An Advance Summary of the work

The subject matter of the thesis has been presented in five chapters. A brief introduction to coordination chemistry has been given in Section A of Chapter-I, whereas Section B and C of the said chapter deal with an outline of Schiff base metal complexes and biological importance of heterocyclic amines and their metal complexes respectively. The infrared spectra of the ligands and their metal complexes studied under this investigation have been discussed in Chapter-II (Section A-G). The infrared spectral data have been utilised to establish the bonding sites of the ligands to the metal ion. The probable geometries of the metal complexes have been proposed on the basis of their electronic spectra and magnetic moment data which have been discussed in Chapter-III along with a brief review of earlier work on the electronic spectra and magnetic properties of different metal ions. Chapter-IV of the thesis deals with the thermal behaviour of the complexes. The synthesis and analysis of the ligands and their metal complexes are described in Chapter-V.

Pharmacological applications of heterocyclic amines, their Schiff bases and their metal complexes described in Section - C of Chapter-I of the present thesis.
strongly advocate the reasons for the tremendous progress and intensive investigation in the field of Schiff base metal complexes. However, the survey of the literature reveals that the synthesis and structure elucidation of metal complexes with Schiff bases obtained by the condensation of the following heterocyclic amines and carbonyl compounds are yet to be studied.

**Heterocyclic amines:**

1. 2-amino-5-p-anisyl-1,3,4-oxadiazole
2. 2-amino-5-p-anisyl-1,3,4-thiadiazole
3. 2-amino-5-mercapto-1,3,4-thiadiazole

**Carbonyl compounds:**

1. Salicylaldehyde
2. Acetylacetone
3. 2-hydroxy acetophenone

Therefore a programme of research was undertaken to prepare metal complexes with the following Schiff bases.

1. 2-salicylideneimino-5-p-anisyl-1,3,4-oxadiazole (HSAOD)
It is further hoped that the complexes, synthesised in the present investigation may be used for clinical trials and prove to be biologically more active and less toxic to human systems than the similar type of complexes already reported.
Some of the results of this research work have been published and some are yet to be published. The reprints of the published work have been incorporated at the end.

**Preparation of Schiff bases:**

The Schiff bases have been prepared by refluxing either in ethanol or glacial acetic acid, equimolecular quantities of heterocyclic amines containing oxadiazole or thiadiazole moieties with various aldehydes or ketones. The ligands are usually of bidentate or bi-bidentate type with the enolic oxygen and azomethine nitrogen as principal donor atoms (Fig. 1).

It is observed that when the carbonyl compound is a β-diketone, such as 2,5-pentanedione, only one of the carbonyl groups undergoes condensation to form the Schiff base. The ligand is believed to exist in solution in a tautomeric equilibrium containing both the keto and the enol forms (Fig. 2). The enol form is stabilised by a higher degree of conjugation of a polyene system and is further reinforced due to the presence of a p-methoxyphenyl ring at the 5-position of the heterocyclic unit. This allows a greater delocalisation of the π-electron over the skeletal chain. This is evident from the appearance of a strong band at \( \sim 35000 \text{ cm}^{-1} \) in the electronic spectra.
of the ligands, characteristic of extended conjugated systems and is assigned to $\pi \rightarrow \pi^*$ transitions. Besides, weaker bands also arise at $\sim 33300 \text{ cm}^{-1}$ and may be due to $n \rightarrow \pi^*$ transitions possibly involving the p-methoxy oxygen atom. On the whole these observations provide a clear picture of the tautomeric equilibrium of the ligands in solution.

On the other hand, when the heterocyclic amine contains a thiol (SH) group at the 5-position, the Schiff base acts as a tetradentate ligand. In such a case, in addition to the phenolic oxygen and the azomethine nitrogen, the ring sulphur and the thiolsulphur also act as the donor atoms. The characteristic $\nu S-H$ vibration observed in the i.r. spectra of the ligands at $\sim 2540 \text{ cm}^{-1}$ is found to be absent in those of the complexes indicating the deprotonation of the $-SH$ group and coordination to the metal ion through sulphur atom. This is substantiated by the appearance of bands around $430 \text{ cm}^{-1}$ in the i.r. spectra of the complexes, characteristic of $\nu M-S$ vibrations. The $\nu C-S-C$ vibrations observed around $680 \text{ cm}^{-1}$ in the i.r. spectra of the ligands ($H_2SMTD$ & $H_2AMTD$) undergoes bathochromic shift in the spectra of the complexes by $10-15 \text{ cm}^{-1}$. This clearly indicates the coordination of the ring hetero sulphur atom to the metal ion. However all the four atoms cannot coordinate to the same metal ion due to steric factor and hence a polymeric
structure as shown in Fig. 8 has been suggested for the complexes of the Schiff bases $\text{H}_2\text{SMTD}$ and $\text{H}_2\text{AMTD}$.

I.R. spectra of the ligands show strong bands in the higher frequency region at $\sim 3300 \text{ cm}^{-1}$ originating due to $\nu \text{OH}$ vibrations. This band is relatively wide and its comparatively low energy is indicative of either inter or intramolecular hydrogen bonding with azomethine or ring nitrogen atoms (Fig. 3-4).

The characteristic breathing modes of vibrations of the heterocyclic diazoles observed at $\sim 910 \text{ cm}^{-1}$ do not appear to undergo any shift on Schiff base formation. The azomethine $\nu \text{C=N}$ vibrations are observed at $\sim 1600 \text{ cm}^{-1}$ and cyclic $\nu \text{C=N}$ vibrations at around $1660 \text{ cm}^{-1}$ in the i.r. spectra of the Schiff bases.

It is noteworthy that the centre of gravity of the hydrogen bonded $\nu \text{OH}$ bands is a measure of the nucleophilicity of the substituent at 5-position of the diazole ring. The nucleophilic character of the methoxy group pushes the electron charge cloud and consequently the azomethine nitrogen acquires a higher degree of basicity (Fig. 5).

Preparation of the metal complexes:

The Schiff base metal complexes isolated in the present study are of the stoichiometries, $\Sigma^\text{M} (\text{SB})_2 \cdot 7$. 
\[ \text{[M(SB)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{7} and [M(SB)(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{7}, where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Hg(II) and SB = schiff base. They were prepared by refluxing in ethanol, the schiff base and the appropriate metal salt in the ratios 2:1 (for ligands HSAOD, HAAAOD, HAAOD, HSATD, HAATD) and 1:1 (for ligands \textsubscript{2}SMTD and \textsubscript{2}AMTD). The chelates are separated out during refluxing in most of the cases and in some cases, usually with the ligands containing the thiazole ring, cooling was necessary. The solids thus separated were digested on water bath, filtered, washed successively with ethanol and ether and dried in vacuo. The complexes are fairly air stable and are insoluble in common organic solvents. However the freshly prepared complexes are sparingly soluble in dioxane and DMF.}

\textbf{I.R. spectra of the complexes:}

The bidentate ligands used in the present study bind the metal ions through the azomethine nitrogen and the enolic oxygen atoms. But in addition to these the quadridentate ligands also utilise the ring sulphur and the thiol sulphur atoms as the bonding sites. The i.r. spectra of the schiff bases display bands in the region 3300-3100 cm\textsuperscript{-1}, which are assigned to the \( \nu \) OH vibrations of the phenolic OH groups. Broadening of this band and the magnitude of shift to a comparatively lower frequency
region from the normal position of a free $\nu OH$ vibration 
(3700-3500 cm$^{-1}$) is due to proximity of the phenolic 
proton to the imine nitrogen and extensive hydrogen 
bonding as a result of deshielding along O-H-N coordinate.

These bands are absent in the i.r. spectra of 
the metal complexes suggesting the deprotonation of 
and coordination through the phenolic oxygen atom. Instead, 
strong and broad bands at $\sim 3400 - 3200$ cm$^{-1}$ are observed 
in the spectra of the complexes of the type $\mathcal{L}^{-} M(SB)_2(H_2O)_2^{-}$ 
which arise due to presence of lattice and/or coordinated 
water molecules. The appearance of bands $\sim 840$ cm$^{-1}$ in 
the i.r. spectra of these complexes characteristic of 
wagging and rocking modes of vibration of water molecules 
indicate the presence of coordinated water. This observation 
is further substantiated by the thermal study which is 
discussed later. The broad trough $\sim 3400-3200$ cm$^{-1}$ and 
the medium intensity band $\sim 840$ cm$^{-1}$ are found to be absent 
in the complexes of the type $\mathcal{L}^{-} M(SB)_2^{-}$.

The characteristic azomethine $\nu C=N$ and phenolic 
$\nu C-O$ bands appearing at $\sim 1600$ and $1260$ cm$^{-1}$ in the i.r. 
spectra of the schiff bases undergo bathochromic and 
hypsochromic shifts respectively in the spectra of all the 
metal complexes, which is a clear manifestation of coordination 
of the ligand through imine nitrogen and phenolic oxygen 
atoms.
The i.r. spectra of the schiff bases containing oxadiazole moieties display bands at ~1680 and 910 cm\(^{-1}\) which are assigned to cyclic \(\gamma\) C=N and \(\gamma\) N-N vibrations respectively. The i.r. spectra of the corresponding metal complexes do not show any change in the vibrational energies of these bands which clearly reflect the nonparticipation of the ring nitrogen and oxygen in coordination. However, in case of the complexes of the schiff base 2-acetylacetaminomino-5-p-anisyl-1,3,4-oxadiazole, it is observed that the i.r. band due to cumulative absorption of \(\gamma\) C=N=\(\equiv\) N is negatively shifted by 10 cm\(^{-1}\) and the characteristic \(\gamma\) N-N band observed at ~910 cm\(^{-1}\) undergoes a hypsochromic shift in the complexes. This is suggested to be due to \(\pi\)-electron interaction of the heterocyclic ring with the hydrogen bonded coordinated water molecules (Fig.6).

Similarly, the characteristic group frequencies due to the thiadiazole ring observed in the i.r. spectra of the schiff bases at ~1395, 1070 and 680 cm\(^{-1}\) are assigned to \(\gamma\) N=C=S, \(\gamma\) N=N and \(\gamma\) C=S=C vibrations respectively. These bands remain unperturbed in the i.r. spectra of the complexes of the type \(\overset{\gamma}{\text{M(SB)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}}}\) indicating that none of the atoms in the thiadiazole ring is coordinated to the metal ion in the respective complexes. But in the i.r. spectra of the chelates with ligands H\textsubscript{2}SMTD and H\textsubscript{2}AMTD, the
involvement of the ring sulphur and thiol sulphur is clearly reflected in the bathochromic shift of \( \nu (C-S-C) \) modes of vibrations and the absence of \( \nu (S-H) \) vibrations.

Additional bands are observed in the spectra of the complexes around 525, 480 and 430 cm\(^{-1}\) which may be assigned to \( \nu M \rightarrow N, \nu M \rightarrow O \) and \( \nu M \rightarrow S \) modes respectively.

**Electronic spectra and magnetic properties of metal complexes:**

**Copper(II) complexes:**

All the copper(II) complexes exhibit normal magnetic moments (1.8-2.1 B.M.) and the electronic spectra show broad bands in the region 16000-13000 cm\(^{-1}\) and intense bands at \( \sim 28000 \) cm\(^{-1}\). The former bands can be assigned to \( 2E_g \rightarrow 2T_{2g} \) transition and the later ones to charge transfer. The broad unsymmetrical hump observed in the visible region of the electronic spectra coupled with the slightly higher value of the magnetic moments than the spin only value (1.7 B.M.) indicates orbital contribution and distortion of octahedral structure.

**Cobalt(II) complexes:**

The cobalt(II) complexes isolated in the present study except the one with the Schiff base 2-salicylidene-imino-5-p-anisyl-1,3,4-oxadiazole exhibit magnetic moments
in the range 4.8-5.5 B.M. The electronic spectra of these complexes display mostly two bands at ~ 14800 and 18000 cm\(^{-1}\) which can be attributed to \(^4T_{1g} \rightarrow ^4A_{2g}(\gamma_2)\) and \(^4T_{1g} \rightarrow ^4T_{1g}(P)(\gamma_3)\) transitions respectively in an octahedral ligand arrangement around the metal ion. In some cases charge transfer bands are also observed at ~ 27000 cm\(^{-1}\). The Co(II) complex with 2-salicylidene-imino-5-p-anisyl-1,3,4-oxadiazole exhibit, at room temperature, magnetic moment value of 4.4 B.M., which is very close to be expected of spin free Co(II) complexes suggesting tetrahedral geometry. Electronic spectrum of this complex shows three bands at ~ 8000, 16000 and 28000 cm\(^{-1}\). The former two bands may be due to \(^4A_{2g} \rightarrow ^4T_{1g}(F)(\gamma_2)\) and \(^4A_{2g} \rightarrow ^4T_{1g}(P)(\gamma_3)\) transitions respectively under an approximately tetrahedral ligand field and the last one may be due to \(L \rightarrow M\) charge transfer.

**Nickel(II) complexes:**

The visible absorption spectrum of the nickel(II) complex with the schiff base 2-salicylidene-imino-5-p-anisyl-1,3,4-oxadiazole shows ligand field bands around 12000 and 17000 cm\(^{-1}\) which are attributed to the transitions \(^3T_{1g}(F) \rightarrow ^3A_{2g}(\gamma_2)\) and \(^3T_{1g}(F) \rightarrow ^3T_{1g}(P)(\gamma_3)\) respectively under a tetrahedral environment around Ni(II) ion. The magnetic moment value of this complex is 4.4 B.M. which supports the above observation. However the schiff base
complexes of Ni(II) ion with the other oxadiazole and thiazole derivatives display ligand field bands in the regions 11000-14000 and 16000-20000 cm⁻¹, which are assigned to $^3_A_2g(F) \rightarrow ^3T_2g(\gamma_1)$ and $^3A_2g(F) \rightarrow ^3T_1g(F)(\gamma_2)$ transitions respectively in an octahedral geometry. In many cases a charge transfer band is also observed $\sim 26000$ cm⁻¹. These Ni(II) complexes show magnetic moment values in the range 2.8-3.2 B.M., expected for octahedral complexes.

The crystal field parameters such as $10Dq$, $B$, $C$, $F_2$ and $F_4$ for all the Co(II) and Ni(II) complexes are calculated from the electronic transition bands which are in close agreement with the values obtained for known Co(II) and Ni(II) complexes. The nephelauxetic ratio ($\beta$) for these complexes are calculated to be less than unity indicating partial covalency in the metal ligand bonds.

Manganese(II) complexes:

It has not been possible to isolate the Mn(II) complexes in case of all the schiff bases. The magnetic moments of various complexes of Mn(II) prepared in this series lie in the range 5-6 B.M., which are in accordance with the values expected for spin only values for 5 unpaired electrons in the octahedral Mn(II) complex involving $sp^3d^2$ hybridisation. The electronic spectra show a series of
bands in the region 600—350 nm. The electronic transitions and the possible assignments are recorded in section-E of Chapter-III. The bands around 26000-25000 cm⁻¹ are assigned to \( ^6A_{1g}(S) \rightarrow ^4E_g(G)+^4A_{1g}(G) \) transition in view of the fact that \( ^4E_g \) and \( ^4A_{1g} \) states are almost degenerate.

**Thermal Analysis:**

The complexes were subjected to thermal analysis in the temperature range 30–650°C at a heating rate of 10°C min⁻¹ with Netzsch simultaneous thermo-analyser-429 by taking 100 mg. of the sample in each case. The thermograms of the complexes of the type \( \text{L}^{-}\text{M(SBI)₂(H₂O)₂} \) show a general pattern with respect to their weight loss. In all the cases no weight loss is observed below 150°C indicating the absence of lattice water or water of crystallisation. However sharp endothermic peaks are observed \( \sim 200-220°C \) in the DTA curves associated with sudden weight loss in the T.G.A. curves corresponding to two molecules of water suggesting the presence of coordinated water. Thereafter a continuous weight loss is observed upto 650-700°C associated with exothermic peaks at the corresponding temperatures indicating the decomposition of the organic ligands and oxidation of the products. Finally a stable arrest is observed and the weight of the residue corresponds to the metal oxides, which is in agreement with the suggested stoichiometry. In case of some Co(II) and Mn(II) complexes there is slight increase in the
mass $\sim 800^\circ C$ which may be attributed to the conversion of oxides from lower to higher oxidation states of metal. It is generally observed that the Cu(II) complexes start losing mass $\sim 200^\circ C$, whereas Zn(II) complexes possess high thermal stability. The complexes with the Schiff bases $H_2SMTD$ and $H_2AMTD$ have comparatively high thermal stability. This behaviour is probably due to the absence of steric strain in the out of plane coordinated polymeric complexes.

The mass loss for the complexes of the type $\left[\text{M(SB)}\right]_2$ starts $\sim 240^\circ C$ and continues slowly and regularly till a horizontal plateau corresponding to the weight of the metal oxide is obtained in the T.G.A. curves. The general order of thermostability is found to be Zn $>$ Cd $>$ Pb $>$ Hg $>$ Ni $>$ Mn $>$ Co $>$ Cu.

Considering the coordination sites of the ligands from the i.r., $^1H$nmr and electronic spectra and the stoichiometry from the analytical and thermal data the following general structures have been proposed (fig. 7-8).