Coordination compounds have received great attention in the field of inorganic chemistry during recent years. The renaissance is due to the important roles they play in a large number of widely differing processes of technological and biological importance. A central metal ion bonded to other atoms, ions or molecules constitutes a coordination compound. The surrounding atoms, molecules or ions are called ligands. The metal ion is usually an electron pair acceptor and ligands are electron pair donors. The nature of bonding in coordination compounds can be predominantly electrostatic or predominantly covalent or intermediate between the two extremes depending on the mode of sharing of electron pairs between the metal ion and the ligands. The number of electron pairs involved in bonding is called the coordination number which is known to have the values from 1 to 12 but 4 and 6 mostly predominate. Ligands are called monodentate, bidentate or polydentate depending on numbers of coordination sites satisfied by them about the metal ion. Ligands, capable of forming a ring structure after coordinating with the metal ion, are called chelating agents and the resulting agglomeration is termed a metal chelate. The phenomenon is called chelation.
The tendency for coordination with ligands has been observed with all metal ions but transition metal ions have proved to be most versatile in this respect. On the other hand, the tendency to donate electron pairs is limited to the more electronegative elements such as carbon, nitrogen, phosphorous, arsenic, oxygen, sulphur, flourine, chlorine, bromine and iodine of groups IV, V, VI and VII of the periodic system. The ability of a ligand to coordinate depends mainly on the nature of atoms or groups present in it i.e. their electronegativity and stereochemistry.

The historical development of the chemistry of coordination compounds dates back from the end of the eighteenth century. In 1978, Tassaert was the first to isolate orange crystals of CoCl$_3$·6NH$_3$ by mixing aqueous solutions of CoCl$_2$·6H$_2$O and ammonia and allowing them to stand in air. Several compounds of this kind were reported in the following century. However, theories prevailing in those days were inadequate to explain the structure of the complexes.

Towards the end of the nineteenth century, research in the field of coordination chemistry was dominated by the Danish Chemist S.M. Jørgensen and Swiss Alfred Werner as well as many others. These two distinguished chemists prepared varieties of amine complexes of
cobalt(III), platinum(II), platinum(IV), chromium(III) and palladium(II) and studied their physical and chemical properties such as transformation, occurrence of isomers, ionisation etc. It was Werner who had the genius to correlate the experimental facts on many different systems. He proposed his coordination theory in 1891 introducing the concept of primary and secondary valences and suggested that the primary valences were those which satisfied the charge of the metal ion and the secondary valences were those used in attaching coordinating groups. According to the theory, the hexammine cobaltic chloride is formulated as: $\text{Co(NH}_3\text{)}_6\text{Cl}_3$ where chloride ions satisfy the primary valences and ammonia molecules satisfy the secondary valences.

The nature of bonding in coordination compounds has been undeniably a challenging and exciting problem since the early days of coordination chemistry. Amongst the earlier workers, G.N.Lewis was the first who laid down the foundation of electronic theory of valence recognizing that stable shells of electrons could be created by the transfer of electrons from one atom to another forming ions or by sharing of two electrons between two atoms forming a covalent bond. There has been phenomenological development on these concepts notably by I.Langmuir, N. V. Sidgwick and L. Pauling which led to the emergence of
FIG. 1.11 THE SPLITTING OF THE 3d LEVELS WHEN A TRANSITION METAL ION IS SURROUNDED OCTAHEDRALLY BY SIX LIGANDS

FIG. 1.12 SPLITTING OF d-ORBITALS IN DIFFERENT CRYSTAL FIELDS
valence bond theory. The theory has been successful in explaining the nature of bonding in most of the compounds and predicting their structures, but was unable to explain the bonding in electron deficient compounds like boron hydrides and certain other facts such as absorption spectra. In order to remove the inadequacy of the valence bond theory, the crystal field theory was revived from the early works of Bethe and Van Vleck.

The crystal field theory treats the interaction between the metal ion and the ligands as a purely electrostatic problem in which the ligand atoms are represented as point charges. At the opposite extremes, the molecular orbital theory describes the metal ligand interaction in terms of molecular orbitals formed by the overlap of ligand and metal orbitals.

The crystal field theory considers the effect of approach of ligands on the d-orbitals of a transition metal ion. The orientation of the five d-orbitals are depicted in Fig.1.1.1 and the approach of the ligands in an octahedral complex by L's. The electrons of the d-orbitals are repelled when ligands approach along the cartesian axes, but the electrostatic repulsion is greater for $d_{x^2}$ and $d_{y^2}$ as compared to $d_{xy}$, $d_{yz}$ and $d_{xz}$ since the lobes of the two former orbitals lie along the direction of approaching ligands. The result is that the energy of
$d_{x^2-y^2}$ and $d_{z^2}$ orbitals is raised relative to the energy of $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals i.e. the degeneracy of the five $d$-orbitals is destroyed. In an octahedral field the $d$-levels are split into an upper group of two ($e_g$) and a lower group of three ($t_{2g}$) orbitals (fig.1.1.2). The energy difference between the two levels is represented by the symbol $\Delta E$ or $10D_q$. It is apparent that the magnitude of splitting depends upon the strength of the crystal field. The splitting of $d$-levels in other symmetries can be considered in a similar way and the relative energy for $T_d$ and $D_{4h}$ fields are also shown in Fig.1.1.2. This theory has been successful in explaining the absorption spectra of the complexes $^5$-$^11$. However, it takes no account of the partly covalent nature of the metal-ligand bonds and therefore whatever effects and phenomenon stem directly from covalence, such as electron spin resonance spectra of $\text{IrCl}_6^-$, are entirely inexplicable by simple crystal field theory.

The molecular orbital theory developed by Hund and Mulliken $^{12}$ for covalent molecules has been extended to construct molecular orbitals of coordination complexes. These orbitals are of the form $^{13}$.

$$\Psi(M.O.) = \zeta(\gamma) + \sum_{i} a_i \psi_i$$
Where $\psi(r)$ represents the wave function of the central metal atom transforming in the molecular point group as the irreducible representation and $\sum_i a_i \chi_i$ is a linear combination of the wave functions of the ligand transforming as the same irreducible representation. The theory has successfully accounted for several features of the complexes.

The most versatile and perhaps the most nearly correct is the ligand field theory which has been developed from an amalgamation of the crystal field theory and molecular orbital theory. Ligand field theory takes into account the extent of metal-ligand interaction by the parameter $D_q$, which can be experimentally determined. The parameter $D_q$ can be theoretically evaluated by taking all metal-ligand interactions into consideration.

The splitting of the metal ion terms of all atomic configurations by the ligand field is dealt within a more sophisticated way by ligand field theory. The most general and useful theoretical treatment for the interpretation of the visible spectra of chelates is proposed by Tanabe and Sugano. The theory depends upon three parameters for interpretation, namely $D_q$, the ligand field parameter which has the same significance as in the crystal field theory and Racah electron repulsion parameters $B$ and $C$. The Racah parameters for free metal ions are determined from atomic
spectroscopy of the ion. From the theoretical viewpoint, these parameters are the numerical values of the coulombic repulsion and exchange integrals between electrons of various states and measure the natural separation of the terms of the metal ion.

Studies on metal complexes of ligands containing sulphur as donor atom is of considerable interest to inorganic chemists in recent years. It is well known that metal complexes of sulphur donor ligands are of special importance due to wide range of their applicability and activity against viruses, protozoa, smallpox, cancer, tuberculosis and certain kinds of tumour.
A  

**SECTION - B**

**A BRIEF OUTLINE ON THE SCHIFF BASE METAL COMPLEXES**

A schiff base is the condensation product of an active carbonyl compound, preferably an aldehyde or a ketone, with a primary amine and contains the azomethine linkage (–C=N–). It forms stable complexes with metal ions due to the formation of five or six membered chelate rings provided the amine and/or the carbonyl compounds possess a second functional group containing a donor atom adjacent to the site of the condensation.

Metal complexes of schiff bases have played a pivotal role in the field of coordination chemistry. A large number of schiff base complexes containing transition and non-transition metal ions and multifarious ligand systems have been isolated. Because of the vastness of the accumulated data in this area, it is not possible to give a complete review here. However in order to provide a background to the present work, a brief outline on the schiff base complexes are described.

In the year 1840 Ettling\(^{15}\) isolated bis(salicylaldimine) Cu(II) (Fig.1.2.1, \(R=H\)) by refluxing a mixture of cupric acetate and salicylaldehyde in aqueous ammonia.

Following his work Schiff\(^{16}\) (1869) prepared the corresponding derivatives (\(R = \text{Aryl}\)) having 1:2
metal-ligand stoichiometry. Since 1931 hectic activities have started and a number of structurally important schiff base complexes (Fig. 1.2 - 1.2.4) with a varieties of aldehydes and amines (Fig. 1.2.5-1.2.8) have been reported.

Metal complexes of schiff bases derived from salicylaldehyde, have been thoroughly studied and well understood. However a few interesting schiff base metal complexes having donor sites of the type ON, ONG, NNO and ONNO etc. are discussed here.

**BIDENTATE LIGANDS**

A series of dimeric copper(II) complexes of general formulation \( \text{Cu}(\text{BSB})\text{Cl}_2 \) (BSB = bidentate schiff base) have been reported. The schiff bases are a number of N-alkyl and N-aryl salicylaldiminates. The binuclear copper(II) complexes are generally prepared by reacting an ethanolic solution of CuCl\(_2\) with bis(N-R-salicylaldimino) copper(II) in chloroform solution. (R=normal, secondary or tertiary alkyl or phenyl group). All the binuclear complexes exhibit pair-wise antiferromagnetism with singlet-triplet separation > 300 cm\(^{-1}\). An interesting feature of this series of copper(II) complexes is that the magnetic behaviour remains invariant from compound to compound unlike the corresponding copper halide adducts of tetradentate salicylaldimine copper(II)
complexes. The ligand field absorption spectra are in keeping with the trans structure. In copper complexes with bidentate salicylaldimines, the ligand field absorption bands in the region 18,000-8,000 cm\(^{-1}\) move to lower energy as the environment about the copper atom tends from planar to tetrahedral. Non-existence of any new band in the above mentioned region is suggestive of square planar environment about each copper atom as shown in Fig. 1. Due to trans-structure, the two copper atoms in each dimer adopt a configuration near to planar with only a small degree of steric distortion towards tetrahedral as the R-group on the salicylaldimine nitrogen becomes more bulky. This has been confirmed by Sinn and Robinson. The corresponding bromo and nitrate compounds, \(\text{Cu(BSB)}X_2\) \((X = \text{Br, NO}_3)\) have similar properties. Substitution at the 5-position of the phenyl ring of the Schiff base, has little influence on the magnetic properties than substitution at the nitrogen atom. Probably, the geometry of Cu-Cu ring is very less sensitive to changes on the phenyl ring. The 1:1 alkylsalicylaldiminates, \(\text{Cu(R-Sal)}Cl_2\) are less antiferromagnetic than the aminoalcohol complexes. The large difference between 2J for the methyl (-295 cm\(^{-1}\)) and ethyl (-460 cm\(^{-1}\)) is attributable to changes in stereochemistry at the copper atom. In both complexes the Cu-Cu bridge is exactly planar, but the geometry at copper deviates from planerily more severely in the methyl complex than in the ethyl complex.
Another class of dimeric copper(II) Schiff base complexes have the general formula \( \text{Cu(R-Sal)}_2 \). The methyl complex has an oxo-bridged structure which is very much similar to that of \( \text{Cu(PyO)}_2 (\text{NO}_3)_2 \). \( \text{Cu(CH}_3\text{-Sal)}_2 \) has an average out-of-plane Cu-O distance of 2.445 Å and an average bridging Cu-O-Cu angle of 100.4°; the corresponding values in \( \text{Cu(PyO)}_2 (\text{NO}_3)_2 \) are 2.44 Å and 102.9°. It is ferromagnetic with \( 2J = +10 \text{ cm}^{-1} \) while \( \text{Cu(CH}_3\text{-Sal)}_2 \) has a value \( 2J = +8 \text{ cm}^{-1} \). This ferromagnetic interaction is entirely consistent with the concept that magnetic behaviour is determined largely by structural characteristics, since these two complexes with similar bridging geometry give rise to similar magnetic behaviour.

The magnetic susceptibility data for the binuclear copper(II) propionates with N-aryl salicylaldimines fit to the Bleany-Bowers equations. The degree of anti-ferromagnetism in the complex \( \text{Cu(Sal-N-Ph)}_2 \) propionate \( 2J = -105 \text{ cm}^{-1} \) is much less compared to the corresponding chloro \( \text{Cu(Sal-N-Ph)}_2 \) \( 2J = -300 \text{ cm}^{-1} \). The reflectance spectral pattern of the propionate which indicate a square planar environment around copper(II) ion is different from the chloride complex to which a pseudo-tetrahedral configuration is assigned. The effective magnetic moment of the propionate
and chloro complexes, at room temperature, are 1.73 and 1.35 B.M. respectively. This difference in magnetic interaction between the chloride and the propionate complexes is attributable to change in structure from carboxylate-bridged to phenolic-oxygen bridged entities.

Copper(II) complexes of the Schiff bases derived from condensation of aryl amine (aniline, o-tolu-ide, m-toluidine and p-toluidine) with 2-hydroxy-5-methyl-acetophenones have been prepared by refluxing an alcoholic solution of copper acetate and the Schiff base for 2-3 hrs. The compounds are dark brown with \( \mu_{\text{eff}} = 1.8-1.9 \) B.M. at room temperature. The electronic spectra are characterised by a single, relatively broad band with maxima at 15,000 cm\(^{-1}\) and a pronounced absorption band near 22,000 cm\(^{-1}\). Tetrahedral copper(II) complexes are expected to give a single broad band in the near i.r. and no band in the region 10,000-20,000 cm\(^{-1}\). Therefore, the present complexes are square-planar. Bands around 15,000 cm\(^{-1}\) are most distinct and most of these are well known d-d bands of copper(II). The phenolic C-O stretching vibration in Schiff bases occurs as a strong band around 1280 cm\(^{-1}\). The hypsochromic shift of this band to 1328-1337 cm\(^{-1}\) on chelation indicates the ortho-OH group to be involved in coordination. The i.r. spectra reveal a single band in the region 485-530 cm\(^{-1}\) due to
vibration and suggest the trans structure for the complex \( ^{48} \) (Fig. 1, 2, 10).

A series of complexes \( \text{CuLX} (\text{HL} = \text{salicylidene}- \text{aminoguanidine, O-hydroxyacetophenoneaminoguanidine, } \ X = \text{Cl, Br, I, NO}_3) \) have been prepared and characterised by magnetic moments, conductance data and i.r. spectra \( ^{49} \). The results indicate that the compounds are square planar and the halogen is probably substituted by water molecule explaining the 1:1 electrolytic behaviour.

There has been much less work on nickel(II) complexes relative to copper(II) systems, but N-alkylsalicylaldimine complexes of nickel(II) are most interesting as far as their magnetic behaviour is concerned both in polar and non-polar solvents. \( \text{Ni(HO-Sal)}^2 \) and \( \text{Ni(MA-Sal)}^2 \) are both diamagnetic solids and become partially paramagnetic in chloroform \( (\mu = 1.1 - 2.2 \text{ B.M./Ni}) \) but fully paramagnetic in pyridine solution \( (\mu = 3.1 \text{ B.M.}) \) \( ^{50} \). The paramagnetism in pyridine is explained by the following equilibrium

\[
\text{Ni(R-Sal)}^2 + 2\text{py} \rightleftharpoons [\text{Ni(R-Sal)}^2(\text{py})_2]^7
\]

which almost shifts to the right at room temperature.

The paramagnetic behaviour in non-coordinating solvents is due to weak axial perturbation on the planar
complexes which causes the triplet state to drop within thermal range. The anomalous paramagnetic behaviour of Ni(Me-Sal)$_2$ is due to an equilibrium between the planar monomeric form and associated species containing one or more paramagnetic nickel(II) ions. The extent of aggregation in Ni(Me-Sal)$_2$ is unknown. But in order to stabilise a triplet ground state, the nickel(II) ion at least, have five-coordination. On this ground a dimeric structure has been proposed through intermolecular Ni...O interactions.

Conversion of Ni(Me-Sal)$_2$ from diamagnetic to paramagnetic species has been possible in solid phase. The diamagnetic green solid on heating above 180°C is transformed to a light green substance with $\mu_{\text{eff}}=3.45$ B.M. and insoluble in non-polar solvents. Heating of the green compound in biphenyl solution at 150-200°C forms an insoluble buff-coloured product having the same composition as the green form and obeying Curie-Weiss law with $\mu=3.1$ B.M. and $\Theta=20^\circ$.

The complexes $\text{Ni}(R-$Sal)$_2$ ($R = \text{C}_2\text{H}_5$, n-Pr, n-Bu, n-pentyl, benzyl and allyl) have been found to be fully paramagnetic (3.1 B.M.) in pyridine solution. Amongst all, the complex Ni(Me-Sal)$_2$ is much more paramagnetic and is believed to be associated to a greater extent. The
most accepted dimeric structure of Ni(CH$_3$-Sal)$_2$ is shown in Fig.1.2.11.

Chelates containing three identical unsymmetrical bidantate ligands can exist in two geometrically isomeric forms, cis and trans as shown in (Fig.1.2.12).

This is an interesting branch of study in the field of schiff base metal complexes. A similar complex tris-(N-salicvlaldimine) Co(III) was suggested to have trans-stereochemistry from dipole moment studies which has been confirmed by nuclear resonance method.

Metal(II) complexes with the schiff base (Fig.1.2.13) obtained by the condensation of N-methyl-S-alkyl dithiocarbazate with 2-hydroxy-1-naphthaldehyde have been reported by Ali and coworkers.

The Cu(II) and Ni(II) complexes, MLX(M=Cu, Ni, L = schiff base, X = NCS, NO$_3$) are reported to be square planar and the Fe(II) complex, FeLCl$_2$ is sulphur bridged.

Mixed ketoimine schiff base complexes (Fig.1.2.14), [MLL']$^-$, (where M = Cu(II) and Ni(II), L = N-1-(2-hydroxy phenyl) ethylene diamine or N-1-(2-hydroxy-p-tolyl) ethylene diamine and L' = N-1-(2-hydroxy-m-tolyl) ethylene diamine or N-1-(6-hydroxy-m-tolyl) ethylene diamine) when subjected to amine...
exchange reactions with ethylene diamine and propylene diamine result in converting the bidentate ligand complexes to tetradentate complexes.

Amongst the crystalline Pd(II) and Zn(II) complexes with schiff bases (Fig.1.2,15) derived from methyl substituted amino,pyridines and salicylaldehydes, the Pd(II) complexes are square planar while the Zn(II) complexes are tetrahedral.

Schiff base metal complexes of Cu(II) and Ni(II) containing chromophore MO₂N₂ with o-hydroxy acetophenoximes have been studied by Khanolkar & Khanolkar and a gross square planar symmetry with intermolecular hydrogen bonding between the two ligand molecules coordinated to the metal ion, has been proposed.

A number of inert azo-mustards (N-C-S) have been prepared and their biological activity have also been studied. Some schiff base mustards have also been subjected to clinical trials which suggest that azomethine linkage plays a very important role in biological reactions.

Coordinative interaction of tin(II) chloride with some schiff bases derived from salicylaldehyde or anisylaldehyde and substituted aniline have been reported.
by Srivastava & coworkers. The formation of the molecular complex is unequivocally indicated by the shift of \(\nu(C=\text{N})\) frequency of the schiff base (Fig. 1.2.16) to the higher wave number side.

The shift to higher wave number side of \(\nu(C=\text{N})\) frequency is also reported earlier. The shifting is attributed to the unshared pair of electron of N-atom being attracted to the metal atom breaking the \(n,\pi\) conjugation with the aniline ring and developing partial positive charge on the nitrogen atom. The aniline ring becomes coplanar with the whole molecule, but the positive charge on the nitrogen hinders the usual conjugation of the azomethine group with the aniline moiety. The removal of the azomethine group from conjugation and its electronic structure analogous to \(-\text{CH} = \text{N}^+ -\text{H}\), increases the frequency of its absorption in the i.r. spectra. The complexes are therefore formed by the overlap of lone pair orbital on the N-atom of the ligand with the empty sp\(^3\) hybridised orbital on the tin, where the schiff base acts as a neutral monodentate ligand, coordinating only through the azomethine nitrogen.

Electronic spectra and acidity constants of schiff base (Fig. 1.2.17) derived from 2-amino-5-phenyl-1,3,4-thiadiazole and various aromatic aldehydes have been studied.
The band around 265-305 nm is assigned to the excitation of the $\pi$-electron of exocyclic and cyclic C=N and the band ~297 nm is suggested to be influenced by the charge transfer interaction occurring in the solute molecule. It is worthy to mention that 1,3,4-thiadiazole ring has been noted for its electron withdrawing character.

Physicochemical study of rearrangement of schiff bases on complex formation have been recently reported. Vibrational spectra of Ni(II) complex with 1,2, diphenyl ethane-dione dihydrazone indicate a trans-structure for the ligand which undergoes transformation to a cis-configuration (Fig.1.2.18) in the metal complexes on the formation of five membered chelate ring.

The trans-structure is belived to be stabilised by greater delocalisation of the $\pi$-electron, whereas in the chelate ring, the symmetry is lowered in the cis-form resulting in an increase in the charge density along C–N bond vectors and increase in the $\tilde{\nu}$ C–N frequency. Similar structural rearrangement of schiff bases on complex formation is also reported by other workers.

Coordination complexes of Cu(II) and Ni(II) with schiff bases, obtained from benzaldehyde, 2-furan
carboxaldehyde and aromatic amines, have been assigned a planar and distorted octahedral configuration (fig.1.2.19).

A large number of distorted octahedral complexes of Cu(II) are also isolated with Schiff bases such as bis(vanilline) ethylene diamine, bis(vanilline) propylene diamine, bis(vanilline) benzidine, bis(vanilline) o-phenylene diamine, vanilline-naphthalamine and bis(vanilline) thiosemicarbazone.

Polymeric octahedral Schiff base complexes of the type \( [M, L_2H_2O_n] \) (where \( M = \text{Mn}^{II}, \text{Co}^{II}, \text{Ni}^{II}, \text{Cu}^{II}, \text{Zn}^{II}, \text{Cd}^{II} \)) are also known and their structures have been proposed based on the elemental, i.r., UV, magnetic moment and thermal studies. Synthesis and characterisation of Fe(III), Co(II), Ni(II) and Cu(II) complexes of 5-phenylazo salicylideneaniline (fig.1.2.20) have also been reported and they are either dimeric or linear polymeric in structure.

Apart from simple aliphatic or aromatic amines, amino acids have also been taken for the preparation of Schiff bases which are in turn utilised for the preparation of Schiff base metal complexes. DL-2-amino butyric acid, L-Valine, -alamine, 3-amino-butyric acid, 4-amino
acids. Co(II) complexes of the schiff bases derived from salicylaldehyde and these amino acids are reported to be octahedral.

Keeping in view, the increased drug activities on complexation, studies on the coordination behaviour of schiff bases derived from some sulpha drugs and substituted 2-hydroxy acetophenones have been taken up by Keemti Lal and coworkers. Schiff bases (Fig. 1.2.21) derived from sulpha furazole, sulpha methoxy pyridazine and sulpha phenazole and 2-hydroxy-5-methyl acetophenone have been synthesized. The study suggests planar structure only for Cu(II) and tetrahedral structures for Mn(II), Fe(II), Co(II) and Ni(II) complexes.

Encouraged by the increased biological activity of schiff bases, some new schiff bases derived from vanilline as possible anticonvulsant have been synthesized. They include anilino-3-methoxy-4-(4-aryl-1-piperazino acetoxy) benzylidene (Fig. 1.2.22) and anilino-3-methoxy-4-{3-mercapto-4-aryl-1,2,4(H)-trizol-5-yl} methylenesoxy benzylidenes (Fig. 1.2.23).

They were screened for anticonvulsant activity against maximal electro shock seizure and pentylene tetrazole induction seizures in mice at a dose of 80 mg/kg with encouraging results.
Furfurylidene benzoyl hydrazone and 5-nitrofurfurylidene-benzoyl hydrazone (L) (Fig.1.2.24) have been synthesised and have been used for the preparation of transition metal chelates of the type $ML_2$ and $M'L_2 \cdot 2H_2O / M =$ Ni(II), Cu(II), Zn(II); $M =$ Mn(II), Fe(II), Co(II). The Schiff bases coordinate through ON atoms behaving as monobasic bidentate ligands depending on the pH of the medium. The complexes have exhibited significant fungitoxicity against Rhizoctonia solani, the causative organism of sheath blight in rice and groundnut plants. Some of the chelates exhibited more toxicity, when compared to Diathane M-45, a commercial fungicide screened in similar condition. The fungitoxicity of the metal chelates was found to be in the order $Cu > Ni > Fe > Zn > Mn > Co$.

Structural studies of Cu(II) and Ni(II) complexes with physiologically active coumarin derivatives; 8-acetyl-umbelliferone and its oxime, hydrazones and thiosemicarbazones are also known. Physiological activity of the ligands and their metal chelates have been evaluated by kymographic studies. Some new coumarins and Schiff bases have also been prepared as possible antibacterial and antifungal agents.

The Schiff base complexes of Ni(II) and Cu(II)-with N,N'-disalicylidene ethylene diamine (MaES) have been
used as a bidentate ligand (complex ligand) (Fig. 1.2.25) in the synthesis\textsuperscript{93} of novel binuclear alkali metal complexes of the general formula \( ^{~}M_{a}ESM_{b}L_{7} \); \( M_{a}ES \) acting as a bidentate complexing agent coordinating through two phenolic oxygen to alkali metal salts \( M_{b}L \) (\( M_{b}L = Li, Na, K \) salts of 1-nitro-2-naphthol); 8-hydroxy quinoline, anthranilic acid as well as alkali metal salts like KSCN, LiCl, NaBr and NaI. The phenolic C-O link retained a considerable amount of partial double bond character in these binuclear complexes.

A large number of substituted salicylidene anils were prepared to study the effect of the substituents on the strength of intramolecular hydrogen bonding between the phenolic proton and the imine nitrogen\textsuperscript{94}. A wide range of electron withdrawing and donating group to vary the basicity of the imine nitrogen and the hydroxyl acidity were substituted in the salicylidene as well as in the aniline ring of the schiff bases. It was found by nmr study that the strength of the hydrogen bonding between the phenolic proton and the imine nitrogen is very much dependent upon the nature of the substituent present in both the rings. Substituent which decrease the basicity of the phenolic oxygen increase the strength of hydrogen bonding while those which decrease the basicity of the imine nitrogen decrease the strength of hydrogen bonding, and vice-versa. The strength of hydrogen bonding is also
enhanced by the electron donating group at C7 in place of aldehydic proton (Fig. 1.2.26).

Ni(II), Cu(II) and Zn(II) complexes of polymeric schiff bases derived from glyoxal and some organic acid monohydrazides and dihydrazides have been synthesized. Inspite of large number of possible coordinating sites present in the schiff base moiety (Fig. 1.2.27) it was observed that only the hydrazide grouping \(-\text{C(O)}-\text{NH-N}<^7\) in the ligand act as a coordinating unit through the azomethine nitrogen. However, when \(R=\text{CH}\), the ligand acts as a tetradeutate one. The stereochemistry around Ni(II) is octahedral, planar around Cu(II) and tetrahedral around Zn(II).

Studies on the fluoroboron derivatives of azomethines (Fig. 1.2.28) obtained by the condensation of o-hydroxy acetophenone or 2-hydroxy-1-naphthaldehyde and alkyl or aryl amines indicate the monomeric nature of the products in boiling chloroform where in the boron atom is found to be tetra coordinated.

The schiff bases derived from 2-hydrazinobenzoazole and salicylaldehyde have been reported earlier to be fungicidal and insecticidal. Recently the ligand and its metal chelates were screened for antifungal activity against three fungi viz Curvularia sp, Fusarium sp, and
Alternaria sp. by spore germination method at room temperature, at various concentration. It was observed that the metal chelates are more active than the ligands and the order of inhibition rate is Cu(II) > Zn(II) > Fe(III) ~ Ni(II) > Co(II) > Mn(II)²⁹.

Schiff bases are well known to have profound biological activities³⁰⁻³⁶. Their ready synthesis and myriad properties have contributed greatly to the study of many biological systems. Schiff base complexes have been suggested as models for enzymes such as galactose oxidase³⁷. Encouraged by these results, a series of new schiff bases derived from 4-substituted and 4,5-disubstituted-2-amino thiazoles and vanilline was synthesized³⁸. Cyclo addition of these schiff bases (Fig.1.2.29) with thioglycolic acid yielded thiazolidone derivatives. Condensation of the schiff bases with chloroacetyl chloride and subsequent reaction with piperidine and morpholine yielded corresponding acetoxy derivatives. They were screened for fungicidal activity.

From the results of the fungicidal tests it is found that the presence of halogen, α-naphthyl and methoxy group in the compound enhances the fungicidal activity. It is also observed that, the schiff bases are more active than the corresponding thiazolidones and acetoxy derivatives.
Most of the binuclear complexes have been prepared from tridentate Schiff bases containing ONO donor atoms. These ligands are prepared by the condensation of salicylaldehyde or acetylacetonate with o-aminophenols, aminoalcohols, \( \alpha \)-aminoacids, and aminothiols. The structural formulae for a series of tridentate ligands in their Schiff base form are shown in Fig. 1, 2, 30-1, 2, 32. The IR spectrum of \( H_2SAF \) in DMSO shows several bands in the hydroxyl stretching frequency region which become weak and shift to lower energy in the solid state due to extensive intramolecular hydrogen bonding. Presence of strong IR bands near 1600 cm\(^{-1}\) are associated with the C=O stretching frequencies. In the \(^1\)H NMR spectra, the resonance peaks at \( \delta = 13.75 \) disappear on addition of D\(_2\)O. This rationalizes the IR assignment of the presence of intramolecularly-bonded hydroxyl groups. The single proton which does not exchange with D\(_2\)O and gives a singlet at \( \delta = 8.95 \), has been assigned to the azomethine proton. Similarly the ligands \( H_2SAE \) and \( H_2SPA \) involve a \( C=O \) linkage strongly hydrogen-bonded to the hydroxyl hydrogen atoms. The band at 1638 and 1635 cm\(^{-1}\) in the IR spectra of \( H_2SAE \) and \( H_2SPA \), respectively, have a strong \( \tilde{\nu} C=O \) component because they shift to higher frequencies in DMSO where the intramolecular hydrogen bond is weakened. The single proton resonance in the \(^1\)H NMR spectra of these ligands occurring near \( 8.2 \delta \) (CDCl\(_3\)) and \( 8.6 \delta \) (DMSO-d\(_6\)) has been assigned to the azomethine proton. The hydroxyl
proton resonance signals are masked by phenyl proton resonance peaks. This upfield shift of the hydroxyl proton compared to \( H_2SAP \) is attributed to the greater shielding of the hydroxyl proton by the more basic nitrogen atoms of the two compounds derived from aliphatic amines.

The interaction of the schiff bases, derived from 5-substituted salicylaldehyde and substituted and unsubstituted aminophenol of the type (Fig.1.2.33) with transition metals have been investigated \(^{110-114}\). The copper complexes have subnormal magnetic moments due to dimerisation in the solid state and may exist in the following three isomeric forms (Fig.1.2.34).

Isomer I has the bridging oxygens from the aminophenol moieties. In isomer II, one bridging oxygen comes from the aminophenol and the other from the salicylaldehyde moiety. The third isomer could have both bridging oxygens from salicylaldehydes \(^{113}\). For the compounds with \( R'' = \text{NO}_2 \) the isomer I is most probable and isomers II and III are ruled out on the grounds of steric interactions \(^{113}\). The electronic spectra of these complexes are very similar and show a multicomponent band system in the range 28500-20000 cm\(^{-1}\) with d-d transition located at 22200 cm\(^{-1}\). The binuclear complexes are convertible to the mononuclear species by pyridine. The
magnetic susceptibility of these complexes have been measured in the range 1.4 to 300K and all show characteristic of magnetically isolated exchange-coupled antiferromagnetic pairs. It has been observed that magnetic properties are markedly influenced by the nature and position of the substituent on the chelate ring. Electron-withdrawing groups attached to salicylaldehyde moiety increase the value of J(exchange integral), but when introduced into the o-aminophenol moiety it causes a decrease in exchange interaction. The following order for $|J|$ for $(R, R')$ has been established$^{114}$.

$$J(H, Cl), J(H, Br) > J(NO_2, NO_2) > J(H, H) > J(H, CH_3) > J(NO_2, H) > J(Cl, H), J(Cl, Cl).$$

This spin-coupling has been explained in terms of Anderson's theory of superexchange.

The synthesis and properties of binuclear copper(II) complexes derived from salicylaldehyde and aminoalcohol have been described$^{115-118}$. Molecular weight determination of the complex $^{2}^{2}Cu(SalN(CH_2)_3O)_2$ in chloroform are in accordance with a binuclear structure. For these complexes, two dimeric configurations are possible viz. (i) with bridging alcoholic oxygen atoms and (ii) with bridging phenolic oxygen atoms. The formation of phenolic bridge between two metal atoms shift phenolic C=O stretching frequency$^{119}$ from $\sim$1540 cm$^{-1}$ to $\sim$1560 cm$^{-1}$ The shift is
not found in these complexes indicating the bridging occurring preferentially through alcoholic oxygen atom. Comparative magnetic studies of the dimeric copper(II) complexes indicate higher magnetic moments for the complexes with bridging phenolic oxygens than those with bridging alcoholic oxygen atoms. The observed magnetic moments of about 0.5 B.M. per copper(II) ion for these complexes are much smaller than those observed in the complexes containing phenolic oxygen bridging. This indicates that the dimeric structure with alcoholic oxygen bridging is more probable.

When the hydroxypropyl group is replaced by the hydroxyethyl or substituted hydroxyethyl, magnetic moments of the complexes at room temperature lie in the range 1.77 - 2.09 B.M. All these complexes possess a five membered ring system. The variation of susceptibility with temperature (80-300K) in linear and on extrapolation, it intercepts the temperature axis at a positive value indicating the presence of ferromagnetic interactions. Molecular weight determination of the complex proves it to be tetrameric. The four copper ions are bridged tetrahedrally. Their normal magnetic moments have been attributed to a negligible \( \pi \)-type super exchange interaction among the four copper(II) ions via the bridging oxygen atoms. The ferromagnetic interaction takes place by a \( \sigma \)-type super exchange,
when three sp$^3$ orbitals of a bridged atom form $\sigma$-bonds with the $d_{x^2-y^2}$ orbitals of three copper(II) ions.

The crystal and molecular structures of $^{\text{5NO}_2}\text{SalN(CH}_2\text{)}_3\text{O}^-\text{Cu}^2-\text{SalN(CH}_2\text{)}_3\text{O}^-\text{Cu}^2$ and $^{\text{5Me}}\text{SalN(CH}_2\text{)}_3\text{O}^-\text{Cu}^2-\text{SalN(CH}_2\text{)}_3\text{O}^-\text{Cu}^2$ have been determined. The former contains dimeric molecules with an intramolecular Cu--Cu distance of 3.0 Å. The intermolecular Cu--Cu separations of 3.6 Å are too long for bonding interaction and the complex is ruled out to be polymeric. The second complex contains well separated dimers. The magnetic moments for these two complexes are 0.3 and 0.26 B.M. respectively and are independent of temperature. Strong antiferromagnetic interaction leads to the singlet-triplet separation of the order of 1000 cm$^{-1}$.

Complexes of the type $\text{Cu}_2^{\text{5RSalN}}\text{RCH}_2\text{OH}_7\text{X}$
($R = -\text{CH}_2\text{-CH}_2\text{-}, -\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-}, -\text{CH}_2\text{-CH(CH}_3\text{)-}, -\text{C(CH}_3\text{)}_2\text{-CH}_2\text{-};$
$X=\text{Cl, NO}_3\text{-, ClO}_4\text{-}$) have been prepared and characterised. Their magnetic properties show significant anion-dependence. Except for $\text{Cu}_2^{\text{5SalN(CH}_2\text{)}_2\text{O}^-\text{OH}_7\text{Cl}}$ and $\text{Cu}_2^{\text{5SalN(CH}_2\text{)}_3\text{O}^-\text{OH}_7\text{Cl}}$, which are antiferromagnetic with phenolic oxygen bridges the temperature range 76–290K. The electronic spectra of the complexes suggest a planar rather than a tetrahedral environment around copper(II) ion except in $\text{Cu}_2^{\text{5SalN(CH}_2\text{)}_3\text{O}^-\text{OH}_7\text{Cl}}$ which shows penta-coordination with trigonal bipyramidal configuration. The complexes are
found to contain dimeric units with phenolic oxygen atoms bridging the two copper(II) ions. The long copper-copper distance (3.29 Å) and low magnetic moment (1.01 B.M. at 300K) rules out the possibility of direct metal-metal interaction for the demagnetisation. The four membered Cu-O ring is planar but unsymmetrical with a short Cu-O distance (1.78 Å) to the oxygen of the ligand chelated to the copper and a long Cu-O distance (2.22 Å) to the oxygen of the other ligand. The geometry around copper is trigonal bipyramidal with the nitrogen end oxygen in the axial positions.

When the complex $\text{Cu}^{2+}\{\text{SalN(CH}_2\text{)}_3\text{O}\}_2$ is treated with HCl in methanol, it transforms to a deep brown crystals having identical physicochemical properties as that of the complex, $\text{Cu}^{2+}\{\text{SalN(CH}_2\text{)}_3\text{OH}\} \times 7_2$.

$\text{Cu}^{2+}\{\text{SalN(CH}_2\text{)}_3\text{O}\}_2 + 2\text{HCl} \rightarrow \text{Cu}^{2+}\{\text{SalN(CH}_2\text{)}_3\text{OH}\} \times 7_2$

The reverse conversion was effected by boiling the deep brown compound in pyridine to get the dark red crystals of $\text{Cu}^{2+}\{\text{SalN(CH}_2\text{)}_3\text{O}\}_2$. The interconversion reaction has not been possible with the complex $\text{Cu}^{2+}\{\text{SalN(CH}_2\text{)}_2\text{O}\}_2$.

Infrared absorption at 790-813, 1005-1022, 1280-1286 and 1488-1495 cm$^{-1}$ in the nitrato complexes suggest that the nitrato is bonded to the metal atom. The electronic spectra of nitrato complexes are characteristic of four coordination with slight distortion from
\[ L = H_2O, \ C_2H_5OH \]

Fig. 1.2.35

\[ \text{Fig. 1.2.36} \]
planarity, indicating the monodentate coordination of the nitrate group (-ONO₂). The perchlorate complexes were obtained as solvate adducts; the magnetic moment (1.18 B.M.) are unusually low and temperature dependent conforming to a binuclear structure as shown in Figure 1,2,35. IR and electronic spectra support this square-pyramidal configuration around each copper atom in the dimer.

Both N-hydroxyethylsalicylaldimine (H₂Lₐ) and N-hydroxypropylsalicylaldimines (H₂Lₐ) are capable of forming mono-, bi- and trinuclear nickel(II) complexes. Mononuclear complexes [NiLX]₇ (L = Lₐ, Lₐ; X = ClO₄, Cl, Br, NO₃) are formed in ethanolic solution by mixing the ligands with NiX₂. But by addition of strong bases, the binuclear complexes [NiLS]₇₂ (S = 2-methyloxyethanol), have been obtained. The trinuclear complexes are prepared only with the ligand Lₐ in acetonitrile. Magnetic data and electronic spectra of the binuclear complexes are consistent with octahedral nickel(II). The IR spectra do not support for phenolic oxygen bridging. As the complexes are prepared in strong basic medium, alkoxy bridging is favoured. Accordingly the binuclear complex has been represented as shown in Fig. 1,2,36. The IR spectra of the trinuclear complexes demonstrate two different modes of coordination of the phenolic oxygen. One of them acts as a bridging oxygen and the other, a terminal one. The electronic spectra and magnetic data
Fig. 1: 2.37
prove the presence of nickel(II) ion in two different octahedral ligand fields in accordance with the structure (Fig. 1.2.37).

Tridentate Schiff bases have been obtained by the reaction of arylhydrazone in absolute ethanol with salicylaldehyde. The ligand (H₂SalR) with copper(II) chloride, forms hydrated complexes of composition Cu(HSalR)(Cl)(H₂O) (R = CH₃, C₆H₅ and p-CH₃OC₆H₄). When R = o-HOC₆H₄ and p-NO₂OC₆H₄, the anhydrous chelates, Cu(HSalR)Cl are formed. A distorted square pyramidal environment around copper(II) ion is suggested for the hydrated complexes whereas the anhydrous chelates possess a square planar arrangement with the chloride ion occupying one coordination site. In both cases the ligand behaves as monobasic tridentate and magnetic moments of the complexes conform to "spin-only" value.

In the IR spectra of these complexes, a strong band appears at 1630 cm⁻¹ while the band due to N-H stretching and νC=O are absent. This band is due to stretching vibration of conjugate C=N=N=C system and is diagnostic of enolisation of hydrazone moiety. The low magnetic moments of Cu(SalR) suggest strong molecular association. Their electronic spectra in nujol show a multicomponent band system over the range 600-730 nm along with a strong CT band at 480 nm. It is consistent with a
square planar geometry. A dimeric structure with bridging hydrazine oxygen has been suggested. In pyridine, these complexes form monopyridine adducts \( \text{Cu(SalR)}(\text{py}) \) (py = pyridine) through rupture of oxygen bridge.

Schiff bases derived from salicylaldehyde and \( \alpha \)-aminoacids are diabasic tridentate with DNO donor sets. They can be prepared as potassium salt, by reacting salicylaldehyde with appropriate amino acids. The IR spectra indicate that the Schiff bases exist in hydroxyaldimine form.

Dropwise addition of nickel acetate to a warm alcoholic solution containing stoichiometric amounts of salicylaldehyde and the amino acid (amino acid, AA=glycine, L-alanine, L-valine, L-leucine, L-methionine, L-phenylalanine) produce quantitatively the binuclear nickel(II) complexes. The complexes contain two molecules of water which is supported by the presence of a strong band at \( \sim 3350 \text{ cm}^{-1} \) in the IR spectra. The electronic spectra and magnetic moment data propose a dimeric octahedral configuration around nickel(II) ion (Fig. 1.2.38). However it is observed that pyridine, DMF and DMSO break the binuclear structure to form mononuclear complexes.

Copper(II) complexes with these Schiff bases have been prepared and their structures are discussed.
Depending on their magnetic moments these compounds are classified into two groups, (i) those having subnormal magnetic moment and (ii) the others with normal magnetic moments. For copper(II) complexes, $\nu_{C=O}$ vibration is observed with 25-30 cm$^{-1}$ higher than those of the corresponding nickel(II) complexes. On reinvestigation of the copper(II) complex with N-salicylidene-L-valinato, it is found to have a tetranuclear configuration and normal magnetic moment at room temperature.

The copper complex of the schiff base formed by salicylaldehyde and 3-amino-1-propanol (SalPA) shows both five-coordination and dimerisation. The fifth coordination site is occupied by a chloride ion which opposes the formation of tetramers. The bridging Cu-O-Cu angle is 110.3° and its magnetic moment at room temperature is 1.1. B.M.

Condensation of o-aminobenzylalcohol with salicylaldehyde, 5-chloro, 5-bromo, 3-methoxy, and 5,6-benzo-salicylaldehyde forms tridentate diabasic schiff bases. The copper(II) complexes exhibit subnormal magnetic moments at room temperature ($\mu_{eff} = 0.98-1.45$ BM). The low magnetic moment is due to super exchange through bridging oxygen atoms of the proposed binuclear structure for these complexes. Absence of band above 1540 cm$^{-1}$ due to phenolic C-O stretching suggests that the alcoholic
oxygens act as the bridge between the two copper atoms. Coordination of nitrogen atoms of the azomethine group is established by the occurrence of a band around 1600-1615 cm\(^{-1}\) due to \(\nu_{C=N}\) stretch. Normally free \(\nu_{C=N}\) stretch appears at \(\sim 1640\) cm\(^{-1}\) in aromatic Schiff bases. The complexes exhibit a d-d band at 15,400-17,000 cm\(^{-1}\) along with a symmetry forbidden ligand \(\rightarrow\) metal CT band around 27,000 cm\(^{-1}\).

Copper(II) complexes of the Schiff base derived from salicylaldehyde, 2-hydroxy-naphthaldehyde and salicylhydrazide or benzoylhydrazide have been prepared and characterised. The complexes have low magnetic moment (\(\mu_{\text{eff}} = 1.15-1.25\) B.M.) at room temperature due to antiferromagnetic spin-spin exchange (\(-J=297\) to 340 cm\(^{-1}\)). The complexes are dimeric with hydrazine (enolic) oxygen bridge. The band due to \(\nu_{C=N}\) vibration in the complexes undergoes a bathochromic shift in comparison to that in the free ligands indicating the coordination of the nitrogen of the Schiff base.

Copper(II) complexes of Schiff base obtained from salicylaldehyde and its 5-chloro, 5-bromo, 5-nitro, 5-ethoxy and 3,5-dichloro derivatives and \(\alpha\)-hydroxybenzyl-amine have been studied. All the complexes have 1:1 metal-ligand stoichiometry with subnormal magnetic moment (0.88-0.98 B.M.) and are involved in strong antiferromagnetic
exchange interaction (-J=482 to 525 cm\(^{-1}\)). Electronic spectra of all these complexes reveal a broad band at 

\[ \sim 15,680-16,810 \text{ cm}^{-1} \]

due to d-d transitions and a band at \[ \sim 23,500-30,000 \text{ cm}^{-1} \] due to forbidden ligand \( \rightarrow \text{metal} \) CT transition. On comparison of IR spectra of these complexes with those of Cu(X-Sal-o-aminophenol), it has been suggested that the bridging in these binuclear complexes occur through benzylaminophenolic oxygen atoms.

Recently the synthesis and characterisation of a binuclear copper(II) complex, \( [\text{Cu(SalPAHP)}]_2 \cdot \text{H}_2\text{O} \) has been described\(^{145}\). The schiff base, (SalPAHP) is derived by the condensation of salicylaldehyde with \((1S, 2S)\)-\((+)-1\)-phenyl-2-amino-1,3-propanediol. In the IR spectra, the position of the phenolic C-O stretching frequency \((1540 \text{ cm}^{-1})\) does not shift to higher energy indicating alcoholic oxygen bridging in the binuclear copper(II) complex.

The electronic spectra of \( [\text{Cu(SalPAHP)}]_2 \cdot \text{H}_2\text{O} \) offer an interesting feature. It has a single broad band at \( \sim 620 \text{ nm} \) which shows solvent dependency. It occurs at 640 nm in the solid state and in toluene solution while in ethanol and pyridine, it is shifted to 626 nm and 547 nm respectively. This suggests solvent coordination to the metal. The position of absorption maximum conforms to either a square-planar or solvated square-pyramidal
configuration around copper. In pyridine a shoulder is found on the low-energy side typical of square-pyramidal copper(II) complexes.

It is well known that metal complexes of sulphur donor ligands are of special importance due to wide range of their applicability and activity against viruses, protozoa, smallpox, cancer, tuberculosis and certain kinds of tumor. Therefore studies on metal complexes of ligands containing sulphur as donor atom is of considerable interest to inorganic chemists in recent years.

Abov and Garebenev have investigated the complexes formed by Co(II), Ni(II), Cu(II) and Zn(II) with schiff base derived from the condensation of thiosemi-carbazide with a number of aldehydes and ketones. They proposed octahedral structure for $\text{M} = \text{Co(II)}$, $\text{Ni(II)}$, $\text{Cu(II)}$ and $\text{Zn(II)}$. But an X-ray structural determination of the nickel complex showed that the complex has a trigonal bipyramidal structure. The condensed product of pyridine-2-aldehyde and thiosemi-cars-carbazide (Fig.1,2,39) forms with iron(II) and nickel(II) stable complexes in which it behaves as a neutral tridentate ligand. The iron complexes $\text{Fe(NSSH)2}^{-} \cdot 7X_2 (X=\text{Cl} \text{ and } \text{Br})$ are spin paired, where as the nickel complexes $\text{Ni(NSSH)2}^{-} \cdot 7X_2 (X=\text{Cl} \text{ and } \text{NO}_3)$ are spin free. The ligand
Fig. 1.2.40

\[
\begin{align*}
R_1 = R_2 &= H, CH_3
\end{align*}
\]

Fig. 1.2.41

\[
\begin{align*}
R &= H, CH_3
\end{align*}
\]

Fig. 1.2.42
when deprotonated yields the complexes $\text{M(NNS)}_{2}^{-7}$ with iron(II) and nickel(II) and $\text{Co(NNS)}_{2}^{-7}\text{Cl}_{3}\text{H}_{2}\text{O}$ with Co(III). On the other hand, the Schiff base derived from o-aminobenzaldehyde and o-(N-dimethylamino)-benzaldehyde with thiosemicarbazide (Fig.1.2.40) give octahedral nickel(II) complexes of the type $\text{Ni(NSH)}_{2}^{-7}\text{Cl}_{2}$ instead of trigonal bipyramidal complexes as stated above.

The Schiff base (Fig.1.2.41) formed by o-methylthiobenzaldehyde and N,N-diethylethylenediamine forms high-spin complexes $\text{M(N-N-SMe)}_{2}^{-7}$; $\text{M=Co(II)}$ and Ni(II); X=Cl, Br, I, and CNS$_{7}$. The nickel halide complexes are five-coordinate in the solid state, whereas in solvent medium, they give rise to temperature-dependent equilibria between tetrahedral and five-coordinate species. The cobalt halide complexes are pseudo-tetrahedral both in the solid state as well as in solution, the cobalt atoms being coordinated to two nitrogen atoms only. In boiling n-butanol, the nickel iodide complex is S-demethylated yielding a brown dimagnetic complex with chromophore Ni(N-N-S)I. 6-Methylpyrid-2-yl-N-(2'-methylthiophenyl) methyleneimine (Fig.1.2.42) forms the mono-ligand complexes, M(SNNMe)$_{2}$; M=Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), X=Cl, Br, I and NCS. Spectral data indicate that in the solid state the manganese(II), iron(II) and cobalt(II) complexes are five coordinate, whereas the
nickel(II) and copper(II) complexes are six-coordinate and polymeric in nature. The bis-ligand complexes, \( [\text{Fe}((\text{SNNMe})_2)_2]^+ \), \( [\text{Ni}((\text{SNNMe})_2)_2]^+ \), and \( [\text{Cu}((\text{SNNMe})_2)_2]^+ \) have also been isolated. The magnetic moment values show that the iron(II) and nickel(II) complexes are respectively low-spin and high-spin types. However it is noteworthy that the bis-6-methyl-pyrid-2-yl-\( N(2'-\text{methyl thiophenyl}) \)methylenemine cobalt(II) complexes viz \( [\text{Co}(\text{SNNMe})_2]^+ \), (where \( X=\text{ClO}_4 \) and \( \text{BF}_4 \)) are spin free, whereas the corresponding complexes of 2-pyridyl-\( N(2'-\text{methyl thiophenyl}) \)methylenemine(Fig.1.2.42, \( R=\text{H} \)) are spin paired.

This difference in magnetic behaviour arises from the lower effective ligand field strength of \( \text{SNNMe} \) (Fig.1.2.42, \( R=\text{CH}_3 \)), presumably due to the steric ligand interference introduced by the methyl group in the 6-position. The magnetic moments of the cobalt complexes are temperature dependent because of a thermal equilibrium between the nearly equienergetic spin-paired and spin-free states of cobalt(II) ion in these complexes.

\( \text{N}(2'-\text{Methyl thiophenyl})-2' \text{ methylthiophenyl methylenemine} \) (Fig.1.2.43, SNS) forms the complexes, \( \text{M(SNS)}_2 \) where \( \text{M=Co(II), Ni(II), X=Cl, Br, I and NCS} \). The electronic spectra indicate that the cobalt(II) halide complexes are five-coordinate, whereas the complex
Fig. 1.2.44

Fig. 1.2.43

Fig. 1.2.45
Co(SNS)(NCS)$_2$ and the nickel(II) complexes are six coordinate and polymeric. The copper(II) complexes, Cu(SNS)$_2$ where X=Cl and Br, are possibly five-coordinate. The bis-ligand complexes of nickel(II), Ni(SNS)$_2$7X$_2$, (X = ClO$_4$ and BF$_4$) are high spin, but the complex Co(SNS)$_2$7(CIO$_4$)$_2$ is low spin with a moment of 1.97 B.M. at room temperature.

The dithiocarbazic acid derivative $\alpha$-N-methyl-5-methyl-$\beta$-N-(2-pyridyl) methylenedithiocarbazate (Fig. 1.2.44) N-NMe-S) acts as a neutral tridentate ligand forming stable complexes with transition metal ions. The complexes M(N-NMe-S)$X_2$; M=Mn(II) and Ni(II), X=Cl, Br, I, NCS$_7$ are probably halogen or pseudohalogen bridged, six-coordinate and polymeric. The structures of the analogous copper complexes are however uncertain. The bis-ligand complexes M(N-NMe-S)$_2$7(ClO$_4$)$_2$ where M=Fe(II), Co(II) and Ni(II)$_7$ and M=Fe(II), Co(II); X=Cl, Br, I and NCS$_7$ have been reported. It is interesting to note that the complexes of the later type with the iron(II) ion is dimagnetic whereas the cobalt(II) complexes are of high spin type.

$\alpha$-N-Methyl-5-methyl-$\beta$-N-(6-methylpyrid-2-yl) methylene dithiocarbazate (Fig. 1.2.45); MeN-NMe-S) also acts as a neutral NNS tridentate ligand and forms stable complexes with iron(II), cobalt(II), nickel(II) and copper(II).
Fig. 1.2.46
However the methyl group in the 6-position of the pyridine moiety increases the tendency of the ligand to form five-coordinate metal complexes. Spectral evidence indicate that the halogen complexes, $M(\text{MeN-NMe-S})X_2$ where $M=\text{Fe(II)}, \text{Ni(II)}$ and $\text{Cu(II)}$; $X=\text{Cl, Br}$ are five coordinate, probably with a distorted trigonal-bipyramidal structure. On the other hand, the thiocyanato complexes $M(\text{MeN-NMe})(\text{NCS})_2$, where $M=\text{Fe(II)}$, and $\text{Ni(II)}$ are six-coordinate with thiocyanato bridges. Bis-ligand complexes of the type $\text{L}^{-}M(\text{MeN-NMe-S})_2$ (ClO$_4$)$_2$ are formed by iron(II), cobalt(II) and nickel(II), but not by copper(II). The complexes $\text{L}^{-}\text{Co(MeN-NMe-S)}_2$ (ClO$_4$)$_2$ and $\text{L}^{-}\text{Co X}_2$, where $X=\text{Cl, Br}$ and CNS and $\text{L}^{-}\text{Fe(MeN-NMe-S)}_2$ (ClO$_4$)$_2$ and $\text{L}^{-}\text{Fe I}_2$ were also obtained. The iron(II) complex $\text{L}^{-}\text{Fe(FeN-NMe-S)}_2$ is diamagnetic$^{156}$.

The bis(S-methylated) derivative, 2(2-3-diaza-4-methylthir-5-thianexa-1,3-dienyl)pyridine (Fig. 1.2.46; N-N-S,Me), forms a number of complexes with manganese(II), cobalt(II), nickel(II) and copper(II). The ligand acts as an NNS tridentate in the complexes, $\text{L}^{-}\text{Ni(N-N-SMe)}_2$ (ClO$_4$)$_2$ and $\text{Ni(N-N-SMe X}_2$ where $X=\text{Cl, Br, I and NCS}$; the later complexes are six-coordinated and anion bridged. The complexes $\text{Co(N-N-SMe}_X_2$ ($X=\text{Cl, Br, I}$) are tetrahedral with the ligand acting as an NN bidentate. On the other hand the nitrato complex $\text{L}^{-}\text{Co(N-N-SMe NO}_3$ is probably five-coordinate in the solid state as well as in solution.
In the complexes $[\text{M}(\text{N-N-SMe})_2]_2^\text{7} \cdot \text{X}_2$ where $\text{M} = \text{Co(II)}$ and $\text{Cu(II)}$; $\text{X} = \text{ClO}_4^-$ and $\text{BF}_4^-$, the ligand behaves as NN bidentate and yields low spin cobalt(II) complexes. The complex $[\text{Cu}(\text{N-N-SMe})_2]_2^\text{7} \cdot \text{BF}_4^-$ is also known.

Pyridine-2-carbaldehyde-S-methylthio-semicarbazone (Fig.1.2.47; pmts) also acts as a tridentate ligand in the complexes of nickel(II) and copper(II). The bis-ligand complexes $[\text{Ni(pmts)}_2]_2^\text{7} \cdot \text{X}_2$ where $\text{X} = \text{ClO}_4^-$, $\text{BF}_4^-$ and $\text{NO}_3^-$ are ionic. Thiocyanate coordination is present in the complex, $\text{Ni(pmts)}_2(\text{NCS})_2$ in which the ligand is bidentate. The complexes $\text{Ni(pmts)}_2 \cdot \text{X}_2$; $\text{X} = \text{Cl, Br}$ are halogen bridged.

All these complexes are six-coordinate including $\text{Cu(pmts)}_2 \cdot \text{X}_2$; (X = Cl, Br, NO$_3$).

Gerbeleu and coworkers have synthesized a number of nickel(II) and copper(II) complexes with 8-quinolinaldehyde (dithiocarbomethoxy) hydrazone (Fig.1.2.48). The ligand behaves as tridentate and the complexes are found to contain varying number of water molecules coordinated to the central metal ion.

Above and Gerbeleu have studied the metal complexes formed by salicylaldehyde-semicarbazone (Fig.1.2.48; DNSH$_2$). This ligand readily loses a proton from the phenolic-group and acts as a singly charged tridentate chelating agent coordinating through the phenolic oxygen, the imino nitrogen and the thione sulphur atoms.
It can also act as a doubly negatively charged tridentate ligand by losing an additional proton from the mercapto group of the tautomeric form (Fig. 1.2.49).

The cobalt(III) complexes $\text{Co(ONSH)}_2\cdot Cl$ and $\text{Co(ONSH)}_2\cdot \text{H}_2\text{O}$, the chromium(III) and iron(III) complexes, $\text{Cr(ONSH)}_2\cdot \text{Cl}$, $\text{Cr(ONSH)}_2\cdot \text{H}_2\text{O}$ and $\text{NH}_4\text{M(ONS)}_2\cdot \text{H}_2\text{O}$, where $\text{M} = \text{Cr(III)}$ and $\text{Fe(III)}$ have been reported. With nickel(II), the above ligand forms a green paramagnetic complex, $\text{Ni(ONSH)}_2(\text{NO}_3)_2$ and a series of reddish brown diamagnetic complexes $\text{Ni(ONS)}_2\cdot \text{B}_2\cdot \text{H}_2\text{O}$ where $\text{B} = \text{H}_2\text{O}, \text{NH}_3, \text{pyridine}$ and aniline. The mode of coordination of the neutral ligand in $\text{Ni(ONSH)}_2(\text{NO}_3)_2$ is in doubt, although the authors assume that the ligand is tridentate and formulate the compound as $\text{Ni(ONSH)}_2(\text{NO}_3)_2$ without any supporting evidence. With copper(II) and zinc(II), the complexes $\text{CuX(ONSH)}\cdot \text{H}_2\text{O}$ ($\text{X} = \text{Cl}$, and $\text{HCO}_2$) and $\text{Zn(ONSH)}_2\cdot \text{X}_2$ ($\text{X} = \text{Cl}$ and $\text{NO}_3$) are formed.$^{162}$

Another nickel(II) complex $\text{NiL(NH}_3\text{)}$, with salicylaldehyde thiosemicarbazone ($\text{H}_2\text{L}$) is reported by Gyepes and coworkers.$^{163}$ Spectral data indicate that the enol form of the ligand (Fig. 1.2.50) coordinates to nickel via the phenolic oxygen, tertiary nitrogen and sulphur atoms. The fourth coordination position is occupied by neutral ammonia molecule:
A square planar complex of nickel(II) NiL(NH$_3$) is formed with resorcinaldehyde thiosemicarbazone (H$_2$L; Fig. 1.2.51). Spectroscopic, magnetic and thermogravimetric data show that coordination of the ligand to the metal ion involves the deprotonated 5H, 2-OH group and the azomethine nitrogen atom$^{164}$.

Mossbauer spectral data have been obtained for the iron(II) and iron(III) complexes of salicylaldehyde thiosemicarbazone and biacetylmonoxime thiosemicarbazone at 80 and 300$^0$K. In the iron(III) complexes, the greater proportion of the iron atoms are in the low spin state even at 323$^0$K. The iron(II) complex of salicylaldehyde thiosemicarbazone and bi-acetylmonoxime thiosemicarbazone are respectively of high spin and lowspin types$^{165,166}$.

Nickel(II) and copper(II) complexes of N-substituted derivative of salicylaldehyde thiosemicarbazone /$^{\text{7}}$OH C$_6$H$_4$-CH=NNRC(S)NH$_2$/ where $R$ = ph, o-tolyl, and styryl $^7$ have been reported$^{167}$. The complex Ni(ONS)$_2$(NO$_3$)$_2$ is six coordinate, while the complexes Ni(ONS)$_2$ (B = H$_2$O and amine) and Cu X(ONS) are square planar.

Adipoin thiosemicarbazone (Fig. 1.2.52; ONSH) forms the complexes /$^\text{7}$M(ONS)$_2$ _7 X$_2$.nH$_2$O /$^\text{7}$ where M = Co(II), Ni(II) and X = Cl, Br, NO$_3$ and NCS$^-$. The involvement of the phenolic oxygen is indicated by the
Fig. 1.2.53

Fig. 1.2.54

Fig. 1.2.55
fact that cyclohexamethiosemicarbazone (Fig. 1.2.53) does not form similar complexes with cobalt(III).

The copper complex of 2-(salicylideneimino) benzene thiol (Fig. 1.2.54; ONSH₂) viz. Cu(ONS) exhibits weak magnetic exchange interaction. It has been suggested that the compound has a polymeric chain structure in which the copper atoms are trigonal bipyramidal and are linked by alternate oxygen and sulphur atoms.

5-Methyl- β-N-(2-hydroxy phenyl)methylene-dithiocarbazates (Fig. 1.2.55; R=H) (ONS₃H₂) and its substituted derivatives (Fig. 1.2.55, R=5-chloro, 5-bromo, 5-nitro and 3-methoxy) act as doubly negatively charged ONS tridentates by the loss of two protons. The square planar complexes M(ONS)B where (M=Ni(II) and Cu(II); B=H₂O and Py, and the octahedral cobalt(III) complexes have been isolated. The copper complexes Cu(ONS) of the 5-chloro, 5-bromo and 3-methoxy salicylaldehyde Schiff bases are red and have anomalously low magnetic moments which decrease with fall of temperature. This behaviour is attributed to antiferromagnetic spin coupling due to oxygen bridged dimeric structure. The moment of the green copper complex of the 5-nitro-salicylaldehyde Schiff base increases with decrease in temperature rising to 2.43 B.M. at 83°K. The magnetic data fit into an expression for a tetrahedral cluster of four ferromagnetically interacting copper atoms.
The acetyl acetone schiff base, 2-hydroxy-4-methyl-5,6-diaza-7-thiono-8-thianone-2,4-diene (Fig. 1.2.56; acacO\textsubscript{SH\textsubscript{2}}) also acts as a doubly negatively charged ONS tridentate ligand and forms complexes M(acacONS), where $M=\text{Ni(II), Pd(II) and Pt(II)}$. These complexes are considered to possess the square planar dimeric thiolo bridged structures (Fig. 1.2.57) and are found to be diamagnetic in nature. But the green complex Cu(acacONS) is found to be ferromagnetic.

The schiff bases, $\alpha$-N-methyl-5-methyl-\(\beta\)-N-(2-hydroxy phenyl) methylene dithiocarbazate (Fig. 1.2.58; \(R=H\)) (HONMeS); its 3-methoxy derivative (Fig. 1.2.58; \(R=\text{OMe}\)), 1-(2-hydroxy phenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-diene (Fig. 1.2.59; \(R=H\)) and its 5-chloro and 5-bromo derivatives (Fig. 1.2.59; \(R=\text{Cl}, \text{Br}\)) (HONMeS), by loss of a proton act as uni-negatively charged ONS tridentate ligands. The complexes Ni(OH\textsubscript{NSMe})\textsubscript{X}, where \(X=\text{Cl}, \text{Br} \) and NCS are dimagnetic and square planar, while Ni(OH\textsubscript{NSMe})\textsubscript{2} is paramagnetic and octahedral. The copper complexes Cu(OH\textsubscript{NSMe})\textsubscript{NO\textsubscript{3}}, Cu(OH\textsubscript{NSMe})\textsubscript{NO\textsubscript{3}}\textsubscript{3}, Cu(S Cl\textsubscript{ONSM}e)\textsubscript{Cl} and Cu(S Br \text{ONSMe})\textsubscript{Cl} display normal magnetic behaviour; but the complex Cu\textsubscript{2}(3MeO\text{ONMeS})\textsubscript{Cl\textsubscript{3}} displays antiferromagnetic interaction between the copper atoms in the dimer. The magnetic data for Cu\textsubscript{3}(ONMeS)\textsubscript{2} Cl\textsubscript{4} and Cu\textsubscript{3}(ONSMe)\textsubscript{2} Cl\textsubscript{4} indicate linear trimeric arrangement with three antiferromagnetically interacting copper atoms.\textsuperscript{172}
Fig. 1.2.59

Fig. 1.2.60

Fig. 1.2.61

Fig. 1.2.62
Tridentate Schiff bases obtained by the condensation of salicylaldehyde or substituted salicylaldehyde with amino phenols, amino alcohols, amino thiophenols and aminothiols have been thoroughly investigated \(^{173-176}\) (Fig. 1.2.60-62). Metal(II) complexes of these Schiff bases are found to exhibit subnormal magnetic moments at room temperature due to antiferromagnetic exchange. Though the Copper(II) complexes are binuclear square planar, where the phenol or the alcoholate (O\(^-\)) of the Schiff bases act as a bridge between the two copper(II) centres, the Co(II) and Ni(II) complexes are reported to be monomers, non-electrolytes with octahedral configuration around the metal ions.

Copper(II) complexes of tridentate dibasic ONO donor Schiff bases derived from o-hydroxy acetophenone, 3-methyl-2-hydroxy acetophenone, 5-methoxy-2-hydroxy acetophenone and o-aminophenol have been prepared\(^{177}\) and dimeric structures have been proposed for the complexes.

Dibasic tridentate Schiff bases derived from o-hydroxy acetophenone and hydroxyalkylamines and having the donor systems ONO have been shown to form boron derivatives of the types \(\left[\text{OEt}\right]_2\text{B(SB)}\_7\) and \(\left[\text{B(SB)}(\text{SBH})\right]_7\), \(\text{SB}^2-\) and \(\text{SB}^2-\) are the anions of Schiff bases \(\text{NO C}_6\text{H}_4\text{C(CH}_3)\_\text{=NROH}, \) where \(\text{R} = -\text{CH}_2-\text{CH}_2-\), \(-\text{CH}_2-\text{CH}_2-\text{CH}_2-\) or \(-\text{CH}(_2\text{H}_5)-\text{CH}_2-\) by the reaction of \(\text{B(OEt)}_3\) with the Schiff
bases in 1:1 and 1:2 molar ratios respectively. The freshly prepared complexes are found to be monomers in boiling benzene and non-electrolytes in DMF\textsuperscript{178-179}.

Syamal and coworkers\textsuperscript{180-182} have reported oxovanadium(IV) complexes with some new tridentate dibasic Schiff bases and observed that the dibasic behaviour of these ligands forces the metal (II) and (III) ions to dimerise or polymerise leading to metal complexes with unusual magnetic properties. The effective magnetic moments of the complexes decrease significantly as the temperature is lowered, indicating the presence of antiferromagnetic exchange with $S=0$ as the ground state. The exchange integral ($J$) of the complexes is in the range 121-245 cm\textsuperscript{-1}. The complexes exhibit the $\nu (\nu=0)$ frequency in the region 910-985 cm\textsuperscript{-1} and the electronic spectral bands are observed around 13000, 18000 and 22000 cm\textsuperscript{-1} due to transitions $\delta xy \rightarrow dxz$, $\delta yz$, $\delta xy \rightarrow dx^2-y^2$ and $\delta xy \rightarrow dz^2$ respectively.

Mixed ligand complexes of Cu(II) with salicylaldehyde and 2-OH-acetophenone as primary ligands and acetoacetanilide and derivatives as secondary ligands with compositions $\left\{^{\mu}CuLL\right\}_n$; LH = salicylaldimine or 2-OH acetophenonimine and LH = acetoacetanilide or derivatives have been prepared\textsuperscript{183}. These complexes are found to undergo amine exchange over the Schiff base on
Fig. 1.2.63
treatment with methylamine, ethylamine and ethanolamine (Fig.1.2.63).

Copper(II) complexes of tridentate dibasic 0 NO donor schiff bases derived from 0-amino phenol and 3-chloro, 4-chloro, 4-methyl and 5-methyl-2-hydroxy acetophenone are also known\(^{184}\). At room temperature, the magnetic moments of these complexes are markedly less than the spin only value (1.73 B.M.) expected for one unpaired electron. The chelates are suggested to attain a four coordinate planar structure presumably by dimerisation of the two tridentate Cu(II) units through an oxygen bridge.

Picolinic acid hydrazide (PH), o-hydroxy acetophenone piconyl hydrazone (APH), o-hydroxy acetophenone isonicotinyl hydrazone (AITH)\(^{185}\) form cationic and neutral five and six coordinated complexes with oxovanadium(IV) of the types \(\overset{\text{VOL}}{\overset{7}{X}}\) and \(\overset{\text{VOL}}{\overset{7}{X}}\), where \(X = \text{Cl, Br, NO}_3, \text{NCS}\). The ligands PH and AITH act as tridentate. The molecular weight, magnetic moment and infrared spectral studies indicate the dimeric nature of the complexes in which the enolic oxygen acts as a bridge.

New organotin and organo-oxy-titanium compounds with schiff bases derived from salicylaldehyde and S-benzyl dithiocarbazate have been prepared\(^{186}\) where the
schiff base acts as a dibasic tridentate ligand by 
enerhio location (fig.1.2,64).

Oxozirconium(IV) complexes with the schiff 
bases derived from salicylaldehyde or substituted 
salicylaldehyde and o-amino benzyl alcohol has also been 
reported recently. The complexes are monomers, 
nonselectrolytes and dimagnetic. The versatile 
coordinating behaviour of tridentate schiff bases is 
amply demonstrated by the synthesis of several new 
iron(III) complexes of the schiff bases derived from 
salicylaldehyde, 5-bromo salicylaldehyde, 4-methoxy 
salicylaldehyde, 3-ethoxy salicylaldehyde, 3-5-dichloro 
salicylaldehyde, 2-hydroxy-1-naphthaldehyde and o-amino-
benzylalcohol. The ligands coordinate through O(Phenolic), 
N(azomethine) and O(alcoholic) atoms. The dimeric nature 
and low effective magnetic moments of the complexes are 
indicative of antiferromagnetic exchange in these complexes. 
A dimeric structure with oxygen as the bridging atom has 
been proposed where the complexes are found to be square 
pyramidal, five coordinate with Fe-O-Fe bridge (fig.1.2.65).

Copper(II), nickel(II), and iron(II) complexes 
with tridentate schiff bases (fig.1.2.66) derived from 
furan-2-carboxaldehyde and polyamines are found to contain 
ONN donor systems. Similarly, Mn(II & III) complexes of 
schiff bases containing ONO donor systems (fig.1.2.67) are 
also not rare.
Fig. 1.2.68

Fig. 1.2.69

Fig. 1.2.70

Fig. 1.2.71
Dibasic tridentate schiff bases containing ONO donor systems reported to be prepared by the condensation of salicylaldehyde or substituted salicylaldehyde either with o-amino benzylalcohol (Fig.1.2.68) or with o-hydroxy benzylamine (Fig.1.2.69) and have been used for the preparation of Zn(II)\textsuperscript{191}, and Co(II)\textsuperscript{192}, Ni(II)\textsuperscript{193} complexes respectively.

Similar type of schiff bases (Fig.1.2.70) are also derived from salicylaldehyde or substituted salicylaldehyde and alcoholamines\textsuperscript{194}. The corresponding Fe(III) complexes are found to be fairly air stable with high thermal stability. Dioxouranium(VI)\textsuperscript{195} and dioxomolybdenum(VI)\textsuperscript{196} complexes with ONO donor schiff bases (Fig.1.2.71) derived from benzoyl-hydrazide and salicylaldehyde or substituted salicylaldehyde are also known.

Dioxo uranium(VI) complexes are also reported\textsuperscript{197} with sulphur donor schiff bases of the ONS type derived from salicylaldehyde or substituted salicylaldehyde and 3-amino-thiophenol (Fig.1.2.72). In these complexes, the absolute coordination number of uranium is found to be six, seven, nine and twelve. The complexes are nonelectrolytes and dimagnetic.

Binuclear Copper(II) complexes of tridentate ONO donor schiff bases derived from salicylaldehyde or
X = H, 5-bromo, 5-methoxy, 3-methoxy, 4-methoxy, 5,6-benzo

Fig. 1.2.72

Fig. 1.2.73

Fig. 1.2.74

Fig. 1.2.75
substituted salicylaldehyde and 3-amino propyl alcohol are also reported. The synthesis of metal chelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II), UO$_2$$^{+2}$ and VO$_2$$^{+2}$ with (α-benzoyl methylebenzylidene imino) benzene sulphonlic acid (Fig. 1.2.73) and 2-(α-benzoyl methyl benzylidene imino) ethane sulphonlic acid (Fig.1.2.74) are reported. The Fe(II), Mn(II), Co(II), Ni(II), Cu(II) and VO$_2$$^{+2}$ chelates display octahedral geometry, Zn(II), and Cd(II) chelates have tetrahedral structures where as Pd(II) chelates show a square planar stereochemistry.

Complexes of 1:1 stoichiometry of Fe(III), Co(II), Ni(II) and Cu(II) with the Schiff base (Fig.1.2.75) derived from 2,4-dihydroxy acetophenone and ethanolamine have been prepared. Cu(II) and Fe(III) complexes are suggested to be of polynuclear and binuclear structures respectively with oxygen bridges in an octahedral geometry.

Cobalt(II) and nickel(II) complexes have been assigned the bipyramidal and tetragonal geometries. Cu(II) and Fe(III) complexes have low magnetic moments as compared to spin only values due to antiferromagnetic interaction in solid state.

Several new dioxouranum(VI) complexes with tridentate dibasic schiff bases derived from pyridoxal
\[ X = \text{o-OH or -COOH} \]

*Fig. 1.2.76*

\[ R = \text{H, CH}_3, \text{CH(CH}_3)_2^- \]

*Fig. 1.2.77*
and 2-aminoethanol, 2-aminoethanethiol, o-aminophenol, o-amino benzylalcohol, benzoyl hydrazide, salicylhydrazide, or aminobenzene sulphonic acid have been synthesized. 

The complexes have the composition $\text{UO}_2\text{L}(\text{B})$, $\text{LH}_2 = \text{tridentate dibasic schiff base}$, $\text{B} = \text{MeOH or EtOH}$ and are monomers. Dioxouranium(VI) complexes with schiff bases derived from pyridoxal end 3-aminothiophenol or thiosemicarbazide have the composition $(\text{UO}_2\text{L})_2$ and are dimeric in nature.

Complexes of Cu(II), Ni(II) and Co(II) with some anionic schiff bases having ONO donor sites have been reported very recently. The schiff bases are derived from salicylaldehyde or furan-2-carbaldehyde by reacting with some aminophenols or aminoacids (Fig. 1.2.76-77).

**TETRADENTATE LIGANDS**

The condensation of salicylaldehyde and ethylenediamine in the ratio 2:1 forms the potentially tetradentate schiff base abbreviated as Salen (Fig.1.2.78). Its copper(II) complex, $\text{Cu(Salen)}_2$ has been established to be a five-coordinate dimer containing two near planar units, linked by non coplanar Cu-O bonds.

Sinn et al. have reported the preparations and properties of a series of complexes of the type...
Fig. 1.2.78
\(\text{Cu(TSB)CuX}_2\_7\) (TSB = tetradentate schiff base, X = halogen). The tetradentate schiff bases are 
N,N'-ethylenebis(salicylaldimine)(ES), N,N'-1,3-propylene-
bis(salicylaldimine)(1,3-PS), N,N'-1,2-propylenebis-
(salicylaldimine)(1,2-PS), N,N'-o-phenylenebis(salicyl-
aldimine)(MPS) etc. These tetradentate salicylaldimines 
forms mononuclear planar complexes with copper(II) and 
nickel(II) salts in which the former is normal paramagnetic 
while the latter is invariably diamagnetic. It has been 
possible to prepare a large number of binuclear complexes 
containing both similar and dissimilar metal atoms from 
these mononuclear "complex ligands". The general method 
involves the mixing of the chloroform solution of the 
"complex ligand" with an alcoholic solution of metal 
halide (MX\(_2\) or M\(_3\)X\(_2\)). The complex \(\text{Cu(TSB)}_7\) functions 
as a bidentate ligand and coordinates to the other metal 
ion through its two phenolic oxygens. All the homonuclear 
complexes of copper(II) are antiferromagnetic and fit into 
the Bleaney-Bowers model. But the heteronuclear complexes 
involving copper(II) with other paramagnetic or diamagnetic 
metals and nickel(II) with other paramagnetic metals have 
normal magnetic properties obeying Curie-Weiss law over 
the temperature range 80-400K. The complexes \(\text{Cu(TSB)}_7\) 
(TSB = ES, 1,2-PS, 1,3-PS and MPS) and \(\text{Ni(ES)}_7\) remain 
essentially planar when they act as ligand. But the 
second metal lying outside the "schiff base moiety" is not 
coplanar with the first metal, rather tends towards
tetrahedral or pseudotetrahedral environment\textsuperscript{208} which has been confirmed by X-ray analysis of the complexes $\left[\text{Cu}(i,3-PS)\text{CuCl}_2\right]_7\text{209}$ and $\left[\text{Cu(Me-Salen)}\text{CuCl}_2\right]_7$. But in the complex Cu(Salen)CuCl\textsubscript{2}, the copper atom which is coordinated to the halides achieve five-coordination by bonding to a chloride of an adjacent dimer. Therefore the complex is a polymeric array of these dimeric units.

Recently Bhattacharya et al\textsuperscript{210-212} have prepared and characterised by spectral and magnetic data, a series of quadridentate Schiff base complexes of copper(II). The complexes have been classified into two types (a) $\left[\text{Cu(TSB)}\text{CuX}_2\right]_7$ (type I) (TSB = symmetrical or unsymmetrical tetradentate Schiff base, $X = \text{Cl}$),
(b) $\left[\text{Cu(TSB)}\text{Cu(A-A)}\right]_7(\text{ClO}_4)_2$ (type II) (A-A = tertiary diamines like 2,2\textsuperscript{'-}bipyridyl, 1,10-phenanthroline and 2(2\textsuperscript{'-}pyridyl)benzimidazole). The ligand TSB (symmetrical) are prepared by the condensation of salicylaldehyde or 2-hydroxyacetophenone with o-phenylenediamine, ethylenediamine and 1,3-propylenediamine, while the unsymmetrical TSB ligands are derived from the condensation of salicylaldehyde, o-phenylenediamine and 2-hydroxyacetophenone, ethylenediamine, 1-3-propylenediamine with salicylaldehyde at one end and 2-hydroxyacetophenone at the other end.

The reflectance spectra of $\left[\text{Cu(TSB)}\text{CuCl}_2\right]_7$ show two bands at 17390 and 11110 cm\textsuperscript{-1} due to $\left[\text{Cu(TSB)}\right]_7$. 
and \( \text{CuCl}_2 \) moieties respectively. In the corresponding complex, \( \text{Cu(TSB)}\text{Cu}(A-A)_7 \text{ClO}_4 \), the band positions are located at 17700 and 14810 cm\(^{-1} \) attributed to the \( \text{Cu(TSB)}_7 \) and \( \text{Cu}(A-A)_7^{2+} \) segments respectively.

The higher d-d band position of \( \text{Cu}(A-A)_7^{2+} \) compared to \( \text{CuCl}_2 \) moiety is due to stronger ligand field of tertiary diamine than the two chlorine atoms. Electronic spectra in ethanol of \( \text{Cu(TSB)}\text{Cu}(2,2'-\text{bipyridyl})_7 \text{ClO}_4 \) exhibits bands at 47000, 42000, 38000(sh), 33250, 32000, 29000, 26000(sh) and 24000 cm\(^{-1} \) corresponding to the transitions of \( \text{Cu(TSB)}_7 \) i.e. 47000, 43000, 38000(sh), 29000, 26000(sh) and 24000 cm\(^{-1} \) without any significant change. It indicates that superexchange interactions in all these complexes involve only the \(-\)orbitals of the metal ions and bridging \( O^{-} \). The \(-\)orbitals of the ligands do not participate in superexchange process.

Diorganotin oxides react with quadridentate Schiff bases to yield complexes of the type \( R_2\text{Sn}(\text{salen}), R_2\text{Sn}(\text{acetophenene}) \) and \( R_2\text{Sn}(\text{benzophenene}) \) where \( R = \text{n-butyl, n-octyl or n-benzyl and salen, acetophenene and benzophenene are the dianion of Schiff bases:} \)

- bis(salicylaldehyde)ethylenediamine, bis(2-hydroxy-5-methylacetophenone) ethylenediamine, bis(2-hydroxy-5-methylbenzophenone) ethylenediamine \( \text{ClO}_4 \). The complex \( R_2\text{Sn(salen)} \) exists both in cis and trans forms with a highly distorted C-Sn-C moiety in solid state. The other
Fig. 1.2.79

\[
\begin{align*}
Y & = H, CH_3 \\
\end{align*}
\]

Fig. 1.2.80

\[
\begin{align*}
Y & = H, CH_3 \\
\end{align*}
\]

Fig. 1.2.81

\[
\begin{align*}
R & = H, CH_3 \\
M & = Ni(II), Cu(II), Pd(II) \\
\end{align*}
\]
complexes, $R_2Sn$ (acetophenone) and $R_2Sn$(benzophenone) however, exist in trans form only both in solid and solution state.

Infrared spectra of all compounds are almost similar to those of the ligands. Negligible change in the group frequencies of the ligands after complex formation is attributable to the fact that bonding of organotin with ONNO set of donor atoms has the same effect as that of the hydrogen bonding in the free ligand. Tin and organotin complexes of quadridentate Schiff bases (Fig. 1.2.79) derived from salicylaldehyde or o-hydroxy acetophenone and thiocarbohydrazide having ONSQ donor system have been synthesized. Coordination of the ligand to tin involves both the deprotonated phenolic (OH) oxygen, thioamide (C=S) sulphur and one of the hydrazone (C=N) nitrogens.

Synthesis of mixed complexes of aluminium with ONNO type quadridentate Schiff bases are also reported by Agrawal and coworkers (Fig. 1.2.80). Dimagnetic Ni(II) and Pd(II) complexes of mixed diamine ligands (Fig. 1.2.81) derived from 2-hydroxy-1-naphthaldehyde and benzoylacetone are reported. The corresponding Cu(II) complexes are paramagnetic in nature with magnetic moment, very close to the spin only value expected for one unpaired electron.
Fig. 1.2.83

\[ \text{M} = \text{Cu}^{(II)}, \text{Co}^{(II)}, \text{Ni}^{(II)} \]

\[ \text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5 \]

Fig. 1.2.83
Tetradentate Schiff bases (Fig. 1.2.82) derived from salicylaldehyde and diamines are reported to undergo structural rearrangement on complex formation with Sn(IV). A series of 1:1 adducts of Tin(IV) iodide with the above Schiff base have been synthesized and have been studied in solid state as well as in solution.

On reacting one mol of acetylacetone with two mols of benzylhydrazide, the Schiff base N,N'-bis (benzamido)acetylacetoneimine(LH₂) is formed, which reacts with Ni(II) chloride to give a sky blue coloured, paramagnetic pseudo-octahedral complex Ni(LH₂)Cl₂. The complex with traces of water results in forming a yellow orange dimagnetic square planar complex (NiL). Cobalt(II) halides when react with this Schiff base in the anhydrous condition form blue coloured polymeric tetrahedral Co(LH₂)X₂ complexes which undergo transformation to the pink ones with traces of water. A bridging polymeric structure has been suggested for the ligand which behaves as quadridentate in its monomeric form.

N,N'-hexamethylene diamine, when reacts with 2,5-dihydroxy acetophenone/propiophenone/benzophenone forms interesting quadridentate Schiff bases (Fig. 1.2.83) containing ONNO donor sites. These have been used to form square planar chelates of Cu(II), Co(II) and Ni(II) ions.
$\text{Fig. 1.2.84}$

$n = 2.3 \quad \text{Fig. 1.2.85}$

$M = \text{Cu(II), Ni(II)} \quad \text{Fig. 1.2.86}$

$R = \text{H, CH}_3 \quad R' = \text{H, CH}_3, \text{C}_2\text{H}_5 \quad \text{Fig. 1.2.87}$
Polyamines have significant role in providing polydentate ligands when they react with compounds containing a carbonyl group at suitable position. For example, furan-2-carboxaldehyde gives a number of polydentate ligands (Fig. 1.2.84-85) with tolyamines which are used for the preparation of Cu(II), Ni(II) and Fe(II) complexes. Similarly stable Cu(II) and Ni(II) complexes with tetradebate schiff bases derived from 2-hydroxy-1-naphthaldehyde and ethylene diamine (Fig. 1.2.86) are reported.

Bhattacharya and coworkers have studied a series of mixed ligand complexes of Cu(II) and Ni(II) containing fused ring systems. The schiff bases are prepared by the reaction of 2-acetyl-1-napthol, salicyaldehyde, 2-hydroxy acetophenone, 2-hydroxy propio-phenone, or 2-hydroxy-1-naphthaldehyde with suitable diamines. The tetradebate schiff bases are found to coordinate through ONNO donor systems (Fig. 1.2.87-88). Antiferromagnetic exchange is observed in some complexes resulting in abnormal magnetic moments. Absence of any significant interaction between the \( \pi \) orbitals of the ligands through the metal ion \( \sigma \) orbitals has been proposed from a study of binuclear Cu(II) complexes involving unsymmetrical tetradebate schiff bases. Binuclear Cu(II) complexes of the type \( ^{\sim} \text{Cu(TSB)} \text{CuX}_{2-7} \) and \( ^{\sim} \text{Cu(TSB)} \text{Cu} (\text{A-A})_{7} (\text{ClO}_4)_{2} \) (Fig. 1.2.90) have been
\[ x = \text{Cl, Br, NO}_3 \]
\[ R = \text{H, CH}_3 \]

**Fig. 1.2.88**

\[ \chi = \text{Cl, CIO}_4 \]
\[ R = (\text{CH}_2)_2 \text{ or } (\text{CH}_2)_3 \]
\[ R_1 = \text{CH}_3 \text{ and } R_2 = \text{H} \]

**Fig. 1.2.89**

\[ R = (\text{CH}_2)_2 \text{ or } (\text{CH}_2)_3 \]
\[ R_1 = \text{CH}_3 \text{ and } R_2 = \text{H} \]

**Fig. 1.2.90**
prepared \( \xi = \text{Cl}, \text{ClO}_4; \text{TSB} = \text{various unsymmetrical schiff bases obtained from condensation of ethylene diamine or 1,3-propylene diamine with salicylaldehyde, at one end and 2-hydroxy acetophenone or 2-hydroxy-1-naphthaldehyde at the other end, and } A-A = 2,2' \text{dipyridyl; } 1,10\text{-phenanthroline or } 2-(2'\text{-pyridyl})\text{benzimidazole}. \)

Room temperature magnetic moment values of the complexes are observed to be much lower than expected for two Cu(II) ions.

Thermogravimetric and polarographic studies of Cu(II) complexes (Fig.1,2,91) with tetradentate schiff base, Bis(salicylidene)-O-alkyl-1-amidinourea has shown \( -\xi^2 \) values to be much less than those of the corresponding parent O-alkyl-1-amidinourea \( ^{224} \) moity. The stability of the complexes with different schiff bases with respect to o-alkyl substituent are reported to be in the order methyl ethyl propyl butyl. The abnormal magnetic properties of the complexes is attributed to the presence of an oxo bridge as supported by IR spectral data.

Complexes of Cu(II), Co(II), Ni(II), UO(II) and UO\(_2\)(II) with tetradentate schiff base \( N,N'\)-ethylene bis(2-hydroxy-4-methyl propiophenoneimine) (Fig.1,2,92) have been prepared \( ^{225} \). Square planar structure are suggested for Cu(II), Co(II) and Ni(II) complexes while oxovanadium(IV) complex.
Fig. 1.2.91

Fig. 1.2.92
In the complexes of trivalent lanthanide ion with Schiff base (Fig.1.2.93) derived from vanillin and triethylene tetramine, the metal ion exhibits eight coordination number. The thermograms of the complex shows the elimination of (OH) (OCH₃) group at low temperature, before the elimination of triethylene tetramine part, corroborating the observation made on the basis of IR spectral data that the phenolic hydroxyl group is not coordinated to the metal ion.

On the other hand, the tetradentate Schiff base, biacetyl (bis-benzoyl hydrazone) BDH) has been reported to coordinate through the enolic oxygen and azomethine nitrogen from a study of its complexes with trivalent rare earth metals. The chelates (Fig.1.2.94) have been synthesized in situ refluxing biacetyl benzoyl-hydrazone and metal salt and are characterised to be neutral, six coordinated and octahedral with the formula \( \text{L}^{−}\text{M(BDH)(OH)(H₂O)}\) \(7\).  

The IR and \(^1\)Hnmr study shows that the Schiff base bis(acetyl acetone) benzidine interacts in enol form and acts as a bifunctional tetradentate ligand (Fig.1.2.95). The thermal analysis of its complexes with trivalent lanthanide proves the presence of one coordinated water molecule.
Fig. 1.2.93

Fig. 1.2.94
Recently, oxovanadium(IV) complexes of some new tetradequate schiff bases (Fig.1.2.96) obtained from 2-hydroxy-1-napthaldehyde and some diamines viz. o-phenylene diamine, ethylene diamine and propylene diamine have been described."229"
Fig. 1.2.95

Fig. 1.2.96

x = \( \textcircled{O} \), \(-\text{CH}_2\text{-CH}_2^-\), \(-\text{CH}_2\text{-CH}_2\text{-CH}_2^-\)
BIOLOGICAL IMPORTANCE OF HETEROCYCLIC AMINES

Heterocyclic compounds containing oxygen, nitrogen and/or sulphur atoms have been found to be useful as potential drugs and their biological importance has been exemplified in recent years. In view of the vastness of the data available in this area, a complete review is really difficult. However, attempt has been made to outline in brief some of the salient features in order to highlight the biological importance of such compounds as potential drugs.

Heterocyclic amine, 1,3,4-oxadiazole is a possible toxophore against a number of harmful organisms. Oxadiazole and its derivatives are also said to possess analgesic and anticonvulsant activities. 1,3,4-oxadiazole moiety and similar heterocyclic residues have been investigated for biological and pesticidal interest. T. Ramalingam and coworkers have reported the synthesis and pharmacology of a number of 2,5-disubstituted 1,3,4-oxadiazole derivatives (Fig.1.3.1,2).

Pharmacological evaluation of these compounds exhibited mild to strong anti-inflammatory and CNS depressant action in experimental animals.

2-aryl-oxymethyl-2-1,3,4-oxadiazolin-5-ones (Fig.1.3.3) and their related compounds exhibited herbicidal
$R = C_{6}H_{5}, NH_{2}, SH, SCH_{2}COOH, SCH_{2}COOC_{2}H_{5}$

$R_{1} = R_{2} = H, 4-CH_{3}, 3,4-(OCH_{3})_{2}$

$R = NH_{2}, SH$  $R_{1}, R_{3}, R_{4} = H, CH_{3}$  $R_{2} = H, Cl$

Fig. 1.3.1

Fig. 1.3.2

Fig. 1.3.3
activities in the range 2,4-D (Na-salt), a commercial herbicide against Argemone Mexicana and Cyperus Rotundus. Some of these compounds also showed fungitoxicity of the order of Diathan M-45 (Manganese ethylene-bis-dithiocarbamate with zinc ion), a commercial fungicide against Aspergillus niger and Helminthosporium Oryzae. The novel exploration of oxadiazon (G-315), the 2-tert-butyl-4-(2,4-dichloro-5-iso-propoxy phenyl)-Δ²-1,3,4-oxadiazoline-5-one which is a broad spectrum commercial herbicide recommended for application on various crops and ornamental plants, has been an incentive for investigation in the field of 1,3,4-oxadiazole herbicides.

Since long, oxadiazoles have been associated with insecticidal, herbicidal, antibacterial, hypoglycemic, antitubercular, antiviral, antifungal and carcinostatic activities. An interesting observation made by Surender Bahadur and K.K. Pandey is that, the parent oxadiazole, 5-(p-anisyl)-1,3,4-oxadiazole-2-thione (Fig.1,3,4) inhibited the growth of bacilli significantly. But this activity was decreased in the manich bases (Fig.1,3,5), derived from it, except those containing the nitro group which inhibited only S. aureus and S. lutea. The insecticidal activity was however enhanced in the manich bases of the type (Fig.1,3,6) and most significantly, when there was incorporation of chloride group.
It is well-known that sulphur containing compounds effect their toxic action by inhibition of acetylcholinesterase which exhibit physiological significance in the nervous system. Thiadiazoles and their derivatives have been found to be potential fungicides, insecticides and bactericides. Similarly, as has been reported by Kirkpatrick, 5-acyl-amino-4,3,4-thiadiazole-2-sulphonamide (Fig. 1.3.7) acts as an efficient pre- and post-emergent herbicide. The versatility of 2-amino-5-substituted-1,3,4-oxadiazole is well reflected in its antimitotic, muscle relaxing and tranquilising property.

Fungicidal and insecticidal screening of 1,3,4-thiadiazole and its derivatives indicate promising drug activities. Experiments on the insecticidal activities were carried out in duplicate on adult male and female cockroaches (Periplanta americana) as the test insect for the compounds (s-acetyl-N-substituted-phenylamine)-arylamino-1,3,4-thiadiazole (Fig. 1.3.8) and some of them have been found to be most potential insecticides.

The antibacterial and insecticidal activity of some thiadiazole derivatives against S. aureus and S. Typhi, E.Coli respectively have been recently investigated by Sengupta and coworkers and promising results were obtained. The aryloxypropionyl thiosemicarbazide and related compounds (Fig. 1.3.9) were screened for antifungal
\[ R \overset{\text{NH}}{\longrightarrow} \begin{array}{c} \text{N} \\ \text{S} \\ \text{S} \\ \text{CH}_2 \end{array} \overset{\text{CO} \overset{\text{NH}}{\longrightarrow}}{\text{S}} \phi \]

**Fig. 13.7**

\[ R_1 \overset{\text{NH}}{\longrightarrow} \begin{array}{c} \text{N} \\ \text{S} \\ \text{S} \\ \text{CH}_2 \end{array} \overset{\text{CO} \overset{\text{NH}}{\longrightarrow}}{\text{S}} \begin{array}{c} \text{N} \\ \text{S} \\ \text{S} \\ \text{CH}_2 \end{array} \overset{\text{CO} \overset{\text{NH}}{\longrightarrow}}{\text{S}} \phi \]

**Fig. 13.8**

\[ R_1 \overset{\text{O}}{\longrightarrow} \begin{array}{c} \text{CH}_3 \\ \text{N} \\ \text{N} \\ \text{NH} \end{array} \overset{\text{X} \overset{\text{NH}}{\longrightarrow}}{\text{N}} \begin{array}{c} \text{N} \\ \text{S} \\ \text{S} \\ \text{CH}_2 \end{array} \overset{\text{CO} \overset{\text{NH}}{\longrightarrow}}{\text{S}} \begin{array}{c} \text{N} \\ \text{S} \\ \text{S} \\ \text{CH}_2 \end{array} \overset{\text{CO} \overset{\text{NH}}{\longrightarrow}}{\text{S}} \phi \]

**Fig. 13.9**

\[ X = 0, 5 \]

\[ R_1 = R_2 = 2-\text{Cl} \]
activity against *H. Oryzae* and *A. Brassicae*. The compounds were found to possess moderate fungicidal activity against these fungi.  

Thiadiazole ring is reported to display fungicidal property by virtue of \(\text{N-C-S-linkage which is a possible toxophore in many pesticides}^{266-267}\).  

1,3,4-thiadiazole derivatives have also been found to possess herbicidal, radioprotective, antitumor, diuretic, bacteriostatic and cystostatic activities. Some new 1,3,4-thiadiazoles having acetamide side chain at 2-position have been prepared recently by Shah and coworkers\(^{268}\). The products (Fig.1.3.10 a,b,c) were screened for antimicrobial activity by cup-plate method using DMF as solvent at a concentration of 10 mg/ml. It was observed that all the compounds were moderately active against *S. Aureas*, but not against *E. Coli*.

Dithiocarbamates of 1,3,4-thiadiazole containing N-aryl/alkyl/morpholino/piperidino/pyrolidino (Fig.1.3.11) residues have been synthesized\(^{269}\) as potential anthelmintic and were screened for anthelmintic activity against *Hymenolepis nana* infection in mice. Encouraging observations were recorded establishing the thiadiazole moiety to be biologically as active as 1,3,4-oxadiazole.
Fig. 1.3-10 (a)

\[
\begin{align*}
\text{R'} & \quad \text{S} \quad \text{NHCOCH}_2 \quad \text{NHR} \\
\end{align*}
\]

Fig. 1.3.10 (b)

\[
\begin{align*}
\text{R'} & \quad \text{S} \quad \text{NH} \quad \text{CH}_2 \quad \text{CO} \quad \text{NHR} \\
\end{align*}
\]

Fig. 1.3.10 (c)

\[
\begin{align*}
\text{R'} & \quad \text{S} \quad \text{NH} \quad \text{CH} \quad \text{CONH}_2 \\
\end{align*}
\]

\[R = \phi, \quad R' = \text{o-nitrophenyl / benzoyl amino methyl}\]

Fig. 1.3.11

\[
\begin{align*}
\text{R} & \quad \text{phenylamino / o-tolylamino / p-anisylamino / morpholino} \\
\end{align*}
\]
Strong CNS depressant, mild hypocholesterolemic and hypotensive action were exhibited on pharmacological evaluation of a number of new s-triazolo[3,4-b]_7-1,3,4-thiadiazole carrying aryl moiety at 2-position and arylxyalkyl group at 5-position. The pathogenic fungi A. flavus and H. Oryzae were found to respond satisfactorily to compounds containing oxadiazole and thiadiazole moieties.
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