CHAPTER - 1
INTRODUCTION
1.1 Schiff Base

A Schiff base (or azomethine), is named after its inventor, Hugo Schiff and it is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen. Schiff bases have the general formula of $R_1R_2C=NR_3$, where $R_3$ is an aryl or alkyl group that makes the Schiff base a stable imine [1]. Generally Schiff bases are prepared under acid or base catalysis or with heat [2]. Schiff bases can be synthesized from a reaction of an aromatic amine and a carbonyl compound by a nucleophilic addition forming a hemiaminal, followed by a dehydration to generate an imine.

The Schiff base formation is really a sequence of two types of reactions, i.e. addition followed by elimination. A large number of aldehydes and ketones have been condensed with various amines to give Schiff bases.

Ligand, a metal surrounded by a cluster of ions or molecule, is used for preparation of complex compounds named as Schiff bases [3]. Schiff bases act as good ligands forming complexes with various metal ions due to their proton donating ability and number of bonding sites which lead to different stereo chemical structures and can also give kinetic and thermodynamic stability to the metal complexes. Though monodentate Schiff base ligands have been synthesized and studied for the complexation with several metal ions, bi, tri and tetratdentate Schiff base ligands, normally known as multidentate ligands, are of great importance because of the chelating property which gives extra stability to the metal complexes and interesting geometries have been observed.
Schiff bases form an important group of compounds in chemistry due to their useful physical and chemical properties and large number of reactions they undergo. They have wide use in industry due to their interesting pharmacological activity. Schiff bases exhibit excellent characteristics and structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural scaffolds [1]. The synthesis of the coordination compounds of the Schiff’s base ligands having N, S-donor binding sites has attracted a considerable attention because of their potential biological activities [4]. The main features of these compounds are their preparative accessibility, diversity, structural variability and versatile coordinating properties [5]. Schiff bases derived from aromatic aldehydes are more stable than those derived from lower aliphatic aldehydes and primary aromatic amines. 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. They are also used in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection due to enhanced selectivity and sensitivity [1]. Heterocyclic ring containing oxygen, sulpher and nitrogen impart special biological activity to these Schiff bases [6]. The chelating abilities and analytical and biological applications of these compounds have attracted remarkable attention [7]. Schiff bases have been widely used in many fields e.g., biological, inorganic, analytical and drug synthesis, as bidentate ligands in the field of coordination chemistry [2]. Schiff bases can be used in the degradation of organic compounds and in radiopharmaceuticals [8].

Many studies initially focus on simple Schiff base ligand such as salophen, salen and acacen but interest quickly shift to more intricate species which have extra functional groups, side chains and more methylene groups in the amine backbone [9].

Schiff bases derived from the salicylaldehyde are well known as polydentate ligands coordinating in neutral forms [10]. Schiff-base ligands derived from salicylaldehyde and chiral amines have been widely applied in enantioselective
cyclopropanation of styrenes [11], asymmetric aziridination of olefins [12], enantioselective epoxidation [13], enantioselective ring opening of epoxides [13], borohydride reduction of aromatic ketones [14], asymmetric oxidation of methyl phenyl sulfide [15], enantioselective oxidation of silyl enol [16] and trimethylsilylcyanation of benzaldehydes [17, 11].

Tetradentate Schiff bases derived from salicylaldehyde and a variety of diamines (1:2 ratio) have been carried out previously. They have been shown that an increase in the methylene chain length allows adequate flexibility for the complexes to change their structure from a planar towards a distorted or pseudo-tetrahedral motif. In addition, the longer chains cause the ligand field strength to decrease [18]. It is well known fact that the Schiff bases containing multiple donor sites plays a key role in the investigation of geometrical structure of coordination compound, which is back bone of the structural chemistry. Tetradentate Schiff bases with a N₂O₂ donor atom set are known to coordinate with various metal ions, and this has attracted many researchers [19]. The ligand was synthesized by the condensation of 2-hydroxyacetophenone with ethylenediamine as reported [20].

Complexing behavior of bidentate and tridentate Schiff bases containing different donor atoms with varying electro-negativities has been well studied. In last some year’s considerable interest has been shown in the complexing behavior of quadridentate Schiff bases [21]. Studies have thrown light on the synthesis of first-row transition metal complexes of some new Schiff bases. Little work seems to have been done on the metal complexes of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and anisidines [22].

1.2 Mixed-Ligand Complexes
Mixed-ligand complexes, in which metal is bound to two different ligands is called ‘ternary complex [MAL] or mixed-ligand complex’. For example complex species MAL were A (primary ligand) and L (secondary ligand) are two different ligands. In formation of ternary complexes, the primary ligand
(A) bond to metal ion M, influences the rate of binding of the secondary ligand L and the effect are corollary to the thermodynamic effects. Thus, strong sigma-donor ligands, which have both sigma and pi-donors, tend to labilize coordinated water molecule leading to a faster rate of replacement of aqua ligand in MA by secondary ligand (L) forming MAL. The strong pi-acceptor ligands do not labilize coordinated water molecule, which implies that the sigma-donor effect of the ligand is compensated by its pi-acceptor properties, leaving unaltered the Lewis acid character of metal ion [23].

Complexes of transition metal(II), which involve derivatives of salicylaldehyde and diamine, have received considerable attention because of their potential as catalysts for the insertion of oxygen into an organic substrate [24]. The synthesis of metal complexes with the electrochemical method was introduced in 1982 by Dennis G. Tuck [25]. The direct electrochemical synthesis of metal complexes has been the subject of interest in recent years [26, 27]. In the application of this technique, which involves the anodic oxidation of a metal in a non-aqueous solution of the ligand precursor, the most important advantages are the simplicity of the technique and high product yield [19].

Transition metals have varying utility and interesting chemistry. Coordination compounds are important due to their role in biological and chemical systems in various ways. It has been observed that metal complexes with appropriate ligands are chemically more significant and specific than the metal ions and original [28]. Currently the significance of metal ions in various biological systems has become important, as they are more powerful inhibitor of an enzyme as compared to uncomplexed biological active compounds. Moreover, the evidences supporting the use of metal complexes in the fight against cancer, tumor, viruses and bacteria have further made this subject a matter of great research interest. There are a large number of metal complexes that are anticancer, antitumor and antibacterial [29]. The complexation of metallic elements with biologically inactive compounds renders them active; and in case the compounds are already active, it makes them more active. The mechanism
involved in enhancing this biological activity upon complexation is still needed
to be further investigated [30].

Much more attention has been devoted by bioinorganic as well as by medicinal
chemists to develop the relationship between the metal ions and their
complexes to use as antitumor and antibacterial agents. In vitro studies have
indicated that some biologically active compounds may become more
carcinostatic and bacteriostatic upon chelation. Such interaction of transition
metal ions with amino acids, peptides and pyrones are of immense biological
importance. Several reviews show that the metallo-organic chemistry of such
compounds greatly influence their biological action highlighting the catalytic
function or metals in many biological processes [31].

Evidences supporting the introduction of metallic elements in several
biological processes are rapidly accumulating. Kirshener et. al. [32] has
investigated the antibacterial, antiviral and anticancer activities of more than
twenty five inorganic compounds which included the metal atom as potentially
significant part of the molecule. They suggested that the transfer of metal ion
from the ligand to the cancer-associated viruses was a mechanism for releasing
the anticancer drug in the locality of the tumor. Due to significant nature of
metallic ions, their metal complexes are now being included in the search for
ideal anticancer drugs [28].

The success of cisplatin and related platinum complexes as anticancer agents
has stimulated a search for other active transition metal complexes and
ruthenium in particular has attracted the researchers [33]. Metal complexes of
ruthenium containing nitrogen and oxygen donor ligands are found to be
effective catalysts for oxidation, reduction, hydrolysis and other organic
transformation [34]. The coordination environment around ruthenium plays the
key role in stabilizing its different oxidation states and hence dictates the redox
properties of the control atoms [35-36].
Oximes and azo dyes have often been used as chelating ligands in the field of coordination chemistry and their metal complexes have been of great interest for many years. The biological importance of oximes and their complexes is very well known [37]. Different oximes and their metal complexes have shown notable bioactivity as chelating therapeutics, as drugs, as inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxides [38-39]. Transition metal complexes with o-hydroxy aromatic oximes have attracted much attention as they exist as cis- and trans- geometrical isomers. Copper complexes are known to assume transstructures while cobalt complexes have cis structures [40].

An important class of natural products which are responsible for the uptake of iron is the siderophores. The probably most prominent example of this class is enterobactin. It has inspired the synthesis of a wide series of non-natural compounds which are used for metal ion binding and medical purposes. However, the efficiency of this artificial chelators to bind iron(III) excels only in few cases the one observed for enterobactin [41]. Metals and metal complexes have played key role in the development of modern chemotherapy. For example, anticancer platinum drugs appear in more chemotherapy regimes than any other class of anticancer agents and have contributed substantially to the success achieved in treating cancer over the past three decades. Metals can play an important role in modifying the pharmacological properties of known drugs after coordinating to a metal [42]. The metal based drugs are also being used for the treatment of a variety of ailments viz. diabetes, rheumatoid arthritis, inflammatory and cardiovascular diseases as well as diagnostic agents [43].

In medicinal chemistry, metal complexes have received limited attention as compared to organic compounds. In fact, many organic compounds used in medicine do not have a purely organic mode of action and require traces of metal ions directly or indirectly for activation or biotransformation. Our health, aging, physiological disorders and diseases are related to the state of the metal
ions and their complexes with biomolecules in the body. Traces of metals are essential for the biological processes as about 30-40% of all known proteins including metalloenzymes require metal cofactors (e.g., Fe, Cu, Zn, Ni, Mn) for their proper folding into an active three dimensional (3-D) structure [44].

1.3 Biochemistry

1.3.1 Biochemistry of Manganese
Manganese is a chemical element, designated by the symbol Mn which is discovered by Johann Gahn of Sweden. It has the atomic number 25. Manganese is a silvery-gray metal resembling iron. It is hard and very brittle, difficult to fuse, but easy to oxidize. Manganese metal and its common ions are paramagnetic. The isotopes of manganese range in atomic weight from 46 u ($^{46}\text{Mn}$) to 65 u ($^{65}\text{Mn}$). Naturally occurring manganese is composed of 1 stable isotope, $^{55}\text{Mn}$. Eighteen radioisotopes have been characterized with the most stable being $^{53}\text{Mn}$ with a half-life of 3.7 million years.

Manganese is actually an extremely important element that the body uses for a variety of things. For instance, we use it to make chemicals that help us digest the food that we eat. Manganese also supports the immune system, regulates blood sugar levels and is involved in the production of energy and cell reproduction. This important element is also important for bone growth. Additionally, manganese works with vitamin K to support blood clotting. Working with the B-complex vitamins, manganese helps to control the effects of stress while contributing to ones sense of well being.

Though it is extremely rare in humans, Percentage Amount in the Human Body: 0.00002%, it is suspected that not getting enough manganese can cause poor bone formation, affect our fertility and the ability for our blood to clot. Birth defects can possibly even result when an expecting mother doesn’t get enough of this very important element. Some researchers are also looking into a link between poor manganese intake and higher skin cancer rates. The fact that manganese is so important to humans, yet deficiencies in humans are so
rare, may indicate that humans have evolved ways to make sure that we don’t ever run out of this element in our bodies. As is the case with most, if not all, elements, we can easily get enough manganese from a good balanced diet. Foods high in manganese include avocados, berries, nuts and seeds, egg yolks, whole grains, green leafy vegetables and legumes (such as peanuts, peas and beans).

Manganese is a critical trace element. Manganese seems to lend a pliant, flexible quality to animal bone. A manganese deficiency in bone leads to brittle, easily broken bones. Manganese also activates several important enzymes, assists in the functioning of metabolism, and aids in the utilization of Vitamin B₁. A manganese deficiency can lead to infertility in mammals.

1.3.2 Biochemistry of Iron
Iron is a chemical element with the symbol Fe (from Latin: *ferrum*) and atomic number 26. It is a metal in the first transition series. Iron surfaces appear lustrous silvery-gray. It is the most common element in the whole planet Earth, forming much of Earth's outer and inner core, and it is the fourth most common element in the Earth's crust. It is produced in abundance as a result of fusion in high-mass stars. Naturally occurring iron consists of four stable isotopes: 5.845% of $^{54}\text{Fe}$, 91.754% of $^{56}\text{Fe}$, 2.119% of $^{57}\text{Fe}$ and 0.282% of $^{58}\text{Fe}$. $^{60}\text{Fe}$ is an extinct radionuclide of long half-life (2.6 million years).

The element iron has many functions in the body. Percentage Amount in the Human Body: 0.006 %. This element is used by the body to make tendons and ligaments. Certain chemicals in our brain are controlled by the presence or absence of iron. It is also important for maintaining a healthy immune system and for digesting certain things in the food that we eat. In fact, plays a vitally important part of how our body obtains energy from our food. The iron we obtain from our diet is an essential part of hemoglobin - the part of our blood that carries oxygen. Iron is essential for blood to work efficiently. If the lack of iron in our bodies is severe, we can get "iron deficiency anemia", which
essentially means that our blood won’t carry enough oxygen to our bodies so we can function normally. Iron deficiency anemia is probably the most common nutritional disease in the world, affecting at least five hundred million people.

Iron is a critical element for life. An iron atom is the center of every hemoglobin molecule, so iron is especially important as an oxygen transport for species with red blood. It is also a constituent of enzymes involved in energy metabolism, and lack of sufficient iron contributes to anemia and reduced resistance to infection. Iron is also an important trace element for plants.

1.3.3 Biochemistry of Cobalt
Cobalt discovered in 1735 by Georg Brandt of Sweden. Named from the German word meaning "goblin", Cobalt has atomic number 27. Cobalt is a shiny, brittle, bluish-gray metal. It is a hard, stable metal unaffected by air or water and only slowly affected by acid. Cobalt is one of the three ferromagnetic metals (cobalt, iron and nickel), so it is often used in alloys for magnets. $^{59}$Co is the only stable cobalt isotope and the only isotope to exist in nature. 22 radioisotopes have been characterized with the most stable being $^{60}$Co with a half-life of 5.2714 years.

Cobalt is another element that is necessary for good human health. While cobalt has no specific function by itself, it forms the core of vitamin B$_{12}$. Without cobalt, Vitamin B$_{12}$ could not exist. The body uses this vitamin for numerous of purposes. B$_{12}$ is necessary for the normal formation of all cells, especially red blood cells. Vitamin B$_{12}$ also helps vitamin C perform its functions and is necessary for the proper digestion of the food that we eat. Additionally, vitamin B$_{12}$ prevents nerve damage by contributing to the formation of the protective sheath that insulates nerve cells. A deficiency of vitamin B$_{12}$ can cause our red blood cells to form improperly. This can prevent our red blood cells from carrying enough oxygen from our lungs to the different parts of our bodies, thus causing a condition called anemia. Symptoms
of anemia include loss of energy, loss of appetite, and moodiness. $B_{12}$ deficiency can also cause nerve cells to form incorrectly, resulting in irreversible nerve damage. This situation is characterized by symptoms such as delusions, eye disorders, dizziness, confusion and memory loss.

The radioactive isotope Co$^{60}$ is a strong gamma ray producer and is used in medical applications, such as a radioactive tracer and a cancer fighter. Cobalt is an essential trace element for many species. It is the core of Vitamin $B_{12}$. It is important in the formation of red blood cells. Low cobalt levels in the soil will cause grazing animals to do poorly.

1.3.4 Biochemistry of Nickel

Nickel is a chemical element with the chemical symbol Ni and atomic number 28. It is a silvery-white lustrous metal with a slight golden tinge. It is one of only four elements that are magnetic at or near room temperature, the others being iron, cobalt and gadolinium. Nickel belongs to the transition metals and is hard and ductile. Naturally occurring nickel is composed of 5 stable isotopes; $^{58}\text{Ni}$, $^{60}\text{Ni}$, $^{61}\text{Ni}$, $^{62}\text{Ni}$ and $^{64}\text{Ni}$ with $^{58}\text{Ni}$ being the most abundant (68.077% natural abundance). 18 radioisotopes have been characterized with the most stable being $^{59}\text{Ni}$ with a half-life of 76,000 years.$^{62}\text{Ni}$ is the "most stable" nuclide of all the existing elements.

Although not recognized until the 1970s, nickel plays important roles in the biology of microorganisms and plants. In fact urease (an enzyme which assists in the hydrolysis of urea) contains nickel. A nickel-tetrapyrrole coenzyme, F430, is present in the methyl coenzyme M reductase which powers methanogenicarchaea. One of the carbon monoxide dehydrogenase enzymes consists of a Fe-Ni-S cluster. Other nickel-containing enzymes include a class of superoxide dismutase and a glyoxalase. Exposure to nickel metal and soluble compounds should not exceed 0.05 mg/cm$^3$ in nickel equivalents per 40-hour work week. Nickel sulfide fume and dust is believed to be carcinogenic and various other nickel compounds may be as well. Sensitized individuals may
show an allergy to nickel affecting their skin, also known as dermatitis. Sensitivity to nickel may also be present in patients with pompholyx. Nickel is an important cause of contact allergy, partly due to its use in jewellery intended for pierced ears. Nickel allergies affecting pierced ears are often marked by itchy, red skin. Many earrings are now made nickel-free due to this problem. The amount of nickel which is allowed in products which come into contact with human skin is regulated by the European Union.

Nickel is known to be an essential trace element for several species of animals. Experimental research shows that when chickens and rats are fed a diet that lacks nickel, they develop liver problems. If they are fed a normal diet, the symptoms do not appear. Animals are not the only ones that need this element to function properly. Bacteria use nickel to make special chemicals called enzymes. These enzymes are necessary for bacteria to function properly.

Though many scientists suspect that nickel is necessary for good human health, it has not been proven. Percentage Amount in the Human Body: 0.00002 %. People with certain liver and kidney diseases are known to have low levels of nickel in their bodies. Also, excess nickel in the body is associated with a high incidence of heart disease, thyroid disease and cancer. In both of these cases, the significance of the amount of nickel in the body is unknown. Some scientists think that nickel affects hormones, cell membranes and chemicals called enzymes. Whatever the case, nickel certainly appears to affect human health, even though we do not know exactly how.

Good sources of nickel include chocolate, nuts, fruits and vegetables. Meats are typically low in this interesting element. Nickel is a necessary trace element to many species. It interacts with iron in oxygen transport. It also stimulates the metabolism, as well as being a key metal in several plant and animal enzymes. Rats raised on a nickel-poor diet tend to develop liver damage.
1.3.5 Biochemistry of Copper

Copper is a chemical element with the symbol Cu (from Latin: *cuprum*) and atomic number 29. It is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; an exposed surface has a reddish-orange tarnish. There are 29 isotopes of copper. $^{63}\text{Cu}$ and $^{65}\text{Cu}$ are stable, with $^{63}\text{Cu}$ comprising approximately 69% of naturally occurring copper. The other isotopes are radioactive, with the most stable being $^{67}\text{Cu}$ with a half-life of 61.83 hours. $^{64}\text{Cu}$ is a radio contrast for X-ray imaging and complexed with a chelate can be used for treating cancer.

Copper is an element that is very important for our good health. Percentage Amount in the Human Body: 0.0001 %. Copper is critically important for dozens of body functions. Copper is a major component of the oxygen carrying part of blood cells. Copper also helps protect our cells from being damaged by certain chemicals in our bodies. Copper, along with vitamin C, is important for keeping blood vessels and skin elastic and flexible. This important element is also required by the brain to form chemicals that keep us awake and alert. Copper also helps your body produce chemicals that regulate blood pressure, pulse, and healing. Current research is looking into other ways copper can affect human health, from protecting against cancer and heart disease, to boosting the immune system. Copper is a necessary trace element to all species. It is a key component of certain enzymes and interacts with iron as hemocyanin, which is important in red blood cell production. The nervous system and bones also need copper. Copper is important to the sense of taste and copper has a distinctive taste that can be detected at very small concentrations.

General symptoms of not getting enough copper in your diet include anemia (a condition in which your blood can’t supply enough oxygen to your body), arthritis (painful swelling of the joints) and many other medical problems.
1.3.6 Biochemistry of zinc

Zinc discovered in 13th Century, its atomic number 30. Zinc is a lustrous, bluish-white metal. It is brittle at room temperature, but becomes malleable when heated to 100 degrees Celsius. Zinc is the 24th most abundant element in the Earth's crust. Zinc has five stable isotopes. $^{64}\text{Zn}$ is the most abundant isotope (48.63% natural abundance). Zinc has 10 nuclear isomers. $^{69m}\text{Zn}$ has the longest half-life 13.76 h. The superscript $m$ indicates a meta stable isotope.

Zinc has been recognized as an essential trace element for plants, animals and humans for more than 70 years. Though the average adult body only contains between 2-3 grams of zinc (a paperclip weighs about one gram), this element has some very important functions. Percentage amount in the human body: 0.003%. Zinc is involved in well over one hundred different reactions in the body. Some of these reactions help our bodies construct and maintain DNA, the molecule that controls how every single part of our bodies is made and works. Zinc is also needed for the growth and repair of tissues throughout our bodies. This extremely important element is used to form connective tissue like ligaments and tendons. Teeth, bones, nails, skin and hair could not grow without zinc. Zinc is widely considered by doctors to be one of the most important elements to a healthy immune system. This unique element is essential for the creation, release and use of hormones in the body. It helps developing fetuses grow correctly and our brains to work right. Additionally, our senses of sight, taste and smell depend on this element. Zinc is a critical trace element for all species. It is a key component in dozens of enzymes. Zinc is important in reproduction and sexual maturation. The metabolism requires zinc to function. An animal with a zinc deficiency needs 50% more food to gain the same weight as an animal with adequate zinc. Zinc is important to the immune system and zinc gluconate has recently become a popular cold medicine. Zinc is important to the senses of taste and smell, bone and skin development.
Not getting enough zinc can have serious effects on our health. Some of the symptoms of zinc deficiency include hair loss, mental apathy and damage to reproductive organs. Decreased growth rate and impaired mental capacity are other symptoms. Additionally, you can loose most of your senses of taste and smell, develop mental disorders and men can even become impotent without enough zinc.

1.4 Application

1.4.1 Catalysts

Transition metal complex-catalyzed oxidation of organic compounds is a field that has been extensively investigated in the past. Most of such catalysts synthesized were based on ligand systems like ethylenediamine [20]. Salen complexes of transition metals have been used in solution asbiomimetic catalysts for oxygen atom transfer and as catalystsfor enantioselective epoxidation, aziridinations, mediatingorganic redox reactions and other oxidative processes [45]. It is also useful as a catalyst in organic synthesis [46]. Co(salen) have been used for catalysing the oxidation of phenols and alcohols with dioxygen as oxidant. Cobalt (II) Salen complex catalyst has been successfully employed in the aerobic oxidation of alkyl aromatics [47]. Copper (II) and zinc (II) complexes based on N,O-bidentate salicylaldimine Schiff base ligands play a role in the catalyst activity [48]. Manganese(II) Schiff base complexes of 1,3-diamino-2-hydroxypropane with salicylaldehyde, 2-hydroxynaphthaldehyde or 2-hydroxyacetophenone ligands were excellent catalysts [49]. Catalytic activity of polymer anchored N,N'-bis(o-hydroxyacetophenone)ethylenediamine Schiff base complexes of Fe(III), Cu(II) and Zn(II) ions in oxidation of phenol [50]. Catalytic activity for alcohol oxidation carried out by ruthenium (II) complexes with 2-hydroxy-1-naphthaldehyde ethylenediimine or 2-hydroxy-1-naphthaldehyde-1,2-propylenediimine or 2-hydroxy-1-naphthaldehydetetramethylenediimine [51]. Catalytic Activity toward Oxidation of Alcoholscarried out by ruthenium(III)
complexes of \( o \)-phenylene diamine or ethylene diamine with salicylaldehyde or \( o \)-hydroxyacetophenone [52].

**1.4.2 Antimicrobial Activities**

Complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with 4-methyl-\( o \)-phenylene diamine and salicylic aldehyde and screened for antimicrobial activity [53]. Antimicrobial activities of Schiff base of 4-aminomorpholine with 2-hydroxynaphthaldehyde compounds have been studied [54]. 2-hydroxynaphthaldehyde and 2-aminophenol and its complexes with nickel and cobalt were biologically active against *Escherichia Coli* and *Bacillus Subtills* [55]. Antimicrobial studies of Cobalt(II), Nickel(II) and Copper(II) complexes of mixed ligands with Schiff base derived from 3-amino 5-methyl isoxazole with 2-hydroxy 1-naphthaldehyde [56]. Metal complexes of Co(II), Ni(II), Cu(II) with 2'- Hydroxyacetophonones and 3, 5 dibromosalicylaldehyde were biologically active [57]. Cu(II), Co(II) and Mn(II) complexes of 3,3’diaminobenzidine with o-hydroxyacetophenone showed good microbial activity [58]. VO(II), Co(II), Ni(II) and Cu(II) with the Schiff bases 2-hydroxyacetophenone/2-chlorobenzaldehyde with 2-amino-4-chlorophenol were tested against the bacteria *Escherichia coli*, *Staphylococcus aureus* and *Streptococcus fecalis* and the fungi *Aspergillus niger*, *Trichoderma polysporum* and *Candida albicans* [59]. Complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with 2-hydroxyacetophenone and hydrazine showed good antimicrobial activity [60]. Ruthenium complexes of Schiff bases salicylaldehyde/\( o \)-hydroxyacetophenone/\( o \)-vanillin/2-hydroxy-1-naphthaldehyde with thiosemicarbazide were screened for their antimicrobial activity against two bacteria and two fungi [61].

Copper(II), Nickel(II) and Oxovanadium(IV) 2-hydroxy-1-naphthaldehyde, 4,5 dichloro-orthophenenediamine and salicylaldehyde were tested against the microbes such as Bacillus subtilis, Staphylococcus aureus, Klebsiella pneumoniae and Escherichia coli [62]. Schiff base of 2-hydroxybenzaldehyde, 2-hydroxy-1-naphthaldehyde with 6,7-dihydro-13\( H \)-dibenzo[e,h] [1,4]dioxonin
-2,11-diamine antimicrobial and anti-yeast activities of the ligands were screened *in vitro* against the organisms [63]. The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with bis(acetophenone)ethylenediamine good antibacterial activity against *Salmonella typhimurium*, *Escherichia coli* and *Serratia marcescens* [64].

Ni(II), Co(II), Mn(II), Cu(II), Fe(III) and Cr(III) complexes of salicylaldehyde, *o*-hydroxy acetophenone and ethylene diamine were tested antimicrobial activity against two strain Gram +ve bacteria (*Staphalococcus aureus*, *Bacillus subtilis*), Gram-ve bacteria (*Salmonella typhimurium*, *Escherichia coli*) and fungus (*Aspergillus oryzae*, *Fusarium species*) [65]. Ruthenium (II) complexes of 2-hydroxy-1-naphthaldehyde ethylenediamine, 2-hydroxy-1-naphthaldehyde -1,2-propylenediimine or 2-hydroxy-1-naphthaldehydetetramethylenediimine. The antibacterial activities of the complexes were screened against *A. hydrophilla* and *Escherchia coli* [51]. Ni(II) complexes of (o-hydroxyacetophenone)ethylenediamine were screened against *Escherchia coli* & *Staphylococcus aureus* bacteria to ass their potential antimicrobial activity [66]. Nickel(II) complexes of *o*-hydroxybenzaldehyde, *o*-hydroxyacetophenone ethylene diamine have been examined against the growth of bacteria *in vitro* to evaluate their anti-microbial potential [67]. Complexes of Co(II) and Cu(II) with *o*-phenylenediamine and 2-Hydroxyacetophenone were tested antimicrobial activity against bacteria (*Bacillus cereus* *Staphylococcus aureus* and *E. Coli*) [68].

**1.4.3 Antifungal Activities**

Complexes of tin(II) 2-hydroxy-1-naphthaldehyde with aniline show antifungal activity [69]. Complexes of manganese(III) 2-hydroxy-1-naphthaldehyde with glycine, L-alanine L-phenylalanine antifungal activities fungus *Candida albicans* [70]. Metal chelates cobalt (II), copper (II), nickel (II) and zinc (II) of 2-Hydroxy-1-naphthaldehyde with sulfonamides were screened for their antibacterial and antifungal activities on different species. Antifungal studies of Cobalt (II), Nickel (II) and Copper (II) complexes of 3-amino 5-methyl
isoxazole with 2-hydroxy 1-naphthaldehyde against two fungi (*R. Saloni* and *A. niger*) [56]. Mixed ligand complexes of the type [M(SB)₂acphen], where M = Mn(II), Co(II), Ni(II), Cu(II) and Cd(II), HSP=3,5-tribromosalicylidineanilin and acphen= bis(acetophenone) ethylenediamine show antifungal activity [71]. Antifungal activities of complex Mn(II) with ligands 2-hydroxy-1-naphthaldehyde and ethylene diamine/ propylene diamine/ butyline diamine and it determined against two fungi (Mucor sp. and Rhizopus sp.) [72].

### 1.4.4 DNA

Complexes of Cu(II), Ni(II), Co(II) and Zn(II) of 4-aminoantipyrine, salicylaldehyde and *o*-phenylenediamine. The nuclease activity of the metal complexes shows only the copper complex cleaves DNA [73]. Cobalt complexes of 1, 3-diamine, 1,3-diaminopropane and 1, 3-diaminopentane with 2-hydroxyacetophenone, DNA binding abilities of all three cobalt complexes have been studied [74]. Copper(II) complex of 2-hydroxy-1-naphthaldehyde and *L*-leucine binds to calf thymus DNA (CT-DNA) [75]. Ruthenium complexes of salicylaldehyde/*o*-hydroxyacetophenone/*o*-vanillin/2-hydroxy-1-naphthaldehyde with thiosemicarbazide, all complexes were tested for its binding with CT-DNA [61]. Ruthenium(II) complexes of *o*-phenylenediamine and salicylaldehyde/*o*-hydroxyacetophenone/*o*-vanillin/2-hydroxy-1-naphthaldehyde, DNA binding studies (*Herring Sperm* DNA) were carried out [76].

### 1.4.5 Miscellaneous Applications

Schiff bases and their metal complexes containing Cu, Ni, Zn and Co were synthesized from salicylaldehyde, 2,4 dihydroxy-benzaldehyde, Glycine and *L*-alanine and possess antitumor activity and their order of reactivity with metal complexes is Ni > Cu > Zn > Co [3]. Copper N-(2-hydroxyacetophenone) glycinate shown to have a potential usefulness in immunotherapy of multiple drug resistant cancers [77]. Antitumor property of the ligand N-(2-hydroxy acetophenone) glycinate and some of its complexes has been studied [78]. The
study on 2-Hydroxy-4-isobutoxy acetophenone oxime has been used for the spectrophotometric determination for Mn(II) [79].

1.5 Literature Survey

The coordination behavior of the triazine ligand with NNO donation sites, derived from 3-benzyl-7-hydrazinyl-4H-[1,3,4]thiadiazolo[2,3c][1,2,4]triazin-4-one (HL), towards some metal ions namely Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were reported by Mohamed G. G., et al. [80]. Soleimani E. [81] was prepared 4,4-dibromobenzilmonoxime (BBOH) and its complexes Na[M(BBO)₃] (where M = Mn(II), Co(II), Cu(II)). The complexes of 2-methoxyhenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) with the general formula: M(C₉H₉O₄)₃·4H₂O, where M(II) = Mn, Co, Ni and Cu [82]. Colak A. T., et. al. [83] were prepared (2-aminomethylpyridinium- pyridinedicarboxylato)copper(II) dihydrate and (8-hydroxyquinolinumpyridine dicarboxylato)copper(II) hydrate. Tas E., et. al. [84] synthesized Schiff-base ligand [N,N-(3,4-benzophenon)-3,5-But2-salicylaldimine and its mononuclear Cu(II), Co(II), Ni(II), Mn(II) and Fe(II) complexes. 3-(4-Carboxy-3-hydroxyphenylaminomethyl)-5-(4-pyridinyl)-1,3,4-oxadizole-2-thione with various metal complexes viz Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, Mn²⁺, Fe³⁺ and UO₂²⁺ were prepared by Solanki D. K., et. al. [85]. The new ligand, N’-[4-(4-chloro-phenyl-sulfonyl)benzoyl]-2-oxoimidazolidine-1-carbohydrazide with complexes of Cu(II), Co(II) and Ni(II) reported by Angelusiu M. V., et. al. [86]. Bis(2-aminobenzaldehyde)malonyl-dihydrazone in the presence of 5-nitroindazole Cu(II) / Ni(II)- chloride prepared by Singh N., et. al. [87]. Vedanayaki S., et. al. [88] synthesized 5-bromo-3-fluorosalicylaldehyde and benzidine with Cu(II), Ni(II) and VO(IV). Raman N., et. al. [7] were reported complexes of Cu(II), Ni(II), Zn(II) and VO(IV) with 3-hydroxy-4-nitrobenzaldehyde and acetylacetone. Numan A. T., et. al. [89] were prepared Bis-1,4-di[N-3-(2-hydroxy-1-amino)-acetophenonylidene]benzylidene and its complexes with (Mn(II), Co(II), Ni(II) and Cu(II)).
Pandya R. N., et. al. [90] synthesized 4-Carboxaldehyde-1-phenyl-3-methyl-2-pyrazolin-5-one condensed with phenylhydrazine to form ligand (HL). These metal complexes are of type [ML₂(H₂O)₂] (M = Mn, Co, Ni and Cu), elemental analysis, magnetic susceptibility, electrical conductance, electronic and infrared data suggest octahedral structure for the metal complexes. Dawood Z. F., et. al. [91] were synthesized nickel(II) complexes with mixed ligands including benzilbis-(semicarbazone) - SCH₂ and one of dithiocarbamate ligands (ammonium pyrrolidenedithio- carbamate - Pyrdtc or ammonium indolinedithio carbamate - Indtc) have been carried out in both neutral and basic medium. Shahid S., et. al. [28] were prepared seven novel and biological active transition metal complexes using 3-nitro-4-hydroxy-6-methyl-pyran-2-one derivative of triacetic lactone as ligand. These data showed that solid complexes of Ni(II), Co(II), Mn(II), Zn(II) and Fe(II) indicated octahedral geometries. New Ni(II), Cu(II) and Co(II) complexes were synthesized 4-([E]-phenyldiazenyl]-2-[(E)-(phenylimino) methyl]phenol (dmpH) by Kurtoglu N. [8].

Rajavel R., et. al. [92] were studied coordination of a biomolecules to the metal ions significantly alters the effectiveness of the biomolecules. In view of the antimicrobial activity ligand [bis-(2-aminobenzaldehyde)] malonyl dihydrazone], metal complexes with Cu(II), Ni(II), Zn(II) and oxovanadium(IV) have been synthesized and found to be potential antimicrobial agents. Emara A. A. A., et. al. [93] were studiedon 4,6-Diacetylresorcinol (DAR) serves as precursor for the formation of different hydrazone ligands, which are di-, tetra- or hexa-basic with two symmetrical sets of O₂N tridentate, O₂N₂ tetradentate or O₄N₂ hexadentate chelating sites. Elzahany E. A., et. al. [94] were prepared Schiff base ligands N-amino rhodanine and each of 2-formylindole and salicylaldehyde with Cr(III), Co(II), Ni(II) and Ag(I), where as Cr(III), Co(III), Ni(II) and Cu (II) have octahedral configurations.
Complexes of Zn(II) and Hg(II) with new Schiff bases ligands of (N,N-bis(4-chlorobenzylidene)propane-1,2-diamine, N,N-bis(3-nitrobenzylidene)propane-1,2-diamine and N,N-bis(4-nitrobenzylidene)propane-1,2-diamine [95]. Shaker S. A., et. al. [10] prepared bidentate schiff base of the P-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-on with salicylaldehyde. Aliyu H. N.,et. al. [96] was synthesized complexes of Cu (II) and Schiff base derived from salicylaldehyde and 2-amino benzoic acid. Thaker B. T. and Bhattacharya P. K. [97] carried out synthesis and characterization of Cu(II) complex with bis[1-(2-hydroxyphenyl)ethylideneamine.

Tetradentate schiff base ligands; 1,3-bis(salicylideneimino)propane, 1,4-bis(salicylideneimino)butane and 1,5-bis(salicylideneimino)pentane and their Cu(II) and Ni(II) complexes were carried out by Chjo K. H., et. al. [98]. Nowicka B., et. al. [99] synthesized the reaction of [M(CN)₄O(H₂O)]²⁻ (M = Mo) with salicylaldehyde and methylamine gave the complex [Mo(CN)₃O(mesal)]²⁻, where Hmesal = N-salicyldenemethylamine. Manganese(III) complexes of the type: (i) [Mn(Sal-o-phen)Bzp].2H₂O, (ii) [Mn(Bzp-o-phen)Sal].2H₂O, (where, Sal-o-phen and Bzp-o-phen are the Schiff bases derived from salicylaldehyde and 1-phenyl-3-methyl-4-benzoyl-2-pyrazoline-5-one and o-phenylenediamine respectively [100]. Saghatforoush L. A., et. al. [101] were describe zinc (II) and cadmium (II) complexes of 2-((E)-(2-(2-(pyridine-2-yl)ethylthio)ethylimino)methyl)-4-bromophenol. Abushamleh A. S., et. al. [102] synthesized (L)-3-acetyl-5-methyl-1-phenyl-4,5-dihydro-1,2,4-triazine-6-one or (L)-3-acetyl-5-benzyl-1-phenyl-4,5-dihydro-1,2,4-triazine-6-one with nickel(II) in the presence of diamine such as: 1,3-diaminopropane, o-phenylenediamine, or ethylenediamine. Studies on N, N’ – bis(Benzoin)-o-phenylenediiminato zinc(II) done by Aliyu H. N. and Abdullahi H. J. [103]. Farias P. A. M. and Bastos M. B. R. [104] were reported copper(II) complexes of N,N’-ethylenebis(salicylideneimine). Koner S., et. al. [105] was prepared azido-bridged Fe(III) schiff base complex of N,N’-bis-
Salicylaldehyde(ethylenediimine) and N,N’-bis-3-methoxy Salicylaldehyde (ethylenediimine).

Complex [Cu(saloph)][(Cu(salobp)₂)Cl] was synthesized from salicylaldehyde and 1,2-phenylenediamine [106]. Two tetradentate ligands, N,N’-bis[4-(benzeneazo)salicylaldehyde]-o-phenylenediamine (H₂L) and N,N’-bis[4-(benzeneazo)salicylaldehyde]ethylenediamine (H₂L’) were formed and their Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) complexes were synthesized by Liu J. et al. [107]. Ti, Fe, Cd, Sn, and Pb (=M) complexes of N,N-bis(salicylidene)-o-phenylenediamine has been investigated by Liu J., et. al. [19]. Panchal P. and Patel M. [64] were reported complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with salicylidene-α-aminothiophenol and bis(benzylidene)ethylenediamine or bis(acetophenone)ethylenediamine. Ni(II), Co(II), Mn(II), Cu(II), Fe(III) and Cr(III) complexes of Schiff base ligand derived from salicylaldehyde, α-hydroxy acetophenone and ethylene diamine was carried out by Maldhure K. A. and Aswar S. A. [108].

Mixed complexes of the type MLL’ where M = Cu(II), Ni(II); L= salicylaldimine and L’= (α-hydroxybenzyl)(ethylideneamine) or o-hydroxydiphenyl enethylenediamine or their derivatives were prepared by Kohli R. and Bhattacharya P. K. [109]. Kannan S., et. al. [110] prepared Ruthenium(II) complexes of 2-hydroxy-1-naphthaldehyde with aniline, α-, m- or p-toluidine. Mittal R., et. al. [22] work done on Cu(II), Ni(II), Co(II), Zn(II), Mn(II) and Cr(III) complexes with the bidentate schiff base 2-hydroxy-1-naphthaldehyde and m-anisidine. Tetradentate schiff base ligands; [1,2-bis(naphthylideneimino)ethane, 1,3-bis(naphthylideneimino)propane, 1,4-bis(naphthylideneimino)butane and 1,5-bis(naphthylideneimino)pentane] and their Ni(II) complexes were synthesized by Jeong B. G., et. al. [111]. 2-Hydroxy-1-naphthaldehyde-2-aminothiazole (HNATS) and its copper complex [Cu(II)-(HNATS)₂] has been investigated by Tang B., et. al. [112]. Sensitive and convenient methods for the spectrophotometric determination of nickel(II) with N,N’-bis(salicylaldehyde) ethylenediamine, N,N’-bis(salicylaldehyde)O-
phenylenediamine and N,N'-bis(2-hydroxy-1-naphthaldehyde)O-phenylenediamine have been developed by El-Shahawi M. S. [113]. Schiff-base N-(1-hydroxy-2-acetophenone)-1-amino-2-phenyleneimine (HL) with 2-hydroxyl-1-naphthaldehyde with Zn, Co, and Cu complexes were prepared by Lashanizadegan M., et. al. [114]. Maparil A. K. and Mangaonkar K. V. [115] were reported mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases N-(2-hydroxy-1-naphthylidene)-2,6-diisopropylaniline and N-(2-hydroxybenzylidene)-2,3-dimethylaniline.

Patel N. H., et. al. [116] prepared Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) complexes with bis(acetophenone)ethylenediamine. Chen D. and Martell A. E. [117] carried out synthesis and characterization of (bis(salicylaldehyde) tetramethylthylediiminato) cobalt(II), (bis(salicylaldehyde)o-phenylene diiminato) cobalt(II), (bis(2-hydroxy acetophenone)ethylenediiminato)cobalt(II), (bis(3,5-dichlorosalicylaldehyde)o-phenylene diiminato)cobalt(II), (bis(3-methoxy salicylaldehyde)o-phenylendiiiminato) cobalt(II), and parent compound (bis (salicylaldehyde)ethylenediiminato)cobalt(II). West D. X., et. al. [118] have been prepared binuclear copper(II) complexes with eight different 2-hydroxy acetophenone 4N-substituted thiosemicarbazones. Two copper(II) complexes with the Schiff base 5-chloro-2- hydroxyacetophenone and salicylhydrazide was synthesized by Dance J. M. [119]. Boghaei D. M. and Lashanizadegan M. [120] were reported nickel(II) and copper(II) complexes of tetradentate Schiff base N-(1-hydroxy-2-acetonaphtone)-1-amino-2-phenyleneimine and N-(2-hydroxyacetophenone)-1-amino-2-phenyleneimine. Schiff-base ligands have been prepared by condensation of 2-hydroxyacetophenone with (1R,2R)-(1,2-diaminocyclohexane, (1S,2S)-(1,2-diphenylethylenediamine by Gao W. T. and Zheng Z. [11]. Saridha K., et. al. [52] were synthesized and characterization of hexa-coordinated ruthenium(III) complexes of the type [RuX2(EPh3)(L)] (E=P or As; X=Cl or Br; L=monobasic tridentate ligand o-phenylene diamine or ethylene diamine with salicylaldehyde or o-hydroxyacetophenone). Complexes of nickel(II) of o-hydroxybenzaldehyde, o-hydroxyacetophenone ethylene diaminewere synthesized by Anant P. et. al.
Habib S. I. et. al. [57] were prepared complexes of Co(II), Ni(II) and Cu(II) have been synthesized with 2'-Hydroxyacetophenones and 3, 5 dibromosalicylaldehyde, all Co(II), Ni(II) complexes have octahedral geometry. Mishra A. P. and Soni M. [121] synthesized new bidentate or tridentate Schiff bases and their VO(II) and Co(II) complexes formed by the condensation of methyl isobutyl ketone with nicotinamide (mna)/2-amino-4-chlorophenol (map) and 2-hydroxy acetophenone with nicotinamide (han)/isoniazide (hai). V. B. Mohankumar et. al. [122] reported complexes of aminoalkanols with 2-hydroxybenzophenone, 2-hydroxy-1-naphthaldehyde, salicylaldehyde, 2-hydroxy acetophenone. Mishra A. P., et. al. [123] prepared coordination complexes of VO(II), Co(II), Ni(II) and Cu(II) with the Schiff bases derived from 2-hydroxyacetophenone/2-chlorobenzaldehyde with 2-amino-4-chlorophenol. Complexes of Chromium and Molybdeum with schiff base bis(2-hydroxyacetophenone)ethylenediiamine was carried out by Ramadan R. M., et. al. [124]. Ali S. A., et. al. [125] synthesized Chromium, Molybdeum and Ruthenium complexes of bis(2-hydroxyacetophenone) ethylenediiamine.

### 1.6 Present Work

The work described in the thesis is in connection with the synthesis of mixed-ligand complexes of type MAB·H₂O [where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); A = N,N’-bis(2-hydroxynaphthaldehyde)ethylenediiamine (ONap-en), N,N’-bis(2-hydroxyacetophenone)ethylenediiamine (OAcPh-en), N,N’-bis(2-hydroxyacetophenone)o-phenylinediamine (OAcPh-opd), N,N’-bis(2-hydroxynaphthaldehyde)o-phenylinediamine (ONap-opd); and B = bis(4-methoxybenzylidene)ethylenediiamine (MeBen-en), bis(4-methoxybenzylidene) o-phenylenediamine (MeBen-opd), bis(benzylidene)ethylenediiamine (Ben-en), bis(benzylidene)o-phenylenediamine (Ben-opd). All these mixed-ligand complexes have been characterized on the basis of physical properties, elemental analysis, magnetic measurements, infrared spectra, electronic spectra, thermo gravimetric analysis and antimicrobial activities. The entire work of the thesis will be divided into five chapters.
Chapter 1: Introduction
In this chapter, general overview on coordination compound, ligand, mixed-ligand complexes, biochemistry of manganese, iron, cobalt, nickel, copper and zinc, applications of coordination compounds as (ligand, mixed-ligand complexes) and literature survey will be discussed.

Chapter 2: Synthesis and characterization of ligands
In this chapter, synthesis and characterization of ligands will be discussed. The ligands have been characterized with help of elemental analysis and infrared spectroscopy.

Chapter 3: Synthesis of mixed ligand complexes
In this chapter, describes experimental methods used for preparation of metal diaqua complexes and metal mixed-ligand complexes.

Chapter 4: Characterization of mixed ligand complexes
In this chapter, characterization of mixed-ligand complexes will be discussed. The complexes have been characterized using physical properties, elemental analysis, magnetic measurements, infrared spectra, electronic spectra and thermo gravimetric analysis.

Chapter 5: Antimicrobial activities
In this chapter, Minimum Inhibitory Concentration (antimicrobial activity) of the compounds will be discussed. MIC has been assayed against two Gram\(^{(-ve)}\) i.e. \textit{E. coli} and \textit{P. aeruginosa}, and three Gram\(^{(+ve)}\) i.e. \textit{S. aureus}, \textit{B. subtilis}, \textit{S. merscences} microorganisms using “Agar diffusion method”. The results show a significant increase in antibacterial activity compared with parentalligands, metal salts and standard drugs.
1.7 Reference


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