

**SYNTHESIS AND CHARACTERIZATION OF SELECTED COPPER (II) MACROCYCLIC
COMPLEXES**

A Dissertation

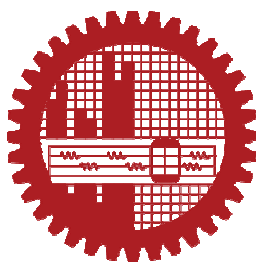
Submitted to the Partial Fulfillment of the Requirement for the Degree of
Master of Science (M. Sc) in Chemistry.

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JANUARY, 2017

CERTIFICATE

This is to certify that the research work embodied in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any university or institution.

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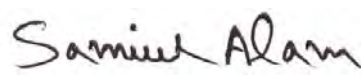
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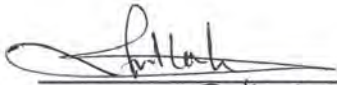
Certification of Thesis
A thesis on
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Roll No.: 1014032703 F, Session: October-2014

has been accepted as satisfactory in partial fulfillment of the requirements for the degree of Master of Science (M. Sc) in Chemistry and certify that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on January 24, 2017.

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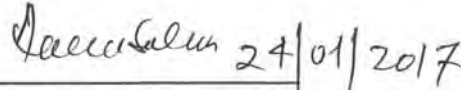
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**Dedicated
To My Beloved
Parents**

ACKNOWLEDGEMENTS

First I would like to express my heartfelt gratitude to and appreciation for my supervisor Prof. Dr. Md. Rafique Ullah for his consistent follow up and as well as for his valuable suggestion ,guidance and encouragement in all aspects needed during the process of my thesis work.

I also feel a great pleasure to convey profound veneration and deep appreciation to my respected teachers, Professor Dr. Nazrul Islam, Professor Dr. Md. Abdur Rashid, Professor Dr. Shakila Rahman, Assistant Professor Dr. Ayesha Sharmin and all other teachers of the Department of Chemistry, BUET for their cordial co-operation and guidance.

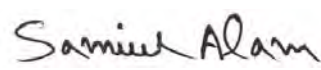
I am very grateful to CASR for giving me financial support of this research work.

I express my thanks to elder brother Mohammad Jakir Hossain and Md. Jahangir Alam who helped me a lot during my research work.

I am highly obliged to Dr. Md. Zakir Sultan, Center for Advanced Research in Sciences, University of Dhaka for elemental analysis.

I am very thankful to department of Chemistry of Buet for the chemicals and equipment that have been provided with during this thesis and also to staff members of the department for their warm approach.

Finally, thanks to my all of friends for their support in sharing ideas and for their continuous encouragement.



Md. Samiul Alam

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LIST OF ABBREVIATION

AAS	Atomic Absorption Spectroscopy
BM	Bohr Magnetron
DMF	Dimethyl Formamide
DMSO	Dimethyl Sulphoxide ($(\text{CH}_3)_2\text{S}=\text{O}$)
EtOH	Ethyl Alcohol
FTIR	Fourier Transform Infra-Red
UV-Vis	Ultra violet-visible
Sc	Specific conductance
Λ_M	Molar conductance
χ_g	Gram magnetic susceptibility
χ_{mol}	Molar magnetic susceptibility
μ	Magnetic moment
μS	Micro Semen
M.pt	melting point
$\text{Scm}^2\text{mol}^{-1}$	Semen centimeter square per mol
μ_{eff}	Effective magnetic moment

SYNTHESIS AND CHARACTERIZATION OF SELECTED COPPER (II) MACROCYCLIC COMPLEXES

ABSTRACT

In this study the template synthesis and characterization of metal ion complexes of Cu (II) are presented. New 16-membered tetraaza macrocyclic complexes of the type $[M(C_8H_{16}N_8O_4)(ClO_4)_2]$, $[M(C_{10}H_{20}N_8O_4)(ClO_4)_2]$, $[M(C_{20}H_{24}N_8O_4)(ClO_4)_2]$, where, M is Cu (II) were synthesized by the template condensation of formaldehyde, acetaldehyde, benzaldehyde with the corresponding hydrated metal salts of $CuCl_2 \cdot 2H_2O$ in aqueous medium. These complexes were distinctly colored and stable to atmospheric conditions. These complexes were characterized by UV-Vis, IR as well as by measurements of their respective molar conductance and magnetic susceptibility. The low molar conductance values obtained in DMSO for these complexes indicated their non electrolyte nature. Furthermore, from their magnetic susceptibility values, UV-Vis spectra and FTIR spectra, these newly prepared complexes were expected to have octahedral geometry, with the respective Cu (II) ion occupying the center of an octahedron.

The complexes $[Cu(C_8H_{16}N_8O_4)(ClO_4)_2]$, $[Cu(C_{10}H_{20}N_8O_4)(ClO_4)_2]$, $[Cu(C_{20}H_{24}N_8O_4)(ClO_4)_2]$, were prepared by the reaction of malonodihydrazide with copper(II) perchlorate hexahydrate in presence of different aldehyde i.e. formaldehyde, acetaldehyde, benzaldehyde respectively in 2:1:2 molar ratio.

GENERAL INTRODUCTION

1.1 INTRODUCTION

The chemistry of macrocyclic complexes has occupied a central role in the development of coordination chemistry. The metal ion and host guest chemistry of macrocyclic ligands has developed rapidly over recent years and now impinges on wide areas of both chemistry and biochemistry. A very large number of synthetic, as well as many natural, macrocycles have now been studied in considerable depth. A major thrust of many of these studies has been to investigate the unusual properties frequently associated with cyclic ligand complexes. In particular, the investigation of spectral, electrochemical, structural, kinetic, and thermodynamic aspects of macrocyclic complexes have all received considerable attention¹.

The macrocyclic complexes of metal ions are synthesized by the reaction of the required metal ion with the preformed macrocyclic ligands, but there are potential disadvantages in this method. The synthesis of a macrocycle in the free form often results in a low yield of the desired product with side reactions where polymerization is predominating. In order to circumvent this problem, the ring-closure step in the synthesis may be introduced to restrict rotation in the open-chain precursor thereby facilitating cyclization. One effective method for the synthesis of macrocyclic complexes involves an *in situ* approach which is commonly referred to as the "metal template effect" method where in the presence of a metal ion the cyclization reaction markedly increases the yield of the cyclic product².

The metal ion plays an important role in directing the steric course of the reaction preferentially toward cyclic rather than polymeric product and

stabilizes the macrocycles once formed³. The chemistry of macrocyclic ligands has been a fascinating area of current research interest to the chemists all over the world. The continued interest and quest in designing new macrocyclic ligands stem mainly from their use as models for protein metal binding sites in biological systems, as models for metallo enzymes, as sequestering reagents for specific metal ions, as models to study the magnetic exchange phenomena, as chemical sensors and batteries, as therapeutic reagents for the treatment of metal intoxication, as medical imaging agents, as catalysts, and in biomedical and fuel cell applications^{4,5}.

Macrocycles are large cyclic molecules which contain donor atoms that can form coordinate bonds with metal centers. As usually defined, macrocyclic ligands are polydentate ligands that contain three or more donor atoms and consist of a minimum of nine atoms⁶. Macrocyclic molecules usually have a central hydrophilic cavity while the exterior of the macrocycles are hydrophobic⁷, therefore, they have the ability to bind to a wide variety of cations, because of this central hydrophilic cavity, and the hydrophobic exterior allows them to solubilize ionic substances in non aqueous solvents and in membrane media⁸. These macrocycles are present in proteins and enzymes and can thus complex readily to heavy metals they get in to the biological system of humans or animals. The complexation of the heavy metal ions with the macrocycle will prevent the heavy metals from being absorbed by the organs in the body.

The metal ion chemistry of macrocyclic ligands has now become a major subdivision of inorganic chemistry. Macrocycles or macrocyclic ligands in inorganic chemistry usually refer to nine membered or greater ring containing

organic molecules usually with twelve or more atoms in which three or more hetero-atom donors such as N, O, S, P, etc binding sites have been interspersed⁹. Consequently, classification of such multidentate macrocyclic ligands is tridentate, tetradentate, pentadentate, etc depending on the number of binding sites. The other way of classifying them is as aza (N), oxa (O), sulfa (S), phospho (P), etc, and a combination of these, depending on the type of hetero-atom(s) involved. Apart from these there had been a traditional classification of such ligands as oxygen donor crown ethers and cryptands and nitrogen donors. The oxygen donor macrocycles tend to complex well with larger alkali and alkaline earth metal ions as well as larger post-transition metal ions such as Pb(II), Tl(I), or Hg(II) due to their tendency to have trigonal planar optimum strain geometry that provides larger cavity¹⁰. The formation of metal complexes is closely related to many naturally occurring ones.

Complexation with such macrocycles has stimulated a number of scientists to synthesize and investigate many macrocycles for their possible binding sites. In general, there are two major factors that determine the selection of macrocycles for metal ion complexation to form stable complexes. Selection of macrocycles for metal ion complexation is based on the size of their cavity, i.e., size match selectivity¹¹ and on the type of donor atom used. Such selection of macrocycles for metal ions or other substrate complexation is critically dependent on the structure of the macrocycles and electronic effects, i.e., charge, polarity, polarizability of the binding site or the type of donor atoms. Some of the major aspect of these are: the number of binding sites, the arrangement of the binding sites, the preferred configuration of the macrocycles that dictate the propensity of the lone pairs to bind metal ion internally or externally to the cavity, the identity of the macrocyclic frame work

and the size of the macrocyclic cavity that determine the flexibility of the ligand and its propensity for metal ion binding.

A number of nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications¹². Macrocyclic compounds and their derivatives are interesting ligand system because they are good hosts for metal anions, neutral molecules and organic cation guests¹³. The metal-ion and host-guest chemistry of macrocyclic compounds are very useful in fundamental studies, e.g., in phase transfer catalysis and biological studies[14]. In situ, one pot template condensation reactions lie at the heart of macrocyclic chemistry¹⁵.

Interest in the study of hexaaza macrocyclic complexes with pendant arms is still growing on account of their unique coordination and structural properties, their utility as bio-inorganic models for cobalamine and catalysis, and their rapidly growing applications as radio pharmaceuticals and magnetic resonance imaging reagents¹⁶. Much work has been done on the electrochemical stabilization of the unusual oxidation states of some transition metals by a variety of macrocyclic ligand types.

Copper is the third most abundant element among the transition metal ions found to be involved in biological processes¹⁷. Copper is a bio-essential element with truly unique chemical characteristics in its two relevant oxidation states I and II. According to its position as the highest homologue of group XII in the periodic table, copper is a very special element. The metal-ligand interaction in Cu(II) complexes is frequently ionic and favours the stabilization of the Cu(II) state through the pronounced Jahn-Teller distortion. Different extent

of axial elongation of the octahedron can produce square-pyramidal, square bipyramidal or square planar geometries.

Copper being an essential trace element, is present in parts per million concentration range in biological systems. The element functions as a key cofactor in a diverse array of biological oxidation reduction reactions¹⁸. Copper containing proteins (hemocyanin, tyrosinase, catecol oxidase etc.,) are involved in various processes in living systems¹⁹.

Therefore in this work, the synthesis and characterization of a new series of 16-membered tetraaza macrocyclic complexes were attempted by the template condensation of Formaldehyde, Acetaldehyde, Benzaldehyde and the corresponding metal salts of Cu (II) in aqueous medium. The General Objectives of this Study are to synthesize and characterize a new series of polyaza macrocyclic complexes of the divalent transition metal ions of Cu (II) accordingly, the specific objectives of the research include:

- I. To synthesize 16-membered tetraaza macrocyclic complexes with Cu (II)
- II. To characterize the as synthesized complexes by various physico-chemical Methods and Instrumental techniques.

1.2 Chemistry of Macrocyclic Complexes

Macrocycles are polydentate ligands that contain at least three donor groups and a minimum of nine atoms within or attached to the macrocyclic ring²⁰. The donors readily form coordinative bonds with metal centres to produce highly stable macrocyclic metal complexes. The first reports of synthetic macrocycles appeared in 1936 when the first synthesis of 1,4,8,11-tetraazacyclotetradecane (cyclam) was reported²¹. However, the field of coordination chemistry of macrocycles exploded in the early 1960s after the publication of articles by Curtis and Thompson on the discovery of the macrocyclic ligand (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) prepared from the condensation of acetone and a nickel complex of ethylenediamine.

Macrocyclic complexes are part of a number of fundamental biological systems. The importance of such complexes has provided a motivation for investigation of the metal ion chemistry of those biological systems as well as of cyclic ligand system²². The development of the field of bioinorganic chemistry has been an important factor in spurring the growth of interest in complexes of macrocyclic compounds²³. A review on macrocycle has revealed the importance of macrocyclic complexes in biological processes such as photosynthesis and dioxygen transport their catalytic properties²⁴, their potential applications as metal extractants and as radio-therapeutic²⁵ and medical imaging agents²⁶. Polyaza macrocyclic complexes with transition metal (II) ions have attracted considerable interest because their structural, equilibrium, and kinetic behaviour differ from those of the non-cyclic analogs²⁷. Metal template syntheses often provide selective routes toward products that are not obtainable in the absence of metal ions. In particular,

formaldehyde has been utilized for cyclization to link two amine moieties. Among 3d metal ions, Ni (II) and Cu (II) have been the most widely investigated species for several reasons; (i) they are often very effective as templating agents in many synthesis, (ii) their complexes display unusually high solution stability.

Even though a large number of tetraaza macrocyclic ligands and their complexes have been synthesized and studied²⁸ only few reports are available for macrocyclic ligands containing six nitrogen donors in a fully saturated macrocyclic framework. During recent years, macrocyclic chemistry has attracted much attention and has become a growing class of research. Macrocyclic complexes are of great importance due to their resemblance to many naturally occurring macrocycles, such as porphyrins and cobalamines. A number of nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications^{29, 30}. Macrocyclic metal complexes of lanthanides, *e.g.*, Gd³⁺, are used as magnetic resonance image (MRI) contrast agents³¹. Macrocyclic metal chelating agents are useful for detecting tumor lesions. The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments³² as well as NMR shift reagents. Furthermore, some macrocyclic complexes have been found to exhibit potential antibacterial activities³³.

Macrocyclic chemistry has attracted the attention of both inorganic and bioinorganic chemists. The synthesis of macrocyclic complexes has been a fascinating area of research and growing at a very fast pace owing to their resemblance with naturally occurring macrocycles and analytical, industrial, and medical applications^{34,35}. Macrocyclic complexes are part of a number of

fundamental biological systems. The importance of such complexes has provided a motivation for investigation of the metal ion chemistry of those biological systems as well as of cyclic ligand systems³⁶. The development of the field of bioinorganic chemistry has been an important factor in spurring the growth of interest in complexes of macrocyclic compounds³⁷. The possibility of using synthetic macrocycle as models for biologically important systems has initiated a broad spectrum of research activities, ranging from synthesis of new ring systems and studies on the properties and functions of macrocyclic complexes to their application in industry, medicine and other fields³⁸.

1.3 LIGANDS

In coordination chemistry, a ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. The bonding between metal and ligand generally involves formal donation of one or more of the ligand's electron pairs. The nature of metal-ligand bonding can range from covalent to ionic. Furthermore, the metal-ligand bond order can range from one to three. Ligands are viewed as Lewis bases, although rare cases are known involving Lewis acidic "ligands." There are many kinds of ligand.

1.4 Strong Field and Weak Field Ligands

In general, ligands are viewed as electron donors and the metals as electron acceptors. Bonding is often described using the formalisms of molecular orbital theory. The Highest Occupied Molecular Orbital (HOMO) can be mainly of ligands or metal character.

Ligands and metal ions can be ordered in many ways; one ranking system focuses on ligand 'hardness'. Metal ions preferentially bind certain ligands. In general, 'soft' metal ions prefer weak field ligands, whereas 'hard' metal ions prefer strong field ligands. According to the molecular orbital theory, the HOMO of the ligand should have an energy that overlaps with the Lowest Unoccupied Molecular Orbital (LUMO) of the metal preferential. Metal ions bound to strong field ligands follow the Aufbau principle, whereas complexes bound to weak field ligands follow Hund's rule. Binding of the metal with the ligands results in a set of molecular orbitals, where the metal can be identified with a new HOMO and LUMO (the orbitals defining the properties and reactivity of the resulting complex) and a certain ordering of the 5d-orbitals.

1.5 CLASSIFICATION OF MACROCYCLIC LIGANDS

Two major areas of complexation have developed over the years with regard to synthetic macrocycles. Those with nitrogen, sulfur, phosphorus, and arsenic tend predominantly to form traditional covalent coordination complexes with transition metal ions. A notable exception to this tendency, however, is the rapidly expanding chemistry of the polyammonium macrocycles, which are capable of forming a variety of complexes with anionic substrates. Oxygen derived macrocycles are noted for complexation with alkali and alkaline earth metal ions, as well as with organic cations and molecular substrates. Macrocyclic ligands are classified, as rings with at least nine members and

three or more donor atoms. Consequently, classification of such multidentate macrocyclic ligands is tridentate, tetradentate, pentadentate, etc depending on the number of binding sites. The other way of classifying them is as aza (N), oxa (O), sulfa (S), phospho (P), etc, and a combination of these, depending on the type of hetero-atom(s) involved.

1.5.1 Polyoxa Macrocycles

Polyoxa macrocycles known more commonly as the crown ethers³⁹. In this category are the polycarbonyls⁴⁰, polylactones⁴¹, polylactams⁴² and carcerands⁴³.

1.5.1.1 Polyether Macrocycles

Polyether macrocycles are the simplest of the polyoxa macrocycles. The commonly used name for these macrocycles is the crown ethers, due to their crown-like structure in the solid state⁴⁴. (As shown in figure 1.1)

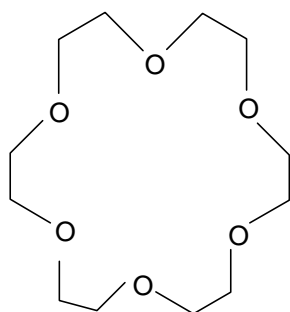


Fig: 1.1

1.5.1.2 Spherands and Hemispherands

These consist of an arrangement of phenyl groups which provide a preorganized cavity for complexation⁴⁵. (As shown in figure 1.2)

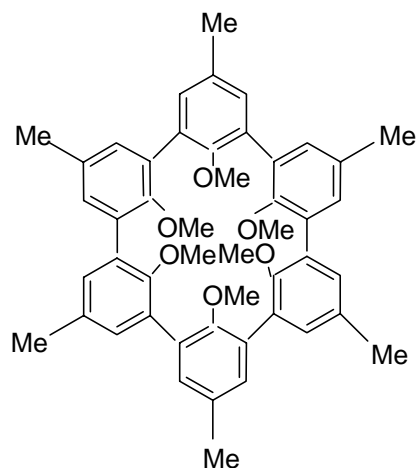


Fig: 1.2

1.5.2 Polythia, Polyphospha, and Polyarsa Macrocycles

Polythia macrocycles are the thioether analogs of the crown ethers⁴⁶. The 'pure' polyphospha macrocycles as opposed to the mixed donor phospho macrocycles⁴⁷. The polyarsa macrocycles comprise one of the least common type of macrocycles⁴⁸. (As shown in figure 1.3)

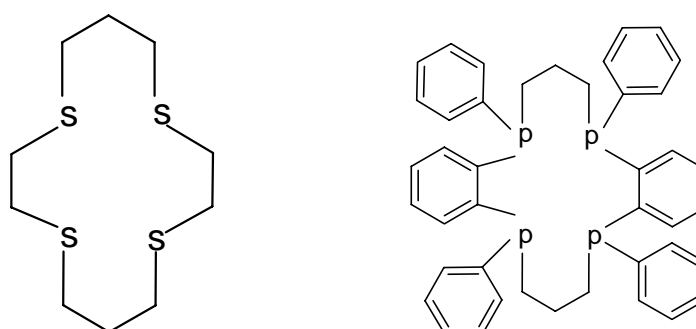


Fig: 1.3

1.5.3 Mixed Donor Macrocycles

1.5.3.1 Simple Mixed Donor Macrocycles

The simple mixed donor macrocycles are made of 'soft' phosphorus and arsenic donors into macrocycles⁴⁹. Mixed oxygen–nitrogen macrocycles are made by the coordination of the aza macrocycles and the oxa crown ethers⁵⁰.

(As shown in figure 1.4)

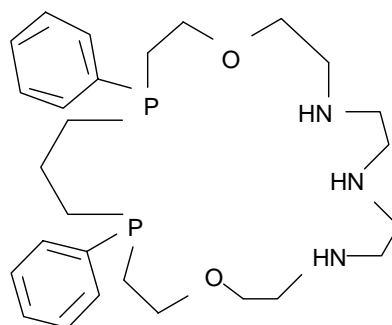


Fig: 1.4

1.5.3.2 Cryptands

Cryptands are bicyclic macrocycles which can contain a variety of donor atoms with bridgehead nitrogen atoms⁵¹. They are highly selective for alkali and alkaline earth metal ions. (As shown in figure 1.5)

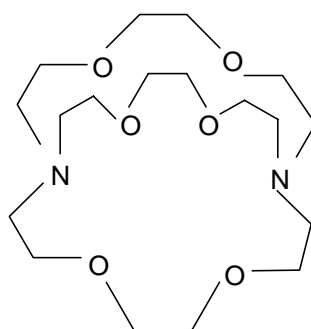


Fig: 1.5

1.5.3.3 Compartmental Ligands

Compartmental ligands are macrocyclic ligands (as well as non-macrocyclic ligands) which contain 'compartments' for housing more than one metal ion⁵². (As shown in figure 1.6)

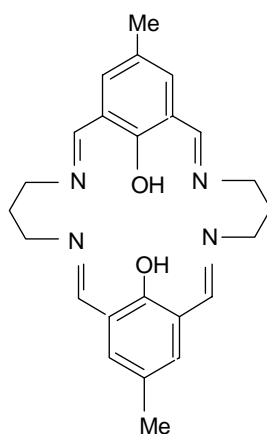


Fig: 1.6

1.5.4 Polyaza Macrocycles

1.5.4.1 Simple Polyaza Macrocycles

The simple polyaza macrocycles has been the effort to achieve functionalized macrocycles in order to expand the chemistry of these ligands by combining the rigid structural aspects of the macrocyclic ring with the more flexible and kinetically labile properties of pendant chains⁵³. (as shown in figure 1.7)

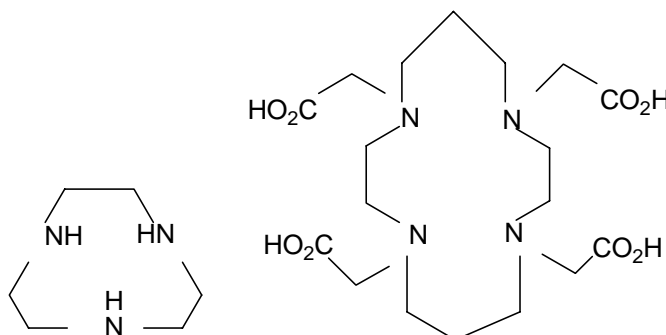


Fig: 1.7

1.5.4.2 Cyclidenes

Cyclidenes are a subset of the polyaza macrocycles and are the lacunar ligands⁵⁴. They coordinate a single metal ion and maintain a 'persistent void' which allows access to small molecules within the vaulted cavity. (as shown in figure 1.8

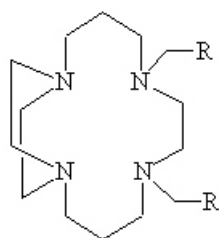


Fig: 1.8

1.5.4.3 Sepulchrates

Sepulchrates are polyaza cage macrocycles. They are noted for their exceptionally strong hold on encapsulated metal ions⁵⁵. (as shown in figure 1.9)

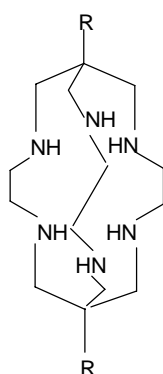


Fig: 1.9

1.5.4.4 Expanded Porphyrins

Expanded porphyrins are macrocycles based on the pyrrolic backbone of porphyrins, but are expanded in size to achieve a larger cavity⁵⁶ or binucleating capabilities⁵⁷. (As shown in figure 1.10)

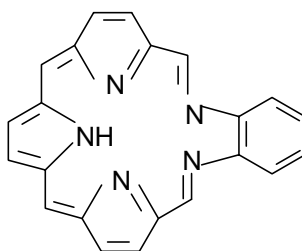


Fig: 1.10

1.6 Schiff Base ligands

Schiff bases are formed typically by the condensation of a primary amine and an aldehyde/ketone. The resultant compound, $R_1R_2C=NR_3$ is called a Schiff base, where R_1 is an aryl group, R_2 is a hydrogen atom and R_3 is either an alkyl or aryl group. However, usually compounds where R_3 is an alkyl or aromatic group are also regarded as Schiff bases. Schiff bases that contain aryl substituents are substantially more stable and readily synthesised, while those which contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerisable⁵⁸, while those of aromatic aldehydes having effective conjugation are more stable. In general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehydes are sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone

donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehydes⁵⁹.

Some examples of open chain Schiff bases: Are given below as in Fig. 1.11

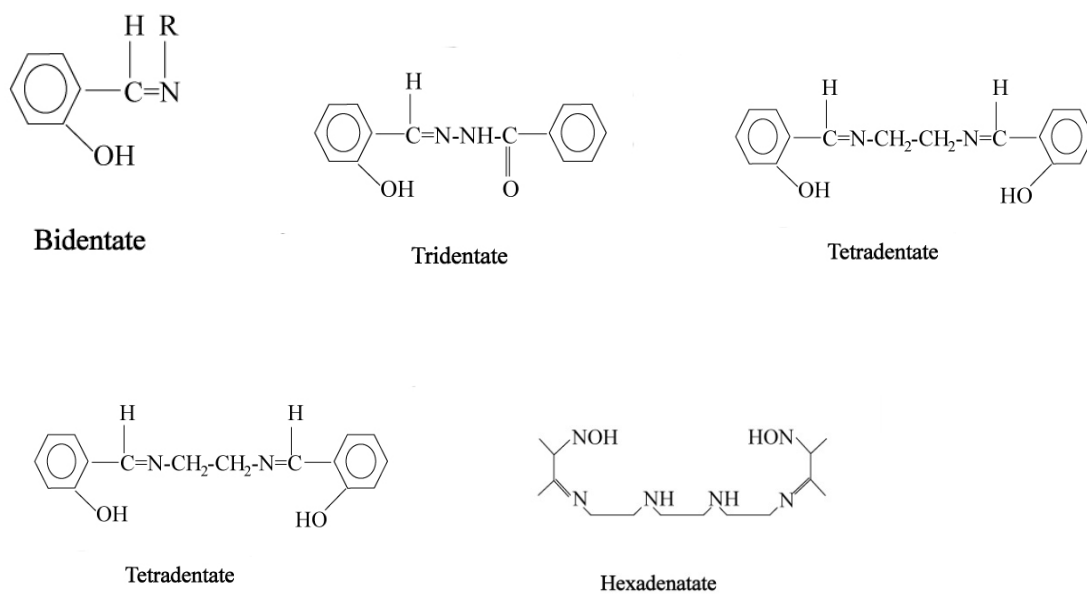


Fig: 1.11

1.6.1 PREPARATION AND MECHANISM OF SCHIFF BASE LIGANDS

A Schiff base is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by C=N-R group. It is usually formed by condensation of an aldehyde or ketone with a primary amine according to the following scheme: (as shown in figure 1.12)

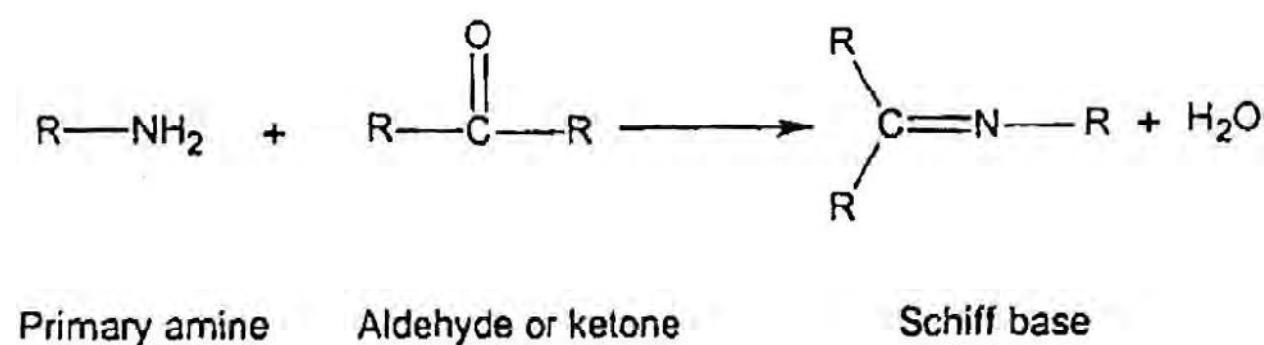


Fig: 1.12

Where R, may be an alkyl or an aryl group. Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable while those of aromatic aldehydes having effective conjugation are more stable.

The formation is generally driven to the completion by separation of the product or removal of water, or both. Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base.

The mechanism of Schiff base formation is another variation on the theme of nucleophilic addition to the carbonyl group. In this case, the nucleophile is the amine. In the first part of the mechanism, the amine reacts with the

aldehyde or ketone to give an unstable addition compound called carbinolamine. The carbinolamine loses water by either acid or base catalyzed pathways. Since the carbinolamine is an alcohol, it undergoes acid catalyzed dehydration. (As shown in figure 1.13)

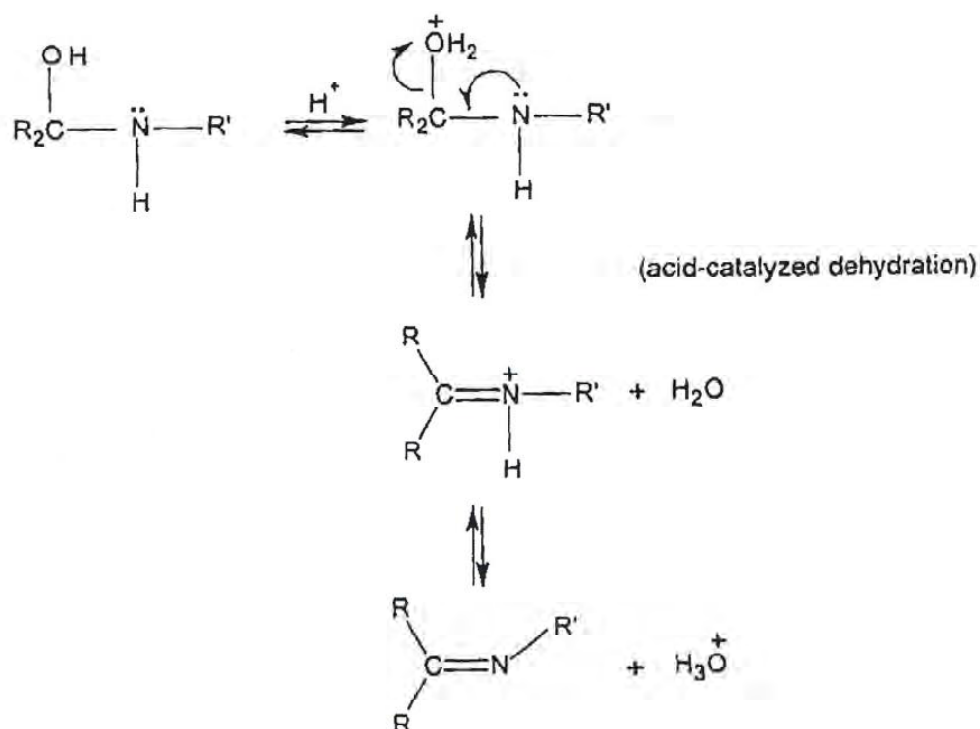


Fig: 1.13

Typically the dehydration of the carbinolamine is the rate-determining step of Schiff base formation and that is why the reaction is catalyzed by acids. Yet the acid concentration cannot be too high because amines are basic compounds. If the amine is protonated and becomes non-nucleophilic, equilibrium is pulled to the left and carbinolamine formation cannot occur.

The dehydration of carbinolamines is also catalyzed by base. This reaction is somewhat analogous to the E_2 elimination of alkyl halides except that it is not a concerted reaction. It proceeds in two steps through an anionic intermediate.

Cycloaddition of Schiff bases to ketenes is highly stereoselective⁶⁰, implying a concerted process. However, a two-step mechanism involving a dipolar intermediate, adequately accounts for the observed stereoselectivity and is strongly supported by mechanistic studies⁶¹ of β -lactam formation via intermediate of the type from Schiff bases and ketenes. (As shown in figure 1.14)

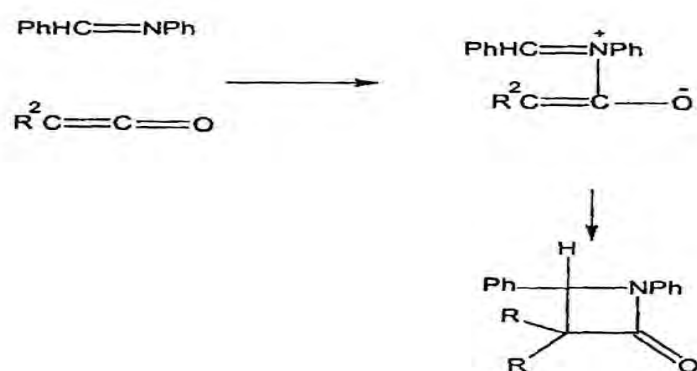


Fig: 1.14

Metal complexes ML_2Cl_2 where M is Fe (II), Co (II), Ni(II), Cu(II), Zn(II) or Cd(II) and L is the Schiff base formed by the condensation of 2-thiophenecarboxaldehyde with 2-aminopyridine, N-(2-thienylmethylidene)-2-aminopyridine (TNAPY) have been reported by Spinu et al⁶². (As shown in figure 1.15)

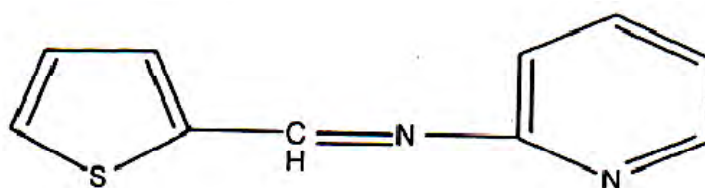


Fig: 1.15

Synthesis, characterization and electrochemical behaviour of Cu, Co, Ni and Zn complexes derived from acetylacetonate and p-anisidine was reported by Raman and coworkers⁶³. These authors have observed that the complexes synthesized by them show fairly good antimicrobial activity. (As shown in figure 1.16)

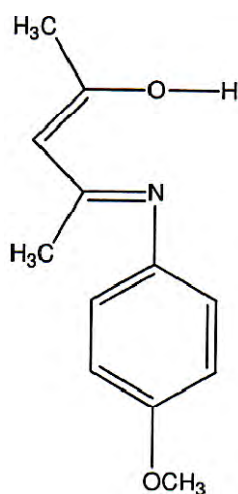


Fig: 1.16

Nair and coworkers⁶⁴ have studied the synthesis and antibacterial activity of some Schiff base complexes. The Schiff bases showed greater activity than their metal complexes. (As shown in figure 1.17)

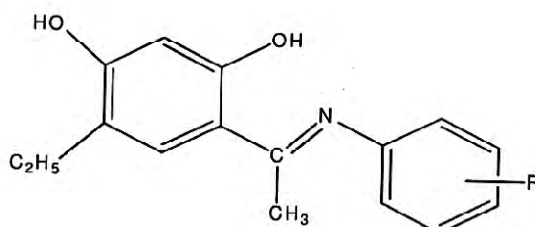


Fig: 1.17

More et al⁶⁵ have reported the synthesis of the following Schiff base. These authors have studied the proton ligand stability constant of the Schiff bases and the formation constants of their transition metal complexes. (As shown in figure 1.18)

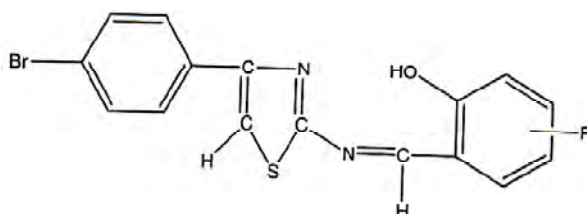


Fig: 1.18

Following two new Schiff bases and transition metal complexes derived from 2,3-diminopyridine (DAPY) and ortho-*vanillin* have been synthesized⁶⁵ and characterized by elemental analysis, magnetic susceptibility measurements, IR and NMR spectra. The Schiff bases and most of the metal complexes display antibacterial activity. (As shown in figure 1.19)

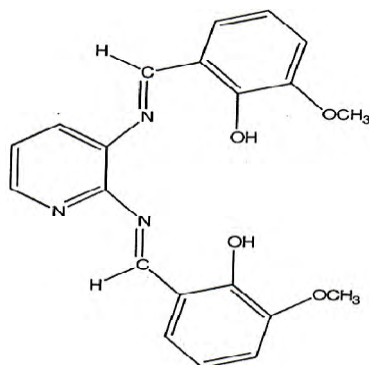


Fig: 1.19

Condensation of 2,2',6,6'-tetraaminobiphenyl with salicylaldehyde gives a binucleating ligand which was used to prepare $\text{Cu}_2(\text{sal-tabp})$, $\text{Ni}_2(\text{sal-tabp})\cdot\text{H}_2\text{O}$ and $\text{Co}_2(\text{sal-tabp})\cdot\frac{1}{2}\text{H}_2\text{O}$ ⁶⁷. (As shown in figure 1.20)

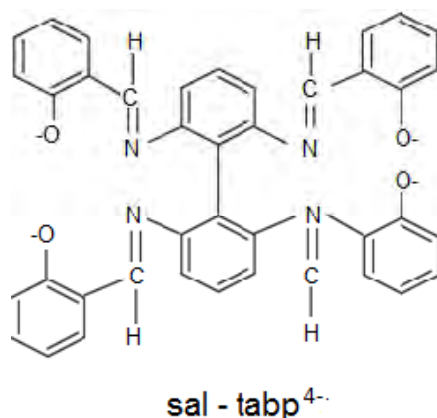
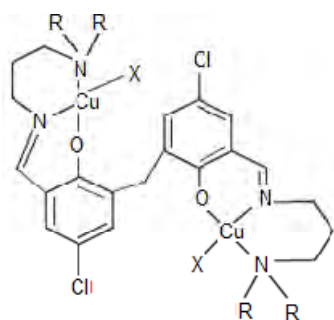


Fig: 1.20

Kanadaswamy et al., synthesised and studied remote donor set of complexes derived from methylene bridged bis (tridentate) ligands with the aim to study the influence of remote donor set of ligands on complex properties ⁶⁸. (As shown in figure 1.21)



R = C₂H₅, CH₃

X = ClO₄⁻, AcO⁻, Cl⁻, Br⁻

Fig: 1.21

Tumer et al., (1999) prepared, characterised and studied the antibacterial activity of binuclear Cu(II), Co(II), Ni(II), VO(II) and Zn(II) complexes derived from 3-hydroxysalicylaldehyde, 4-hydroxysalicylaldehyde and 5-bromosalicylaldehyde with N-(pyridyl)-2-hydroxy-3-methoxyaminobenzylamine⁶⁹. (As shown in figure 1.22)

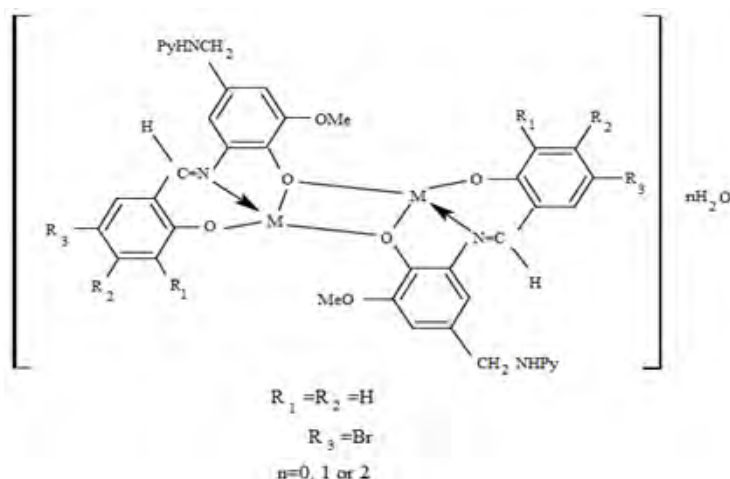


Fig: 1.22

Ghames prepared, the structural and electrochemical studies of Co(II), Ni(II), Cu(II) and Cd(II) complexes with a new symmetrical N₂O₂ Schiff base and crystal structure of the ligand 1,2-di[4-(2-imino-4-oxopentane)phenyl]ethane was also studied⁷⁰. The coordination occurs through the N₂O₂ system. (As shown in figure 1.23)

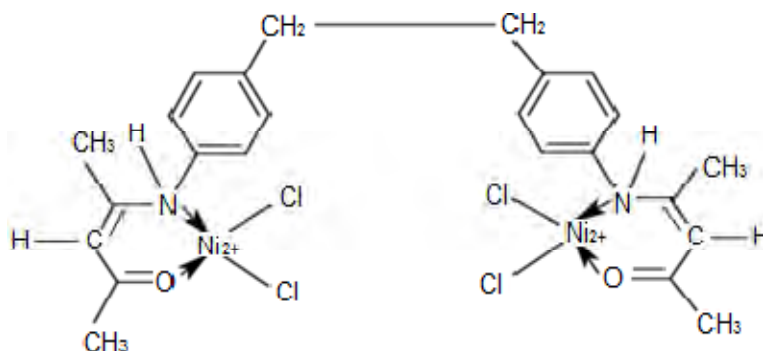


Fig: 1.2

Tumer et al., synthesized and characterized divalent metal [Cd(II), Cu(II), Co(II), Ni(II), Zn(II)] complexes⁷¹. Their electrochemical, catalytic, thermal and antimicrobial studies have also been carried out. (As shown in figure 1.24)

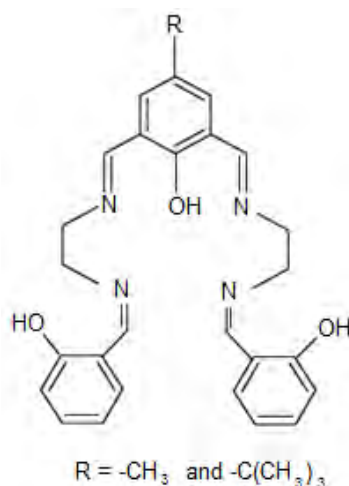


Fig: 1.24

Ahmed et al., (2009) prepared and characterised binuclear dichloro-bridged copper (II) complexes, the ligands have been synthesised by the condensation of acetyl acetone and p-phenylenediamine⁷². (As shown in figure 1.25)

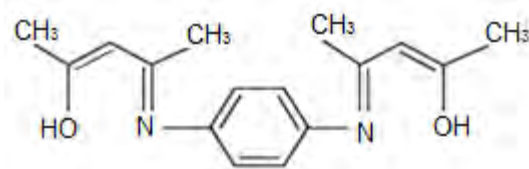


Fig: 1.2

1.7 Macrocyclic complexes have the following characteristics.

- i. A marked kinetic inertness both to the formation of the complexes from the ligand and metal ion.
- ii. They can stabilize high oxidation state, that are not normally readily attainable, such as Cu (III) or Ni(III).
- iii. They have high thermodynamic stability than the formation constants for non-macrocyclic N_4 ligand. Thus for Ni(II) the formation constant for the macrocyclic tetradentate Ni complex is about five orders of magnitude greater than that for the non-macrocyclic tetradentate Ni complex

1.8 Cu (II) Chemistry of Macrocyclic complexes

The Cu (II) ion with its d^9 configuration in octahedral and tetrahedral environment is highly susceptible to Jahn-Teller distortion. Octahedral complexes without any distortion are expected to have only one d-d absorption band corresponding to ${}^6T_{2g} \rightarrow {}^3E_g$ Transition, while for distorted octahedral complexes several weak absorption bands are observed around 16000 cm^{-1} and often a broad band in the near IR region. Cu (II) is usually found in tetragonal coordination environment, with four short equatorial bonds and one or two axially elongated bonds due to the Jahn-Teller effect, though some four coordinate tetrahedral and planar complexes are known. The tetragonally distorted Cu (II) complex shows three absorption bands corresponding to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$. However, tetrahedral complexes are expected to give a single, broad band corresponding to ${}^6T_{2g} \rightarrow {}^3E_g$ transition in the near IR region. For square planar, three d-d bands corresponding to ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow 2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ are observed. The Cu (II) ion is classified as a borderline hard acid; therefore nitrogen and oxygen donors followed by chlorine and sulphur have dominated its coordination chemistry. Magnetic moments of Cu (II) complexes are generally in the range 1.7 to 2.2 B.M⁷³.

1.9 Methods of Synthesis of Macrocyclic Complexes

The stability of the macrocyclic complex was attributed to the fixed geometrical placement of the ligand donor atoms. This effect was first illustrated with acyclic triamine by Busch and co-workers in 1970. In 1975 presented further evidence of the coordination strength of cyclic tridentate amines by determining formation constants of the Cu (II), Ni(II), and Zn(II) complexes. Until recently polyaza macrocycles, which are quadridentate such as cyclam and related ligands with extensive varieties of modification including different degree of saturation and ring size had been the most widely studied ones due to their relationship to porphyrin as well as their stability and selectivity in complexing with various transition metal ions. Template assisted condensation of amines with formaldehyde macrocyclic products ⁷⁴.

1.10 Template synthesis of Copper (II)

Template Schiff base condensations between dicarbonyl compounds and diamines are among the successful and most popular methods for macrocycle synthesis⁷⁵. The term “template” has been widely used since the early sixties. The routine use of metal template procedures for obtaining a wide range of macrocyclic systems⁷⁶, Metal template condensation reactions are simple “one-pot reactions”, cheap and high yielding.

Macro cyclic complexes are best prepared with the aid of metal ions as templates to direct the condensation reaction which, ultimately ends with ring closure⁷⁷. Copper is a bio essential element in all living systems. It is a component of many metallo proteins and plays a vital role in electron transfer reactions of many cellular processes. However, excessive copper can be very toxic resulting in severe diseases⁷⁸. Recently, numerous research groups have reported novel copper (II) complexes with organic ligands showing antifungal and antibacterial properties against several pathogenic fungi and bacteria⁷⁹. Diethylmalonate acts as an efficient locking fragment in the Cu (II) directed synthesis of 16-membered tetraaza-macrocycles.

1.11 AIM OF THE PRESENT WORK

Macrocyclic complex compounds are an immense field in chemistry, especially in coordination chemistry and in bio-inorganic chemistry.

Macrocycles are important and powerful ligands in transition metal coordination chemistry for the following reasons: 1) they mimic important biological ligands developed long ago by nature, for example the porphyrin prosthetic group of many metalloproteins, 2) they impart thermodynamic and kinetic stabilities to their metal complexes uncommon or non-existent with ligands of lesser types. For the purposes of this dissertation, a macrocycle is defined as a cyclic compound with nine or more members including at least three donor atoms. These impart exceptional kinetic and thermal stabilities to the complexes, dramatically accentuating the advantages of macrocyclic ligands, both (1) and (2) above.

In the nature a lot of macrocyclic compounds are known (e.g. haemoglobin, myoglobin, vitamin B₁₂ coenzymes where the metal atoms are Fe, Co and the basic macrocyclic unit is porphyrin but have different functional groups to the macrocycles). The chemical properties of some macrocyclic compounds resemble those of antibiotics.⁷⁹ For instance, macrolactones resemble the natural metabolites such as nonactin and monactin.

In the recent years considerable attention has been given to the synthesis of macrocyclic complexes.^{80-82.} These complex compounds have been used as a model system of biologically important materials, such as porphyrin and corins.

Some of the macrocyclic ligand cannot be easily prepared from the reactants.⁸³
In that case the complex compounds could be synthesized by template method. The desire macrocyclic ligand can be isolated by stripping the complex compounds.^{84, 85} Macrocyclic tetraaza complex of Ni²⁺ act as catalyst to reduce CO₂ to CO and Fe²⁺, Mn³⁺ porphyrins have been most commonly studied catalyst.^{86, 87.}

In view of the extensive use as drugs and significant pharmacological activities of macrocyclic complexes and their derivatives, it is desired to synthesize macrocyclic complexes of Cu (II) . Synthesized macrocyclic complexes and their derivatives are expected to have microbial activity.

Therefore, considering the rapid increasing importance of macrocyclic ligand and their complexes in biology and in medicine the present work as follows:

Synthesis of some new macrocyclic complexes by the reactions of malonodihydrazide with Cu (II) perchlorate in the presence of formaldehyde, acetaldehyde and benzaldehyde will be characterised by elemental analysis, UV visible and IR spectral analysis, magnetic moment and conductance measurements and some other physical properties.

METHODS AND MATERIALS

2.1 PHYSICAL MEASUREMENTS

2.1.1 Weighing

The weighing operation was performed on a electronic balance.

2.1.2 Determination of melting points of the complexes

The melting point of each product was measured using the melting point apparatus. The melting point of each product was determined following the instruments operation procedure, which required appearance of a sharp melting point in case of a pure solid.

2.1.3 Infra Red (IR) Spectroscopy Spectrum Analysis

The infrared (IR) spectra of the as synthesized complexes were recorded by FT-IR spectrophotometer in the range of 4000-400 cm^{-1} using pressed pellet sampling technique (KBr discs). A few mg IR-grade KBr was placed in a mortar (the amount of KBr taken was sufficient to cover an area of about 20 mm^2 to a depth of 1mm). The KBr was ground in the mortar until there was no crystallinity and then small amount of each complex sample was added (amount of taken was enough to cover an area of about 4 mm^2 to an average of a depth of 0.5 mm). After the sample was ground to the KBr until it was uniformly distributed throughout the KBr, some of the ground mix was finally transferred to pellet making die. The desired pellet was made and its FTIR spectrum of the pellet was recorded over the range of 4000-400 cm^{-1} . Infrared spectra disc were recorded as KBr with a SHIMADZU FTIR-8400 infrared spectrophotometer.

2.1.4 UV-Visible Spectroscopy Spectrum Analysis.

The electronic spectra measurements were used for assigning the stereo chemistry of metal ions in the complexes based on the positions of absorption bands including d-d transition peaks. The electronic absorption spectra are often very helpful in the appraisal of results offered by the other methods of structural investigation.

2.1.5 Conductivity

The conductivity cell was normally cleaned three times with water and finally rinsed three times with acetone and allowed to dry in air.

Conductivity measurements of the present complexes were carried out in dimethyl sulfoxide (DMSO). The conductivity viz. the molar conductivities were calculated by using the formula.

$$\kappa = (1000/C) \times \text{cell constant} \times \text{observed conductivity}$$

Where 'C' represents the concentration of the respectively complex in mol/L.

Generally 10^{-3} M solutions of complex were employed for this purpose. The conductance measurements were made at room temperature using by digital conductivity meter and a dip type cell with a polarized electrons.

2.1.6 Magnetic moments

i. Working principle of the balance:

The magnetic susceptibilities of the isolated complexes were determined by Gouy's method.

The following general expression for mass susceptibility in C.G.S units may be derived in the same manner for the traditional Gouy method.

$$\chi_g = l/m[C(R-R_0) + \chi_{\text{vair}}A] \dots \dots \dots (i)$$

Where,

C = Constant of proportionality

R = Susceptibility of the tube with sample

R_0 = Susceptibility of the empty tube

l = Length of the sample (in cm)

m = Mass of the sample (in gm)

A = Cross-section area of the tub (in cm^2)

χ_{vair} = Volume Susceptibility of the displaced air, for powdered sample

the air correction term χ_{vair} may normally be ignored.

C the const of proportionality is related to the calibration constant of a given balance by the formula.

$$C = C_{\text{Bal}} / 10^9 \dots\dots\dots(ii)$$

From (i) and (ii), we get

$$\chi_g = C_{\text{Bal}} \times l \times (R - R_0) / 10^9 \times m \dots\dots\dots(iii)$$

ii. Calibration of the balance

The magnetic susceptibility Balance (M.S.B) must be calibrated at its intended work place. The balance is to be used mainly for solid sample, then a solid calibrant (preferably) $[\text{Hg Co (SCN)}_4]$ is recommended since some of the systemic errors in packing may cancel. The constancy of the calibration was checked using a sealed off sample of MnCl_2 solution.

iii. Procedure

1. The Zero knob of the magnetic susceptibility was turned until numerical display shows zero (000) and calibration sample $[\text{HgCo(SCN)}_4]$ was inserted into sample holder. It was allowed settled reading the numerical display.
2. Reading was recorded and calibration constant was calculated from the formula.

$$C = \text{Blac} = C_{\text{Tube}} / (R - R_0)$$

$$= (1766.842) / \{2830-17\}$$

$$= 2.086 \dots\dots\dots (iv)$$

From (iii) and (ii) we get,

$$\chi_g = 2.086 \times l \times (R-R_0) / 10^9 \times m \dots\dots\dots (v)$$

iii. Operation of the “Balance”

1. The range knob was turned to the XI scale then it was allowed to 10 minutes warm up period before use.
2. The zero knob adjusted until the display reads 000. The zero was adjusted on each side.
3. An empty sample tube of known weight was placed into the tube guide and was taken the reading R_0 .
4. The sample was packed and sample mass, m in grams and the sample length l in cm.
5. The packed sample tube was placed the tube guide and was taken the reading R .

The mass susceptibility, χ_g is calculated using.

$$\chi_g = 2.086 \times l \times (R-R_0) / 10^9 \times m.$$

The temperature was read from thermometer situated in the balance room.

iv. The Magnetic Moment

From the measurement of magnetic moment one can find the number of unpaired electrons present in the system and the possible configuration and also the structure.

If substance is placed in a field of intensity H gauss, then B , the magnetic induction of the field within the substance is given by,

$$B = H + 4\pi I$$

Where,

I = Intensity of magnetism induced by the field.

I / H = is called the volume susceptibility of the substance and is given the symbol χ_v . In most cases a more useful quantity is the magnetic susceptibility per unit mass susceptibility, χ_g equal to χ_v/d where d is the density of the substance in gm/cm^3 . It was convenient to regard χ_v as dimensionless and χ_g as having the dimensions of reciprocal density.

The molar susceptibility χ_m is equal mass susceptibility χ_g multiplied by the formula weight of the substance. ($\chi_m = \chi_g \times \text{molecular weight}$)

$$\text{Here } (\mu_{\text{eff}}) = 2.828 (\chi_m \times T)^{1/2}$$

The magnetic moment was calculated using the above equation.

The magnetic moment due to electron spin of unpaired electron were calculated from the Equation: $\mu = (n(n+2))^{1/2}$

Where n is the number of unpaired electrons.

For some metal ion systems, there may also be spin and orbital contribution to the magnetic moment, which make the measured value to be somewhat larger.

Table 2.1: Unpaired spins and magnetic moments

No. of Unpaired electrons	Total spin angular moment (S)	Magnetic moments μ (Bohr Magnetons)(B.M)s
1	0.5	1.73
2	1	2.83
3	1.5	3.87
4	2	4.90
5	2.5	5.92

The idea on magnetic measurements can be applied to understand the stereochemistry of metal complex.

2.1.7 Metal Estimation

A known weight of the complex was taken into a conical flask and to it concentrated, H_2SO_4 (0.5) was added. It was fumed down to dryness and the process was repeated. Conc. HNO_3 , (0.5ml) was then added and conc. HClO_4 (0.5 ml) were added too. The mixture was fumed to dryness. The process of the adding acids and fuming down to dryness was added to dissolve the residue and then the metal was estimated complexometrically⁸⁸. Using EDTA (EDTA = Ethylenediamine tetraacetic acid) and DMG (DMG = Dimethyl glyoxime) excellent agreement of result were found.

2.1.8 Elemental analysis

Micro analysis for carbon hydrogen and nitrogen were obtained by using Kjeldahl Method.⁸⁹

2.2 PURIFICATION OF THE SOLVENTS

2.2.1 Ethanol

About 1.25g of clean and dry magnesium turnings and 0.125g of iodine were placed in dry 500 mL round bottle flask containing 40 mL of reagent Ethanol. The flask was then fitted with a condenser carrying a calcium chloride guard tube on the top. The mixture was warmed until, the iodine had disappeared; heating was continued until all the magnesium was converted into ethoxied, then 250 mL of absolute ethanol was added and the mixture was refluxed for one hour. After cooling, the ethanol was distilled directly into a vessel in which it was stored, by resembling the condenser for downward distillation via a splash head adapter. Then the dry ethanol was collected into a receiving flask from which it was stored into an air tight bottle.

2.2.2 Acetone

The acetone was heated under reflux with successive quantities of potassium per manganese until the violet coloured persisted. It was the dried with anhydrous potassium carbonate, Filtered from the desiccant and distilled. Precaution was taken to exclude moisture. i.e. a calcium chloride guard tube was used.

2.3 NAME OF THE CHEMICALS/REAGENTS USED AND SUPPLIERS

Copper (II) perchlorate hexahydrate	E. Merck
Copper (II) carbonate	E. Merck
Acetone	E. Merck
Absolute ethanol	BDH
Dimethyl sulfoxide (DMSO)	E. Merck
Formaldehyde	James Burrough Ltd. (England)
Acetaldehyde	BDH
Cinnamaldehyde	BDH
Crotanaldehyde	BDH, England
Benzaldehyde	E. Merck
Para Nitro Benzaldehyde	BDH, England
Para Chloro Benzaldehyde	BDH, England
Hydrazine hydrate	E. Merck
Dimethylformamide (DMF)	BDH
Diethylmalonate	May & Baker Ltd.

All chemicals were used as supplied except purification of the solvent.

EXPERIMENTAL

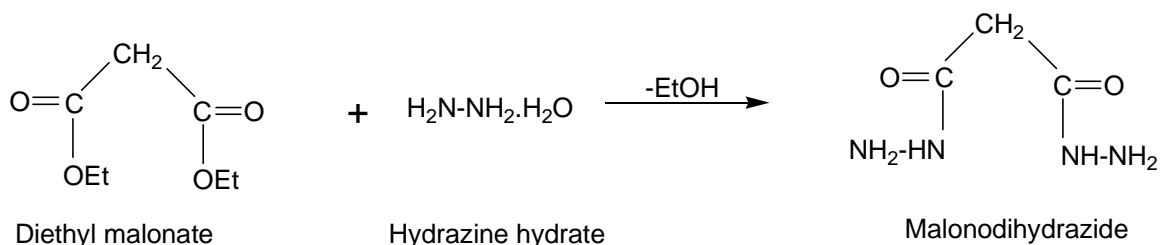
3.1 PREPARATION OF COMPLEXES

3.1.1 Preparation of malonodihydraide $C_3H_4N_2O_2$.

Diethyl malonate (8.080 g, 50 mmol) and hydrazine hydrate (5.006 g, 100 mmol) were mixed together in a beaker with constant stirring at ambient temperature. The reaction was carried out without solvent. The precipitate was form when the solution was turned from yellowish to white. After the precipitation the product was filtered off on a buckner funnel and washed with ethanol and dried in a vacuum desicator over anhydrous $CaCl_2$. A silky white amorphous product 8.800g was obtained (60% yield). The melting point of the compound was recorded at $125^{\circ}C$ - $130^{\circ}C$.

The substance was soluble in water and Dimethyl formamide (DMF) and insoluble in ethanol, methanol, dichlormethane, diethylether, petether, carbon tetrachloride and n-hexane.

Reaction of the preparation of the ligand:



3.1.2 Preparation of Metal Perchlorate.

Metal perchlorate was prepared from analytically pure metal carbonate by treatment with 70% perchloric acid. The treatment was done in the following way:

About 100 mL 70% perchloric acid was taken in a 250 mL beaker and then copper carbonate was added slowly with continuous stirring. The addition of copper carbonate was continued until the bubbles were disappeared. Access amount of copper carbonate was added and kept it 12 hours to ensure the complete of the reaction. Then water and alcohol mixture was added with continuous stirring and filtered. The resulting solids were filtered, washed with ethanol till free from excess acid and recrystallized several times from ethanol. Copper perchlorate is partially soluble in alcohol. Copper perchlorate solution was also standardized by iodometric titration.

3.1.3 PREPARATION OF MACROCYCLIC COMPLEXES OF Cu (II).

3.1.3.1 Preparation of $[\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$ Complex 1

To the solution of malonodihydrazide $\text{C}_3\text{H}_8\text{N}_4\text{O}_2$ (0.528 g, 4 mmol was dissolved in 10 mL water) and formaldehyde solution (0.320 g, 4 mmol 37%) was added. To the above mixture copper (II) perchlorate hexahydrate (0.741 g, 2 mmol in 10 mL water) was added and the whole mixture was refluxed with constant stirring for two hours at room temperature. A light blue precipitate was formed immediately. Then the product was filtered off on a buckner funnel washed with ethanol and dried in a vacuum desicator over anhydrous CaCl_2 .

The melting point of the compound was 224-227⁰C and yield was 1.89 g (70%). The compound was soluble in DMF, DMSO and insoluble in chloroform, ethanol, and acetone.

3.1.3.2 Preparation of [Cu (C₁₀H₂₀N₈O₄) (ClO₄)₂] complex 2

To the solution of malonodihydrazide (0.792 g, 6 mmol in 10 mL water), acetaldehyde (0.264 g, 6 mmol in 10 mL water) was added. To the above mixture copper (II) perchlorate hexahydrate (1.112 g, 3 mmol in 10 mL water) was added and the whole mixture was refluxed with constant stirring for 6 hours and cooled down. A yellow green precipitate was filtered off on a buckner funnel. The product was washed with ethanol. The product was dried in a vacuum desicator over anhydrous CaCl₂.

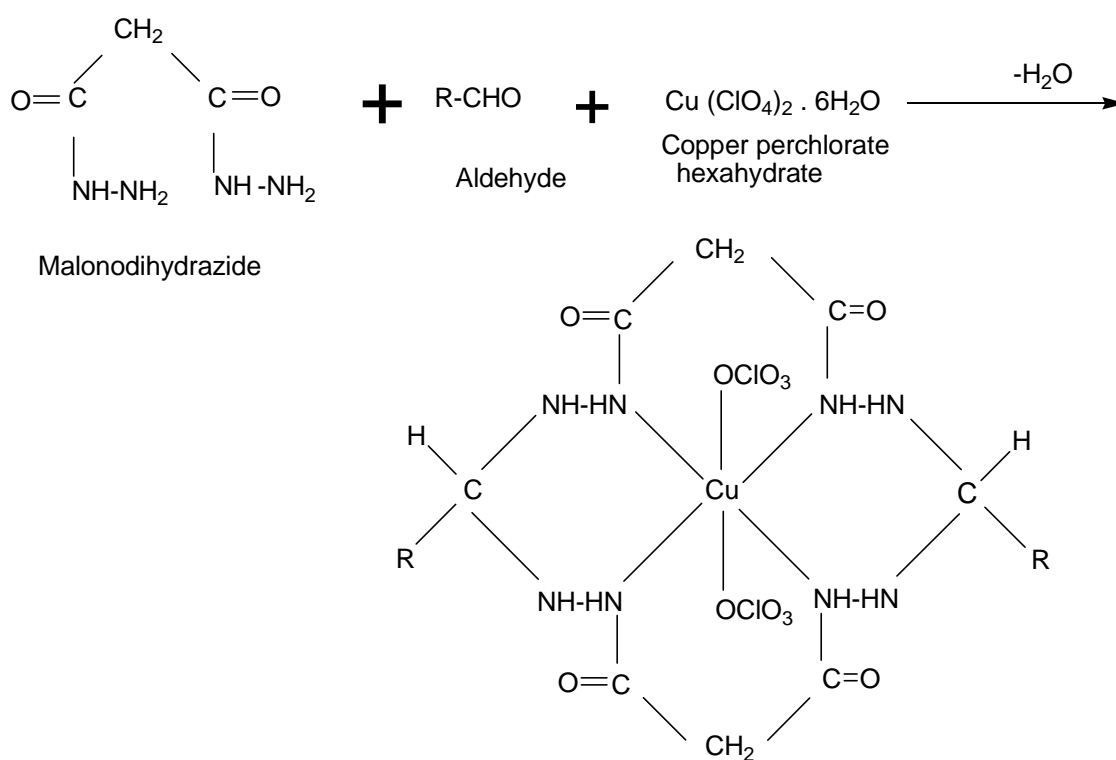
The melting point of the compound was 232-237⁰ C and yield was 1.41 g (65%). The compound was soluble in DMF, DMSO and insoluble in acetone, alcohol and chloroform.

3.1.3.3 Preparation of [Cu (C₂₀H₂₄N₈O₄) (ClO₄)₂] complex 3

To the solution of malonodihydrazide, C₃H₈N₄O₂ (0.528 g, 4 mmol in 10 mL water) and benzaldehyde (0.528 g, 4 mmol) were mixed together. To the above mixture copper (II) perchlorate hexahydrate (0.7410 g, 2 mmol in 10 mL water) was added and the whole mixture was refluxed with constant stirring for 4 hours and cooled down to room temperature. An off white precipitated was formed. The product was filtered off on a buckner funnel and washed with ethanol. The product was dried in a vacuum desicator over anhydrous CaCl₂.

The melting point of the compound was 251-256⁰C and yield was 1.01 g (75%).
 The compound was soluble in DMF, DMSO and insoluble in acetone, ethanol, water and chloroform.

Reaction of the preparation of the complexes:



Where, R = H, CH₃ -, C₆H₅ -

RESULTS AND DISCUSSION

In this work, new macrocyclic complexes of the metal ions Cu (II) were synthesized from formaldehyde, acetaldehyde and benzaldehyde in aqueous solution and the products were characterized by solubility tests, melting point determination, elemental analysis, metal estimation, conductivity and magnetic susceptibility measurements as well as by spectroscopic techniques.

4.1 Characterization of metal complexes

4.1.1 Solubility tests

Qualitative tests were performed to determine the solubility of synthesized Cu (II) complexes (1-3) in six different solvents. The results obtained from observation are summarized as shown below in Table 4.1.

Table 4.1: The solubility of Cu (II) complexes (1-3) in different solvents

No	Solvent	Copper complex
1	Ethanol	Insoluble
2	Acetone	Insoluble
3	DMSO	Soluble
4	DMF	Soluble
5	Water	Insoluble
6	Chloroform	Insoluble

According to the results, it can be said that the solubility behavior of the Cu(II) complexes (1-3) for non-electrolytic in nature.^{90, 91}

4.1.2 Results of melting point determination (Test of purity)

Results of the melting point determination for the as-synthesized copper complexes (1-3) are presented in Table 4.2 below.

Table 4.2: Mean differences in the melting points of the complexes (1-3).

Complex	Melting point ($^{\circ}\text{C}$)	Mean difference
1. $[\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$	224 – 227	3
2. $[\text{Cu}(\text{C}_{10}\text{H}_{20}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$	232 – 234	2
3. $[\text{Cu}(\text{C}_{20}\text{H}_{24}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$	251 – 254	3

The accepted melting point value for a pure organic solid compound must be sharp at a specific temperature but in some cases it could be acceptable if falling within a narrow temperature difference (range) of 0.5 to 2 $^{\circ}\text{C}$ between replicate measurements. If a compound is contaminated with even small amount of impurity, its melting point falls in large temperature range. Since the mean melting point differences for these complexes show slight deviation from the acceptable range, it can be suggested that these complexes (1-3) contained some impurity. The fact that their melting point difference are not very much exaggerated that (not large difference) may leave us some room to assume that the contaminants (impurities) could not be attributed to the formation of mixed products from any parallel or side reaction.

4.1.3 Results of conductivity measurement

The results obtained from the measurements of specific conductance of a 3×10^{-4} M solutions of the respective complexes (1-3) in DMSO at different temperature are summarized in Table 4.3 below.

Table 4.3: Measurement of conductance of Copper complexes (1-3).

Sample	Solvent	Temperature($^{\circ}$ C)	Specific conductance(μ S/cm)
1. $[\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$	DMSO	23.1	1.44
		24.5	1.56
		25.4	1.76
		Mean	1.58
2. $[\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$	DMSO	24.6	4.32
		25.3	4.50
		25.9	4.80
		Mean	4.54
3. $[\text{Cu}(\text{C}_{20}\text{H}_{24}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$	DMSO	23.4	2.51
		24.3	2.65
		25.6	2.75
		Mean	2.63

As indicated in Table-4.3 (above), Since the above value of conductance of Cu (II) complexes (1-3) is indeed below the value assigned ($49 \mu\text{S/cm}$ in DMSO) for non- electrolyte.

4.1.4 Elemental analysis and Metal estimation

The elemental analyses (C, H and N) and metal estimation data of the complexes are consistent with the proposed formula.

Table 4.4: Elemental Analytical data of compounds (1-3).

No	Compounds	%C		%H		%N	
		Calculated	Found	Calculated	Found	Calculated	Found
1	[Cu(C ₈ H ₁₆ N ₈ O ₄)(ClO ₄) ₂]	17.43	17.21	2.90	2.79	20.34	20.40
2	[Cu(C ₁₀ H ₂₀ N ₈ O ₄)(ClO ₄) ₂]	20.74	20.51	3.45	3.50	19.36	19.11
3	[Cu(C ₂₀ H ₂₄ N ₈ O ₄)(ClO ₄) ₂]	34.16	34.10	3.41	3.23	15.94	15.78

From the elemental analysis it is observed that the found value is almost equal to calculated value, which is indicated that elemental analysis data gave supportive evidence for successful formation of the complexes.

Table- 4.5: Physical appearance and Metal estimation of compounds (1-3).

No	Compounds	Yield%	Colour	M %	
				Calculated	Observed
1	[Cu(C ₈ H ₁₆ N ₈ O ₄)(ClO ₄) ₂]	70	Olive green	11.53	10.91
2	[Cu(C ₁₀ H ₂₀ N ₈ O ₄)(ClO ₄) ₂]	65	Yellow green	10.97	10.45
3	[Cu(C ₂₀ H ₂₄ N ₈ O ₄)(ClO ₄) ₂]	75	Off white	9.04	8.91

From the observed data table it is showed that the amount of copper metal ion is almost equal to calculated value, which is indicated the formation of complex with the copper metal ion.

4.1.5 Magnetic susceptibility of Cu (II) complexes

Magnetic susceptibility of the complexes was determined using a magnetic balance. The effective magnetic moment (μ_{eff}) was calculated using the formula

$$\mu_{\text{eff}} = 2.824(\chi_{\text{M}}T)^{1/2}$$

Magnetic susceptibility of the complexes was recorded at room temperature. The magnetic moment measurement data (Table 4.6) of the Cu (II) complexes (1-3) showed (1.24-1.77) B.M. This result indicates that the Cu (II) complex is paramagnetic with effective magnetic moment (μ_{eff}) the range of (1.24 - 1.77) BM.

It can be assumed that the Cu (II) ion should exist in the complex with only one unpaired electron occupying one of the upper energy d-orbital's with $d^9 (t_{2g}^6 - e_g^3)$ configuration.

Table 4.6: Magnetic susceptibility of Cu (II) complexes (1-3).T=301K

No	Compounds	Sample Length , l in cm	Weight of the sample , m in gm	Susceptibility Of the empty tube , R_0	Susceptibility Of the sample with test tube , R	Mass susceptibility $\chi_g \times 10^{-6}$ C.G.S unit	Molecular Weight , M	Molar Susceptibility $\chi_m \times 10^{-3}$ C.G.S unit	μ_{eff} B.M
1	[Cu(C ₈ H ₁₆ N ₈ O ₄)(ClO ₄) ₂]	2.9	0.0794	-59	-32	2.057	550.5	1.124	1.77
2	[Cu(C ₁₀ H ₂₀ N ₈ O ₄)(ClO ₄) ₂]	3.3	0.0626	-38	-31	0.769	578.5	0.442	1.24
3	[Cu(C ₂₀ H ₂₄ N ₈ O ₄)(ClO ₄) ₂]	2.6	0.093	-67	-66	0.583	754.5	0.439	1.33

4.1.6 UV-Vis absorption spectra

For many coordination compounds, the electronic absorption spectrum provides a convenient method for determining the magnitude of the effect of ligands on the d-orbitals of a transition metal ion and this helps us to study its effect on coordination compound of any geometry. The UV-Vis spectra transitions are generally broad because vibrational and rotational energy levels are superimposed on top of the energy levels.

Two absorption bands, assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions were observed in the spectra of both Cu (II) complexes. As these transitions are shifted towards the lower and higher frequencies, respectively it can be confirmed that coordination of the ligands to the metal ions has most possibly occurred. Charge transfer transitions are generally intense compared with ligand field transitions, the former (CT transitions) give rise to intense absorption bands whereas the later (d-d transition) give much weaker bands.

The complexes showed (Fig. 4.1) a band at 590 nm represent the d-d transition of ${}^6T_{2g} \rightarrow {}^3E_g$ for d^9 configuration of Cu (II) suggested they octahedral geometry⁹². The band observed due to 415 nm assigned to the $\pi \rightarrow \pi^*$ transition of the macrocyclic ligand. These absorption bands are in the range of literature value for an octahedral complex.

4.1.7 IR spectra of Cu (II) complexes

The infrared spectra of the complexes (1-3) are shown in Fig (4.2-4.4). The infrared spectral data (Table 4.7) of the complexes showed a strong and broad band at (3216-3253) cm^{-1} which is assigned for the $\nu(\text{N-H})$ stretching^{93,94}. Due to coordination the $\nu(\text{N-H})$ stretching of the amide group goes to the higher frequency at (3238, 3253) cm^{-1} region as compared to the starting material malonodihydrazide⁹⁵. In the complexes the terminal- NH_2 groups of malonodihydrazide condensed with the aldehyde moiety form a new secondary-NH group which may appear as a strong and broad band. [The starting material malonodihydrazide have three $\nu(\text{N-H})$ bands at (3248, 3213, 3050) cm^{-1} . The bands at (3248, 3050) cm^{-1} for the asymmetric and symmetric $\nu(\text{N-H})$ stretching of the terminal NH_2 moiety and 3213 cm^{-1} for amidic (N-H) group].

The complexes showed a broad band at (2979-3078) cm^{-1} is suggested for the $\nu(\text{C-H})$ stretching of aliphatic moiety⁹². The complexes showed a strong band at (1662-1685) cm^{-1} which represent the $\nu(\text{C=O})$ of NH-NH-CO-CH_2 moiety⁹². Three or four band at (621-1162) cm^{-1} region also indicated the $\nu_1, \nu_2, \nu_3, \nu_4$ bands of (ClO_4^-) moiety. These stretching frequency is suggested the coordination of perchlorate moiety to the metal through the O atom^{96, 97}. A medium band at (416-445) cm^{-1} region is tentatively attributed to the $\nu(\text{M-N})$ mode^{93, 94} indicating the coordination of the ligand to the metal through the nitrogen atom.

Table – 4.7: Important infrared spectral bands of compounds (1-3).

No	Compounds	V(C-H) cm ⁻¹	V(C=O) cm ⁻¹	V(NH) cm ⁻¹	V(M-N) cm ⁻¹	V(ClO ₄) cm ⁻¹
1	[Cu(C ₈ H ₁₆ N ₈ O ₄)(ClO ₄) ₂]	3022	1685	3253	418	1154 1083 626
2	[Cu(C ₁₀ H ₂₀ N ₈ O ₄)(ClO ₄) ₂]	2979	1682	3238	416	1122 1091 626
3	[Cu(C ₂₀ H ₂₄ N ₈ O ₄)(ClO ₄) ₂]	3078	1662	3216	445	1162 1069 621

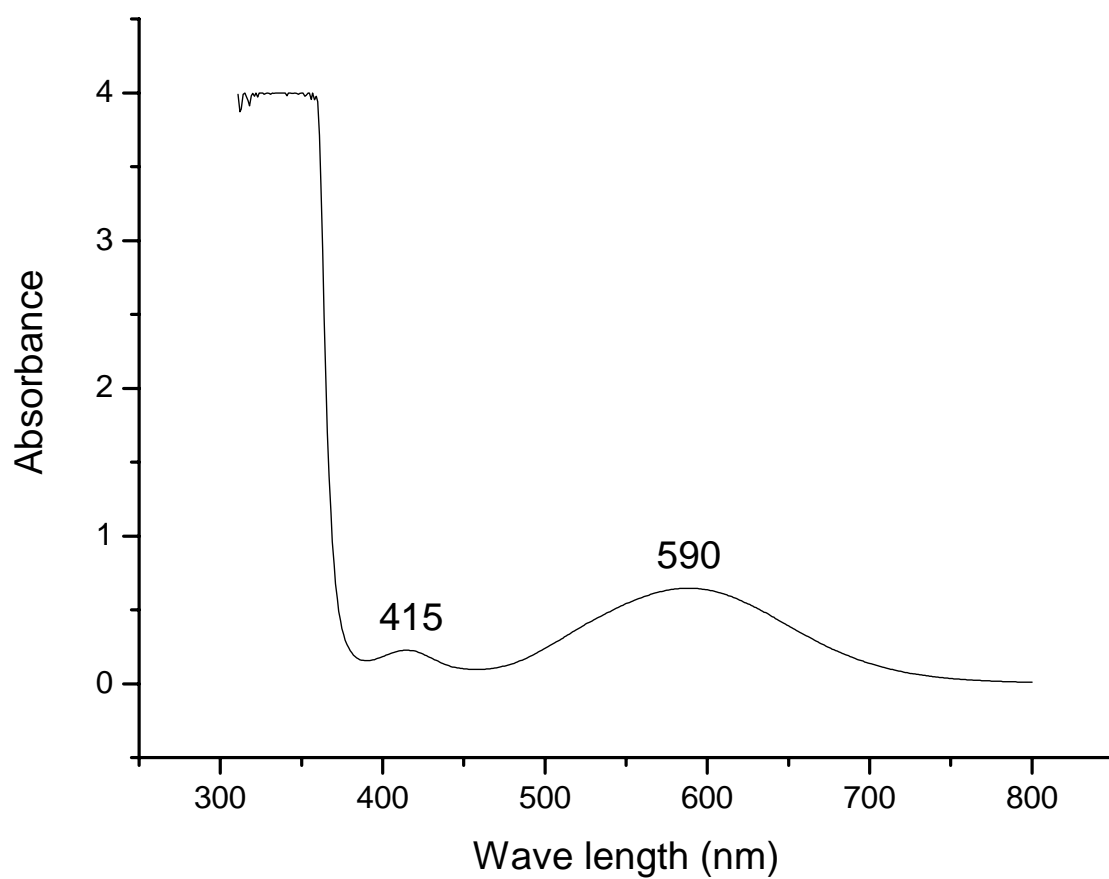


Fig-4.1: UV-Visible Spectrum of $[\text{Cu} (\text{C}_8\text{H}_{16}\text{N}_8\text{O}_4) (\text{ClO}_4)_2]$ Complex 1.

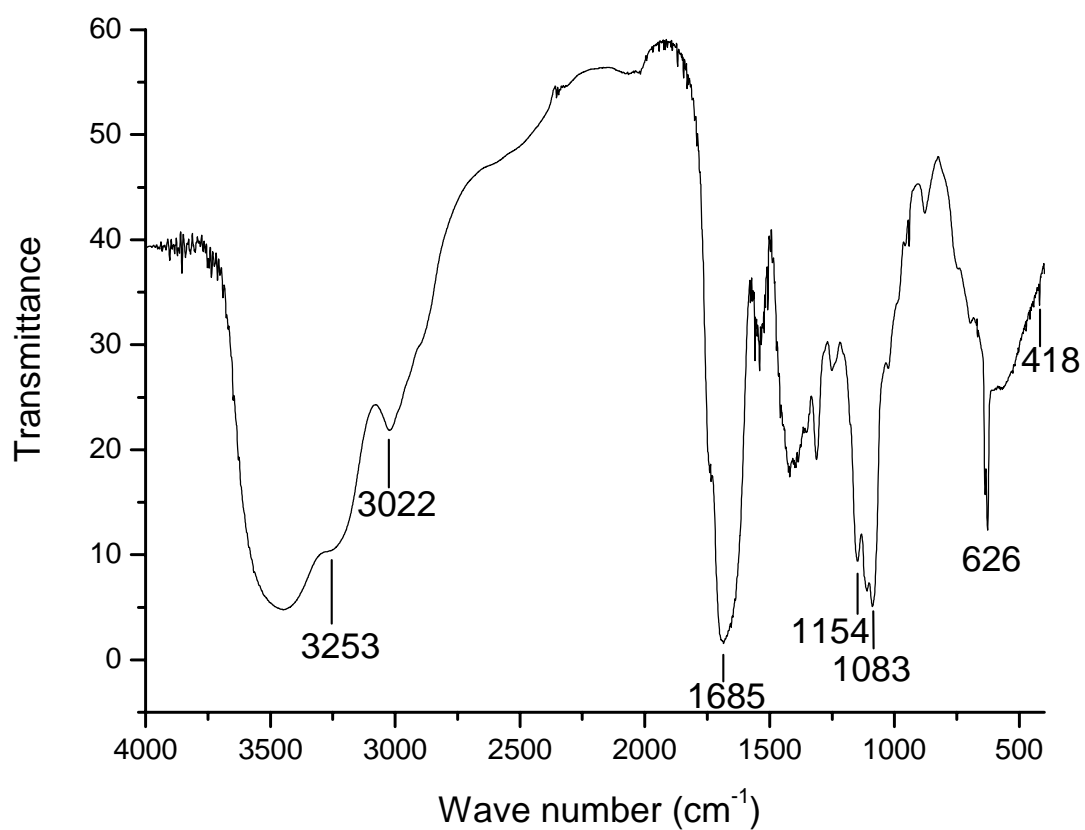


Fig-4.2: Infrared Spectrum of $[\text{Cu} (\text{C}_8\text{H}_{16}\text{N}_8\text{O}_4) (\text{ClO}_4)_2]$ complex 1.

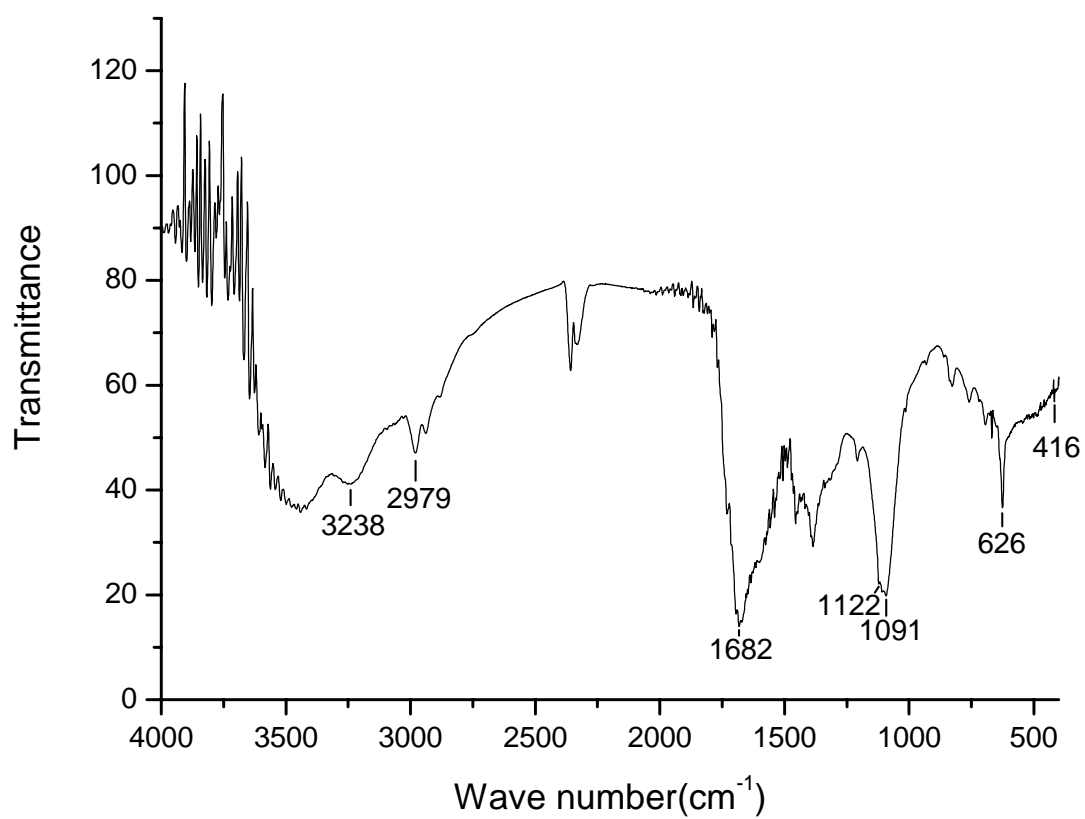


Fig-4.3: Infrared Spectrum of $[\text{Cu}(\text{C}_{10}\text{H}_{20}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$ complex 2.

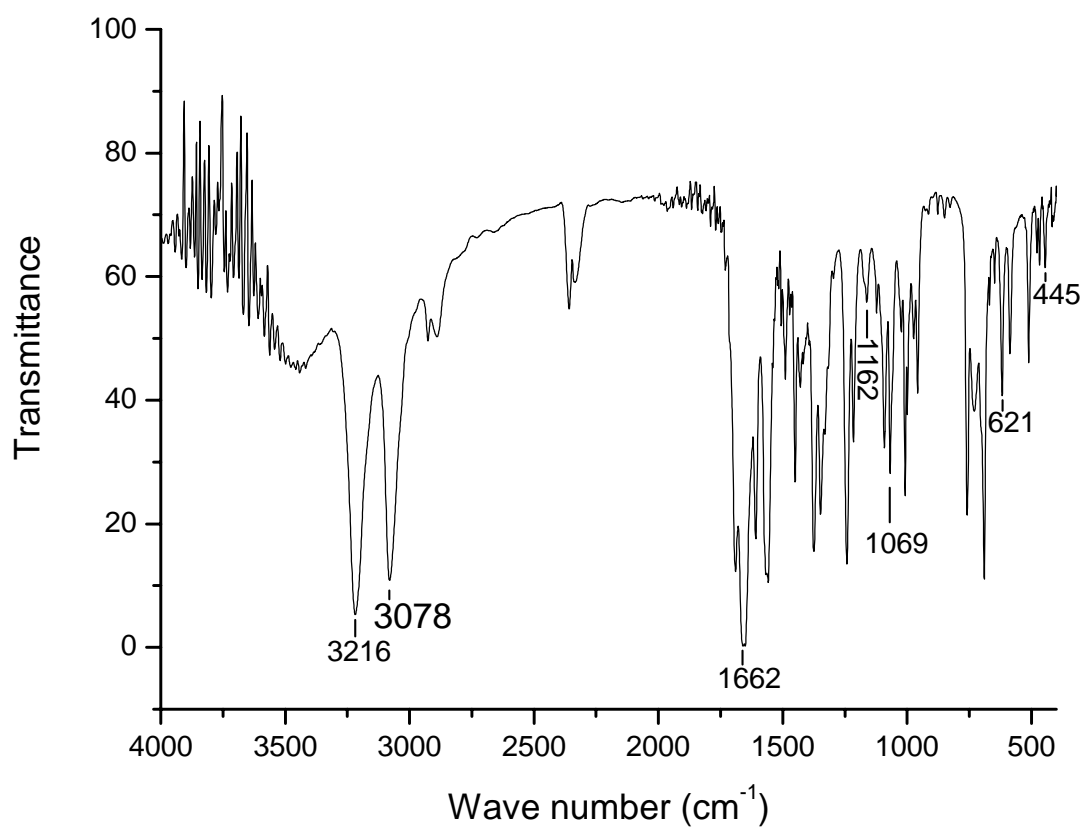
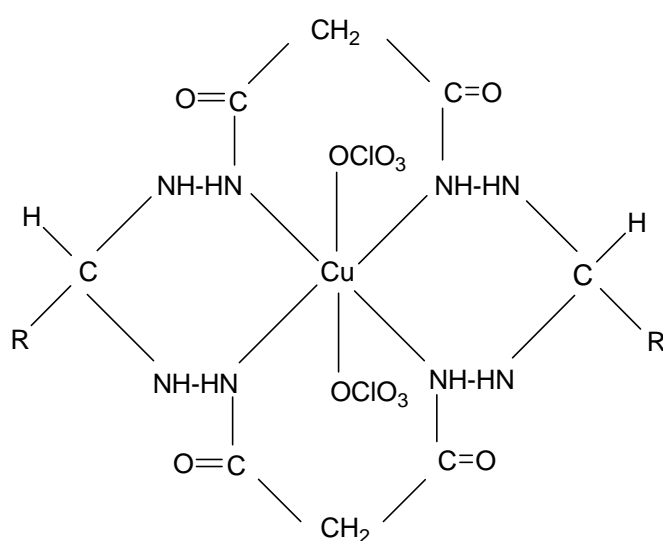


Fig-4.4: Infrared Spectrum of $[\text{Cu}(\text{C}_{20}\text{H}_{24}\text{N}_8\text{O}_4)(\text{ClO}_4)_2]$ complex 3.

4.2. Structural Elucidation of the complexes

Based on the magnetic moment, elemental analysis, FTIR, conductance, and UV data, it can be proposed that the Cu (II) complex may have an octahedral geometry. The complexes are thought to be formed as a result of template condensation of aldehydes, malonodihydrazide with corresponding metal perchlorate of Cu (ClO₄)₂. It was expected that this template reaction should result in 16-membered tetraaza macrocyclic complexes.



Where, R = H, CH₃ -, C₆H₅ -

Fig-4.5: Probable structure of the complexes

5. SUMMARY AND CONCLUSION

5.1. Summary

The main objective of this study was to synthesize and characterize a new series of tetraaza macrocyclic complexes of Cu (II) metal ions derived from the template condensation of formaldehyde, acetaldehyde, benzaldehyde, and corresponding metal salts $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in aqueous medium. The synthesized complexes of Cu (II) were characterized by using UV-Vis, FT-IR as well as by conductivity and elemental analysis, magnetic susceptibility measurements, and melting point and solubility determinations. Furthermore, their magnetic susceptibility values, UV-Vis spectra and FTIR spectra give supportive evidences for the possible formation of the proposed octahedral geometry for the copper (II) complexes.

5.2. Conclusion

New Cu (II) complexes (1-3) were prepared from the template condensation of formaldehyde, acetaldehyde, benzaldehyde and corresponding metal salts $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in aqueous medium. Various spectroscopic and analytical method such as, UV-Vis, elemental analysis, conductivity measurement and magnetic susceptibility were adapted for the characterization of the complexes (1-3). The results suggested that Cu (II) complexes obtained by the direct template methods presumably octahedral geometries. The IR spectral data gave supportive evidence for the successful formation of the complexes.

Some of the physical data obtained from melting point and solubility determination suggested the purity of the complexes (1-3).

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