CHAPTER I
INTRODUCTION

1.1 Importance of coordination compounds

Coordination chemistry is the most widely developed field in the last few decades. They play a vital role in nature as exemplified by the function of macromolecules such as haemoglobin, chlorophyll etc. that regulate various enzymatic processes in biological systems. Many enzymes contain coordinated metal ions as their active centres.

Today the study of coordination compounds has emerged as one of the major center of attraction for the inorganic chemist. It covers a comprehensive range of fascinating and theoretical applications. In synthetic work they continue to provide a challenge in the laboratory. In industry coordination compounds play key roles in homogeneous and heterogeneous [1-3] catalysis, biological catalyst [4], purification of water [5], analytical chemistry [6], solvent extraction [7] and photography [8]. They are also used as dyes [9], photoactive materials [10], and also used as electroluminescent materials [11], non-linear optical materials [12] and pharmaceuticals [13-15]. Coordination compounds are used as chemosensors [16-18] and they also act as corrosion inhibitors [19, 20]. They are essential in many life processes such as oxygen transfer and metal ion control. In fact the rapidly developing field of bioinorganic chemistry is centered on the presence of metal complexes in the biological systems. Moreover, the study of coordination compounds has enabled the inorganic chemist to make significant progress in refining the concept of chemical bonding and to explain the influence of bonding on the various properties of the compounds.
1.2 Schiff base ligands

Schiff base was first reported by Hugo Schiff in 1864 [21]. Among the complexing ligands, Schiff bases are having special interest due to their preparative accessibility and structural variety. Both aldehydes and ketones form Schiff base; however the formation takes place less readily with ketones than with aldehydes. Schiff bases derived from aliphatic aldehydes are unstable and are readily polymerizable. The presence of a dehydrating agent normally favors the formation of Schiff base. The common Schiff bases are crystalline and feebly basic in nature. They are characterized by the presence of an azomethine group –RC=NR’, where R and R’ are alkyl, cycloalkyl, aryl or heterocyclic group. Often they are referred to as anils, imines or azomethines. Schiff bases are widely designed by varying the chemical environment about the –C=N- group. The presence of a lone pair of electron in the sp$^2$ hybridized orbital on the imino nitrogen atom makes the azomethine group more significant. Schiff bases with an additional donor atom closer to the imino nitrogen form stable chelate with many metal ions. The essential requirement of the Schiff base which can act as model to mimic the oxygen carrying property of natural system is that it should possess at least two nitrogen donors, with the others being nitrogen, oxygen, sulphur or combination of the three.

1.3 Methods of synthesis of Schiff bases

Most commonly Schiff bases are prepared by the condensation of carbonyl compounds and amines in suitable conditions and in different solvents with the elimination of water molecules.
The preparation of Schiff bases and their complexes can be carried out by the following two methods:

a. **Direct synthesis**: In this method, the isolation and purification of Schiff bases are carried out before complexation. The complexes are then prepared by treating the metal ion and Schiff bases. One of the advantages of this method is that it is possible to perform the spectral characterization of complexes by comparing with the spectral data of the ligands.

b. **Template synthesis**: In this method, the syntheses of complexes are carried out without the isolation of Schiff bases by interacting carbonyl compound, amine and the metal salt in a one-step reaction.

The formation of a Schiff base from aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis, or upon heating.
The mechanism of Schiff base formation is another variation on the theme of nucleophilic addition to the carbonyl group. In this case, the nucleophile is the amine. In the first part of the mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called carbinolamine. The carbinolamine loses water by either acid or base catalyzed pathways. Since the carbinolamine is an alcohol, it undergoes acid catalyzed dehydration.

Typically the dehydration of the carbinolamine is the rate-determining step of Schiff base formation and that is why the reaction is catalyzed by acids. Yet the acid concentration cannot be too high because amines are basic compounds. If the amine is protonated and becomes non-nucleophilic, equilibrium is pulled to the left and carbinolamine formation cannot occur. Therefore, many Schiff base synthesis are best carried out at mildly acidic pH.
The dehydration of carbinolamines is also catalyzed by base. This reaction is somewhat analogous to the E2 elimination of alkyl halides except that it is not a concerted reaction. It proceeds in two steps through an anionic intermediate. Thus the Schiff base formation is really a sequence of two types of reactions, i.e. *addition* followed by *elimination*.

### 1.4 Coordination behaviour of Schiff bases

Ligands are classified according to the number of donor atoms contained and are known as uni, di, tri, or quadridentate ligands. When donor sites of a ligand occupy two or more coordination positions on the same central metal ion, a complex possessing a closed ring is formed. The phenomenon of ring formation is called chelation and ring formed is called chelate ring. Schiff bases primarily possess nitrogen donor atoms, though many can act as bi-, tri-, tetra- or polydentate mixed donor capabilities. In general, the donor nature of the ligands depends both on the type of aldehyde/ketone used and the nature of primary amine/diamine.
For several reasons, Schiff bases have been found to be the most convenient and attractive ligands for forming complexes. First, steric and electronic effects around the metal core can be finely tuned by an appropriate selection of bulky and/or electron withdrawing or donating substituents incorporated into the Schiff bases. Secondly, the two donor atoms N and O of the chelated Schiff base exert two opposite electronic effects: the phenolate oxygen is a hard donor and stabilizes the higher oxidation state of the metal atom; whereas the imine nitrogen is a border line donor and stabilizes the lower oxidation state of the metal ion [22]. Thirdly, Schiff bases are currently prepared in high yield through one-step procedures via condensation of common aldehydes with amines, in practically quantitative yields. While sulphur donor ligands, being soft bases, prefer to combine with late transition elements and with metal ions in lower oxidation state, the ONS donor Schiff bases can show symbiosis [23]. The presence of soft sulphur atom softens the hardness of the oxygen atom, and this enables such ligands to form a large number of complexes with structural diversity

1.5 Schiff base transition metal complexes

Metal complexes of Schiff bases are generally prepared by treating suitable metal salts with Schiff base ligands. There is a continuing interest in metal complexes of Schiff bases due to the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands. They readily coordinate with a wide range of transition metal ions yielding stable and intensely coloured metal complexes, some of which have been shown to exhibit interesting physical and chemical properties and potentially useful biological activities [24]. Cozzi [25] in his review explained in detail about five synthetic routes that are commonly employed for the preparation of Schiff base metal complexes (Scheme 1.1)
Scheme 1.1. Preparation of Schiff base complexes

Route 1 involves the use of metal alkoxides (M(OR)_n). Alkoxides of early transition metals (M = Ti, Zr) are commercially available and easy to handle. Metal amides M(NMe_2)_4 (M = Ti, Zr) are also employed as the precursors in the preparation of Schiff base metal complexes (Route 2). The reaction occurs via the elimination of the acidic phenolic proton of the Schiff bases through the formation of volatile NHMe_2. Other synthetic routes include treatment of metal alkyl complexes with Schiff bases (Route 3) or treatment of the Schiff base with the corresponding metal acetate under reflux conditions (Route 4). The synthetic scheme presented in route 5 which is quite effective in obtaining salen-type metal complexes consists of a two-step reaction involving the deprotonation of the Schiff bases followed by reaction with metal halides. Deprotonation of the acidic phenolic
hydrogen can be effectively done by using NaH or KH in coordinating solvents and the excess sodium or potassium hydride can be eliminated by filtration.

There are certain metallo-elements without which the normal functioning of the living organism is inconceivable. These metallo-elements are called, 'metals of life'. These are Na, Mg, K and Ca. Among the transition elements are V, Cr, Mn, Mo, Fe, Co, Ni, Cu and Zn. These elements are present at trace and ultra-trace quantities but play vital roles at the molecular level in a living system. These transition elements are known to form Schiff base complexes. During the last few decades there has been great interest in the chemistry of transition metal complexes because of their extensive applications in wide ranging areas [26].

1.6 Applications of Schiff base metal complexes

1.6.1 Industrial applications

The iridium(III) complexes containing 2,3-diphenylquinocxalines are highly efficient and pure-red emitting materials for electrophosphorescent organic light emitting diodes [27]. Organometallic complexes possessing a third-row transition metal element are crucial for the fabrication of highly efficient organic light-emitting diodes (OLEDs). Schiff base complexes containing Zn(II) are now a days used as electroluminescent materials eg; bis[salicylidene(4-dimethylamino)aniline]zinc(II) complex exhibits very good light emission and charge transporting performance in organic light emitting diodes (OLEDs). A novel electroluminescent material, 6,7-dicyano-2,3-di-[4-(2,3,4,5-tetraphenylphenyl) phenyl]quinoxaline (CPQ), which can be used as a multifunctional material in organic light-emitting diodes (OLEDs) [28]. Metal complexes of Schiff bases have wide application in asymmetric epoxidation of
unfunctionalised olefins [29, 30] used in dye industry [31], antifertility and enzymatic agents [32].

1.6.2 Schiff base transition metal complexes in catalysis

Schiff base complexes play a central role in various catalytic reactions and the activity of these complexes varies with the type of ligands, coordination sites and metal ions. Metal complexes with vacant coordination site can act as catalysts for two reasons. Firstly, they can have several oxidation states and can take part in electron transfer reactions. Secondly, they can provide sites at which reactions can take place. This feature gives them a high probability to form the suitable intermediates required for preceding the catalytic reactions. They can show catalytic behaviour when dissolved in solutions or in solid state and act as homogeneous or heterogeneous catalysts. Literature reports reveal that Schiff base complexes are more selective in catalysing various reactions, such as hydroxylation [33], aldol condensation [34], oxidation [35-37], hydrogenation [38, 39], polymerization [40, 41], epoxidation [42, 43] etc. They are also used as catalysts in various biological systems.

1.6.3 Pharmaceutical and Biological applications

Many Schiff bases are known to be medicinally important and are used to design medicinal compounds. Nitro and halo derivatives of Schiff bases are reported to have antimicrobial and antitumor activities [44]. Some drugs have increased activity when administrated as metal chelated and inhibit the growth of tumours [45].

The biological activity of Schiff bases either increase or decrease upon chelation with metal ions. In azomethine derivatives, the C=N linkage is essential
for biological activity, Several azomethine have been reported to possess remarkable antibacterial [46-48], antifungal [49-51], anticancer [52-54], antioxidant [55, 56], insecticidal [57], anti-HIV [58], antitumor [59, 60], in vitro cytotoxic [61-63], anti-inflammatory [64, 65] and antimalarial [66] activities. The mechanism of working of such compounds may be on the basis of hydrogen bond formation by the azomethine group (-C=N-) at the active centers of cellular entities, which cause the interferences in normal cellular phenomenon. Many transition metal complexes have been utilized as probes of DNA structure, as agents for mediation of strand scission of duplex DNA and as chemotherapeutic agents. Coordination of organic compounds with metal ions causes drastic change in the biological properties of the ligand and the metal ion moieties. Transition metal complexes with their varied coordination environments and tunable redox and spectral properties are able to interact with duplex DNA in various ways. Many Schiff base metal complexes have DNA binding [67-69] and DNA cleavage [70-72] activities.

1.7 Importance of compounds chosen for study

4-aminoantipyrine

4-aminoantipyrine is a metabolite of aminopyrine with analgesic and anti-inflammatory properties. Pyrazolone is a five-membered lactam ring compound containing two nitrogen atoms and ketone in the same molecule. Lactam structure is an active nucleus in pharmacological activity. 4-Aminoantipyrine has an N-phenyl group and a –CH group on either side of a polar carbonyl group, thus resembling N-substituted amides. The carbonyl group in 4-aminoantipyrine is a potential donor due to the large dipole moment (5.48 D) and strong basic character. Pyrazolone is an active moiety as a pharmaceutical ingredient, especially in the class of nonsteroidal anti-inflammatory agents used in the treatment of arthritis and other musculoskeletal
and joint disorders. The term pyrazolone sometimes refers to nonsteroidal anti-inflammatory agents. Antipyrine (also called phenazone) is a pyrazolone class analgesic agent in otic solutions in combination with other analgesic such as benzocaine and phenylephrine. Pyrazolone derivatives, as lactam structure related compounds, are also widely used in preparing dyes and pigments. 4-Aminoantipyrine possibly can be used as an intermediate for the synthesis of pharmaceuticals especially antipyretic and analgesic drugs. It is also used in the colorimetric determination of phenols.

Three modes of coordination must be considered for the system, unidentate with bonding through either oxygen or the amino nitrogen or chelation utilizing both these donors. Depending upon the form (neutral, protonated) of the ligand precursor, it is possible to obtain either neutral or protonated forms of the ligands. 4-aminoantipyrine regulate the performance of metals in a large variety of catalytic transformations [73]. Antipyrine derivatives are reported to exhibit analgesic and anti-inflammatory effects [74-77], antiviral [78], antibacterial [79] activities and have also been used as hair colour additives [80] and to potentiate the local anesthetic effect of lidocaine [81]. These compounds have been used in spectrophotometric determination of metal ions. Many of these reagents give intense colours with transition metal ions, providing sensitive probes [82] and some of them can also coordinate to rare earth ions to form metal complexes with interesting structures [83]. Antipyrine Schiff base derivatives can serve as anti-parasitic agents and their complexes with platinum(II) and cobalt(II) ions have been shown to act as antitumor substances [84].

In recent years, there has been a considerable interest in the chemistry of antipyrine and its derivatives. The coordinating behaviour of 4-aminoantipyrine has
been modified into a flexible ligand system by condensation with a variety of reagents like aldehydes, ketones etc.

1,10-Phenanthroline

1,10-Phenanthroline is an inhibitor of metallopeptidases, with one of the first observed instances reported in carboxypeptidase A. Inhibition of the enzyme occurs by removal and chelation of the metal ion required for catalytic activity, leaving an inactive apoenzyme. 1, 10-Phenanthroline targets mainly zinc metallopeptidases, with a much lower affinity for calcium. It is widely believed that the iron chelator 1, 10-phenanthroline (phen) is able to fully block the Fenton reaction by forming a complex [Fe(phen)$_3$]$^{2+}$, also known as ferroin that cannot react with H$_2$O$_2$. The synthetic chemical nuclease, [Cu(1,10-phenanthroline)$_2$]$^{2+}$, has stimulated research within metallonuclease development and in the area of cytotoxic metallodrug design. This agent is “promiscuous” as it binds both DNA and protein biomolecules, without specificity, and induces general toxicity to a diversity of cell lineages.

Aminophenols

Aminophenols are important to the pharmaceutical industry, since they have antibacterial and antitubercular action. Schiff bases obtained by the condensation of 2-aminophenol with some aldehydes/ketones find application as antituberculosis compounds. They also find application in the biophysical and clinical studies as metal ligand luminescence probes [85] and light-emitting devices (LEDs) [86]. 2-Aminophenol is an intermediate in the synthesis of dyes. It is particularly useful in yielding metal-complex dyes when diazotized and coupled to a phenol, naphthol, or other aromatic or resonant dye species. Metal complex dyes using copper or chromium are commonly used for producing dull colors.
1.7.1 Importance of the various metal ions used

Human body contains seven major and twenty-two trace elements. Trace elements play important structural, electrochemical and catalytic functions in the body. Their excess or deficiency may cause certain diseases. Transition metals exist in biological systems as stable complexes. These complexes are able to undergo ligand exchange with components of the biological system. Among the metal ions, d-block elements play important role in many biological reactions.

Cobalt is essential for many organisms including mammals. It activates a number of enzymes. Co(II) is found to be the most successful classes of oxygen carriers among the non-porphyrin dioxygen carriers. Co(II) complexes of Schiff base ligands give first real clue to the probable nature of the metal-dioxygen interaction [87-90]. The cobalt atom in porphyrin complexes is coordinated to four nitrogen atoms which form the basic skeleton for a highly conjugated tetrapyrrole system. In the analogous Schiff base complexes, two oxygen and two nitrogen or four nitrogen atoms constitute an annulene type of framework around the metal ion. Stynes and Ibers [91] have pointed out that the nature of equatorial ligands has an important role in stabilizing dioxygen complexes.

Nickel is an essential trace element. Chick and rats having deficient diet of nickel show impaired liver functions and morphology. It stabilizes polysomes and involves as active metal in several hydrogenases. Researchers have become interested in the coordination chemistry of nickel complexes as models for the active sites in nickel containing enzymes. There are six nickel enzymes so far discovered and they are: urease, NiFe hydrogenases, methyl coenzyme M reductase, carbon monoxide dehydrogenase, acetyl coenzyme A synthase and more recently nickel superoxide dismutase [90].
Copper is ubiquitous in plants, animals and its redox chemistry is involved in a variety of biological oxidation processes. Copper usually binds to proteins in living organisms. Copper is utilized very extensively in biological systems, to perform a large variety of functions, from electron transfer to oxygen transport. There are nine classes of copper enzymes and proteins; (i) electron-transfer enzymes (ii) ‘blue’ oxidases (iii) ‘non-blue’ oxidases (iv) monooxygenase (v) dioxygenases (vi) terminal oxidase (vii) superoxide degradation (viii) dioxygen transport (ix) nitrogen cycle enzymes [90].

Zinc is one of the most important metal ions in biology, and is more often found in metalloenzymes. Zinc is essential for the normal growth and development of mammals and is present to the extent of 1.4 to 2.3 g in the human body. In the body, about 18 zinc metalloenzymes and 14 zinc-ion activated enzymes have been found to be present. In aqueous solution, zinc exists in +2 oxidation state. It acts predominantly as a Lewis acid and is found in many metalloenzymes such as carboxypeptidase and carbonic anhydrase [90]. Recently confirmed function of zinc in proteins is to recognize base-sequences in DNA and regulate the transfer of genetic information during the replication of DNA. These so called “zinc finger” proteins contain 9-10 Zn(II) ions [91].

1.8 Review (4-AAP Schiff base metal complexes)

Raman et al [92] have reviewed the most important results on syntheses, spectral, magnetic, redox, structural characteristics, antimicrobial and DNA cleavage of the metal complexes with heterocyclic Schiff bases derived from 4-aminoantipyrine.
In the crystal structure of the centro symmetric title complex, 
\[\text{bis-[\mu-(E)-1,5-dimethyl-2-phenyl-4-(3-pyridyl-methyl-eneamino) pyrazol-3(2H)-one] bis-\{dibromido-[(E)-1,5-dimethyl-2-phenyl -4-(3-pyridylmethyl-ene-amino)-pyrazol-3(2H)-one]manganese(II)\}}, \ [\text{Mn}_2\text{Br}_4(\text{C}_{17}\text{H}_{16}\text{N}_4\text{O})_4], \] the Mn atom adopts a trigonal-bipyramidal geometry and the ligand adopts monodentate and bidentate bridging coordination modes [93].

Some novel metal complexes of UO$_2$(VI) with Schiff bases derived from 4-aminoantipyrine and 5-bromosalicylaldehyde/p-anisaldehyde have been synthesized and characterized by elemental analyses, IR, UV, $^1$H NMR spectra, thermal studies, magnetic and conductance measurements [94].

A series of transition metal complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), VO(IV), Hg(II) and Cd(II) have been synthesized from the Schiff base (H$_2$L) derived from 4-aminoantipyrine, 3-hydroxy-4-nitrobenzaldehyde and 2-aminophenol. The structural features have been arrived from their elemental analyses, magnetic susceptibility, molar conductance, mass, IR, UV-Vis., 1H NMR and ESR spectral studies [95].

Few transition metal complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), VO(IV), Hg(II) and Cd(II) have been synthesized from the Schiff base, derived from 4-aminoantipyrine, salicylaldehyde and 4, 4'-diaminodiphenylmethane. The structural features have been arrived from their elemental analyses, magnetic susceptibility, molar conductance, FAB Mass, IR, UV-Vis., 1H NMR and ESR spectral studies [96].

N$_2$O$_2$ donor type Schiff bases have been designed and synthesized by condensing acetylaceto-4-aminoantipyrine/acetoacetanilido-4-aminoantipyrine with 2-amino benzoic acid. Solid metal complexes of the Schiff bases with Cu(II), Ni(II),
Co(II), Mn(II), Zn(II), VO(IV), Hg(II) and Cd(II) metal ions were synthesized and characterized by elemental analyses, magnetic susceptibility, molar conductance, FAB Mass, IR, UV-Vis., $^1$H NMR, and ESR spectral studies [97].

Neutral complexes of Cu(II), Ni(II), Co(II), VO(II) and Zn(II) have been synthesized from the new Schiff base derived from curcumin and 4-aminoantipyrine. The structural features of the complexes have been determined from their microanalytical, magnetic susceptibility, molar conductance, IR, UV-Vis., $^1$H-NMR, mass and ESR spectral data [98].

The reactions of mono(cyclopentadienyl) titanium (IV) trichloride and bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride with Schiff bases, derived by condensing 4-aminoantipyrine with benzaldehyde (L$_1$), furfuraldehyde (L$_2$), pyridine-4-carboxaldehyde (L$_3$) or salicylaldehyde (L$_4$H), have been studied in anhydrous tetrahydrofuran or dichloromethane and products of types $[\text{Cp}_2\text{M}(\text{L})\text{Cl}]\text{Cl}$, $[\text{CpTiCl}_3(\text{L})]$ (L = L$_1$, L$_2$ or L$_3$); $[\text{Cp}_2\text{M}(\text{L}_4)\text{Cl}]$, $[\text{CpTiCl}_2(\text{L}_4)]$, $[\text{CpTi}(\text{L}_4)_2]\text{Cl}$ [M = Ti IV or Zr IV] have been isolated. Tentative structures are proposed for these complexes based upon elemental analyses, electrical conductance and spectral (electronic, IR, $^1$H NMR and $^{13}$C NMR) data [99].

A series of transition metal complexes of Cu(II), Ni(II), Co(II) and Zn(II) have been synthesized from the Schiff base derived from 4-aminoantipyrine, salicylaldehyde and o-phenylene diamine. The structural features have been arrived from their elemental analyses, magnetic susceptibility, molar conductivity, FAB-mass, IR, UV-Vis., $^1$H NMR and ESR spectral studies [100].

N-(2-hydroxy-1-naphthaldene)-4-aminoantipyrine has been synthesized. The structure is determined by X-ray diffraction method and elemental analysis. The geometry has been obtained from the density functional theory (DFT) method and
the B3LYP method employing the 6-31G* basis sets. The calculated results propose that the latter is close to the experimental data [101].

A series of transition metal complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Hg(II), and VO(IV) have been designed and synthesized from the Schiff base derived from cinnamidene-4-aminoantipyrine and 2-aminophenol by involving the carbonyl group of 4-aminoantipyrine. The structural features have been arrived from their elemental analyses, magnetic susceptibility, molar conduction, FAB mass, IR, UV-Vis, \(^1\)H NMR and ESR spectral studies [102].

Schiff bases prepared by condensation of 4- aminoantipyrine and various aromatic aldehydes followed by reaction with thiosemicarbazide. These thiosemicarbazones are potential ligands toward transitions metal ions. The reaction of copper (II) salts with 4[N- (benzalidene)amino]antipyrine thiosemicarbazone (BAAPTS), 4[N-(4′-methoxybenzalidene) amino]antipyrine thiosemicarbozzone (MBAAPTS), 4[N-(4-dimethylaminobenzalidene)amino]antipyrine thiosemicarbazone (DABAAPTS) and 4[N-(cinnamalidene)amino]antipyrine thiosemicarbazone (CAAPTS) resulted in the formation of solid complexes with the general composition CuX\(_2\).\(\text{H}_2\text{O}\)(L)(X = Cl, Br,NO\(_3\),NCS or CH\(_3\)COO; L = BAAPTS, MBAAPTS, DABAAPTS or CAAPTS). These complexes were characterized through elemental analysis, molecular weight, electrical conductance, infrared, electronic spectra and magnetic susceptibilities at room temperature [103].

The formation mechanism and photochromic property of a novel solid state Schiff base compound derived from 4-aminoantipyrine and 3,5-diiodosalicylaldehyde is investigated using density functional theory with and without the presence of water [104].
A series of transition metal complexes of Cu(II), Ni(II), Co(II) and Zn(II) have been designed and synthesized using a Schiff base (L) derived from 4-aminoantipyrine, benzaldehyde and o-phenylenediamine. The structural features were derived from their elemental analyses, magnetic susceptibility and molar conductivity, as well as from mass, IR, UV-Vis, 1H-NMR and ESR spectral studies [105].

The Schiff base pyridine-2-carboxylidene-4-aminoantipyrine and its perchlorate have been prepared and characterized by elemental analysis, IR spectra and single-crystal X-ray crystallography analysis [106].

Transition metal complexes of Schiff base ligand (L) derived from thiophene 2-carboxaldehyde and 4-aminoantipyrine have been synthesized and characterized using spectroscopic, magnetic susceptibility measurements, conductivity methods and thermal studies and thermal analysis were performed [107].

Transition metal complexes of Co(II), Ni(II) and Cu(II) metal ions with general stoichiometry [M(L)X]X and [M(L)SO₄], where L = 3,3'-thiodipropionic acid bis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline) and X = NO₃⁻, Cl⁻ and OAc⁻ have been synthesized and structurally characterized [108].

Some novel metal complexes of oxomolybdenum(V) and dioxomolybdenum(VI) with a Schiff base derived from 4-aminoantipyrine and 2,4-dihydroxyacetophenone have been synthesized and characterized [109].

Ni(II) and Ru(II) complexes of heterocyclic Schiff base, 3-hydroxyquinoxaline-2-carboxylidene-4-aminoantipyrine, have been synthesized and characterized by elemental analysis, FT-IR, UV-vis diffuse reflectance
spectroscopy, FAB-Mass, TG-DTA, AAS, cyclic voltammetry, conductance and magnetic susceptibility measurements [110].

Two antipyrine derivates, 4-(3,4-dihydroxybenzylideneamino)antipyrine (DHBAP), and 4-(2,3,4-tri hydroxybenzylideneamino)antipyrine (THBAP), are structurally similar Schiff bases derived from the condensation of 3,4-dihydroxybenzaldehyde and 2,3,4-tri hydroxybenzaldehyde with 4-aminoantipyrine in methanol solutions [111].

The Schiff base (HL) ligand is prepared via condensation of 4-aminoantipyrine and 2-aminobenzoic acid. The ligand and its metal complexes were characterized based on elemental analysis, mass, IR and $^1$H NMR spectra, solid reflectance, magnetic moment, molar conductance and thermal analyses (TGA, DrTGA and DTA) [112].

Two structurally similar Schiff bases are derived from the condensation of 2,3-dichlorobenzaldehyde or 2,5-dichlorobenzaldehyde with 4-aminoantipyrine in methanol solution. The compounds are characterized by elemental analysis, FT-IR, FT-Raman, UV-vis and X-ray single crystal diffraction techniques. Density functional calculations were performed to further optimize and characterize them [113].

The Schiff base 2,3-dimethyl-1-phenyl-4-(2,5-dihydroxyacetophenone)-5-pyrazolone (DHAAP) has been prepared by reacting 4-aminoantipyrine with 2,5-dihydroxyacetophenone and a series of metal complexes with this ligand were synthesized by reaction with Cu(II) having the compositions [Cu(DHAAP)$_2$(Cl)$_2$], [Cu(DHAAP)$_2$(NO$_3$)$_2$], [Cu(DHAAP)$_2$(ClO$_4$)$_2$], [Cu(DHAAP)$_2$(CH$_3$COO)$_2$] and [Cu(DHAAP)$_2$(NCS)(Cl)] (where DHAAP = dihydroxyacetophenoneazoantipyrine). The complexes were characterized on the basis of elemental analyses, molar
conductance, magnetic susceptibility data, UV-Visible, IR, ESR, thermal and X-ray diffraction studies [114].

Metal complexes of Schiff base (HL) ligand was prepared from 4-aminoantipyrine and 2-aminophenol and characterized using spectral techniques. IR spectra show that HL is coordinated to the metal ions in a uninegatively tridentate manner with NNO donor [115].

Neutral complexes of Co(II), Ni(II), Cu(II), and Zn(II) have been synthesized from the Schiff bases derived from 3-nitrobenzylidene-4-aminoantipyrine and aniline (L1)/p-nitro aniline (L2)/p-methoxy aniline (L3) in the molar ratio 1:1. The structural features have been determined from microanalytical, IR, UV-Vis, ¹H-NMR, mass and ESR spectral data [116].

A series of transition metal complexes of Cu(II), Ni(II), Zn(II) and VO(IV), were synthesized from the Schiff base (L) derived from 4-aminoantipyrine, 3-hydroxy-4-nitrobenzaldehyde and acetylacetone. The structural features were arrived from their elemental analyses, magnetic susceptibility, molar conductance, Mass, IR, UV-Vis., ¹H NMR and ESR spectral studies [117].

A series of transition metal complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Hg(II) and Sn(II) have been synthesized from the Schiff base (L) derived from 4-aminoantipyrine and 4-fluoro-benzaldehyde using traditional synthetic methodology and microwave-induced organic reaction enhancement (MORE) technique. Structural features were obtained from elemental analysis, molar conductivity, ¹H NMR, mass, UV-Vis. and FTIR spectroscopy and X-ray diffraction. [118].
The Schiff's bases 2-alkyl-4-oxo-3,4-dihydro-2H-1,2-benzothiazine 1,1-dioxides have been synthesized for the first time, their structures in solution and in the crystalline state and their ability to form complexes have been investigated [119].

The Schiff base, 3-hydroxyquinoxaline-2-carboxylidine-4-aminoantipyrine, was synthesized by the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde with 4-aminoantipyrine [120].

The coordination compounds of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Zr(OH)$_2$(II), MoO$_2$(II) and UO$_2$(II) with the Schiff base derived from the condensation of 3-formylsalicylic acid and 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one have been synthesized at different pH. The coordination compounds have been characterized on the basis of elemental analyses, molecular weight, spectral (IR, reflectance, ESR and NMR) studies and the magnetic susceptibility measurements [121].

Schiff base synthesized from pyridoxal, a vitamin and 4-aminoantipyrine has been reported. This Schiff base acts as a tridentate ligand, which form very stable complexes with the lanthanide metals La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Er. The structure of the ligand and complexes were characterized [122].

A bidentate Schiff base, synthesized from 4-aminoantipyrine and vanillin forms stable complexes with transition metal ions such as Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). Their structures have been investigated by elemental analysis, infrared spectroscopy, electronic spectroscopy, NMR spectroscopy; thermo gravimetric analysis and electron spin resonance spectroscopy [123].
The reaction of cis-[RuCl$_2$(DMSO)$_4$] with salicylaldehyde semicarbazone in ethanol resulted in the chemoselective cleavage of the CN bond of the Schiff base, forming a complex in which the semicarbazide remains coordinated to the metal. Reactions of cis-[RuCl$_2$(DMSO)$_4$] with 4-aminoantipyrine derivatives of salicylaldehyde, 2-hydroxy-1-naphthaldehyde and o-vanillin, CN cleavage was observed in all three cases yielding the same compound, [RuCl$_2$(DMSO)$_2$(4-aminoantipyrine)]. The reactions, under the same experimental conditions did not show any cleavage with unsubstituted /N- substituted thiosemicarbazones of salicylaldehyde and 2-hydroxy-1- naphthaldehyde. All the complexes have been characterized by analytical and spectroscopic techniques [124].

Two Schiff bases, N’-(5-bromo-2-hydroxy-3-methoxybenzylidene)-4-methoxybenzohydrazide and 4-{{[1-(5-bromo-2-hydroxy3-methoxyphenyl)methylidene]-amino}-1-methyl-2-phenyl-1,2-dihydropyrazol-3-one, have been synthesized by the reaction of 5-bromo-3-methoxysalicylaldehyde with 4-methoxybenzohydrazide and 4-aminoantipyrine, respectively. The compounds were characterized by elemental analysis and X-ray single crystal determination [125].

Cu(II) complexes have been synthesized from the Schiff base ligands derived from furfurlyidene-4-aminoantipyrine and aniline (L$_1$)/p-nitroaniline (L$_2$)/ p-hydroxyaniline (L$_3$). They were characterized using analytical and spectral techniques [126].

The Schiff base 4-[(anthracene-9-ylmethylene)amino]-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one has been synthesized in high yield by reaction of anthracene-9-carbaldehyde and 4-aminoantipyrine. The structure of this new
compound was confirmed by elemental analysis, IR, $^1$H NMR, $^{13}$C NMR and GC-MS spectral data [127].

A few mononuclear complexes of oxomolybdenum(V) and dioxomolybdenum(VI) with a Schiff base derived from 4-aminoantipyrine and o-vanillin have been synthesized and characterized. The complexes have general formulae [MoO(AAPOV)Cl$_2$X] and [MoO$_2$(AAPOV)ClX] where AAPOV = 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxy benzylidene amino)pyrazol-5-one and X = Cl, NCS, NO$_3$ or ClO$_4$. The ESR spectrum of the complex [MoO(AAPOV)Cl$_3$] in the solid state exhibits a single line pattern [128].

Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base derived from vanillinidene-4-aminoantipyrine and o-phenylenediamine have been synthesized and characterized by elemental analysis, $^1$H NMR, $^{13}$C NMR, molar conductance, infrared, electronic, magnetic measurements, cyclic voltammetry, powder XRD and SEM [129].

A series of transition metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were synthesized from the Schiff base ligand derived from 4-aminoantipyrine, furfural and o-phenylenediamine. The structural features were derived from their elemental analyses, infrared, UV-vis, NMR, TGA, ESR and conductivity measurements [130].

Some copper complexes have been synthesized and characterized of the formulae [Cu(L$_1$)(OAc)], [CuL$_2$(H$_2$O)], [CuL$_3$(H$_2$O)], [CuL$_4$(OAc)], [CuL$_5$(H$_2$O)] [CuL$_6$], [CuL$_7$], [CuL$_8$](OAc) and [CuL$_9$], where L$_1$-L$_9$ represents Schiff base ligands [derived by the condensation of 5-hydroxyflavone with 4-aminoantipyrine (L$_1$), o-aminophenol (L$_2$), o-aminobenzoic acid (L$_3$), o-aminothiazole (L$_4$), thiosemicarbazide (L$_5$), 4-aminoantipyrine-o-aminophenol (L$_6$), 4-aminoantipyrine-o-aminobenzoic acid (L$_7$),
4-aminoantipyrine-o-aminothiazole (L8) and 4-aminoantipyrine-thiosemicarbazide (L9)]. The spectral and magnetic results of the Cu(II) complexes exhibit square planar geometry [131].

Schiff base metal complexes of Cu(II), Ni(II), Co(II) have been synthesized from a new tetradentate ligand, 2-((E)-1,5-dimethyl-2-phenyl-3-((E)-quinolin-8-methyl)-2,3-dihydro-1H-pyrazol-4-ylimino)methyl)phenol. The ligand and its metal complexes have been characterized on the basis of elemental analysis, electronic, infrared, $^1$H NMR and $^{13}$C NMR spectral studies. [132].

Complexes of the type [M(L)X$_2$], where M = Co(II), Ni(II) and Cu(II), have been synthesized with novel NO-donor Schiff’s base ligand, 1,4-diformylpiperazine bis(4-imino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) which is obtained by the acid catalyzed condensation of 1,4-diformylpiperazine with 4-aminoantipyrine [133].

Potentially tridentate Schiff bases $H_2$nap and $Hoap$ have been synthesized by the condensation reaction of 4-aminoantipyrine with 2-aminobenzaldehyde and salicylaldehyde, respectively. The reaction of $H_2$nap with [ReOBr$_3$(PPh$_3$)$_2$] and cis-[ReO$_2$I(PPh$_3$)$_2$] (1) gives rise to the products [Re(nap)Br$_2$(PPh$_3$)]Br (2) and [ReO(OEt)(Hnap)(PPh$_3$)]I (3), respectively. In (2) the ligand nap is coordinated as a tridentate imido-imino-ketone, while in 3Hnap is bonded as an amido-imino-ketone. The reaction of $Hoap$ with [ReO$_2$I(PPh$_3$)$_2$] affords the product [ReO(OMe)(oap)(PPh$_3$)]I (4). Spectroscopic data and the X-ray crystal structures of compounds 2-4 were also reported [134].

Some ternary NNO type Schiff bases and their Cu(II) and Zn(II) chelates have been synthesized using curcuminyl-4-aminoantipyrine and aniline/substituted aniline (p-Cl, p-NO$_2$ and p-CH$_3$). They have been characterized by elemental
Transition metal complexes of Cu(II), Ni(II), Co(II), Zn(II) and VO(IV) have been synthesized from the Schiff base ligand (L) derived from 4-aminoantipyrine and 5- bromo salicylaldehyde. The structural features of Schiff base and metal complexes were determined from their elemental analyses, thermogravimetric studies, magnetic susceptibility, molar conductivity, ESI-Mass, IR, UV-Vis, $^1$H NMR and ESR spectral studies [136].

4-aminoantipyrine derived Schiff bases and their metal complexes have been synthesized and characterized. Their structural features and other properties were deduced from the elemental analysis, magnetic susceptibility and molar conductivity as well as from mass, IR, UV-vis, 1H NMR and EPR spectral studies [137].

The Schiff base compound synthesized by the condensation reaction of 4-amino-1,5-dimethyl-2-phenylpyrazole-3-one and benzaldehyde was studied by single-crystal X-ray diffraction [138].

The coordination complexes of VO(II), Co(II), Ni(II) and Cu(II) with the Schiff bases derived from isatin with 3-chloro-4-fluroaniline and 2-pyridinecarboxaldehyde with 4-aminoantipyrine have been synthesized by conventional as well as microwave methods and characterized. The antimicrobial results indicate that the metal complexes are better antimicrobial agents as compared to the Schiff bases [139].

4-aminoantipyrine derived Schiff base and its four mixed ligand complexes have been synthesized and characterized. The binding properties of metal
complexes with DNA have been investigated by electronic absorption spectra and viscosity measurements showing that the complexes have the ability of interaction with DNA by intercalative mode. The effect of the metal complexes on DNA was carried out as pUC19 DNA [140].

Cu(II) complexes of molecular formula, \( [\text{CuL}_1(\text{OAc})], [\text{CuL}_2(\text{H}_2\text{O})], [\text{CuL}_3(\text{H}_2\text{O})], [\text{CuL}_4(\text{H}_2\text{O})], [\text{CuL}_5(\text{H}_2\text{O})] \) where \( \text{L}_1-\text{L}_5 \) represents Schiff base ligands by the condensation of 3-hydroxyflavone with 4-aminoantipyrine (\( \text{L}_1 \))/o-aminophenol (\( \text{L}_2 \))/o-amino benzoic acid (\( \text{L}_3 \))/o-amino thiazole (\( \text{L}_4 \))/thio semicarbazide (\( \text{L}_5 \)), have been prepared. They have been characterized using analytical and spectral techniques [141].

The \textit{in vitro} antifungal activities of few novel 4-aminoantipyrine derived Schiff bases and their metal complexes were tested against fungi such as Aspergillus niger, Fusarium solani, Culvularia lunata, Rhizoctonia bataicola and Candida albicans [142].

A series of transition metal complexes of Co(II), Ni(II), Cu(II), Zn(II) and VO(IV) with biological activity, have been synthesized involving the Schiff bases 2,3-dimethyl-1-phenyl-4-(5-chloro-2-hydroxy benzyldeneamino)-pyrazol-5-one (5-Cl SALAAP), \( \text{L}_1 \) and 2,3-dimethyl-1-phenyl-4-(3-ethoxy-2-hydroxy benzyldeneamino)-pyrazol-5-one (3-OEt SALAAP), \( \text{L}_2 \) derived from 4-amino antipyrine and 5-chloro salicylaldehyde/3-ethoxy salicylaldehyde respectively. Structural features have been obtained from their IR, 1H NMR, ESI Mass, UV-Vis, thermo gravimetric studies, elemental analysis, molar conductance and magnetic susceptibility measurements [143].

New binuclear Co(II) and Cu(II) complexes of ONO tridentate heterocyclic Schiff base derived from 4-aminoantipyrine with salicylaldehyde have
been synthesized and characterized on the bases of elemental analysis, UV-Vis., FT-IR, molar conductivity and magnetic measurements [144].

Schiff base analogues of 4-aminoantipyrine have been synthesized by the condensation reaction with substituted benzaldehydes and then evaluated for their antioxidant and anti-inflammatory activities. Some of the synthesized complexes exhibited antioxidant and anti-inflammatory activities [145].

The synthesis and characterization of three hexa-coordinated Ru(II) Schiff base complexes of the type \([\text{RuCl(CO)(B)L]}\) (B = PPh\(_3\)/AsPh\(_3\)/py and L = monobasic tridentate Schiff base ligand derived by the condensation of salicylaldehyde with 4-aminoantipyrine) were reported. IR, electronic, NMR and mass spectral data of the complexes were discussed [146].

Metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) with ligands (L\(_1\)H and L\(_2\)) derived from 4-aminoantipyrine, 2-hydroxy-3-formylquinoline, and isatin have been synthesized and characterized by the elemental analysis, conductance measurements, magnetic susceptibility and spectral analysis [147].

Transition metal complexes of tetradentate N\(_2\)O\(_2\) donor Schiff base ligands containing 2-hydroxybenzylidene-4-aminoantipyrine and amino acids (alanine/valine) abbreviated to KHL\(_1\)/KHL\(_2\) have been synthesized. All the metal complexes have been fully characterized with the help of elemental analyses, molecular weights, molar conductance values, magnetic moments and spectroscopic data [148].

Neutral tetradentate N\(_2\)O\(_2\) complexes of Co(II), Ni(II), Cu(II), Zn(II) and VO(II) have been synthesized using the 1-phenyl-2,3-dimethyl-4-imino-(2-hydroxybenzylidene)-pyrozol-5-(\(\alpha\)-imino)-indole-3-propionic acid (H\(_2\)L). All the
complexes were characterized by elemental analysis, molar conductivity, magnetic susceptibility data, IR, $^1$H-NMR, UV-Vis, FAB-Mass, and EPR spectral studies [149].

Hexacoordinated organosilicon complexes of type $R_3Si(L)$ ($R = ethyl, butyl, phenyl; HL = ligand, obtained by the condensation of 4-aminoantipyrine with 2-hydroxyacetophenone, 2-hydroxybenzophenone, 2-hydroxybenzaldehyde, and 2-hydroxynaphthaldehyde) have been reported [150].

Schiff base composed with 9-anthraldehyde and 4-aminoantipyrine have been synthesized and characterized as a fluorescent probe in the presence of Fe(III). The method of Job's plot indicated the formation of 1:1 complex between probe and Fe(III) and the possible binding mode of the system has also been proposed. Moreover, other examined metal ions had no effect on the detection of Fe(III) [151].

A series of Pt(II) and Pd(II) complexes have been synthesized by template condensation of 4-methoxybenzaldehyde, benzaldehyde, 4-chlorobenzaldehyde and 4-nitrobenzaldehyde, with 4-aminoantipyrine (4-AAP) in the presence of $K_2PtCl_4/PdCl_2$ to form complexes of the type $[M(L_n)Cl_2]$ (where $M = Pt(II)$ or Pd(II)). The corresponding Schiff base complexes mixed ligand were prepared by condensation of $[M(L_n)Cl_2]$ with ethanolamine (LH). On the basis of elemental analysis, IR, $^1$H NMR and $^{13}$C NMR, electronic spectra, conductance measurements, magnetic susceptibilities and thermal analysis. [152].

The proton-ligand dissociation constant of 4-(4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino)-phenol and 4-(4-amino-1,5-dimethy l-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino)-benzoic acid and metal-ligand stability constants of their complexes with metal ions Mn(II), Co(II), Ni(II) and
Cu(II) have been reported. The effect of temperature and the corresponding thermodynamic parameters (ΔG, ΔH and ΔS) have been investigated [153].

Metal complexes of Schiff base (L) ligand via condensation of 4-chlorobenzaldehyde and 4-aminoantipyrine, metal complexes were characterized based on elemental analysis, mass, IR and NMR spectra, magnetic moment, molar conductance and cyclic voltammetry (CV) [154].

4-(4-nitrobenzalideneamino)antipyrine (NBAA) have been synthesized from 4-aminoantipyrine and p-nitrobenzaldehyde and characterized with various physico-chemical techniques. X-ray diffraction patterns show amorphous nature for all NBAA thin films except UV irradiated thin film which shows amorphous nature with some crystallinity but with small amount. The effect of UV irradiation as well as the effect of annealing on the optical properties of NBAA thin films was also reported [155].

A Schiff base derived from 2-pyridine formaldehyde and 4-aminoantipyrine was synthesized and characterized as a fluorescent probe. In the presence of Al(III), the fluorescent intensity has a dramatic enhancement over other examined metal ions in aqueous solution [156].

A novel Schiff base has been synthesized using the bioactive ligand obtained from 4-aminoantipyrine, 3,4-dimethoxybenzaldehyde and 2-aminobenzoic acid. Its Co(II), Ni(II), Cu(II) and Zn(II) complexes have also been synthesized and characterized [157].

Cu(II) and Zn(II) complexes of bidentate Schiff base ligand, synthesized via condensation of 4-aminoantipyrine and 2-aminothiazole. The ligand has been
characterized on the basis of elemental analysis, mass, IR, $^1$H NMR, UV-Visible and ESR spectra. [158].

The synthesis of complex combinations of Cu(II) and Zn(II) with Schiff base obtained by the condensation reaction of 4-aminoantipyrine with benzaldehyde and 2-amino-3-methyl-butanoicacid. Structural features of synthesized compounds were determined by analytical and spectral techniques [159].

Seven imine derivatives obtained by condensation of appropriate aldehydes and salicylaldehydes with 4-aminoantipyrine has been investigated in terms of Intramolecular hydrogen bond structure. On the base of $^1$H, $^{13}$C and $^{15}$N NMR measurements in solution and in the solid state, it has been observed that all compounds which can form such structure exist as OH forms with strong H-bonds to nitrogen atom. The influence of antipyrine moiety seems to be the major factor defining H-bond structure [160].

1:2 Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with the Schiff base ligand Indal-4-AAP, derived from indole-3-carboxaldehyde and 4-aminoantipyrine has been synthesized and characterized by elemental analyses, mass, IR, electronic spectra, magnetic moment, molar conductance and cyclic voltammetry. The DNA cleavage activity of the ligand and its complexes has been assayed on pUC18 DNA using gel electrophoresis [161].

An acyclic Schiff base ligand containing N$_2$O$_3$ donor atoms has been synthesized by the condensation reaction of 2,6-diformyl-4-ter-butylphenol and 4-aminoantipyrine. The synthesized ligand and complexes of the metal ions Cr(III), Fe(III), Co(II),Ni(II),Cu(II) and Zn(II) were characterized by $^1$H NMR, $^{13}$C NMR, mass spectrometry, UV-Visible, FTIR, atomic absorption, elemental analysis (C,H,N.), molar conductivity and magnetic susceptibility measurements [162].
1.9 Scope of the present investigation

Schiff bases and their complexes have significant importance in chemistry. Every year number of reports has been published on the preparation of these compounds and their applications in various fields. A potential group of Schiff base complexes which have received comparatively less attention is those derived from heterocyclic systems. Heterocyclic compounds are found widely in nature and are essential to many biochemical processes. Heterocyclic Schiff base complex can be served as versatile materials as a multidentate ligand bearing hetero atoms, such as $N, S, O, P$ etc. Aim of the present investigation has been to work on metal chelates of Schiff base, derived from heterocyclic systems.

The literature survey indicates voluminous work turned out by researchers all over the globe. 4-aminoantipyrine contain imine group (Schiff's bases) which are considered as ‘privileged ligands’ have the ability to stabilize different metals in different oxidation states. Taking into consideration the preeminent importance assumed, the present investigation was taken up, which deals with synthesis, characterization, and biological studies on i) Metal complexes with Schiff base derived from furfuraldehyde, 4-aminoantipyrine and 2-aminobenzothiazole ii) Mixed ligand metal complexes of Schiff base with 1,10-phenanthroline. iii) Mixed ligand metal complexes of Schiff base with 2-amino phenol. The metal ions chosen for the study are cobalt, nickel, copper and zinc. The Schiff base is abbreviated as FAAPBT. 1,10-phenanthroline is abbreviated as Phen and 2-aminophenol is abbreviated as AP.
The metal complex systems reported are:

1. **FAAPBT M(II) complexes** (M= Co, Ni, Cu, Zn).

2. Mixed ligand complexes of M(II) with **FAAPBT** and **Phen** (M= Co, Ni, Cu, Zn).

3. Mixed ligand complexes of M(II) with **FAAPBT** and **AP** (M= Co, Ni, Cu, Zn).

The objectives are:

- To study the stoichiometry of the Schiff base metal complexes and mixed ligand metal complexes.
- To investigate the binding sites of the ligands.
- To formulate stereochemistry of Schiff base and mixed ligand metal complexes.
- To study the redox behaviour, thermal stability, grain size and surface morphology of Schiff base and mixed ligand metal complexes.
- To study antimicrobial activity of Schiff base and mixed ligand metal complexes.
- To evaluate the DNA binding ability of Schiff base metal complexes and mixed ligand metal complexes.
- To study the DNA cleavage of Schiff base metal complexes and mixed ligand metal complexes.
• To carry out anti tuberculosis activity of 1, 10-phenanthroline mixed ligand metal complexes.

• To evaluate the cytotoxicity of the mixed ligand metal complexes.

• To study the anticancer activity of the mixed ligand metal complexes

• To perform docking studies of all the synthesized complexes

The Schiff base ligand was synthesized and characterized by elemental analysis, IR, $^1$H NMR and DART mass spectral measurements. The complexes were synthesized and characterized by elemental analysis, molar conductance, IR,$^1$H NMR, DART mass, electronic, magnetic, ESR, CV and TGA. The grain size and the surface morphology of the complexes were studied using XRD and SEM techniques. An attempt was also made to study, antibacterial, antifungal, DNA binding, cleavage, SOD, anti-tuberculosis of selected system, cytotoxicity and anticancer activity of mixed ligand metal complexes. Docking studies of the synthesized compounds were also carried out.