

The development of coordination chemistry occurred slowly throughout the nineteenth century; it was in the last two decades with the work of Denmark and Alfred Werner in Switzerland, that the heart and soul of this discipline namely coordination chemistry took shape. The growth of coordination chemistry has been three dimensional encompassing breadth, depth and applications. The ongoing respect for the evolving science is apparent is the five noble prizes that have been impinged heavily on the subject Alfred Werner 1913; M. Eigen 1967; Wilkinson and Fischer, 1973; H. Tanabe 1983; Cram, Lehn and Pedersen 1987. The first Werner and last Cram, Lehn and Pedersen in the list recognized the old and new realness of coordination chemistry specifically.¹ Coordination chemistry encompasses a great diversity of substances and phenomenon.²

The separation of geometrical isomers of $[\text{Co}(\text{NH}_3)\text{Cl}_2]\text{X}$ optical resolution of $\text{cis-}[\text{Co}(\text{NH}_3)(\text{en})\text{Cl}]\text{X}_2$ are some examples, which revolutionized the foundation of classical chemistry. The growth in understanding the coordination chemistry has been greatly stimulated by the developments in catalysis and understanding its role in biochemistry. The key components of coordination compounds are metals, ligands and metal-ligands interactions. Metals are generally from 'd' and 'f' block elements and are characterized by their variable oxidation states, coordination numbers. Ligands may be anions, cations or neutral molecules, polyatomic ligands that bond through single atom are termed as monodentate ligands that form rings by bonding atom are said to be chelating ligands, chelating ligands may be further classified as bidentate, tridentate and tetradentate etc. depending on the number of donor atoms available for bonding to central metal atoms^{3,4}.

Metal complexes play a vital role in analytical chemistry in chemical industries and in understanding a variety of biological process. The rapidly developing field of bioinorganic chemistry in recent years centered on the presence of coordination complexes in living system. The applications of coordination complex formation reactions are in use since early days the detection, separation and estimation of metals both in macro and micro scales.

Coordination compounds are not only limited for synthesis and stereochemistry, Chemical industry, Pharmaceutical labs, Textiles, Geo-science, Oceanography, Agriculture, Bio-inorganic chemistry etc. in recent years. Some more recent and some what existing applications of metal complexes observed are in the photolytic splitting of water producing hydrogen. This process has an immense

potential for generating a non polluting fuel which may be an ultimate solution to save the world from a severe crisis in the future due to non-availability of fossil fuels. The knowledge of the factors that govern the stability and reactivities of metal complex and the nature of the metal ligand bond provide a fundamental basis for understanding the behavior of metal complexes.

The rapidly developing field of Bio-Inorganic chemistry in recent years, entered as the presence of coordination complexes on living systems. The use of gold complexes in the treatment of tuberculosis, arthritis etc. several significant researches unequally proved the effective usefulness of metal complexes in biology, in the treatment of several diseases ⁵ like small pox, viral diseases and certain kinds of tumors and for metal detoxification in case of metal poisoning.

Metals play a predominant role in biological life kingdom. The correct proportion of metals is a must for normal growth and normal health both, the excess and deficiency of many metals, not synthesized in the body like other nutrients, lead to metal poisoning, metabolic disorders and skeletal abnormalities. Many of us heard the common and some what sarcastic statement, from our elders, that they have silver in the hair, gold in the teeth and lead in the bones. Strange as it may seem at first sight, all three metals can have an effect on living systems.

Silver and its salts have anti bacterial properties and are used as disinfectants due to their germicidal effects^{6,7} for example Silver Nitrate(AgNO_3) in diluted solution is administered to the eyes of new born as a prophylactic agent against gonorrhoeal infections ^{8,9}.

Gold compounds, like Aurofin(2,3,4,6-tetra-o-acetyl-1-thio- β -D-glucopyranosido-S)triethyl phosphine gold(1)^{10,11} are applied as oral drugs against rheumatoid arthritis^{11,12}.

Cisplatin, $\text{Cis}-(\text{NH}_3)_2 \text{PtCl}_2$, which is successfully employed world wide as an anticancer drug^{13,14} or lithium carbonate which is given to patient with certain mental disorders¹⁵.

Lead is one of the oldest metal known to man and its toxicity was recorded already by Greek and Arab Scholars¹⁶ lead interest with the metabolism and action of essential metals, particularly Ca, Fe, Zn and Pb can act as an effective substitute¹⁷. It is harmful mainly through its neurotoxicological effects.

The interaction of Zn(II) and Cd(II) ions with biomolecules is one of the most studied fields in coordination chemistry. Zinc is the second most abundant trace metal in the human body and can be considered as non toxic to humans. It is essential for the structure regulation and catalytic action of over 300 enzymes. Cadmium is a very toxic metal widely used in many industrial process¹⁸. Silanes are organofunctional hybrid organic, inorganic chemicals, historically used as coupling agents for adhesion between organic and inorganic material, such as glass fiber reinforced polymeric composites¹⁹.

The importance of metal complexes in the biological action of certain drugs²⁰ has been realized only in the past few decades. The metal complexes seem to best upon the active sites of the drugs, certain physical properties etc. It has been found that majority of the metal complexes possessing biological activities are chelates several reviews have been reported on the relationship of metal complexes to biological response.

Schiff's base

Schiff's bases are an important class of ligands in coordination chemistry and have many applications in various fields³. The most common method of obtaining Schiff's base is simple condensation of primary amines with aldehydes or ketones. The chemistry of Schiff's base complexes continues to attract many researchers because of its wide applications in Analytical chemistry, Catalysis, Food industry, Dye industry, Fungicidal and Agro chemical activity.²¹⁻²⁴

In addition; they have also been used as biological models for oxygen carriers. In chemical science the chelating characterization of Schiff's base transition metal complexes containing different donor atoms such as nitrogen, oxygen and sulphur exhibit enhanced applications in the advanced chemical fields like anticancer, anti-tuberculosis, anti-inflammatory, antiviral, anti-HIV²⁵⁻²⁹, fungicide, insecticide, anthelmintic, antipruritic, anti-helicobacter pylori activities³⁰⁻³², has also in technological fields like electroplating, photography polymers, hair spray, cosmetics, perfumes, printing technology and environmental sciences.

The coordination compounds are characterized depending on the nature of metal-ion, the donor atom, the structure of the ligand and metal-ligand interaction, usually a metal-ion does not forms a bonds of same strength with two different donor atoms, similarly a particular donor atom cannot form bonds of same strength with different metal-ions.

A survey of the literature shows that besides investigating electronic structure, bonding and stereochemistry of metal complexes, an increasing number of studies have been devoted to the dynamics and mechanisms of reaction of metal complexes. The classical applications of complex formation in analysis and other laboratory practices have been refined and sophisticated to such a degree that it is now possible to monitor concentration of species at unbelievably low levels, viz., in the range of a fraction of a micro gram per milliliter of solution based on several characteristics such as color, catalytical activity etc.

The number of coordination compounds, including organometallics, have been synthesized with a variety of organic substrates these are important, not only academically but also technologically, because of their useful catalytic properties. Apart from the study of their potential use in the laboratory, industry, drugs and medicinal therapy, more recent and exciting applications of complexes include photolytic decomposition of water producing hydrogen.

It has long been known that intake of metals by plants and animals are necessary for life to flourish. But until recently little was known for the precise functions of metals. In most of the cases, metals are found to be in complexed form with the organic moieties in the biological systems. Many complexes and the complex forming reagents are known for their use as drugs in certain diseases and also for metal detoxication in the case of metal poisoning.

Few Metals play a very important role in the biological kingdom. There would have been no life without the essential of transition and non-transition metals. Their correct proportion is a must for normal growth and normal health, both, the excess and deficiency of many metals, not synthesized in the body like other nutrients, lead to metal-poisoning, metabolic disorders and skeletal abnormalities. The essential metals in the body may be considered to be in two categories bulk metals and trace metals, bulk metals (sodium, potassium, magnesium and calcium) constitute about one percent of the human body weight. Whereas trace metals (manganese, iron, copper, cobalt, zinc, molybdenum, vanadium and chromium) represent less than 0.010% of the same. A 70 kg man has approximately 170 g of potassium in his body of which about 9.0 g are in the blood and 3.0 g in the tissue fluid. The same man requires only about 5.0 g of iron.

In biological system, most of the essential metals cannot occur in the form of free metal ions under the prevailing pH conditions of the system and presence of

numerous complex forming and chelating species in biological materials. Some of these are amino acids, hydroxyacids, nucleic acids, etc., together with inorganic ligands such as chlorides, nitrates, bicarbonates and carbonates, phosphates, etc., due to the presence of the above substance; the metallic cations enter into more or less strong complexation with these complex forming species.

The presence of Copper in ceruloplasmin haemocyanine, amine oxidase. Polyphenoloxidase, lactase, Nickel in human serum albumin. Zinc in carboxy peptides, magnesium in chlorophyll and ATP etc. are proved to be essential for biological activity and establish the fact of occurrence of metal complexes in biological systems. Many enzyme reactions are directly metal ion dependent so that dialysis or addition of chelating agents may lead to loss of activity, which may be regained, if further metal is added. Examples include the magnesium, calcium and manganese activated phosphoryl transferases, copper activated polyphenol oxidase and zinc activated alkaline phosphates.

The transition metals are characterized by their ability to form a wide range of coordination compounds in which the octahedral, tetrahedral and square-planar geometries are predominant. Based on this, several complexes of the Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) and Manganese(II), are well known.

The development in the field of coordination chemistry during the past three decades has indeed been phenomenal. The interest in the metal complexes now embraces area ranging from purely academic synthesis to large-scale industrial production. This tremendous growth of coordination chemistry was due to the availability of several modern physical techniques such as IR. UV-Vis. NMR and ESR spectral methods, which are of great help in elucidating the structures of metal complexes³³⁻³⁵. Thermal techniques such as TG, DTG, DTA and DSC are also help for studies of these complexes.

The Coordination compounds are widely used in analytical chemistry for the identification and extraction of metal ions in cation exchange resins and in solvent-extraction for the preparation of radioactive metals. They are used as catalyst in many industrial processes like Wacker process, Monsanto process etc. They are also used as gravimetric reagents, e.g. dimethylglyoxime, 8-hydroxyquinoline, they play an important role in colorimetric, spectrometric and polarographic analysis.

Werner's ideas about coordination number and geometrical arrangement were accepted. However, there still remained the intriguing questions of the nature of the bond which held the ligand to the metal-ions. The studies of Werner and his contemporaries followed by the ideas of Lewis³⁶, Langmuir³⁷ and Sidgwick³⁸ who put forward his Effective Atomic Number (EAN) on electron pair bond led to the idea that ligands are the groups which can in some way donate electron pairs to metal ions, thus forming a so called coordinated link. This approach to bonding in complexes was extended by Pauling³⁹ and developed in to the valence bond theory (VBT) of metal ligand bonding. This theory enjoyed great and virtually exclusive popularity during 1930 and 1940. But in 1950 it was supplemented by the crystal field theory (CFT). The CFT was first expounded in 1929 by H. Bethe⁴⁰. This was further developed between 1930 and 1940 by physicists, mainly J. H. Vanvlenck⁴¹ and his students and rediscovered in 1950 by several theoretical chemists into ligand field theory (LFT). The LFT as it is used today has evolved out of a purely electrostatic CFT. While the crystal field theories focus attention entirely on the metal ion d-orbitals, the molecular orbital theory (MOT) takes in to account the ligand orbital another approach is the so called angular overlap model (AOM).

A Brief review of DNA Studies:

In some of the bioactive ligands with low molecular weight which also recognize and interact with DNA, are of chemical and medicinal significance as potential artificial gene regulators or cancer chemotherapeutic agents^{42,43}. The investigation of interactions between double stranded DNA and DNA binding agents is crucial for understating biochemical process as replication, repair, recombination and expression of genes. In principle, the possible binding mechanism of ligands to double stranded dsDNA can be divided into sequence specific binding and binding mode that lack sequence specificity. Specific binding between ligand (protein) receptor (dsDNA) often termed as molecular recognition is the basis for the interaction of many transcription factors with DNA. Small agents bind unspecifically or with lower sequence specificity to dsDNA are often capable of influencing or inhibiting these processes and intrinsically exhibit magnetic properties. Consequently these molecules find application as Pharmaceuticals mainly in the treatment of Cancer others are employed as straining agents.⁴⁴

Deoxyribonucleic acid (DNA) is the primary target molecules for most anticancer and antiviral therapies according to cell biologists. Investigations on the

interaction of DNA with small molecules are important in the design of new types of pharmaceutical molecules. Since the chemical nuclease activity of transition metal complexes was discovered in 1980, studying the interaction model and the mechanism of transition metal complexes with DNA and exploring the application of metal complexes in anti-neoplastic medication, molecular biology and bio-engineering have become hotspots in recent years. Some kind of metal complexes interacted with DNA could induce the breakage of DNA strands by appropriate methods. In the case of cancer genes after DNA strands are cleaved, the DNA double strands break. The replication ability of cancer is destroyed⁴⁵. Metal complexes play an essential role in Agriculture, Pharmaceutical and Industrial chemistry⁴⁶ the metal complexes of Schiff's bases have also received much attention. These complexes not only play an important role development of coordination chemistry but also in catalysis enzymatic reaction, magnetism, molecular architectures⁴⁷⁻⁴⁹ and exhibit interesting biological activities⁵⁰⁻⁵²

A Brief review of some Metals:

Copper (II)

The Cu(II) having a single electron outside the completed 3d shell, exhibit oxidation states of +1, +2 and +3. The di-positive state is the most important one for copper. The '3d⁹' configuration makes copper(II) susceptible to Jahn-Teller distortion when placed in environment of cubic symmetry, i.e. regular octahedral or tetrahedral and this has performed effect on its stereo chemistries.

Copper complexes have an important applications in organic chemistry for oxidations, halogenation, coupling reactions, etc.⁵³ phenol oxidation by copper-amine complexes⁵⁴ provide model for phenol oxidizing enzymes. Copper(II) complexes play a important role in biological and pharmaceutical activities. Such as anti-tumor Scavenger effects on OH[•] and O₂^{-•} radicals⁵⁵ and specifically Cu(DMG)₂ shows high activity against cancer⁵⁶ and shows more life span to the extent 200-300%.

Cobalt(II)

Cobalt exhibits various oxidation states ranging from +1 to +5. The most common oxidation states are +2 and +3. The coordination compounds of Cobalt(II) exhibit diversity in coordination number, geometry, stability, liability and other aspects of their chemistry. Several studies have been oriented towards understanding and application of these important substances. Cobalt(II) is basically associated with

three different types of stereochemical configurations such as tetrahedral, octahedral, square planar, and trigonal bipyramidal. The tetragonal is a rare possible one. Cobalt complexes with tetra-dentate Schiff's base ligands were proposed as a model molecule for Vit. B₁₂⁵⁷.

Nickel(II)

Nickel(II) exhibits various oxidation states ranging from +1 to +4. Nickel (II) complexes mainly exist in square-planar structure. Numerous interesting studies on Nickel(II) complexes have been reported in literature⁵⁸. Nickel(II) can also form several pentadentate complexes. Five coordinated Nickel(II) complexes with a trigonal bipyramidal⁵⁹ and square pyramidal geometry have been characterised⁶⁰. Nickel(II) chelates with distorted trigonal prismatic structure⁶¹ have also been reported.

Zinc (II)

Zinc is a part of enzyme carbonic anhydrase, which is take part in conversion of CO₂ to carbonic acid in plants. Zinc is also present in horse-liver alcohol dehydrogenase. Deficiency of zinc in animals results in stunted growth and male sexual immaturity. The toxicity of zinc is too low, +1 and +2 are oxidation states of zinc. Zinc(I) does not occur in the normal conditions only spectroscopic species have been found. Like mercury, Zn₂⁺² ion also exists⁶². Zinc(II) complexes are essentially diamagnetic due to filled d¹⁰ configuration. The Zinc(II) complexes can have 4, 5 and 6 coordination numbers. It is invariably seen that zinc forms only tetrahedral complexes with coordination number 4.

Five coordinated complexes either possess square pyramidal or trigonal bipyramidal structures. Complexes having coordination number 6 are octahedral. Many polymeric structures involving bridging groups are reported. Certain complexes show even coordination number 7. Mainly zinc is utilized in the form of alloy to prepare containers, as toxicity is too low.

Cadmium(II)

The Cadmium in living organisms is highly toxic, it affects the kidney and liver, cadmium shows oxidation states +1 and +2, cadmium(I) has been isolated in solid state in which it is present as Cd⁺² ion. Cadmium(II) is well known to form a large variety of compounds and complexes. Four coordinated complexes are tetrahedral. Five coordinated complexes are not found as frequently as in zinc. Six coordinated complexes have octahedral structure and are of common occurrence.

Cadmium is used as control rods and shielding for nuclear reactors because of its high neutron absorbing capacity.

A brief review of Schiff's base ligands and their metal complexes

A Schiff's bases have drawn a considerable attention since such ligands dominate the area of higher coordination number and from kinetic and thermodynamic point of view. The chemistry of Schiff's bases is its wide application in food industry and dyes industry, analytical chemistry, catalysis fungicidal and agrochemical activity⁶². The Schiff's bases are the condensed products of aldehyde and primary amines and are the good chelating agents. This is evident from the volumeness literature documented in the literature⁶³.

A variety of Schiff's bases containing various donor sites have been tried for the complexation and the structures were deduced with the aid of spectral and magnetic data. Azomethines and their complexing capabilities have been enlightened in a considerable number of review articles⁶⁴⁻⁶⁷. Amidst abundance of information pouring into literature on the metal complexes with ligands containing O, N & S donor atoms. Schiff's bases have claimed enormous portion of interest, because of their varied complexing ability. But here the literature pertaining to bidentates only is reviewed⁶⁸. The bidentate Schiff's base ligands containing one active center and one donor center form complexes with transition metals. Which are generally 1:2 adducts and / or dimeric or polymeric in nature.

Hydrazones are a special group of compounds in the Schiff's bases. They are characterized by the presence of $>C=N-N<$ groups. The presence of two inter-linked nitrogen atoms separates this from imines, oximes, etc. Hydrazones in general, are prepared by refluxing the stoichiometric amounts of the appropriate hydrazide and aldehyde or ketone dissolved in a suitable solvent. The compounds usually crystallized on cooling it is recrystallized from a suitable solvent. Hydrazides have been successfully tried for preparing the complexes with transition metals both NH_2 and $C=O$ groups involve in the bond formation⁶⁹.

Coordination behavior of ligands

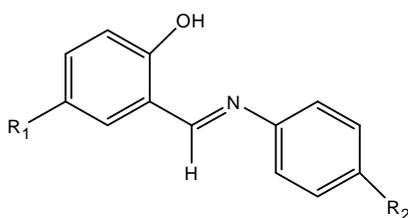
The azomethine and their complexing capabilities have been enlightened in many review articles.⁷⁰⁻⁷⁴ various studies have shown that the (C=N) azomethine group has considerable biological importance. Schiff's bases considered as an useful chelating agent when a suitable functional groups e.g., -OH, -SH, COOH, etc., are present sufficiently close to azomethine group so as to form stable five or six

membered chelate ring with metal ion. By changing nature and position of the donor atoms and groups, it is possible to control the size of the chelate ring formed and exploit the effect of substitution. All these factors make Schiff's bases good chelating agents and potential reagents.

A review of literature, the different type of potential Schiff's bases on the basis of their donor atoms set has been attempted. Based on the donating sites, further Schiff's bases are classified as monodentate, bidentate, tridentate, tetradentate and polydentate ligands containing O, N and S donor atoms. Such type of donor site ligands have been tried for their complexation and the structures were deduced with the aid of analytical and spectral data.

Monodentate Schiff's bases

The basic strength of C=N group is not sufficient to obtain stable complexes by coordination of the imino nitrogen atom to the metal ion. Hence, the presence of at least one of the other group is required to stabilize metal-nitrogen bond. Aryl groups are attached to either O or N generally stabilizes the Schiff's base by resonance. Monoamine Schiff's base as *N*-benzylidene-aniline derivatives, **Fig. 1(1)** is known in the literature.⁷⁵



Where $R_1 = R_2 = \text{H, Cl, CH}_3, \text{OCH}_3$ and NO_2 .

Fig. 1(1)

Bidentate Schiff's bases

Bidentate Schiff's bases are the most useful ligands for preparing metal complexes. Potential bidentate ligands depending on their donor atom set has been given below.

N, O and N, N donor atom set

Numbers of metal complexes were synthesized by using Schiff's bases having N, O and N, N donor sets. Since in N, O donor set oxygen is often represented by OH group. These Schiff's bases generally act as chelating mono amines. Hydrazides have been synthesized and complexed with transition metals, both NH_2 and C=O groups are involved in the bond formation⁷⁶ **Fig.1(2)**.

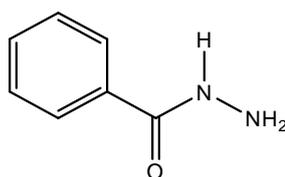


Fig.1(2)

There are number of examples for potential bidentate ligands with N, O donor sets derived⁷⁷ from 2-hydroxyaldehydes **Fig. 1(3)** and N, N donor sets from *p*-anilines **Fig. 1(4)**.

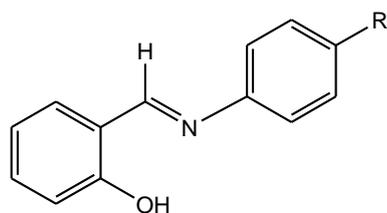


Fig. 1(3)

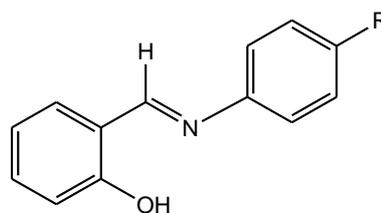


Fig. 1(4)

Where R=H,CH₃ or Cl

Raman *et al.*,⁷⁸ have reported a new bidentate Schiff base ligands derived from 4-aminoantipyrine and *o*-acetoacetotoluidide and its Cu(II), Co(II), Ni(II) and Zn(II) complexes of the type ML₂ and are characterized by micro analytical data, conductance measurement, magnetic susceptibility data, IR, electronic, ¹H NMR and mass spectra. These results indicated that all these complexes are monomeric in nature and having square planar geometry. **Fig.1(5)**

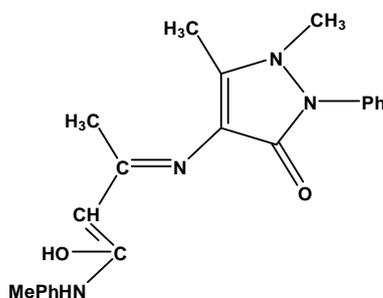


Fig. 1(5)

Chohan *et al.*,⁷⁹ reported a bidentate Schiff's base ligands derived by β -diketones and amino acid derived compounds and its Cu(II), Co(II), Ni(II) and Zn(II) complexes of the type M(L)₂(H₂O) and are characterized by elemental analysis, molar

conductance, magnetic moments, IR and electronic spectral measurements. These spectral measurements indicate octahedral geometry. **Fig. 1(6)**

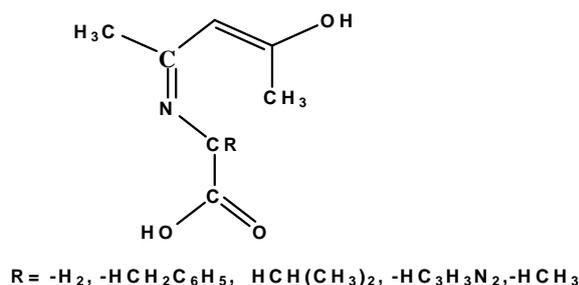


Fig. 1(6)

A new series of twelve Co(II) and Ni(II) complexes with N-isonicotinamido-2', 4'-dichlorobenzaladimine (INH-DCB) with the general formula MX₂.n(INH-DCB) [Where M=Co(II) or Ni(II), X= Cl⁻, Br⁻, NO₃⁻, NCS⁻, n =2; X= ClO₄⁻, n =3] have been reported by Ram *et al.*,⁸⁰. These complexes were characterized by elemental analysis, IR, electronic spectra, magnetic susceptibility and conductance measurements. An octahedral geometry has been suggested for all the complexes. **Fig.1(7)**

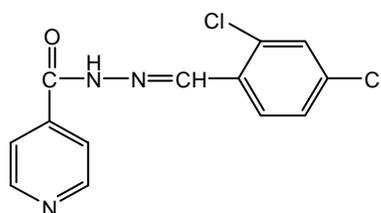


Fig. 1(7)

Tridentate Schiff's bases

There are large number of tridentate Schiff's bases containing ONN, NNS, NOO and NSO donor sets.⁸¹ these may be generally derived from the bidentate analogous by the addition of another donor group. It must be pointed out that the oxygen donor atom of such ligands may often act as bridge between two metal centers giving polynuclear complexes of some tridentate ligands. **Fig.1(8)** and **Fig.1(9)**

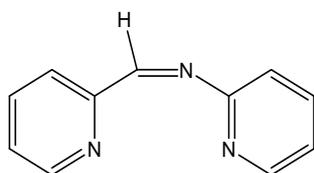


Fig. 1 (8)

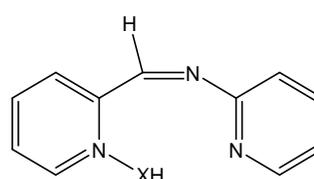


Fig. 1 (9)

Where X=O or S

Sancak *et al.*,⁸² have reported Cu(II), Ni(II) and Fe(II) complexes with a new substituted 1,2,4-triazole Schiff's base derived from 4-amino-5-(thien-2-ylethyl)-2,4-dihydro -3H-1,2,4-triazol-3-one and 2-hydroxy naphthaldehyde and these were characterized by elemental analysis, IR, magnetic moment, electronic, mass spectral data, ¹H NMR and ¹³C NMR spectra. The Schiff's base is coordinated to the metal ion in a tridentate manner with OON donors. The spectral data indicate that octahedral geometry for Cu(II) and Fe(II) and Square planar for Ni(II) complex **Fig. 1(10)**.

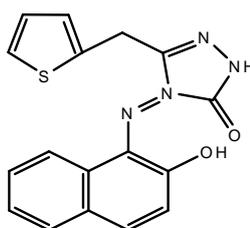


Fig.1(10)

Sathisha *et al.*,⁸³ have reported the synthesis, structure, electrochemistry, spectral and biological studies of Cu(II), Co(II), Ni(II) and Zn(II) complexes of thiocarbohydrazone ligands of the type $[M(L)X].2H_2O$ where $M = Cu(II), Ni(II)$ and $X = Cl, CH_3COO$ having Square planar geometry and $[M(L)_2.2H_2O]$ where $M = Co(II)$ and $Zn(II)$ having octahedral geometry. It is evident from spectral data all the complexes are mononuclear in nature.

The ligands coordinate to the metal ion through sulphur atom after deprotonation, nitrogen of azomethine and carbonyl group in tridentate manner. The complexes are soluble in organic solvents. Molar conductance values in DMF indicate non electrolytic nature of the complexes. **Fig. 1(11)**

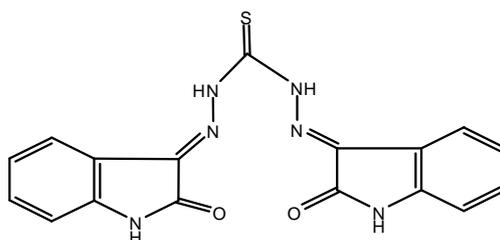


Fig 1 (11)

Nair *et al.*,⁸⁴ have reported Cu(II), Co(II), Ni(II) and Zn(II) complexes of the tridentate Schiff's base ligands derived from vanillidene and β -alanine of the type MLX where L = Schiff's base ligands and X=water molecule. These are characterized by elemental analysis, conductivity measurement, IR and electronic spectral data.

Tetradentate Schiff's base

The Tetradentate Schiff's bases with N_2O_2 and N_2S_2 donor set have been studied for their ability to coordinate with metal ions. The characterization of complexes obtained by their Schiff's base ligands are determined by electronic nature of the ligands as well as by their conformational behavior.⁸⁵ Tetradentate Schiff base of ethylene diamine may be mainly classified as I acen **Fig. 1(12)**, II salen **Fig. 1(13)** and III moxen **Fig. 1(14)**.

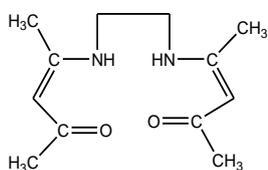


Fig.1(12)

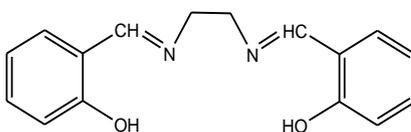


Fig.1 (13)

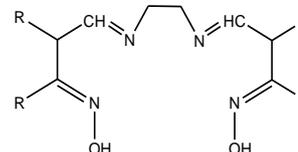


Fig.1 (14)

Berger *et al.*,⁸⁶ have give the clear structural information due to mainly the complexity of the IR spectra. The Mossbauer spectroscopy has proved useful in providing such information for organotin compounds, and it was thought worthwhile to study these inorganic-tin adducts using Mossbauer techniques.⁸⁷ **Fig. 1(15)** and **Fig. 1(16)** give the structure information.

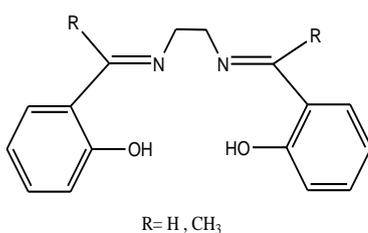


Fig. 1(15)

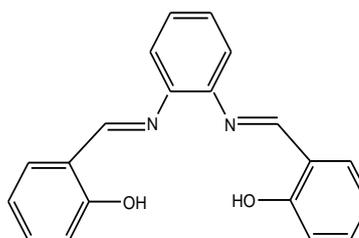
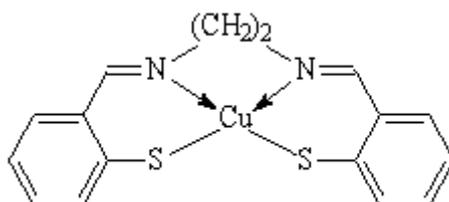


Fig. 1(16)

Branca *et al.*,⁸⁸ have carried out an electron spin resonance spectral analysis of Cu(II) complexes of bis(mercaptobenzylidene)diamine **Fig. 1(17)** and have arrived at

the configuration around the Cu(II) ion, namely squareplanar. They have calculated the various parameters using computer simulated programs.



(Fig.17)

The transition metals from complexes of varied coordination number and especially Co(II), Ni(II) and Cu(II) complexes are formed as a result of expansion of the coordination sphere. Such a phenomenon occurs frequently with square planar complexes by taking one or two Schiff base ligands giving rise to penta and hexa coordinated complexes.

The difference type in color of certain Co(II) and Ni(II) complexes in different solvents is often attributed to this effect substitution to form complexes higher coordination numbers. It has been studied the uptake of biacetyl by bis-pyridylhydrozone Ni(II) complexes in benzene and calculated the stability constants from spectral changes due to the expansion of coordination sphere around the metal ion **Fig.1(18)**. Sacconi and Bertine⁸⁹ have reported similar type of ligands while trying to prepare a Cu(II) complex containing ethylenediamine and acetylacetone **Fig.1(19)**. Morgan et.al.,⁹⁰ obtained a green color complex having the following structure.

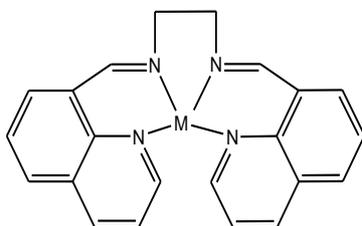


Fig.1(18)

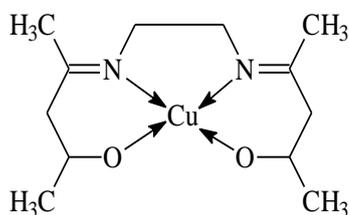


Fig.1(19)

The X-ray analysis of the structure of Cu(II) chelate shows that the acetyl acetone rings are considerably conjugated with possible preponderance of the structure derived from ketamine from of the ligand. The chelate molecule is expected to be planar but form some puckering in the central chelate ring it is slightly concave towards the centre. The Co(II) complex of such base has also been reported.⁹¹ Evings

et al.,⁹² have prepared Sn(IV) and organotin (IV) complexes **Fig.1(20)** with N, N'-ethylenen(acetylideneimine). The complexes are monomeric. The spectroscopic data suggest distorted octahedral structure with non linear C-Sn-C unit for (Me)₂ Sn EDTA. The complexes of other metals are also known.⁹³⁻⁹⁶.

The most interesting observation is due to Tanaka and Kono⁹⁷ who observed the impact of lengthening of hydrocarbon chain between the two azomethine groups on the color of the Cu(II) complex **Fig. 1(21)** with change in number(n) from 2 to 6 the color of the complexes changed from yellowish green to pale blue. Similar synthesis have been tried in the cases of Co(II) and Ni(II). It is found that the lengthening of hydrocarbon bridge has profound impact on the geometry of Co(II) complexes.

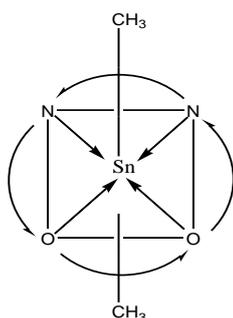


Fig. 1(20)

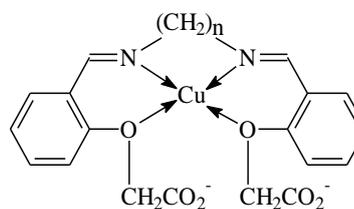


Fig. 1(21)

In an event to study the implication of extensive conjugation of coordinated imines on bonding and structure, Natarajan *et. al.*,⁹⁸ have prepared 2-hydroxychalcone imines and its Co(II), Ni(II) and Cu(II) complexes, the magnetic and spectral studies have indicated that the intensive conjugation of C=N group does not facilitate the attack of imines. All complexes have squareplanar configurations. The other type of chalcone complexes are also reported in the literature⁹⁹ Cu(II) complexes with 2, 2'-dihydroxychalconeimines are also known in the literature, and they have square planar geometry.¹⁰⁰

Importance of Benzofurans

The many of the compounds with benzofuran moiety are more abundantly occurring in nature, in particular plant kingdom after such products with benzofuran nucleus are possessing pharmacological properties. During last several years the more interest in synthetic products having benzofuran moiety has put forward a development of benzofuran chemistry in spectacular fashion.

Benzofuran compounds have created interest to the chemists, because, they occur in nature in a variety of structural forms which is from a simple molecule such as 5-methoxy benzofuran to a very complicated molecules like morphine A and B. The seed oil plant “Egonoki” which is much common in Japan is known to contain a benzofuran derivative called “Egonal”. It is an effective synergist for rotenone pyrethrum against house flies, mosquitoes, aphids and many other insects¹⁰¹. Bakers yeast contains a benzofuran derivative, which acts as an antioxidant and prevents haemorrhagic liver neurosis in rats and haemolysis of red cells in vitamin deficient rats¹⁰².

The plant extract “Ammirisnga L” has been used from long time as home remedy to relief spasma of all kinds and also cure for leucoderma¹⁰³, Moncrieff¹⁰⁴ has investigated the basic compound provalin in furocommarin, which is useful in medicine for the treatment of leucoderma. Joseph Nodman et. al.,¹⁰⁵ have synthesized 2-acetylbenzofuran which acts as diuretic and choleric agent. Sridhar et. al.¹⁰⁶ have synthesized 3-methyl/5-methoxybenzo furan-2-carbamate and carbamide derivatives of biological interest. The benzofuran derivatives having nitro group is more important for practical properties of benzofurans¹⁰⁷.

Vaidya et.al.,¹⁰⁸ have prepared few aryl and aryloxyalkly-5-nitrofurans-2-carbamates having antibacterial and antifungal activities. Benzofurans and furanochromes are known to posses various pharmacological properties¹⁰⁹.

Khellin as furanochromone is well known for its physiological activity¹¹⁰. Keeping in mind Khellin is of therapeutic activity, several 2, 3 aroylbenzofuran bearing phenolic groups were found to show a marked spasmolytic activity¹¹¹. Spath and Gruber¹¹² have reported that Khellin has a selective antispasmodic effect upon the ureter, bronchial mussels, gall bladder and bile duct. Khellin is found to be a potent coronary Vasodiolor¹¹³, inhabits gastric ulcers and intestinal activity¹¹⁴. It is also useful in the treatment of heart diseases and whooping cough.

Bouet et. al.,¹¹⁵ have synthesized 2-furaldehyde-4-phenylsemicarbazone **Fig. 1(22)** and its Co(II), Ni(II), Cu(II) and Cd(II) complexes.

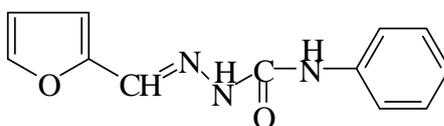


Fig.1 (22)

It is interesting to note that ligand appears to be bidentate in case of Cu(II), Ni(II) and Co(II) complexes and a tridentate in case of Cd(II) complexes giving dinuclear structure.

Singh et. al.,¹¹⁶ have synthesized 2-furoylhydrazone of 2-acetylthiophene and 2-acetylfuran **Fig.1(23)** and **Fig.1(24)** and their Cu(II), Co(II), Ni(II), Zn(II) and Mn(II) complexes, later they have also synthesized Fe(III) complexes with the same ligand¹¹⁷.

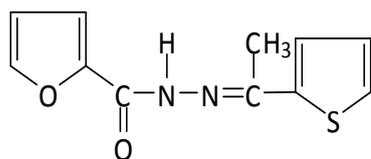


Fig. (23)

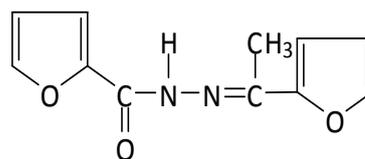


Fig. (24)

Chohan and Rauf¹¹⁸ have reported the nicotinoyl hydrazone of 2-furfural thiophen-2-aldehyde and pyrrol-2-aldehyde, **Fig.1(25)** and their Co(II), Ni(II) and Cu(II) complexes.

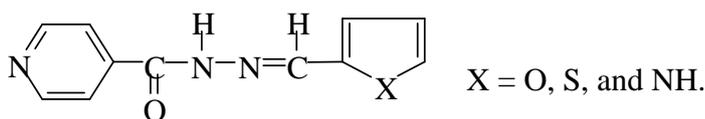


Fig. 1(25)

The ligands are coordinated to the metal ions through carboxyl-O, azomethine-N and the heteroatom O, S or N. The ligands also exhibited Keto-enol tautomerism.

A lot of work has been done on simple 2,3-substituted benzofuran and benzofuro [3,2-d] pyrimidine derivatives¹¹⁹ and Schiff's base derived from 3-amino-2-benzofuran carboxylate, 3-amino-2-benzofurancarboxamide with substituted benzaldehydes/ substituted salicylaldehyde/acetophenones¹²⁰. Halli et. al.,¹²¹ have reported several metal complexes and have characterized them by elemental analysis, chemical and spectral studies.

One of the best functionality, which has been frequently used in the literature for development of pyrazole ring system is carbonylhydrazide ($-\text{CO}=\text{NHNH}_2$). Based on this we evolved a synthetic strategy that involves the modification of carbonylhydrazide group located on furan moiety of benzofuran nucleus in to the

desired benzofuran ring system. The benzofuran-2-carboxyl hydrazide **Fig. 1(26)** and 3-methoxybenzofuran-2-carboxyl hydrazide, **Fig.1(27)** as described by Tanaka.¹²²

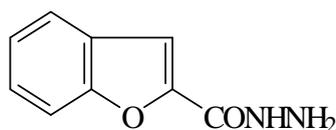


Fig. 1(26)

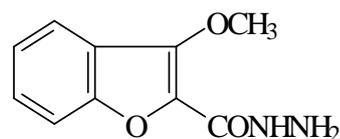


Fig. 1(27)

Hiremath et. al.,¹²³ have reported the complexes of 3-acetylamino-2-benzofuran carboxamide(L) **Fig.1(28)** with Co(II), Ni(II), Cu(II), Cd(II) and Hg(II) metal have been synthesized and characterized on the basis of elemental analysis, IR. electronic spectra, magnetic moments and conductance measurement studies.

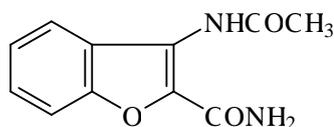


Fig. 1(28)

These results indicates that polymeric octahedral structure may be proposed for the Cu(II), Ni(II) and Cd(II) complexes and monomeric octahedral structure for Co(II) and Hg(II) complexes.

The above authors also reported¹²⁴ the complexes of the type $MLCl_2$ ($M=Co(II)$, $Ni(II)$, $Cu(II)$ and $Cd(II)$) and ML_2Cl_2 [$M=Zn(II)$, $Hg(II)$, $UO_2(II)$ and $Th(IV)$] and Schiff's base derived from 4-hydrazinobenzofuro[3,2-d] pyrimidine and 4-hydroxy-3-aldehydo diphenyl **Fig.1(29)** have been reported and characterized on the basis of analytical and spectral data.

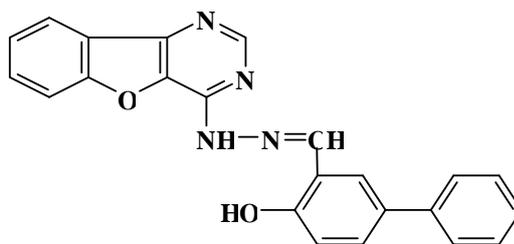


Fig. 1(29)

The ligand field parameters have been evaluated for Co(II), Ni(II) and Cu(II) complexes which suggest an octahedral geometry for each of them. The IR spectral data reveal the bidentate nature of the ligand.

Hiremath et. al¹²⁵, have reported complex of the type $MLCl_2$ where $M=Co(II)$, $Ni(II)$, $Zn(II)$ and $Cd(II)$ and $L=3$ -acetyl-amino-2-benzoylbenzofuran, have been synthesized and characterized by elemental analysis, electrical conductance, magnetic moment, IR and electronic spectral data. These results indicated that $Co(II)$, $Ni(II)$ and $Cu(II)$ complexes are polymeric octahedral while $Zn(II)$ and $Cd(II)$ complexes are monomeric tetrahedral. The ligand behaves as bidentate in all the complexes.

The above authors also reported¹²⁶, the Schiff's base derived from the condensation of 3-amino-2-benzofuran carboxamide/ethyl-3-amino-2-benzofuran carboxylate with substituted benzaldehyde / acetophenone have been synthesized **Fig. 1(30)**. The complexes have been characterized by elemental analysis, magnetic susceptibility, conductance, ESR and IR spectral data.

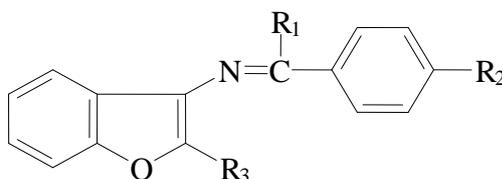


Fig. 1(30)

I, $R_1 = H$, $R_2 = OCH_3, H, Cl, NO_2$ and $R_3 = CONH_2/COOC_2H_5$

II, $R_1 = CH_3$, $R_2 = H$, and $R_3 = CONH_2/COOC_2H_5$.

The spectral study shows that Schiff's base behaves as a neutral bidentate in all the complexes. The ligands and their complexes have been evaluated for their antibacterial and anthelmintic activities.

Halli et.al¹²⁷, have reported the complexes type MLX_2 where $M=Co(II)$, $Ni(II)$, $Zn(II)$, $Cd(II)$ and $Hg(II)$ and $L=(E)-N'$ -((thiophen-2-yl)methylene)benzoyl benzofuran-2-carbohydrazide, have been synthesized and characterized by elemental analysis, electrical conductance, magnetic moment, IR and electronic spectral data. These results indicated that $Co(II)$, $Ni(II)$ and $Cu(II)$ complexes are polymeric octahedral while $Zn(II)$ and $Cd(II)$ complexes are monomeric tetrahedral. The ligand behaves as bidentate in all the complexes. The DNA cleavage activities of all of the complexes were studied by the agarose gel electrophoresis method.

Lot of work has been done in our laboratory for the last three decades on the synthesis of various substituted benzofuran carbohydrazides, which served as good precursor for large number of novel heterocyclic system.

Present work

In view of the biological importance of Schiff's base ligands and there metal complexes, in the present investigation we thought it is worthwhile to synthesize Schiff's base ligands by the condensation of benzofuron -2-carbohydrazide with 2-acetylpyridine / 2-acetylthiophene / Acetophenone / p-methoxyacetophenone / p-chloroacetophenone / 3-methyl-2-thiophene carboxaldehyde / 4-methylthiobenzaldehyde and 3-ethoxy-4-hydroxybenzaldehyde and there metal complexes by using metal ions Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II). The synthesized Schiff's based ligands are as follows.

1. BCAP: N'-(1-(pyridin-2-yl)ethylidene)benzofuran-2-carbohydrazide
2. BCAT: N'-(1-(thiophen-2-yl)ethylidene)benzofuran-2-carbohydrazide
3. BCACP: N'-(1-phenylethylidene)benzofuran-2-carbohydrazide
4. BCMeOACP N'-(1-(4-methoxyphenyl)ethylidene)benzofuran-2-carbohydrazide
5. BCClACP: N'-(1-(4-chlorophenyl) ethylidene)benzofuran-2-carbohydrazide.
6. BCMeTPC: N'-(3-methylthiophen-2-yl)methylene)benzofuran-2-carbohydrazide.
7. BCMeTB: N'-(4-(methylthio)benzylidene)benzofuran-2-carbohydrazide.
8. BCEtHB: N'-(3-ethoxy-4-hydroxybenzylidene)benzofuran-2-carbohydrazide.

All the metal complexes have been characterized on the basis of elemental analysis, spectral studies, magnetic and conductivity measurements, X-ray diffraction and Thermal analysis all the ligands and complexes were screened for their antibacterial and antifungal activity. The details are discussed in the succeeding chapters.

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