SYNTHESIS AND CHARACTERIZATION OF APPROPRIATE MACROCYCLIC COMPLEXES OF NICKEL (II) METAL ION

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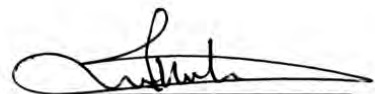MACROCYCLIC COMPLEXES OF Ni (II) METAL ION
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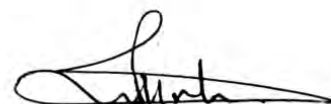Roll No.: 1014032704 F, Session: October-2014

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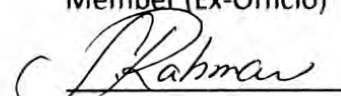
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To my parents, who sacrificed

every personal comfort

to see me through my basic education

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LIST OF ABBREVIATION

AAS	Atomic Absorption Spectroscopy
BM	Bohr Magnetron
DMF	Dimethyl Formamide
DMSO	Dimethyl Sulphoxide $(CH_3)_2S=O$
EtOH	Ethyl Alcohol
FTIR	Fourier Transform Infra-Red
UV-Vis	Ultra violet-visible
Sc	Specific conductance
Λ_M	Molar conductance
X_g	Gram magnetic susceptibility
X_{mol}	Molar magnetic susceptibility
μ_{eff}	Magnetic moment
μS	Micro Semen
M.pt	Melting point
Scm^2mol^{-1}	Semen centimeter square per mol
μ_{eff}	Effective magnetic moment

SYNTHESIS AND CHARACTERIZATION OF APPROPRIATE MACROCYCLIC COMPLEXES OF NICKEL (II) METAL ION

ABSTRACT

In this study of some macrocyclic complexes of Ni (II) containing a ligand with tetraaza tetrahydrazin moiety were prepared by template condensation of malonodihydrazide ($C_3H_8N_4O_2$) with different aldehydes. A new macrocyclic complexes of the type [Ni($C_8H_{16}N_8O_4$)(ClO_4)$_2$], [Ni($C_{10}H_{20}N_8O_4$)(ClO_4)$_2$] and [Ni($C_{20}H_{24}N_8O_4$)(ClO_4)$_2$]were synthesized by the template condensation of aldehydes, malonodihydrazide with corresponding metal perchlorate of Ni(ClO_4)$_2$ in water medium. The complexes were distinctly colored and stable to atmospheric conditions. These complexes were characterized by UV-Vis, IR as well as by the measurements of their respective specific conductance and magnetic susceptibility. The specific conductance values obtained in DMSO for all the complexes indicated their nonelectrolyte nature. Furthermore, from their magnetic susceptibility values, UV-Vis electronic and FTIR spectra, the newly prepared complexes were expected to have octahedral geometry, with the respective divalent metal ion Ni (II) occupying the center of an octahedron.

GENERAL INTRODUCTION

1. INTRODUCTION

Nickel is silver-white, with high electrical and thermal conductivities and MP 1452^0C, and it can be drawn, rolled, forged, and polished. The trend toward decreased stability of higher oxidation states continues with nickel so that only Ni (II) occurs in the ordinary chemistry of element. However, there is a complex array of stereochemistry associated with this species. The higher oxidation states are relatively rare but are gaining in importance. Both Ni (I) and Ni (II) species are being studied because of possible involvement of these oxidation states in nickel-containing metalloenzymes[1].

Macrocyclic chemistry is a field of coordination chemistry that has bases for a vast number of important naturally occurring and synthesized macrocycles and their complexes. It is a very active and rapidly growing field of research that overlaps with interesting fields of chemistry such as catalytic chemistry, biomimetic chemistry and supramolecular chemistry to which a number of scientists have been attracted.

Macrocycles are large cyclic molecules which contain donor atom 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 atoms[2]. Macrocyclic molecules usually have a central hydrophilic cavity while the exterior of the macrocycles are hydrophobic[3].This

kind of arrangement provide the ability to the macrocyclic molecule to bind to a wide variety of cations such that the hydrophilic cavity would allow the metal ion to be fixed at the center of the molecule, while the hydrophobic exterior would enable the resulting complex to solubilize ionic substances in non-aqueous solvents and membrane media[4]. Macrocycles are generally present in proteins and enzymes and can thus complex readily to heavy metals they get in to the biological system of human beings or animals. Thus this kind of complexation of heavy metal ions with these types of macrocycles will actually prevent the heavy metals from being absorbed by the organs in the body.

A very large number of synthetic and natural macrocycles have 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 attention .For example Casella compared complexes of tetraaza macrocycles with their open-chain analogues. They opted to apply the term "macrocyclic effect" to extra stability of the former assuming this to be a logical extension of the well-known chelate effect[5].

The author gave more insight of the "Macrocyclic effect '' for attributing very high thermodynamic stability and extreme kinetic inertness of transition metal complexes of polyazamacrocyclic ligands for their versatility and enhanced use for many industrial applications[5].

Transition metal macrocyclic complexes have received much attention as an active part of metalloenzymes as biomimic model compounds due to their resemblance with natural proteins like hemerythrin and enzymes[6,7].The metal ion chemistry of macrocyclic ligands has now become a major subdivision of inorganic chemistry. The macrocyclic complexes of metal ions can be 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 hinder this problem, the "metal template effect" method involves for the synthesis of macrocyclic complexes; where in the presence of metal ions in the cyclization reaction markedly increase the yield of the products. 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 formed[8].

The effect of metal ions in promoting certain cyclization reactions was initially discovered in 1928 when the dark blue complex of the macrocycle was obtained by a template reaction as a side product formed during the preparation of phthalimide by reaction of phthalic anhydride and ammonia in an iron vessel. This dark blue compound was later shown to be Fe (II) complex of the highly conjugated macrocycle phthalocyanine which, as mentioned before, bears a strong structural resemblance to the natural porphyrine systems[9].

The value of macrocyclic molecules presses closely when Pedersen and Frensdorff discover on dibenzo [18] crown-6[10]. This observation led to the discovery of the

coordination power of crown ethers which then led to the synthesis of other macrocycles with a variety of donor atoms, such as nitrogen, oxygen, sulphur and phosphorus[11].

The significance extends from large number of life composing and naturally occurring complexes to vast number of synthetically made ones for diverse biological and nonbiological functions. Some of the important and life giving naturally occurring macrocyclic metal complexes are the iron porphyrin of hemoglobin, the cobalt-Corrine of vitamin B_{12}, the magnesium-hydroporphyrin of chlorophyll and the crown ethers and cryptands of alkali and alkaline earth metals[12]. The above mentioned naturally occurring macrocyclic compounds have been known for a long time, but it is only in the last 30 years that a large number of synthetic macrocyclic compounds have been prepared and investigated.

Importance of complexes containing macrocyclic ligands has led to considerable effort being invested in developing reliable and inexpensive synthetic routes for these compounds. These macrocycles which contain varying combinations of aza (N), oxa (O), phospha (P) and sulfa (S) ligating atoms can be tailored to accommodate specific metal ions by the fine tuning of ligand design features, such as the macrocyclic hole size, nature of the ligand donors, donor set, donor array, ligand conjugation, ligand substitution, number and sizes of the chelate rings, ligand flexibility and nature of metal. Aza-type ligands appear very promising for potential use as antifertile, antibacterial, antifungal agents and as biological properties[13].

A variety of azamacrocycle compounds are formed by Mannich condensations of amines with an aldehyde, usually methanol, in the presence of a templating metal ion, usually Ni (II) or Cu (II) (though the reactions are often facile with Pd (II), Pt (II), or Au (III)). Condensations of methanol and ammonia with combinations of mono-, di-, tri-, tetra-, and penta amines form a variety of bis and tricyclic azamacrocycle compounds. It was found, that smaller metal ions prefer to bind to a system that would provide 6 membered rings, while larger metal ions prefer to form 5- membered rings[2].

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 reagents[11]. In general, these new tetraaza macrocycle complexes may serve as models for metalloenzymes act as protein metal binding sites in biological systems, serve as models to study as therapeutic reagents for the treatment of metal toxification as well as help for extractions of ions by transport through artificial and natural membrane[14].

1.1. Chemistry of Macrocyclic Complex

There are three reasons why macrocyclic ligands often yield complexes which show unusual properties : I) Complex formation geometrical factors, arising from the cyclic nature of the ligands ,II) If the cycle is fully conjugated and incorporates (4n+2) π electrons then enhanced electron delocalization and ligand stability are characteristic of the resulting Huckel aromatic system and III) Macrocyclic ligand

complexes are almost always found to be considerably more stable thermodynamically and kinetically than their corresponding open chain analogues[2].

Macrocyclic development began in the late 1960 with initial applications focused towards modeling biological processes such as ion transport. These macrocycles initially include the oxygen based crown ethers of Pedersen and cryptands of Lehn[14].Both of which exhibit high selectivity toward alkali and alkaline earth metal ions. Several years later the concept of "pre-organized" cavity resulted in the synthesis of cavitands. For selective encapsulation of metals is so as to be used in metal ion extraction. The recognition of the importance of the complexes of macrocyclic ligands has led to considerable efforts being invested in developing reliable and inexpensive synthetic routes for these compounds[15].

Synthetic macrocycles are a growing class of compounds with a wide range of different molecular topologies and sets of donor atoms[16]. The studies of macrocycles have undergone tremendous growth in recent years and their complexation chemistry with a wide variety of metal ions has been extensively studied. Macrocyclic complexes are considered to mimic the synthetic models of metalloporphyrins and metallocorrins due to their intrinsic structural properties.[17,18]

Macrocyclic complexes have received special attention because of their mixed soft–hard donor character and versatile coordination behavior and their pharmacological properties, i.e. Toxicity against bacterial growth.[19,20,21] In recent

years the chemistry of macrocyclic metal complexes has attracted the interest of both inorganic and bioorganic chemists because metals have an esteemed place within medical biochemistry which has led to developments in cancer care, infection control and Diabetes.[22]They have been widely explored for their antitubercular, antitumor and anti HIV.[23,24]

1.2 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.[25,26]

1.3 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-oritals.

1.4 CLASSIFICATION OF MACROCYCLIC LIGANDS

Macrocyclic ligands are defined as cyclic molecules generally consisting of organic frames into which heteroatoms, capable of binding to substrates, have been interspersed. Some reports of 'synthetic' macrocycles (as opposed to the naturally occurring species such as porphyrins, Corrine, and chlorines) appeared as early as 1936, when the first synthesis of 1,4,8,11-tetraazacyclotetradecane was reported.[27]Nonetheless, the field only began to blossom in the early 1960s with the pioneering work of Busch[28] and Curtis' discovery of the nickel mediated condensation of $[Ni(en)_3]^{2+}$ with acetone.[29]The early macrocycles were synthesized with an eye to mimicking biologically occurring macrocycles such as the porphyrins, corrins, chlorins, and, more recently, the corphins. Another area of macrocyclic development began in the late 1960s and initial applications were focused toward modeling biological processes such as ion transport. These macrocycles initially included the oxygen-based crown ethers of Pedersen,[30]and the mixed oxygen–nitrogen bicyclic cryptands of Lehn[31]both of which exhibit high selectivity toward alkali and alkaline earth metal ions. Several years later, the

concept of 'preorganized' cavities resulted in the synthesis of the cavitands by Cram.[32]

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. Oxygenderived macrocycles are noted for complexation with alkali and alkaline earth metal ions, as well as with organic cations and molecular substrates. In this latter situation, associations tend to be electrostatic in nature, and in many instances hydrogen-bonding interactions are vital to complex formation. Macrocyclic ligands will be classified, for the purposes of this article, as rings with at least nine members and three or more donor atoms. In a number of cases of unique structural units, elegant descriptive names have developed, which more appropriately describe the macrocyclic shape. Macrocycles will be classified as to donor types and, within the donor types, specific classifications of macrocycles will be noted where applicable.

1.5 Polyaza Macrocycles

1.5.1 Simple Polyaza Macrocycles

The tetraaza macrocycle had been the most studied because of the relationship of these molecules to naturally occurring tetraaza macrocycles, such as the porphyrins and corrins. Currently, with interest in metal–metal interactions, increased activity has occurred in the area of larger macrocycles capable of

incorporating more than one metal ion.[33]Interest in the smaller triaza macrocycles has also accelerated in recent years.[34]Added to 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 chains as in fig.-1.1
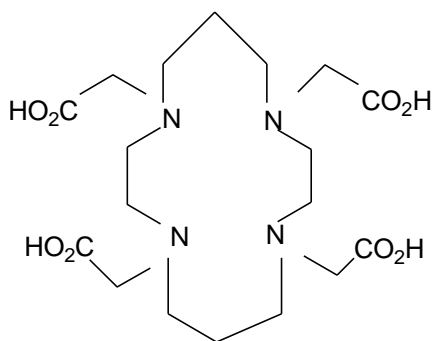
Fig. 1.1 Functionalized macrocycle

1.5.2 Sepulchrates

Sepulchrates are polyaza cage macrocycles. They are noted for their exceptionally strong hold on encapsulated metal ions.[35] (as in figure 1.3)
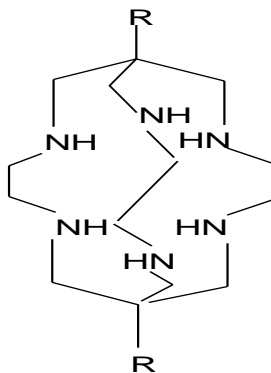
Fig. 1.2 Sepulchrate

1.5.3 Expanded Porphyrins

Expanded porphyrins are macrocycles based on the pyrrolic backbone of porphyrins, but are expanded in size to achieve a larger cavity or binucleating

capabilities which provide another mechanism for achieving complexation of morethan one metal ion. They are joined by a bridge linking two simple macrocycles.[36](as in figure 1.4)
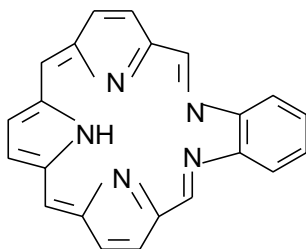
Fig. 1.3 Expanded porphyrin

1.6 Mixed Donor Macrocycles

1.6.1 Simple Mixed Donor Macrocycles

The simple mixed donor macrocycles at one time were the major source of study of the influence of the incorporation of 'soft' phosphorus and arsenic donors into macrocycles.[37]Mixed oxygen–nitrogen macrocycles have been studied quite extensively, since they serve as bridges for examining the coordination tendencies of the aza macrocycles and the oxacrown ethers.[38](as in figure 1.5)
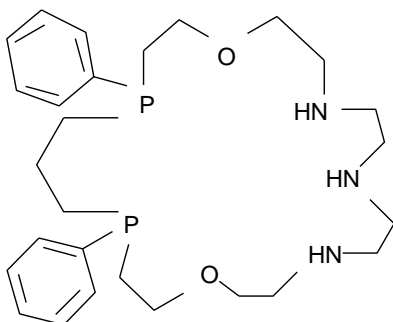
Fig. 1.4 Mixed donor macrocycle

1.6.2 Cryptands

Cryptands are bicyclic macrocycles which can contain a variety of donor atoms with bridgehead nitrogen atoms. They are highly selective for alkali and alkaline earth metal ions.(as shown in figure 1.6)
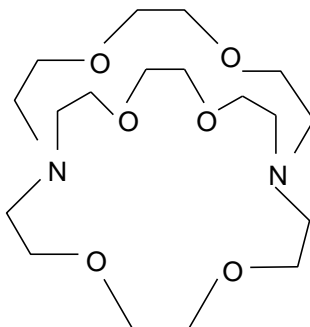
Fig.1.5 Cryptand

1.6.3 Compartmental Ligands

Compartmental ligands are macrocyclic ligands which contain 'compartments' for housing more than one metal ion.[39](as in figure 1.7)
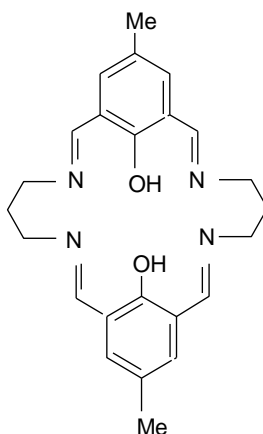
Fig. 1.6 Compartmental ligand

1.7 Polyoxa Macrocycles

Polyoxa macrocycles comprise an extensive area of research.[40]Some of these macrocycles have been utilized predominantly for purposes other than metal ion complexation.[41]

1.7.1 Polyether Macrocycles

Polyether macrocycles arethe simplest of the polyoxamacrocycles. The commonly use name for these macrocycle is the crown ethers, due to their crown-like structure in the sold state. These molecules have been extensively studied as complexing agents for the alkali and alkaline earth metal ions.(as shown in figure 1.8)
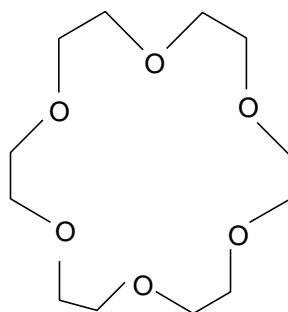
Fig. 1.7 Crown ether

1.7.2 Spherands and Hemispherands

These consist of an arrangement of phenyl groups which provide a preorganized cavity for complexation.[42](as shown in figure 1.9)
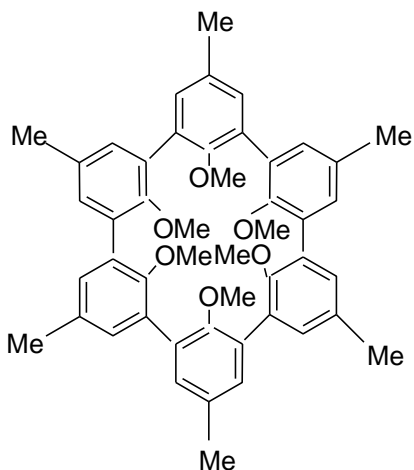
Fig. 1.8 Hemispherand

1.7.3 Polythia, Polyphospha, and Polyarsa Macrocycles

Polythia macrocycles have been known since the 1930s.[43]These are the most extensively studied macrocycles in line after the polyoxa and polyaza macrocycles. The 'pure' polyphospha macrocycles were first reported in 1975.[44]These macrocycles have been found to complex a variety of transition metals, but have not received the same attention as the more readily accessible polyaza and polyoxa macrocycles. The polyarsa macrocycles comprise one of the least common types of macrocycles.[45](as shown in figure 1.9)
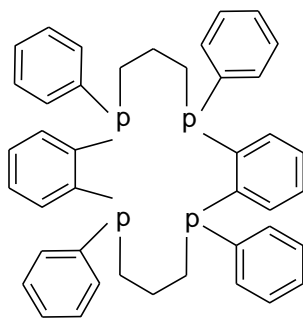
Fig. 1.9 Polyphospha macrocycle

1.8 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. Schiff bases are generally bidentate, tridentate tetradentate, or polydentate ligands capable of forming very stable complexes with transition metals. They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reacting with a metal ion. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, e.g., biological, inorganic and analytical chemistry.[46,47] Applications of many new analytical devices require the presence of organic reagents as essential compounds of the measuring system.

Transition metals are known to form Schiff base complexes and Schiff bases have often been used as chelating ligands in the field of coordination chemistry. Their metal complexes have been of great interest for many years. It is well known that N, O and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules.[48]Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications.[49,50,51] They serve as models for biologically important species and find applications in biomimetic catalytic reactions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities.

There are certain metallo-elements without which the normal functioning of living organism is inconceivable. Among these metallo-elements so called, 'metals of life', four members form an island. These are Na, Mg, K and Ca, the transition

elements are V, Cr, Mn, Fe, Co, Ni, Cu and Zn. These elements are present at trace and ultra-trace quantities and play vital roles at the molecular level in a living system. These transition elements are known to form Schiff base complexes.

Schiff base metal complexes have been known since the mid nineteenth century[52] and even before the general preparation of the Schiff base ligands themselves. Schiff base metal complexes have occupied a central place in the development of coordination chemistry after the work of Jorgensen and Werner.[53]Ettlings isolated a dark green crystalline product from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia. Schiff prepared complexes of metal-salicylaldehyde with primary amines.[54]Subsequently, Schiff[55] prepared complexes from the condensates of urea and salicylaldehyde. Delephine prepared complexes by reacting metal acetate, salicylaldehyde and a primary amine in alcohol and demonstrated a 2:1 stoichiometry.[56]

The study of binuclear and polynuclear complexes of transition metal ions has received a growing attention in recent years. It has been an interesting area for chemists, physicists and biologists, since these complexes form the basis of several research fields such as bioinorganic chemistry, magneto chemistry, material science, catalysis, super conductivity and multi electron redox chemistry etc.[57,58]

The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configurations and structural labiality and are sensitive to the molecular environment. 2-hydroxy Schiff base ligands and their complexes

derived from the reaction of derivatives of salicylaldehyde with amines have been extensively studied in great details for their various crystallographic structural and magnetic features.[59, 60, 61]

Although several kinds of metal ions are found, metallo proteins with transition metal ions are numerous. The main reason for the preference of transition metal ions over the other metal ions is ultimately due to their unique features such as the flexibility to adopt more than one-coordination geometries and the ability to exist in multiple oxidation states. Natural systems utilize one or both of these features for their feasible biological transformations.

A rational control of the nuclearity of transition metal complexes is important to design systems with the desired properties as some of these applications require the presence of more than one metal centre in the particular complex. Indeed, binuclear complexes may have different reactivity than mononuclear counterparts, thereby enabling transformations inaccessible to single metal ions.[62] For instance; nucleic acid hydrolysis is postulated to be facilitated by the cooperative action of two metal ions.[63]

Metal ions play an important role in living system both in growth and in metabolism. The active sites of the biomolecules[64] are coordination complexes comprising of one or more metal ions. The potential relation and those of synthetic coordination complexes has contributed significantly to the emergence of interdisciplinary field of bioinorganic chemistry. The bioinorganic chemistry[65] forms the molecular basis of all possible interactions between the biological

molecules and metal ions which is inturn applied in the field of medicine, biology, environmental sciences, catalysis and technology.

The Ni (II) ions play a central role in biological redox metalloenzymes like plastocyanin, hemocyanin, azurin, galactose oxidase and others.[66] Nickel compounds are present in the active sites of urease and are used extensively in the design and construction of new magnetic materials.

1.9 PREPARATION AND MECHANISM OF SCHIFF BASE LIGANDS

The formation of a Schiff base from an aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis, or upon heating. 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.

$$
\underset{\text{Ketone}}{R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R} \quad + \quad \underset{\substack{\text{primary}\\\text{amine}}}{R\text{-}NH_2} \rightleftharpoons \underset{\substack{NHR\\\text{Carbinolamine}}}{R-\overset{\overset{\displaystyle OH}{|}}{C}-R}
$$

$$
\underset{\substack{\text{N-Substituted}\\\text{imine}}}{R-\overset{\overset{\displaystyle NR}{\|}}{C}-R}
$$
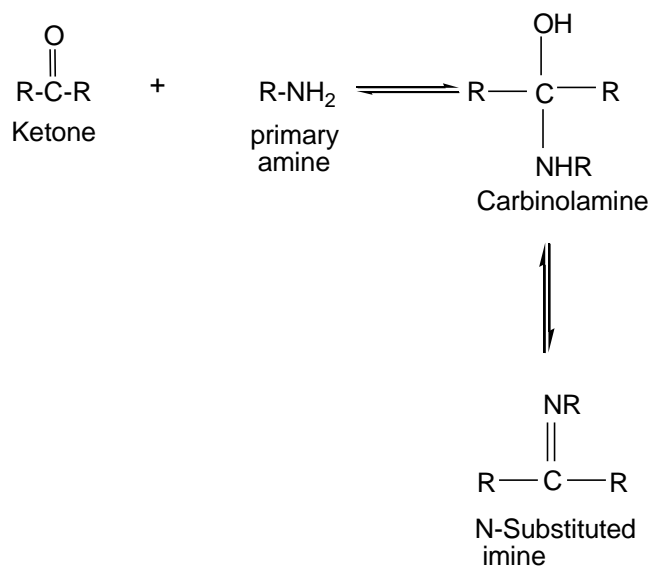
Fig. 1.10 Mechanism of Schiff base formation

The mechanism of Schiff base formation is another variation on the theme of neucleophilic addition to the carbonyl group. In this case, the neucleophile 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.

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-neucleophilic, equilibrium is pulled to the left and carbinolamine formation cannot occur. Therefore, many Schiff bases synthesis are best carried out at mildly acidic pH.The dehydration of carbinolamines is also catalyzed by base. This reaction is somewhat analogous to the E2 elimination of alkyl halides except that it is not a concerted reaction. It proceeds in two steps through an anionic intermediate.[67]

1.10 Macrocyclic complexes have the following characteristics.[68]

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.

1.11 Ni (II) Chemistry

The electronic configuration of the Ni (II) is d^8, in this divalent state it forms a very extensive series of compounds; and it is the most common oxidation state of nickel. Basically Ni(II) complexes are octahedral, tetrahedral and square-planar. For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. Octahedral and square planar geometries are the most usual. Some structures are complicated by interconversions between square planar and tetrahedral, or square planar and octahedral coordination. Three spin-allowed transitions are expected for octahedral nickel complexes which assigned to $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(P)$. Magnetically, square planar complexes of Ni(II) are diamagnetic. Octahedral nickel (II) complexes have relatively simple behavior. Ni(II) should have two unpaired electrons, and the magnetic moments ranging from 2.83-3.4 B.M. depending on the magnitude of the orbital contribution. Octahedral nickel (II) complexes having $^3A_{2g}$ ground state are expected to have three spin allowed transitions $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}$ (P) and $^3A_{2g} \rightarrow ^3T_{1g}$ (F) in the ranges of 7000- 13000 cm^{-1}, 11000-20000 cm^{-1} and 19000-27000 cm^{-1} respectively[69] two spin forbidden transitions:$^3A_{2g} \rightarrow ^1Eg$ and $^3A_{2g} \rightarrow ^1T_{2g}$ are also observed near the second spin allowed transitionand between second and third spin allowed transitions respectively. Octahedral nickel (II) complexes have two unpaired electrons and thus possess magnetic moments ranging from 2.9 to 3.4 B.M. depending on the orbital angular momentum contribution.[70]

1.12 Methods of Synthesis of Macrocyclic Complexes

The stability of the macrocyclic complex was attributed to the fixed geometrical placement of the ligand donor atoms.[71]This effect was first illustrated with acyclic triamine by Busch and co-workers in 1970. In 1975 (Yang and Zompa) 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[72].

Until recently polyaza macrocyles, 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.[73]

1.13 Template Synthesis of Ni (II) Complex

Some reports on synthetic macrocycles appeared as early as in 1936 when the first synthesisof 1, 4, 8, 11-tetraaza cyclotetradecane cyclam, compound was reported. Nevertheless, the field only began to blossom in the early 1960's, with the pioneering work of Busch and Curtis that led to the discovery of nickel mediated condensation of [Ni $(en)_3]^{2+}$ and acetone.[74] Template condensation of coordinated amines with formaldehyde in the presence of metals is useful for the synthesis of saturated polyazamacrocyclic complexes containing $N-CH_2-N$ linkages. Here, the nickel (II) and copper (II) complexes of the hexaaza macrocyclic ligand has been synthesized by the reaction described below. The reaction product largely depends upon the molar ratio of the reactants employed.[75]

Formaldehyde is a good reagent to link two amine moieties and, therefore, metal-directed reaction of coordinated amines and formaldehyde is useful for the preparation of various types of fully saturated polyaza macrocyclic complexes containing N-CH$_2$-N linkages. For example, the 14-membered hexaaza macrocyclic complex [ML$_2$]$^{2+}$ (M = Ni (II)) can be prepared by the one-pot reaction of formaldehyde with ethylenediamine and methylamine in the presence of the metal ion. It has been revealed that the reactions are simple and selective synthetic routes toward saturated polyaza macrocyclic complexes that could not be prepared by other methods.

1.14 AIM OF THE PRESENT WORK

The macrocyclic complexes have attracted the attention of both inorganic and bioinorganic chemists in recent years.[76]Naturally occurring macrocycles were shown to be capable of activity transport metal ion across membranes, beginning with valiomycin.[77]Synthetic macrocyclic ligands have been shown to form very stable complexes with alkali and alkaline earth metal cations. These complexes can be used as models for investigation of ion transport throughout membrane in biological systems.[78] The potentiality of tetraaza synthetic macrocyclic complexes as models for more complex natural system is now well recognized.[79]In these macrocyclic complexes, both the metal ion and the size of the ring play an important role. The saturated macrocycles with various numbers of their ring membered have been synthesized consistently. These compounds have produced interesting information concerning both the stabilities and structure of their metal complexes.[80] It has also been suggested that these are suitable for the

treatment of various allergies, asthma and influenza.[81] Several organolead compounds find uses as good algicides, herbicides and also as anticancerous agents.[82,83,84] The applications[85,86,87] of macrocyclic compounds in bioinorganic chemistry, catalysis, extraction of metal ions from solution and the activation of small molecules gave impetus to this endeavor.

In the nature a lot of macrocyclic compounds are known e.g. hemoglobin, myoglobin, vitamin B_{12} coenzymes where the metal atoms are Fe, Co, and the basic macrocyclic unit is prophyrin but have different functional group to the macrocycles. The chemical properties of some macrocyclic compounds resemble those of antibiotics.[88] For example; macrolactones resemble the natural metabolites such as nonatine and monactine.

In the recent years considerable attention have been given to the synthesis of macrocyclic complex.[89,90,91] These complex compounds have been used a model system of biologically important materials, such as porphyrin and corins.

Some of the macrocyclic ligands cannot be easily prepared from the reactants.[92] In that case the complex compounds could be synthesized by template method. The desire macrocyclic ligand can be isolated by the complex compounds.[93,94] Macrocyclic complex of Ni^{2+} act as catalyst to reduce CO_2 to CO and Mn^{2+} porphyrins have been most commonly studied catalyst.[95]

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 Ni (II). The 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 biological system and in medicine the present work is as follows:

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

METHOD AND MATERIALS

2.1 Materials and Apparatus

2.1.1 Chemical Reagents

All the chemicals used for synthesis of metal complexes were of analytical grade. These included Nickel perchlorate hexahydrate, malonodihydrazide, formaldehyde, acetaldehydeand benzaldehyde. In addition to, analytical grade reagents like conc. HNO_3 as well as solvents such as C_2H_5OH, DMSO, DMF, acetone, chloroform, toluene etc. were used for various purposes.

2.1.2 Weighing

The weighing operation was performed on an Electronic balance using SHIMADZU, DL-220H, JAPAN.

2.1.3 Determination of melting points of the Complexes (Test for Purity)

The melting point of each product was measured prior to all other analytical determination using the melting point apparatus to determine its purity based upon appearance of a sharp melting point. The melting point of each product was determined (using Biocote, Model No. SMP 10) following the instruments operation procedure, which required appearance of a sharp melting point in case of a pure solid.

2.1.4 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 of 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 1 mm). The KBr was ground in the mortar until there was no crystallinity and then a small amount of each complex sample was added (amount taken was enough to cover an area of about 4 mm^2 to an average of depth of 0.5 mm). After the sample was ground in 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 were recorded as KBr with a SHIMADZU FTIR-8400 infrared spectrophotometer.

2.1.5 UV-Visible Spectroscopy Spectrum Analysis

The electronic spectra measurements were used for assigning the stereo chemistries of metalions in the complexes based on the positions of absorption bands including possible d-d transition peaks. The electronic absorption spectra are often very helpful in the appraisal of results offered by other methods of structural investigation. The UV-Vis spectra were recorded with a SHIMADZU, MODEL-1601 PC, JAPAN.

2.1.6 Conductivity

The specific conductance of the complexes was determined by using a EUTECH CON 510 conductometer. Conductivity measurement of the present complexes was carried out in dimethyl sulfoxide (DMSO)

2.1.7 Magnetic Moments

i. Working principle of the balance

The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance (MSB) is the result of collaboration with professor D.F. Evans of imperial college London and is designed as a replacement for a traditional Gouy balance system the evans method uses the same configuration as the Gouy method but instead of measuring the force which a magnet exerts on the sample, the equal and opposite force which the sample exerts on a suspended permanent magnet is observed.

The M.S.B. works on the basic of a stationary sample and moving magnets. The pairs of magnets are placed at opposite ends of a beam so placing the system in balance. Introduction of the sample between the poles of one pair of magnets produces a deflection of the beam, which is registered by means of phototransistor. A current is made to pass through a coil mounted between the poles of the other pair of magnets, producing a force restoring the system to balance. At the position of equilibrium, the current passed through the coil is proportional to the force exerted by the sample and can be measured as a voltage drop.

The following general expression for mass susceptibility χ_g may be derived in the same manner for the traditional Gouy Method.

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

Where,

C = Constant of probability

R = Susceptibility of the tube with sample

R_o= Susceptibility of the empty tube

l = Length of the sample (in cm)

m = Mass of the sample (in g)

A = Cross-section area of the tube (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 constant of proportionality is related to the calibration constant of a given balance by the formula.

$C = C_{Bal}/10^9$ ....(ii)

From (i) and (ii), we get

$\chi_g = C_{Bal} \times l \times (R - R_o)/10^9 \times m$ ....(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, the solid celebrant (preferably) [HgCo(SCN)$_4$] is recommended since some of the systemic errors in packing 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 [HgCo(SCN)$_4$] was inserted into sample holder. It then allowed settle reading the numerical display.

2. Reading was recorded and calibration constant was calculated from the formula.

C = Blac = C_{Tube}/(R-Ro)

= (1766.842)/ {2830-17}

= 2.086 ………………………………………………. (iv)

From (iii) and (ii) we get,

χ_g = 2.086 x l x (R-R_o)/10^9 x m.. …………………………………..(v)

iv. Operation of the "Balance"

1. The range knob was turned to the XI scale 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 tube of known weight was place into the tube guide and was taken the reading Ro.

4. The sample was packed and noted the 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.

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

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

v. The Magnetic moment

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

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

$B = H + 4\pi l$

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 $\chi_{v/d}$ where d is the density of the substance in g/cm^3. It is 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.($\chi_m = \chi_g \times$ molecular weight)

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

The magnetic moment was calculated using the above equation. The magnetic moments due to electron spin of unpaired electrons were calculated from the Equation: $\mu = (n(n+2))^{\frac{1}{2}}$.

Where n is the number of unpaired electrons.

For some metal ion systems, there may also be an orbital contribution to the magnetic moment, and 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 Magneton)
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 complexes.

2.1.8 Metal Estimation

A known weight of the complex was taken into a conical flask and to it concentrated, (0.5M) H_2SO_4 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 complexometrically. Using EDTA (EDTA = Ethylenediamine tetraacetic acid) and DMG (DMG = Dimethyl glyoxime) excellent agreement of result were found.

2.1.9 Elemental analysis

A CHN analyzer is a scientific instrument which can determine the elemental concentrations in a given sample. It is used to measure C, Hand N. Sample sizes may differ depending on system, but most often in around a few mg. For some sample matrices larger mass is preferred due to sample heterogeneity. This instrument uses combustion to oxidize the sample into sample compounds which are then detected with thermal conductivity detection or infrared spectroscopy. Separation of interference is done by chemical reagents.

2.1.10 Thermo Gravimetric Analysis

TGA of the complexes is recordedunder nitrogen atmosphere at the heating rate of 10^0C/min (using TGA-50, SHIMADZU, JAPAN).

2.2 NAME OF THE CHEMICALS/REAGENTS USED AND SUPPLIERS

Nickel (II) perchlorate hexahydrate   Flleuka

Nickel(II) Carbonate   E. Merck

Acetone   E. Merck

Absolute ethanol   BDH,England

Dimethyl sulfoxide (DMSO)   E. Merck

Formaldehyde James   Bur rough Ltd. (England)

Acetaldehyde   BDH,England

Cinnamaldehyde   BDH,England

Hydrazine hydrate   E. Merck

Dimethylformamide (DMF)   BDH,England

Diethylmalonate   May & Baker Ltd.

Benzaldehy   BDH,England

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

EXPERIMENTAL

3.1 PREPARATION OF COMPLEXES

3.1.1 Preparation of malonodihydrazide[96] $C_3H_8N_4O_2$

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 precipitation was stared to form when the solution was turned from yellowish ting to shite. After the precipitation the product was filtered off on a Buckner funnel and washed with ethanol three times and dried in a vacuum desiccator over anhydrous $CaCl_2$. A silky white amorphous product 8.800 g was obtained (60% yield). The melting point of the compound was recorded at 125^0C-130^0C.

The substance was soluble in water, Dimethyl formamide(DMF), DMSO and insoluble in ethanol, methanol, dichloromethane, diethyl ether, pet ether, carbon tetrachloride and n-hexane.

Reaction of the preparation of the ligand:
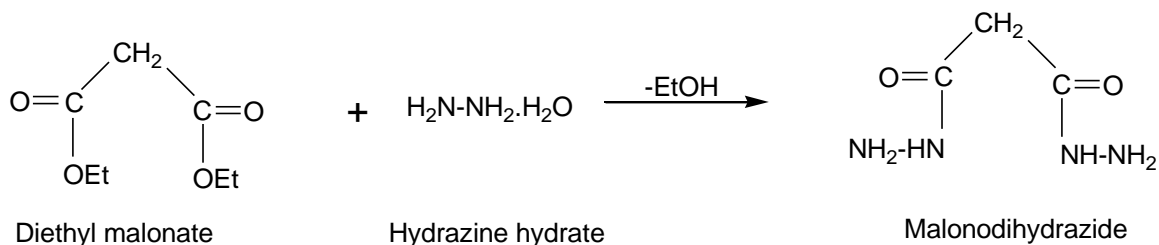
Fig. 1.11 Reaction of the formation of the malonodihydrazide

3.1.2 Preparation of Metal Perchlorate.

Metal perchlorate was prepared from analytically pure metal carbonate by treatment with 70% per chloric acid (AR). The treatment was done in the following way:

About 100 mL 70% per chloric acid was taken in a 250 mL beaker and then metal carbonate e.g. Nickel carbonate was added slowly with continuous stirring. The addition of Nickel carbonate was continued until the bubbles were disappears. Access amount of Nickel carbonate was added and kept it 12 hours to ensure the complete of the reaction. Than water-alcohol mixture was added with continuous steering and filtered. The resulting solids were filtered, washed with ethanol till free from excess acid and recrystallized several times from ethanol. (Nickel perchlorate is partially soluble in alcohol).

3.1.3 PREPARATION OF MACROCYCLIC COMPLEXES OF Ni (II).

3.1.3.1 Preparation of [Ni($C_8H_{16}N_8O_4$)(ClO_4)$_2$] complex 1.

To the aqueous malonodihydrazide, $C_3H_8N_4O_2$(0.793 g, 6 mmol in 10 mL water) formaldehyde solution (0.477 g, 6 mmol 37%) was added. To the above solution nickel(II) perchlorate hexahydrate (1.088 g, 3 mmol in 10 mL water) was added and the whole mixture was refluxed with constant stirring for two hours and cooled down. A light blue precipitate was formed immediately. The product was washed with ethanol for three times and dried in a vacuum desiccator over anhydrous $CaCl_2$. The melting point of the compound was 213^{0}C-216^{0}C and yield

was 1.793 g (75%). The compound was soluble in DMSO and insoluble in acetone, ethanol, water and chloroform.

3.1.3.2 Preparation of [Ni ($C_{10}H_{20}N_8O_4$)(ClO_4)$_2$] complex 2

To the solution of malonodihydrazide (0.527 g, 4 mmol in 10 ml water) acetaldehyde (0.18 g, 4 mmol in 10 mL water) was added. To the above mixture with nickel(II) perchlorate hexahahydrate (0.731 g, 2 mmol in 10 mL water) was added and the whole mixture was refluxed with constant stirring for 12 hours and cooled down. A yellow precipitate was formed. The precipitation was filtered off on a buckner funnel and washed with water and ethanol three times. The product was dried in a vacuum desiccator over anhydrous $CaCl_2$

The melting point of the compound was 224^0C-226^0C and yield was 0.850 g (55%). The compound was soluble in DMSO and insoluble acetone, alcohol, chloroform.

3.1.3.3 Preparation of [Ni ($C_{20}H_{24}N_8O_4$)(ClO_4)$_2$] complex 3

To the solution of malonodihydrazide, $C_3H_8N_4O_2$ (0.527 g, 4 mmol 10 in mL water) benzaldehyde (0.529 g, 4 mmol) solution was added. To the above mixture of nickel(II) perchlorate hexahydrate (0.733 g, 2 mmol in 10 mL water) and the whole mixture was refluxed with constant stirring for 3 hours and cooled down. The brown precipitate was formed. The product was filtered off on a Buckner funnel and washed with water and ethanol three times. The product was dried in a vacuum desiccator over anhydrous $CaCl_2$.
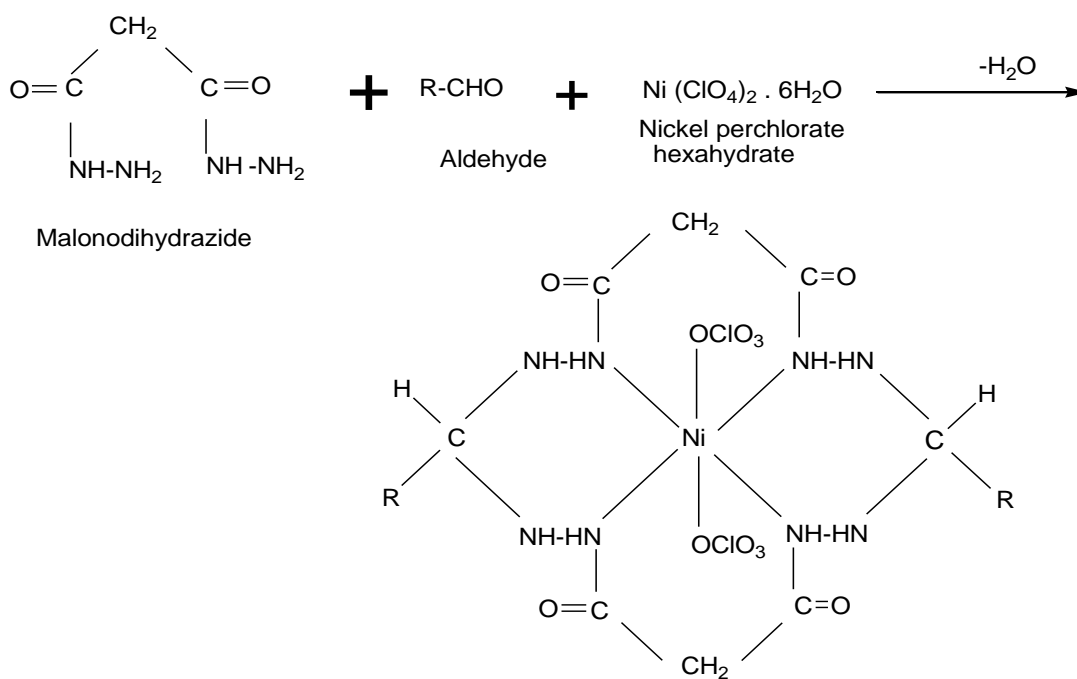
The melting point of the compound was 242^0C-244^0C and yield was 0.93 g (60%). The compound was soluble in DMSO and insoluble in chloroform, water and acetone.

The probable path way of the reaction is:

Where, R = H, CH_3 - , C_6H_5 -

Fig. 1.12 Reaction of the formation of macrocyclic complexes

RESULTS AND DISCUSSTION

In this work, new macrocyclic complexes of the metal ion Ni(II) were synthesized from malonodihydrazide,formaldehyde,acetaldehyde, benzaldehyde in water medium and the products were characterized by solubility, FT-IR, UV-VIS, melting point determination, conductivity and magnetic susceptibility measurements.

4.1 Characterization of the Metal Complexes

4.1.1 Solubility

Qualitative test were performed to determine the solubility of each of the as synthesized Ni(II) complexes in six different solvents. The results obtained from observation are summarized as shown in Table 4.1 below

Table-4.1: The Solubility of Ni (II)) Complexes in different solvents.

No.	Solvent	Nickel complexes
1.	Acetone	Insoluble
2.	Ethanol	Insoluble
3.	Water	Insoluble
4.	Chloroform	Insoluble
5.	DMSO	Partial Soluble
6.	DMF	Partial Soluble

According to the result, it can be said that the solubility behavior of the complexes may be suggestive of their nonelectrolyte nature.

4.1.2 Results of melting point determination (purity Test)

Results of the melting point determination for the as-synthesized metal complexes are presented in Table 4.2 below.

Table 4.2: Mean differences in the melting point of complexes

No	Complexes	Melting point (^{0}C)			
		Test 1	Test 2	Average mean difference	Purity
1.	$[Ni(C_8H_{16}N_8O_4)(ClO_4)_2]$	213-216	214-218	3.5	Not pure
2.	$[Ni(C_{10}H_{20}N_8O_4)(ClO_4)_2]$	224-226	223-227	3	Not pure
3.	$[Ni(C_{20}H_{24}N_8O_4)(ClO_4)_2]$	242-244	243-246	2.5	Not pure

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 differences (range) of 0.5 to 2^{0}C between replicate measurements. If a compound is contaminated with even small amounts of an impurity, its melting point will take place in a large temperature range. Of the mean melting point differences for both complexes show the results slight deviate

from the acceptable range suggesting that the compounds contained impurity. The fact that their mean melting point differences are not very much exaggerated that (not large differences) may leave us some room to assume that the contaminate (impurity) could not be due to formation of mixed products (from parallel or side reaction).

4.1.3 Results of specific conductance measurements

The results obtained as such from measurements of specific Conductance of 3 x 10^{-4}M solution of the respective complex at different temperature are summarized in Table 4.3 below.

Table 4.3: Measurement of Specific Conductance of Nickel complexes

No.	Complexes	Solvent	Temperature (^{0}C)	Specific conductance (μS/cm)
1.	$[Ni(C_8H_{16}N_8O_4)(ClO_4)_2]$	DMSO	25.4	1.56
2.	$[Ni(C_{10}H_{20}N_8O_4)(ClO_4)_2]$	DMSO	25.3	1.86
3.	$[Ni(C_{20}H_{24}N_8O_4)(ClO_4)_2]$	DMSO	25.2	1.49

According to the results given in table 4.3, since the specific conductance of the complexes in DMSO have fallen within the range of 1.49-1.86 μS/cm and this range is actually below the value (4.9 μS/cm in DMSO) assigned for non-electrolytes.[97]

4.1.4 Magnetic susceptibility measurements

Magnetic susceptibility of the complexes was determined using very sensitive instrument known as a magnetic susceptibility balance. Magnetic susceptibility measurements were recorded at room temperature. Ni (II) should have two unpaired electrons, and the magnetic moments ranging from 2.83-3.4 B.M. depending on the magnitude of the orbital contribution. The magnetic moment measurement data of the Ni(II) complexes showed (2.82-3.14) B.M. This follows to assume that the Ni (II) ion exist in a high spin d^8 ($t_{2g}^6 e_g^2$) octahedral environment in its complex.

Table 4.4: Magnetic moment measurement data of the Ni (II) complexes

No	Compounds	Samle Length , l in cm	Weight of the sample , m in g	Suscep-tibility of the empty tube , R_0	Suscep-tibility of the sample with test tube , R	Mass suscep-tibility $x_g \times 10^{-6}$ cm^3/g	Molecular Weight , M	Molar Suscepti-bility $x_g \times 10^{-3}$ cm^3/mol	μ_{eff} B.M
1	$[Ni(C_8H_{16}N_8O_4)(ClO_4)_2]$	3.4	0.0594	-65	-15	5.97	545.69	3.258	2.89
2	$[Ni(C_{10}H_{20}N_8O_4)(ClO_4)_2]$	2.9	0.0466	-60	-8	6.750	573.2	3.874	3.14
3	$[Ni(C_{20}H_{24}N_8O_4)(ClO_4)_2]$	3.8	0.0346	-42	-20	5.04	697.6	3.77	2.82

4.1.5 Elemental Analysis and Metal Estimation

The elemental analysis data measured by CHN Analyzer and metal estimation data of the complexes are consistent with the proposed formula which is given below

Table 4.5:Elemental analysis data of the complexes

No	Compounds	%C		%H		%N	
		Calculated	Found	Calculated	Found	Calculated	Found
1	$[Ni(C_8H_{16}N_8O_4)(ClO_4)_2]$	17.59	17.19	2.93	2.12	20.52	20.10
2	$[Ni(C_{10}H_{20}N_8O_4)(ClO_4)_2]$	20.92	20.30	3.48	3.11	19.52	19.41
3	$[Ni(C_{20}H_{24}N_8O_4)(ClO_4)_2]$	34.39	33.9	3.44	3.25	16.05	15.98

Table 4.6: Metal estimation data of the complexes

No	Compounds	% yield	Colour	M %	
				Calculated	Found
1	$[Ni(C_8H_{16}N_8O_4)(ClO_4)_2]$	75	Light blue	10.76	10.19
2	$[Ni(C_{10}H_{20}N_8O_4)(ClO_4)_2]$	55	Yellow	10.23	9.98
3	$[Ni(C_{20}H_{24}N_8O_4)(ClO_4)_2]$	60	Brown	8.41	8.35

4.1.6 UV-Vis (Electronic) absorption spectra

In general 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 the metal and it helps us to study this effect for coordination compounds of any geometry. UV absorbance is generally broad because vibrational and rotational energy levels are superimposed on top of the electronic levels. There are two absorption bands, assigned to n→π* and π→π* transitions, are found in the spectra of the complexes, both are shifted towards lower and higher frequencies, respectively confirming the coordination of the ligands to the metal ions, Charge transfer transitions are generally intense compared with ligand field transitions, i.e., charge transfer gives rise to intense absorptions whereas d-d bands are much weaker.

In the UV-Vis spectrum of Ni (II) a band 367 nm could be assigned to π→π*transition of the macrocyclic ligand. Another band at 540 nm can be assigned to d-d band transitions. The absorption bands at 540 nm can be assigned to $^3A_{2g}{\rightarrow}^3T_{1g}$ (P) and $^3A_{2g}{\rightarrow}^3T_{1g}$(F) which favors octahedral geometry. These absorption bands are in the range of literature value for octahedral complex.

Table 4.7: UV- Visible absorption maxima of compound

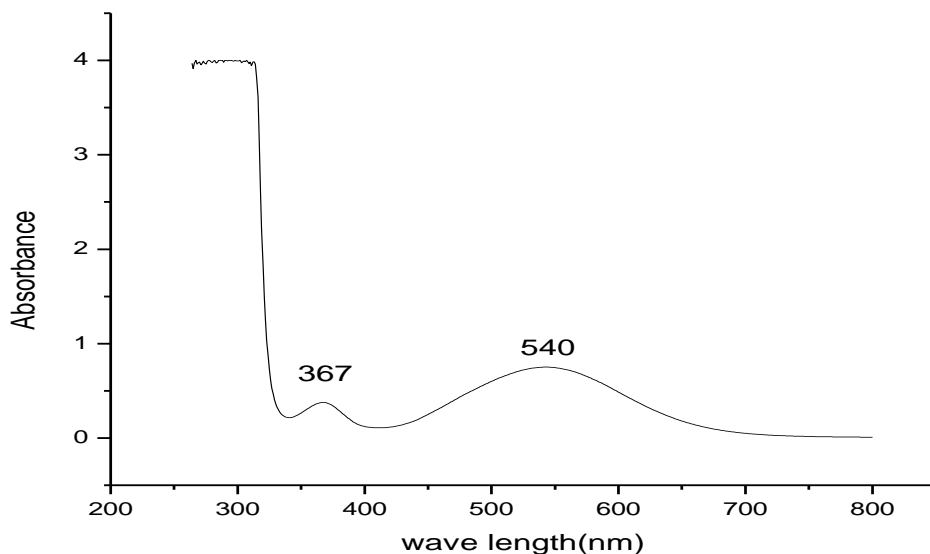| No	Compounds	λmax (nm)
1	$[Ni(C_8H_{16}N_8O_4)(ClO_4)_2]$	367,540

Fig-4.1: UV-Visible Spectrum of Ni (II) Complex 1

4.1.7 IR spectra of Nickel complexes

Due to coordination the v(N-H) stretching of the amide group goes to the higher field at (3246, 3265) cm^{-1} region as compared to the starting material malonodihydrazide. In the complexes the terminal-NH2group of malonodihydrazide condensed with the aldehyde moiety forms a new secondary

1-NH group which may appear at the same region as to the amide-NH group as a result the v(N-H) band appear as a strong and broad band. [The starting material malonodihydrazide have three v(N-H) bands at (3248, 3213, 3050) cm^{-1}. The bands at (3248, 3050) cm^{-1} for the asymmetrie and symmetric v(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 (2920-2972) cm^{-1} is suggested for the v(C-H) stretching of

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aliphatic moiety.[98]The complexes showed a strong band at (1649-1674) cm^{-1} which represent the v(C=O) of NH-NH-CO-CH2 moity.[99]Three or four band at (625-1145) cm^{-1} region also indicated the v_1,v_2,v_3,v_4 bands of (ClO$_4^-$) moiety. These stretching frequency is suggested the coordination of perchlorate to the metal through the O atom.[100,101,102] A medium band at (407- 412) cm^{-1} region is tentatively attributed to the v (M-N) mode[103,104] indicating the coordination of the ligand to the metal through the nitrogen atom.

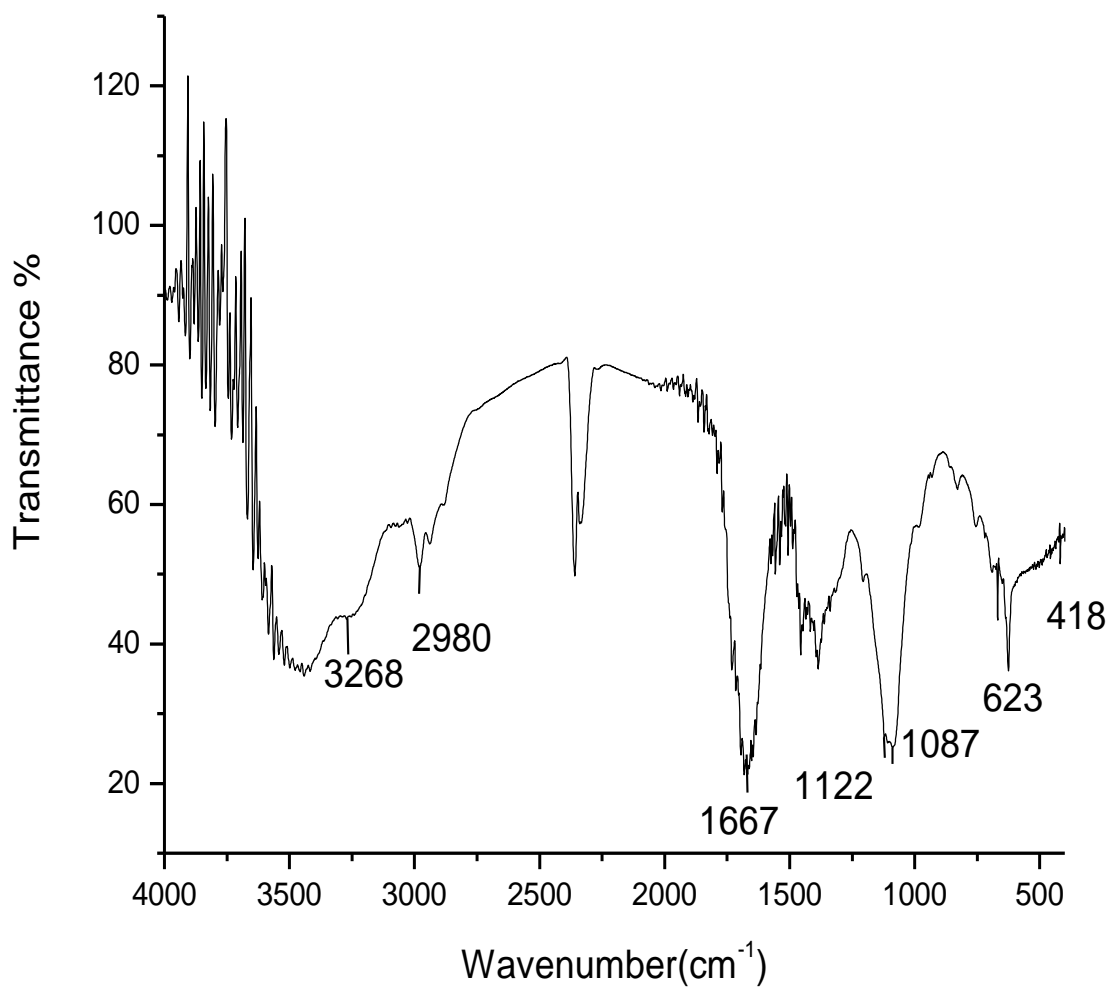Table 4.8: Important infrared spectral bands of compounds

No	compounds	V(C-H) cm^{-1}	V(C=O) cm^{-1}	V(N-H) cm^{-1}	V(M-N) cm^{-1}	V(ClO$_4$) cm^{-1}
1	[Ni(C$_8$H$_{16}$N$_8$O$_4$)(ClO$_4$)$_2$]	3017	1689	3270	418	1147 1087 624
2	[Ni(C$_{10}$H$_{20}$N$_8$O$_4$)(ClO$_4$)$_2$]	2980	1667	3268	418	1122 1087 623
3	[Ni(C$_{20}$H$_{24}$N$_8$O$_4$)(ClO$_4$)$_2$]	2919	1647	3213	426	1156 1073 687
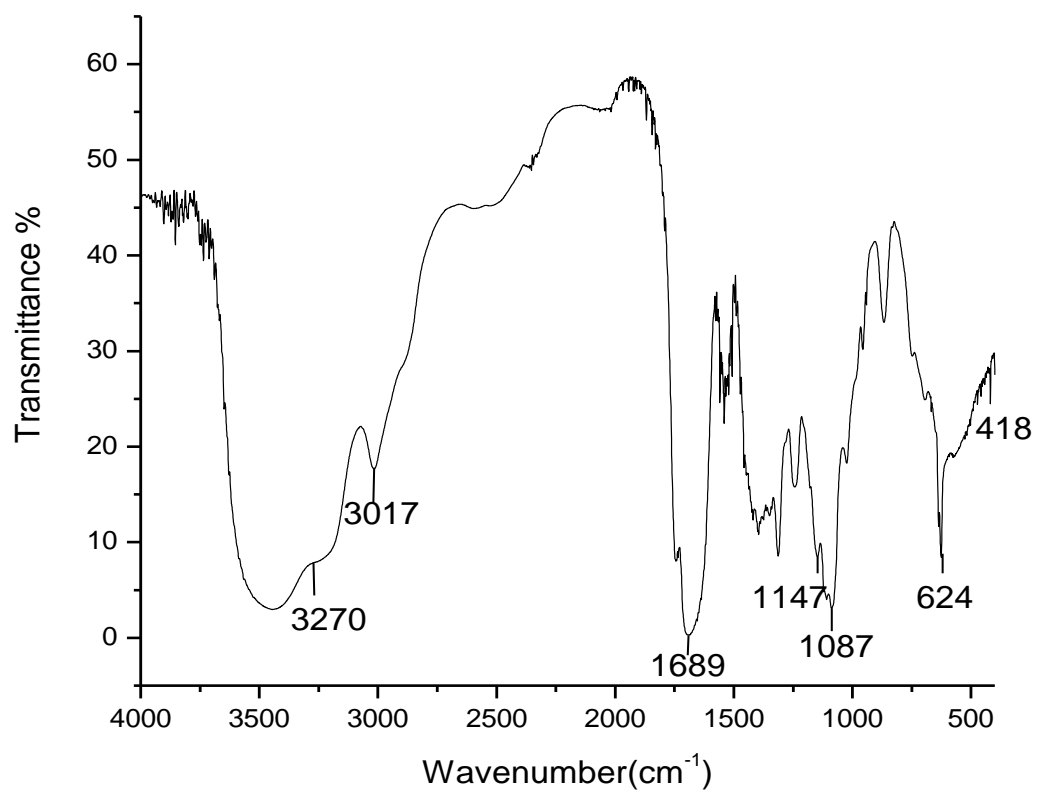
Fig-4.2: Infrared Spectrum of [Ni (C$_8$H$_{16}$N$_8$O$_4$)(ClO$_4$)$_2$] complex

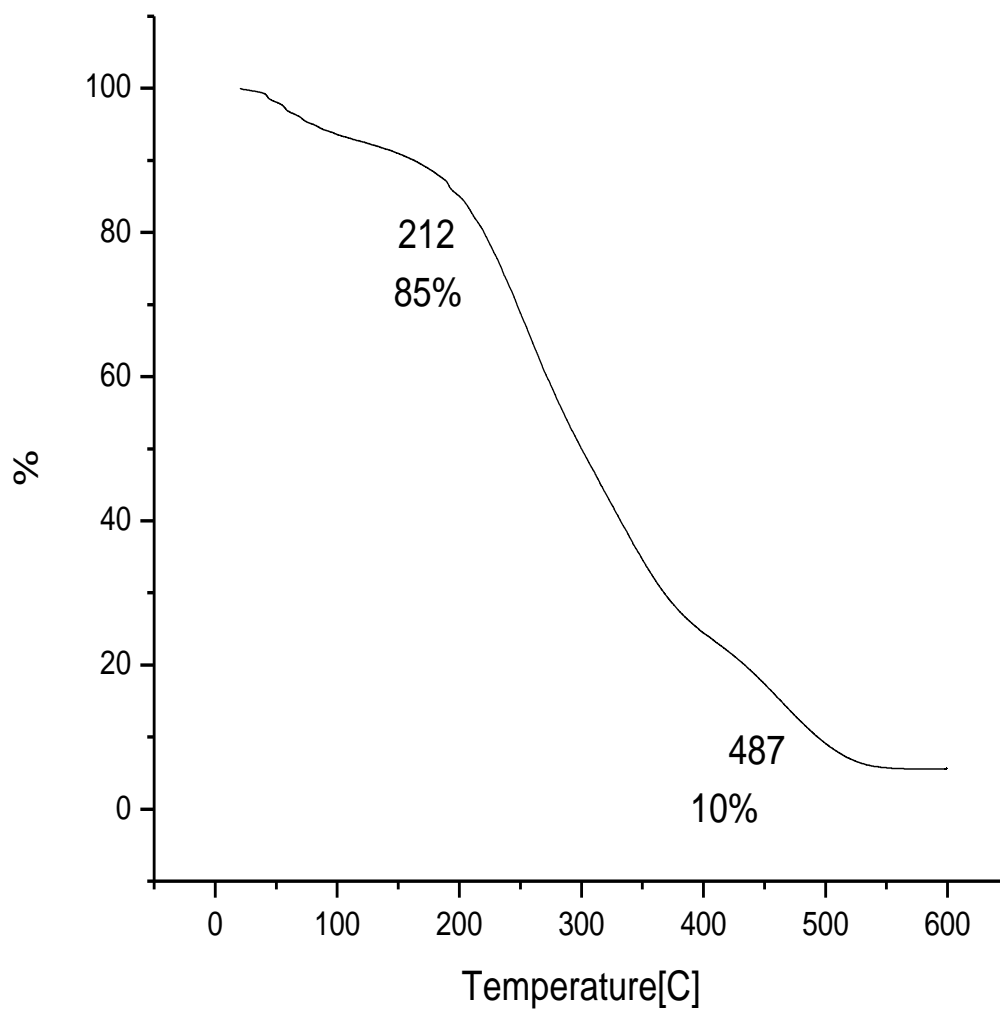**Fig-4.3: Infrared Spectrum of [Ni (C₁₀H₂₀N₈O₄)(ClO₄)₂] complex**
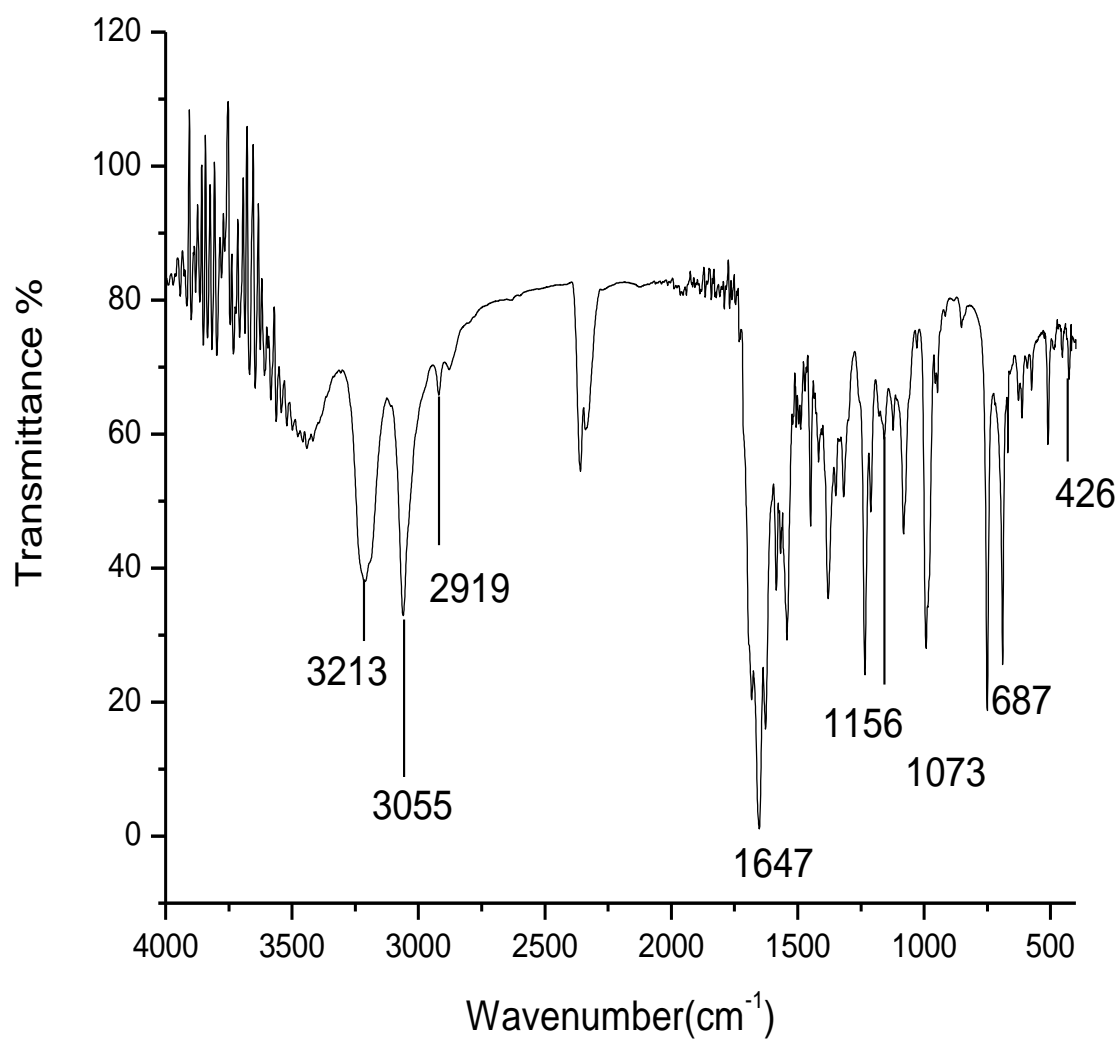
Fig-4.4: Infrared Spectrum of [Ni (C$_{20}$H$_{24}$N$_8$O$_4$)(ClO$_4$)$_2$] complex

4.1.8 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis of the complexes was recorded under nitrogen atmosphere at the heating rate of 10^0C/min. The complex [Ni $(C_8H_{16}N_8O_4)(ClO_4)_2$] is stable up to 216^0C and shows a continuous weight loss up to 472^0C. Then the whole complex gets decomposed in a single step. This corresponds to the loss of two malonodihydrazide ligands and two perchlorates (observed weight 80%, theoretical weight 82%). The complex [Ni $(C_{10}H_{20}N_8O_4)(ClO_4)_2$] is stable up to 212^0C and shows a continuous weight loss up to 487^0C. Then the whole complex gets decomposed in a single step. This corresponds to the loss of two malonodihydrazide ligands and two perchlorates (observed weight 75%, theoretical weight 78%). The complex [Ni $(C_{20}H_{24}N_8O_4)(ClO_4)_2$] is stable up to 217^0C and shows a continuous weight loss up to 550^0C. Then the whole complex gets decomposed in a single step. This corresponds to the loss of two malonodihydrazide ligands and two perchlorates (observed weight 82%, theoretical weight 85%).
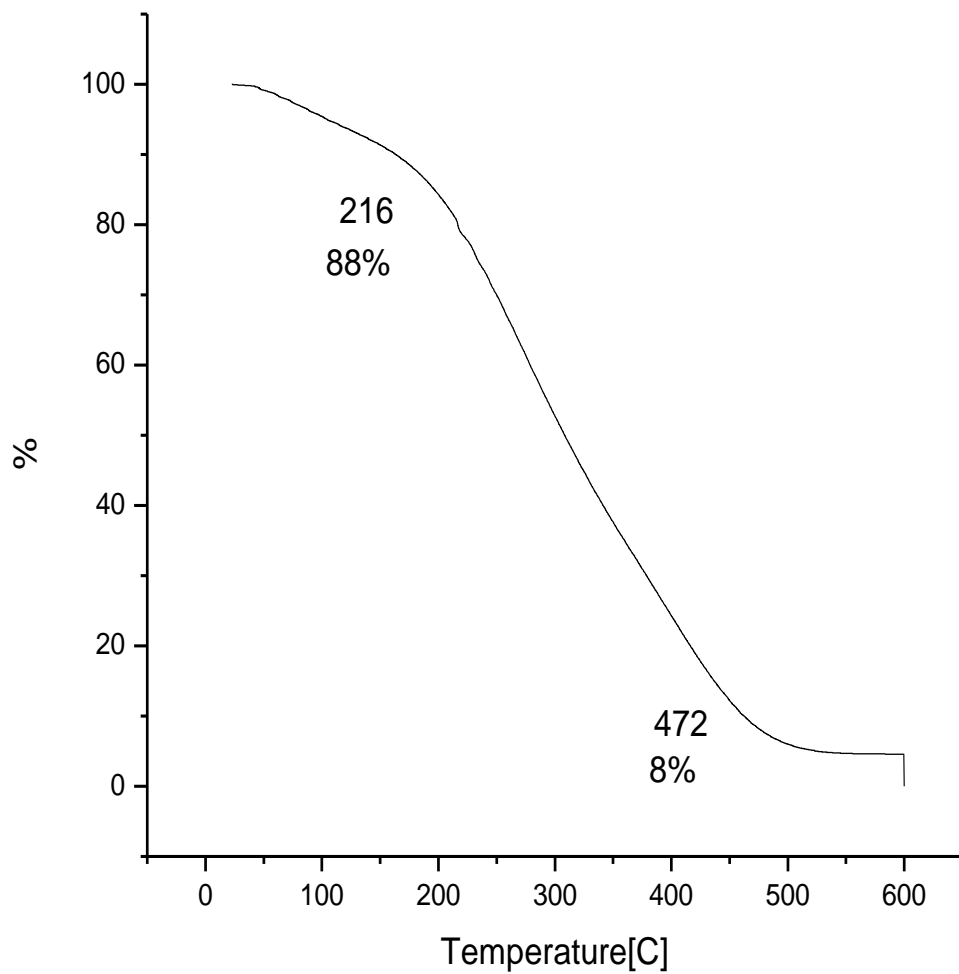
Fig-4.5: Thermo Gravimetric Analysis of [Ni (C$_8$H$_{16}$N$_8$O$_4$)(ClO$_4$)$_2$] complex

Fig-4.6: Thermo Gravimetric Analysis of [Ni (C$_{10}$H$_{20}$N$_8$O$_4$)(ClO$_4$)$_2$] complex
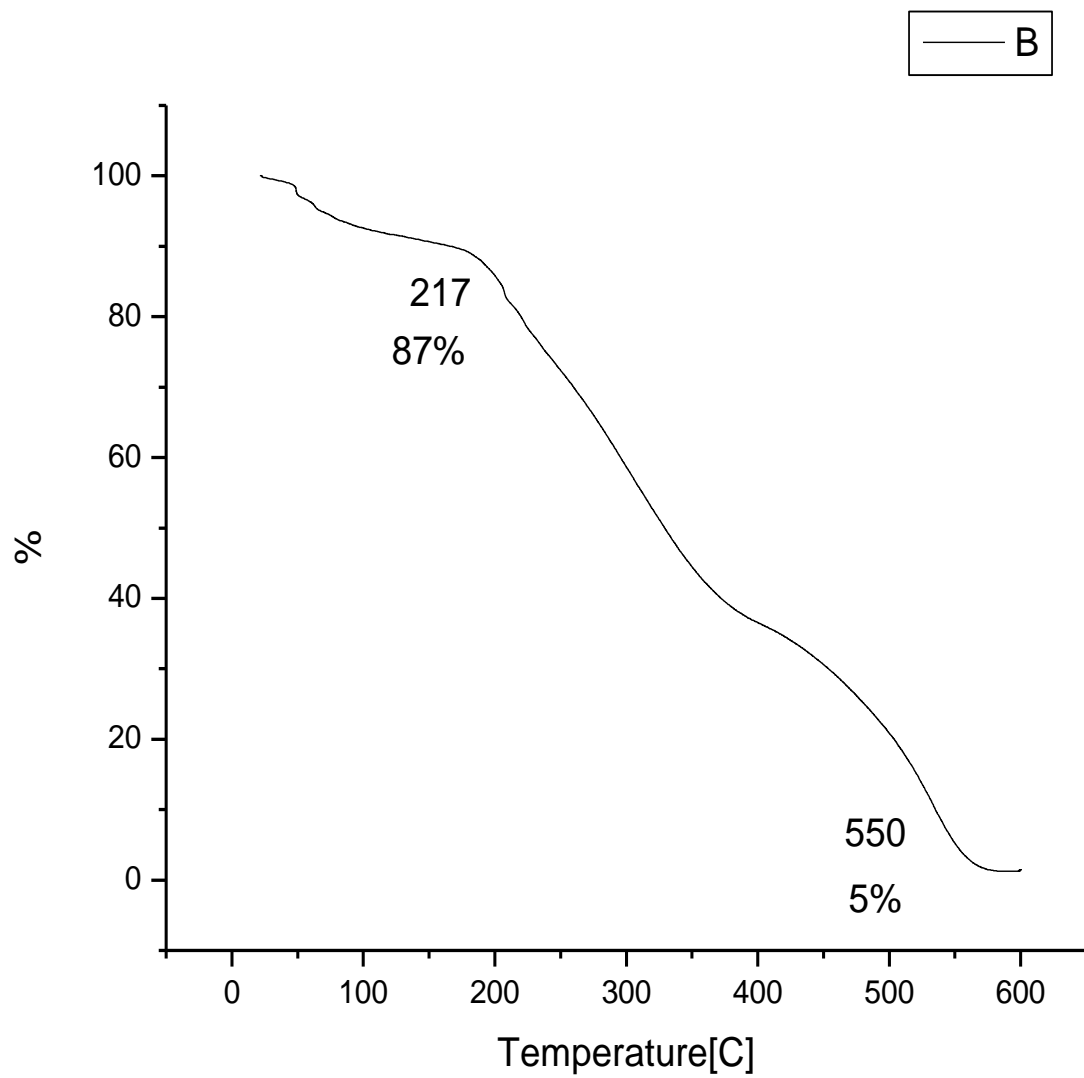
Fig-4.7: Thermo Gravimetric Analysis of [Ni (C$_{20}$H$_{24}$N$_8$O$_4$)(ClO$_4$)$_2$] complex

4.2. Structures of Complexes

Based on the magnetic moment, FTIR, conductance, Elemental analysis, TGA and spectral data, proposed geometries of Ni(II) complexes were octahedral .These complexes wereformed as a result of template condensation of aldehyde, malonodihydrazide with corresponding metal perchlorate of $Ni(ClO_4)_2$. The result was expected to produce a mixture of the mononuclear 16-membered tetraaza macrocycle complex .

 The probable structure of the complex is given below:
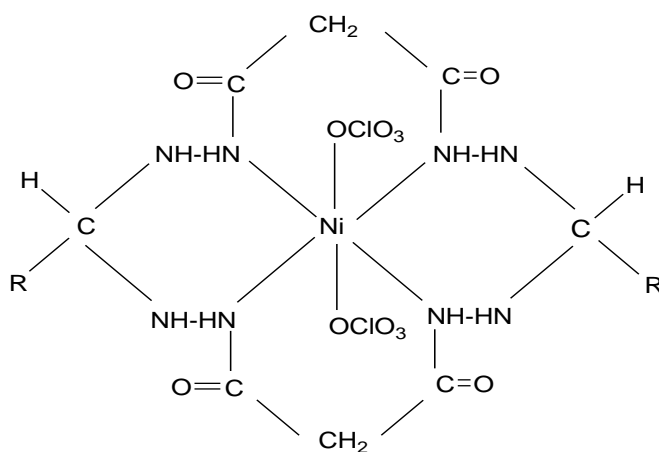
Where, R = H, CH_3 - ,C_6H_5 -

 Fig-4.8: Probable structure of the complexes

5. Conclusion

New Ni (II) complexes (1-3) were prepared from the template condensation of formaldehyde, acetaldehyde, benzaldehyde and corresponding metal salts $NiCl_2.2H_2O$ in aqueous medium. Various spectroscopic and analytical methods such as, UV-Vis, elemental analysis, conductivity measurement and magnetic susceptibility, TGA etc. were adopted for the characterization of the complexes (1-3). The results suggested that Ni (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).

References

1. F.A Cotton and G, Wilkinson,"Further properties of atoms, molecules and Chemical bonds. In: advanced inorganic chemistry: A comprehensive text, 2nd edn.Interscience", New York, PP.140. 5th ed. P. 344 ,1966,1988.

2. L.F. Lindoy, "The chemistry of macrocyclic ligand complexes", Cambridge University press New York. Chemical Society Revision, 4, 421-441, 1989.

3. R.M. Izatt., D.J.Eatough, K.Pawlak and J.S.Bradshaw. "Synthesis coordination and organometallic chemistry". Chemistry Revision ,95, 2529, 1991.

4. P.Arranz, C.Bazzicalupi, A.Bencini, S.Ciattini, P.Fornasari, C.Giorgi and B.Altancoli, "Co-ordination chemistry of amino pendant arm derivatives of 1,4, 7-triazacyclononane", Dalton Trans., 1934-1944.Inorganic Chemistry, 40, 6383-6389, 2001

5. I. G. Casella, E. Desimoni, T.R.I. Caldi, "Study of a nickel-catalysed glassy carbone electrode for detection of carbohydrates in liquid chromatography and flow injection analysis", American Chemical Society, 248,117-125,1991

6. AK. Chaudhary, M. Nokubo, GR reddy, SN Yeola "Detection of Endogenous Malondialdehyde-deoxyguanosine adducts in human liver", American chemical Society, 293,1991

7. S. Chandra and R. Kumar, Chromium(III) complex with different chromosphers macrocyclic ligands: synthesis and spectroscopic studies, Turky J.Chem.,30,77-87, 2006.

8. M.N Hughes and J.Wiley 1981. "The Inorganic Chemistry of Biological Processes", 2nd ed. Inorganic Chemistry; 4th Ed; Harper Collins college publishes; New York,1981

9. F. Moser and A.Thomas, "Synthesis and properties of a soluble conjugated poly(azomethine) with high molecular weight", Macromolecules., 31, 2676-2678,1963.

10. B. Bosnich, C.Poon, M .Tobe. "Principles of mononucleating and binucleating ligand design", Chemistry Revision, 104, 349 – 383,1965.

11. K.P. Wainwright,"Applications of Polyaza macrocycles with nitrogen attached pendant arms", A.G. sykes, Ed., Academic press, Sandiego.52.pp.293-334. Coordination Chemical Revision, 166, 35-90,2001.

12. R.B King, "Advances in Plutonium Chemistry", Encyclopedia of Inorganic Chemistry., 4,2000,1995.

13. W.Christensen, R.M.Izatt,. "Progress in Macrocyclic Chemistry Education". J.J., NewYork, vol.3, chapt.1. p. 1., 1987.

14. S.M. Omar "Synthesis and Spectral Studies of 15-and16- Membered Diamide Diimine Tetraaza Macrocyclic Metal Complexes".Asian General Chemistry,1231-1238,115-123,2009, Main group Chemistry, 53-59,2007.

15. C.J.Pedersen,J.M.Lehn "Cryptands in Comprehensive supramoleculer Chemistry, Journal of American Chemical Society, Elsevier: Oxford, Vol. 1, pp 153–211 ,1967.

16. B Dietrich, J.M.Lehn, J.P.Savage,"Cryptands in Comprehensive Supramolecular Chemistry"; Gokel, G. W. Ed; Elsevier: Oxford; Vol. 1, pp 153–211, 1969.

17. S. Chandra, D.Jain, A.K.Sharma and P.Sharma , "Coordination Modes of Schiff Base Pentadentate Derivative of 4- Aminoantipyrine with Cobalt (II), Nick(II) and Copper (II) Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies" 14, 174-176, 2009.

18. B.H. Mruthyunjayaswamy, M.O.Ijare, B.Imkar and Y.Jadegou"Synthesization Characterization and Biological Activity of Symmetric Dinuclear Complexes Derived from a Novel Macrocyclic Compartmental Ligand", Journal of Brazil Chemical Society,16,783-789,2005.

19. K.Shankar,M.Ashok,P.Reddy,R.,Rohini andV.Ravinder Spectroscopic characterization and antibacterial activities of Mn (III) complexes containing the tetradentate aza Schiff base ligands, International Journal of Chemistry Teaching Research , 1,777-783,2009.

20. T Rosu, S.Pasculescu, V.Lazar, C.Chifiriuc and R.Cernat, "Copper (II) Complexes with Ligands Derived from 4-Amino-2, 3-dimethyl-1-phenyl-3-pyrazoline- 5-one, Molecules,11, 904-914,2006.

21. V.C. Filho, R.Correa, Z.Vez, J.B.Calixto, R.J.Nunes, T.R.Pinheiro, A.D.Andricopulo ,R.A Yunes. Further Studies on Analgesic Activity of Cyclic Imides,Farmaco ,53, 55-57,1998.

22. Turhan-Zitouni,G., M.Sivaci, F.S.,Kilic, K.Erol,Synthesis of Some Triazolyl-antipyrine Derivatives and Investigation of Analgesic Activity, England Medical Chemistry, 36,685-689,2001.

23. N. Raman, J.Joseph, A.Sakthivel Synthesis, "structural characterization and antimicrobial studies of novel Schiff base copper (II) complexes", Journal of Chile Chemical Society, 54(4),354-357,2009.

24. G.S Rajiv, S.K.Ibrahim, S.S.Syed and M.S.Dastager, Template Synthesis Charact-erization and antimicrobial activity of Schiff base complexes of V(IV), Fe(III), Zr and W(VI) Metal Ions, Journal of Pharmacy Research, 4(12), 4681-4682,2011.

25. Y.,Inouye,T.Kanamori, M.Sugiyama, T.YoshidaKaike, M.Shionoya, H.Fujioka and E.Kimura , "Differential Contribution of metal complexation and dimerisation to the chemotherapeutic potential of bicyclen-Zn2 complex against human immune deficiency virus", Biology Pharmcetical Bull.,19(3): 456-458,1996.

26. Cotton, Frank Albert, Geoffrey Wilkinson, Carlos, A. Murillo "Advanced Inorganic Chemistry", 13, 135, 1999.

27. Miessler, Gary L.; Donald Arthur Tarr, Inorganic Chemistry,642, 1999.

28. J. Van Alphen, Recl. Trav. Chim. Pays-Bas, 55, 835,1936.

29. M. C. Thompson and D. H. Busch, Chem. Eng. News, 57,1962.

30. N. F. Curtis, J. Chem. Soc., 4409,1960.

31. C. J. Pedersen, J. Am. Chem. Soc., 89, 7017,1967.

32. B. Dietrich, J.-M. Lehn, and J.-P. Sauvage, Tetrahedron Lett., 2889,1969.

33. J. Almy, D. C. Garwood, and D. J. Cram, J. Am. Chem. Soc., 95, 2961,1973.

34. A. Bianchi, M. Micheloni, and P. Paoletti, Pure Appl. Chem., 60, 525,1988.

35. P. Chaudhuri and K. Wieghardt, Prog. Inorg. Chem.,35, 329,1987.

36. D. H. Busch and C. Cairns, in "Progress in Macrocyclic Chemistry" eds. R. M. Izatt and J. J. Christensen, Wiley, New York, Vol. 3, Chap. 1, p. 1,1987.

37. A. M. Sargeson, Pure Appl. Chem., 56, 1603,1984.

38. I. Murase, K. Hamada, and S. Kida, Inorg. Chim. Acta,54, L171,1981.

39. L. Lindoy, Y. Inoue and G. W. Gokel, Dekker, "Cation Binding by Macrocycles"New York, Chap. 16,p. 599,1990.

40. D. E. Fenton, U. Casellato, P. A. Vigato, and M. Vidali, Inorg. Chem. Acta, 62, 57, 1982.

41. Y. Inoue and G. W. Gokel eds, "Cation Binding byMacrocycles", Dekker, New York, 1990.

42. D. J. Cram, S. Karbach, Y. H. Kim, L. Baczynskyj, andW. Kalleymeyn, J. Am. Chem. Soc., 107, 2575,1985.

43. D. J. Cram, Angew. Chem., Int. Ed. Engl., 25, 1039,1986.

44. N. B. Tucker and E. E. Reid, J. Am. Chem. Soc., 55,775,1933.

45. J. Ennen and T. Kauffmann, Angew. Chem., Int. Ed. Engl.,28, 118, 1981.

46. L. Horner, H. Kunz, and P. Walach, Phosphorus Relat. Group B Elem., 6, 63,1975.

47. Z. Cimerman, S. Miljanic and N. Galic, Croatica Chemica Acta, 73 81,2000.

48. A. Elmali, M. Kabak and, Y. Elerman, J. Mol. Struct., 477 ,151,2000.

49. D.H. Brown and W.E. Smith, Enzyme Chemistry-Impact and Applications, Chapmann and Hall, London, 1990.

50. K. Singh, M.S. Barwa and P. Tyagi, Eur. J. Med. Chem., 42 ,394,2007.

51. P.G. Cozzi, Chem. Soc. Rev., 33 ,410,2004.

52. S. Chandra and J. Sangeetika, J. Ind. Chem. Soc., 81, 203,2004.

53. H. Schiff, Ann. Chem. Pharm., 150, 193,1869.

54. C. K. Jorgensen, Acta Chem. Scand., 11,73,1957.

55. H. Schiff, Ann. Chem. Pharm., 150,193,1869.

56. H. Schiff, Ann. Chem. Pharm., 151,186,1869.

57. M. Delepine, Bull. Soc. Chim., 21 ,943,1899.

58. V. Cassel1ata, P. Vigato, D.E. Fenton and M. Vidali, Chem. Soc. Rev., 79,199,1979.

59. J. Sessler and J. Sibcr, Tetrahedron, 49,8727,1993.

60. M. Yildiz, Z. Kilic and T. Hökelek, J. Mol. Struct., 441,1998.

61. Y. Sunatsuki, Y. Motoda and N. Matsumoto, Coord. Chem. Rev., 226,199,2002.

62. D.P. Kessissoglou, M.L. Kirk, M.S. Lah, X. Li, C. Raptopoulou, W.E. Hatfield and V.L. Pecoraro, Inorg. Chem., 31,2935,1992.

63. A.L. Gavrilora and B. Bosnich, Inorg. Chim. Acta, 352,24,2003.

64. C. Liu, M. Wang, T. Zhang and H. Sun, Coord. Chem. Rev., 248,147,2004.

65. J.A. Ibers and R.H. Holm, Science, 209 ,223,1980.

66. E. Bouwman and J. Reedijk, Bioinorganic Catalysis, 2nd Edn, Ed. J. Reedijk, E. Bouwman, Marcel Dekkar Inc. New York, pp. 1,1999.

67. J.A. Halfan, V.G. Toung and W.B. Tolman, Angew Chem. Int. Ed., 35,1687,1996

68. E. Kwiatkowski, M. Kwiatkowski, Inorg. Chim. Acta 117,145,1986.

69. N.Raman, J.Joseph, A.Sakthivel "Synthesis, structural characterization and antimicrobialstudies of novel Schiff base copper (II) complexes", Journal of Chile Chemical Society, 54(4), 354-357, 2009.

70. R. Gao and L.J.Zheng "Highly enantioselective hydrophosphonylation of aldehydescatalyzed by tridentate Schiff base Aluminum (III) complexes", Angew Chemical International Education., 47, 392–394,1976.

71. G.Vuckovic, V.Stanic,S.P.Hasty, M.A. Nikolic, J. Mrozinski. 2005. Cobalt (II) complexeswith aromatic carboxylates and N-functionalized cyclam bearing 2-pyridylmethylpendant arms. Journal of Serbian Chemical Society, 70,11-21,2005.

72. G.Karabocek.,Y.Kiseok, Soo-Kyung and Chang-Su.Template synthesis and characterizationof copper (II) complexes of polyaza non-macrocyclic ligands,chemistry department, Taegu Universty,713-714,1996.

73. G.Sureshan. Y.Kiseok, Soo-Kyung and Chang-Su "Template synthesis and characterization of copper (II) complexes of polyaza non-macrocyclic ligands", chemistry department, Taegu University, 713-714, 1996.

74. Gutta Ghames.,"Synthesis and characterization of some new series of Zn(II),Co(II) andCu(II) complexes of tetradentate tetraaza Macrocycles and pent bis(macrocycle)", Graduate thesis of A.A.U.454,27,2002.

75. Wei-Hau Wang , M.Sosa-Torres, R.Toscano"Synthesis, crystal structures and theoreticalstudies of four Schiff bases derived from 4-hydrazinyl-8-(trifluoromethyl) quinoline,Journal of Chemical Crystallography" 31, 129,2001.

76. Fabbrizzi, Comments Inorg. Chem, 4, 33 1985.

77. R. Rajavel, M .Senthil and C. Anitha "Synthesis, Physical Characterization andBiological Activity of Some Schiff Base complexes E-Journal of Chemistry" 5(3) 620-626, 2008.

78. L. Bellamy, "Infrared Spectra of Complex Molecules London" p.175,vol 1,1954.

79. D.H.Busch,andN.F, Curtis. "Distinctive coordination chemistry and biological significanceof complexes with macrocyclic ligands. Academicals Chemical Researche".11, 392-400, 1978.

80. R.Yang, and L.J.Zompa. "Highly enantioselective hydrophosphonylation of aldehydescatalyzed by tridentate Schiff base Aluminum (III) complexes", Angew Chemical International Education., 47, 392–394, 1976.

81. G.K.Shin, Y.Kiseok, Soo-Kyung and Chang-Su "Template synthesis and characterization of copper (II) complexes of polyaza non-macrocyclic lligands", chemistry departmentTaegu University, 713-714, 1996.

82. Z. H. Zhong, X-Z You and Q-C Yang, Polyhedron, 13, 195,1994.

83. C. Moore and B.C. Pressman, Biochem. Biophys. Res. Commun,15, 562, 1964.

84. R. M. Izatt and R. M. Nelson, Science, 164, 443, 1969.

85. W. U. Malik, R. Bembi and R. Singh, Inorg. Chim. Acta, 68,223, 1983.

86. M. Fujiwara, H. Wakita, T. Matsushtta and T. Shono, Bull.Chem. Soc. Japan, 63, 3443, 1990.

87. I. Prokopenko, N. N. Liatvinov, D. M. Klimova, R. A.Dmitriena, V. P. Ilin, T. L. Mazurina, O. A. Pugacheva, K. K.Kuznetsova and T. A. Kiril Kina, Gig. Sanit., 2, 9, 1989.

88. G. Fernandez Leborans and M. A. Antonia Garcia, ActaProtozool., 27, 141, 1988.

89. J. L. Stauber and T. M. Florence, Water Res., 23, 907, 1989.

90. M. R. Moors and P. A. Meredith, Arch. Toxicol., 42, 87, 1979

91. M. Mitewa and P. R. Bontcher., Coord. Chem. Rev., 136, 129,1994.

92. I. Ito, M. Kato, M. Yamashito and H. Ito, J. Coord. Chem., 15,29, 1986.

93. M. P. Mertes and K. B. Mertes, Acc. Chem. Res., 23, 413, 1990.

94. M. Sezgin, A. D. Beduck, S. Ertul and A. Kocak; Synth React,Inorg. Met-Org. Chem., 21, 269.

95. N. F. Curtis, Coord. Chem. Rev., 3, 3, 1967.

96. C. J. Pedersen, J. Atn. Chem. Soc., 89, 7017, 1967.

97. R. D. Hancoock and M. P. Ngwenya, J. C. S. Dalton. Trans.,2911, 1987.

98. E. P. Kyba, G. W. Gokel, E. de Jong K. Koga, L. R. Sousa, M.G. Siegel, L. Kaplan, G.D.Y. Sogah and D.J. Cram. J. Org.Chem, 42, 4173, 1977.

99. V. L. Goedken, J. Molin-case and Y. Whang., J. C. S. Chem.Comm., 2, 337, 1973.

100. C. J. Cairns R. A. Heckman, A. C. MelnyK, W. M. Davis and D.H. Bush, J. C. S. Dalton, Trnas., 2505, 1987.

101. K. S. Patel and A. A. Adeniyi, "Syn, Reat Inorg. Met-orgn. Chem. 21, 1331, 1991.

102. D. L. Pavia, G. M Lampman & G. S. Kriz, Jr. "Introduction to Spectroscopy" Saunders College Edi., Philadelphia.

103. R. E Cook, and P. J. Robinson, J. Chem. Res., 9S) 267, (M) 2772 ,1982.

104. A. A. Schilt, "Perchloric Acid and Perchlorates", The G. Frederick Smith Chemical Co., Columbus, Ohio, 1979.