CHAPTER - I

Introduction and Literature Survey
The father of coordination chemistry Alfred Werner helped to rationalize the formulation of coordination compounds by putting forward the theory of coordination compounds in 1893 [1]. His theory not only gave bright insight stereo chemical aspects of coordination compounds but also stimulated much work in the preparation of a variety of coordination compounds. When quantum mechanics was introduced and applied to chemistry not only much progress was made in many theoretical aspects of chemistry but also a significant contribution was made in understanding the concept of molecular orbital and ligand field theories. Further the application of quantum mechanics to chemistry gave an insight into understanding the forces, which bond atoms together [2-3]. Coordination chemistry is one of the broad areas that cover various applications. This field has now leaped into many areas of science and technology viz, analytical chemistry, medicinal chemistry, metallurgy, industrial chemistry, so on and so forth.

The nature of coordination compound depends on the metal ion, the donor atom, the structure of the ligands and the metal-ligand interaction [4]. One of the most important problems in the coordination chemistry has been the nature and strength of metal-ligand bond. Normally, a metal ion does not form bonds of equal strength with two different donor atoms. Similarly, a particular donor atom does not form bonds of the same strength with different metal ions [5].

The coordination chemists are interested mainly in stereo chemical, thermodynamic, kinetic, spectral and magnetic properties of coordination compounds. Apart from these, there has been a growing interest in the role of the metal ions and their complexes in biological systems. It is a well known fact that, about six metals are very much essential for human life even though they are present in ultra trace quantities. Alkali, alkaline earth metal complexes of crown ethers and cyclic ligands play an important role in the biological systems. The complexes of copper and iron are involved in biological systems as oxygen carriers; there is a growing interest in understanding the mechanism
of oxygen binding, structure of oxygen containing compounds and to develop synthetic oxygen carriers [6-8]. Similarly, involvement of molybdenum in nitrogenous enzymes leads to nitrogen carrying compounds that might be used in nitrogen fixation [9].

Recently many applications have been developed, most important being in the field of catalysis and analytical chemistry. Iron complex \([\text{Fe}_4(\text{CO})_{10}\text{NSiMe}_4]\) used for the hydrogenation of methacrylate, 2,4-dimethylbutadiene, cyclobutene [10] etc. The complex \([\text{RhCl (PPh}_4)_4]\) known as Wilkinson’s catalyst is largely used in the homogeneous hydrogenation. It is highly active catalyst for the hydrogenation of alkenes [11]. Wilkinson et al have shown that, the complex \([\text{RhCl (PPh}_4)_4]\) and complexes derived from it can be used for the preferential and related complexes have been used on the partial hydrogenation of soybean oil [12]. Molybdenum(VI) and Tungsten(VI) dioxo complexes have been used in the epoxidation of alkenes [13-14].

Coordination chemistry has played major role in medicine. Coordination compounds have been used in the treatment or diagnosis of diseases. In some cases, coordination compounds can be formed in the body to handle dysfunction due to metal poisoning. There are many principal areas for the use of transition metal complexes in medicine.

Many metal complexes of azo, formazan, azomethine, nitroso, anthraquinone and phthalocyanine ligands find an important applications in the field of photography, catalysis and some modern high technology industries such as electronics. Some complexes are used as pigments and dyestuffs in textile and paper industry [6]. Recently, several phthalocynides have found new applications in electronics etc, piezoelectric and electrochemical devices, xerography, laser disc memory, photovoltaic cells and chemical sensors [6].

Hydrogen production using bi and polynuclear complexes of metallloporphyrins and metallophthalocyanides in the presence of visible light is attracted much interest as photo sensitizers for photo reduction of hydrogen from water [6]. The application of metal complexes in photolytic
decomposition for the production of hydrogen with stimulated the research for regenerating non-polluting fuel, which can be the ultimate solution to the future energy crisis faced by the world due to imminent exhaustion of the fossil fuels.

Coordination chemistry has also its greatest application in the field of hydrometallurgy. Use of carboxylic acid extractant to remove Fe(III) from solution of the earth metals has been reported. Versatic acid has been used for the production of pure Eu(III), La(III) and Y(III) oxides. Development of new water soluble chelating agents and their use as extracting agents via solvent extraction or ion exchange methods has tremendously helped the isolation of lanthanides and actinides and separation of individual elements.

“The ever increasing application of metal complexes in various fields of science is the driving force for the research and development in coordination chemistry”.

**Triazoles**

1,2,4-Triazole display biological activity such as inhibition of cholinesterase, interference with mitosis and reversible denaturation of serum proteins [15] and its derivatives have become very useful compounds in medicine, agriculture and in many fields of technology [16]. The metal complexes of substituted 1,2,4-triazole derivatives have been extensively investigated in previous reports [17-19]. Recently, several complexes of various transition and inner transition metals with substituted 1,2,4-triazole ligands have been reported from our laboratory [20-23]. There is growing interest in the studies on the metal complexes of Schiff bases derived from substituted triazoles which are well known bactericides [24], pesticides [25], insecticides [26] and potential fungicides [27].

**Hydrazones**

Hydrazones are a special group of compounds in the Schiff base family. They are characterized by the presence of >C=N-N=C<. The presence of two inter linked nitrogen atoms separates this from imines, oximes etc. Hydrazones,
in general, are prepared by refluxing the stoichiometry amounts of the appropriate hydrazide and aldehydes or ketone dissolved in a suitable solvent.

Compound to simple hydrazone Schiff bases, acyl, aroyl and heteroacryol Schiff bases have an additional donor sites >C=O. The additional donor sites make then more flexible and versatile. This versatility that has made hydrazones good polydentate chelating agents that can form a variety of complexes with various transition and inner transition metals and has attracted the attention of many researchers.

Depending on the experimental conditions, hydrazones are obtained; which have application as biologically active compounds [28] and as analytical reagents [29]. As biologically active compounds, hydrazones find applications in the treatement of diseases such as tuberculosis [30-31], leprosy and mental disorder [28]. Tuberculostatic activity is attributed to the formation of stable chelates with transition metal present in the cell. Thus many vital enzymatic reactions catalyzed by these transition metals cannot take place in the presence of hydrazones [32-34]. Hydrazones also act as herbicides, insecticides, nematicides, rodenticides and plant growth regulators. They exhibit spasmolytic activity, hypertensive action and activity against leukemia, sarcomas and other malignant neoplasm. They are also used as effective sterilants for houseflies [35]. They possess anthelmintic activity also [36]. The biological activity of hydrazones is not limited to transition metal complexes only. Recently, many hydrazones with lanthanides have shown remarkable biological activity, mainly antibacterial activity [37] and pharmacological activity [38].

Hydrazones are used as plasticizers and stabilizers for polymers, polymerization initiators, antioxidants etc; They act as intermediates in preparative chemistry. In analytical chemistry, hydrazones find application in detection, determination and isolation of compounds containing the carbonyl group. More recently, they have been extensively used in detection and
determination of several metals. They also find applications as indicators and spot test reagents [29].

The study of complexes of hydrazones is interesting from the structural point of view. It is their ability to exist in keto, enol or in special cases mixed keto-enol form depending on experimental conditions. Infrared spectrometry is extensively used to study these compounds. Ligands with the chromophore groups –CO-NH-N< can enter the inner sphere of the complexes either in the keto or enol form. This tendency depends on a number of factors such as pH of the medium employed in the synthesis of the complexes, the nature of the substituents attached to the carbonyl carbon atom, nitrogen atom, the anion of metal salt used and the metal ion. If the ligand exists in the keto form in the complexes, one would expect that the –NH and >C=O stretching vibrations, whereas the absence of both these frequencies is the characteristic of the enol form in the complexes. These studies in combination with ¹H NMR data can be used to confirm the keto or enol tautomerism.

**Macrocyclic Compounds**

Coordination chemistry of macrocyclic ligands has been a fascinating area of current research interest to the inorganic chemists all over the world. The continued interest and quest in designing new macrocyclic ligands stem mainly from their use as models for protein-metal binding sites in a substantial array of metalloproteins in biological systems, as synthetic ionophores, as models to study the magnetic exchange phenomena, as therapeutic reagents in chelate therapy for the treatment of metal intoxication, as cyclic antibiotics that owe their antibiotic actions to specific metal complexation, to study the guest-host interactions and in catalysis. Recognition of the importance of complexes containing macrocyclic ligands has led to a considerable effort being invested in developing reliable inexpensive synthetic routes for these compounds.

Several classes of macrocyclic ligands have been reported, such as saturated polyazamacrocycles, imine Schiff base macrocycles, oxoazolidine-
containing macrocycles, polyoxamacrocycles, polyoxaazamacrocycles, polyoxa-and oxaazacoronands, crown ethers, lariat crown ethers, cryptands, cavitands, calixarenes, hemispherands, catenanes, podands, compartmental macrocyclic ligands which form homo-and heterodinuclear complexes, structurally reinforced macrocycles, redoxive responsive macrocycles, photoresponsive macrocycles, pH-responsive macrocycles, chromogenic macrocycles, siderophores, sepulchrare, spherands, molecular clefts, bibracchial macrocycles and macrocycles containing pendant arms have been synthesized.

**Survey of the Previous Work**

As the work embodied in the thesis mainly deals with the metal complexes of Schiff bases derived from triazoles, hydrazones, thiocarbohydrazones, 2,6-diformyl-4-methyl phenol and macrocyclic compounds, here, the discussion is confined to metal complexes of above mentioned compounds and their derivatives.

The tridentate Schiff bases with heterocyclic amines containing ONS donor sequence have been tried for complexation with transition metals such as Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). Of these Cu(II) complexes, the ligand shows bivalent tridentate behavior and forms dimeric complexes, this has been substantiated by the subnormal magnetic moments and electronic spectra [39-42].

Garg *et al.*, [43] have synthesized Co(II), Ni(II) and Cu(II) complexes of 5-mercapto-1,2,4-triazoles and they have assigned distorted octahedral geometry for these complexes.
Gadag and Gajendragad [44] have been prepared the nickel(II) and copper(II) complexes with 3-methyl and 3-ethyl derivatives of 4-amino-5-mercapto-1,2,4-triazole and they have high spin octahedral type configuration.

\[ \text{M} = \text{Co(II) and Ni(II)} \]

Literature also records the complexing ability of 3-aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazoles with bivalent metal ions [45]. In this case, x-ray studies reveal that, the complexes possess cubic structure and fungi toxicity of the complexes and the free ligands have been evaluated against *H. Oryzae*.

Pannu *et al.*, [46] have been reported Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of 4n-butyl-4H-1,2,4-triazole, in which ligand shows bidentate behavior in all the complexes except those of Cd(II) and Hg(II).

Badiger and Patil *et al.*, [47] have been reported the complexes of Co(II), Ni(II) and Cu(II) with 3-substituted-4-(4’-substituted-salicyldeneimino)-5-mercapto-1,2,4-triazoles and they have assigned the tetrahedral configuration for Co(II) and Ni(II) complexes on the basis of magnetic and spectral data. In case of Cu(II) complexes the ligand show bivalent tridentate behavior involving O, N, S-donor system. All the complexes are four coordinated and polymeric nature.

Zaydoun *et al.*, [48] have been reported the Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) halide complexes with 1,2,4-triazoles. Their structures are discussed on the basis of electronic and magnetic data and they have assigned the pseudo-octahedral geometry for all the complexes. The complexes are polymeric and metallic ions are bridged by triazoles and halogens. The compounds studied generally exhibit antiferromagnetic coupling.
Jia-Cheng Liu and coworkers [49] have reported Cu(II) complexes with 1,2,4-triazole and end-on azido bridging ligands. They have assigned the Cu(II) ions are strongly antiferromagnetic nature on the basis of their magnetic and crystal structures.

Depree et al., [50] have been studied the Pb(II) and Cu(II) complexes with macrocyclic Schiff bases derived from [2+2] cyclisation reaction of 3,5-diacetyl-1H-1,2,4-triazole and 1,3-diaminopropane using Pb(II) template ions. The macrocycle provides four nitrogen atoms, two imine and two triazolate donors as equatorial donor atoms to each of the two metal ions in the macrocycle. The Cu(II) complexes have been structurally characterized by X-Ray diffraction and three different structural types can be distinguished: monomeric, trimeric and polymeric.

Chohan et al., [51] used 1,1'-disubstituted ferrocenes have been prepared and used as chelating ligands in the preparation of Cu(II) compounds with a variety of anions such as nitrate, sulfate, oxalate, and acetate. These compounds have been characterized by physical, spectral, and analytical methods. Screening of these derivatives against pathogenic bacterial such as S.
aureus, E. coli, P. aeruginosa, and K. pneumonia showed all of them to possess varied bactericidal activity. The Cu(II) complexes were found to be consistent with the proposed square planar structure of the Cu(II) complexes.

Wesley R. Browne and coworkers [52] have reported the Ru(II) complexes with Schiff bases derived from 2,2'-bipyridine and H₂(Metr)₂ 2,5-bis(5'-methyl-4'H-[1,2,4]triaz-3'-yl)pyrazine. All these complexes have been characterized by various physico-chemical techniques. They have been very well explained about photoluminescence and photochemical reaction of above said complexes.

Recently Bhat et al., [53] have been studied the Ag(I), Tl(I), Zn(II), Hg(II), Cd(II), Pd(II), Co(II), and Ni(II) with 4-[(4-dimethylamino-benzylidene)-amino]-5-ethyl-2,4-dihydro-[1,2,4]triazoles-3-thione and 4-[(benzylidene)amino]-6-(t-butyl)-4H-[1,2,4-triazene-3-thione-5-one and they have been assigned the octahedral structures for the Co(II) and Ni(II), tetrahedral for the Zn(II), Hg(II), Cd(II) complexes, linear polymeric structures for the Ag(I), Tl(I) complexes and a square-planer structure for the Pd(II) complex.
Recently Liang Shen and co-workers have studied [54] the crystal structure of centrosymmetric dinuclear complex of \([\mu-2,10,15,23\text{-}\text{tetramethyl-3,6,9,12,13,16,19,22,25,26,27,28\text{-}\text{dodecaazatricyclo[22.2.1]hexacosa-1 (26),2, 9 11(28),13,15,22,24(27)\text{-}\text{octaene-12,25\text{-}diido-k}^5\text{N}^{13},\text{N}^{16},\text{N}^{19},\text{N}^{22},\text{N}^{25}:2k^5\text{N}^3,\text{N}^6\text{N}^9 \text{N}^{12},\text{N}^{26}]\text{-bis[diaquomanganese(II)]dichloride hexahydrate.}}\) They have assigned the Mn(II) centre is an approximately pentagonal-bipyramidal environment.

\[\text{(a)}\]

\[\text{(b)}\]

\[\text{(c)}\]

\[\text{(d)}\]

Alexander Eisenwiener et al., [55] have studied the Cu(II) and pt(II) complexes with a series of pyrazole and triazole based dinucleating ligands have been synthesized and their complexation potential for metal ions, which exhibit square planar coordination geometry has been studied. In the case of \(\text{Cu}^{2+}\) the complexation equilibria in solution have been determined using pH
titrations. Species with 1:1 stoichiometry \([\text{CuLH}]\) 2:1 stoichiometry \([\text{Cu}_2\text{LHm}]\), and of dimeric nature \([\text{Cu}_2\text{L}_2\text{Hp}]\), have been detected and their overall stability constants have been measured.

Recently K. Singh et al., [56] have studied the Co(II), Ni(II) and Zn(II) complexes with Schiff bases synthesized by the reaction of \(p\)­nitrobenzaldehyde, \(o\)-nitrobenzaldehyde and \(p\)-toluylaldehyde with 4-amino-5-mercapto-1,2,4-triazole. Which are characterized by Physico-chemical studies suggest that, an octahedral geometry for the cobalt(II), nickel(II) and zinc(II) complexes.

These complexes have been screened for antibacterial activity against three Gram-positive (\(S.\ aureus, S. epidermidis\) and \(B.\ subtilis\)) and two Gram-negative (\(S.\ typhi\) and \(P.\ aeruginosa\)) bacterial strains, and results compared with the activity of the free ligands. The metal complexes were found to be more potent against one or more bacterial strains than the free ligands.
Very recently Nali et al., [57] studied a pentacoordinated Cu(II) complex, [Cu(H2O)(L1)(L2)(NO3)](NO3)(H2O) (1; L1=1,2,4-triazole-5-one, L2=1,10-phenanthroline) has been synthesized and characterized. An X-ray structure analysis of 1 revealed that, the Cu(II) centre has a distorted square pyramidal environment with a second weakly bonded nitrate (Cu–O 2.550Å) giving rise to a pseudo-octahedral coordination geometry. Weak interactions such as π-π stacking and hydrogen bonding (especially C–H----O hydrogen bonds) have significant effects in configuring the 3D packing of the complex.

Recently David Olea et al. [58] have been studied Nanoprocessability of a one-dimensional oxalato-bridged cobalt(II) complex with 1,2,4-triazole. The polymer {[Co(ox)(Htr)2]2H2O}n (ox = oxalate dianion; Htr = 1,2,4-triazole) (1) has been synthesized and characterized by FT-IR spectroscopy, thermal analysis, variable-temperature magnetic measurements and X-ray diffraction methods. They studied its processability, as nano-rings, fibres and single chains which has been achieved by scission of part of the metal–ligand bonds with ultrasound and posterior re-organization of the oligomers on surface. A new feature is the observation for the first time of circular structures of a coordination polymer that is linear in the solid state. Reaction formation of this polymer at low concentration of the reactants has been also shown as a suitable way for the isolation of nano-fibres on HOPG (Highly Oriented Pyrolytic Graphite).
1.10-1.30 nm

L= ridget N-containing ligands such as Pyridines, Triazoles derivatives or Purine bases

As compared to the Schiff bases, hydrazones are more flexible in their coordinating sites and reactive groups in the molecule may either show monovalent tridentate, bivalent tridentate or monovalent bidentate behavior. A survey of literature on the synthesis and characterization of the metal complexes formed of various types of hydrazones is presented in the following paragraphs.

Sacconi [59-60] has opened up the vast field of salicylaldehyde aroylhydrazone coordination chemistry and this has been pursued by many others wherein, the complexes of these ligands with various transition, non-transition metal ions have been prepared and characterized by physicochemical data which indicate that, the ligands show different coordinating behavior towards the metal ions forming with them the complexes of different compositions and structures [61-64].

Lions and co-workers [65-70] have carried out detailed physicochemical investigations on the divalent Cr, Mn, Co, Ni, Cu, Zn, Cd, Hg and Sn complexes of pyridine-2-aldehyde-2-pyridylhydrazone.

Patil et al. [71] have synthesized Ni(II) complexes with Schiff bases derived from thiocarbohydrazide and substituted saclicylaldehydes and thiocarbohydrazide and benzoin. Which are characterized by elemental analyses, magnetic, conductance and spectral data and suggested a square planer configuration for these complexes.

Patil et al., [72] have also reported tin(IV) complexes with nickel(II) thiocarbohydrazones and they have demonstrated that Ni(II) complexes of thiocarbohydrazones having square planar configuration react with tin(IV)
chloride and as a result of this square planar Ni(II) complexes got change their configuration to octahedral. The complexes were identified by the elemental analyses and characterized by spectral and magnetic data.

Lanthanide(III) nitrate complexes with 2-hydroxy-1-naphthaldehyde, 1-isonicotinoylhydrazone (LH) having the general formula \([\text{Ln} \ (\text{L})_2 \ \text{NO}_3]\) where \(\text{Ln}=\ \text{La, Pr, Nd, Sm, Gd, Dy, and Y}\) have been synthesized and characterized by analytical, magnetic, conductance and spectral data [73]. The ligand acts as a monovalent terdentate donor and nitrate ion is coordinated monodentately offering a coordination number of seven to the lanthanide ion.

Yongxiang and Zhao Gang [74] have studied the lanthanide (III) complexes of acetylferrocene benzoylhydrazone Schiff base and characterized by elemental analyses, spectral, molar conductance and thermal data. It was found that, the ligand coordinates to the central ions in the keto form and some chloride ions and water molecules participated in coordination to the metal ion.

Dioxymolbdenum(VI) complexes of Schiff bases derived from carbohydrazide, thiocarbohydrazide and salicylaldehyde by Carrillo et al [75]. These complexes have been characterized by elemental analysis, spectral and X-Ray diffraction data. The X-Ray crystal structures of the title complexes are described as hexacoordinated.
Havinale et al., [76] have studied Co(II), Ni(II) and Cu(II) complexes of malonoanilic acid hyrazones. Which are characterized on the basis of analytical, conductivity, magnetic, spectral, ESR and thermal data. They have been reported that, the ligands behave in a dibasic tetradeinate manner in all the complexes accept in the case of Cu(II) complexes where they act as dibasic tridentate ligands with ONO donor sequence. Co(II) and Ni(II) complexes have octahedral geometry while Cu(II) complexes have square-planar structures.

Trivalent lanthanide complexes of acetone isonicotinoylhydrazone (AINH) having an empirical formula Ln(AINH)₃ Cl₃ where Ln= La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y have been prepared and studied by various physicochemical techniques [77]. AINH behaves as a neutral, bidentate ligand coordinating through the carbonyl oxygen and azomethine nitrogen.

Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and Hg(II) complexes of hyrazones derived from benzoic, p-methyl or p-nitro substituted acid hydrazide and furan-2-carboxaldehyde have been reported; wherein, the ligands coordinated in bi- and/or tridentate manner [78].

Dey et al., [79] have reported Co(II) complexes with schiff bases derived from diacetyl bis(4-methoxybenzoyl hydrazone). The stereochemistry of the isolated solid complexes has been discussed by elemental analyses, molar conductance, magnetic and spectroscopic data, in which the ligands act as a monobasic quadradeinate or dibasic quadradeinate ONNO donor sequenence.
Cu(II) and Ni(II) complexes of benzoic acid [(furan-2-yl) methylene] hydrazide (BFMH), benzoic acid [(furan-2-yl) ethylened] hydrazide (BFEH), benzoic acid [(thiophene-2-yl) methylene] hydrazide (BTMH), benzoic acid [1-(thiophene-2-yl) ethylened] hydrazide (BTEH), 2-furanyl carboxylic acid (benzylidene) hydrazide (FCBH) and 2-thiophenyl carboxylic acid (benzylidene) hydrazide (TCBH) have been synthesized by Reddy et al., [80] and they have been characterized by elemental analyses, conductivity, magnetic, spectral and ESR data. The electronic and magnetic values suggest an octahedral structure for all Ni(II) complexes, planar geometry for copper(II) complexes of BFMH, BTMH, FCBH and TCBH ligands and an octahedral geometry for the Cu(II) complexes with BFEH and BTEH ligands.

Singh and Agrawal [81] have synthesized Co(II), Ni(II), Cu(II) and Zn(II) complexes of pyridine2-carboxaldehyde thiobenzoyl hydrazone and characterized by magnetic, electronic and ESR spectral studies suggest high-
spin octahedral geometry for all the Ni(II) and Co(II) complexes and distorted octahedral geometry for Cu(II) complexes.

\[ \text{M} = \text{Co, Ni & Zn} \]
\[ \text{X} = \text{Cl, Br & NCS} \]

Crystal and molecular structure of 2-hydroxy-1-naphthaldehyde isonicotinoyl hydrazone (NIH) and its Fe(III) complex have been synthesized by Richardson and Bernhardt [82]. In this study, they have examined the structure and properties of NIH and its Fe\textsuperscript{III} complex in order to obtain further insight into its anti-tumor activity. Two tridentate NIH ligands deprotonated upon coordination to Fe(III) in a meridional fashion to form a distorted octahedral high-spin complex. Solution electrochemistry of [Fe(NIH-H)\textsubscript{2}]\textsuperscript{+} shows that, the trivalent oxidation state is dominant over a wide potential range and that, the Fe(II) analogue is not a stable form of this complex. The fact that, [Fe(NIH–H)\textsubscript{2}]\textsuperscript{+} cannot cycle between the Fe(II) and Fe(III) states suggests that the production of toxic free-radical species, e.g. OH\textsuperscript{•} or O\textsubscript{2}\textsuperscript{•–}, is not part of this ligands cytotoxic action. This suggestion is supported by cell culture experiments demonstrating that, the addition of Fe(III) to NIH prevents its anti-proliferative effect. The chemistry of this chelator and its Fe(III) complex is discussed in the context of understanding its anti-tumor activity.
Recently Warad et al., [83] have synthesized Zr(IV), VO(IV), Co(II), Ni(II) and Cu(II) complexes with Schiff bases derived from carbohydrazide with various aldehydes and which are characterized by elemental analysis and spectral methods. On the basis of elemental analysis and spectral data, square antiprism, square pyrimid and square planer structures have been proposed. The biological activities of all isolated ligands and their metal complexes have been studied by screening the compounds against micro organisms such as *E. coli, S. aureus, A. niger* and *C. albicans*.

Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with N-benzoyl-N'-2-furanthiocarbohydrazide have been synthesized by Singh and Kushawaha [84]. The complexes have been characterized by elemental analyses, magnetic, electronic, IR, NMR, ESR, FAB-mass and mossbauer spectral studies. The biological activities have been screened against several bacteria and fungi. They have assigned octahedral geometry for Mn(II), Co(II) and Ni(II) complexes, high spin square pyramidal geometry for Fe(II) complex and square pyramidal geometry for Cu(II) complex.

Recently, Khalil et al., [85] have synthesized Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and UO$_2$(VI) complexes with Schiff bases derived from 2-amino-4-hydrazino-6-methyl pyrimidine with o-hydroxyacetophenone. The structure of the ligand was elucidated by IR and $^1$H NMR spectra which indicated the presence of three different coordinating groups, the oxygen atom of the phenolic OH group, the nitrogen atom of the azomethine, C=N group and one of the nitrogen atoms of the heterocyclic ring. The ligand behaves either as a tridentate ($N_2O$ sites) neutral, mono- or di-basic ligand or as a bidentate (NO sites) monobasic ligand depending on the pH of the reaction medium and the metal ion.
The IR spectra of the binuclear complexes indicated that, the oxalate anion acts as a bridging tetradentate ligand. Elemental analyses, IR, electronic and ESR spectra as well as conductivity and magnetic susceptibility measurements were used to elucidate the structures of the newly prepared metal complexes. Square-planar geometry is suggested for the Cu(II) complex, octahedral geometry for the Fe(III) Ni(II) complexes, tetrahedral geometry for the Co(II) and Zn(II) complexes and pentagonal-bipyramidal geometry for the UO2(VI) complex.

Very recently, Chattopadhyay et al., [86] have synthesized five seven- or eight-coordinated manganese complexes of hydrazone ligands have been prepared. Three seven-coordinated neutral Mn(II) complexes: [Mn(dapA2)]n (1), [Mn(dapB2)(H2O)2] (2), [Mn(dapS2)(H2O)2] (3) have been synthesized from the bis-Schiff bases of 2,6-diacetylpyridine: dap(AH)2, dap(BH)2 and dap(SH)2 (AH=anthraniloyl hydrazide, BH=benzoyl hydrazide, SH = salicyloyl hydrazide) respectively. Two eight-coordinated Mn(II) complexes: [Mn(dapS)2] (4) and [Mn(dapB)2] 3H2O (5) have been synthesized from the mono-Schiff bases dapBH and dapSH, respectively. The complexes have been characterized by elemental analyses and spectral data. The mono-Schiff bases are monoanionic and the bis-Schiff bases are dianionic. The octa-coordinated mono-Schiff base complex 4 adopts a dodecahedral geometry, while the hepta-coordinated bis-Schiff base complex 1 forms a one-dimensional linear polymeric chain.
Very recently, Murakan and Mohanan [87] have studied Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes which have been synthesized with Schiff bases derived from isatin monohydrazone with 2-hydroxy-1-naphthaldehyde. The complexes were characterized on the basis of elemental analyses, molar conductance, magnetic and spectral studies. Analytical data reveal that, the Ni(II), Cu(II) and Zn(II) complexes possess 1:1 metal–ligand ratios and that, Mn(II), Fe(II) and Co(II) complexes exhibit 1:2 ratios. Infrared spectral data suggest that the bishydrazone behaves as a monobasic tridentate ligand with ONO donor sequence towards the metal ions. X-Ray diffraction study of the Co(II) complex indicated an orthorhombic crystal lattice. The EPR spectral data show that, the metal–ligand bond has considerable covalent character. The electrochemical behavior of the Co(II) complex was investigated by cyclic voltammetry (CV). Antibacterial tests of the ligand and the metal complexes were also carried out and it has been observed that the complexes are more potent bactericides than the ligand.
Coordination Compounds of Binucleating Macrocyclic Compounds

In 1970 N.H. Pikington and R. Robson [88] were the first to report the synthesis of the macrocyclic binucleating ligand framework of the following type by simply combining 2,6-diformyl-4-methylphenol (DFMP), 1,3-diaminopropane and various M^{2+} cations of the first transition series under template conditions.

Symmetrical coordination compounds (R1 = R2 = (CH₂)₃) for M^{2+} = Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+} and Zn^{2+} less than two years later, H. Okawa and S. Kida [89] used a linear synthetic strategy, building unsymmetrical (R1 ≠ R2) binuclear coordination compounds in a step-wise fashion for Cu^{2+} and Ni^{2+}. Since, these reports many authors have utilized these synthetic strategies to synthesize a variety of symmetrical and unsymmetrical binuclear phenoxide bridged coordination compounds containing a very wide variety of metal ions, chelating groups and substituents (R, R') [90-98].

Diaminomaleonitrile-a Precursor to Symmetrical Robson-Type Macrocycles

It was suggested in 1928 [99] that, the tetramer obtained via base polymerization of hydrogen cyanide had the structure of Diaminomaleonitrile. This structure was not confirmed until 1961 when Penfold and Lipscomb [100] obtained a single crystal X-Ray diffraction structure of the molecule. In the years that followed, there were surprisingly few reports of the use of DAM in coordination chemistry, possibly due to its unusual reactivity.
Diaminomaleonitrile is a very attractive precursor for the formation of symmetrical Robson-type coordination compounds. The binuclear M$^{2+}$ coordination compounds that, should result after templating the [2+2] condensation of a 2,6-diformyl-(R) phenol (R = CH$_3$, t-Bu) and DAM. These are very interesting compounds, which may be studied from a number of points of view.

Mandal et al., [101] have studied dicopper(II) complexes with macrocyclic Schiff bases derived from 2,6-diformyl-4-methylphenol and 1,3-diaminopropane. Which have been characterized by magnetic, electrochemical (CV) and X-Ray crystal studies. Antiferromagnetically coupled Cu(II) complexes which exhibit cyclic voltammetry involving two one-electron oxidation steps and two one-electron reduction steps with the formation of Cu(III)-Cu(III) and Cu(I)-Cu(I) and mixed oxidation species.

Alexander and Kumar [102] have synthesized lanthanide(III) and yttrium(III) complexes with 18-membered macrocyclic Schiff bases derived
from 2,6-diformyl-4-methylphenol and 1,2-aminobenzene. Which are characterized by elemental analyses, magnetic, spectral, conductance and thermal data suggest that, the central metal ion was coordinated with four nitrogen and two oxygen donors of the macrocyclic and two oxygen donors of a bidentate chelating nitrate ion and a water molecule. Metal ion exhibit the coordination number of nine.

Richard Robson et al., [103] have studied Ni(II) complexes with tetra nucleating macrocyclic Schiff base derived from two molecules of 2,6-diformyl-4-methylphenol and two molecules of 2,6-bis(aminomethy)-5-methylphenol. It is well characterized by X-Ray crystal structure. The molecule is situated around a crystallographic 2-fold axis of symmetry and four nickel ions are located almost at the corners of a square perpendicular to the axis and a pseudo-octahedral arrangement around each nickel ion is completed by a central $\mu_4$-hydroxo group located on the 2-fold axis with its hydrogen pointing away from the Ni$_4$ plane.
Dinuclear Cu(II) complexes with Schiff bases derived by template condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane have been synthesized by Thompson et al., [104] and characterized by X-Ray crystal studies. The square-pyramidal geometry of copper(II) complexes were suggested by X-Ray crystallographic studies.

Lacroix and Daran [105] have reported conductivity and magnetic properties of trifluoromethylated dinuclear copper(II) complexes with Schiff bases derived from 1,3-diaminopropane and 2,6-diformyl-4-trifluoromethylphenol and tetracyanoquinodimethane. The magnetic properties recently have been investigated for Robson-type Cu(II) dimmers, in which each metal is weakly bonded to a ligand.

Spectral and electrochemical properties of a new series of unsymmetrical bis(phenoxo) bridged macrocyclic binuclear manganese(III)
complexes have synthesized by Kandaswamy and co-workers [106]. Two reduction couples were observed for all the complexes in the negative potential region (0.00 to -1.60V) \[ \text{Mn}^{III}_2 \rightarrow \text{Mn}^{II}_2 \text{Mn}^{III} \rightarrow \text{Mn}^{II}_2 \]. The first one electron reduction is observed around -0.90 V and the second around -1.30 V. In other positive potential region (0.00 to +1.00 V) two oxidation couples are observed for all the complexes \[ \text{Mn}^{III}_2 \rightarrow \text{Mn}^{III}_2 \text{Mn}^{IV} \rightarrow \text{Mn}^{IV}_2 \]. The first one electron oxidation is observed around +0.25 V and the second around +0.60 V.

Martin Schröder and co-workers [107] have studied magnetochemistry of binuclear Co(II), Ni(II) and Cu(II) complexes of 2,6-diformyl-4-methylphenol dioxime (2-hydroxy-5-methylbenzenedicarbaldehyde dioxime) and which have been characterized by X-Ray crystallographic data. In all the complexes, the two dioxime ligands are monodeprotonated at the phenolic oxygen and oximes are linked by hydrogen bonds, which results in a pseudo-macrocyclic framework. Magnetic susceptibility measurements on the complexes over the range 2.5-340K confirm that, the complexes are antiferromagnetically coupled.
David Hendrickson and co-workers [108] have studied variation of magnetic exchange interaction in a series of six-coordinate Fe(II), Co(II) and Ni(II) complexes and which are characterized by spectral data. An increase in antiferromagnetic exchange interaction was expected for a six-coordinated complex compared to the analogous five-coordinated complex as a consequence of improved orbital overlap from the metal ion being in the plane of the binucleating ligand for the six coordinated complex. This was not realized, possibly because of the increased ligand field splitting in the six-coordinated complex attenuated the increased antiferromagnetic interaction.

Jingcai Yao and co-workers [109] have studied a tetranuclear zinc(II) complex of a [4+4] macrocyclic Schiff base ligand derived from 2,6-diformyl-4-methylphenolate (sdmp) and 1,5-diamino-3-(1-hydroxyethyl)azapentane (dhap). The structure of the complex has been determined by X-ray techniques, indicating that, the hydroxyethyl group of the amine, dhap has been eliminated in the process. For comparison, the reaction of sdmp with diethylenetriamine has also been carried out. The resulting product has been characterized by its infrared and positive ion FAB mass spectra, which turned out to be a mixture of the corresponding [3+3] and [4+4] macrocyclic Schiff bases together with the common [2+2] mode.
Recently, Martin Schröder et al., [110] studied mononuclear and binuclear zinc(II) compartmental macrocyclic complexes of macrocyclic Schiff-bases formed by the [2+2] template condensation of 2,6-diformyl-4-methylphenol with 1,2-diaminoethane: \([H_2L_1]\), 1,3-diaminopropane: \([H_2L_2]\), 1,4-diaminobutane: \([H_2L_3]\) and 2,6-diacyl-4-methylphenol with 1,2-diaminoethane: \([H_2L_4]\) have been determined. Two different coordination environments are observed in \([Zn_2(L^1)(\mu-OAc)(OAc)]\).CHCl₃; which contains both a five and a six-coordinated \(Zn^{II}\) centre, with one acetate bridging two metal ions and a monodentate acetate bound to the six-coordinate \(Zn^{II}\) ion.
Very recently, Ni(II), Pd(II) and Zn(II) complexes of Schiff bases derived from 1,3-diaminopropane with a protected thiophen dialdehyde have been synthesized by Christine J. McKenzie and co-workers [111]. The Ni$^{2+}$ complex of the 2 + 2 macrocycle contains two square-planar nickel (II) ions and shows an arrangement similar to one observed previously the $\mu$-S atoms of the thiophenolate groups are pyramidal and lie on the same side of the plane defined by the four N atoms of the macrocycle to give a V-shaped molecule. By contrast, the Zn$^{2+}$ complex of the 2 + 2 macrocycle undergoes oligomerisation to yield a bowl-shaped hexanuclear complex that includes $\mu_3$-carbonate anion.

Very recently, Avaji et al.,[31] have synthesized and characterized the complexes of La(III) with Schiff bases derived from 3-substituted-4-amino-5-hydrazino-1,2,4-triazole and substituted salicylaldehydes. These complexes have been characterized on the basis of elemental analyses, spectral, magnetic and thermal studies.
La(III) and Th(IV) complexes with Schiff base derived by the condensation of thiocarbohydrazide and thiophene-2-aldehyde have been reported from this laboratory [403]. These complexes have been characterized on the basis of elemental analyses, spectral, magnetic and thermal studies.

Recently, Ni(II) complexes of terphthalic acid hydrazones also reported [31A]. These complexes have been characterized on the basis of elemental analyses, spectral, magnetic and thermal studies.

Co(II), Ni(II) and Cu(II) complexes of Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole with indole-3-aldehyde [31B] reported from this laboratory. These complexes have been characterized on the basis of elemental analyses, spectral, magnetic and thermal studies.
Very recently, La(III) and Th(IV) complexes with Schiff bases derived from 2,6-diformyl-4-methylphenol and bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl) alkanes [31C] have been reported. These complexes have been characterized on the basis of elemental analyses, spectral, magnetic and thermal studies.
AIM OF THE PRESENT RESEARCH WORK

In recent years there has been lot of interest shown in the synthesis and physico-chemical properties of transition metal complexes with substituted 1,2,4-triazoles. Triazoles and their derivatives have been proved to be effective bactericides [112], pesticides [113], fungicides [114-115] and insecticides [116-117]. Many Schiff bases derived from either heterocyclic amines or aldehydes have been studied for their ability to form complexes with the transition metals [118-127].

The metal complexes of Schiff bases have been widely investigated because of their structural features, unusual properties and their relevance to biological processes. The metal complexes of 4n-butyl-4H-1,2,4-triazole have been reported to act as a systemic protectant, fungicide against leaf rust for both spring and winter wheat. Mercapto derivatives of triazoles have great antiviral and antiinflammatory activities [128-129]. The Schiff bases are known to possess tuberculostic [130], fungicidal [131], bacteriostatic [132] activities. Patil and Coworkers studied the antimicrobial activities of triazole derivatives [133]. They have exhibited promising results. Besides their pharmaceutical and agricultural uses, triazole derivatives have been used in the field of polymers [134] and for making photographic chemicals [165] and dyestuffs [136]. Benzaldehyde derivatives of 3-methyl-4-amino5-mercapto-1,2,4-triazole has been evaluated for its coordinating abilities [137]. This ligand exists in the thiol form and it is reported that, Cu(II) undergoes reduction to Cu(I) while forming the complexes with this ligand.

Hydrazones constitute an important class of organic compounds because of their coordinating capability, analytical and industrial potentiality and biological activity.

The coordination chemistry of these compounds has assumed over the years, new dimensions owing to the fact that, they exhibit varied ligational behavior towards different metal ions and manifest novel structural features in the metal complexes [28-38, 138-142].
Hydrazones find wide applications in the synthetic chemistry for the preparation of compounds of most diverse structure and in analytical chemistry for the identification and isolation of carbonyl compounds and for the detection and determination of a large number of metal ions [143-144]. They also find use as plasticizers, polymerization, initiators, stabilizers for polymers, antioxidants, etc. [145].

In biological front, many of the hydrazones are reported to be physiologically active and find application in the treatment of several dreadful diseases; they show spasmolytic activity, hypotensive action and activity against leukaemia, sarcomas and other malignant neoplasms [145, 146-148]. Further they act as acaricides, herbicides, antibacterial and antifungal agents, plant growth regulators, nematocides, rodenticides, insecticides etc. [149-151, 145].

The biological activity of these compounds has often been considered to be due to their ability to form complexes with the metals present in the biosystem [152]. In many instances, the metal ion association exerts effect on the activity of the free ligand [153-156].

A survey of the literature reveals that, no work has been carried out on the synthesis of metal complexes with some following new Schiff bases (1-6). These ligands have three donor sites of SNO sequence with varied coordinating abilities which may lead to varied bonding and stereochemical behavior in complexes with different metal ions. This aroused our interest in synthesizing and elucidating the structures of transition [Co(II), Ni(II) and Cu(II)] and innertransition [La(III) and Th(IV)] metal complexes with new triazole Schiff bases and hydrazones.

1. Schiff bases derived from 3-substituted-4-amino-5-hydrazino-1,2,4-triazole and substituted salicylaldehydes (Fig.1).
2. Schiff bases derived from 2,6-diformyl-4-methylphenol and bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl) alkanes(Fig.2).
3. Bishydrazines derived from 3-substituted-4-amino-5-hydrazino-1,2,4-triazoles and 2,6-diformyl-4-methyl phenol (Fig.3).
4. Bishydrazines derived from terephthalic acid hydrazide and substituted salicylaldehydes (Fig.4).

5. Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole with indole-3-aldehyde (Fig.5).

6. Schiff base derived by the condensation of thiocarbohydrazide and thiophene-2-aldehyde (Fig.6).

All the complexes have been characterized on the basis of various physico-chemical techniques.

Because of the biological properties associated with the triazoles and hydrazine moieties, we have evaluated some Schiff bases and their metal complexes for their antibacterial and antifungal activities against *E. coli*, *P. aeruginosa*, *B. cereus* and *S. aureus* (Bacteria), *A. niger* and *A. fumigates* (Fungi).