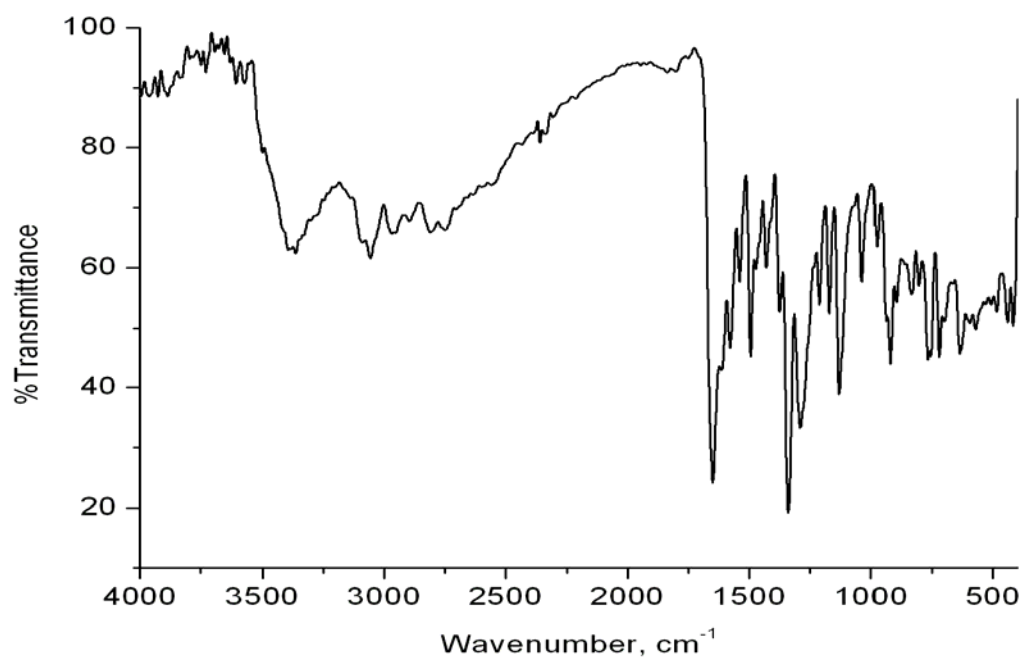

Figure 4.4: *FTIR spectrum of [Co(qlh)(OAc)].2H₂O*

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Figure 4.5*: FTIR spectrum of [Ni(qlh)(OAc)(H₂O)₂].H₂O*
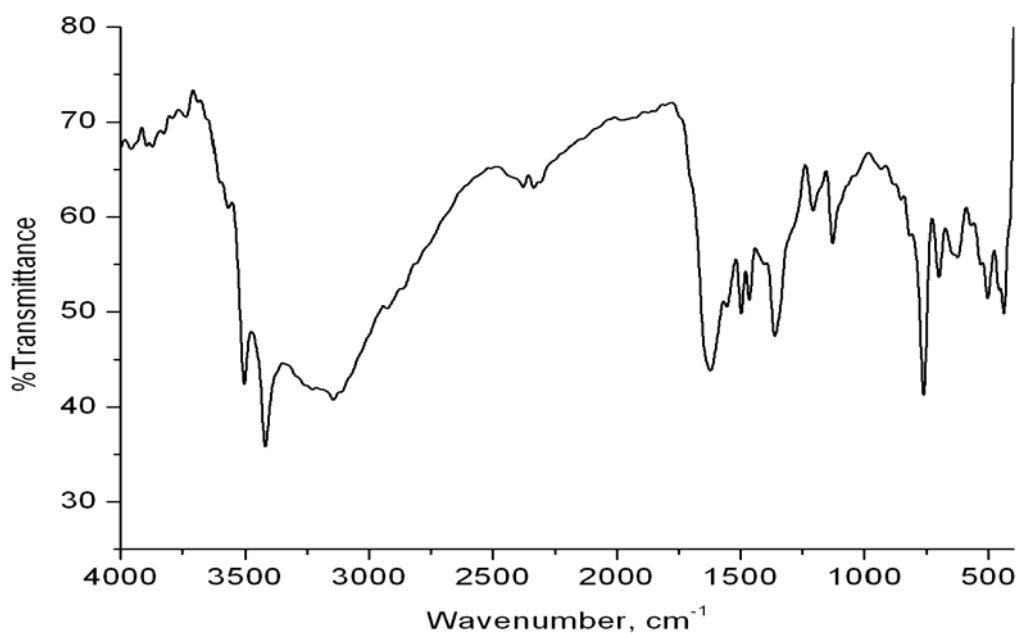
Figure 4.6: *FTIR spectrum of [Cu(qlh)Cl]. 2H₂O*

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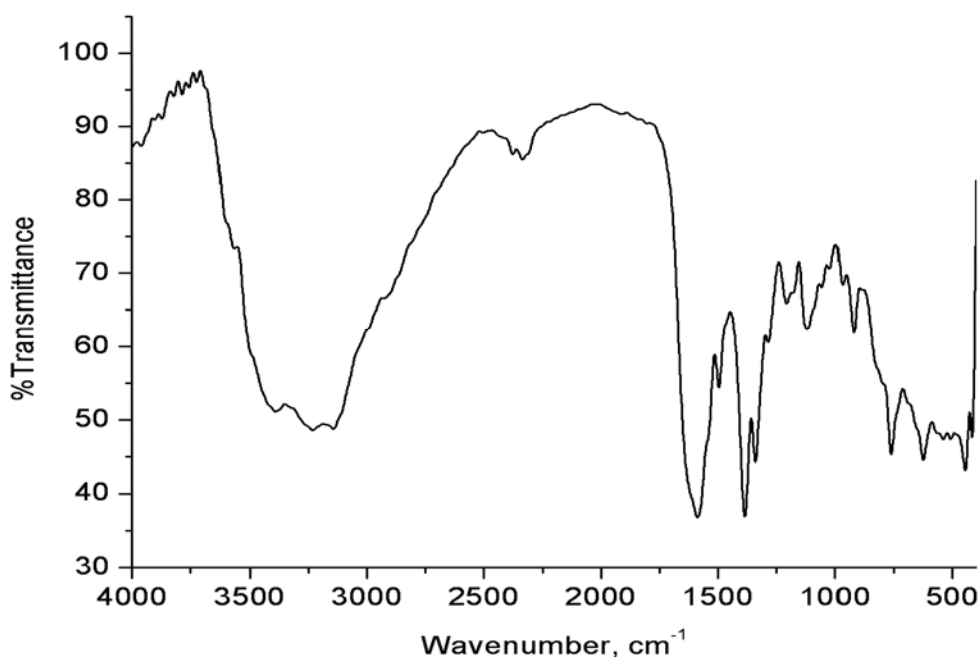
Figure 4.7: *FTIR spectrum of [Zn(qlh)(OAc)].2H$_2$O*

4.3.3 Electronic spectra

The UV–Vis spectra of the Schiff base complexes in methanol (~5x10^{-4} molar) were recorded in the range 50000-10000 cm^{-1}, and are given in Figures 4.8–4.13. The spectral bands and their assignments are listed in Table 4.4. For all the complexes the bands observed between 28500 to 50000 cm^{-1} are identical and might be due to π–π* transitions and intraligand charge transfer transitions of quinoxaline ring, imidazole ring and azomethine C=N moiety. The forbidden n–π* transitions are not observed.

The electronic transitions from $^6A_1$ ground state of manganese(II) to higher energy states are spin-forbidden and these transitions are difficult to observe in the spectrum. The spectrum of [Mn(qlh)(OAc)] contains bands at 27550 and 20200 cm^{-1}, which corresponds to $^6A_1{\rightarrow}^4E_1$(D) and $^6A_1{\rightarrow}^4T_1$(G) transitions. Similar observations has been made in the case of tetrahedral manganese(II) complexes [15, 16].

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The ground state of high spin octahedral Fe(III) complexes is $^6A_{1g}$. The four lowest energy bands are expected for such complexes the transition from $^6A_{1g}$ to $^4T_{1g}$, $^4T_{2g}$, ^4E_g, and $^4A_{1g}$, excited states. The Fe(III) complex exhibits only a charge transfer band at 27700 and a weak shoulder at 24400 cm^{-1}. The charge transfer band might have obscured the weak forbidden d-d transitions. However, the shoulder band might be due to the $^6A_{1g} \rightarrow {}^4T_{1g}$ transition expected for the iron(III) octahedral complexes [17].

The spectrum of the cobalt(II) complex contains a d-d band at 16670 cm^{-1}, which corresponds to $^4A_2 \rightarrow {}^4T_1(P)$ transitions [15]. There is a charge transfer band at 27400 cm^{-1}. In addition to the solution spectrum, the spectrum of the cobalt(II) complex is taken in nujol to get more information about the geometry around cobalt. The geometry can be distinguished by analyzing the near IR region of the electronic spectrum. The low-energy multiplets at 8000 and 7500 cm^{-1} in the mull spectrum indicates the tetrahedral geometry of the cobalt(II) complex and this band might be due to $^4A_2(F) \rightarrow {}^4T_1(F)$ transition [18, 19]. The electronic spectrum of the cobalt(II) complex in nujol mull is presented in Figure 4.14.

Spectrum of the nickel(II) complex exhibits three shoulders at 23600, 17760 and 9800 cm^{-1} which indicates an octahedral geometry around nickel atom [20] and these bands corresponds to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively.
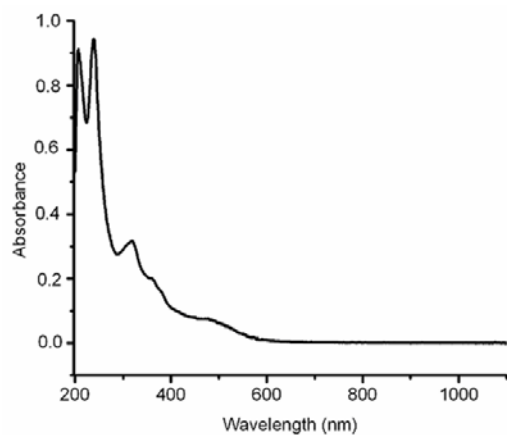
The spectrum of [Cu(qlh)Cl].2H$_2$O gives a weak broad band in the visible region, 13000 to 19000 cm^{-1} assignable to $^2B_{1g} \rightarrow {}^2E_g$ transition. The bands at 25900 and 15500 cm^{-1} correspond to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions. It indicates the square planar geometry of the complex around copper atom [15, 21]. The zinc(II) complex exhibits only an intra ligand charge transfer transition at 31250 cm^{-1}. No d-d transitions are expected for d^{10} zinc complexes.
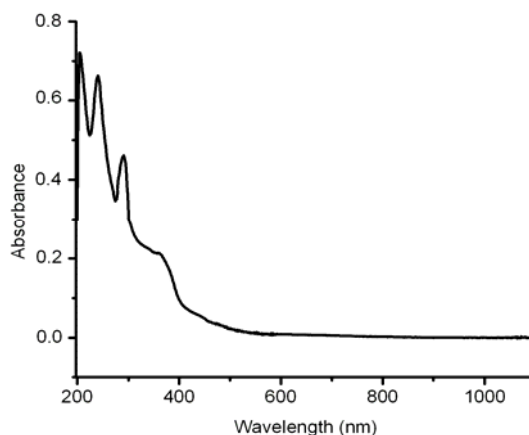
Table 4.4: *UV-Vis spectral data of the complexes in methanol*

Compound	Absorption maxima cm^{-1}	log ε (ε in L mol^{-1} cm^{-1})	Tentative assignments
[Mn(qlh)(OAc)]. 2H$_2$O	42000	3.36	$\pi-\pi^*$
	31650	2.89	$\pi-\pi^*$
	27550	2.08	$^6A_1\rightarrow^4E(D)$
	20200	1.90	$^6A_1\rightarrow^4T_1(G)$
[Fe(qlh)Cl$_2$].2H$_2$O	41700	3.72	$\pi-\pi^*$
	31050	3.23	$\pi-\pi^*$
	27700	3.20	CT
	24400	1.95	$^6A_{1g}\rightarrow^4T_{1g}$
[Co(qlh)(OAc)].2H$_2$O	40000	3.37	$\pi-\pi^*$
	27400	3.14	CT
	16670	1.95	$^4A_2\rightarrow^4T_1(P)$
	8000*		$^4A_2\rightarrow^4T_1(F)$
	7500*		
[Ni(qlh)(OAc)(H$_2$O)$_2$].H$_2$O	39840	3.53	$\pi-\pi^*$
	27300	3.27	CT
	23600	1.60	$^3A_{2g}\rightarrow^3T_{2g}$
	17760	1.48	$^3A_{2g}\rightarrow^3T_{1g}$
	9800	0.97	$^3A_{2g}\rightarrow^3T_{1g}(P)$
[Cu(qlh)Cl]. 2H$_2$O	41700	3.75	$\pi-\pi^*$
	31300	3.33	CT
	25900	2.47	$^2B_{1g}\rightarrow^2A_{1g}$
	15500	1.90	$^2B_{1g}\rightarrow^2E_g$
[Zn(qlh)(OAc)].2H$_2$O	42200	3.63	$\pi-\pi^*$
	31250	3.24	CT

* in nujol

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Figure 4.8: *The UV-Vis spectrum of [Mn(qlh)(OAc)]. 2H₂O*

Figure 4.9: *The UV-Vis spectrum of [Fe(qlh)Cl₂].2H₂O*
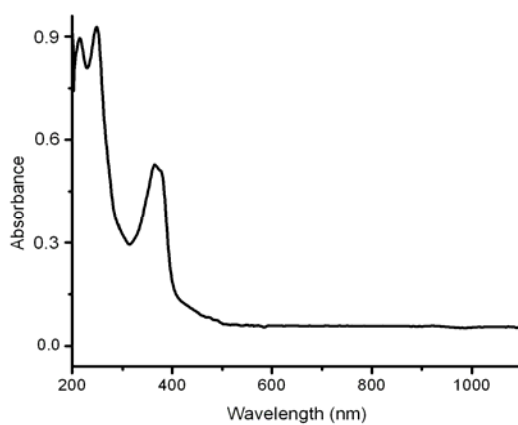
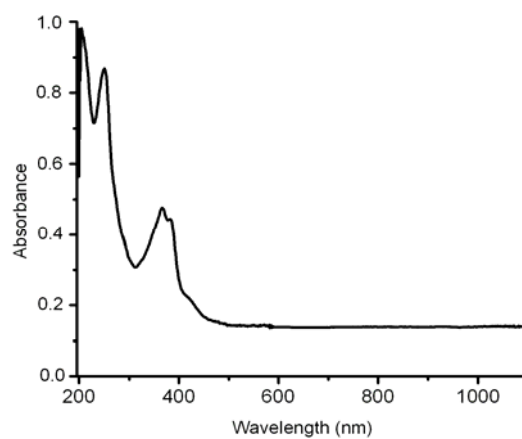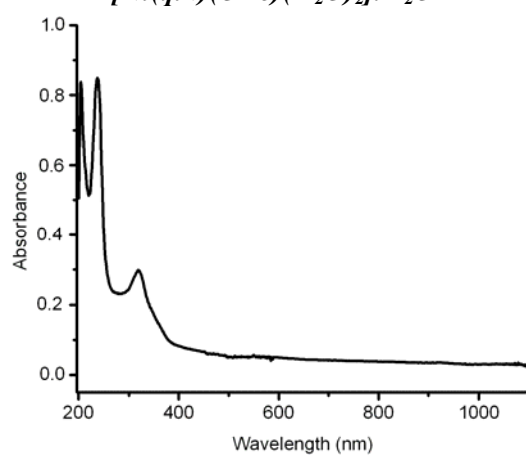**Figure 4.10:** *The UV-Vis spectrum of [Co(qlh)(OAc)].2H₂O*

Figure 4.11: *The UV-Vis spectrum of [Ni(qlh)(OAc)(H₂O)₂].H₂O*
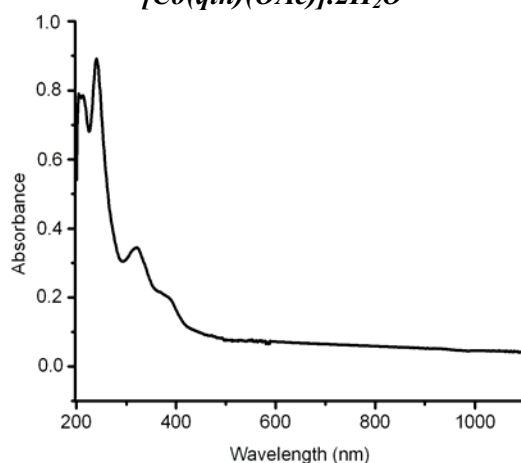
Figure 4.12: *The UV-Vis spectrum of [Cu(qlh)Cl]. 2H₂O*

Figure 4.13: *The UV-Vis spectrum of [Zn(qlh)(OAc)].2H₂O*

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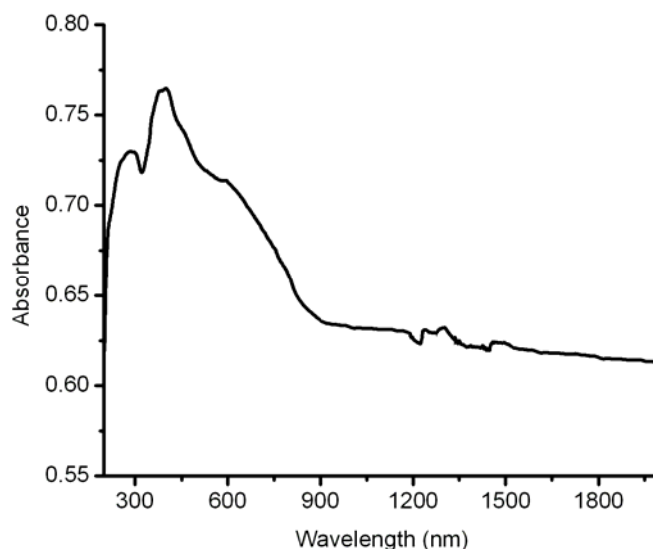
Figure 4.14: *UV-Vis spectrum of [Co(qlh)(OAc)] in nujol mull*

4.3.4 Thermal analysis

There is weight loss below 120 ºC in all complexes suggesting the presence of lattice water molecules [22]. The thermogravimetric analysis data of the complexes upto 200 ºC give an indication about number and nature of water molecules in the complex (Table 4.5). A loss of one lattice water and two coordinated water molecules in the nickel(II) complex is observed in the temperature range 50-210 ºC. Above 350 ºC, the complexes begin to decompose and finally give the corresponding metal oxide. All the compounds are found to be thermally stable and exhibit multi stage decomposition pattern. The TG-DTG plots of the complexes are given in Figures 4.15–4.20. Thermal results show good agreement with the molecular formula arrived from the analytical data.

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Table 4.5: The thermogravimetric analysis data below 200 ºC

Complex	Temperature range, ºC	% loss	Fragment lost	Nature of water lost
[Mn(qlh)(OAc)].2H$_2$O	60–120	8.3	2 H$_2$O	Lattice water
[Fe(qlh)Cl$_2$(H$_2$O)].H$_2$O	55–125	4.1	1 H$_2$O	Lattice water
	160–210	3.9	1 H$_2$O	Coordinated water
[Co(qlh)(OAc)].H$_2$O	60–120	4.3	1 H$_2$O	Lattice water
[Ni(qlh)(OAc)(H$_2$O)$_2$].H$_2$O	50–110	3.8	1 H$_2$O	Lattice water
	120–210	7.5	2 H$_2$O	Coordinated water
[Cu(qlh)Cl].2H$_2$O	70–140	8.5	2 H$_2$O	Lattice water
[Zn(qlh)(OAc)].2H$_2$O	50–130	7.9	2 H$_2$O	Lattice water
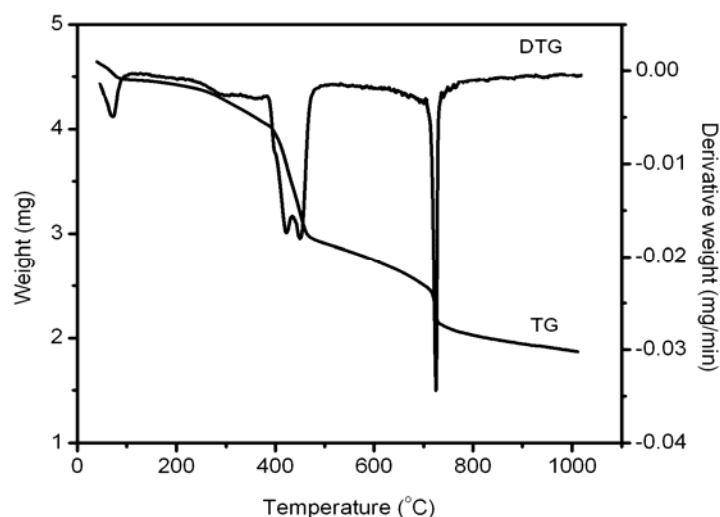
Figure 4.15: *The TG/DTG plot of [Mn(qlh)(OAc)].2H$_2$O*
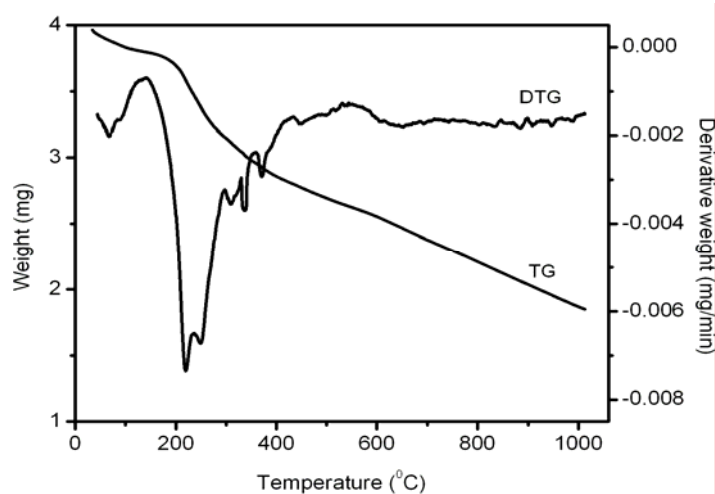
Figure 4.16: *The TG/DTG plot of [Fe(qlh)Cl$_2$(H$_2$O)].H$_2$O*
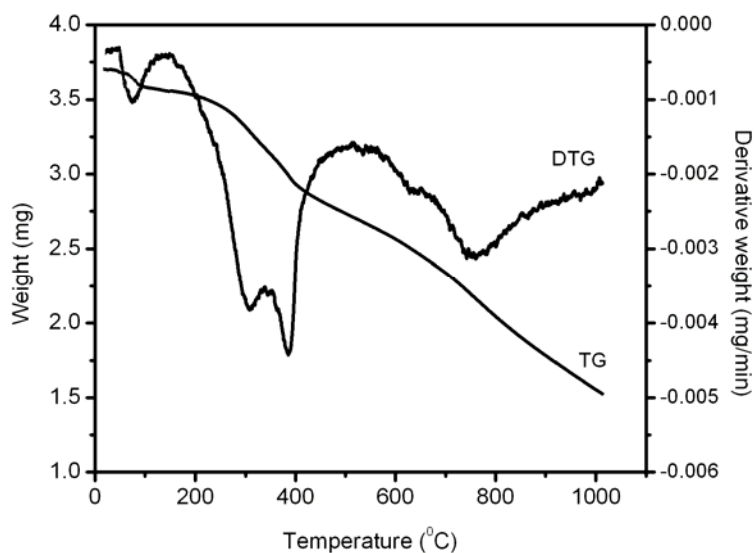
Figure 4.17: *The TG/DTG plot of [Co(qlh)(OAc)].H₂O*
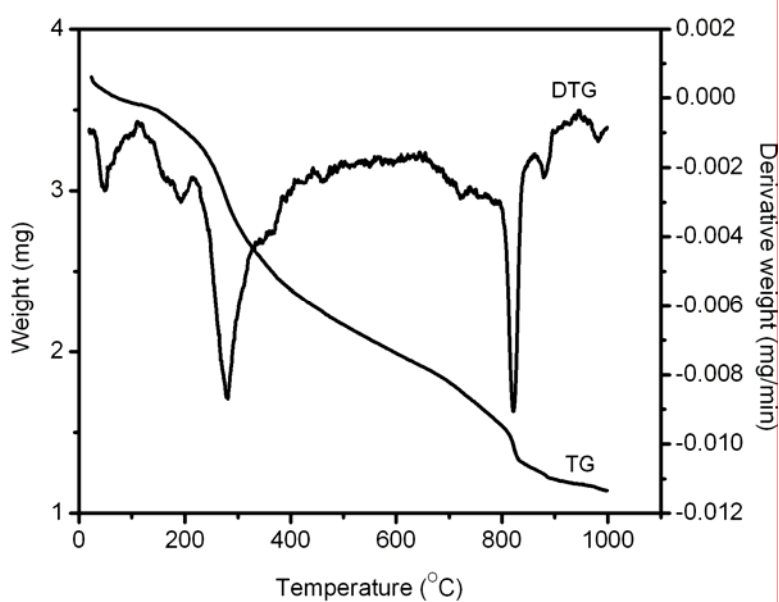
Figure 4.18: *The TG/DTG plot of [Ni(qlh)(OAc)(H₂O)₂].H₂O*

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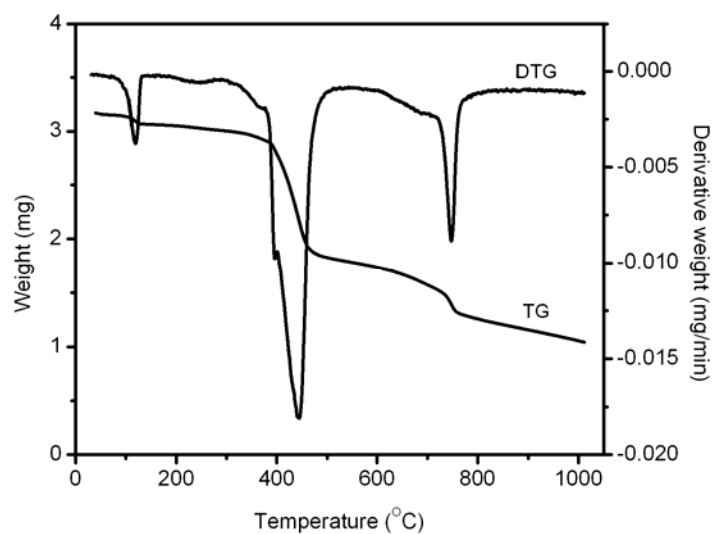
Figure 4.19: *The TG/DTG plot of [Cu(qlh)Cl]. 2H₂O*
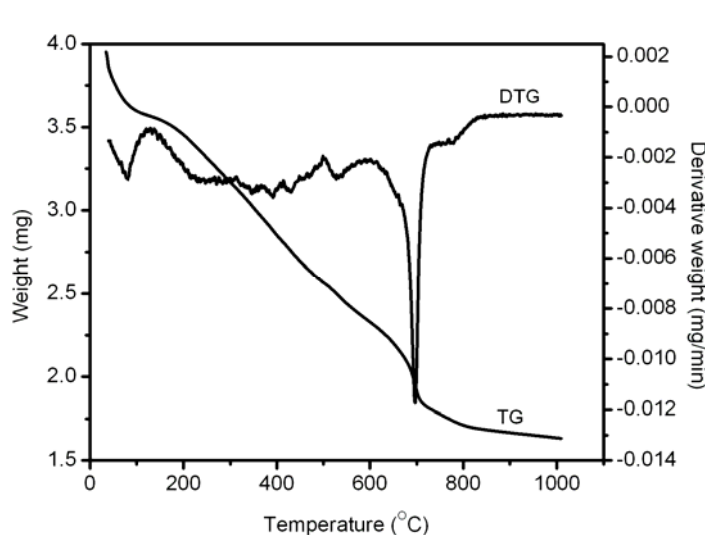
Figure 4.20: *The TG/DTG plot of [Zn(qlh)(OAc)].2H₂O*

4.3.5 EPR spectra

The EPR spectrum of the Mn(II) complex in polycrystalline state gives a broad signal with a *g* value of 2.11. At room temperature (28±2 °C), Mn(II) complexes give very broad signals, which are due to dipolar interactions and enhanced spin lattice relaxation. The EPR spectrum of the manganese(II) complex in DMF at LNT exhibits six lines arising due to hyperfine interaction between the

unpaired electrons of the manganese(II) ion (I=5/2) with a g and A value of 1.99 and 0.00836 cm^{-1} respectively (Figure 4.21). This hyperfine spectrum of six lines corresponds to m_I = ±5/2, ±3/2, ±1/2, resulting from allowed transitions (Δm_s = ±1, Δm_I = 0).
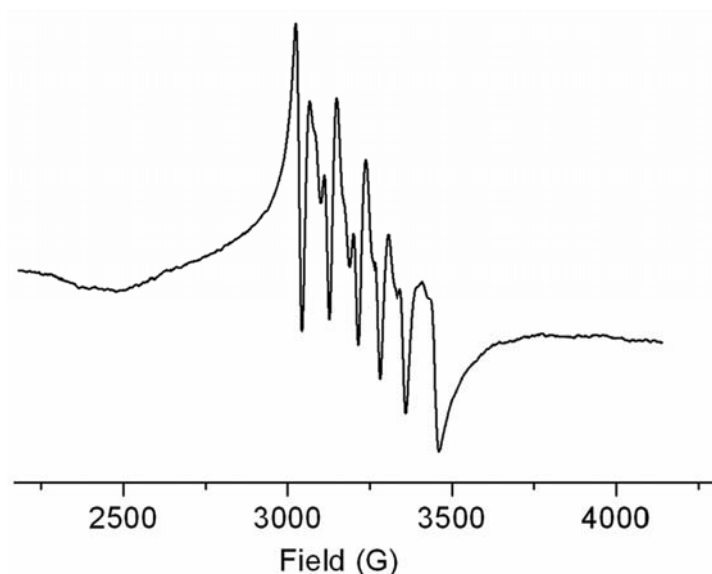
Figure 4.21: *The EPR spectrum of [Mn(qlh)(OAc)(H₂O)₂].H₂O in DMF at LNT*

A pair of low intensity forbidden lines lying between each of the two main hyperfine lines is observed in the frozen solution spectra of the complexes. The forbidden lines in the spectrum arise due to the mixing of the nuclear hyperfine levels by the zero-field splitting factor of the Hamiltonian [23, 24].

In polycrystalline state EPR spectrum of the copper(II) complex gives an isotropic spectrum with a g value of 2.07. The EPR spectrum of the copper(II) complex in DMF at 77 K suggest that the copper(II) species is placed in two different environments [25]. The complicated nature of the spectrum is due to the presence of Cu(II) species in a square planar geometry and to those in octahedral geometry, which might be due to attachment of DMF (highly coordinating solvent) to the square planar species [26].

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To overcome this problem, we repeated the spectral analysis in chloroform and got an axial spectrum with a $g_\parallel$ value of 2.21 and $g_\perp$ value of 2.07. The trend $g_\parallel > g_\perp > g_e$ (g_e is the g value of the free electron, 2.0023) observed for copper(II) complex shows that the unpaired electron is most likely localized in $d_x{}^2-d_y{}^2$ orbital of copper(II) ion and the features of the spectrum are characteristic of an axial symmetry [27, 28]. The EPR spectrum of the copper(II) complex in DMF and that in chloroform are presented in Figures 4.22 and 4.23 respectively.
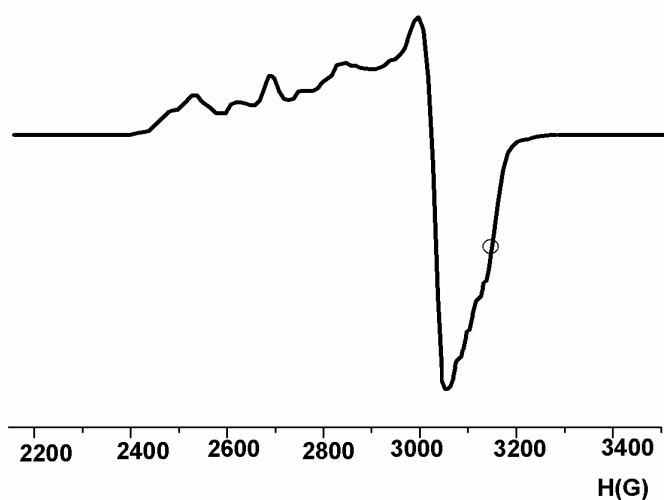
Figure 4.22: *The EPR spectrum of [Cu(qlh)Cl].2H₂O in DMF at LNT*
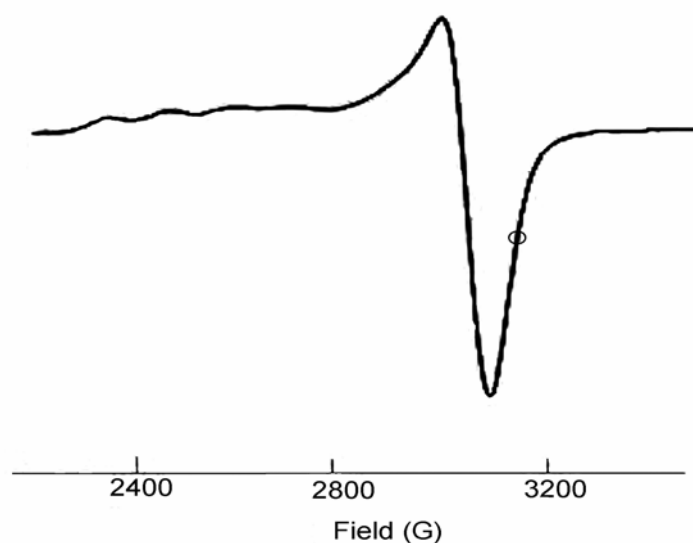
Figure 4.23: *The EPR spectrum of [Cu(qlh)Cl].2H₂O in chloroform at LNT*

4.3.6 ^{1}H NMR spectrum of [Zn(qlh)(OAc)].2H$_2$O

The proton NMR spectrum of zinc(II) complex of qlh was taken in d$_6$-DMSO (Figure 4.24). The N-H proton resonates at 8.75 ppm [29], which is comparable to the reported value of histidine NH. Jacobsen [30] analyzed the NMR spectrum of an octapeptide which contains histidine as one of its building block. In the spectrum of peptide, the histidine NH resonates at 8.4 ppm. The protons of water molecules appear as a broad signal at 3.9–4.3 ppm. The aromatic protons appear as a multiplet at 7.60–8.50 ppm. The azomethine –CH proton appears as a singlet at 9.45 ppm, which is in the range expected for azomethines [31–34]. Imidazole ring protons resonate at 6.80–7.00 ppm. Acetate protons gave a chemical shift of 2.08 ppm. The spectral data of the zinc(II) complex is given in Table 4.6. The proton which is α to the amino and carboxyl moiety gives a chemical shift value of 2.70 ppm and the β protons resonates at 2.90 ppm.

Table 4.6: *^{1}H NMR Spectroscopic data of [Zn(qlh)(OAc)].2H$_2$O*

Compound	Chemical shift, δ (ppm)	Assignment
[Zn(qlh)(OAc)].2H$_2$O	9.45	(s, 1H, azomethine)
	8.75	(s, 1H, NH)
	7.60–8.50	(m, 4H, Ar)
	6.80–7.00	(m, 2H, imidazole)
	3.9–4.3	(br, water of hydration)
	2.08	(s, 3H, acetate)
	2.70	(t, 1H, ali. histidine)
	2.90	(d, 2H, ali. histidine)
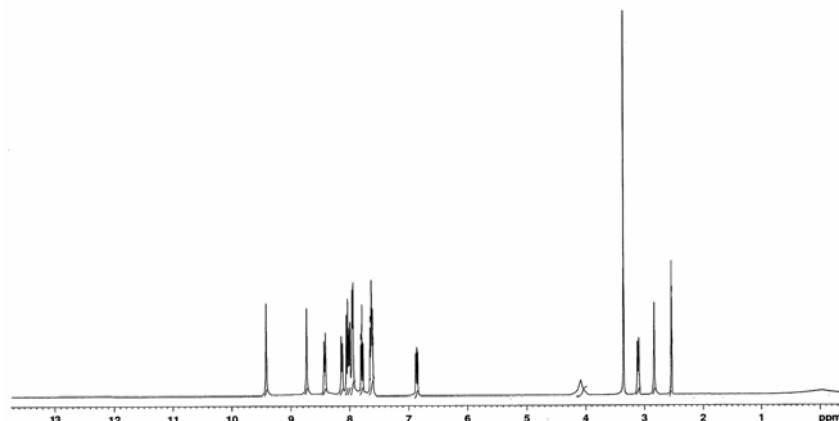
Figure 4.24: *^{1}H NMR spectrum of [Zn(qlh)(OAc)].2H$_2$O*

4.4 CONCLUSIONS

In summary we have accomplished the facile synthesis of six complexes of the Schiff base quinoxaline−2−carboxalidine−L−histidine by template method and characterized them by elemental analysis, conductivity studies, magnetic susceptibility measurements, IR, UV−Vis, EPR and thermal analysis. The ligand qlh acts as a tridentate ligand. The physicochemical and spectral data reveal an octahedral geometry for the Fe(III) and Ni(II) complexes, a tetrahedral structure for manganese(II), cobalt(II) and zinc(II) complexes and a square planar geometry for the copper(II) complex. The proposed structures of the complexes are given in Figure 4.25.
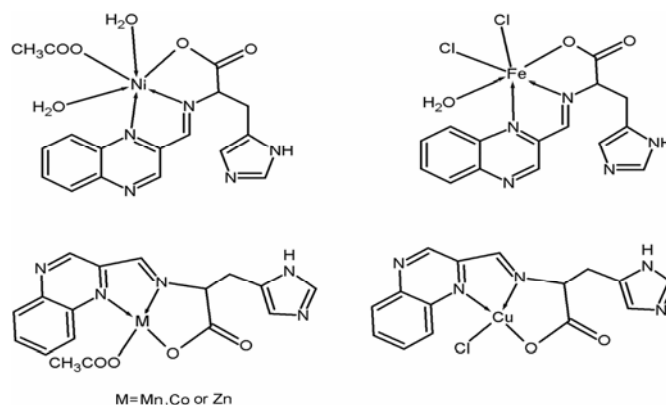
Figure 4.25: *Suggested structures of the complexes of quinoxaline−2 carboxalidine−L− histidine (solvated water molecules are omitted)*

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3-Hydroxyquinoxaline–2–carboxalidine–2– amino –5–methylphenol complexes of manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II)

Contents

5.1 Introduction

5.2 Experimental

5.3 Results and discussion

5.4 Conclusions

References

5.1 INTRODUCTION

The syntheses of ONO donor Schiff base complexes attract considerable attention due to its applications in catalysis, photonics and medicine [1-3]. The Schiff base derived from salicylaldehyde and 2–aminophenol is well studied [4-7]. Several metal chelates coordinated through the Schiff base ONO donors have been studied as oxygen carriers and they are useful models for bioinorganic processes [8, 9]. Patel *et al.* [10, 11] reported the crystal structures of the copper(II) complex of N-(salicylidene)anthranilic acid with imidazole, 2,2'-bipyridine or 1,10-phenanthroline as coligands. These complexes were screened for superoxide dismutase activity. The ONO donor Schiff bases derived from salicylaldehyde and their transition metal complexes can be considered as non-enzymatic models for pyridoxal amino acid systems. The chemistry of the metal complexes of ONO donor Schiff bases is quite interesting because of their biological applications [12-15].

Quinoxalines with ortho hydroxy groups are of particular interest due to their ability to form tautomers. They can form complexes in either neutral keto form or enolic form as given in Figure 5.1. Eventhough quinoxalines and their compounds have been extensively studied [16-21], the reports on the quinoxaline based Schiff bases are very scanty. The synthesis and characterization of quinoxaline-2-carboxaldehyde with 2-aminophenol was previously reported [22]. Our aim was to prepare new tridentate ONO donor Schiff base from 3-hydroxyquinoxaline-2-carboxaldehyde and 2-amino-5-methylphenol and study the nature of its complexes.
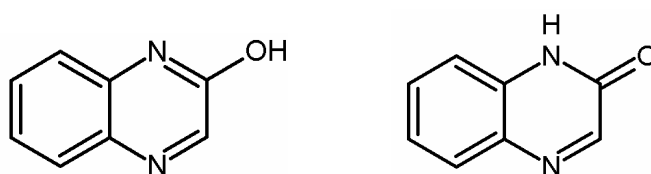
Figure 5.1: *Tautomeric forms of 2−hydroxyquinoxaline*

We have synthesized the Schiff base, 3-{(*E*)-[(2-hydroxy-4-methylphenyl) imino]methyl} quinoxalin-2(1*H*)-one, by condensation reaction. The Schiff base is an ONO donor and it can act as a monobasic or dibasic ligand due to the formation of tautomers. In solid state the keto form is predominant and it easily enolise in solution to form diol. The results of the studies on the complex formation of this ligand with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions are presented in this chapter.

5.2 EXPERIMENTAL

5.2.1 Materials and methods

The preparation of 3−hydroxyquinoxaline−2−carboxaldehyde and techniques employed for the characterization of ligand and metal complexes are given in chapter II.

5.2.2 Synthesis of 3-{(*E*)-[(2-hydroxy-4-methylphenyl) imino]methyl} quinoxalin-2(1*H*)-one (hamp)

To an aqueous solution of 3–hydroxyquinoxaline–2–carboxaldehyde (1.742 g, 10 mmol, in 500 mL distilled water), 3–4 drops of conc. HCl was added. To this solution was added dropwise 2–amino–5–methylphenol (1.231 g, 10 mmol) in methanol (20 mL). The solution was stirred for 6 hours. The red coloured Schiff base formed was filtered, washed with water and dried over anhydrous calcium chloride. The crude product was recrystallised from absolute ethanol. Formation of hamp is presented in scheme 5.1.

(Yield: 75 %, MP: 220 ºC)
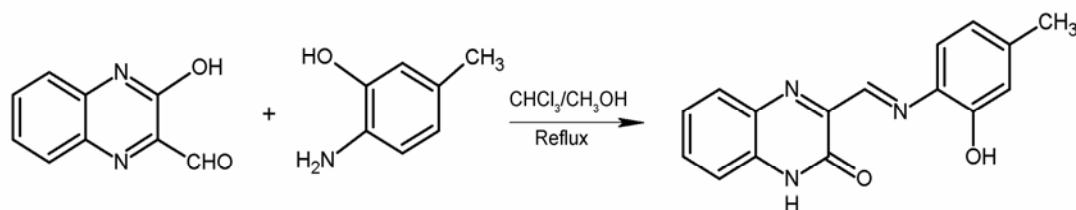
Scheme 5.1: *The formation of hamp by condensation*

5.2.3 Preparation of Complexes

The Schiff base, hamp, (0.01 mol, 0.279 g) was dissolved in 50 mL methanol. To this solution a solution of metal compound (0.01 mol: manganese acetate tetrahydrate 0.245 g, ferric chloride 0.162 g, cobalt acetate hexahydrate 0.249 g, zinc acetate 0.219 g, cupric acetate 0.198 g or nickel acetate 0.249 g) in methanol (30 mL) was added. The solution was then refluxed for an hour and was then kept at room temperature (28±2 ºC) after reducing its volume by evaporation. The precipitate formed was filtered, washed with methanol and kept in a desiccator. The formation of metal complexes is given in Scheme 5.2.

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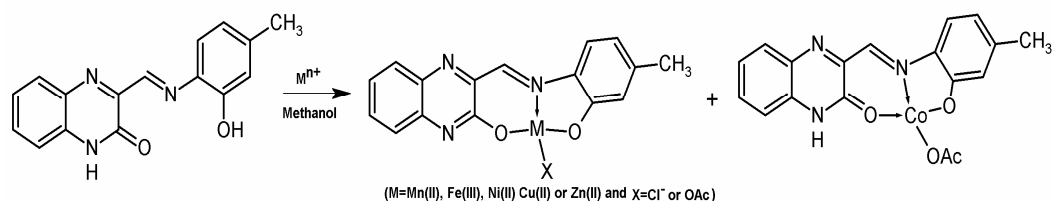
Scheme 5.2: *The formation of metal complexes of hamp*

5.3 RESULTS AND DISCUSSION

The complexes are stable in air and non-hygroscopic. They are soluble in common solvents like ethanol, methanol, acetonitrile and DMF. The analytical data (Table 5.1) reveal that all the complexes are formed in metal:ligand ratio of 1:1. Further the molecular formula of the complexes given in the table agrees well with the analytical data. The very low conductance values (Table 5.2) of the complexes in DMF indicate the non-electrolytic nature of the complexes [23].

Table 5.1: *Analytical data of qamp and its complexes*

| Compound | Colour | Yield (%) | Analytical data. Found (calculated)% | | | | |
			C	H	N	M	Cl
hamp	Red	85	69.15 (68.81)	4.55 (4.69)	14.05 (14.00)	-	-
[Mn(hamp)(H$_2$O)].H$_2$O	Brown	45	51.36 (52.19)	3.29 (4.11)	10.89 (11.41)	14.85 (14.92)	-
[Fe(hamp)Cl(H$_2$O)$_2$]	Black	58	47.43 (47.50)	3.77 (3.74)	10.45 (10.39)	13.67 (13.80)	8.69 (8.76)
[Co(hamp)(OAc)(H$_2$O)$_2$].H$_2$O	Violet	71	47.96 (48.01)	4.71 (4.70)	9.15 (9.33)	13.11 (13.09)	-
[Ni(hamp)(H$_2$O)].H$_2$O	Black	65	51.49 (51.66)	4.11 (4.06)	11.39 (11.30)	15.73 (15.78)	-
[Cu(hamp)(H$_2$O)]	Black	80	53.21 (53.55)	3.66 (3.65)	11.69 (11.71)	17.77 (17.71)	-
[Zn(hamp)(H$_2$O)]	Brown	70	53.19 (53.28)	3.67 (3.63)	11.66 (11.65)	18.17 (18.13)	-

Table 5.2: *Conductivity and magnetic moment data of complexes*

Compound	λ_m[#]	μ_{eff} (B.M)
[Mn(hamp)(H$_2$O)].H$_2$O	13	5.75
[Fe(hamp)Cl(H$_2$O)$_2$]	18	5.40
[Co(hamp)(OAc)(H$_2$O)$_2$].H$_2$O	21	4.95
[Ni(hamp)(H$_2$O)].H$_2$O	9	3.84
[Cu(hamp)(H$_2$O)]	17	2.10
[Zn(hamp)(H$_2$O)]	11	-

[#] Molar conductivity (in Mho cm^2 mol^{-1}), 10^{-3} Molar solution in DMF

5.3.1 ^{1}H NMR spectrum of hamp and [Zn(hamp)(H$_2$O)]

The ^{1}H NMR spectrum of hamp and that of the zinc(II) complex are given in Figures 5.2 and 5.3. The spectral data are summerised in Table 5.3. Because of the low solubility in CDCl$_3$, the NMR spectra of the Schiff base and zinc(II) complex were made in deuterated DMSO. The spectral features suggest that the compound exist as keto tautomer. The co-existence of the tautomers is not observed. The broad singlet observed at 12.85 ppm is due to phenolic –OH proton. The broadness of the band indicates considerable hydrogen bonding in the Schiff base. The peak observed at 11.52 ppm is due to NH proton [24-26]. The azomethine proton resonates at 9.15 ppm which is a singlet [27]. The multiplet observed around 6.40-8.30 ppm is due to aromatic protons of quinoxaline ring and phenolic ring. The peak due to methyl protons is observed at 2.26 ppm as a singlet.

The NMR spectrum of the zinc(II) complex is given in Figure 5.3. The phenolic OH and NH signals which are found at 12.85 and 11.52 ppm in the spectrum of the ligand are not seen in the spectrum of the Zn(II) complex indicating the enolisation of the Schiff base in zinc(II) complex and participation of the phenolic OH group in chelation with proton displacement [28, 29]. The signals due to azomethine proton are shifted upon complexation, which is probably due to

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the donation of the lone pair of electrons by the nitrogen to the central metal atom [30]. ^{1}H NMR spectrum gives the aromatic and quinoxaline protons as a number of complex multiplets in the region δ 7.10–7.98 ppm. The methyl group attached to the phenolic ring is observed at 2.22 ppm as a singlet. The broad singlet in the region 3.51– 3.80 ppm indicates the presence of a water molecule in the complex.

Table 5.3: ^{1}H NMR Spectroscopic data of hamp

Compound	Chemical shift, δ (ppm)	Assignment
hamp	12.85	(s br, 1H, OH)
	11.52	(s, 1H, NH)
	9.15	(s, 1H, CH azomethine)
	6.40-8.30	(m, 7H, Ar H)
	2.26	(s, 3H, CH3)
[Zn(hamp)(H$_2$O)]	9.30	(s, 1H, CH azomethine)
	7.10-7.98	(m, 7H, Ar H)
	3.51-3.80	(br s, 2 H, water)
	2.22	(s, 3H, CH3)
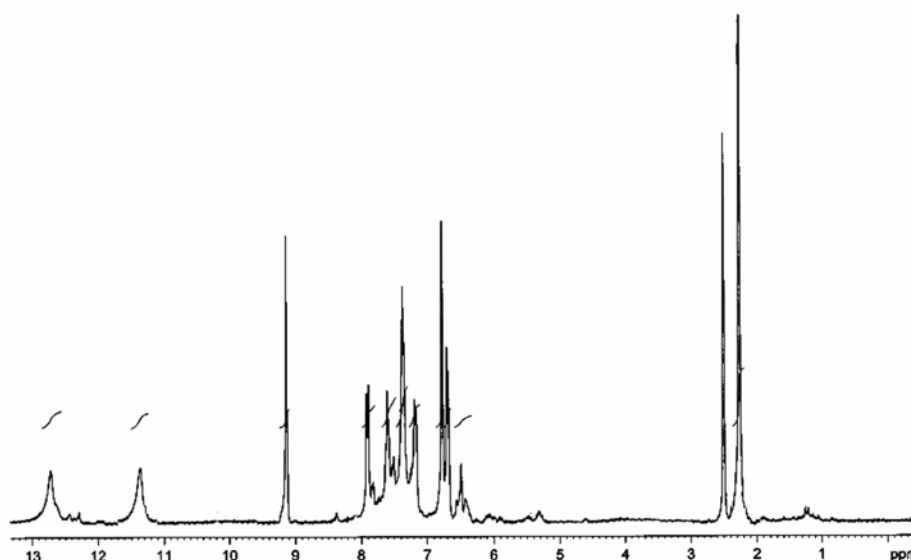
Figure 5.2: ^{1}H NMR spectrum of hamp
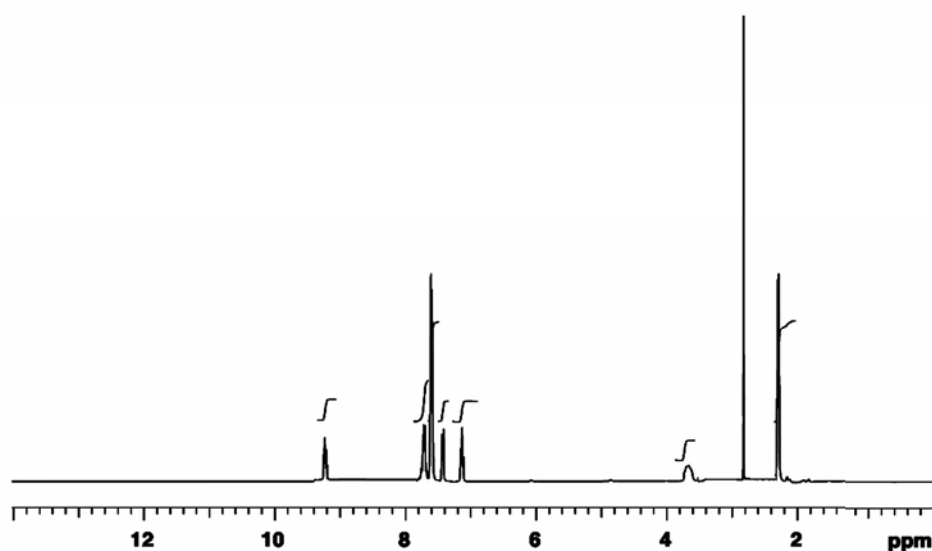
Figure 5.3: *^{1}H NMR spectrum of [Zn(hamp)(H$_2$O)]*

5.3.2 Magnetic susceptibility measurements

The magnetic moment values (at 28±2 ºC) of the complexes are shown in Table 5.2. The μ_{eff} value of the Mn(II) complex was found to be 5.75 B.M. as expected for high spin d^5 system. The iron(III) complex shows a magnetic moment of 5.80 B.M. The cobalt(II) complex has a magnetic moment of 4.95 B.M. and the high magnetic moment value is as expected for high spin Co(II) octahedral complex. The higher magnetic moment is due to the orbital contribution [31]. The nickel(II) complex exhibits a magnetic moment value of 3.84 B.M., which is in the normal range observed for tetrahedral Ni(II) complexes. The higher value of magnetic moment compared to the expected spin only value is due to the orbital contribution [32]. The magnetic moment of the copper(II) complex is 2.10 B.M. which suggest absence of Cu−Cu interactions. The higher value indicates a tetrahedral structure.

5.3.3 Infrared spectra

The infrared spectral bands and the assignments are given in Table 5.4. The IR spectra of ligand and complexes are given in Figures 5.4 to 5.10. The band at

3386 cm^{-1} in the spectrum of hamp is due to the OH stretching vibrations. The ligand exhibits azomethine C=N stretching at 1609 cm^{-1} and C=N of quinoxaline ring at 1571 cm^{-1} [33-37]. There is a sharp intense band at 1665 cm^{-1}, which shows the presence of a keto group in the compound and confirms the existence of tautomerism for the 2-hydroxyquinoxaline moiety.

Most of the bands due to the free ligand are present in the spectra of complexes. A new broad band at around 3300 cm^{-1} is seen for all the complexes which may be due to the presence of hydrated or coordinated water molecule [38]. The azomethine C=N stretching is observed at a lower frequency than that for the ligand. This negative shift in C=N stretching frequency is an indication of coordination of nitrogen [39-41]. For all the complexes the phenolic C-O stretching occurs at higher wavenumber when compared to that of the ligand indicating the deprotonation and coordination of the hydroxyl groups. In addition, the FTIR spectra of all complexes, except that of the cobalt(II) complex, do not contain $v(C=O)$, which indicates the enolisation of the keto group in solution. The strong band observed at 1633 cm^{-1} for the cobalt(II) complex suggests that the Schiff base acts as a monobasic tridentate ligand. Appearance of new bands in the spectra of all complexes in the regions 500–450 and $420–400 \text{ cm}^{-1}$ has been attributed to $v(M–O)$ and $v(M–N)$, respectively.

Table 5.4: *IR spectral data of hamp and its complexes*

Assignments (in cm^{-1})	v (OH)	v (C=O)	v (C=N) *	v (C–O)$^{\#}$	v (M–O)	v (M–N)
hamp	3386	1665	1609	1254	-	-
[Mn(hamp)(H$_2$O)].H$_2$O	3376	-	1592	1260	492	417
[Fe(hamp)Cl(H$_2$O)$_2$]	3450	-	1589	1259	490	424
[Co(hamp)(OAc)(H$_2$O)$_2$].H$_2$O	3390	1633	1604	1255	473	414
[Ni(hamp)(H$_2$O)].H$_2$O	3370	-	1601	1257	484	409
[Cu(hamp)(H$_2$O)]	3361	-	1602	1259	472	414
[Zn(hamp) (H$_2$O)]	3365	-	1603	1259	471	417

* azomethine, $^{\#}$ phenolic
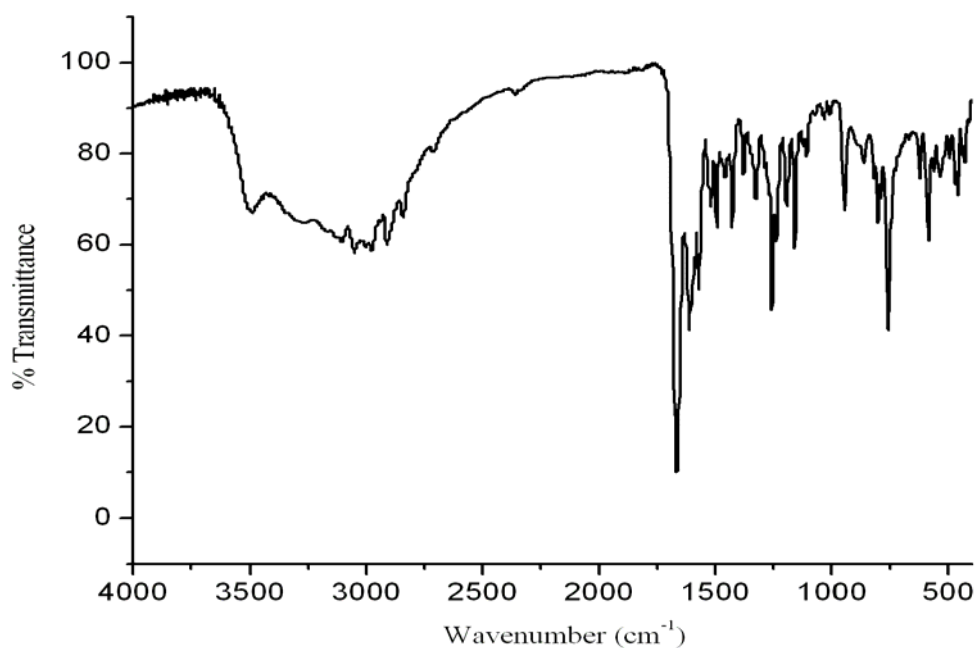
Figure 5.4: *FTIR spectrum of the Schiff base hamp*
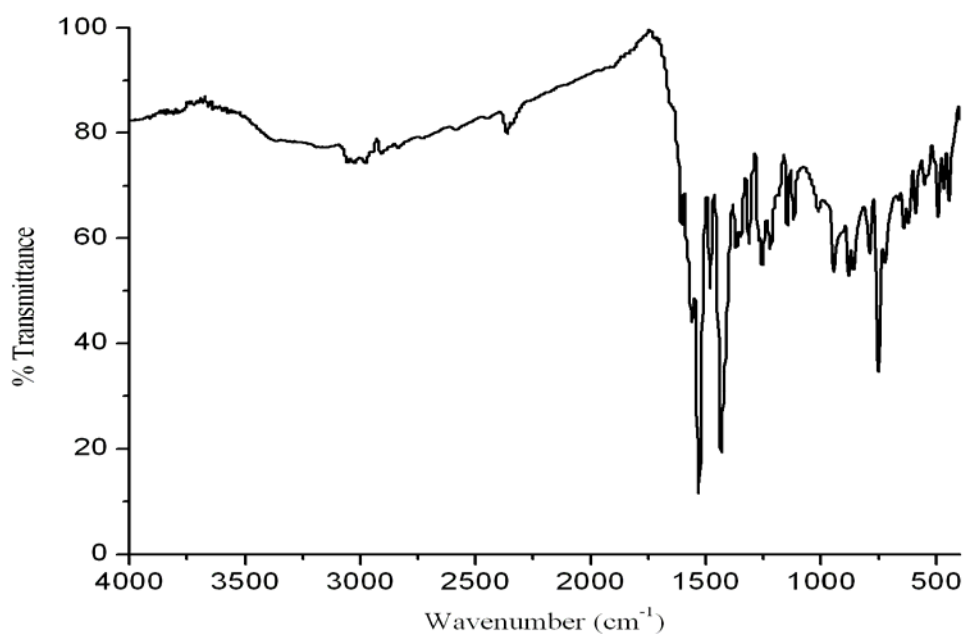
Figure 5.5: *FTIR spectrum of [Mn(hamp)(H₂O)].H₂O*

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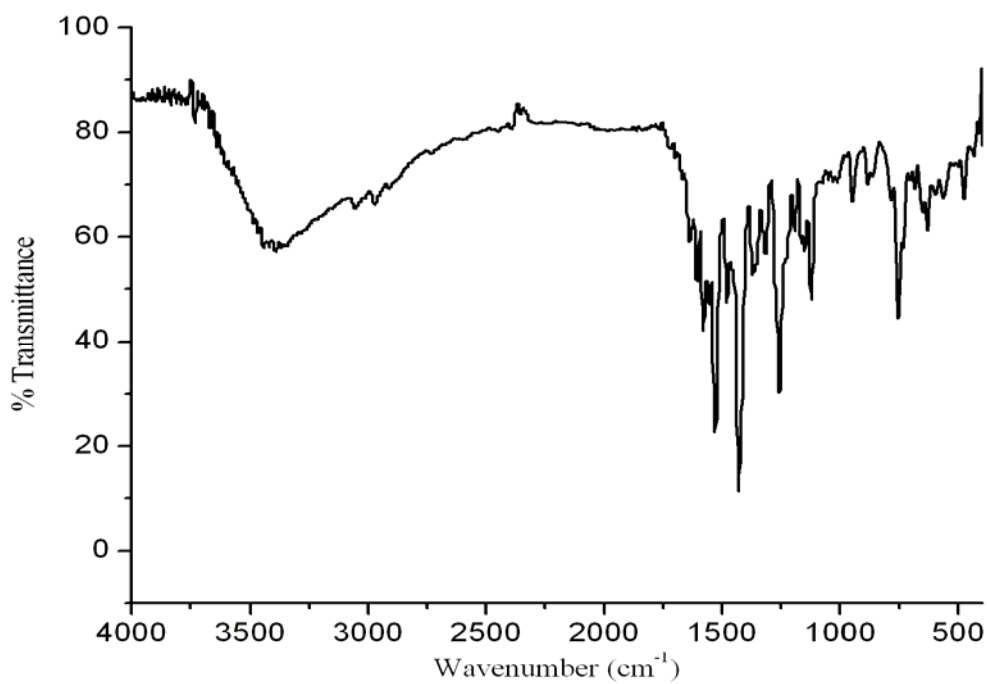
Figure 5.6: *FTIR spectrum of [Fe(hamp)Cl(H₂O)₂]*
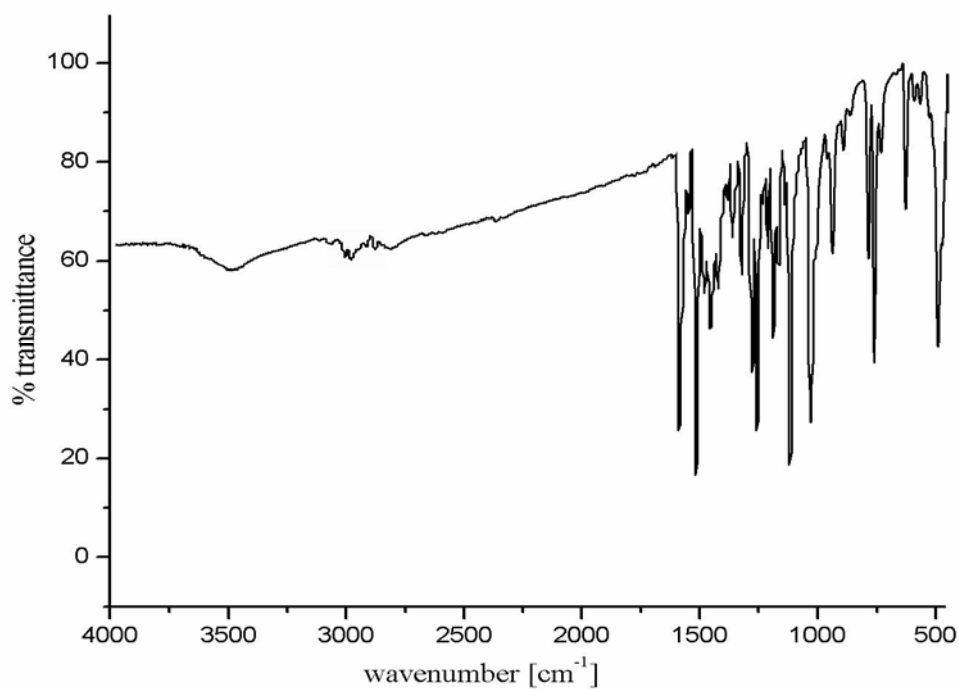
Figure 5.7: *FTIR spectrum of [Co(hamp)(OAc)(H₂O)₂].H₂O*
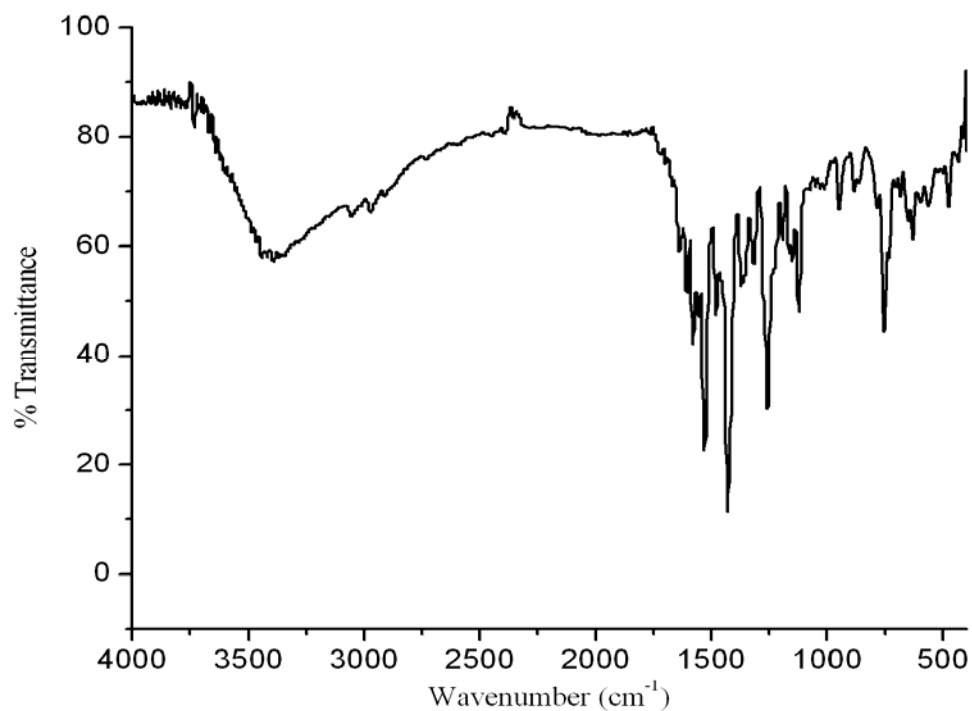
Figure 5.8: *FTIR spectrum of [Ni(hamp)(H₂O)].H₂O*
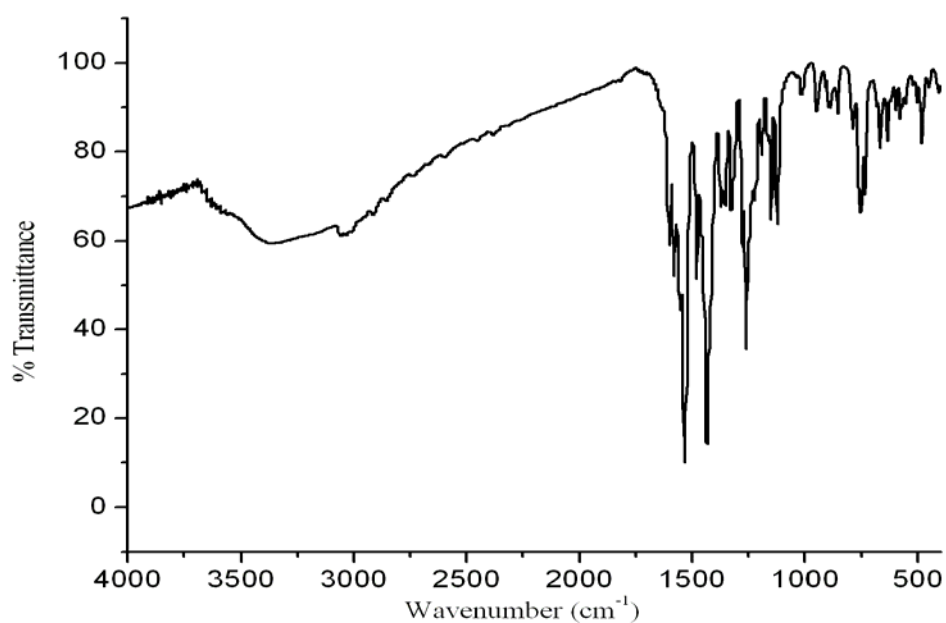
Figure 5.9: *FTIR spectrum of [Cu(hamp)(H₂O)]*

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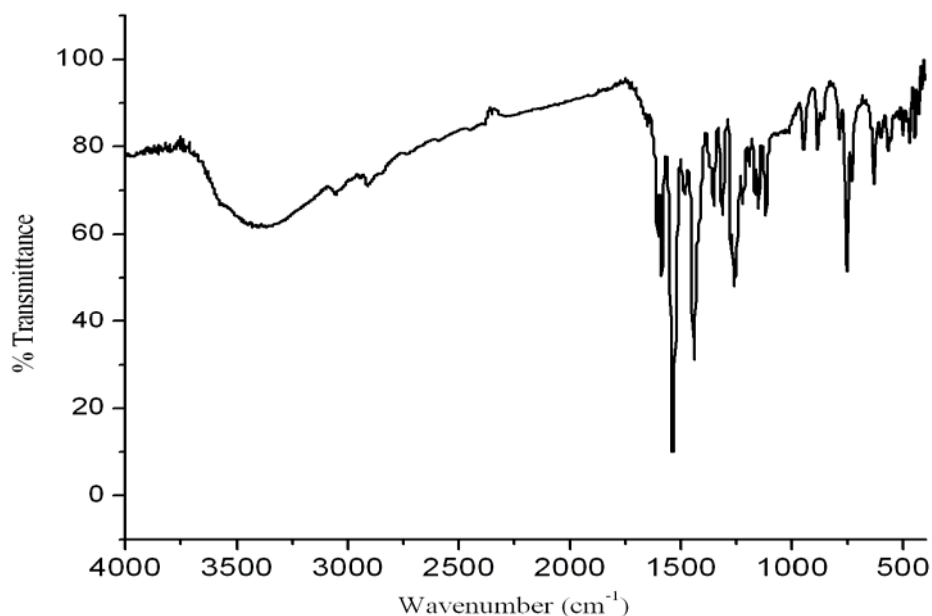
Figure 5.10: *FTIR spectrum of [Zn(hamp)(H₂O)]*

5.3.4 Electronic spectra

The electronic spectral data of the Schiff base and complexes are presented in Table 5.5. Spectra are taken in methanol ($\sim5\times10^{-4}$ molar) and are given in Figures 5.11-5.17. The spectral bands due to solvent, which have been observed above 45000 cm^{-1}, are omitted [42]. The ligand shows absorptions at 30800 and 24000 cm^{-1}. These bands are attributed to benzene π–π^*, imino π–π^* and quinoxaline π–π^* transitions of the Schiff base. In complexes, the intense bands observed above 30000 cm^{-1} are due to charge transfer and intraligand transitions.

The electronic spectrum of the manganese(II) complex in methanol contain two intense broad bands at 29800 and 21500 cm^{-1}. The weak d-d bands are masked by these charge transfer bands [43]. To get more information about geometry, the UV-Vis-NIR spectrum of the Mn(II) complex is taken in nujol mull (Figure 5.18). In the near IR region of the mull spectrum a multiplet is observed around 6200 cm^{-1}.

Such low energy bands are characteristic of tetrahedral manganese(II) compounds. The spectrum of the Fe(III) complex exhibits a weak shoulder band at 23200 cm^{-1} which may be assigned to the $^6A_{1g} \rightarrow T_{2g}(G)$ transition and indicates an octahedral geometry of the complex [43].

In the electronic spectrum of Co(II) complex the d–d transitions are almost masked by the high-intensity charge transfer bands. However, a shoulder is observed around 17000 cm^{-1} which may be assigned to the $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transition and transitions in this region have been reported for octahedral Co(II) complexes [32].

The solution spectrum of the nickel(II) complex shows two charge transfer bands at 29000 and 21400 cm^{-1}. The d-d bands are observed at 16100 and 11000 cm^{-1} which is due to $^3T_1 \rightarrow ^3T_2$ and $^3T_1 \rightarrow ^3T_1(P)$ transitions. The spectrum of the nickel(II) complex is also taken in nujol mull in the UV-Vis-NIR region (Figure 5.19). The near IR band characteristic of the $^3T_1(F) \rightarrow ^3A_2(F)$ transition of tetrahedral nickel(II) appears at 7100 cm^{-1} for this complex.

The copper(II) complex exhibits intense charge transfer bands at 23800 and 20400, and the band observed at 17000 cm^{-1} is due to the $^2T_2 - ^2E_2$ transition. A band is observed in the NIR region of the mull spectrum of the copper(II) complex at 6400 cm^{-1}. A band in this region has been reported for the tetrahedral copper(II) complexes (Figure 5.20) [43, 44]. The zinc(II) complex exhibits a charge transfer transition at 20300 cm^{-1}.

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Table 5.5: *The UV-Vis spectral data*

Compound	Absorption maxima (cm^{-1})	log ε (ε in L mol^{-1} cm^{-1})	Assignment
hamp	30800	3.09	$\pi \rightarrow \pi^*$
	24000	3.18	$\pi \rightarrow \pi^*$
[Mn(hamp)(H$_2$O)]H$_2$O	44640	3.50	$\pi \rightarrow \pi^*$
	29800	3.11	CT
	21500	3.17	CT
[Fe(hamp)Cl(H$_2$O)$_2$]	42900	3.36	$\pi \rightarrow \pi^*$
	36400	3.27	$\pi \rightarrow \pi^*$
	29070	3.26	CT
	23200	2.66	$^6A_{1g} \rightarrow T_{2g}(G)$
[Co(hamp)(OAc)(H$_2$O)$_2$].H$_2$O	43510	3.64	$\pi \rightarrow \pi^*$
	29000	3.36	CT
	21400	3.42	CT
	17000	3.40	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
[Ni(hamp)(H$_2$O)]H$_2$O	43200	3.68	$\pi \rightarrow \pi^*$
	30000	3.26	CT
	21300	3.39	CT
	16100	2.44	$^3T_1 \rightarrow {}^3T_2$
	11000	2.25	$^3T_1 \rightarrow {}^3T_1(P)$
[Cu(hamp)(H$_2$O)]	29500	3.45	$\pi \rightarrow \pi^*$
	23800	3.43	CT
	20400	3.53	CT
	17000	2.47	$^2T_2 \rightarrow {}^2E_2$
[Zn(hamp)(H$_2$O)]	41600	3.30	$\pi \rightarrow \pi^*$
	23800	3.33	CT
	20300	3.40	CT

Figure 5.11: *The UV-Vis spectrum of hamp*
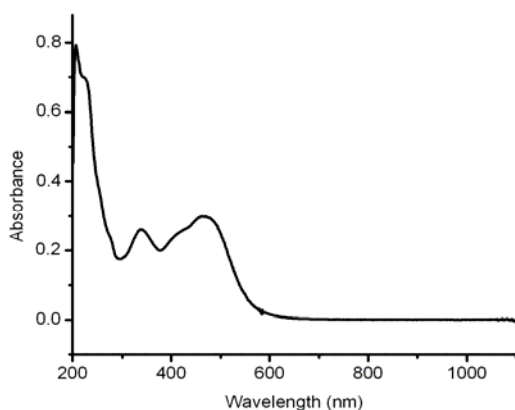
Figure 5.12: *The UV-Vis spectrum of [Mn(hamp)(H₂O)]*
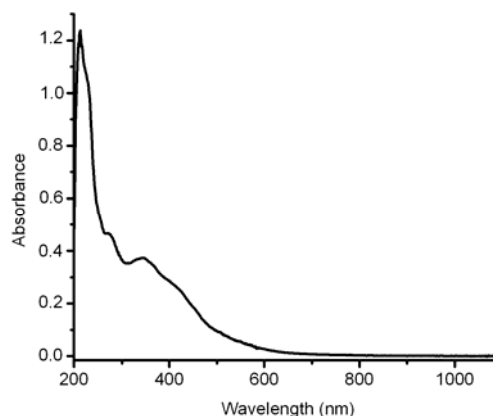
Figure 5.13: *The UV-Vis spectrum of [Fe(hamp)Cl(H₂O)₂]*
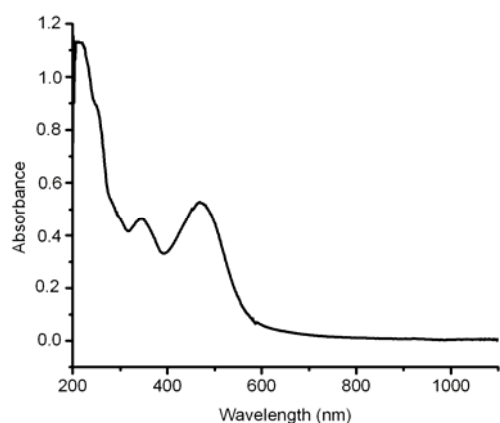
Figure 5.14: *The UV-Vis spectrum of [Co(hamp)(OAc)]*
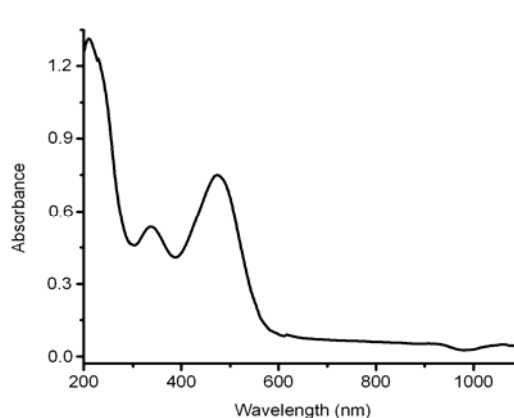
Figure 5.15: *The UV-Vis spectrum of [Ni(hamp)(H₂O)]*
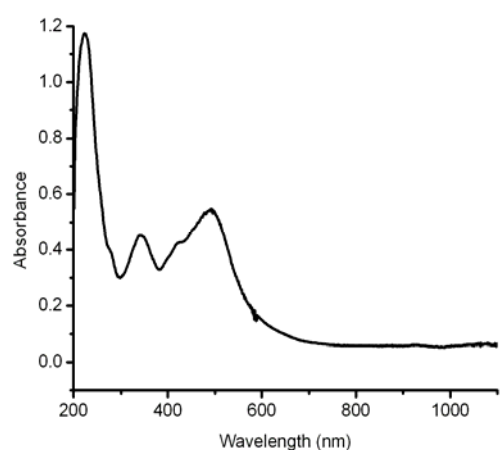
Figure 5.16: *The UV-Vis spectrum of [Cu(hamp)(H₂O)]*
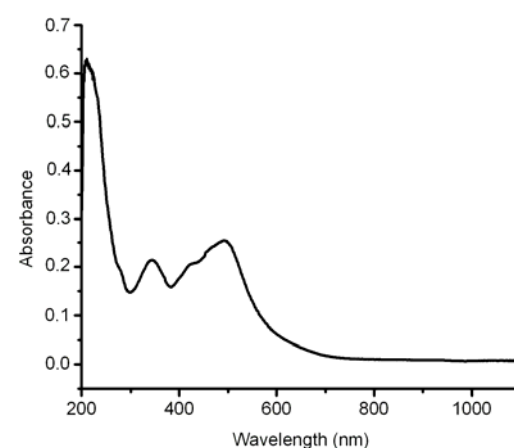
Figure 5.17: *The UV-Vis spectrum of [Zn(hamp)(H₂O)]*
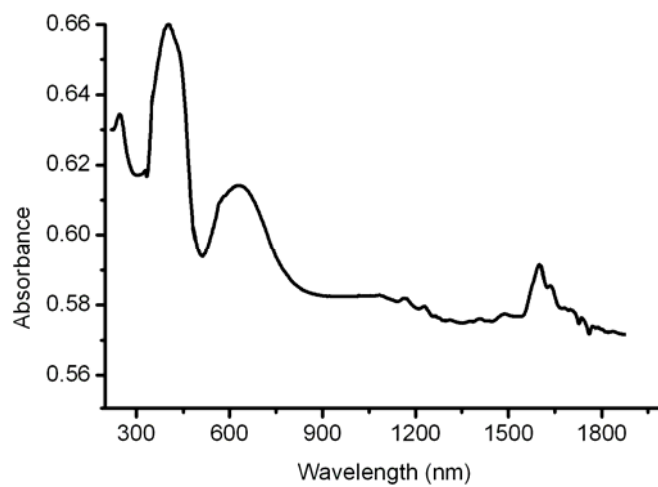
Figure 5.18: *The UV-Vis spectrum of [Mn(hamp)(H₂O)] in nujol mull*
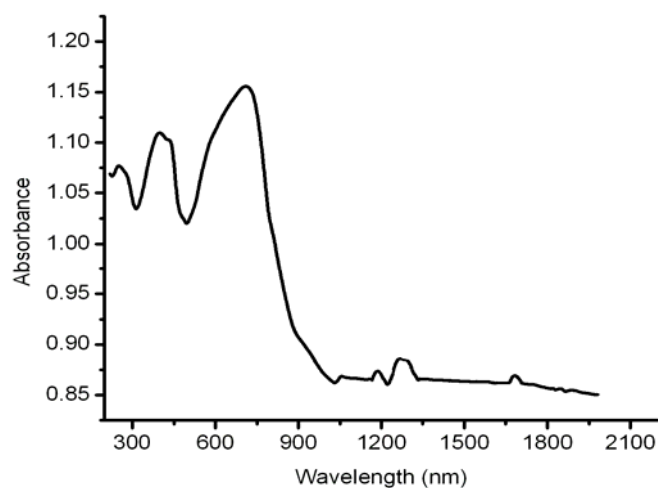
Figure 5.19: *The UV-Vis spectrum of [Ni(hamp)(H₂O)] in nujol mull*

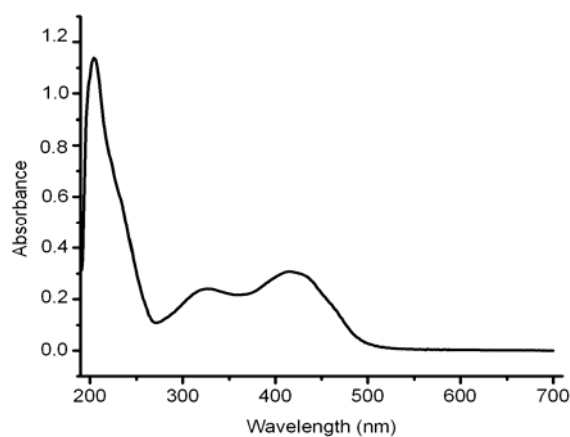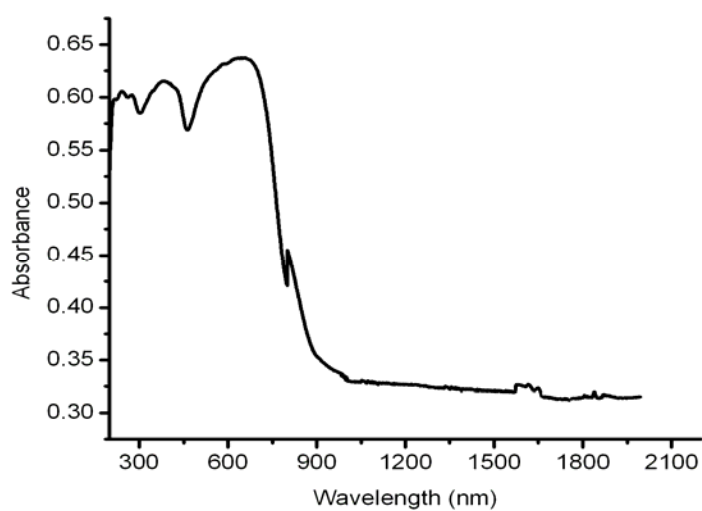**Figure 5.20:** *The UV-Vis spectrum of [Cu(hamp)(H₂O)] in nujol mull*

5.3.5 Thermal analysis

The TG–DTG curves are presented in Figure 5.21–5.27 and the TG data in the temperature range 50-250 °C is given in Table 5.6. The ligand decomposes in two steps in the range 150–600 °C. The loss of lattice water molecule occurs in manganese(II), cobalt(II) and nickel(II) complexes below 125 °C. Loss of coordinated water in these complexes occurs in the range 130–250 °C. In the case of the Ni(II) complex, the weight loss corresponding to one lattice water and one coordinated water occurs in a continuous step from 60 to 190 °C. Above 250 °C organic part of the complexes begins to decompose. The iron(III) and copper(II) complexes show two step decomposition. Decomposition of the nickel complex takes place in three steps and the decomposition of the cobalt complex takes place in five steps.

Table 5.6: *Thermogravimetric analysis data below 200 ºC*

Complex	Temperature range, ºC	% loss	Fragment lost	Nature of water lost
[Mn(hamp)(H$_2$O)]H$_2$O	60-110	5.0	1 H$_2$O	Lattice water
	130-190	4.8	1 H$_2$O	Coordinated water
[Fe(hamp)Cl(H$_2$O)$_2$]	160-210	8.8	2 H$_2$O	Coordinated water
[Co(hamp)(OAc)(H$_2$O)$_2$]H$_2$O	50-110	3.9	1 H$_2$O	Lattice water
	150-210	8.4	2 H$_2$O	Coordinated water
[Ni(hamp)(H$_2$O)]H$_2$O	60-190	9.7	2 H$_2$O	Lattice water Coordinated water
[Cu(hamp)(H$_2$O)]	140-195	5.2	1 H$_2$O	Coordinated water
[Zn(hamp)(H$_2$O)]	140-180	4.6	1 H$_2$O	Coordinated water
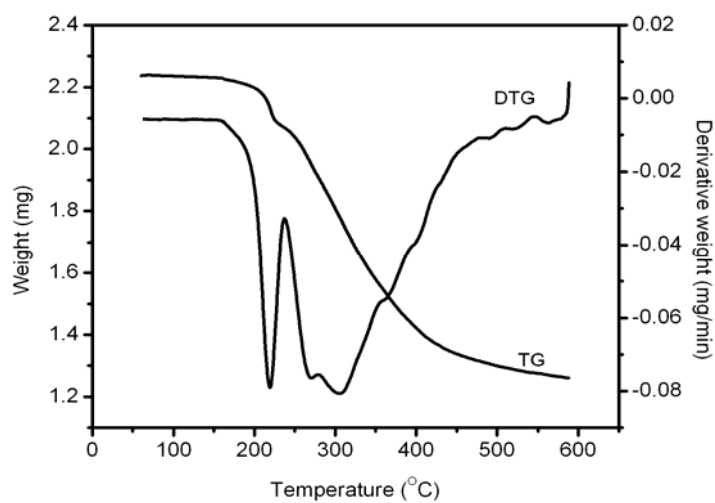
Figure 5.21: *TG-DTG of hamp*

Figure 5.22: *TG-DTG of [Mn(hamp)(H₂O)]H₂O*
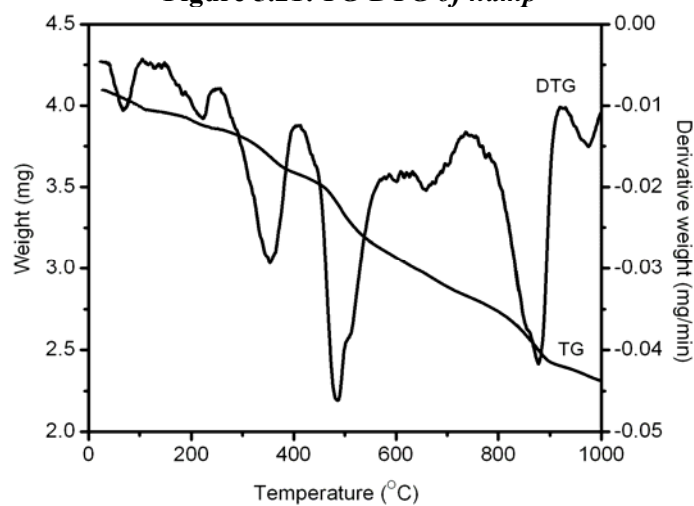
Figure 5.22: *TG-DTG of [Mn(hamp)(H$_2$O)]H$_2$O*
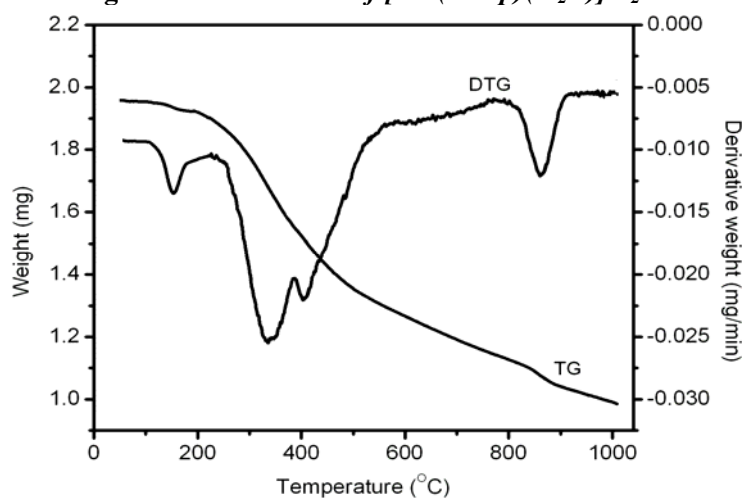
Figure 5.23: *TG-DTG of [Fe(hamp)Cl(H$_2$O)$_2$]*

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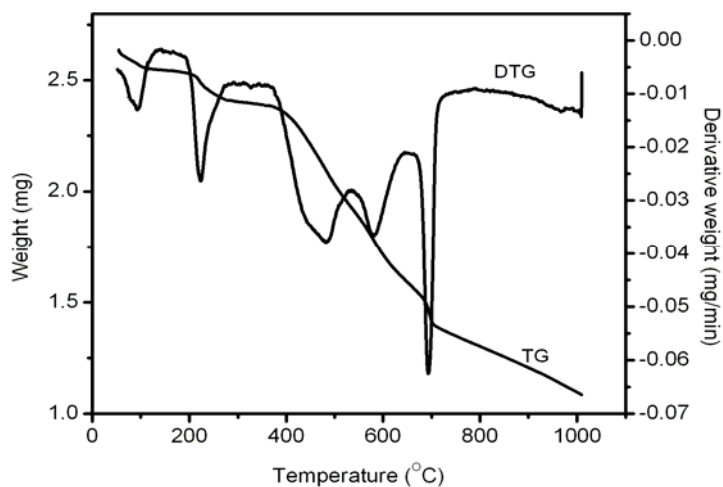
Figure 5.24: *TG-DTG of [Co(hamp)(OAc)(H₂O)₂]H₂O*
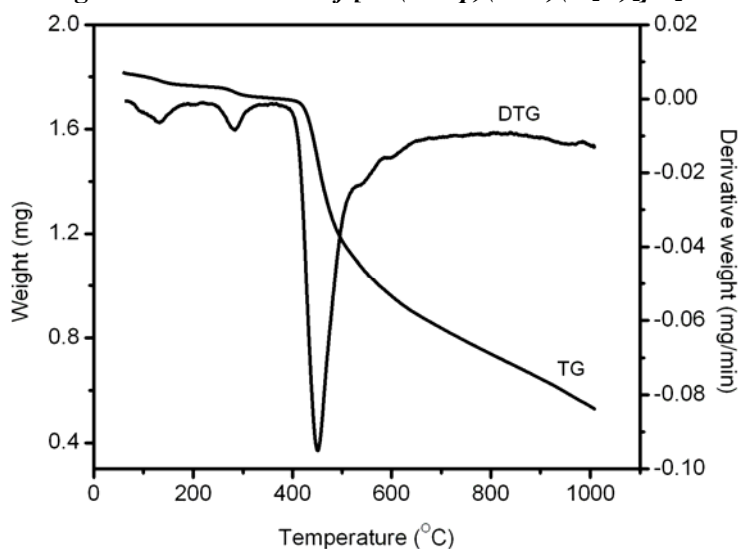
Figure 5.25: *TG-DTG of [Ni(hamp)(H₂O)]H₂O*
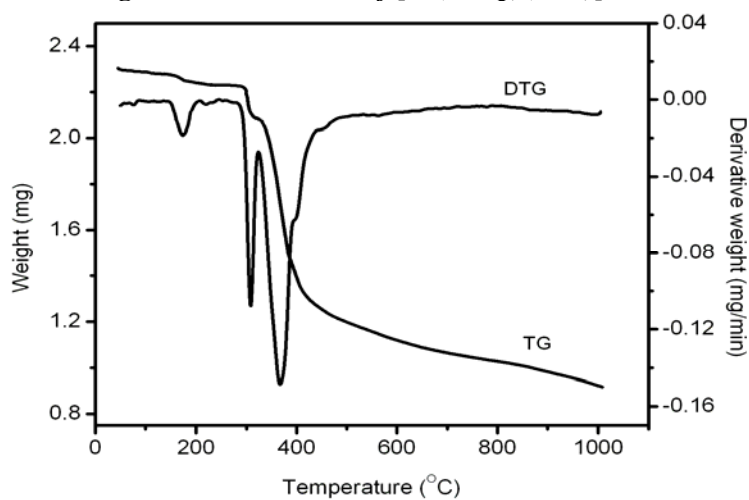
Figure 5.26: *TG-DTG of [Cu(hamp)(H₂O)]*

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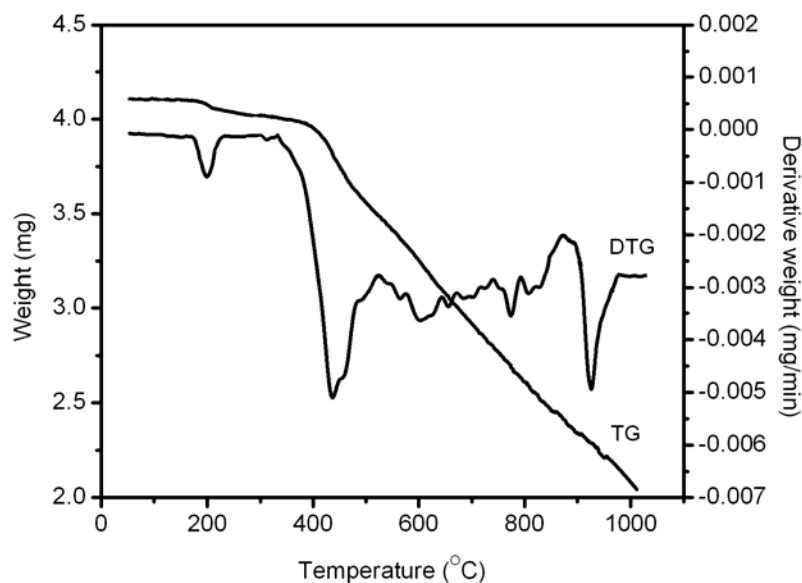
Figure 5.27: *TG-DTG of [Zn(hamp)(H₂O)]*

5.3.6 EPR spectra

In polycrystalline state, manganese(II) complex gives a broad signal with a *g* value of 2.06 [45]. The spectrum at 77 K in DMSO (Figure 5.28) exhibits six hyperfine lines. The lines are poorly resolved, which may be due to the poor glass formation. The spectrum gives a *g* value of 1.99 with an A value of 0.00929 cm^{-1}.

In polycrystalline state EPR spectrum of the copper(II) complex gives an isotropic spectrum with a *g* value of 1.99 (Figure 5.29). This may be due to the extensive exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation. Solution state EPR spectrum of the copper complex was recorded in DMF at 77K. The *g*$_∥$ value is found to be 2.08 and *g*⊥ is 1.99. The spectrum clearly indicates axial features [46].
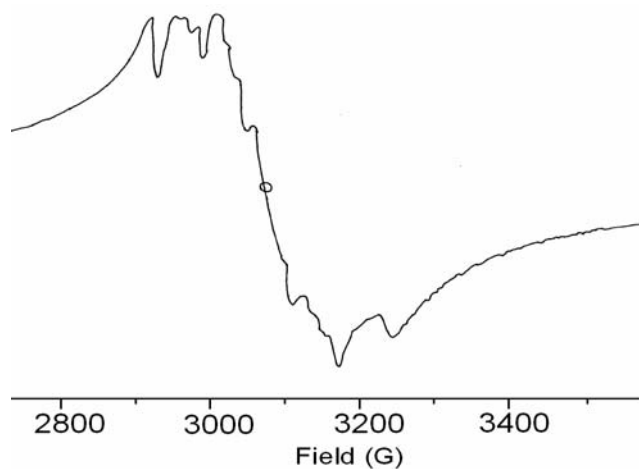
Figure 5.28: *EPR spectrum of [Mn(hamp)(H$_2$O)]H$_2$O in DMSO, 77 K*
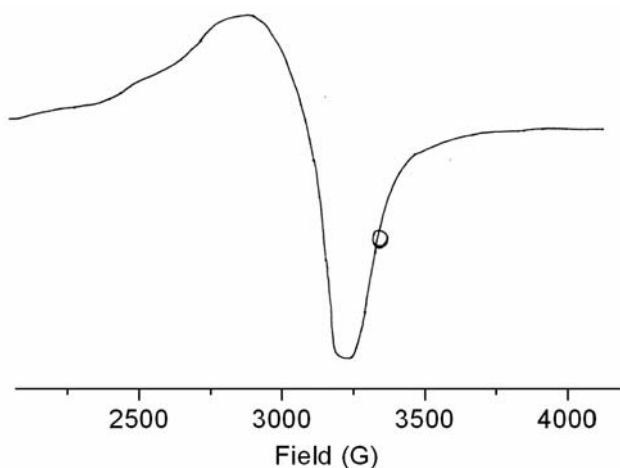
Figure 5.29: *EPR spectrum of [Cu(hamp)(H$_2$O)] in polycrystalline state*

5.4 CONCLUSIONS

A new Schiff base derived from 3-hydroxy quinoxaline-2-carboxaldehyde and 2-amino-5-methylphenol and its complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and characterized. Based on the physicochemical and spectroscopic studies we propose the following structures for the complexes (Figure 5.30).

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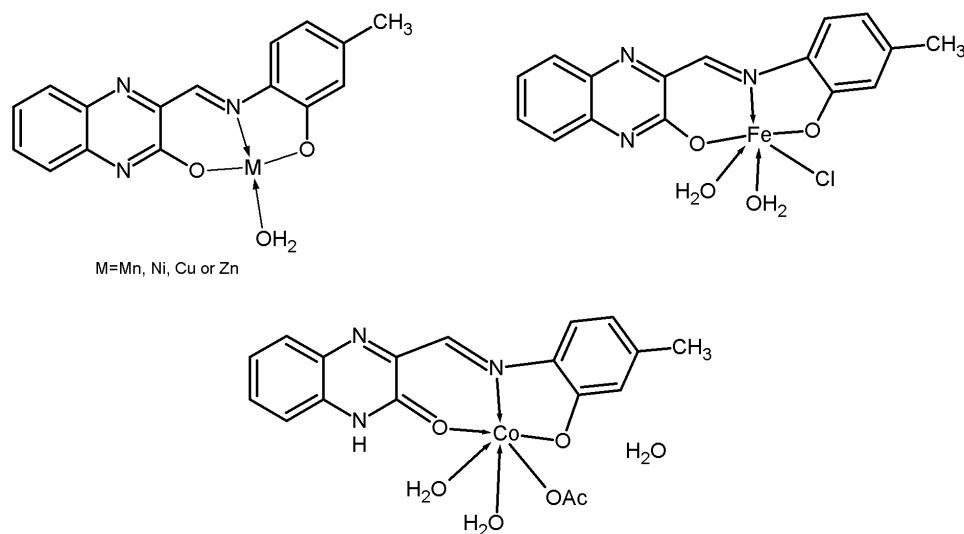
Figure 5.30: *The proposed geometry of complexes*

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3-Hydroxyquinoxaline–2–carboxalidine–2–amino thiophenol complexes of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II)

C o n t e n t s

6.1 INTRODUCTION

The interest in studying Schiff bases containing ONS donors arose from their significant antifungal, antibacterial, and anticancer activities [1, 2]. In addition, the presence of both a hard and a soft donor group in one ligand increases the coordination ability towards hard as well as soft acidic metals. The structural features of the ONS donor salicylidine Schiff base complexes were reviewed by Soliman and Linert [3]. Anaconda and coworkers have shown that the condensation of an aldehyde or a ketone with 2-aminobenzenethiol does not lead to isolation of the corresponding Schiff base, but to the isolation of benzothiazoline [4, 5]. Nevertheless, in solution, the benzothiazolidine may exist in equilibrium with its tautomeric Schiff base which could be stabilized as its metal complex and cannot be isolated free of its associated metal ion. Bouwman *et al.* [6] reported the coexistence of the Schiff base *N*-(2'-*tert*-butylbenzylidene)-2-aminothiophenol and the ring closed 2-(2-*tert*-butylthiophenyl)benzothiazolidine in solution. The structure of the compounds in equilibrium mixture is given in figure 6.1. The

presence of a metal ion can prevent the formation of benzothiazolidines and can act as a templating agent for the formation of the Schiff base [7].
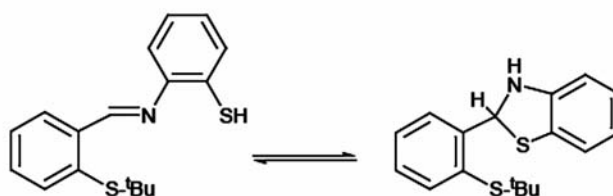
Figure 6.1: Schematic drawing of *N*-(2'-*tert*-butylbenzylidene)-2-aminothiophenol and 2-(2-*tert*-butylthiophenyl)benzothiazolidine in equilibrium

The Schiff base ligand generated by condensing 2-aminothiophenol with salicylaldehyde exhibits a remarkably diverse chemistry. Most importantly, the Schiff base, which is not the stable form of this noncoordinated molecule, undergoes ring closure to form benzothiazoline compounds [8-10]. Benzothiazoline compounds find application in medicine as as antiulcer drugs [11]. These compounds get rearranged to form the dianionic form of the Schiff base which can be stabilized by coordination to metal ion centers. There are many reports on the Schiff base complexes derived from 2-aminothiophenol with salicylaldehyde [9, 10, 12, 13]. But Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde and 2-aminothiophenol are hithero unknown.

We have synthesized the benzothiazoline compound, 3-(2,3-dihydro-1,3-benzothiazol-2-yl)quinoxalin-2(1*H*)-one, which is abbreviated as btq. The formation of btq is given in scheme 6.1. In solution btq gets rearranged to form the corresponding Schiff base in presence of metal ion as given in scheme 6.2. In such condition, the Schiff base exhibits tautomerism and its keto/enol form is able to complex with metal ions. We have synthesised the Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of this new Schiff base, 3−hydroxyquinoxaline−2−carboxalidine−2−aminothiophenol (hatp) and the complexes have been characterized by various physicochemical and spectroscopic techniques. In this chapter, the results of our studies on these complexes are presented.
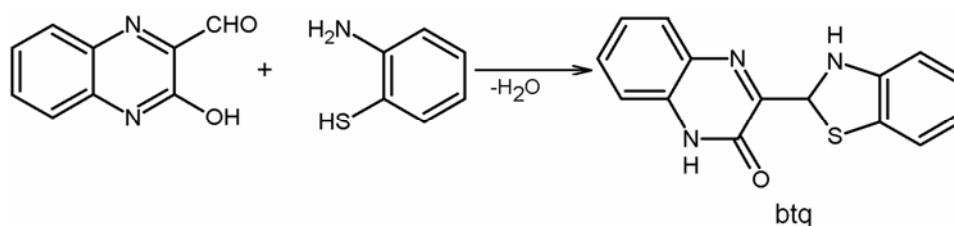
Scheme 6.1: *The formation of btq by ring closure*

6.2 EXPERIMENTAL

6.2.1 Materials and methods

The procedures for the preparation of 3-hydroxyquinoxaline-2-carboxaldehyde and the techniques employed for the characterization of btq and metal complexes are given in chapter II.

6.2.2 Preparation of 3-(2,3-Dihydro-1,3-benzothiazol-2-yl)quinoxalin-2(1*H*)-one

The compound, 3-(2,3-dihydro-1,3-benzothiazol-2-yl)quinoxalin-2(1*H*)-one, was prepared by taking an aqueous solution of 3−hydroxyquinoxaline −2−carboxaldehyde (1.742 g, 10 mmol, in 500 mL distilled water) which is acidified using 3–4 drops of con. HCl. To this solution was added a solution of 2−aminothiophenol (1.07 mL, 10 mmol) in methanol (20 mL) dropwise. The solution was stirred for 6 hours. The precipitated Schiff base was filtered, washed with water and dried over anhydrous calcium chloride. The crude product was recrystallised from absolute ethanol. Yield: 2.3 g (81.73 %)

6.2.3 Preparation of Complexes

The complexes of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) were prepared by the following general procedure:

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The compound btq (0.29 g, 1 mmol) dissolved in methanol (30 mL) was mixed with the solution of the metal salt (1 mmol: 0.245 g of $Mn(OAc)_2.4H_2O$, 0.249 g of $Co(OAc)_2.4H_2O$, 0.2488 g of $Ni(OAc)_2.4H_2O$, 0.1705 g of $CuCl_2.2H_2O$ or 0.2195 g of $Zn(OAc)_2.2H_2O$) in methanol (10 mL) and was stirred for 3 hours at room temperature (27±2 ºC). The precipitate formed was filtered off, washed with cold methanol, and dried in vacuum over anhydrous calcium chloride.

Our attempts to synthesize iron(III) complex of the Schiff base were not successful. In this case, we could get only the starting compound.
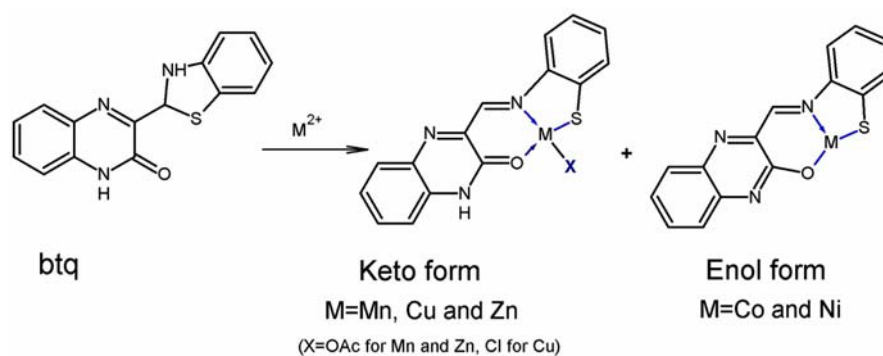
Scheme 6.2: *Formation of metal complexes of btq*

6.3 RESULTS AND DISCUSSION

Spectral data of the yellow compound isolated from the reaction of 3-hydroxyquinoxaline-2-carboxaldehyde and 2–aminothiophenol indicate that the compound does not have the expected open chain imine, but has a benzothiazoline structure as depicted in scheme 6.1. Similar reactions leading to the formation of benzothiazolines from 2–mercaptoanilines have been reported [7-9, 11, 12]. The product 3–(2,3–dihydro–1,3–benzothiazol–2–yl)quinoxalin-2(1*H*)–one (abbreviated as btq) was characterized by elemental analysis, IR and ^{1}H NMR spectra. The Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes were prepared by the stoichiometric reaction of the metal chloride/acetate with the compound, btq. The complexation

reaction proceeds with the rearrangement of btq to the corresponding Schiff base, hatp.

The colour, yield and elemental analyses data of btq and the complexes of its rearranged form, hatp, are given in Table 6.1. The molar conductivity values (table 6.2) in 10^{-3} M DMF solutions suggest non-electrolytic nature of the complexes [14]. The analytical data reveal the metal ligand ratio as 1:1 for all the complexes.

Table 6.1: *Analytical data of btq and complexes of hatp*

Compound	Colour	Yield (%)	Analytical data. Found (calculated)%					
			C	H	N	S	M	Cl
btq	Yelow	80	64.15 (64.04)	4.25 (3.94)	14.63 (14.94)	11.44 (11.40)	-	-
[Mn(hatp)(OAc)(H₂O)₂]	Red	56	48.38 (47.45)	3.85 (3.98)	9.95 (9.76)	7.50 (7.45)	12.45 (12.77)	-
[Co(hatp)(H₂O)₃]	Brown	75	43.68 (43.91)	3.70 (4.18)	10.33 (10.24)	8.07 (7.81)	14.79 (14.36)	-
[Ni(hatp)(H₂O)₃]	Red	63	45.37 (45.95)	3.28 (3.86)	10.60 (10.72)	8.09 (8.18)	15.31 (14.97)	-
[Cu(hatp)Cl]	Violet	70	47.38 (47.50)	2.40 (2.66)	11.12 (11.08)	8.42 (8.45)	16.41 (16.75)	8.92 (9.35)
[Zn(hatp)(OAc)]	Brown	78	50.17 (50.44)	3.28 (3.24)	10.60 (10.38)	8.09 (7.92)	16.31 (16.16)	-

Table 6.2: *Conductivity and magnetic moment data of complexes*

Compound	λ_m#	μ_{eff} (B.M)
[Mn(hatp)(OAc)(H₂O)₂]	20	5.80
[Co(hatp)(H₂O)₃]	11	5.18
[Ni(hatp)(H₂O)₃]	16	3.27
[Cu(hatp)Cl]	14	1.95
[Zn(hatp)(OAc)]	12	-

Molar conductivity (in Mho cm² mol⁻¹), 10⁻³ Molar solution in DMF

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6.3.1 ¹H NMR spectra of btq and [Zn(hatp)(OAc)]

The ¹H NMR spectra of the compound btq and that of [Zn(hatp)(OAc)] complex were recorded in d₆-dimethylsulphoxide solution using TMS as the internal standard. The chemical shifts of different protons of compound btq and of the zinc(II) complex are listed in table 6.3. Proton NMR spectra of btq and the zinc(II) complex are given in figures 6.2 and 6.3. The compound, btq, exhibits a doublet at 7.16 ppm due to thiazolidine CH (*J*=5Hz) [6] and a multiplet at 7.4–8.3 ppm due to the two NH protons and 8 aromatic protons [15]. In the NMR spectrum of the diamagnetic zinc(II) complex, the azomethine proton appears at 8.93 ppm as a singlet [16] and the three acetate protons appear as a singlet at 1.23 ppm. The aromatic protons are observed in the region 7.0–7.9 ppm as a multiplet. Thus the spectrum of the zinc(II) complex is quite different from that of the compound, btq and the spectral data clearly reveal that the ring opening of btq occurs in presence of metal ion.

Table 6.3: *¹H NMR Spectroscopic data of btq and [Zn(hatp)(OAc)]*

Compound	Chemical shift, δ (ppm)	Assignment
btq	7.16	(d, 1H, CH benzothiazoline)
	7.44-8.30	(m, 9H, Ar H and benzothiazoline NH)
	12.00-13.00	(m, 1H, NH/OH quinoxaline)
[Zn(hatp)(OAc)]	1.23	(s, 3H, CH₃ acetate)
	7.00-7.90	(m, 8H, Ar. H)
	8.93	(s, 1H, CH azomethine)
	12.20	(br s, 1H, NH)
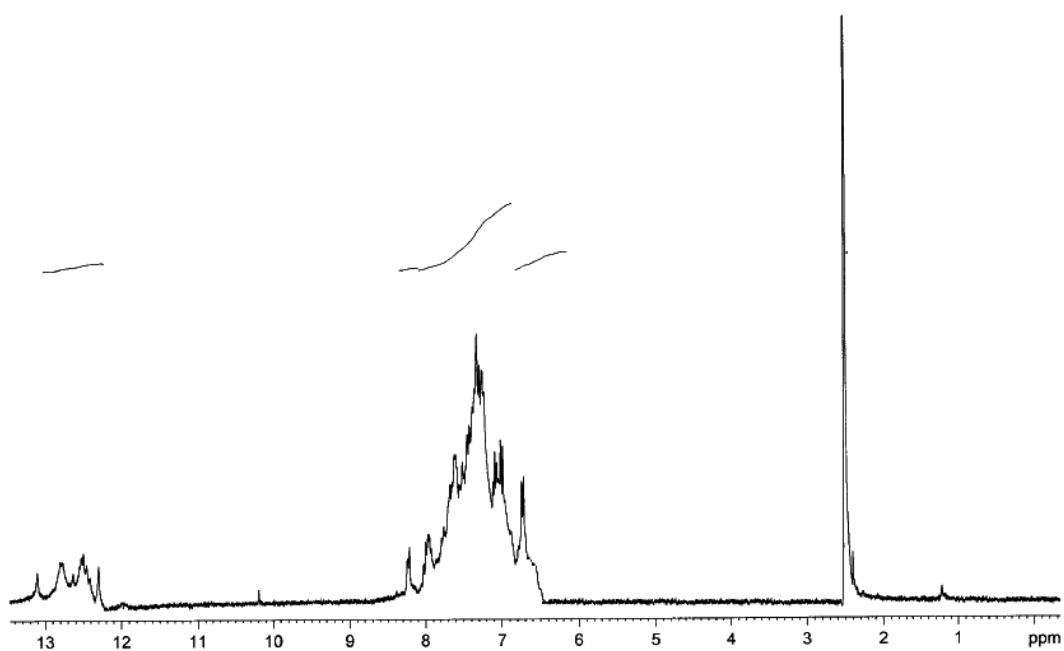
Figure 6.2: *NMR spectrum of btq*
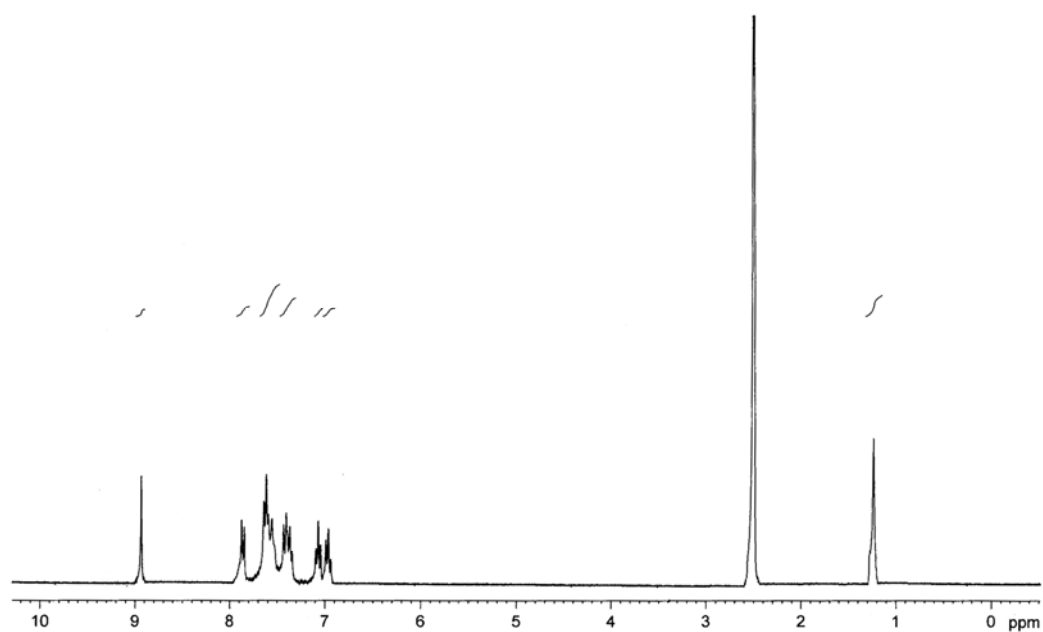
Figure 6.3: *NMR spectrum of [Zn(hatp)(OAc)]*

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6.3.2 Magnetic susceptibility measurements

The magnetic moment values of the complexes are presented in table 6.2. The μ_{eff} value of 5.80 B.M. for manganese(II) complex corresponds to the presence of five unpaired electrons and gives no specific information about its stereochemistry. The octahedral and tetrahedral cobalt(II) complexes differ in their magnetic properties. Because of the intrinsic orbital angular momentum in the octahedral ground state, there would be considerable orbital contribution, and effective magnetic moment values for such compounds at room temperature lie between 4.7 to 5.2 B.M. The complex, $[Co(hatp)(H_2O)_3]$, exhibits a magnetic moment of 5.18 B.M. which suggests an octahedral geometry for the complex [17, 18]. The nickel(II) complex is also octahedral, as it exhibits a μ_{eff} value of 3.27 B.M. [19]. The copper(II) complex has a magnetic moment of 1.95 BM, which indicate that the four coordinated complex is not tetrahedral.

6.3.3 Infrared spectra

The most important IR spectral bands of the btq and metal complexes of hatp are listed in Table 6.4. The benzothiazoline in presence of metal ion rearranges to form the Schiff base and the resulting Schiff base can act either in a monoanionic tridentate (keto form) or in a dianionic tridentate (enol form) manner as given in Scheme 6.2. The formation of benzothiazoline was confirmed by the absence of bands due to $\nu(SH)$ in the spectra of btq (Figure 6.4) [20]. Two absorption bands at 3375 and 3325 cm^{-1} due to $\nu(NH)$ of the amide tautomer and benzothiazoline ring respectively suggest the existence of btq in keto form in the solid state. In the case of tautomeric quinoxaline derivatives, particularly quinoxaline-2-ones, the IR stretching frequencies of the C=O and C=N (quinoxaline ring) vary from compounds to compounds [21]. It is not easy to assign a particular range for these two types of stretching frequencies. Mamedov *et al.* reported a series of quinoxaline-2-one compounds, which exhibit the C=O stretching in the region 1680–1665 cm^{-1} and quinoxaline C=N stretching in the

region 1600–1620 cm^{-1} [22-24]. In the IR spectrum of btq, the C=O and quinoxaline C=N stretching frequencies occur at 1665 and 1609 cm^{-1} respectively. The bands can be easily distinguished on the basis of their intensity, as the ν(C=O) will be more intense than ν(C=N).

The complexes exhibit a broad band in the range 3100–3500 cm^{-1}, due to the OH stretching of water molecules (Figures 6.5-6.9) [25]. The (N–H) stretching is also observed in the same region. However, we could not differentiate them due to the broadness of the peak. The Schiff base exists in the enol form in the cobalt(II) and nickel(II) complexes, which is evidenced by the disappearance of band due to (C=O) stretching. But it exists in the keto form in the manganese(II) copper(II) and zinc(II) complexes as there is a strong band around 1650 cm^{-1} for these complexes [26]. In these cases coordination of the ligand to metal ion is in a monoanionic tridentate manner. All the complexes exhibit the azomethine stretching in the region 1600–1640 cm^{-1} and the C–O (phenolic) stretching band is observed in the range of 1200–1300 cm^{-1} [27]. Conclusive evidence of the bonding is also shown by the appearance of new bands in the region 430-470 and 400-420 cm^{-1} in the spectra of the complexes due to (M–O) and (M–N) stretching vibrations [28-31].

Table 6.4: *IR spectral data of btq and its complexes*

Assignments (in cm^{-1})	ν(OH) / ν(NH)	ν(C=O)	ν(C=N)[#]	ν(M–O)	ν(M–N)
btq	3375, 3325	1665	-	-	-
[Mn(hatp)(OAc)(H$_2$O)$_2$]	3300 b	1650	1637	431	419
[Co(hatp)(H$_2$O)$_3$] H$_2$O	3400 b	-	1629	465	422
[Ni(hatp)(H$_2$O)$_3$]	3400 b	-	1624	445	404
[Cu(hatp)Cl]	-	1676	1605	427	406
[Zn(hatp)(OAc)]	-	1657	1599	505	420

[#] azomethine, b-broad
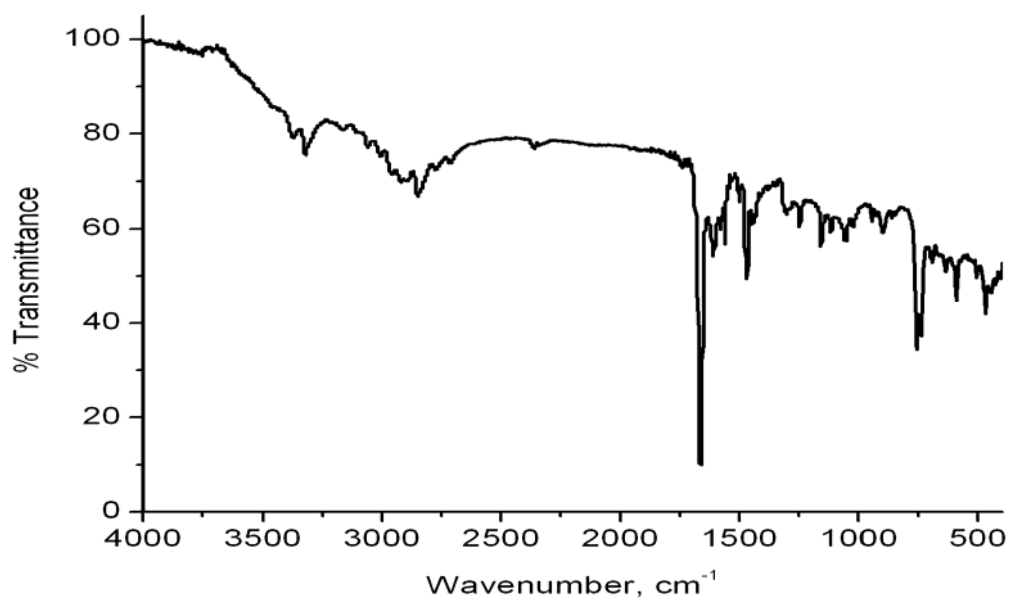
Figure 6.4: *IR spectrum of btq*
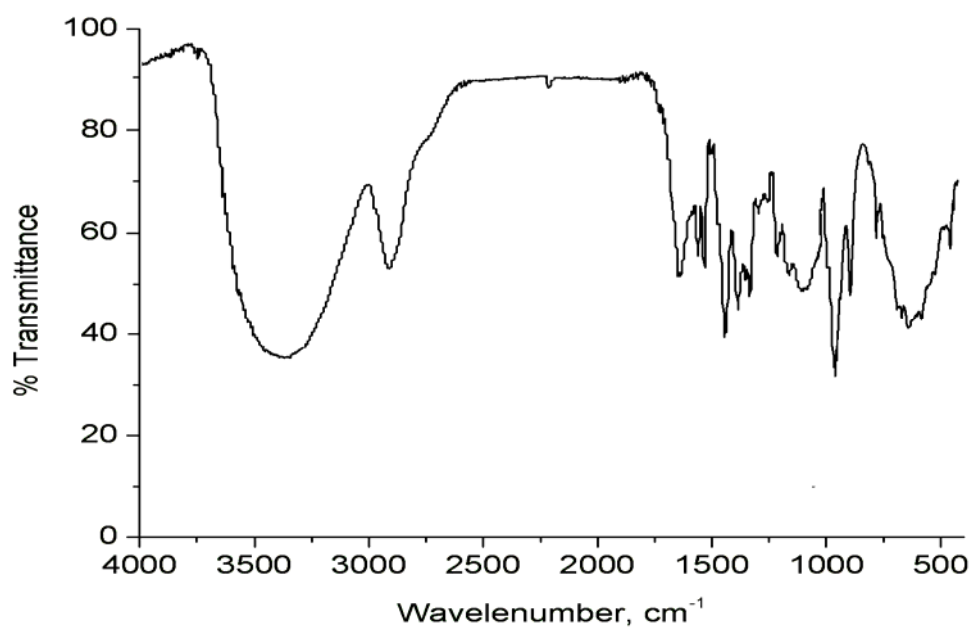
Figure 6.5: *FTIR spectrum of [Mn(hatp)(OAc)(H$_2$O)$_2$]*
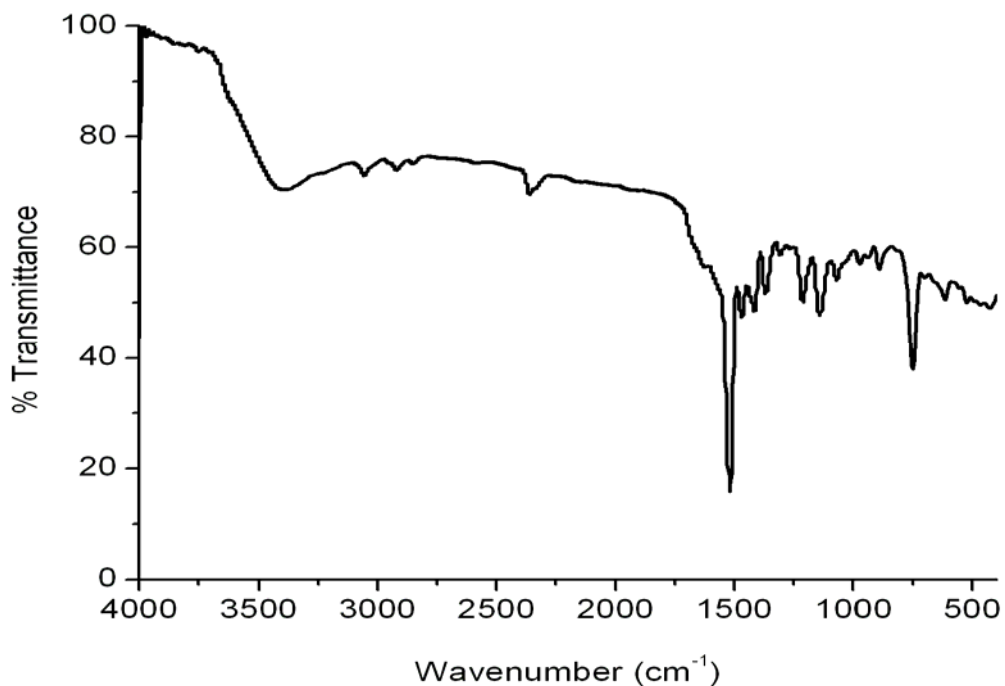
Figure 6.6: *FTIR spectrum of [Co(hatp)(H₂O)₃] H₂O*
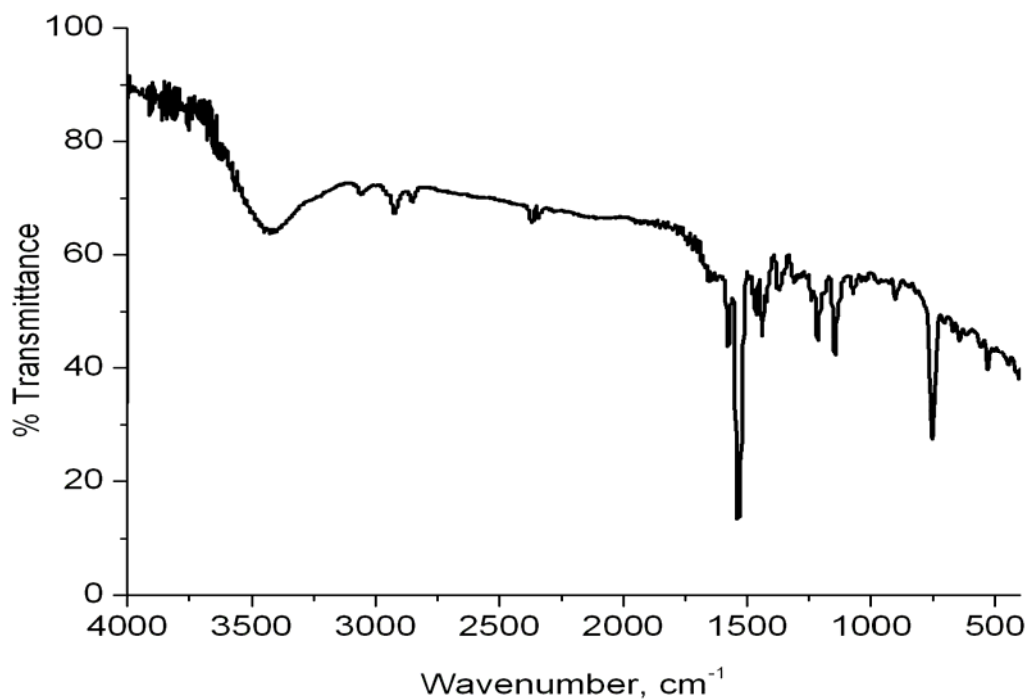
Figure 6.7: *FTIR spectrum of [Ni(hatp)(H₂O)₃]*

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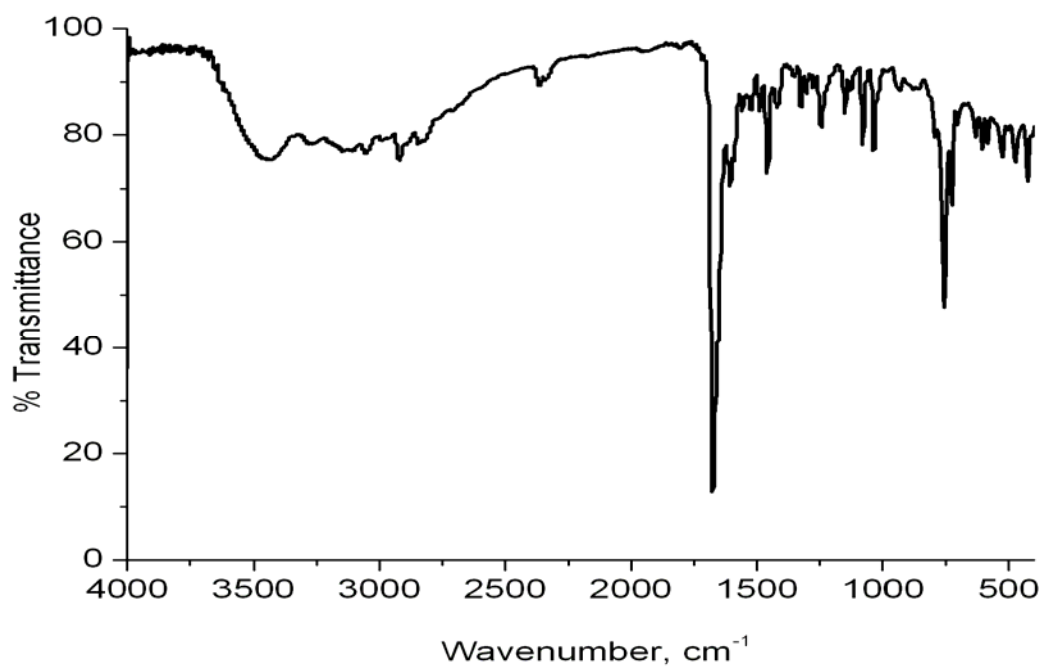
Figure 6.8: *FTIR spectrum of [Cu(hatp)Cl]*
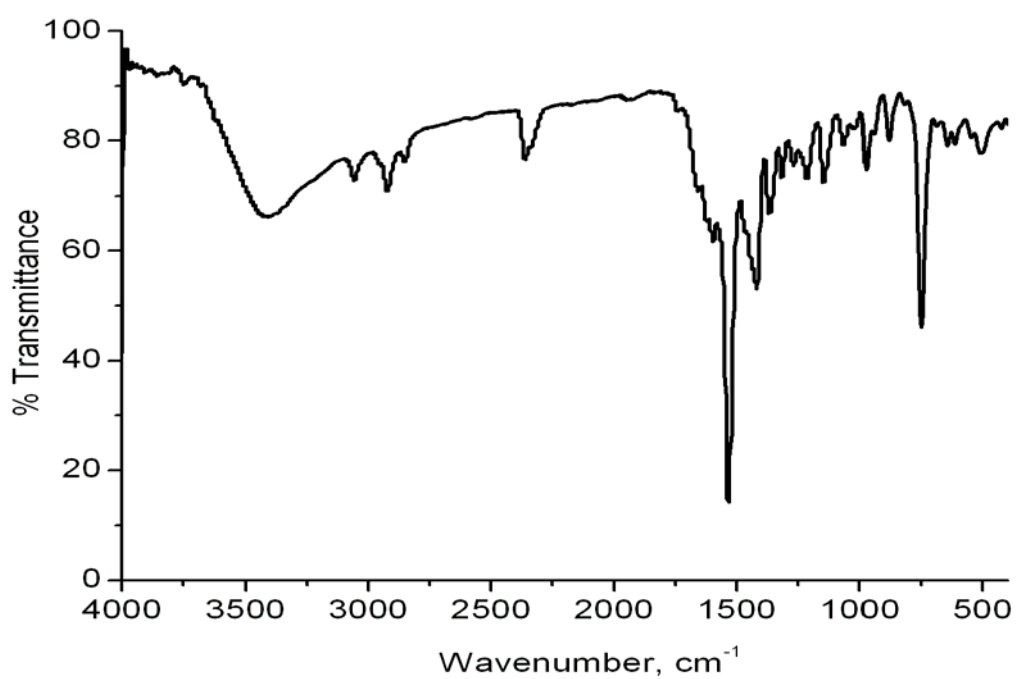
Figure 6.9: *FTIR spectrum of [Zn(hatp)(OAc)]*

6.3.4 Electronic spectra

The UV–Vis spectra of the compound btq and the complexes of hatp are recorded in methanol in the wavelength range from 50000–10000 cm^{-1}. Electronic spectra of btq and the complexes of hatp are given in Figures 6.10-6.15. Spectral data are presented in Table 6.5. The bands at 37700 and 29000 cm^{-1} are attributed to quinoxaline π–π* and phenyl π–π* transitions respectively. The band at 25000 cm^{-1} is assigned to the n–π* transition of azomethine group and ring (C=N) groups.

The manganese(II) complex exhibits bands at 23500 and 21400 cm^{-1}, which can be assigned to $^6A_{1g} \rightarrow {}^4E_g(G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions expected for the octahedral complexes of Mn(II) [32]. These transitions are forbidden and the intensity of the bands is found to be very low (log ε <1). The spectrum also shows bands at 24800 and 29600 cm^{-1} due to the metal to ligand to metal charge transfer transitions.

No d-d transitions were observed for the cobalt(II) complex. The complex exhibits a broad charge transfer band with a maximum at 19200 cm^{-1}, which might have obscured all the d-d transitions expected for an octahedral complex [33].

The three spin allowed electronic transitions are expected for octahedral nickel(II) complexes. The shoulder bands observed at 21370, 19530 and 11325 cm^{-1} can be assigned to the transition from $^3A_{2g}$ to $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ respectively. Furthermore intensities of these bands are very low as expected for the octahedral complexes [17, 32].

The copper(II) complex exhibits ligand to metal charge transfer transitions at 27800 and 24700 cm^{-1}. The d-d bands observed at 20200 and 17500 cm^{-1} are due to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions expected for the square planar copper(II) complexes [34]. Two charge transfer transitions are observed at 29900 and 23500 cm^{-1} for the zinc(II) complex.

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Table 6.5: *UV-Vis spectral assignments of btq and complexes*

Compound	Absorption maxima (cm^{-1})	log ε (ε in L mol^{-1} cm^{-1})	Assignment
btq	37700	4.07	$\pi \rightarrow \pi^*$
	29000	3.62	$\pi \rightarrow \pi^*$
	25000	2.97	$n \rightarrow \pi^*$
[Mn(hatp)(OAc)(H$_2$O)$_2$]	37750	4.06	$\pi \rightarrow \pi^*$
	29600	2.54	CT
	24800	1.11	CT
	23500	0.90	$^6A_{1g} \rightarrow {}^4E_g(G)$
	21400	0.70	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
[Co(hatp)(H$_2$O)$_3$] H$_2$O	37000	3.89	$\pi \rightarrow \pi^*$
	32900	3.46	$\pi \rightarrow \pi^*$
	24600	2.63	$n \rightarrow \pi^*$
	19200	3.60	CT
[Ni(hatp)(H$_2$O)$_3$]	37700	3.95	$\pi \rightarrow \pi^*$
	29400	3.13	$n \rightarrow \pi^*$
	24700	3.69	CT
	23400	3.66	CT
	21400	2.18	$^3A_{2g} \rightarrow {}^3T_{2g}$
	19500	1.14	$^3A_{2g} \rightarrow {}^3T_{1g}$
	11300	1.17	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
[Cu(hatp)Cl]	37700	3.96	$\pi \rightarrow \pi^*$
	27800	3.54	CT
	24700	3.32	CT
	20200	2.95	$^2B_{1g} \rightarrow {}^2E_g$
	17500	2.85	$^2B_{1g} \rightarrow {}^2A_{1g}$
[Zn(hatp)(OAc)]	37750	3.92	$\pi \rightarrow \pi^*$
	29900	3.46	CT
	23500	3.30	CT
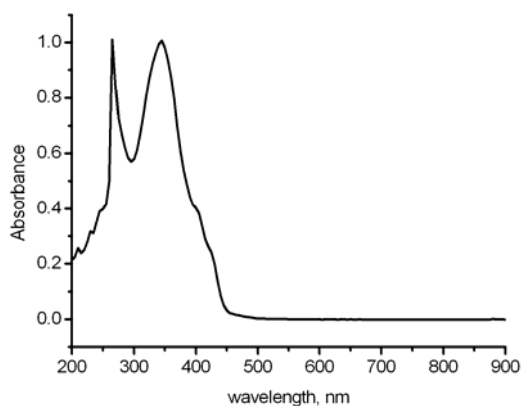
Figure 6.10: *The UV-Vis spectrum of btq*
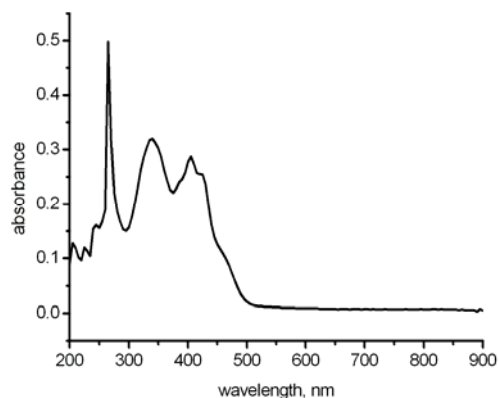
Figure 6.11: *The UV-Vis spectrum of [Mn(hatp)(OAc)(H₂O)₂]*
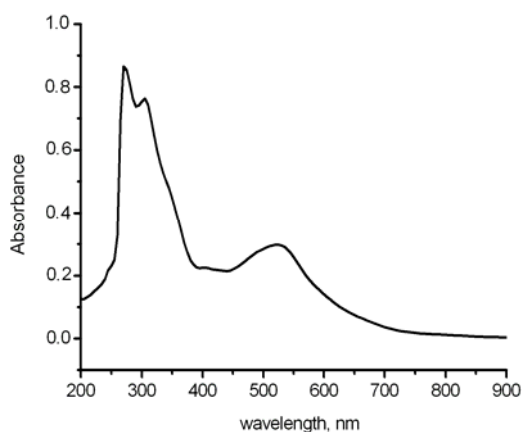
Figure 6.12: *The UV-Vis spectrum of [Co(hatp)(H₂O)₃] H₂O*
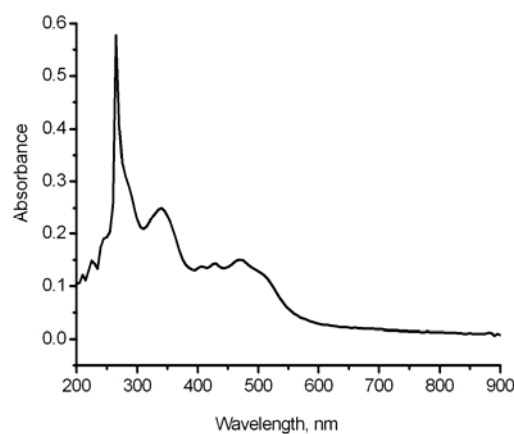
Figure 6.13: *The UV-Vis spectrum of [Ni(hatp)(H₂O)₃]*
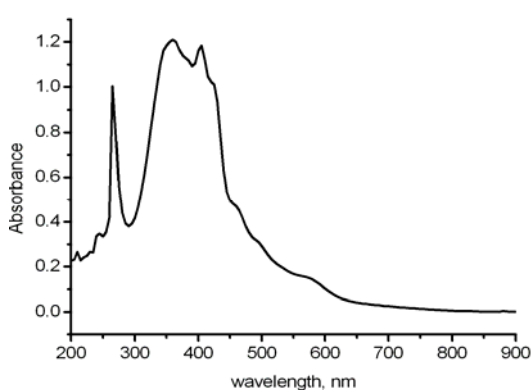
Figure 6.14: *The UV-Vis spectrum of [Cu(hatp)Cl]*
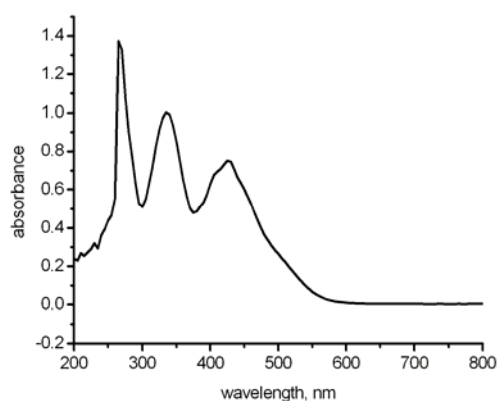
Figure 6.15: *The UV-Vis spectrum of [Zn(hatp)(OAc)]*

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6.3.5 Thermal analysis

Thermal stability of the btq and complexes of hatp was investigated using TG–DTG under nitrogen atmosphere with a heating rate of 10 ºC min^{-1} over a temperature range of 40–1000 ºC. The TG-DTG plots of btq and the complexes are given in figures 6.16-6.21. The compound btq exhibits a two stage decomposition which begins at 130 ºC. The weight loss observed for the cobalt(II) complex in the range 90-120 ºC indicates the presence of three lattice water molecules. The weight loss observed in the region 150-200 ºC for the manganese(II), cobalt(II) and nickel(II) complexes can be attributed to the loss of coordinated water molecules [35-37]. Table 6.6 presents the thermogravimetric analysis results below 220 ºC. The TG data suggest the presence of three coordinated water molecules in the cobalt(II) and nickel(II) complexes and two coordinated water molecules in the manganese(II) complex exhibit multi stage decomposition pattern. The data also show good agreement with the molecular formula of the complexes arrived from the analytical data.

Table 6.6: *Thermogravimetric analysis data (below 220 ºC)*

Complex	Temperature range, ºC	% loss	Fragment lost	Nature of water lost
[Mn(hatp)(OAc)(H$_2$O)$_2$]	140-210	8.4	2 H$_2$O	Coordinated water
[Co(hatp)(H$_2$O)$_3$] H$_2$O	90-120	4.5	1 H$_2$O	Lattice water
	130-200	13.3	3 H$_2$O	Coordinated water
[Ni(hatp)(H$_2$O)$_3$]	140-220	13.7	3 H$_2$O	Coordinated water
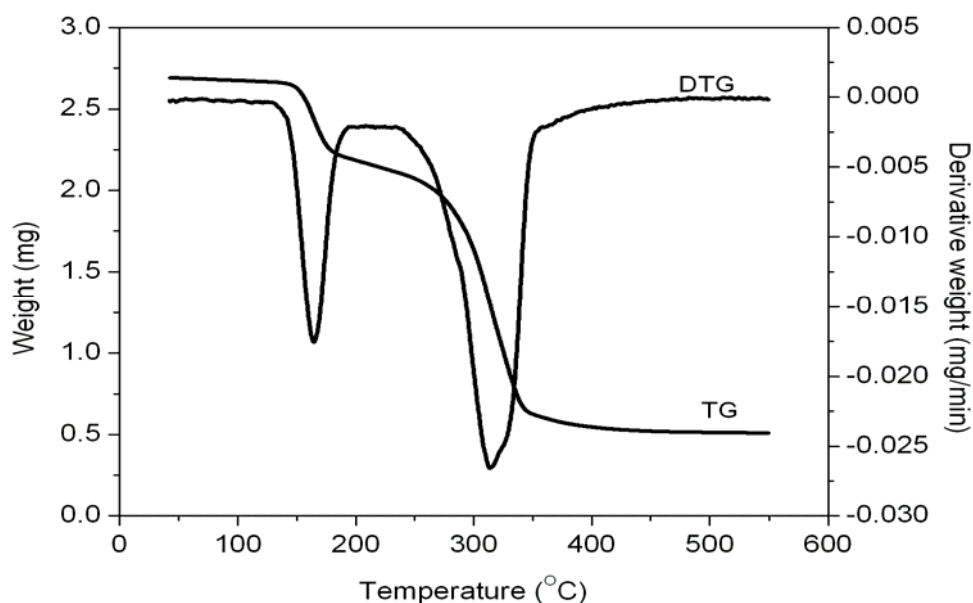
Figure 6.16: *TG-DTG of btq*
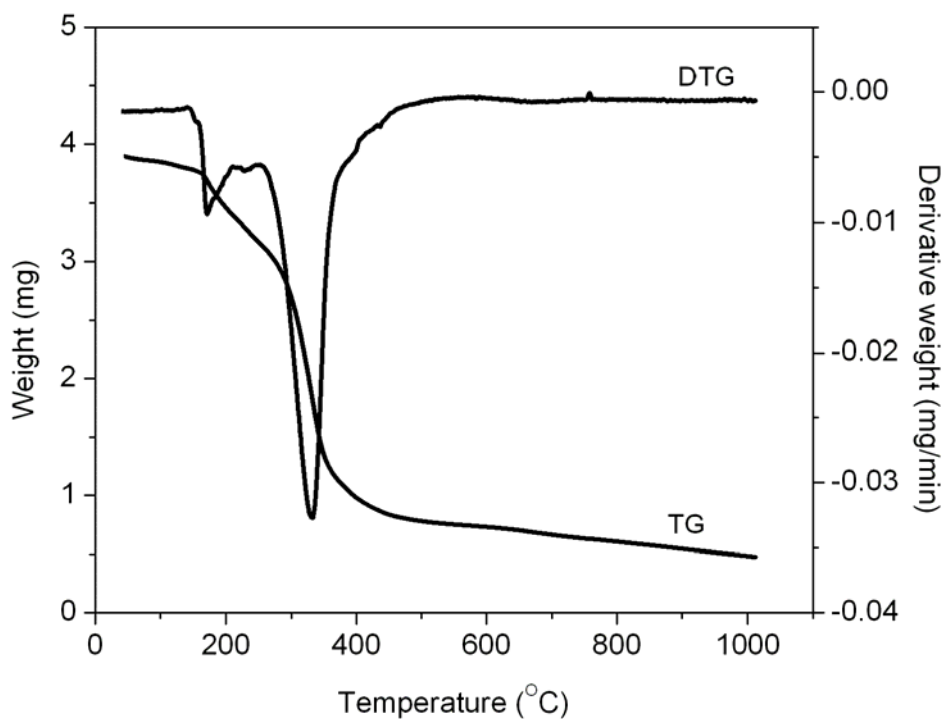
Figure 6.17: *TG-DTG of [Mn(hatp)(OAc)(H₂O)₂]*

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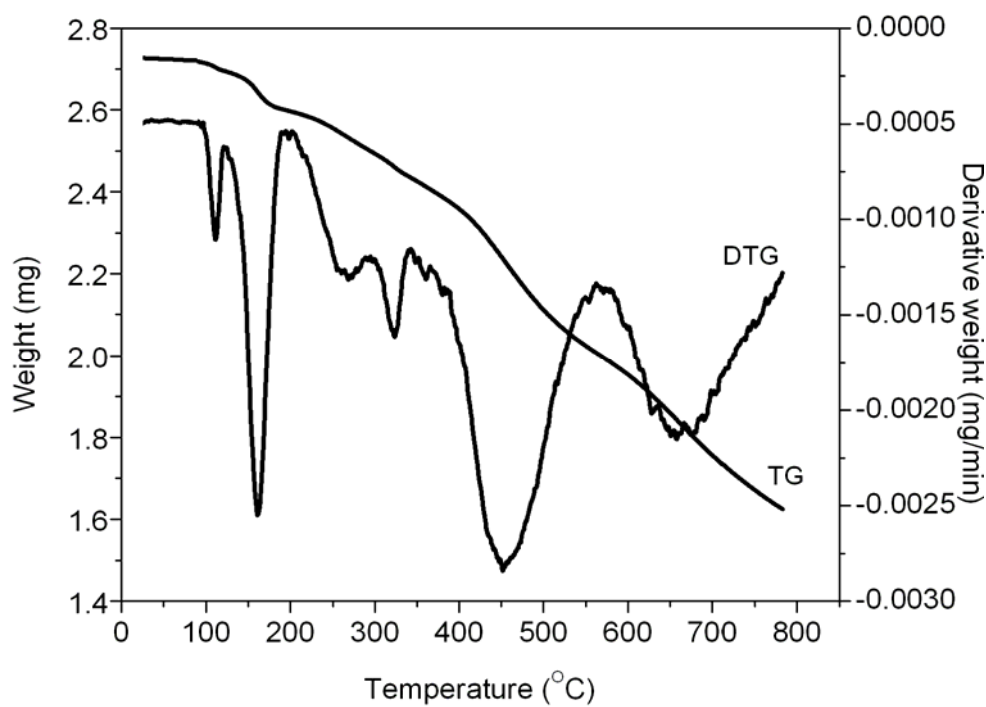
Figure 6.18: *TG-DTG of [Co(hatp)(H$_2$O)$_3$]H$_2$O*
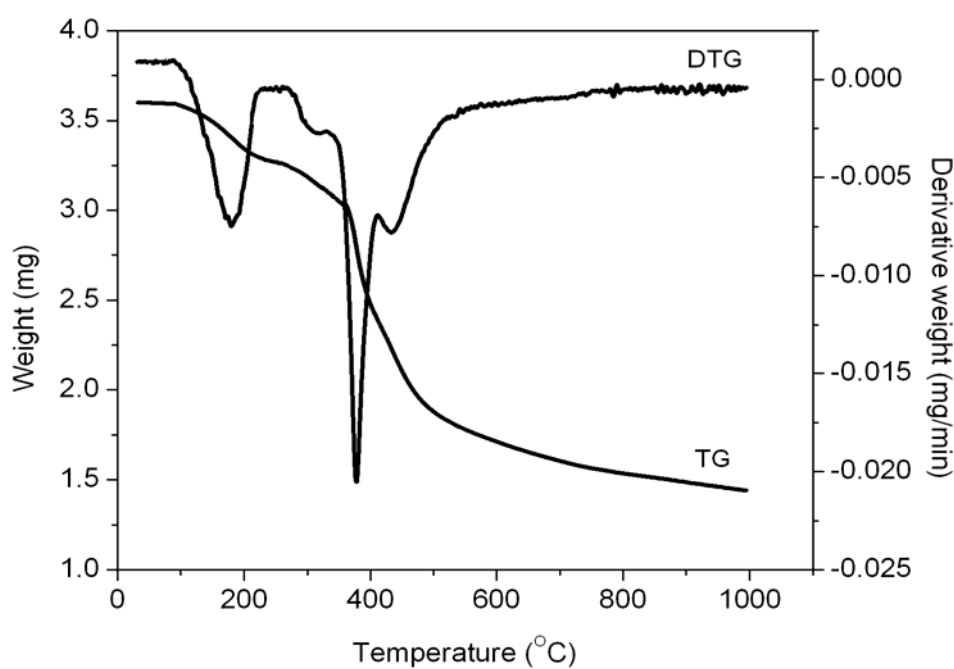
Figure 6.19: *TG-DTG of [Ni(hatp)(H$_2$O)$_3$]*
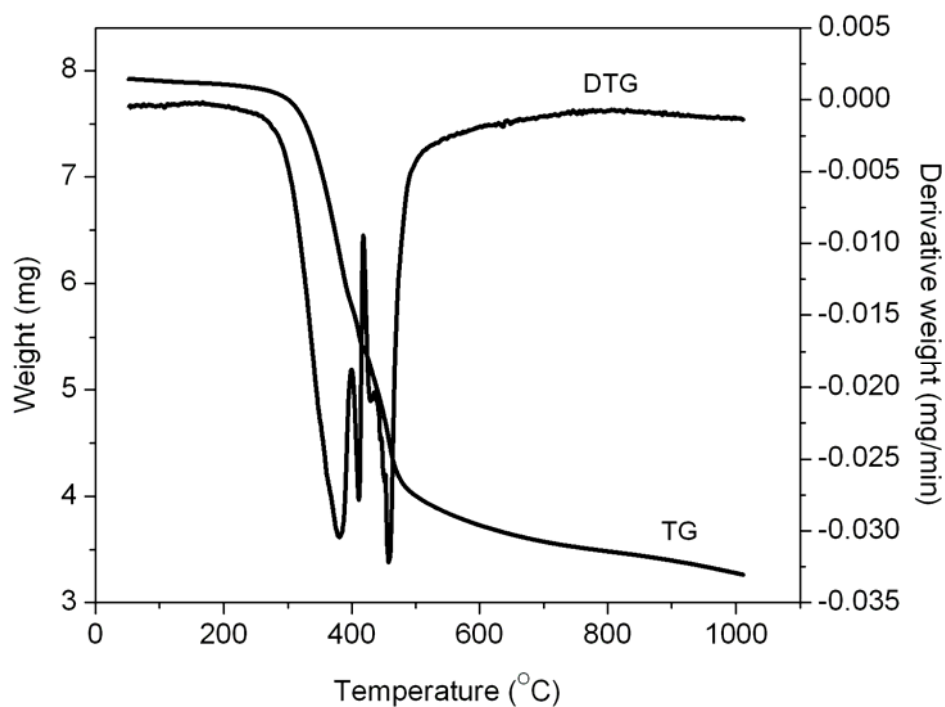
Figure 6.20: *TG-DTG of [Cu(hatp)Cl]*
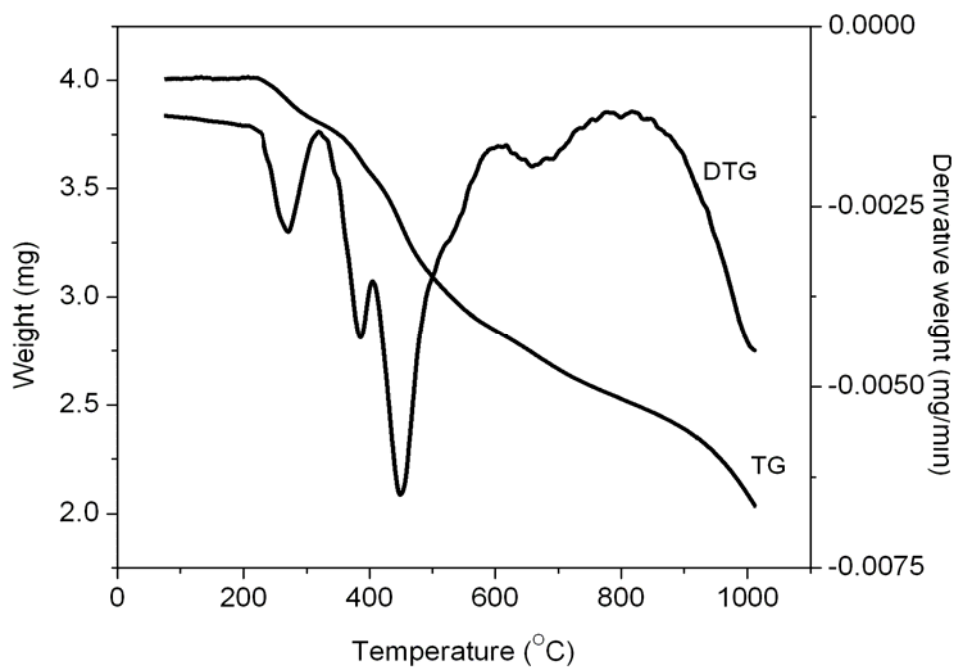
Figure 6.21: *TG-DTG of [Zn(hatp)(OAc)]*

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6.3.6 EPR spectra

The EPR spectra of the Cu(II) and Mn(II) complexes in the polycrystalline state at 298 K and in solution (DMSO) at 77 K were recorded in the X–band, using 100 kHz field modulation and the g tensors were calculated relative to the standard marker TCNE (g=2.003).

The solid state EPR spectrum of the Mn(II) complex is characterized by the broad isotropic spectrum with a g value of 1.98. The solution spectrum in DMSO at LNT gives six hyperfine lines which indicate the six allowed transitions. The low intensity spin forbidden transitions are observed in between the lines [38]. The spectrum gives a *g* value of 1.98 with an A value of 0.00851 cm^{-1} (Figure 6.22).

The copper(II) complex in polycrystalline state exhibits an isotropic spectrum with a g value of 1.97. This type of spectra gives no information on the electronic ground state of the Cu(II) ion present in the complexes [39]. EPR spectrum of the copper(II) complex in DMSO at liquid nitrogen temperature (figure 6.23) gives a g$_\parallel$ value of 2.20 and g⊥ value of 2.08. The spectrum clearly reveals axial features (g$_\parallel$>g⊥>2.0023), which suggests a B$_{1g}$ ground state and a square planar geometry for the copper(II) complex [40, 41].
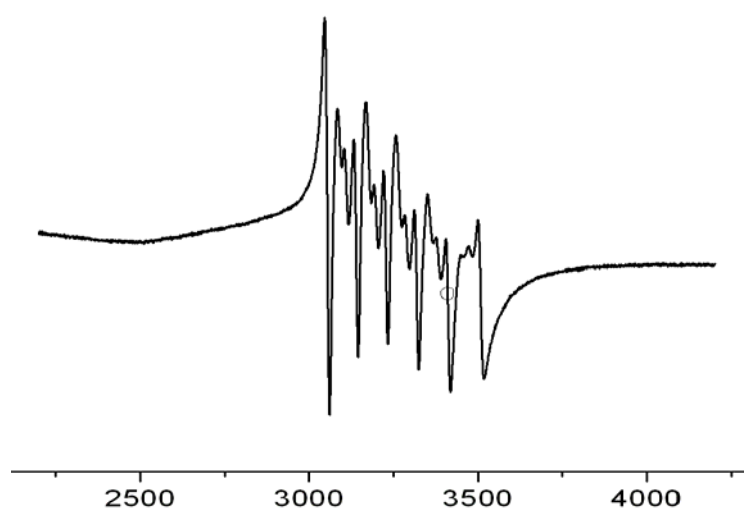
Figure 6.22: *EPR spectrum of the Mn(II) complex in DMSO at LNT*

Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study
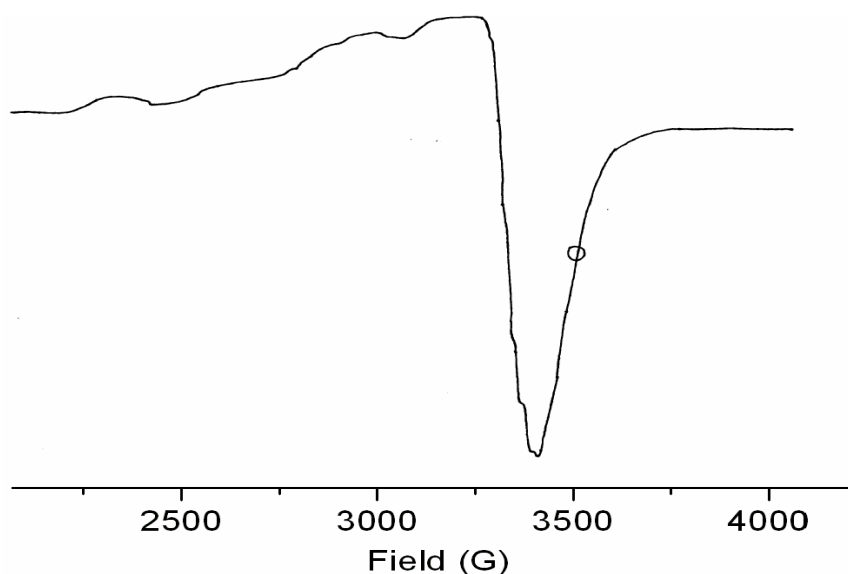
Figure 6.23: *EPR spectrum of the copper(II) complex in DMSO at LNT*

6.4 CONCLUSIONS

A novel benzothiazolidine derivative, 3-(2,3-dihydro-1,3-benzothiazol-2-yl)quinoxalin-2(1*H*)-one, has been synthesized and characterized by elemental analysis, IR and NMR spectra. This compound (btq) gets rearranged to form tridentate ONS donor Schiff base, hatp, in the presence of metal ions. Like the other 3-hydroxy derivatives of quinoxalines, the compounds btq and hatp exhibit prototropic tautomerism. The Schiff base, hatp may get coordinated either in the keto form or in the enol form. All the complexes were characterized by physicochemical and spectroscopic techniques. These studies suggest that the copper(II) complex is square planar, zinc(II) complex is tetrahedral and the manganese(II), cobalt(II) and nickel(II) complexes are octahedral in geometry (figure 6.24).
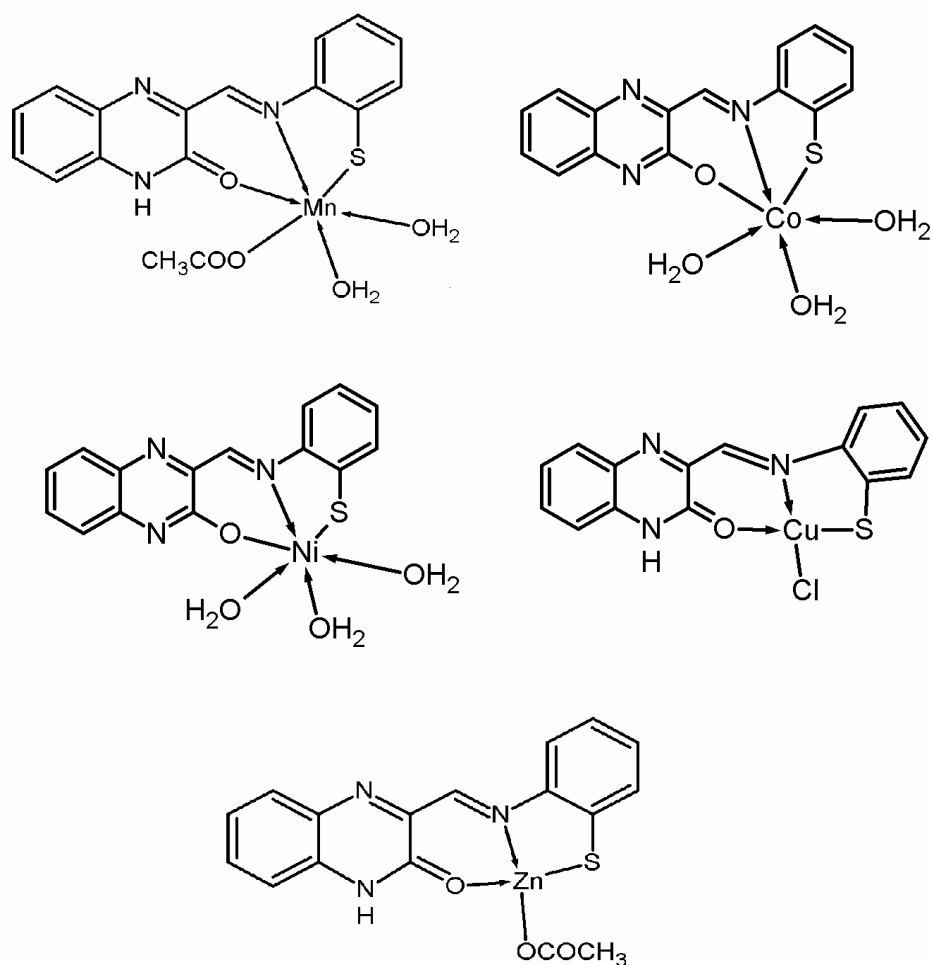
Figure 6.24: *The proposed geometry of the complexes*

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Catalytic activity of the Schiff base complexes in some oxidation reactions

The oxidation of organic compounds is an important and widely used reaction in laboratory scale organic synthesis as well as in large scale. There are hundreds of different reagents and methods available for the oxidation of organic compounds. The selections of solvent, oxidant, reaction conditions such as temperature, pressure and number of reaction steps are crucial in affecting the speed of reaction and the type and qauntity of side-product produced. The Schiff base transition metal complexes are a family of attractive oxidation catalysts for a variety of organic substrates because of their cheap and easy synthesis and their chemical and thermal stability [1]. Important oxidation reactions include the transformation of alcohols to either the corresponding carbonyl compounds or carboxylic acids, the oxidation of sulfides to sulfoxides, alkenes to epoxides and diols, and the activation of hydrocarbons *etc.*

This chapter deals with the studies on the use of the Schiff base complexes as catalysts in the hydroxylation of phenol, oxidation of cyclohexane and oxidation

of benzyl alcohol and is divided into three sections. Section 7.1 deals with studies on the liquid phase hydroxylation of phenol. The section 7.2 presents the studies on the oxidation of cyclohexane and section 7.3 deals with the studies on catalytic activity of the copper(II) Schiff base complexes in the oxidation of benzyl alcohol.

7.1 SCHIFF BASE COMPLEXES AS CATALYST TOWARDS THE LIQUID PHASE CATALYTIC HYDROXYLATION OF PHENOL

7.1.1 Introduction

Liquid phase hydroxylation of phenol to catechol and hydroquinone using simple oxidants like O_2 and H_2O_2 is an important reaction. The oxidation of organic substrates with aqueous hydrogen peroxide is very attractive from the viewpoint of industrial technology and synthetic organic chemistry since aqueous hydrogen peroxide is cheap, environmentally clean and easy to handle [2, 3]. Catechol and hydroquinone are two of the many phenolic derivatives of high value. They are widely used as photographic chemicals, antioxidants [4, 5], polymerization inhibitors, flavoring agents, and medicine [6, 7]. A number of novel estrane skeletons have been synthesized using catechol estrogens [8].
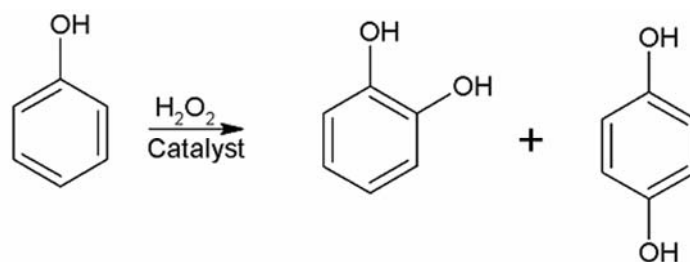
Scheme 7.1.1: *Catalytic hydroxylation of phenol to get Catechol and hydroquinone*

The catalytic hydroxylation of phenols in heterogenized systems has been reported in many cases [9-14]. Transition metal complexes containing nitrogen and phenolic oxygen donor atoms are of considerable interest in inorganic and biomimetic chemistry due to their potential application in catalysis, their biological relevance, and potentially interesting magnetic properties [15-20]. In the present study the phenol hydroxylation reaction was carried out using copper(II),

manganese(II), iron(III) and cobalt(II) complexes of ONN, ONO and ONS donor Schiff bases. Suitable reaction conditions have been optimized to give maximum hydroxylation.

7.1.2. Experimental

7.1.2.1. Materials and methods

The details of the synthesis and characterization of the complexes are outlined in the previous chapters. The products obtained are analyzed in a Chemito 8510 gas chromatograph with OV-17 column. Materials used in the catalytic activity studies are listed in chapter II.

7.1.2.2. Catalytic activity study

The catalytic activity study towards the hydroxylation of phenol was carried out in a 50 mL two necked RB flask fitted with a water cooled condenser. In a typical reaction, an aqueous solution of 30 % H_2O_2 (2.67 mL, 25 mmol) and phenol (2.2 mL, 25 mmol) were mixed in 10 mL of acetonitrile and the reaction mixture was heated at 343 K with continuous stirring in an oil bath. The complex (15 mmol) was added to the reaction mixture and the reaction was considered to be started at this time. During the reaction, the products were analyzed using a gas chromatograph after specific interval of time by withdrawing small aliquot. Quantification was done after considering the response factors of the reagents and products obtained using standard mixtures. The effects of various parameters such as concentration of the oxidant and catalyst, temperature and time of the reaction were studied to see their effect on the reaction product pattern.

7.1.3. Results and discussion

Liquid phase hydroxylation of phenol catalyzed by the Schiff base complexes using H_2O_2 as an oxidant was studied in CH_3CN. Although it is difficult to explain the effect of solvent and to identify the solvent parameters that are

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responsible for controlling the reaction rate, solvent plays a very significant role in controlling the overall % conversion. Abbob *et al.* [21] proposed that for phenol hydroxylation reaction, the solvent has a moderate influence on the ratio of Catechol to hydroquinone. In the current study acetonitrile was found to be the best solvent. As hydroxyl group present on phenol is ortho and para directing, the hydroxylation of phenol is expected to give two products *viz.* catechol and hydroquinone [22] as shown by scheme 7.1.1. Para benzoquinone is also likely to be formed due to the further oxidation of hydroquinone [23]. In the current study, formation of the benzoquinone is not observed or the percentage of benzoquinone formed may be below the detection limit.

7.1.3.1 Catalytic activity of the metal complexes towards phenol hydroxylation: Screening studies

The catalytic activities of the prepared Mn(II), Fe(III), Co(II) and Cu(II) complexes are screened for their activity towards phenol hydroxylation reaction. The results of these studies are given in Table 7.1.1. The reaction conditions employed are given in the experimental part. Almost all the complexes show good activity. The activities of these cobalt complexes are slightly lower than that of copper(II), iron(II) and manganese(II) analogues of the investigated Schiff bases. Similar observations were made by Wyk and co-workers [22, 24]. The major product of the reaction was found to be catechol in all cases [25]. The cobalt(II) complex of qamp is found to be inactive, which may be due to the coordinative saturation. In [Co(qamp)$_2$]H$_2$O two molecules of the Schiff bases are tightly bound the metal ion, so that it is unable to bind with the oxygen to form the intermediate. The complex, [Cu(qamp)Cl], was found to be the most active catalyst with ~16 % conversion.

Table 7.1.1: *Catalytic activity of the metal complexes towards phenol*

hydroxylation

Catalyst	% C	% Products		% S (Cat)	Cat/HQ
		Cat	HQ		
[Cu(qamp)Cl]	16.10	14.48	1.62	89	8.9
[Cu(qlh)Cl]2H$_2$O	15.67	12.26	3.41	78	3.5
[Cu(hamp)(H$_2$O)]	7.90	7.45	0.45	94	16.5
[Cu(hatp)Cl]	5.52	4.65	0.87	84	5.3
[Mn(qamp)(OAc)]H$_2$O	11.70	10.30	1.40	88	7.3
[Mn(qlh)(OAc)]2H$_2$O	7.71	6.72	0.99	87	6.8
[Mn(hamp)(H$_2$O)]H$_2$O	10.48	9.41	1.07	89	8.8
[Mn(hatp)(OAc)(H$_2$O)$_2$]	4.28	3.90	0.38	91	10.2
[Fe(qamp)Cl$_2$]	9.29	7.95	1.34	86	5.9
[Fe(qlh)Cl$_2$ (H$_2$O)]H$_2$O	8.17	7.09	1.08	87	6.5
[Fe(hamp)Cl(H$_2$O)$_2$]	10.41	8.21	2.20	79	3.7
[Co(qlh)(OAc)]H$_2$O	4.76	4.31	0.45	91	9.6
[Co(hamp)(OAc)(H$_2$O) $_2$]H$_2$O	5.23	4.11	1.12	78	3.7
[Co(hatp)(H$_2$O)$_3$]H$_2$O	3.28	2.65	0.63	81	4.2
[Co(qamp)$_2$]H$_2$O	Negligible				

% C: percentage conversion, Cat: catechol, HQ: hydrquinone, % S: percentage selectivity

To acquire suitable reaction conditions for maximum transformation of phenol, [Cu(qamp)Cl] (the catalyst which showed highest activity during the screening studies) was studied in detail by varying the following reaction conditions: effect of the amount of catalyst, effect of temperature, effect of H$_2$O$_2$ concentration and effect of time.

7.1.3.2 Effect of reaction conditions on phenol hydroxylation of [Cu(qamp)Cl]

7.1.3.2.1. Effect of time

The appropriate reaction time is the main assurance for the perfect reaction. The catalytic hydroxylation of phenol, using H$_2$O$_2$ as oxidant was studied as a function of time. Too long a time appears to be unfavorable for phenol hydroxylation [26]. Table 7.1.2 shows that the fit reaction time is two hours. There

was no significant change in the conversion and selective formation of catechol beyond three hours [20].

Table 7.1.2: *The influence of reaction time*

Time (hr)	Phenol conversion (%)	Product distribution (%)	
		Catechol	Hydroquinone
1	11.66	11.25	0.41
2	16.10	14.48	1.62
3	16.19	14.52	1.67
4	16.90	14.65	2.25
5	17.31	14.51	2.80

reaction temperature 343 K; catalyst 1.5 mmol; phenol:H_2O_2 (molar ratio)=1:1; acetonitrile 10 mL

7.1.3.2.2. Effect of temperature

Table 7.1.3 presents the effect of reaction temperature on hydroxylation of phenol. Five different temperatures (303, 323, 333, 343 and 353 K) were considered, while keeping the other parameters same for the catalytic performance in 10 mL of CH_3CN. Below 343 K, conversion of phenol was very poor. At the same time above 343 K, decomposition of H_2O_2 gets accelerated which is not beneficial to phenol hydroxylation [24]. Thus, 343 K is the minimum required temperature to supply sufficient energy to reach the energy barrier of phenol transformation.

Table 7.1.3: *The influence of temperature*

Temperature K	Phenol conversion (%)	Product distribution (%)	
		Catechol	Hydroquinone
303	0	0	0
323	1.23	1.23	0
333	8.20	7.23	0.97
343	16.10	14.48	1.62
353	16.57	14.40	2.17

reaction time 2 h; catalyst 1.5 mmol; phenol:H_2O_2 (molar ratio)=1:1; acetonitrile 10 mL

7.1.3.2.3. Effect of amount of catalyst

The reaction when carried out in the absence of catalyst did not yield any products. The effect of amount of catalyst on the rate of reaction is illustrated in table 7.1.4. Five different amounts (1, 3, 5, 7 and 9 mg) of the catalyst [Cu(qamp)Cl] were used for the fixed amount of phenol (2.2 mL, 25 mmol) and oxidant (2.67 ml, 25 mmol) in 10 mL CH₃CN. An amount of 10 to 20 mmol gave comparable results in both cases with *ca.* 14–16 % phenol conversion in 2 h of reaction time at 343 K. Lowering the amount of catalyst resulted in the poor conversion [11]. Thus, 1.5 mmol of catalyst was considered to be sufficient enough to give good performance. The conversion to products is not monotonic in its catalyst dependence. As expected for a homogeneous catalytic process, the conversion increases linearly with catalyst concentration over most of the available range of the variable, but eventually it decreases. Bush *et al.* [27] made similar observations. The decrease in conversion at high catalyst concentrations could arise from competitive formation of catalytically inactive dimeric μ-oxo- and/or μ-peroxo- bridged metal species. Such metal species are not active in catalyzing this reaction.

Table 7.1.4: *The influence of the amount of catalyst*

Catalyst weight, g (mmol)	Phenol conversion (%)	Product distribution (%)	
		Catechol	Hydroquinone
0.18 (0.5)	3.30	3.27	0.03
0.36 (1.0)	14.38	13.54	0.84
0.54 (1.5)	16.10	14.48	1.62
0.72 (2.0)	14.36	12.90	1.46
0.90 (2.5)	13.01	10.32	2.69

reaction time 2 h; reaction temperature 343 K; phenol:H₂O₂ (molar ratio)=1:1; acetonitrile 10 mL

7.1.3.2.4. Effect of H₂O₂ concentration

Amount of H₂O₂ concentration has great influence on reaction rate. Table 7.1.5 presents the effect of H₂O₂ concentration on reaction rate. The influence of

oxidant on reaction was monitored using five different amounts of aqueous 30 % H_2O_2 viz. 15, 20, 25, 30 and 35 mmol for a fixed amount of phenol (2.2 mL, 25 mmol) and catalyst (1.5 mmol) in 10 mL CH_3CN. The lowest H_2O_2 concentration results in only ca. 3 % phenol hydroxylation. Other two concentrations give comparable results. This information suggests that H_2O_2/phenol ratio of 1:1 is ideal for the maximum conversion as well as maximum efficiency. Thus, the larger concentration of oxidant is not an essential condition to maximize phenol conversion.

Table 7.1.5: *The influence of H₂O₂ concentration*

Hydrogen peroxide (mmol)	Phenol conversion (%)	Product distribution (%)	
		Catechol	Hydroquinone
15	3.27	3.27	0
20	7.57	7.44	0.13
25	16.10	14.48	1.62
30	13.37	11.81	1.56
35	15.00	13.17	1.83

reaction time 3 h; reaction temperature 343 K; catalyst 1.5 mmol; acetonitrile 10 mL

7.1.4 Conclusions

The catalytic activity of the prepared complexes was studied in the liquid-phase hydroxylation of phenol using H_2O_2 as an oxidant. Catechol and hydroquinone are the sole products of the reaction. The copper(II), manganese(II), iron(III) and cobalt(II) were screened for their activity towards the hydroxylation of phenol. Detailed study of the catalytic activity of the complex, [Cu(qamp)Cl], that gave maximum conversion in the screening studies was carried out by changing the different parameters like concentration of the oxidant and catalyst, reaction time, reaction temperature and the nature of solvent. It was also found that there exists an optimum value for the amount of catalyst as well as temperature and time, after which conversion decreases or remains more or less the same.

7.2 SCHIFF BASE COMPLEXES AS CATALYST TOWARDS THE OXIDATION OF CYCLOHEXANE

7.2.1. Introduction

The natural oil and gas constituents contain a large amount of hydrocarbons. The functionalization of hydrocarbons has been identified as a key research strategy for the development of economical and sustainable global carbon management. Undoubtedly one of the most important functionalizations is selective oxidation. It is already known to oxidise aliphatic or cycloaliphatic compounds in the liquid phase using oxygen or hydrogen peroxide to corresponding alcohols and/or ketones. The chemical inertness of hydrocarbon makes the activation of C-H bonds really difficult, usually requiring drastic conditions, such as high temperature and pressure [28]. The selective oxidation of cyclohexane to cyclohexanone or cyclohexanol is of great industrial importance [29]. Over one billion tonnes of cyclohexanol and cyclohexanone are produced each year worldwide, which are mostly used in the manufacture of the polymers Nylon-6 and Nylon-6,6 [30, 31]. In the industrial process the cyclohexane is first oxidised to cyclohexanol and cyclohexanone using cobalt based homogeneous catalyst (4% conversion and 70-80 % selectivity towards cyclohexanol) and from the products, the adipic acid or ε-caprolactone is obtained [32]. High temperature and pressure (423–433 K and 0.9 MPa) are required to form cyclohexanol and cyclohexanone [33]. The subsequent oxidation to adipic acid uses nitric acid as oxidant which is a very unfriendly reagent [34]. As early as 1876, Fenton has found that iron(II) salts in an acidic aqueous solution using hydrogen peroxide as oxidant is capable of oxidising alkanes. Many mechanisms have been proposed for this reaction, mostly those involving OH· or OOH· and other involves reactive high valent metal ion species [35-37].

Cyclohexane oxidation is an interesting reaction in the past decades. In 1993, Schuchardt *et al.* published a review article entitled "Why is it interesting to study cyclohexane oxidation" [38]. In the review they presented new ideas on how

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to improve the industrial cyclohexane oxidation reaction. In continuation of the previous review in 2001, they published another review article on "the cyclohexane oxidation continues to be a challenge" [30]. The review point towards the development of new catalysts to oxidise cyclohexane under mild conditions. The usage of metal complexes as catalyst for activation of hydrocarbons was initially developed with metalloporphyrins and later on applied on Schiff base complexes [39-42]. Groves *et al.* [43] did pioneering work towards utilisation of metalloporphyrins as the catalyst for cyclohexane oxidation. Cyclohexane oxidation using Schiff base complexes is an interesting area of research nowadays [44-47].

In the present study we have carried out the oxidation of cyclohexane using the oxidant hydrogen peroxide. The catalysts used are copper(II), iron(III) and manganese(II) complexes derived from the Schiff bases qamp, hatp, hamp and qlh.

7.2.2. Experimental

7.2.2.1 Materials and methods

The details of the synthesis and characterization of the complexes are outlined in the previous chapters. The products obtained are analyzed in a Chemito 8510 gas chromatograph with carbowax column. The adipic acid was determined by titration with sodium hydroxide. Materials used in the catalytic activity studies are listed in chapter II.

7.2.2.2 Catalytic activity study: oxidation of cyclohexane

The cyclohexane oxidation was carried out by the published procedure [48]. The reactions were carried out in acetonitrile as solvent, using hydrogen peroxide as the oxidant, and the copper(II), iron(III) or manganese(II) complexes as the catalysts. In a typical reaction, an aqueous solution of 30% H_2O_2 (1.06 mL, 10 mmol) and cyclohexane (1.08 mL, 10 mmol) were mixed in 5 mL of acetonitrile and the reaction mixture was heated at 343 K with continuous stirring in an oil

bath. The complex (0.010 mmol) was added to the reaction mixture and the reaction was considered to be started at this time. During the reaction, the products were analyzed using a gas chromatograph after specific interval of time by withdrawing small aliquot. Assignments of products were made by comparison with authentic samples. The effects of various parameters such as concentration of oxidant and catalyst, temperature and time of the reaction were studied in order to see their effect on the reaction product pattern.

7.2.3. Results and discussion

Oxidation of cyclohexane catalyzed by Schiff base complexes using H_2O_2 as the oxidant was studied in CH_3CN. To choose the best solvent, the oxidation reactions were carried out in common solvents under the same conditions. The results indicate that acetonitrile provided the best oxidation medium for higher substrate conversion and selectivity of cyclohexanol. It is interesting to note that acetonitrile was successfully used for many oxidation reactions [49-52]. Furthermore, the volatility of acetonitrile is lower than that of other solvents under open-wide system, so the utilization factor of acetonitrile is more here than that of other solvents. Therefore a lower environmental contamination is expected in such cases and acetonitrile is a suitable solvent for the oxidation of cyclohexane. The products obtained for the oxidation reaction are cyclohexanol, cyclohexanone and adipic acid as shown by scheme 7.2.1.
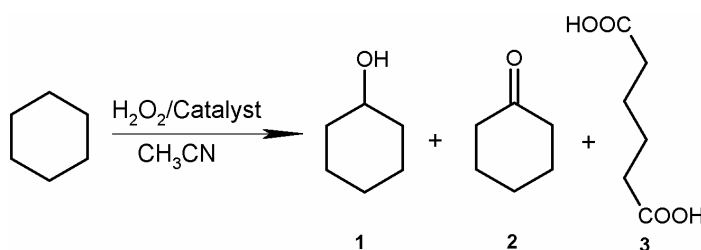
Scheme 7.2.1: *Oxidation of cyclohexane to cyclohexanol (1), cyclohexanone (2) and adipic acid (3).*

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7.2.3.1 Catalytic activity of the metal complexes towards cyclohexane oxidation: Screening studies

The catalytic activities of the prepared Mn(II), Fe(III) and Cu(II) complexes are screened for their activity towards cyclohexane oxidation reaction. The results of these studies are given in table 7.2.1. The reaction conditions employed are given in section 7.2.2.2. Almost all the complexes show good activity. The major product of the reaction was found to be cyclohexanol. Other products are cyclohexanone and adipic acid. Adipic acid formed was determined titrimetrically at the end of the reaction [48]. These products are of special interest in the nylon manufacture as well as the building blocks for a variety of commercially useful products. The copper(II) and iron(III) complexes are found to be more active compared to manganese(II) complexes. [Cu(qamp)Cl] and [Fe(qlh)Cl$_2$H$_2$O]H$_2$O are found to be the most active catalysts with ~30 % conversion. Both of the catalysts show good selectivity towards cyclohexanol (around 70 %). Control reactions were carried out in the absence of the catalysts and no oxidation products were observed.

Table 7.2.1: *Catalytic activity of the metal complexes towards cyclohexane oxidation*

Catalyst	% C	% Products			% S (C-nol)
		C-nol	C-one	AA	
[Cu(qamp)Cl]	30.94	22.17	6.56	2.21	72
[Cu(qlh)Cl]. 2H$_2$O	27.29	16.81	8.58	1.90	62
[Cu(hamp)(H$_2$O)]	15.00	12.05	1.72	1.23	80
[Cu(hatp)Cl]	11.36	6.92	3.43	1.11	61
[Mn(qamp)(OAc)].H$_2$O	7.12	3.02	2.11	1.89	42
[Mn(qlh)(OAc)]. 2H$_2$O	7.42	3.21	2.89	1.32	43
[Mn(hamp)(H$_2$O)].H$_2$O	3.28	1.80	1.03	0.45	55
[Mn(hatp)(OAc)(H$_2$O)$_2$]	4.88	2.10	2.50	0.28	43
[Fe(qamp)Cl$_2$]	18.37	10.70	6.46	1.21	58
[Fe(qlh)Cl$_2$(H$_2$O)]. H$_2$O	30.12	20.68	6.99	2.45	69
[Fe(hamp)Cl(H$_2$O)$_2$]	29.99	16.33	11.99	1.67	54

% C: percentage conversion, C-nol: cyclohexanol, C-one: cyclohexanone, AA: adipic acid, %

S: percentage selectivity

In order to acquire suitable reaction conditions for maximum transformation of cyclohexane, [Cu(qamp)Cl] (the catalyst which showed highest activity during the screening studies) was studied in detail by varying the following reaction conditions: effect of the amount of catalyst, effect of temperature, effect of H_2O_2 concentration and effect of time.

7.2.3.2 Effect of reaction conditions on cyclohexane oxidation of [Cu(qamp)Cl]

The catalytic activity was investigated using various reaction conditions of temperature, amount of catalyst, time, oxidant to substrate ratio etc. in order to find out the optimum conditions for the oxidation reaction.

7.2.3.2.1. Effect of variation of time

The dependence of activity of [Cu(qamp)Cl] in phenol hydroxylation on the reaction time is displayed in Table 7.2.2. It is observed that cyclohexane oxidation was affected by reaction time and the conversion increases with time [43]. The cyclohexane conversion and the selectivity towards cyclohexanol were found to be enhanced with the increase of the contact time, and the reaction acquires steady state after 3 h.

Table 7.2.2: *The influence of reaction time*

Time (hrs)	% C	% C-one	% C-nol	% AA
1	16.14	2.70	12.23	1.21
2	27.53	5.90	20.18	1.45
3	30.94	6.56	22.17	2.21
4	32.31	6.55	23.54	2.22
5	32.55	6.97	23.05	2.53

catalyst: 0.01 mmol, H_2O_2: 1.06 mL, cyclohexane: 1.08 mL, acetonitrile: 5 mL, temperature: 343 K.

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7.2.3.2.2. Effect of temperature

Table 7.2.3 presents the effect of reaction temperature on oxidation of cyclohexane. Four different temperatures (303, 323, 343 and 363 K) were considered, while keeping other parameters same as mentioned above. The catalyst employed is found to be active even at room temperature. But the conversion rate was very poor. As temperature increased, the conversion was found to increases [54]. The optimum temperature for carrying out the reaction is 343 K. There is a slight decrease in conversion above 343 K, which may be due to the accelerated decomposition of hydrogen peroxide [55]. So, 343 K is selected as the optimum temperature for carrying out cyclohexane oxidation reaction.

Table 7.2.3: *The influence of reaction temperature.*

Temperature (K)	% C	% C-one	% C-nol	% AA
303	7.82	1.87	4.33	1.62
323	20.15	2.93	15.18	2.04
343	30.94	6.56	22.17	2.21
363	28.97	4.00	22.73	2.24

catalyst: 0.01 mmol, H_2O_2: 1.06 mL, cyclohexane: 1.08 mL, acetonitrile: 5 mL, time: 3 h

7.2.3.2.3. Effect of amount of catalyst

The reaction when carried out in the absence of catalyst did not yield any products. The effect of amount of catalyst on the rate of reaction is illustrated in table 7.2.4. Five different amounts of the catalyst [Cu(qamp)Cl] were used without changing the other reaction parameters. On increasing the catalyst amount, the degree of conversion increased for all complexes as expected [56]. Thus, 0.01 mmol of catalyst was considered to be sufficient enough to give good performance. It is observed that at higher catalyst concentration there is a slight decrease in % conversion. Koda *et al.* [57] reported similar observations in the aerobic oxidation of cyclohexane catalyzed by {5,10,15,20-tetrabis (pentafluorophenyl) porphyrinato}

iron(III) chloride. The decrease in conversion and selectivity may be due to the formation of metal-oxo species [27, 58].

Table 7.2.4: *The influence of the amount of catalyst.*

Catalyst weight, mg (mmol)	% C	% C-one	% C-nol	% AA
0.45 (0.001)	4.57	1.8	2.45	0.32
1.8 (0.005)	13.77	2.9	9.43	1.44
3.6 (0.01)	30.94	4.56	20.17	2.21
5.4 (0.015)	32.11	6.57	21.65	3.89
7.2 (0.02)	31.56	7.95	19.89	3.72

H_2O_2: 1.06 mL, cyclohexane: 1.08 mL, acetonitrile: 5 mL, temperature: 343 K, time: 3 h

7.2.3.2.4. Effect of H_2O_2 concentration

The effect of hydrogen peroxide concentration on the rate of reaction was studied by keeping the other parameters constant. These studies indicate that the conversion increases with increase in the volume of hydrogen peroxide. But the higher concentration of hydrogen peroxide will lead to the higher yield of adipic acid, which is formed as an over oxidation product [59].

Table 7.2.5: *The influence of H_2O_2 concentration.*

H_2O_2 (mmol)	% C	% C-one	% C-nol	% AA
5	4.98	1.02	3.28	0.68
10	30.94	6.56	22.17	2.21
15	31.50	6.87	22.09	2.54
20	33.00	6.98	23.29	2.73
25	34.28	6.41	23.70	4.17

catalyst: 15 mmol, time: 3 h, cyclohexane: 1.08 mL, acetonitrile: 5 mL, temperature: 343 K

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7.2.4 Conclusions

The catalytic activity of the prepared complexes was studied in the cyclohexane oxidation using H_2O_2 as an oxidant. Cyclohexanol, cyclohexanone and adipic acxid are the products. The selectivity was found to be greater for cyclohexanol. Detailed study of the catalytic activity of the complex, [Cu(qamp)Cl], that gave maximum conversion in the screening studies was carried out by changing the different parameters like reaction time, reaction temperature, concentration of the oxidant and catalyst. It was also found that there exists an optimum value for the amount of catalyst as well as temperature and time, after which conversion decreases. Increase in the amount of H_2O_2 has a positive effect on the reaction.

7.3 COPPER(II) SCHIFF BASE COMPLEXES AS CATALYST TOWARDS THE OXIDATION OF BENZYL ALCOHOL

7.3.1 Introduction

The oxidation of organic substrates is an important reaction in organic synthesis. Among them oxidation of benzyl alcohol to benzaldehyde is an industrially important reaction. Chlorine free benzaldehyde is a versatile chemical intermediate widely used in the manufacture of pharmaceuticals, perfume and flavouring chemicals [60]. Several research groups have developed different catalytic methods for oxidation of benzyl alcohol to benzaldehyde. Among the various methods, transition metal Schiff base complex catalysed oxidation is worth mentioning [61]. The oxidation of methoxy substituted benzyl alcohol especially veratryl alcohol which is a typical model compound for non lignin monomer and the enzyme lignin peroxidase has been studied [62-64]. Ruthenium(III) complexes of the monobasic tridentate ligand, formed by the condensation of o-phenylenediamine or ethylenediamine with salicylaldehyde or o-hydroxyacetophenone is found to catalyse the benzyl alcohol oxidation [65]. Solvent-free reactions are of general interest because of their potential in

combinational chemistry, simple processes, easy work-up, low cost and reduction in noxious waste materials [66]. However, only a limited number of such useful oxidation procedures have been reported [67-69].

Considering the important role of copper in enzymatic oxidations, it is hardly surprising that copper is frequently used in oxidation reactions in everyday laboratory practice. The Wacker Process, which uses a catalyst containing palladium and copper chlorides, is used for converting alkenes into alcohols and is a good example of an industrially important large scale oxidation reaction [70]. This chapter discusses the oxidation of benzyl alcohol to benzaldehyde, using small amount of copper(II) complexes in combination with hydrogen peroxide.

7.3.2. Experimental

7.3.2.1. Materials

The details of the synthesis and characterization of the complexes are outlined in the previous chapters. The products obtained are analysed in a Chemito 8510 gas chromatograph with OV-17 column. Materials used in the catalytic activity studies are listed in chapter II.

7.3.2.2. Catalytic activity study

The catalytic activity study towards the oxidation of benzyl alcohol was carried out in a 50 mL two necked RB flask fitted with a water cooled condenser. In a typical reaction, benzyl alcohol (3.11 mL, 30 mmol) and 30% H_2O_2 (4.8 mL, 45 mmol) were mixed and the reaction mixture was heated in an oil bath with continuous stirring at 343 K. An appropriate amount of catalyst (30 mmol) was added to the hot mixture and the reaction was continued. The progress of the reaction was determined by analyzing the reaction mixture using a gas chromatograph by withdrawing small aliquots of the reaction mixture at specific interval of time.

7.3.3. Results and discussion

Solvent free catalytic oxidation of benzyl alcohol was studied using hydrogen peroxide as the oxidant and copper(II) complexes as the catalysts. Generally benzyl alcohol oxidation gives benzaldehyde, benzoic acid and benzyl benzoate. We haven't detected any benzyl benzoate. The reaction was highly selective towards benzaldehyde. Slight amount of benzoic acid is also formed.

7.3.3.1 Catalytic activity of the metal complexes towards benzyl alcohol oxidation: Screening studies

The catalytic activities of the prepared Cu(II) complexes are screened for their activity towards benzyl alcohol oxidation reaction. The results of these studies are given in table 7.3.1. The reaction conditions employed are: time of 4 hours, temperature 343 K, substrate:catalyst:oxidant is 2:2:3. All the complexes show good activity. The major product of the reaction was found to be benzaldehyde. [Cu(qlh)Cl]2H$_2$O is found to be the most active catalysts with ~38 % conversion and very good selectivity towards benzaldehyde. In the absence of catalyst, no significant amount of benzaldehyde was produced indicating that hydrogen peroxide alone is unable to oxidise benzyl alcohol to benzaldehyde. In the endeavor to a greener benzyl alcohol oxidation the solvent-free reaction is more exciting [71]. In some cases, solvent-free reactions proceed efficiently [72, 73].

Table 7.3.1: *Catalytic activity of the metal complexes towards cyclohexane oxidation*

Catalyst	% C	% Products			% S (BAl)
		BAl	BAc	BB	
[Cu(qamp)Cl]	35.75	32.30	3.45	nd	90
[Cu(qlh)Cl]2H$_2$O	38.50	36.88	1.62	nd	96
[Cu(hamp)(H$_2$O)]	27.89	24.02	3.87	nd	86
[Cu(hatp)Cl]	13.66	12.45	1.21	nd	91

% C: percentage conversion, Bal: benzaldehyde, BAc: benzoic acid, BB: benzyl benzoate, % S: percentage selectivity

7.3.3.2 Effect of reaction conditions on benzyl alcohol oxidation of [Cu(qlh)Cl]2H$_2$O

The catalytic activity was investigated using various reaction conditions of temperature, amount of catalyst, time, oxidant to substrate ratio etc. in order to find out the optimum conditions for the oxidation reaction.

7.3.3.2.1. Effect of variation of time

The time dependence of catalytic solvent free oxidation of benzyl alcohol was studied by performing the reaction of benzyl alcohol (3.11 mL, 30 mmol) with 30% H$_2$O$_2$ (4.8 mL, 45 mmol) in the presence of 30 mmol of catalyst at 343 K with constant stirring. The percentage of conversion was monitored at different reaction times. The conversion was found to increase with time. It was seen that 38.50% conversion was observed at 4 h. When the reaction was allowed to continue for 12 h, 52 % conversion was observed.

Table 7.3.2: *The influence of reaction time*

Time (hrs)	% C	% BAl	% BAc
1	16.53	15.78	0.75
2	21.10	20.02	1.08
3	27.96	26.53	1.43
4	38.50	36.88	1.62
12	52.00	45.20	6.80

catalyst: 30 mmol, H$_2$O$_2$: 4.8 mL, benzyl alcohol: 3.11 mL, temperature: 343 K.

7.3.3.2.2. Effect of temperature

The effect of temperature on the oxidation of benzyl alcohol using [Cu(qlh)Cl].2H$_2$O as catalyst was investigated at four different temperatures viz. 303, 323, 343 and 363 K, keeping the other parameters fixed: namely benzyl alcohol (3.11 mL, 30 mmol), 30% H$_2$O$_2$ (4.80 mL, 45 mmol), catalyst (30 mmol)

and reaction time (4 h). The results are shown in table 7.3.3, which reveals that 5.76, 17.19, 38.50 and 41.86 % conversion were found corresponding to 303, 323, 343 and 363 K respectively. On increasing the temperature from 343 to 363 K, only very little improvement in conversion was observed, so that a temperature of 343 K was considered to be optimum [74].

Table 7.3.3: *The influence of reaction temperature.*

Temperature (K)	% C	% BAl	% BAc
303	5.76	5.76	0
323	17.19	16.81	0.38
343	38.50	36.88	1.62
363	38.86	37.05	1.81

catalyst: 30 mmol, H_2O_2: 4.8 mL, benzyl alcohol: 3.11 mL, time: 4 hrs.

7.3.3.2.3. Effect of amount of catalyst

The amount of catalyst has a significant effect on the oxidation of benzyl alcohol. Four different amounts of catalyst viz., 10, 20, 30 and 40 mmol were used, keeping all the other reaction parameters fixed: namely benzyl alcohol (3.11 mL, 30 mmol), 30% H_2O_2 (4.80 mL, 45 mmol), temperature 343 K and reaction time (4 h). The results obtained are given in table 7.3.4, indicating 17.68, 31.97, 38.50 and 40.10 % conversion corresponding to 10, 20, 30 and 40 mmol catalyst respectively.

Table 7.3.4: *The influence of the amount of catalyst*

Catalyst weight (mmol)	% C	% BAl	% BAc
10	17.68	17.27	0.41
20	31.97	30.64	1.33
30	38.50	36.88	1.62
40	40.10	37.89	2.21

temperature: 343 K, H_2O_2: 4.8 mL, benzyl alcohol: 3.11 mL, time: 4 hrs.

7.3.3.2.4. Effect of H₂O₂ concentration

To determine the effect of H_2O_2 on the oxidation of benzyl alcohol to benzaldehyde, we have used four different benzyl alcohol: H_2O_2 molar ratios (2:1, 1:1, 1:1.5 and 1:2) keeping other parameter fixed: namely benzyl alcohol (3.11 mL, 30 mmol), catalyst (30 mmol), temperature 343 K and reaction time (4 h). The results are shown in table 7.3.5. A benzyl alcohol to H_2O_2 molar ratio of 2:1 and 1:1 resulted in 19.53 and 26.44 % conversion, and when benzyl alcohol to H_2O_2 molar ratio was changed to 1:1.5, conversion increased to be nearly 38.50%, keeping all other conditions similar. However, conversion was found to be almost the same at 39.19% when the benzyl alcohol to H_2O_2 molar ratio was further changed to 1:2.

Table 7.3.5: *The influence of H₂O₂ concentration.*

H₂O₂ (ml)	% C	% BAl	% BAc
1.60	19.53	19.01	0.52
3.20	26.44	25.51	0.93
4.80	38.50	36.88	1.62
6.40	39.19	37.42	1.77

catalyst: 30 mmol, benzyl alcohol: 3.11 mL, time: 4 hrs, temperature: 343 K.

7.3.4 Conclusions

The catalytic activity of the prepared complexes was studied in the benzyl alcohol oxidation using H_2O_2 as an oxidant. The products obtained are benzaldehyde and benzoic acid. The selectivity was found to be greater for benzaldehyde. The copper(II) complexes of hatp, hamp, qamp and qlh were screened for their activity towards the oxidation. Detailed study of the catalytic activity of the complex, $[Cu(qlh)Cl]2H_2O$, that gave maximum conversion in the screening studies, was carried out by changing the different parameters like catalyst amount, reaction time, reaction temperature and amount of oxidant. At optimum

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conditions [Cu(qlh)Cl]2H$_2$O gives very good selectivity (96 %) towards benzaldehyde.

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Conclusions and future prospects

The attempts to design new tridentate Schiff base complexes and their utilization as oxidation catalysts are the main goals of this work. Details regarding the synthesis, spectral characterization and catalytic applications of some new transition metal complexes of the Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde or quinoxaline-2-carboxaldehyde are presented in this thesis.

Schiff bases play a key role in the development of coordination chemistry. Schiff bases have different denticity and basicity, which will influence the stability and properties of the complex. The Schiff base complexes may be synthesized by template method, rearrangement of heterocycles in the presence of metal ions or by direct ligand synthesis followed by complexation. They find application as catalysts, medicines, biocidal agents, fluorescent materials, dyes and corrosion inhibitors. They are found to catalyse a large number of organic transformations and play an important role in asymmetric catalysis, as chiral Schiff bases are able to transmit chiral information to produce non racemic products. Quinoxaline based Schiff bases are versatile chelating ligands due to the presence of two heterocyclic nitrogen atoms in the ring. This chapter presents an overview of the chemistry of Schiff bases and their complexes and the application of Schiff base complexes as catalysts especially with regard to phenol hydroxylation, cyclohexane oxidation and benzyl alcohol oxidation. The scope of the present work is also given in chapter 1. Details regarding the general reagents, experimental techniques employed and the synthesis of quinoxaline-2-carboxaldehyde and 3-hydroxyquinoxaline-2-carboxaldehyde are presented in chapter 2.

Chapter 3 deals with the synthesis and characterization of the Schiff base quinoxaline-2-carboxalidine-2-amino-5-methylphenol (qamp) and its manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes. The complexes have the general empirical formula [M(qamp)$_2$] for the cobalt(II),

nickel(II) and Zn(II) complexes, [Fe(qamp)Cl$_2$] for the iron complex, [Mn(qamp)(OAc)] for the manganese complex and [Cu(qamp)Cl] for the copper complex. All the complexes are stable and are non electrolytes in DMF. On comparing the infrared spectrum of the ligand with that of the complexes, a shift in stretching frequencies of azomethine (C=N), quinoxaline (C=N) and phenolic (C-O) is observed supporting the tridentate nature of the ligand. The electronic spectral and magnetic moment studies of the complexes reveal an octahedral geometry for the Co(II) and Ni(II) complex, a tetrahedral geometry for Mn(II) complex, square pyramidal geometry for Fe(III) complex and square planar geometry for Cu(II) complex. Crystal structure determination of the cobalt(II) and nickel(II) complexes are carried out. Crystal structures of [Co(qamp)$_2$].H$_2$O and [Ni(qamp)$_2$].H$_2$O confirm the octahedral geometry of the complexes. Each of the crystals is a racemic mixture of two crystallographically independent enantiomers of the complex. The molecules exhibit a two dimensional chain structure parallel to [010] plane, formed by O–H…N and O–H…O intermolecular hydrogen bonding and π–π stacking interaction.

The synthesis and characterization of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base, quinoxaline−2−carboxalidine−L−histidine (qlh) are presented in chapter 4. This Schiff base cannot be isolated and the syntheses of the complexes were carried out by template method in which aldehyde, amine and metal compound are refluxed in 1:1:1 molar ratio. The analytical data show that the complexes have the general empirical formula [M(qlh)(OAc)] for the manganese(II), cobalt(II) and zinc(II) complexes and [M(qlh)Cl] for the copper(II) complex, [M(qlh)(OAc)(H$_2$O)] for the nickel(II) complex and [M(qlh)Cl$_2$(H$_2$O)] for the iron(III) complex. All the complexes are found to be stable and conductivity studies show that the complexes are non electrolytes in DMF. FTIR spectra indicate that bands due to histidine and quinoxaline-2-carboxaldehyde are present in complexes, while C=O stretching was found to be absent, which indicates the formation of the Schiff base complex. The ^{1}H NMR spectrum of the zinc(II) complex also confirms the formation of the

Schiff base, in which the azomethine CH resonates at 9.45 ppm. All the results of our study clearly demonstrates that the ligand is monobasic tridentate ligand. The physicochemical and spectral data reveal an octahedral geometry for the Fe(III) and Ni(II) complexes. The manganese(II), cobalt(II) and zinc(II) complexes are found to be tetrahedral; while the copper(II) complex has a square planar geometry.

Chapter 5 is a discussion on the synthesis and characterization of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base 3-{(*E*)-[(2-hydroxy-4-methylphenyl)imino]methyl} quinoxalin-2(1*H*)-one (hamp). The ligand exhibits tautomerism in solution. The analytical data reveal that all the complexes are formed in the metal:ligand ratio 1:1. All the complexes are stable and non electrolytes in DMF. The proton NMR spectrum of hamp indicate that the ligand exists as the keto tautomer. NMR spectrum of the zinc(II) complex suggests the enolisation of hamp on complexation. IR spectral studies reveal that the ligand acts as a tridentate ONO donor and it can coordinate either in keto form or in enol form. In all the complexes, there is a shift in azomethine stretching frequency towards lower wavenumbers suggesting the coordination of imine nitrogen. FTIR spectra further reveal that the Schiff base in the cobalt(II) complex exists in the keto form while that in all other complexes exists in the enol form. The physicochemical and spectral data suggest a tetrahedral geometry for the Mn(II), Ni(II), Cu(II) and Zn(II) complexes. The iron(III) and cobalt(II) complexes are octahedral in geometry.

A novel benzothiazolidine derivative, 3-(2,3-dihydro-1,3-benzothiazol-2-yl)quinoxalin-2(1*H*)-one (abbreviated as btq) and the Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base (abbreviated as hatp), which is formed by the rearrangement of btq, has been synthesized and characterized. The formation of ring closed benzothiazoline compound will get rearranged to form the form the tridentate ONS donor Schiff base in the presence of metal ions. All the complexes are stable and non electrolytes in DMF. The Schiff base may get coordinated either in the keto form or in the enol form. The ^{1}H NMR spectra of the compound btq and

that of [Zn(hatp)(OAc)] complex are taken in DMSO-d_6. The thiazolidine CH of btq exhibits a doublet at 7.16 ppm which indicates the ring closure. In the NMR spectrum of the diamagnetic zinc(II) complex, the azomethine proton appears at 8.93 ppm as a singlet. The FTIR spectra of the hatp complexes suggest that the Schiff base exists in the enol form in the cobalt(II) and nickel(II) complexes, which is evidenced by the disappearance of band due to (C=O) stretching. But it exists in the keto form in the manganese(II) copper(II) and zinc(II) complexes, these complexes exhibit strong ν(C=O) bands at 1650, 1676 and 1657 cm^{-1} respectively. On the basis of physicochemical and spectroscopic techniques, the copper(II) complex is found to be square planar and the zinc(II) complex is tetrahedral. The manganese(II), cobalt(II) and nickel(II) complexes are octahedral in geometry. The details of these results are presented in chapter 6.

Chapter 7 deals with the studies on the use of the Schiff base complexes as catalysts in some oxidation reactions and is divided into three sections. Section 7.1 deals with studies on the liquid phase hydroxylation of phenol. The section 7.2 presents the studies on the oxidation of cyclohexane and section 7.3 deals with the studies on catalytic activity of the copper(II) Schiff base complexes in the oxidation of benzyl alcohol.

Catalytic activity of the prepared complexes in the liquid-phase hydroxylation of phenol was studied using H_2O_2 as an oxidant. Catechol and hydroquinone are the sole products of the reaction. The copper(II), manganese(II), iron(III) and cobalt(II) complexes were screened for their activity towards the hydroxylation of phenol. The major product of the reaction was found to be catechol in all cases. The cobalt(II) complex of qamp is found to be inactive, which may be due to the coordinative saturation. In [Co(qamp)$_2$].H_2O two molecules of the Schiff bases are tightly bound the metal ion, so that it is unable to bind with the oxygen to form the intermediate. The complex, [Cu(qamp)Cl], was found to be the most active catalyst with ~16 % conversion. Detailed study of the catalytic activity of the complex, [Cu(qamp)Cl], that gave maximum conversion in the screening

studies, was carried out by changing the different parameters like the concentration of catalyst and oxidant, reaction time and reaction temperature. It was also found that there exists an optimum value for the amount of catalyst as well as temperature and time, after which conversion decreases or remains more or less the same. It is observed that the order of activity of the metal ions follows the order; copper(II)>manganese(II)~iron(III)>cobalt(II). The catalytic activity of the complexes of hatp is found to be lower compared to that of the other Schiff base complexes.

The catalytic activity of the prepared complexes was studied in the cyclohexane oxidation using H_2O_2 as an oxidant. Cyclohexanol, cyclohexanone and adipic acxid are the products. The selectivity was found to be greater for cyclohexanol. The copper(II), manganese(II) and iron(III) complexes were screened for their activity towards the oxidation. Detailed study of the catalytic activity of the complex, [Cu(qamp)Cl], that gave maximum conversion in the screening studies, was carried out by changing the different parameters like the concentration of catalyst and oxidant, reaction time and reaction temperature.

The catalytic activity of the prepared complexes was studied in the benzyl alcohol oxidation using H_2O_2 as an oxidant. The products obtained are benzaldehyde and benzoic acid. The selectivity was found to be greater for benzaldehyde. The copper(II) complexes were screened for their activity towards the oxidation. Detailed study of the catalytic activity of the complex, [Cu(qlh)Cl]2H_2O, that gave maximum conversion in the screening studies, was carried out by changing the different parameters like the concentration of catalyst and oxidant, reaction time and reaction temperature. Complexes of qlh and qamp, which are ONO donor ligands, show highest activity towards benzyl alcohol oxidation.

FUTURE PROSPECTS

Transition metal complexes derived from quinoxaline Schiff bases and their catalytic activity studies are the central topic of research described in this thesis.

The major goal of coordination chemists nowadays is to develop new complexes that have potential applications. The reports on transition metal complexes derived from quinoxalines are scanty. Since quinoxaline moiety contains two heterocyclic nitrogen atoms, it is possible to prepare coordination polymers. The ligand is easily modifiable in order to control the geometries and nuclearities of the complexes formed. The utilization of quinoxaline Schiff base complexes in medicine, catalysis, photonics and electronics are not fully explored.

This thesis also deals with the catalytic activity studies of transition metal complexes derived from quinoxalines towards some oxidation reactions. In the current study the exact nature of the catalytically active species is not studied. Detailed kinetic studies are necessary for the better understanding and future development of the efficient catalysts. Kinetic studies would expose several aspects of these reactions, such as rate constants and order of the reaction, pH and solvent dependency, and the active species responsible for catalytic activity. Furthermore, a broader range of substrates should be studied to investigate and correlate the selectivity and activity correctly to the structures of the catalysts. From the combined catalytic, mechanistic and kinetic studies of metal complexes using systematically varied structures of the ligands, certainly more powerful catalysts are likely to be developed.

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List of publications

1 Synthesis, characterization and the crystal structure of a new Cobalt(II) Schiff base complex with quinoxaline-2-carboxalidine-2-Amino-5-methylphenol; Manju Sebastian, V. Arun, P.P. Robinson, P. Leeju, Digna Varghese, G. Varsha and K.K.M. Yusuff; *Journal of Coordination Chemistry* 63 (2010) 307-314.

2 Metal-induced rearrangement of benzothiazoline ring: Synthesis and characterization of transition metal complexes of an ONS-donor Schiff base; Manju Sebastian, V. Arun, P. P. Robinson, K.K.M. Yusuff, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* (Accepted)

3 Template synthesis and spectral characterization of some Schiff base complexes derived from quinoxaline-2-carboxaldehyde and L-histidine; Manju Sebastian, V. Arun, P.P. Robinson, P. Leeju, G. Varsha, Digna Varghese and K.K.M. Yusuff; *Journal of Coordination Chemistry* (Communicated)

4 Synthesis, structural characterization and catalytic activity study of Mn(II), Fe(III), Ni(II), Cu(II) and Zn(II) complexes of quinoxaline–2–carboxalidine–2–amino–5–methylphenol: Crystal structure of the nickel(II) complex, Manju Sebastian, V. Arun, P. P. Robinson, Annu Anna Varghese, Rani Abraham, E. Suresh, K.K.M. Yusuff ; *Polyhedron* (Communicated)