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CHAPTER I

INTRODUCTION

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Multimetallic species occupy an important position in modern inorganic chemistry. The awareness of the importance of such complexes has prompted wide ranging research investigations on these compounds in the last two decades. Among these, polynuclear Copper(II) complexes form a subject of special interest owing to their varied applications in the field of bioinorganic chemistry as models for understanding the different metal activated enzymatic processes. Further, they have potential in industrial homogeneous catalysis.

Several such complexes containing two or more metal ions, linked to each other within the complex through one or more shared entities, referred to as " bridging groups ", have been studied.[1-12] The structures of such complexes have often been correlated to their characteristic spectral and magnetic properties.[13-19] In some cases, the structures have independently been determined by using X-ray diffraction analysis of single crystals.[20-25]

A summary of the literature reveals that the published data on the multicentred Copper(II) complexes can be classified into the following four types.

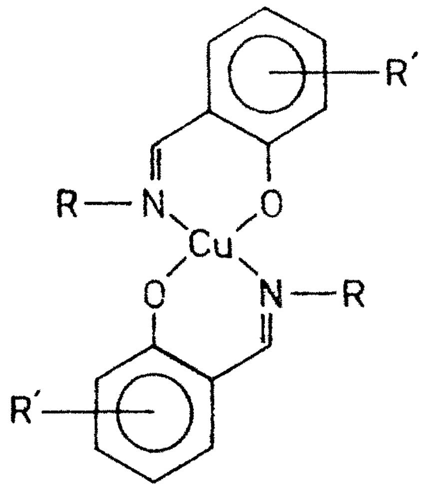


Figure I 1

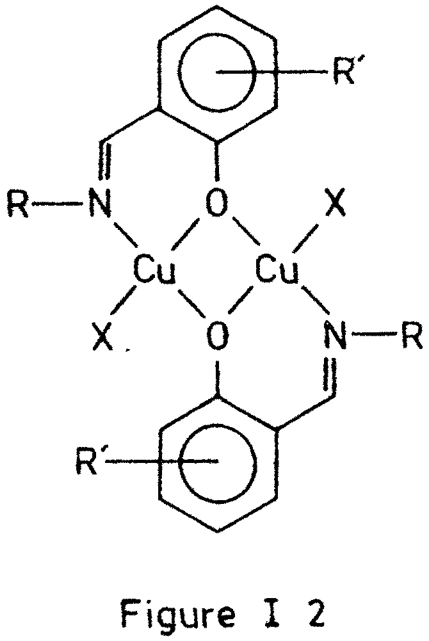


Figure I 2

1 Binuclear Complexes Derived From Bidentate Schiff Base Complexes [M(BSB)]

The complexes of bidentate schiff base (BSB) (I) can be considered as simple bidentate ligands with two oxygen atoms acting as donors.[26-40] When this [M(BSB)] is made to react with MX_2 ($X = Cl^-$, Br^- or NO_3^-), a binuclear complex with a rearranged structure (II) is obtained.[28] This can be illustrated in the case of $[Cu(BSB)CuCl_2]$ complex as shown in Figures I 1 and I 2.

The bonding between salicylaldiminato complex and metal halide most likely occurs by dative bonding via the two phenolic O^- of the bidentate complex ligand. Properties of these binuclear complexes have been explained in terms of a trans structure. The trans structure allows the two Copper atoms to adopt a configuration nearer to planar with only a small amount of steric distortion towards tetrahedral, as the R-group on the BSB nitrogen becomes bulkier..

2 Binuclear Complexes Derived From Tridentate Schiff Base Complexes [M(TrSB)]

Like bidentate schiff base complexes, tridentate schiff base complexes can also act as " Complex Ligands ". In the binuclear complexes involving tridentate schiff base, obtained by the condensation of o-hydroxyaldehyde with

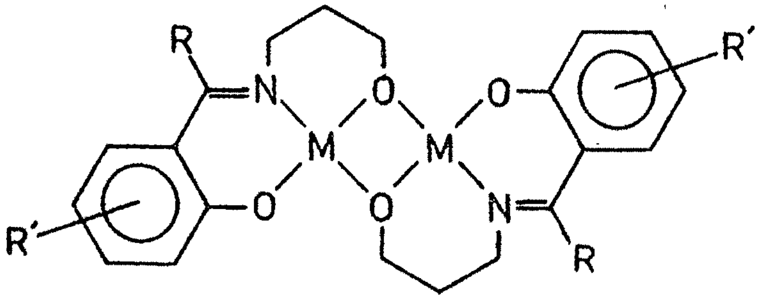


Figure I 3

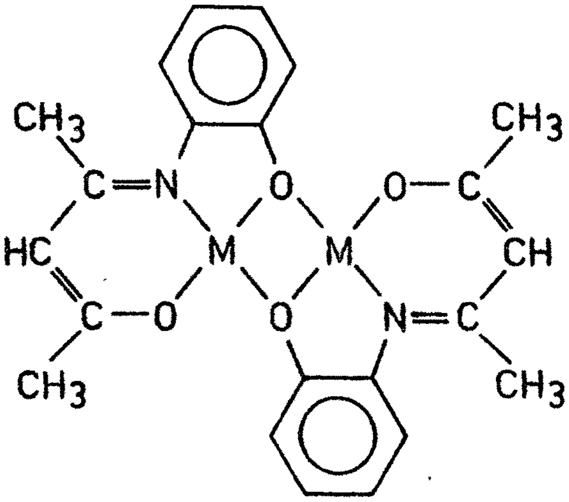


Figure I 4

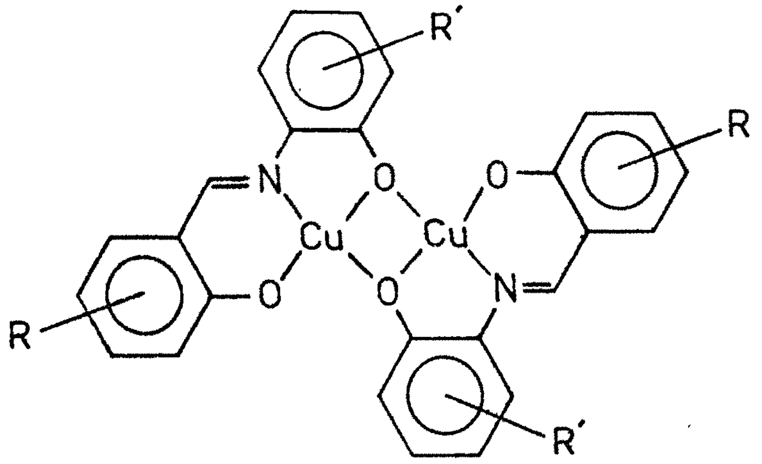


Figure I 5

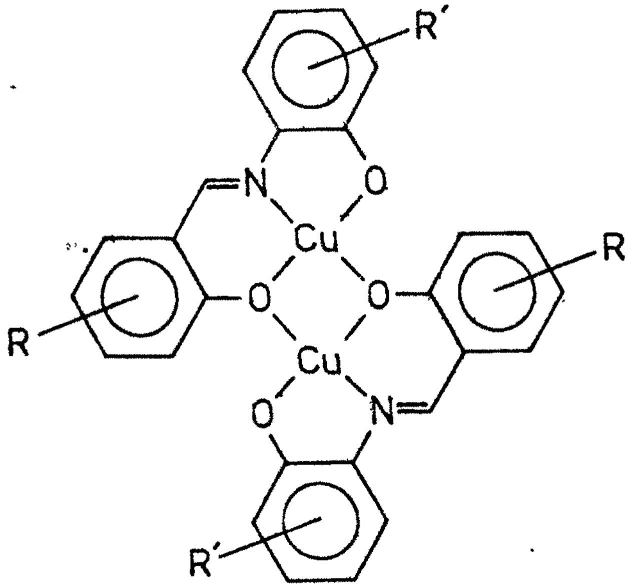
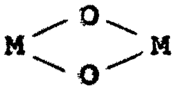


Figure I 6

alkanolamine, bridging occurs more readily via alcoholic oxygen (Figure I 3).[15,21,41-44] This has been confirmed from the X-ray diffraction study of few complexes.

Binuclear complexes of Copper(II), Iron(III) and Cobalt(III) derived from tridentate schiff base complexes obtained by condensation of salicylaldehyde with o-hydroxybenzylamine, have been studied by Syamal and coworkers.[45-56]

In the complexes, shown in Figure I 4, involving tridentate schiff base obtained by the condensation of aminophenol with β-diketone,  bridging occurs more readily via phenolic oxygen than the O^- of ketoamine part.[57-63] Bridging through phenolic O^- has been confirmed by IR spectral and X-ray diffraction studies in cases where phenolic and ketoamine oxygen occur in the same complex.

Hatfield[64] and Ginsberg[65] studied binuclear complexes of tridentate schiff base complexes obtained by the condensation of substituted or unsubstituted salicylaldehyde with substituted and unsubstituted o-aminophenols. They have obtained two structural isomers (Figures I 5 and I 6) and no choice of the bridging O^- can be made a priori.

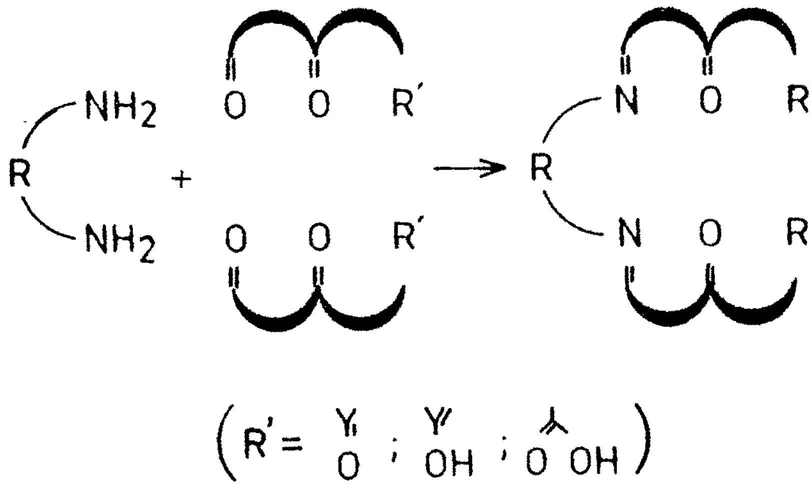


Figure I 7

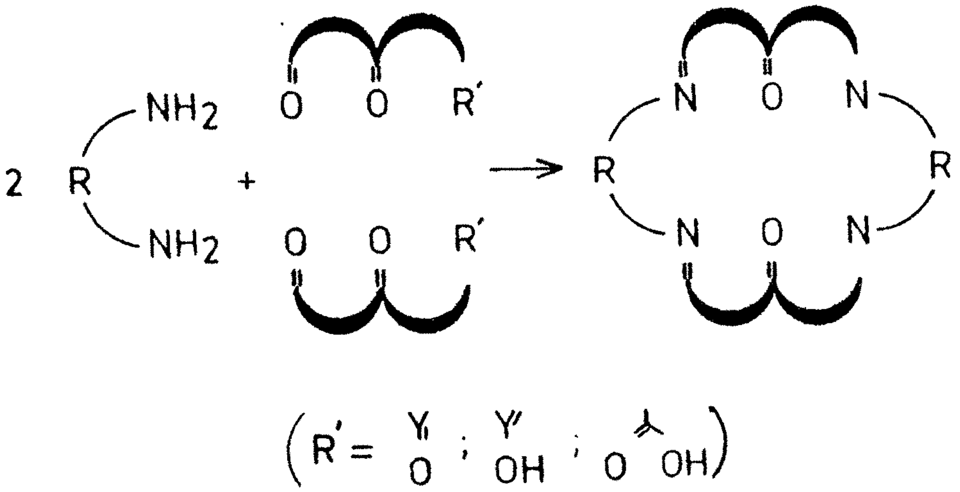


Figure I 8

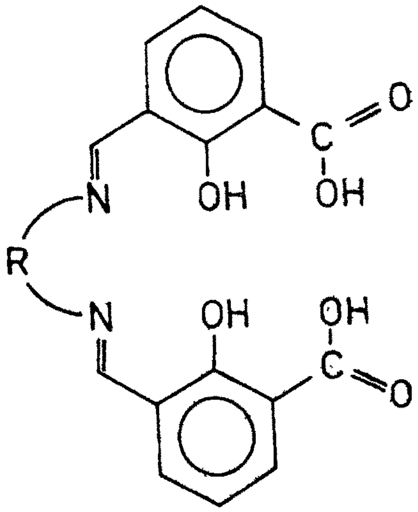


Figure I 9

3 Binuclear Complexes Derived From Compartmental Ligand

Two decades ago Robson initiated a series of studies concerning the rationale of synthetic approach to cluster compounds.[5,66] Through this work he introduced the concept of a macrocyclic binucleating ligand i.e. " a ligand capable of securing two metal ions in close proximity ". This definition can be extended to include acyclic ligands having similar properties studied in the present thesis.

Compartmental ligands can be prepared by the reaction of diamines with (i) β-triketones, (ii) keto-carboxylic acids and (iii) keto-phenols resulting in schiff bases (Figures I 7 to I 11).

i) β-triketones

When two β-triketone molecules condense with one diamine molecule, it will result in a compartmental ligand having an O - O donating compartment and an O - N donating compartment (Figure I 7). Whereas, if two diamine molecules react in a similar fashion, cyclic ligand results, which can, by the reaction with metal ions, produce macrocyclic binuclear complex (Figure I 8).[67-74]

ii) keto-carboxylic acid

Second class of ligands (Figure I 9), capable of offering dissimilar adjacent coordination

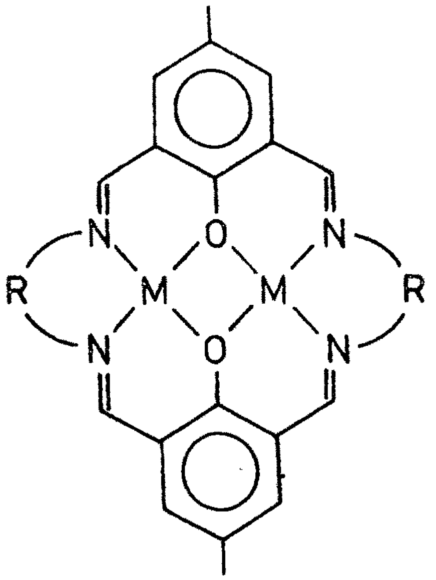


Figure I 10

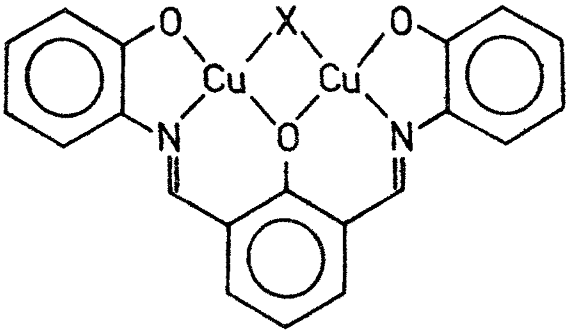


Figure I 11

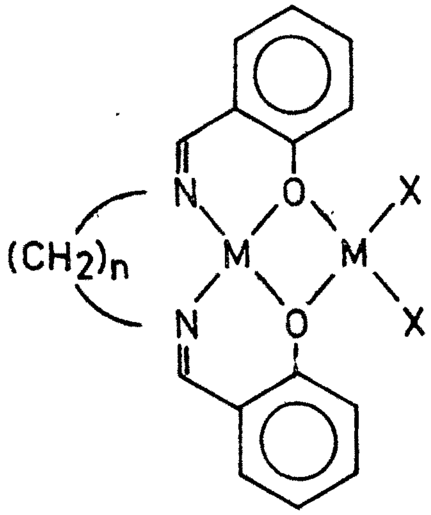


Figure I 12

compartments is derived from the reaction of α,ω-diamines with 3-formylsalicylic acid. Various homo- and hetero- binuclear complexes of this ligand have been synthesised.[9,11,19,75-82]

iii) keto-phenols

Formation of closed double compartment homo- and hetero- binuclear complexes, bridged through O^-, have also been reported in the case of macrocyclic schiff base ligands obtained by condensing 2-hydroxyisophthaldehyde with α,ω-diamines (Figure I 10).[8,12,83-93]

Binuclear complexes of Copper(II) have also been obtained by the treatment of cupric isobutyrate with the schiff bases derived from the reaction of o-aminophenol or alkanolamine with 3-formyl-5-methyl-salicylaldehyde (Figure I 11).

4 Binuclear Complexes Derived From Tetradentate Schiff Base Complexes [M(TSB)]

Sinn and Harris[3] have reported bi- and tri- nuclear complexes of the type $[M(TSB)MX_2]$ and $\{[M(TSB)]_2 M\}(ClO_4)_2$, where TSB represents various tetradentate schiff bases derived from salicylaldehyde or 2-hydroxyacetophenone (Figure I 12).

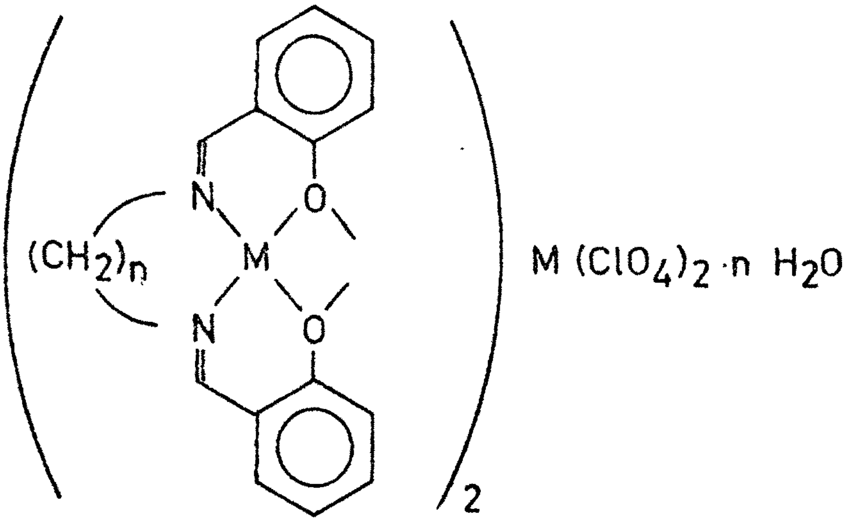


Figure I 13

The mononuclear complex of the tetradentate schiff base has an additional lone pair of electrons over the two phenolate O^-. They can get coordinated with the Copper(II) of another CuX_2 molecule resulting in the formation of homobinuclear complex. However, if the TSB complex of metal ion is made to react with the chloride of another metal ion, a heterobinuclear complex is formed and when TSB complex is made to react with metal perchlorate in 2 : 1 proportion, a trinuclear complex results (Figure I 13).

In all the cases of bi- and tri- nuclear complexes, bridging is through the phenolate O^-. Thus, in the formation of these complexes, the coordination number of coordinated oxygen atoms is raised to three.

Magnetic And Spectral Properties Of Binuclear Copper(II) Complexes

Antiferromagnetic compounds can be generally classified into two broad subgroups.[96] The first type consists of metal oxides in which magnetic exchange occurs over the entire crystal lattice giving rise to long range ordering. Under the second type are those complexes, in which the exchange is between different cation centres within the same molecule, leading to short range ordering. These two types can be called inter- and intra- molecular antiferromagnets,

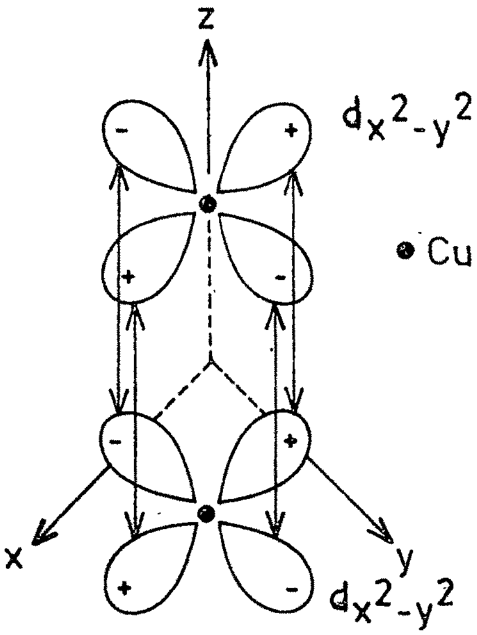


Figure I 14

respectively. Obviously, the binuclear Copper(II) complexes belong to the latter type.

Magnetic exchange interactions are often useful in elucidating the structure of polynuclear complexes having paramagnetic centres. It was the temperature dependence of magnetic susceptibility[97-99] and the ESR spectrum[97,100-103] of the compound copper acetate monohydrate, that led to the prediction of its binuclear structure.[104,105] At this point it is worthwhile to mention the generally accepted mechanisms of exchange interaction and discuss them with reference to the binuclear complexes. Mainly, following two types of mechanisms[96] are operating.

1 Direct Interaction

This involves the direct overlap of the orbitals containing the unpaired electrons. This mechanism is the one considered to be responsible for exchange interaction in Copper(II) acetate monohydrate. In this molecule, weak overlap between the $d_{x^2-y^2}$ orbitals of each Copper atom gives rise to a δ type bond as shown in Figure I 14. Martin and Figgis[106] and Kettle[107, 108] have confirmed that the distance between two Copper centres is such that a weak metal-metal interaction is possible.

The symmetry of the molecule approximately corresponds

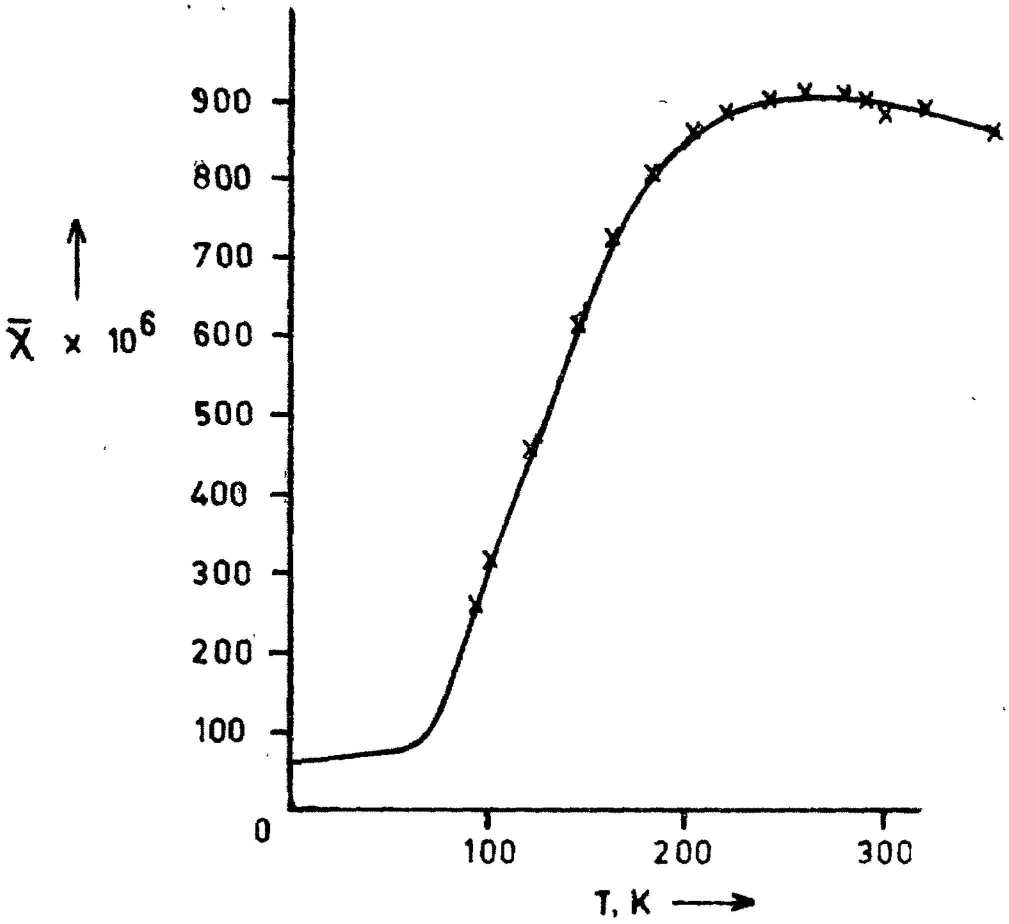
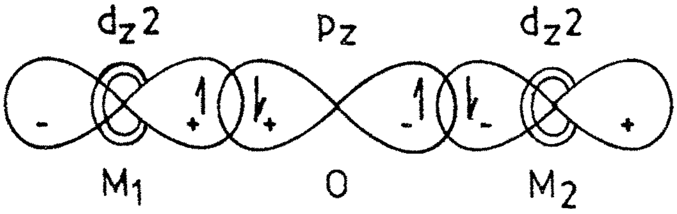

900
800
700
600
500
400
300
200
100
0
$\bar{\chi} \times 10^6$
100
200
300
T, K

Figure I 15

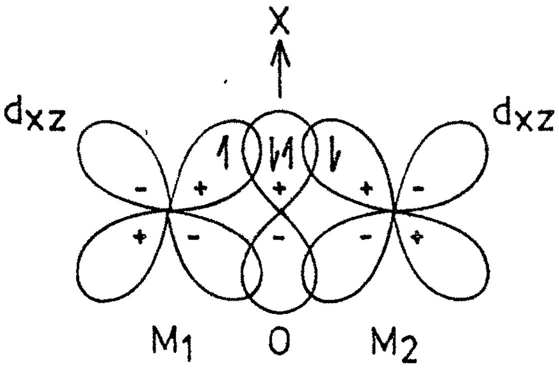
to D_{4h} and under this geometry the $d_{x^2-y^2}$ orbitals on each Copper combine to give a b_{1g} bonding and a b_{2u} antibonding orbital. At lower temperature, the two available electrons get paired up in the b_{1g} bonding orbital, and give rise to a diamagnetic ground state for the molecule. This is a singlet state. An excited triplet state is attained if one of the electrons is promoted to b_{2u} antibonding orbital, the resulting configuration being $b_{1g}^{2}\ b_{2u}^{0}$ or $b_{1g}^{1}\ b_{2u}^{1}$. Since the separation between b_{1g} and b_{2u} levels is not much, an excited triplet state must be appreciably populated at normal temperatures to account for the subnormal magnetic moment. With increasing temperature, electron pass to b_{1u} level in more molecules and there is an increase in the magnetic moment. The observed variation in χ_m with temperature (Figure I 15), therefore, results from the thermal population of the spin triplet state. It may be added that the overlap between the metal $d_{x^2-y^2}$ orbitals is very weak and is not to be considered as a metal-metal bond.

2 Superexchange

The superexchange interaction, resulting in antiferromagnetism, is an indirect exchange involving the interaction of electrons of opposite spins on the two interacting cations via an intermediate anion. This mechanism also involves orbital overlap, but here, in



ⓐ σ bonding



ⓑ π bonding

Superexchange in a linear M-O-M system

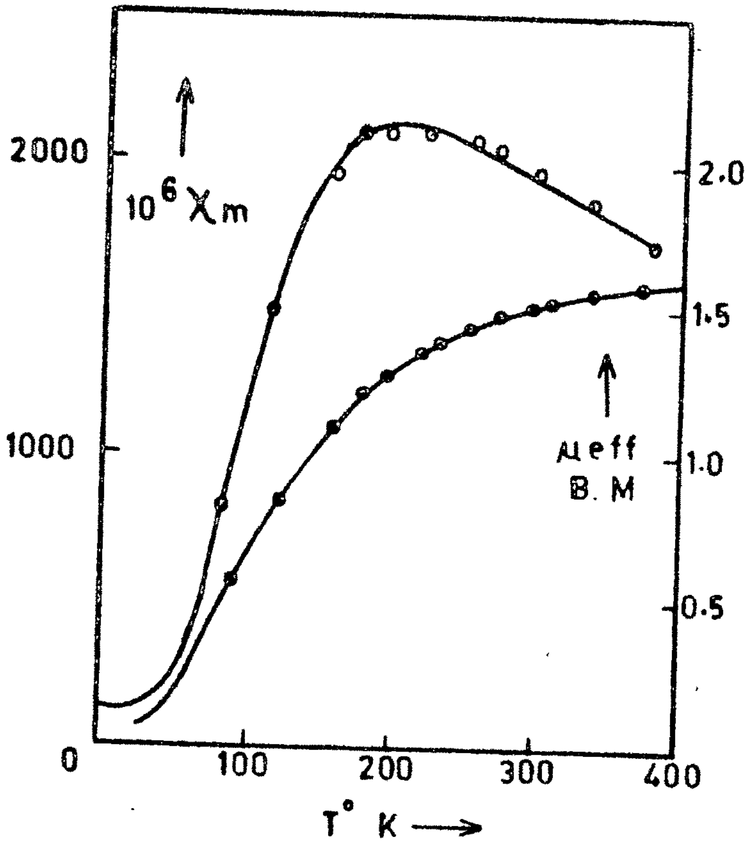
Figure I 16

addition to the metal d orbitals, the filled orbitals of the intervening anion also take part. This is explained by the help of Figure I 16.

In Figure I 16, a hypothetical M_2O, where M is a transition metal ion with a single electron has been considered. In a linear M-O-M arrangement the interaction may occur through two ways, either σ bonding or π bonding, as shown in Figure I 16 a and b, respectively.

A simple pictorial representation of the exchange process involves an electron with positive spin on M_1 pairing with one of the electrons in the bridging oxygen p orbital which has a negative spin. This leaves the other electron of oxygen p orbital with positive spin. When this electron with positive spin interacts with the electron on the other metal ion, the latter is induced to have negative spin. Thus, through the spin polarization the electron spins on the two metal ions are aligned antiparallel resulting in antiferromagnetic ordering.

Systematic study, of the X-ray diffraction patterns, ligand field spectra and low temperature magnetic susceptibility of $[Cu(TSB)CuX_2]$ type complexes was carried out by Sinn and coworkers.[109-115] They observed that the magnetic moments are subnormal and decrease with decreasing temperature. In the case of these binuclear Copper complexes,



$J = -166 \ \mathrm{cm}^{-1}$

$g = 2.11$

Figure I 17 (Ref. 3, 112)

Copper(II) - Copper(II) distance is comparatively larger and hence it seems unlikely that the direct exchange due to overlap of copper 'd' orbitals is significant.

The possible exchange path way is superexchange involving σ overlap of Copper $d_{x^2-y^2}$ and oxygen p_x orbitals. This interaction gives rise to a diamagnetic ground state and an excited paramagnetic triplet state. The separation between the two states is equal to 2J, where J is the value of spin exchange interaction. This determines the extent to which the triplet state is populated at a given temperature. The temperature dependence of χ_m is given by Bleaney and Bower's equation[100,101] as

$$\chi_m = \frac{2g^2\beta^2N}{3\ kT}\left[\frac{1}{1+\frac{1}{3}\ e^{(-2J/kT)}}\right] + N\alpha$$

If $2J \geqslant kT$, all the molecules are in singlet ground state and the binuclear complex is diamagnetic. When $2J \simeq kT$, the magnetic susceptibility depends on the Boltzman population of the states. For the case of the complex, $[Cu(salen)CuCl_2]\ H_2O$, it has been shown that there is a close agreement between the χ_m (corrected) or μ_{eff} values (——) calculated from Bleaney and Bower's equation and the values (∘) obtained experimentally (Figure I 17).

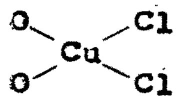
The magnitude of J can be calculated from a fit of the experimental data of χ_m and T to the above equation or may be estimated from T_{max} (the temperature at which χ_m is maximum) in the plot of T against magnetic susceptibility by using the relation[116] $J = 1.6\ k\ T_{max}$.

Albeit the magnetic properties of the complexes are very dependent upon temperature, Sinn and Robinson[32] found that they are not significantly sensitive to pressure upto 3000 atms, indicating that there is little difference in volume between the singlet and triplet forms of the molecules.

For the exchange interaction to occur between the two Copper(II), it is necessary that the binuclear complex should have a planar structure. Any distortion from planarity would reduce the overlap of Copper(II) $d_{x^2-y^2}$ orbitals with oxygen p_x orbital and the exchange interaction is weakened. A convenient measure of the degree of distortion from planarity is the angle τ between the plane Cu_2O bridge and that of the remaining ligands. For a complete planar structure it will be zero and will increase with tetrahedral distortion at the two Copper(II) centres. On this basis, superexchange in $[Cu(BSB)CuX_2]$ complexes (Figure I 2) should be more than that in $[Cu(TSB)CuX_2]$ complexes (Figure I 12).[21] It is actually observed that $[Cu(BSB)CuX_2]$ complexes exhibit much larger singlet-triplet separation (300 cm^{-1} or more) and the magnetic property does not differ significantly from complex to complex. In $\left[Cu(TSB)CuX_2\right]$ complexes the J value is less and the magnetic property differs among individual complexes. These properties have been explained on the basis of trans structure of $\left[Cu(BSB)CuX_2\right]$ complexes. The trans structure helps the complex to attain greater planarity and hence the exchange interaction is more. In complexes $\left[Cu(BSB)CuX_2\right]$, if R groups on N are bulkier, there is steric hindrance leading to Td distortion and magnetic moment goes up.

The band position in the ligand field spectra of these complexes also show that the Copper(II) in these binuclear complexes is in square planar field.[27,117] With the substitution of bulkier R groups, there is tetrahedral distortion with λ_{max} moving to higher wavelengths. Thus, there is a linear relationship between the wavelength of the d-d transition band and the magnetic moments of the complexes. The same relationship holds good in $\left[Cu(TrSB)CuX_2\right]$ complexes (Figure I.3) also.

Jonassen and coworkers[30,34,41,118-121] have also shown the existence of linear relation which could be interpreted in terms of continuous stereochemical change of Copper(II) ions between planar and tetrahedral configurations. An increase in the degree of planar configuration results in a blue shift in the d-d band and low magnetic moment due to a greater orbital overlap between metal and bridging O atoms.

The two phenolate O^- of the TSB are in the cis position in $[Cu(TSB)CuX_2]$ complexes. In $[Cu(TSB)]$ itself, the geometry of the ligand around Copper(II) is distorted from planarity.[111] In all binuclear complexes formed on coordination with $CuCl_2$, the  segment has a pseudo tetrahedral structure. This induces more planarity on the $[Cu(TSB)]$ part. It was observed by Sinn and Harris[27] that, if one of the metal ions is in a planar environment, the adjacent metal ion will be distorted away from planarity, and vice versa. As distortion from planarity increases, there is lowering in the antiferromagnetic interaction. At the same time, with tetrahedral distortion there is lowering in the ligand field with consequent increase in λ_{max}. Thus, linear relationship between magnetic moment and λ_{max} values holds good in $[Cu(TSB)CuX_2]$ complexes also.

In case of $[Cu(TSB)CuX_2]$ complexes, it was observed[111,114] that there is a steady increase in the magnetic moment and λ_{max} values as we move to the TSB with increasing length of the carbon chain joining the nitrogen atoms. The reason lies in the fact that, with increasing chain length, there is an increased distortion in the geometry of the $[Cu(TSB)]$ from planar to pseudo tetrahedral form.[111]

In these three types of complexes substitution over the phenyl ring of the schiff base can affect the J value to the extent they alter the M-O-M bridge via alteration of molecular packing. Nature of R over $>$C=N- part in $[Cu(TSB)CuX_2]$ complexes does not affect the properties significantly. TSB derived from 2-hydroxyacetophenone or 2-hydroxybenzophenone forms binuclear Copper(II) complexes with magnetic moment not significantly different from the complexes of TSB derived from salicylaldehyde.[34,36,115,122]

In case of the binuclear complex, $[Cu(salen)CuCl_2]$ it was observed that there is a possibility of linkage of the halogen with the Copper(II) of the adjacent molecule, making it five coordinated and weakening one of the Cu-O bonds. This results in a weakening of the antiferromagnetic interaction and lowering of J values.[28]

In $[Cu(TSB)CuX_2]$ complexes, when X = NO_3^-, [44] the second oxygen of the already coordinated NO_3^- is in close proximity to the Copper(II) of another binuclear complex. Thus, there is formation of a weaker Cu—O bond due to intramolecular interaction and the geometry at each Copper(II) is square pyramidal. This apical bond reduces the superexchange overlap, resulting in reduction of J value. The way it is brought about is not very clear because the M-O-M bridge angle is not affected significantly.

The spectral characteristics of the binuclear complexes show some interesting characteristic features. In case of [Cu(BSB)CuX$_2$] and [Cu(TrSB)CuX$_2$] complexes of bidentate and tridentate schiff bases[27] only one d-d band is observed although it is slightly shifted from the band position of the mononuclear complex. This shows that the two Copper(II) centres have equivalent ligand fields in both bidentate and tridentate schiff base binuclear complexes. The position of the band also shows that the structure of the two centres is planar and this is in keeping with the trans structure.

In [Cu(TSB)CuX$_2$] complexes, however, there are two non-equivalent Copper(II) centres and hence two bands are observed. In the CuCl$_2$ part, bonded to two phenolate O^- of the [Cu(TSB)], Copper(II) is in a pseudo tetrahedral enviornment and hence band is observed in the region 8 000 - 12 000 cm^{-1} as expected in tetrahedral complexes of Copper(II).[123] The original band of mononuclear TSB complex (occuring at $\sim$ 17 000 cm^{-1}), shows a shift on coordination with CuCl$_2$. The band shifts to the higher energy region indicating that the complex ligand becomes more planar when it coordinates with CuCl$_2$. This energy shift confirms that there is formation of binuclear complex.

The discussions, so far, clearly reveal in general, the interesting spectral and magnetic properties shown by multicentred Copper(II) complexes. In the present work an attempt has been made to formulate correlations between structural, magnetic and spectral properties of some selected binuclear Copper(II) complexes of TSB with non-equivalent Copper(II) centres. With this in view, complexes of the type $\left[Cu(TSB)Cu(A\text{-}A)\right](ClO_4)_2$, where A-A corresponds to tertiary diamines, have been prepared. Binuclear complexes containing unsymmetrical tetradentate schiff base complexes and saturated tetradentate mannich base complexes have also been studied to find correlation between magnetic superexchange and spectral properties. Lastly, some trinuclear Copper(II) complexes have been studied.