# CHAPTER I

# INTRODUCTION

## 1.1 General Introduction :

Schiff's bases are those compounds which contain (⊃C=N-) group and are usually synthesised by the reaction of a primary amine and an active carbonyl compound (aldehyde or ketone).

Metal complexes with Schiff's bases as ligands have been amongst the most widely studied co-ordination compounds[1-13]. Early work in this field was carried out using Salicylaldehyde. Pfeiffer was the pioneer of this work. He and his co-workers have published a series of papers[14] on Schiff's base complexes by using copper (II) as metal.

The Schiff's base metal complexes can be synthesised by three different procedures :

(i) Reaction of metal ion with preformed Schiff's base.
(ii) Reaction of metal aldehyde complex with primary amine.
(iii) Reaction of metal amine complex with an aldehyde or a ketone.

Schiff's base complexes have been studied extensively due to various reasons like manifestation of novel structural features[15-17], abnormal magnetic properties[18-19] and relevance to biological processes[20].

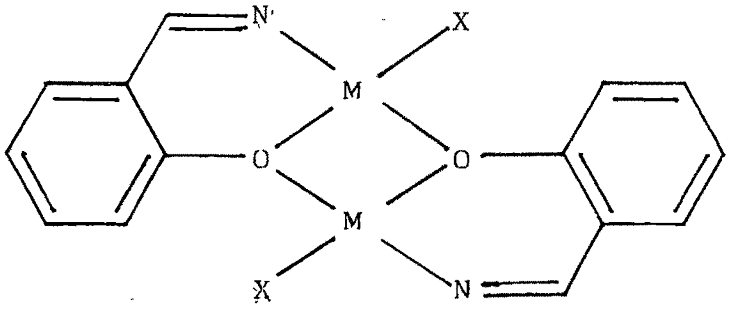
Several Schiff's base complexes containing two or more metal ions, linked to each other within the complex through one or more shared entities referred to as "bridging groups" have been studied[21-24]. There is an increasing evidence that binuclear transition - metal complexes have played important roles in the development of co-ordination chemistry. In one role they have served as models for more complex systems of polymetallic or cluster-catalyzed reactions. Secondly the recent applications of mixed - metal systems in organic synthesis[25]. They act as models in bioinorganic chemistry[26-27]. The development of a large number and variety of binucleating ligands has led to the successfull synthesis of a variety of homo- and hetero - binuclear metal complexes[28-31]. An evolution started a decade ago toward hetero - bimetallic complexes, but still limited number of these complexes are known and fully structurally characterised.

As per literature binuclear Schiff's base complexes can be classified into the following types[32] :

(1) Binuclear complexes derived from bidentate schiff's base which are of two types :

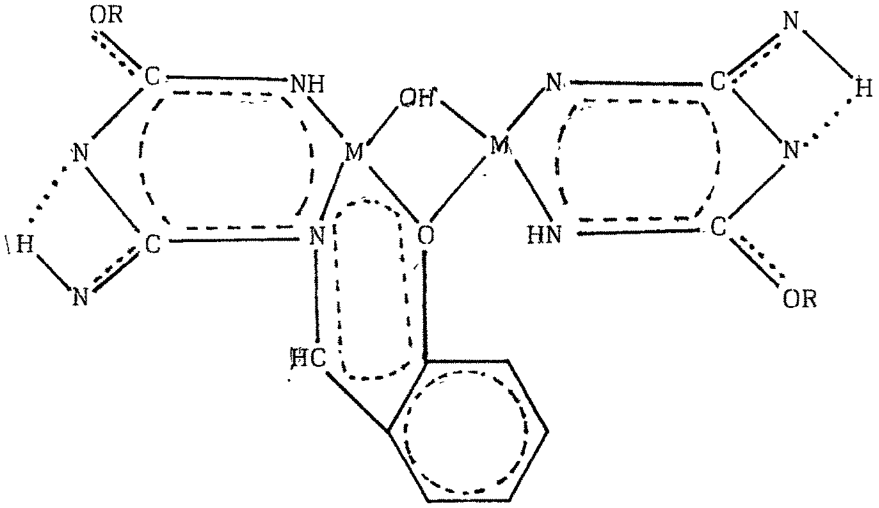
  (i) Symmetrical (Fig. 1.1)[33].

  (ii) Unsymmetrical (Fig. 1.2)[34]



X = Cl , Br   $H_2O$   etc.

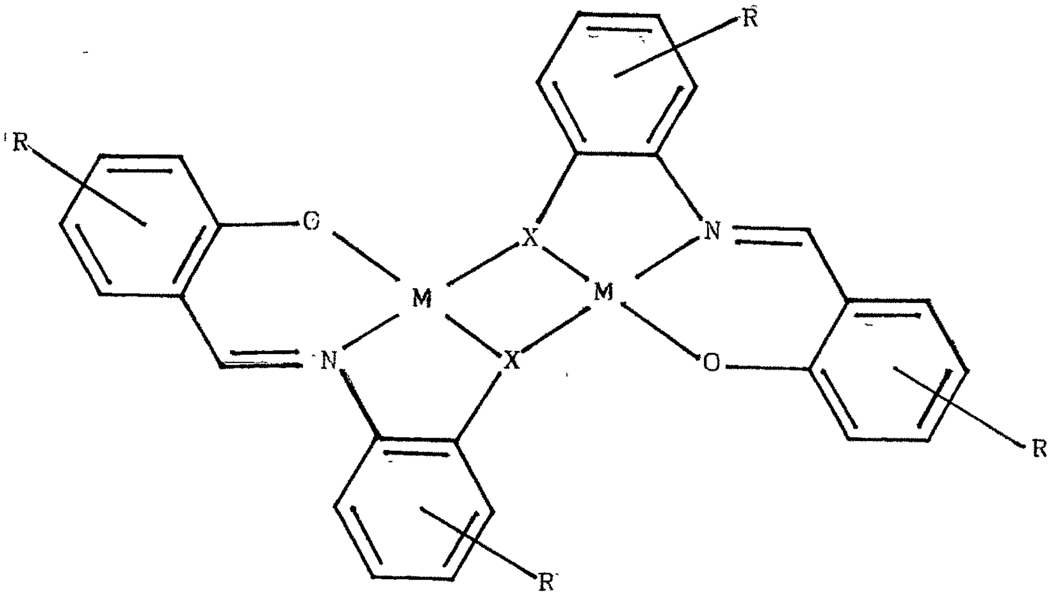
(Fig. I.1)



(Fig. I.2)

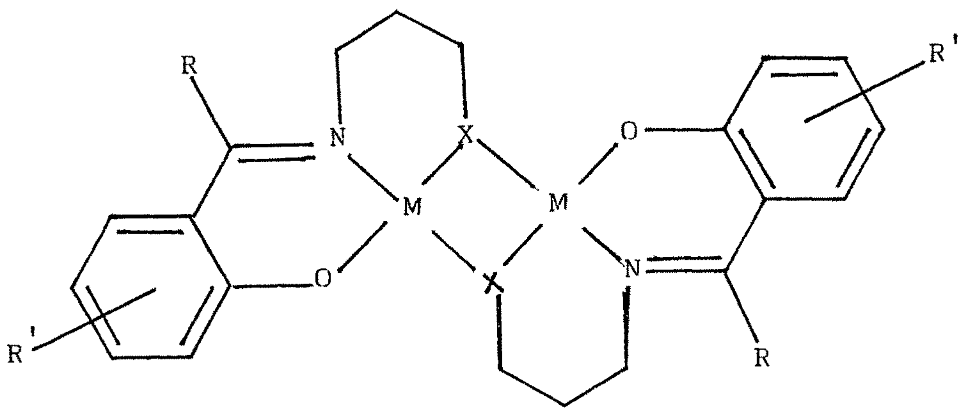
(2) Binuclear complexes derived from tridentate Schiff's base where :

- (i) bridging occurs via phenolic oxygen or sulpher (Fig. 1.3)[24].
- (ii) bridging occurs via alcoholic oxygen or sulpher (Fig. 1.4)[22,35].
- (iii) bridging occurs via carboxylic group (-COO$^-$) (Fig.1.5)[35]



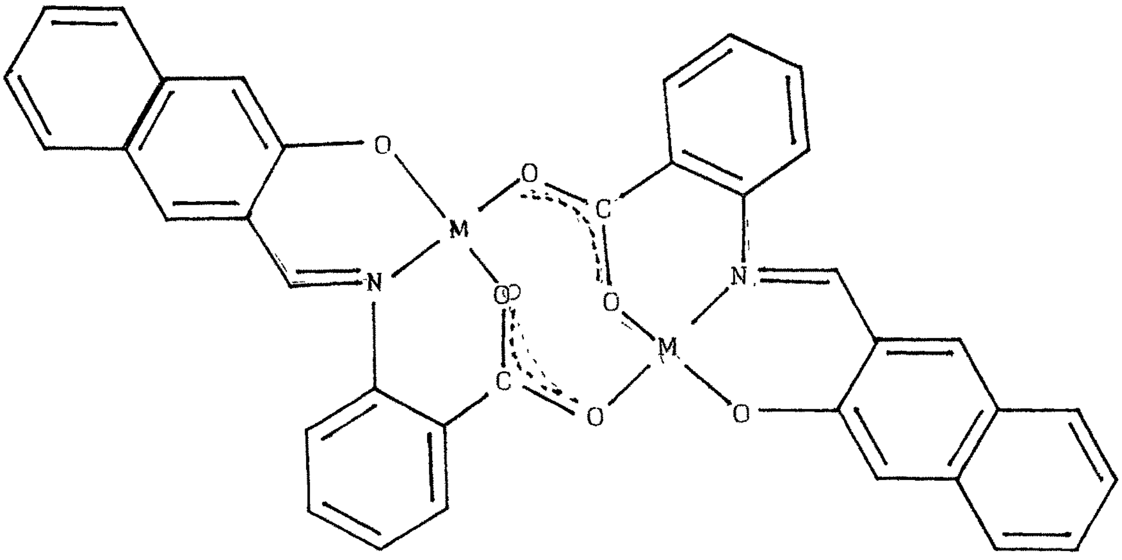
X = S or O

(Fig. I.3)



X = O or S

(Fig. I.4)

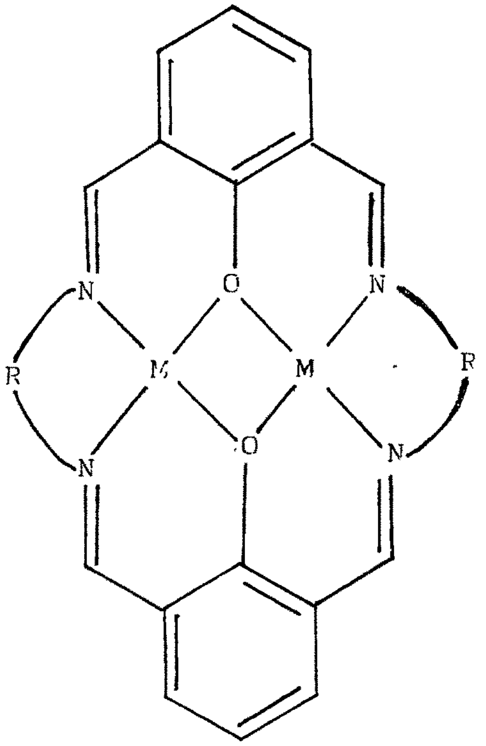


(Fig. I.5)

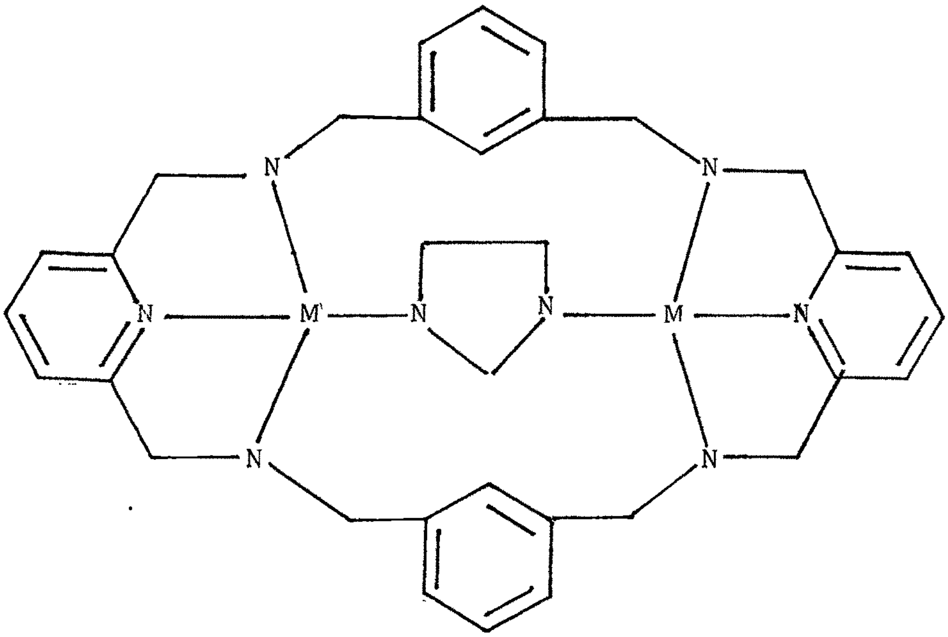
3) Binuclear complexes Derived from compartmental ligand (a macrocyclic binucleating ligand).

(i) with similar co-ordination sites (Fig. 1.6)[37] & (Fig. 1.7)[38].

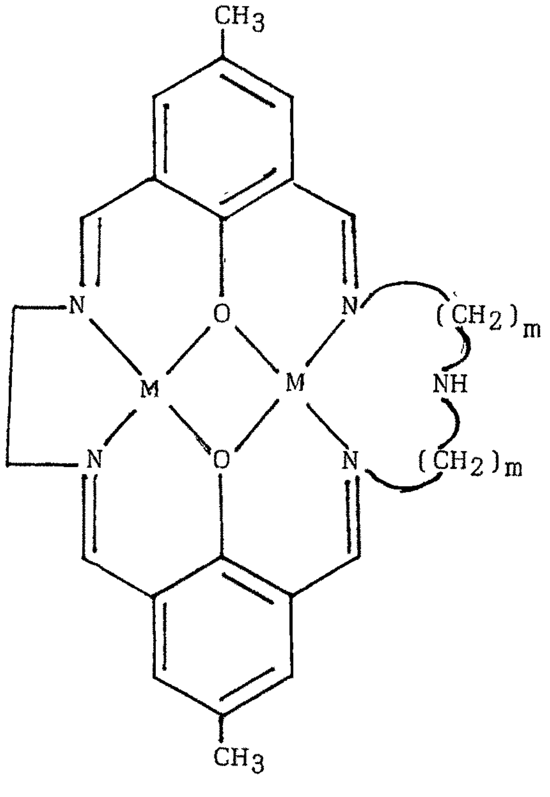
(ii) with dissimilar co-ordination sites (Fig. 1.8)[39].



(Fig. I.6)



(Fig. I.7)

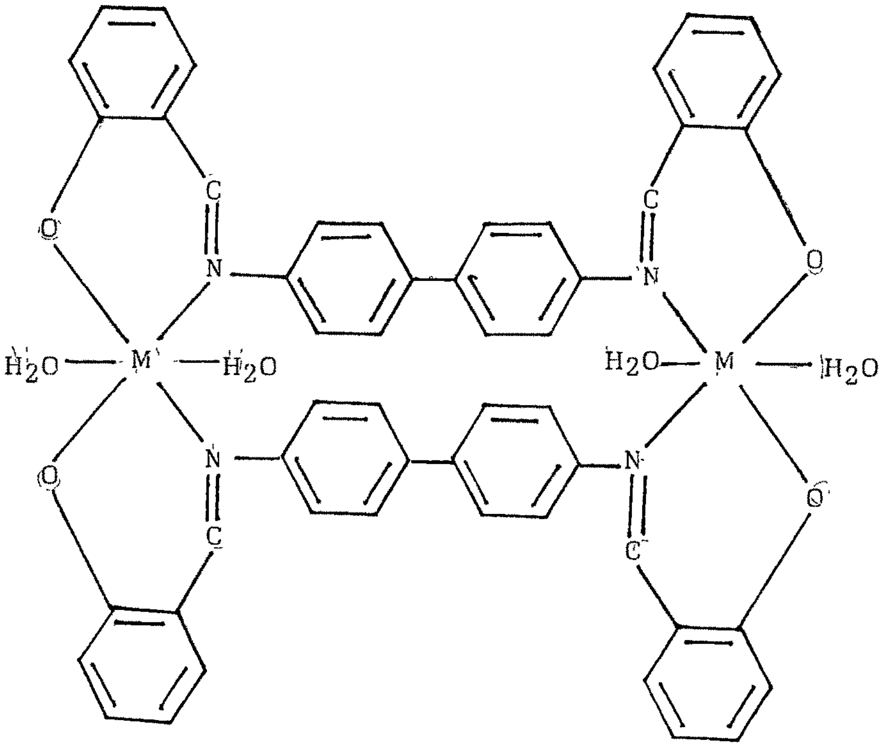


(Fig. I.8)

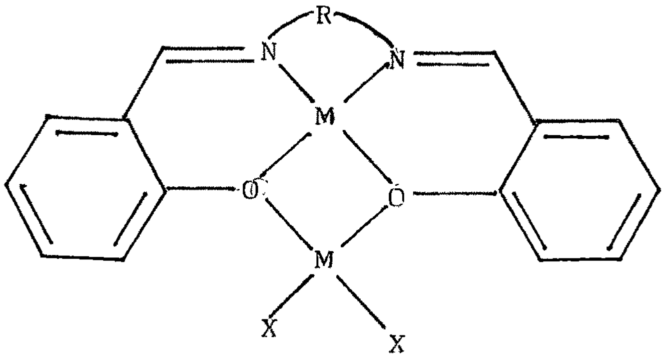
4) Binuclear complexes derived from tetradentate Schiff's bases, which are of two types :

(i) Symmetrical (Fig. 1.9)[40].

(ii) Unsymmetrical (Fig. 1.10)[41].



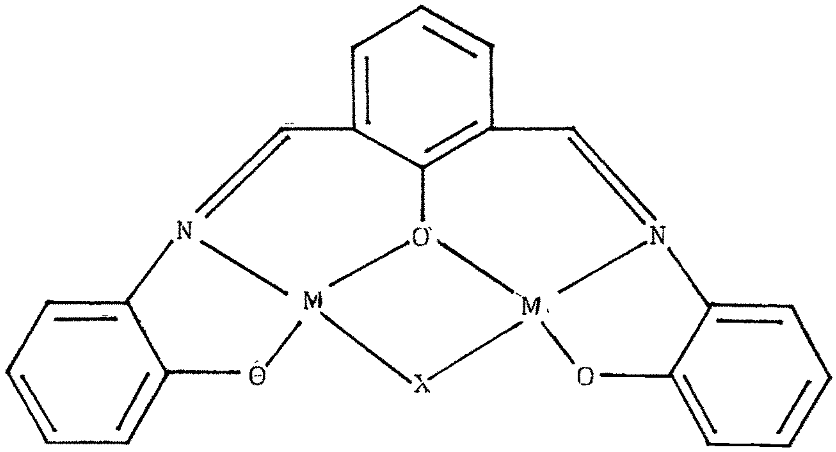
(Fig. I.9)



X = $Cl^-$, $Br^-$ or $NO_3^-$

(Fig. I.10)

5) Binuclear Complexes derived from Pentadentate schiff's bases (Fig. 1.11)[42].



X = OR, Cl$^-$ etc.

(Fig. I.11)

The literature survey has reported that schiff's bases and their complexes possess good luminescence and pigmentation properties[43-45]. A number of schiff's base complexes also reported to be of great utility in pharmacological and biological aspects[46-47]. These properties change with structure of the ligand and nature of the metal ion.

## 1.2 LUMINESCENCE :

Luminescence is most conveniently defined as the radiation emitted by a molecule, or an atom in the visible region, after it has absorbed energy to go to an excited state. Luminescence consists of fluorescence and phosphorescence and it generally occurs in molecules having $\pi$-electron system[48].

Much work is reported in the field of luminescence studies of metal complexes at recent international conferences held in U.S.A. and Japan on photophysics (ICL'93) and photochemistry (10th International Symposium on Photochemistry and Photophysics of Co-ordination Compounds). The work on polynuclear and molecular cluster complexes have drawn more attention of the scientists in these conferences. There is also luminescence work reported on organic Schiff's bases, but unfortunately their complexes have not been studied.

The study of several azomethine compounds has shown that the main structural factor determining the luminescence properties is the presence of $>C=N-$ group with lone pair electrons at the nitrogen atom[49]. The $>C=N-$ group may be regarded as an intermediate between the ethylene group $>C=C<$ and azo group $-N=N-$. These compounds exhibit properties typically observed in diarylethylenes and azo compounds. At the same time, the asymmetry of the $>C=N-$ group is the reason why compounds of this class display some very special properties inherent only in them[49]. The literature also shows that the eliminattion of rotation of N-phenyl ring radiationless transitions are reduced, more over due to a higher participation of unshared pair of nitrogen electrons of azomethine bond is responsible for increase in luminescence intensity on complex formation[44].

During the fluorescence process the active molecule undergoes some change due to exciting radiation and it is only when the active molecule is destroyed, fluorescence takes place. Hence the intensity of fluorescence is determined by the rate at which active constitutes are destroyed.

In organic compounds with aromatic, cyclic or closed ring structure more fluorescence is observed. Heterocyclic or six membered compounds are bases of fluorescence.

It is well known that Ru(II) and Os(II) polypyridine compounds exhibit Luminescence from the lowest triplet metal to ligand charge transfer excited states[50].

It is also revealed from the literature that exoergonic energy transfer between two directly connected units is so fast to cause 100% efficient luminescence quenching of the higher energy unit and sensetisation of the lower energy one. For the symmetrical compounds the luminescence is very simple emission, originating from the lowest excited state, which is metal to bridging ligand charge transfer (MLCT)[51].

The luminescence behaviour of nonsymmetric compound is more complicated. The lowest excited state is located on (M-L) unit. Besides luminescence bands of these units an emission band at shorter wevelength is also observed, which is characteristics of (M-L) units[52].

The energy transfer from the central units to the peripheral ones is 100% efficient because the process is exoenergic and donor acceptor units are directly connected. However energy transfer from higher energy units to the lower energy one exhibits a low efficiency, since the two units are separated by two higher energy units.

Charge transfer L ⟶ M or M ⟶ L are always higher energies compared to M ⟶ M charge transfer (d - d) transitions[50]. Excited states resulting from the promotion of an electron from metal or ligand orbital into a conduction or otherwise delocalised bands can give rise to fluorescence in transition metal complexes[53]. The transition may be either magnetic or electric dipole and may be symmetry allowed or forbidden. Emission from spin allowed or forbidden states have been observed.

Most fluorescent metal chelates compounds emit upon making the reverse transitions, that is made upon excitation i.e. $\pi^* \longrightarrow \pi$. Because of the nature of combining states the emission spectrum of a typical fluorescent metal chelate will consist of a rather broad band having a half band width greater than 2000 $cm^{-1}$ (60 mμ) at room temperature[54].

Under certain conditions the metal chelates may emit fluorescence denoted as $m^* \longrightarrow m$. Subsequent to energy transfer, if some excitation energy has passed to a resonance level of metallic ion, a relative transition may occur from the resonance levels to the ground state. Because of this, the pathway involves a radiative combination of atomic orbitals and fluorescence would be characterised by a relatively narrow band width[55].

Metal chelate fluorescence has been reported on which emission accompanies the charge transfer step $\pi^* \longrightarrow n$. The band in the emission spectrum in this case would be somewhat narrow than the usual $\pi^* \longrightarrow \pi$ band because one of the combining orbital is localised on the metallic ion, but the band would be broader than narrow $m^* \longrightarrow m$ band because one of the combining state is centered on the ligand[56].

Introduction of auxochromic groups often produce only minor shifts in wave lengths of maximum absorption and minor changes in the intensity of the absorption by their chelates. The fluorescence intensity, however may change markedly with such ligand modifications. The effect of these structural changes on the relative energies of the $\pi$ & $\pi^*$ orbitals are rather small hence the minor shift in the positions of the absorption and fluorescence spectral band[57].

However small structural changes may profoundly affect the efficiency of certain energy transfer steps. In certain cases the added substituent may have non-bonding (n) electrons, and if these are more easily excited than $\pi$ electrons i.e., if an n, $\pi^*$ excited states is lower in energy than the lowest $\pi$, $\pi^*$ excited state a quenching may result[58].

The influence of the metallic ion on the fluorescence characteristics of a metal chelate compound is of major importance from the analytical view point. Only those ions which are diamagnetic when co-ordinated and are not themselves easily reduced, can normally be expected to form fluorescent metal chelate compounds[59].

The metallic ions perturb slightly the energies of the ligand, this will have marked effect on the intensity of fluorescence because metal ion strongly affects the efficiency of the various pathways available for dissipating the excitation energy of the chelate. Chelates of heavier metal ions show decrease in fluorescence intensity[60].

In some transition metal chelates intramolecular energy transfer from the ligand to excited "d" levels of the transition metal ion $d^* \longrightarrow d$ transition follow accompanying by emission of a narrow band fluorescence. Interaction between d-orbitals of the chelated transition metal ion and $\pi$ orbitals of the ligand also introduces some molecular character into the "d" orbitals as a result spectral band width for $d^* \longrightarrow d$ transition will be greater than those for $f^* \longrightarrow f$ transitions[61].

The introduction of hydroxyl group with donor properties increases fluorescence intensity. Introduction of Cl, Br groups show no substantial change in the fluorescence properties of the compound. Introduction of nitrogen, quenches fluorescence. The absence of hydrogen bonding produces either blue shift or the red shift of emission in complexes is expected[43].

## 1.3 Biological Activity :

A number of Schiff's base complexes reported to be of greater utility in pharmacological and biological aspects[46-47,62-63]. 8-Hydroxy quinoline and its metal chelates are well known potential bactericides and fungicides[46]. Also La(III) and Th(IV) salicylanilide complexes are good fungicidal and bactericidal agents[64].

It has been reported that complexes containing sulfur atom are bacterial static agents[65]. Some Schiff's base complexes of Mn(II), Co(II), Cu(II) and Ni(II) are reported to be antifungal and antibacterial agents[62]. Recently much work has been reported on biological activity of metal Schiff's base complexes at 29th ICCC held in Switzerland.

From these and related observations it has been suggested that an azomethine linkage is perhaps an essential structural requirement for such activity. Furthermore, co-ordination of biologically active ligands with metals often results into the formation of compounds of enhanced activity[66]. In Indian Ayurvedic system copper has been described to posses strong antileprotic activity[67], and its compounds are frequently used in pharmaceutical preparations for the treatment of various skin diseases including Psoriasis and Leprosy[68]. The metal ions are known to play a vital role in metabolic and toxicological function in the biological systems.

The metal chelates are more biologically active than free ligands, this may be due to chelation which reduces the polarity of the metal ion. This increases the hydrophobic character of the metal chelate and favours the penetration through liploid layers of micro-organism memberane[69].

The biological activity is found to change with structural changes. The presence of Cl, - $OCH_3$, $-OC_2H_5$, -OH groups enhance the activity. The metal chelates of aliphatic and aromatic diamines are reported, which show that amino group linked with different chain length has different effect according to structures[70].

Zinc complexes are reported to be more fungicides and bactericides compare to Copper and Nickel complexes.

The presence of heterocyclic ring in the complex molecules increases the potential activity[70]. The biological activities of metal chelates are very selective. The complexes which are effective on one type of test organism may not be toxic for other type of organisms. The water soluble and liquid complexes are more effective and convenient to apply.

## 1.4 Pigmentation Properties :

One of the most fascinating features of modern chemistry is the ever increasing interest by metal complexes of organic compounds. Their importance is well known in many fields, and the technology of dyes and pigments where considerable progress has been made during the past few decades. Some indication of the importance of metal complexes in this field is shown by the wide variety of metal complex dyes and pigments which have been employed commercially. These include copper, chromium, cobalt and nickel complexes[71-73].

The post treatment of direct dyed cotton with copper salts has been employed for many years as a method for improving wash - and light-fastness[74]. Most metal complexes produce dyes of high light-fastness for wool (mostly between 6 and 7).

Azomethines bear a formal resemblence to azo compounds and many parallels exist in the co-ordination chemistry of the two series of compounds.

Metallizable azomethines as dyestuffs have been widely investigated and tridentate diaryl -azomethines having different substituents, such as -OH, O-alkyl, -SH, S-alkyl, -$NH_2$, -COOH & -$OCH_2COOH$ in ortho positions were examined[75]. The metal complexes of tetradentate azomethines with copper and nickel are reported to have high light-fastness, their trinctorial strength and brightness are inadequate for them to be of value as pigments.

It appears that the variations in fastness between dyes of similar constituents are not related to change in substituents. It is possible that the light-fastness of metallized dyes, as in case of direct cotton dyes, is related to their degree of aggregation within the fiber than to the chemical structure[73]. The metal chelates are capable of establishing linkage with protein or cellulose molecules and a stable metal dye fiber complex is formed. It is further observed that cellulose - metal bond is weaker than protein - metal bond, hence they are effective dyes for woolen clothes. The stability of dyes of various diamines are reported, and found that aromatic diamines are better dyes than aliphatic ones. The binuclear schiff's base complexes of Cu(II) and Ni(II) are reported to be very good pigments for synthetic fibers[70].

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## AIMS AND OBJECTIVES

Much interest has been evinced in the last few years in the study of homo - & hetero - bimetallic and multimetallic complexes, which have occupied an important position in the Modern Inorganic Chemistry.

The awareness of the importance of such complexes has prompted a wide range of investigation on these compounds. The interest in these compounds arises from their various applications in the field of bio-inorganic, textile and luminescence.

The schiff's bases and their complexes are the most widely studied coordination compounds in the above mentioned fields, and have acquired a central role in the development of coordination chemistry.

This has led us to synthesise Some novel tailored molecules possessing above mentioned properties. A successful attempt has been made in the present work to synthesise binuclear metal chelates and characterise as well as to study their various applications in various fields like bioactivity, pigmentation and luminescence.

Here we are presenting the results of our studies on Cu(II), Ni(II) and Zn(II) binuclear Complexes of different series of binucleating schiff's base ligand systems derived from condensation of some aliphatic and aromatic diamines with different substituted aromatic aldehydes and aromatic dialdehyde with amino acids too.