CHAPTER: 1

Introduction

1. Introduction

For a long time, magnets have found a wide range of applications in science, technology and domestic life. From audio or videotapes to door closures and car parts, they are present everywhere. Making of these magnets makes use of the bulk magnetic property of materials which are essentially metallic. Metal oxides have been experimented on in few cases. Molecular and macromolecular materials are also encountered widely but in different areas such as plastics, woven synthetics, display technology, optics, etc. However, molecular magnets belong to a field which is still at an early stage of development. Research interest in this field is motivated by the need for a better understanding of the fundamental principles that govern magnetic behavior, in particular when moving from isolated molecules to three dimensional solids, as well as the need for new improved materials. The trend towards the miniaturization of electronic devices to the ultimate scale – the molecular one – is a further force driving the expansion of the field. While the biological world provides numerous examples, it also demonstrates that the route is feasible.

Molecular magnets are the systems where a permanent magnetization and magnetic hysteresis can be achieved (although usually at extremely low temperature) not through a three-dimensional magnetic ordering, but as a purely one-molecule phenomenon. It has begun in 1951 with the study of a dinuclear complex, copper acetate [1], but it was only in the 1980s that the first molecular – based solids exhibited spontaneous magnetization below their curie temperature [2]. The observations provided a strong impetus for the study of bi- and multimetallic systems.

Although multimetallic complexes were known early in the development of modern coordination chemistry, it is only over past 30 years that special attention has been devoted to their preparation and properties. As was the case for analogous organometallic compounds, the 1970s were a period of high expectations for multimetallic coordination complexes. It was generally assumed that properly designed multimetallic systems would provide new reactivity patterns and physical properties. Multimetallic systems were expected to have greater oxidizing and reducing power, the neighboring metals were expected to "cooperate" in promoting reactions, and electronic interactions between metals might lead to distinct physical properties. These and other expectations led to the rapid development of the field that, in its initial phase, provided a variety of polynucleating ligands. The physical properties of the complexes were reported sometimes in great detail. In some cases special physical properties were observed, but the systems yielded few examples of unique reactivity patterns. Under these circumstances one would have expected interest in the area to subside after the initial burst of activity. Enthusiasm for the area, however, has been maintained by one major factor, the rapid growth in the understanding of the functions, reactivities, and structures of metalloprotiens.

It was especially disconcerting to coordination chemists, particularly those who worked on multimetallic systems, to find that the nature had constructed numerous multimetallic proteins [3, 4], complexes that perform an extraordinary array of catalytic transformations, few of which had been anticipated or reproduced in nonprotein systems. These continuing biological discoveries have inspired coordination chemists to persist in developing the area from an inorganic viewpoint. The task of finding functional analogues for these proteins can be a daunting task in most cases because the function performed by the protein is not only controlled by the immediate coordination sphere but is also affected by the larger protein structure. Even so, the study of analogues of metalloproteins can be instructive even if the biological function is not entirely reproduced because such studies help to define the parameters, which may guide reactivity in the protein.

There are several ligands in the biological systems, which possess more than one coordination centers. In the presence of excess of metal ions, they can quite easily from homo or hetero binuclear or polynuclear complexes [5-13]. The study of these transition metal complexes are of great interest because they provide the opportunity to study the mechanism of superexchange interaction between paramagnetic ions and the role of the metal ions in multielectron redox reactions and in the activation of small molecules such as O_2 and N_2. They also serve as models for some metalloproteins whose biological functions are associated with metal center in pairs

[14-17]. Even the study involving polynucleating ligands is important to ascertain their ability to form multinuclear species and their use as models for the coordination environment of the metal ions at the polynucleating biosites. They are also of interest, as potential homogeneous catalysts, mimicking the role of oxidases and oxygenases in the biosystems.

There are both homo and heterobimetallic species known in the biological systems. The homobimetallic systems include hemethryrin (Fe, Fe) [18-20], hemocynin (Cu, Cu) [21,22], tyrosinase (Cu, Cu) [27-25] and several multi copper oxidases (Cu, Cu) [26]. The cytochrome C oxidase (Fe, Cu) [27, 28] and super oxide dismutase are example of heterobimetallic systems [29]. In order to understand the biological functions of these metallobiomolecules, and to understand the role of the metal ions involved in the biological reactions, many model binuclear complexes involving binucleating ligands have been studied in detail [30-35].

Since 1970, when Robson introduced the term "binucleating ligand" for polydentate chelating ligands, capable of simultaneously binding two metal ions [36], there has been steady increase in the number and types of such ligands synthesized. There are mainly two classes of the binucleating ligands [37]. They are as follows:

1. The first group consists of those ligands forming binuclear complexes in which the metals share at least one donor atom that provide a bridge ("bridge donor sets"). The ligands giving these complexes have been collectively termed as compartmental ligands [38].
2. The second group consists of those ligands forming complexes in which donor atoms are not shared and so isolated donor sets exist.

1.1. Compartmental ligands:

The ligands in this class are predominantly 2,6-disubsituted phenols and thiophenols, 1,3,5-triketones and β-ketophenols and schiff bases derived from them. In these the central phenolic or keto oxygen or thiophenolic sulphur atoms can act as the bridging donor atoms. Ligands derived from 2,6-disubstituted phenols and thiophenols, 1,3,5-triketones can be either of the following three types:

1.1a. Macrocyclic form derived from a "2+2" condensation reaction (**Fig 1.1**)

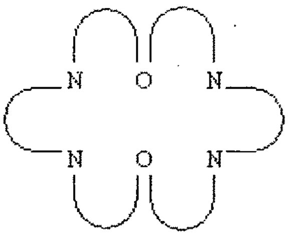
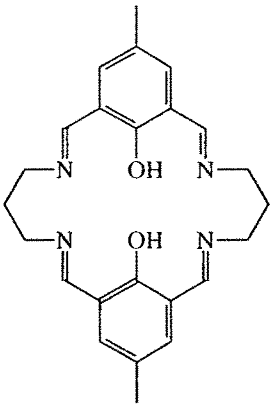
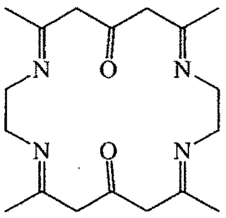


Fig.1.1 Compartmental ligands, macrocycle (N_4O_2).

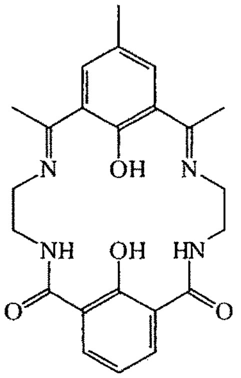
The macrocycles may be either symmetrical, (**1.1a.1** and **1.1a.2**) or nonsymmetrical, (**1.1a.3**), in nature. In the non-symmetrical macrocycles spatial differences may occur in the coordination sites but the donor sets remain equivalent.



1.1a.1 (ref. 39, 40)



1.1a.2 (ref. 41)



1.1a.3 (ref. 42)

1.1b. "End-off" acyclic compartmental ligands: (Fig 1.1b)

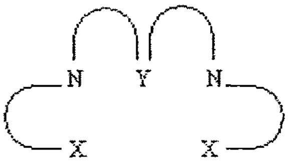
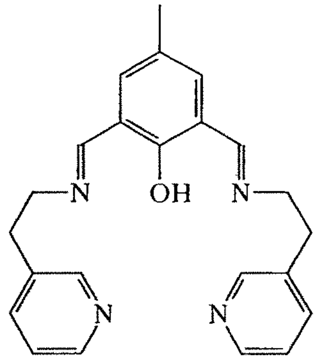
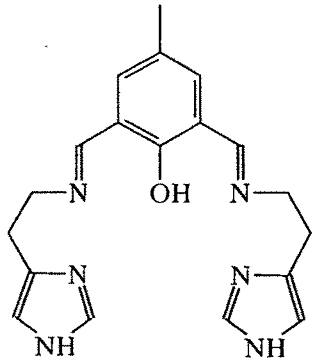


Fig. 1.2 Compartmental ligands "end off" (N_2YX_2: X= N, OSi; Y= O, S);

The "End-Off" acyclic compartmental ligands are modified forms of macrocycles in which one donor bridge is removed. They provide only one endogenous bridging donor and so have a labile bridging site available between the metal sites into which a variety of anions (X^-) can be introduced as exogenous bridges. This subclass gives a wide range of donor atom combinations with essentially the same basic structural framework and has, in principle, the potential to bind molecules such as dioxygen, or dinitrogen, at the exogenous bridging site, (**1.1b.1** and **1.1b.2**).



1.1b.1 (ref. 43)



1.1b.2 (ref. 43)

1.1c. "Side-off" acyclic compartmental ligands: (Fig. 1.3).

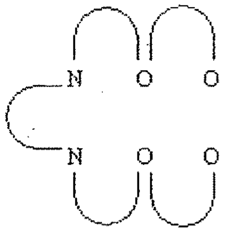
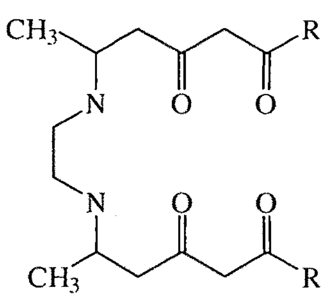


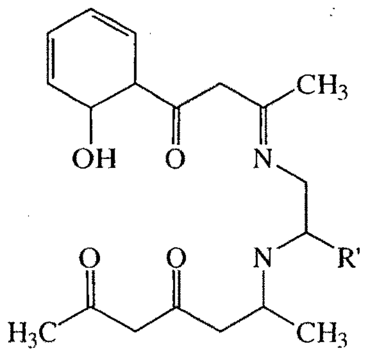
Fig.1.3 Compartmental ligands, "side-off" (N_2O_4)

"Side-off" acyclic compartmental ligands are the forms of macrocyclic ligands in which one non-donor bridge is absent. They are derived from a "2+1" condensation of a 1,3,5-triketone, β-ketophenol, or 3-formylsalicylic acid with an α,ω-alkanediamine. Acyclic ligands are prepared which present adjacent, dissimilar coordination compartments, i.e. "O_2O_2" and "N_2O_2" donor sets. Symmetric and non-symmetric ligands are available, (**1.1c.1** and **1.1c.2**).



R = CH_3, C_6H_4-, tBu-

1.1c.1(ref. 44-46)



R' = various bridging groups

1.1c.2 (ref. 47)

1.2. Ligands with Isolated donor sets:

In the complexes of this type of ligands, the donor atoms are not shared. A wide spectrum of ligands and bridges are available in this type. The ligands with isolated donor sets are mainly of four types.

1.2a. Extendable macrocycles and related systems:

Binucleating ligands having isolated donor sets within extendable macrocycles and related systems are the molecules similar to those described in the earlier section except that the bridging atom is not shared. Instead there are separate coordination groups capable of accommodating two metal ions (**Fig. 1.4**).

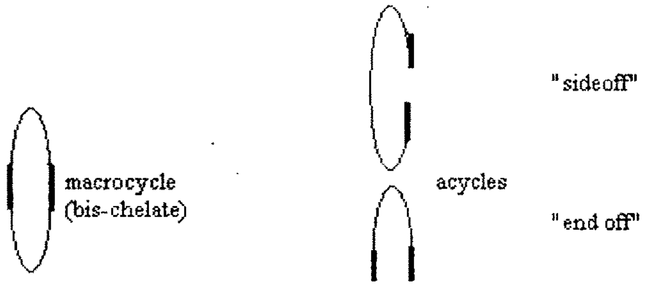
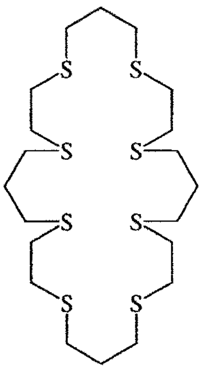


Fig. 1.4 Isolated donor sets within extendable macrocycles.

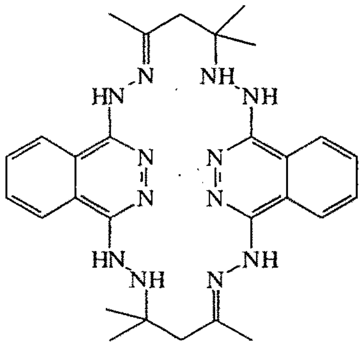
The first example of macrocycle capable of circumscribing two metal ions completely was octadendate macrocyclic thioether, (**1.2a.1**), reported by Busch in

1970 [48] and also of the macrocycle, (**1.2a.2**), derived from the template reaction of 1,4-dihydrazinophthalazine with acetone in the presence of nickel (II) ions [49].

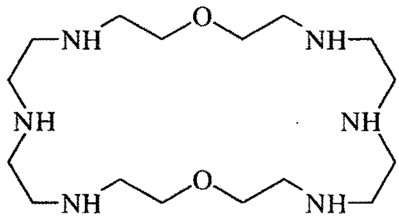
Macrocyclic binucleating ligands based on two chelating subunits of the diethylene triamine type (**1.2a.3**), and related ligands bearing two diagonally disposed pyridine groups, (**1.2a.4**), have been developed by Lehn and his groups [50].



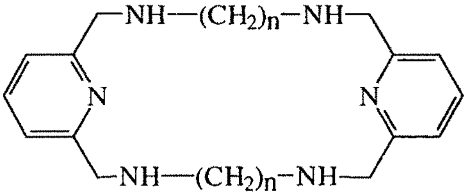
1.2a.1 (ref.48)



1.2a.2 (ref.49)



1.2a.3, N_6O_2, (ref. 50)



1.2a.4 (ref. 50)

(n = 4, N_4Py_2 and n = 5, N_4Py_2)

1.2b. Eextendable macrobicycles. (Fig. 1.5)

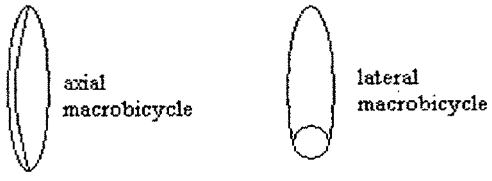
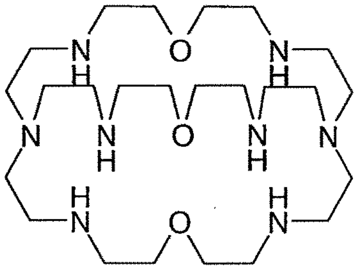


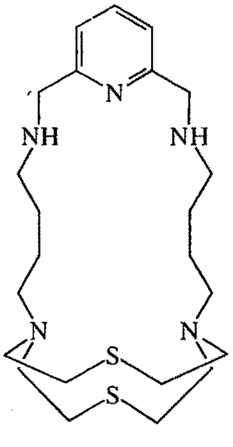
Fig. 1.5 Isolated donor sets within extendable macrobicycles.

1.2b.1 Axial macrobicycles: Extendable macrobicycles have been constructed from two relatively simple ligand combinations. Axial systems may be directly related to a combination of tripodal ligands, and lateral systems may be considered as a combination of a chelate and a macrocycle [50]. The ligand, (**1.2b.1**) [51] has been synthesized, together with a series of derivatives, and provides an ellipsoidal cavity which is capable of binucleation. Binuclear Zn^{2+},Cu^{2+} and Co^{2+} complexes have been reported.



1.2b.1 (ref. 51)

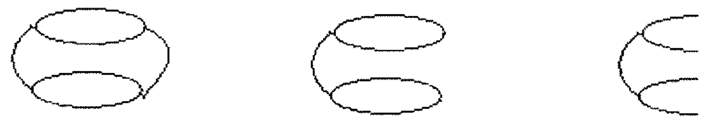
1.2b.2 Lateral macrobicycles: Lateral macrobicyclic systems may be prepared when a chelating subunit is bridged over a macrocycle. Such a system is (**1.2b.2**) in which the 2,6-(bis(aminomethyl)pyridine sub unit is present together with the 12-membered diaza-dithia-macrocycle [50].



1.2b.2 (ref. 50)

1.2c. Extendable macrotricycles and related systems:

Isolated donor sets can be derived from planar macrocycles and related systems constraining to stack one above each other. **(Fig. 1.6)**



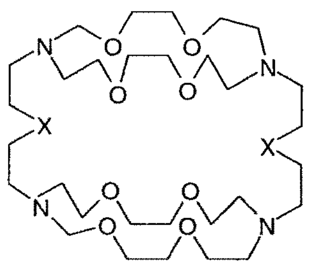
cylindrical macrotricycle

bis-macrocycle

"wishbone" polypode

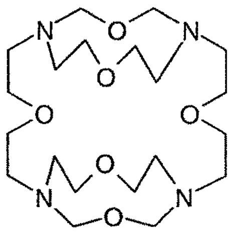
Fig. 1.6 Isolated donor sets derived from planar macrocycles constrained to stack one above each other.

1.2c.1 Cylindrical macrotricycles: Cylindrical macrotricyclic molecules can be devised by face-to-face linkage of two macrocycles by two bridges. The first cylindrical macrotricyclic ligands described were polyoxamacrotricycles, **(1.2c.1)**, **[50]**. The microtricyclic ligands, **(1.2c.2)**, **[52]** gave a bis-silver nitrate complex.



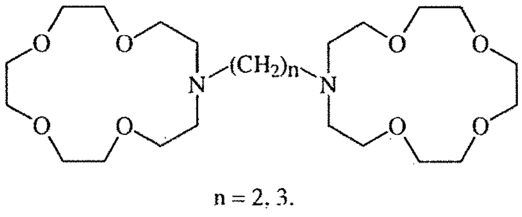
1.2c.1 (ref. 50)

(X = O or CH_2 or NH or o-phenylene)

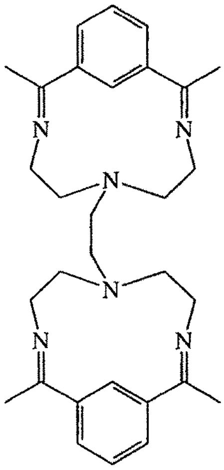


1.2c.2 (ref. 52)

1.2c.2 Bis-macrocycles: Removal of one linking chain from the cylindrical macrotricycles lead to the formation of bis-macrocycles which may exist in one of the many orientations available between extreme of syn- or anti- conformation. Synthetic bis-macrocycles are represented by **1.2c.3** [53] and **1.2c.4** [54]. Homobinuclear Cu (II) complexes with ligand, **1.2c.4** have been synthesized and show some antiferromagnetic exchange.



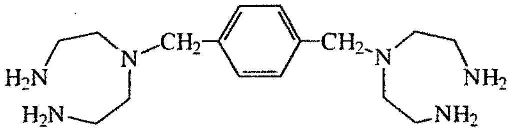
1.2c.3 (ref. 53)



1.2c.4 (ref. 54)

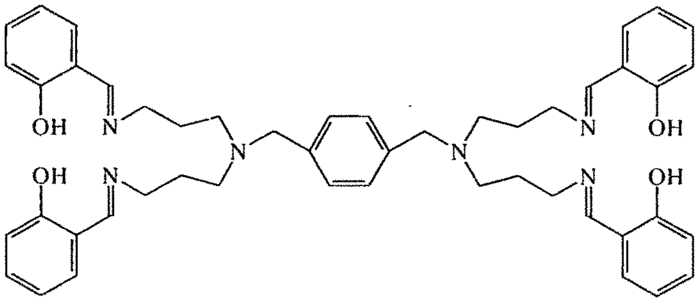
1.2c.3 Polypodal ligands: Polypodal ligands, or "wish bones" have been constructed by opening up each macrocycle in the bis-macrocycle,

The work of Martell and coworkers [55-58] showed that polypodal ligands based on the separation of two tridentate donor groups by a para-xylene bridge could be prepared incorporating phosphorous [55], nitrogen [56, 57] or arsenic donor atoms [58]. The ligand (**1.2c.5**) readily complexes two metals such as copper (II) or cobalt (II) and with later can act as an efficient dioxygen carrier [57].

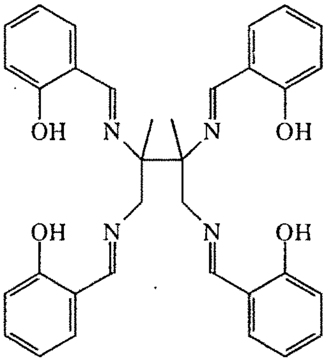


1.2c.5 (ref. 55-58)

Further examples of polypodal ligands stem from the work of Kida et al, **1.2c.6** [59] and **1.2c.7** [60]. Binuclear Cu (II) complexes have been prepared from these ligands and show little magnetic exchange properties.



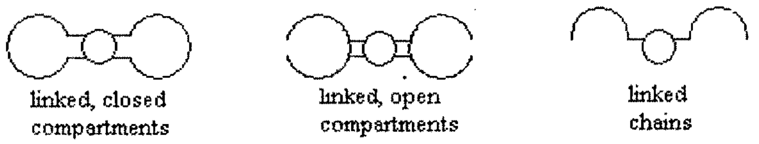
1.2c.6 (ref. 59)



1.2c.7 (ref. 60)

1.2d. Ligands with isolated donor sets separated by aromatic, or other, bridging functions:

These type of binucleating ligands can be broadly classified as in **Fig. 1.7**


linked, closed compartments

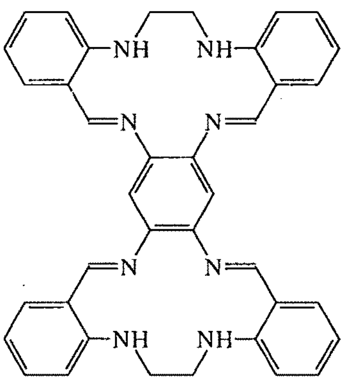
linked, open compartments

linked chains

Fig. 1.7 Isolated donor sets separated by aromatic, or other, bridging functions.

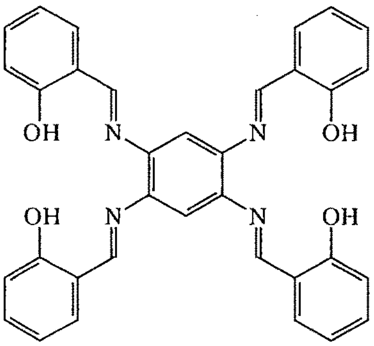
Separated donor sets:

1.2d.1 Linked-closed compartments: An example of this type of ligands is the bicyclic octadentate ligand consisting linked-closed compartments (**1.2d.1**). It was prepared by condensation of the components, tetraaminobenzene and 4,7-diaza-2,3,8,9-dibenzodecane-1,10-dione. Homobinuclear complexes of copper (II) and nickel (II) have been prepared from this ligand [61].

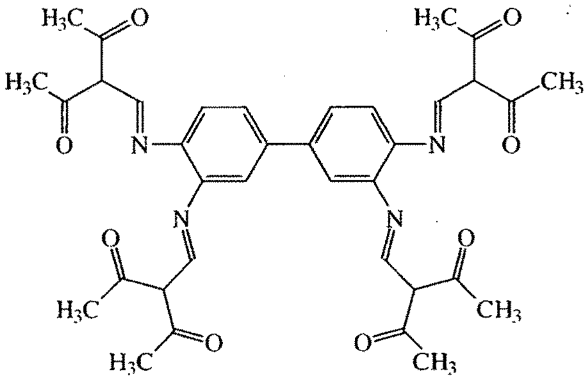


1.2d.1 (ref. 61)

1.2d.2 Linked-open compartments: Linked-open compartments related to the above subclass. Representative species are shown in **1.2d.2** [62] and **1.2d.3** [63]. Structural modifications have been made to **1.2d.2** in order to make the homobinuclear metal complexes of it. Substitutions have been made into the salicylaldehyde precursors.

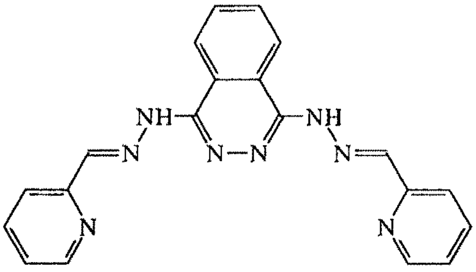


1.2d.2 (ref. 62)

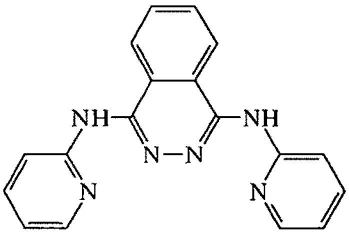


1.2d.3 (ref. 63)

1.2d.3 Linked-open chains: Representatives of binucleating ligands of this class, derived from 1,4-dihydrazinophthalazine, are **1.2d.4** [64] and **1.2d.4** [65]. The complex with ligand (**1.2d.5**) has been used in studies on catecholase activity [66].



1.2d.4 (ref. 64)



1.2d.5 (ref. 65)

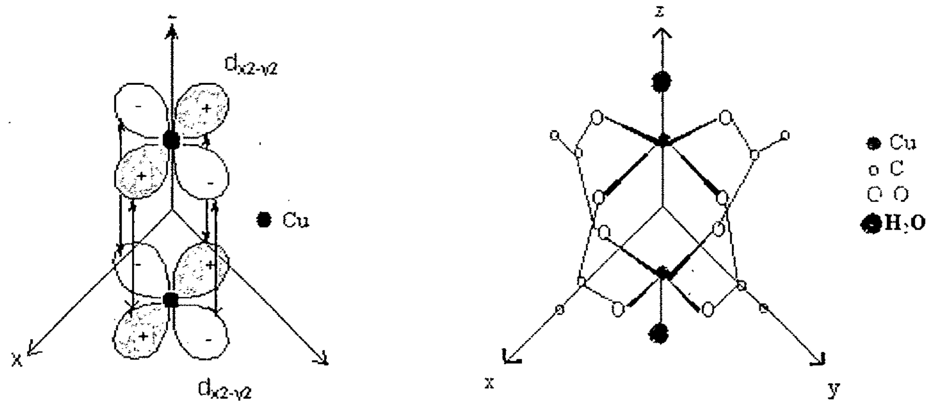
1.3. Magnetic Interactions:

The magnetic exchange in the compounds can be generally classified into two sub groups. The first type consists of metal oxides in which magnetic exchange occurs over the entire crystal lattice giving rise to a long range ordering. Under the second type are those complexes, in which the exchange is between different cation centers within the same molecules, leading to short range ordering. These two types can be called inter- and intra- magnetic exchange, respectively. Obviously, the binuclear transition metal complexes belong to later type.

Intramolecular magnetic exchange in binuclear complexes can take place in three different ways.

1.3.1 Direct metal – metal interaction:

In this type of interaction the spin exchange results by direct overlap of the orbitals of the paramagnetic metal centers containing the unpaired electrons. Figgis and Martin [1] in 1956 first put forth the idea that the antiferromagnetic interaction in $[Cu(CH_3CO_2)_2(H_2O)]_2$ is due to the existence of a δ-bond between the copper ions as shown in **Fig. 1.8**. Later it was proved to have superexchange interaction. Other metal acetates e. g. Chromium acetate, Molybdenum acetate and Rhodium acetate were shown to be diamagnetic due to M-M interaction [67-68]. This arises when, the two metal ions are held closely by binucleating ligands, oriented in such a way that the metal orbitals containing unpaired electrons are directed to overlap with each other. There is pairing of electron spins over the two metal centers, resulting in diamagnetism.



(a) (b)

Fig. 1.8 (a) An illustration of the δ-bonding in and (b) the structure of copper (II) acetate monohydrate. (after Figgis and Martin [1]).

1.3.2 Super exchange interaction:

The idea of "super-exchange" [69, 70] was originally put forth by Anderson [69]. This involves an exchange of the spins over two paramagnetic centers mediated by the orbitals present over an intermediate anion. In this mechanism, in addition to the metal d- orbitals, the filled orbitals of the intervening anion also take part. This can be explained with the help of **Fig. 1.9**

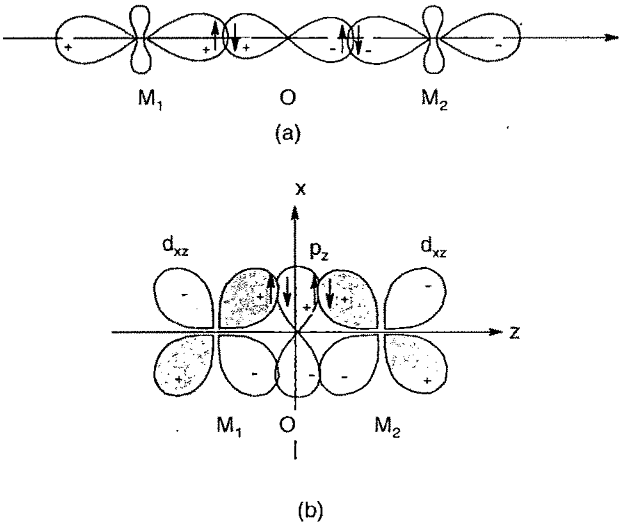


Fig. 1.9 Superexchange in a linear M-O-M system. An example of superexchange via (a) σ – bonding, and (b) π – bonding.

If, for example, a binuclear complex of a transition metal ion with a single unpaired electron involving O bridge is considered, in a linear M-O-M arrangement, the interaction may occur in two ways. There can be σ – bonding, or there can be π – bonding as shown in **Fig. 1.9a** and **Fig. 1.9b**, respectively.

A simple pictorial representation of the spin 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 this interacts with the electron on the other metal ion, the later 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.

Although, the main interest was in the O bridged binuclear copper (II) complexes, various complexes with halide or S bridge have been studied [71]. It has been pointed out that S or Br bridging in copper dimers should lead to stronger antiferromagnetism than O or Cl bridging respectively [72]. In case of exo-hydroxo or endo-alkoxo or endo-phenoxo bridging in binuclear copper (II) complexes there is overlap of the d_{x2-y2} orbital of the two copper (II) centers with the filled p_x orbital of the bridging O. This gives rise to a diamagnetic ground state and a paramagnetic triplet state, with a separation in energy of 2J, where J denotes the value of spin exchange interaction **Fig. 1.10**.

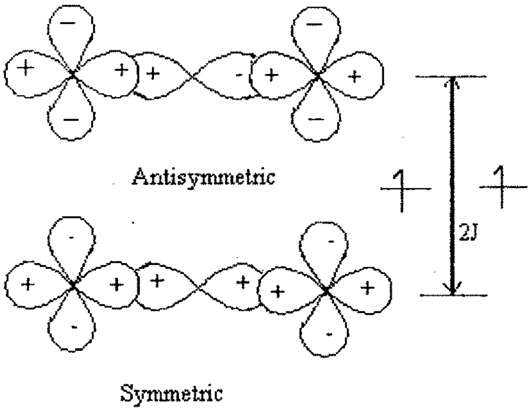


Fig. 1.10

For the dihydroxo – bridged copper (II) dinuclear species, the linear correlation between Cu-O-Cu bridging angle and the singlet – triplet energy gap (J) was first observed by Hodgson and Hartfield [73-80]. An antiferromagnetic interaction was found when the Cu-O-Cu angle was larger than 97.5°, but when the Cu-O-Cu angle was smaller than 97.5° a ferromagnetic interaction was observed to be present. Several theoretical approaches were applied to understand the behavior of the antiferromagnetic and ferromagnetic interaction of such dihydroxo – bridged copper (II) dinuclear species [81-88]. A linear correlation was established between the coupling constant J and the Cu-O-Cu angle.

In addition to the optimum value of the M-L-M angle (θ), the planarity of the binuclear core structure is also an important requirement, for the electronic interaction to take place [89, 90]. Kahn et al and Sinn et al showed the dependence of the value of J on the dihedral angle, between two copper coordination planes in O – bridged non planar dimers. There is maximum antiferromagnetic interaction between the magnetic orbitals, when the coordination planes are planar, θ being 0. Any distortion of the binuclear core structure from planarity, resulting in increase in dihedral angle, reduces the overlap of copper (II) d_{x2-y2} orbitals with the bridging oxide ion orbitals, and as a consequence the exchange interaction is weakened.

A trigonal planar geometry, (sp^2 hybridization) of the bridging atom, leads to good overlap between the copper (II) d_{x2-y2} orbitals and the bridging oxide ion orbitals with consequent strong antiferromagnetic coupling. As the geometry of the bridging atom approaches pyramidal / tetrahedral geometry, (sp^3 hybridization) with concomitant development of dihedral angle between adjacent copper – ligand planes, the J value approaches to zero, or becomes overall positive, and gives rise to ferromagnetism.

An interesting observation was made by Hendrickson and coworkers [91]. In case of the transition metal complexes of the binucleating ligand formed by the condensation of 2,6-diformyl-4-methyl phenol and 1,3-diaminopropane. The net antiferromagnetic interaction decreases monotonically in the series Cu (II) ($J = -294$ cm^{-1}), Ni (II) ($J = -27$ cm^{-1}), Co (II) ($J = -9.3$ cm^{-1}) and Fe (II) ($J = -4.2$ cm^{-1}), and finally becomes a net ferromagnetic exchange interaction with the Mn (II) complex where $J = + 0.2$ cm^{-1}. They attributed the variation in J value across the series to (1) the changing number of unpaired electrons and associated exchange pathways and (2) the increasing M – ligand plane distance in going from Cu (II) to Mn (II).

1.3.3 Magnetic exchange interactions propagated by multiatom bridges:

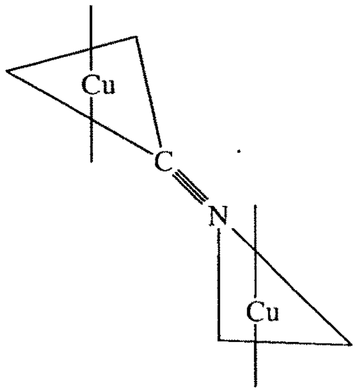
Apart from the two kinds of interactions mentioned above, magnetic exchange interactions have been observed to be taking place between metal centers bridged by more than one atoms [92]. Study of this type of magnetic exchange is also important to understand the mechanism of the thermal electron transfer between paramagnetic centers well separated by large organic molecules [93] and also biological electron transport over large distances [94–96]. Several studies have been carried out to determine the criteria for strongest magnetic exchange through multiatomic bridges. A variety of bridging groups have been considered.

1.3.3a Cyanide, Azide and Related Bridges:

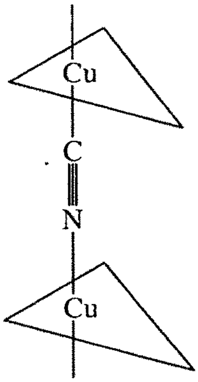
Cyanide ions are known to bridge in an end- to –end fashion between transition metal ions in polymeric and dimeric complexes [97, 98]. Hendrickson and coworkers reported the X – ray structure and the presence of a weak antiferromagnetic exchange interaction [99, 100] for $[Cu_2(macro)_2(CN)](ClO_4)_3$, where macro is the macrocyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Four binuclear copper (II) complexes, each with a single end – to – end cyanide bridge have been prepared. All four binuclear cations exhibit intramolecular antiferromagnetic interactions as summarized below:

Compounds	J (cm^{-1})
$[Cu_2(macro)_2(CN)](ClO_4)_3$	-4.8
$[Cu_2(bipy)_4(CN)](PF_6)_3$	-9.4
$[Cu_2(phen)_4(CN)](PF_6)_3$	-29.0
$[Cu_2(tren)_2(CN)](PF_6)_3$	-88.0

The copper (II) coordination geometries approximate to trigonal bipyramidal in all four of these complexes. The first three complexes essentially have a CN^- bridging from one equatorial position to another equatorial sites as indicated in **1.3.1a** In the case of tren complex the CN^- bridges from one axial coordination site to another axial site, as in structure **1.3.1b**.



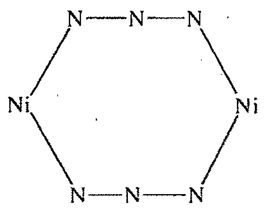
1.3.1a



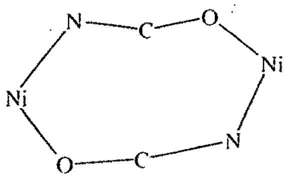
1.3.1b

It is clear that the tren complex exhibit the largest antiferromagnetic interaction, for d_{z2} ground states are present and the CN^- ion bridges directly between the main lobes of the two unpaired – electron d_{z2} orbitals. Of the three other binuclear complexes, the phen complex exhibits the largest interaction. This is the result of the fact that phen has more restricted "bite" than either of the two non – bridging ligands and consequently the copper coordination geometry in the phen complex is more distorted from trigonal bipyramidal. The increased distortion could result in a change in the orientation of the z – axis relative to the cyanide bridge, which brings the main lobe of the dz^2 orbital into overlap with the σ cyanide orbitals, or the increased distortion could mix in some amount of d_{x2-y2} into the ground state.

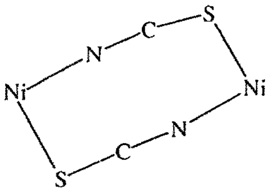
Ginsberg et.al. [101], Duggan and Hendrickson [102-105] synthesized series of nickel (II) complexes with the composition $[Ni_2(tren)_2X_2](BPh_4)_2$, where X is N_3^-, NCO^-, NCS^-, or $NCSe^-$. The most important factor in determining J in this series is the symmetry of the bridging units in these complexes, **1.3.2.** The extent of net antiferromagnetic exchange decreases, in the case of the N_3^- complex with $J = -35\ cm^{-1}$, NCO^- complex ($J = -4.4\ cm^{-1}$) and then becomes net ferromagnetic for the NCS^- ($+2.4\ cm^{-1}$) and $NCSe^-$ ($+1.6\ cm^{-1}$) complexes. The antiferromagnetic interaction in the azide – bridged complex reflects the symmetry of the bridging and N-N-Ni angle of 135°. It is the 90° C-S-Ni angle in the NCS^- complex that sets stage for the net ferromagnetic interaction in this complex. P. Talukder [106] reported end-to-end single cynato and thiocynato bridged copper (II) polymeric complexes. The magnetic susceptibility data show slight antiferromagnetic coupling. The low values of J are consistent with the equatorial-axial disposition of the bridge in polymers. J. Shi et al [107] also studied, thiocynato bridged polynuclear copper (II) complexes. An ESR and variable temperature susceptibilities measurements reveal that there exists a strong antiferromagnetic coupling between the bridging copper (II) ions. The strong antiferromagnetic interaction is attributed to the good magnetic orbital overlap via the $\mu_{1,3}$-SCN- bridge.



1.3.2a N_3^-



1.3.2b NCO^-

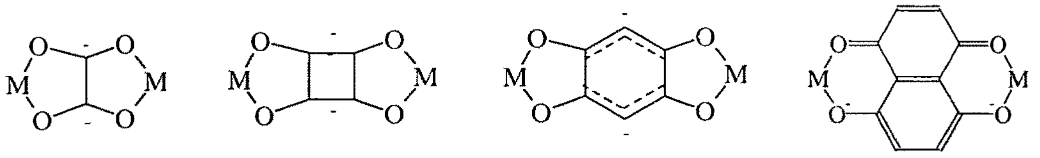


1.3.2c NCS^-

Felthouse et al. [108] had reported that two N_3^- ions can support an exchange interaction between two copper (II) ions. The series of the complexes $[Cu_2(dien)_2(N_3)_2]X_2$ was prepared and characterized, where "dien" is dpt, Me_5dien, or Et_5dien and X is BPh_4^- or ClO_4^-. The X – ray structure of the Me_5dien- BPh_4^- species was determined to find Cu-Cu = 5.2276 A° in this complex that has $J = -6.5$ cm^{-1}. In the whole series of complexes the J value ranged from 0 to –11.1 cm^{-1}. Thompson et al studied, extensively, azide bridged binuclear copper (II) complexes and effects of non bridging ligand on the values of J, indicated ferromagnetic to antiferromagnetic exchange [109]. O. Kahn and his colleagues studied azido bridge as an exogenous ligand [110, 113]. Several other workers [112-115] reported DFT calculations and nature of the magnetic coupling in such asymmetric end-on and end-to-end N_3-bridges. Results show that the double asymmetric end-on bridge produce antiferromagnetic coupling while end-to-end ones can present ferro – or antiferromagnetic coupling depending on the coordination sphere.

1.3.b Oxalate, Oxime, and Related Bridges:

Copper acetate is the very first member of the series of compounds synthesized with multiatom bridges. Studies on binuclear complexes with di- or tri- atomic bridges have been reviewed by Hendrickson [116]. The basic mechanism of super exchange i.e. the conveyance of the unpaired spin from one metal to the other through the orbitals of the bridging atoms can be considered to be applicable for the case of multiatom bridges also. If this would be the only criterion for the magnetic exchange, the extent of interaction would be dependent only on the distance between two metal centers or the number of the bridging atoms. In a series of binuclear complexes bridged by oxalate [117-125], squarate [117, 126] and the dianion of 2,5-dihydroxybenzoquinone [108], as shown in **1.3.3a to 1.3.3d** , the largest interaction is found for the μ – oxalate complex as expected on the basis of the Cu – Cu separation, but the next largest interaction is found for the dihydroxy benzoquinone complex and not the squarate complex [108, 117].



a. (Oxalate) b. (Squarate) c. (DHBQ) d. (DHNQ)

(1.3.3a to **1.3.3d)**

Amongst several other studies reported are the comparison between the magnetic exchange via squarate, naphthazarin, quinizarin [127], and aromatic diamines. Magnetic exchange parameter and intramolecular Ni-Ni distances in the series $[Ni_2(tren)_2(bridge)](BPh_4)_2$ were determined. All four binuclear cations exhibit intramolecular antiferromagnetic interactions as summarized below :

Compounds	J (cm^{-1})	Ni-Ni, A°
$[Ni_2(tren)_2(Ox)](BPh_4)_2$	-16.0	5.4
$[Ni_2(macro)_2(Sq)](ClO_4)_2$	-0.4	6.9
$[Ni_2(tren)_2(DHBQ)](BPh_4)_2$	-1.1	7.9
$[Ni_2(tren)_2(DHNQ)](BPh_4)_2$	-0.1	8.1

A general conclusion can be drawn from all these studies. As pointed out earlier by Hendrickson [127] the magnetic exchange through multiatomic bridges does not depend on the distance between the paramagnetic centers, it depends more on the symmetry and energy of the exchange propagating orbitals.

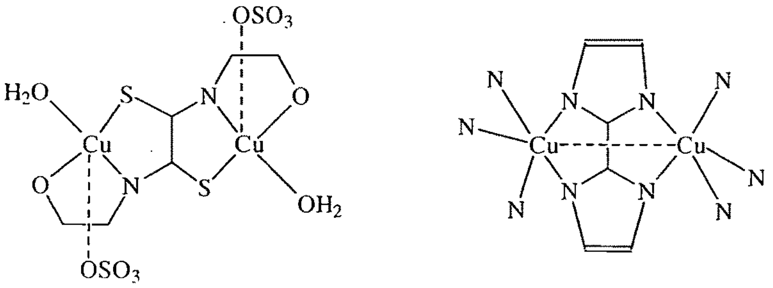
Extensive studies have been carried out by Kahn and coworkers [128, 129] and other groups [130] on the oxalate bridged complexes. Kahn and coworkers could 'tune' the magnetic exchange in these complexes by varying the non bridging ligands [131]. These observations paved a way for designing the binuclear complexes with desired magnetic properties. Several complexes of ligands derived from oxalate, like oxamates and oxamidates, have been extensively studied. The studies have concluded that all these complexes are strongly exchange coupled with the values of J increasing in the order [132] -

$$\text{oxalate} < \text{oxamato} < \text{oxamidato}$$

The magnetic exchange could be tuned in the μ-oxamido complexes also by varying the nature of the ligand [133].

M. Julve et al [134-136], reported heterobimetallic oxalato-bridged M(II) Re(IV) complexes, (M = Cu, Mn, Fe, Co). A very weak antiferromagnetic coupling between Cu(II) and Re(IV) and Mn(II) Re(IV) occurs, whereas a significant ferromagnetic interaction between Re(IV) and Fe, Co was observed. Orthogonality between magnetic orbitals in these binuclear complexes lead to ferromagnetic coupling and distortion in the coordination geometry introduce some orbital overlap, turning the interaction weakly antiferromagnetic.

In di – μ-aqua-bis{μ- {N,N'-bis(2-hydroxy ethyl) dithiooxamidato(2-)-N, O, S : N', O', S'}-bis{aqua copper (II) sulphato copper (II) } i.e. $[Cu_2S_2C_2(N(CH)_2\ OH_2)(H_2O)_2]SO_4$ **(1.3.4a)** the bridging of the dithiooxamide ligand results in very strong antiferromagnetic coupling ($J = -523\ cm^{-1}$), despite the Cu.........Cu distance of 5.65 A° [137]. By contrast, the planar bridging role of the 2,2'-bibenzimidazolate dianion in μ-2,2'-bibenzimidazolate bis (1,1,4,7,7-pentamethyl diethylene triamine) dicopper (II) tetraphenylborate i.e. $[Cu_2(Me_5dien)_2(biim)](BPh_4)_2$ **(1.3.4b)** results in zero exchange coupling ($J \sim 0.5\ cm^{-1}$) between the copper (II) atoms separated by 5.49 A° [138]. Several other scientists have studied the extent of magnetic exchange in binuclear complexes of oximato and related bridging groups [139-142].

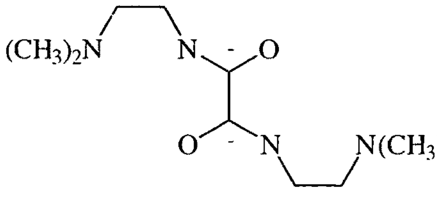


(a) (b)

1.3.4a $[Cu\ S_2C_2(N(CH_2)_2OH_2)(H_2O)_2]SO_4$

1.3.4b $[Cu_2(Me_5dien)_2(biim)](BPh_4)_2$

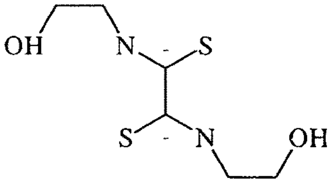
Yoshino and Nowacki [143] reported the structure of $[Cu_2(DMAEO)(NCS)_2(DMF)_2]$, where DMF is N, N' – dimethylformide and DMAEO is (**1.3.5a**)



1.3.5a

Each copper (II) ion has a square – pyramidal coordination geometry with an axial DMF ligand and one NCS$^-$ ligand completing the square plane. Felthouse [144] reported the magnetic susceptibility for this complex from 270 to 81.6 °K. The data were least squares fit to give $J = -291\ cm^{-1}$. This is a particularly strong interaction in view of the large Cu-Cu distance of 5.153 A°.

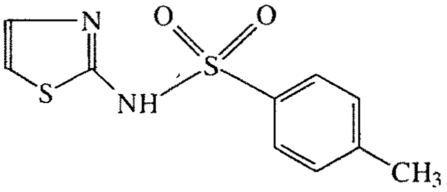
Kahn and coworkers [145] studied the antiferromagnetic exchange in two isomeric binuclear copper (II) complexes bridged by the following dithiooxamide (**1.3.5b**)



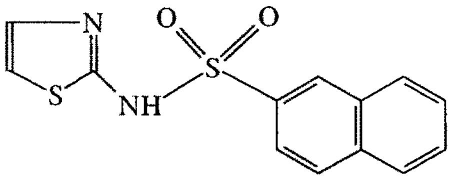
1.3.5b

Strong antiferromagnetic interactions with J = -297 cm^{-1} and –261.5 cm^{-1} were found in spite of large Cu-Cu distance of 5.61 and 5.65 A°, respectively.

J. Borras et al [146] reported dinuclear copper (II) complexes with N-substituted sulfonamide ligands i.e. [Cu_2(tz-tol)$_4$] (1) and [Cu_2(tz-naf)$_4$] (2) where Htz-tol = N-(thizole-2yl)toluenesulfonamide and Htz-naf = N-(thizole-2yl)naphthalenesulfonamide (**1.3.6a** and **1.3.6b)**



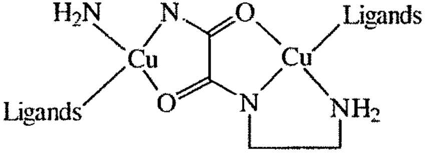
1.3.6a Htz-tol



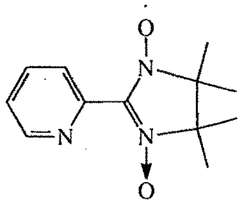
1.3.6b Htz-naf

The coordination geometry of the copper (II) in the dinuclear entity of 1 and 2 is distorted square planar with two N-thiazole and two N-sulfonamide atoms. Magnetic susceptibility data shows strong antiferromagnetic coupling with 2J = -121.3 cm^{-1} for compound (1) and 2J = -104.3 cm^{-1} for compound (2). The lower value of J in complex (2) is affected by naphthalene groups, bulkier size decreases the effective overlapping of metal orbitals with MOs of ligands.

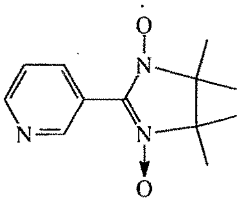
D. Zhang et al [147] studied trans-oxamido bridged copper (II) binuclear units [Cu(oxen)(PYNN)]$^{2+}$, (**1.3.7a)** forming helical chains. The ligands used were oxen = N,N-bis(2-aminoethyl)oxamide] and pyridine-substituted nitronyl nitroxide radicals (o-, m- and p-). (**1.3.7b** to **1.3.6d**)



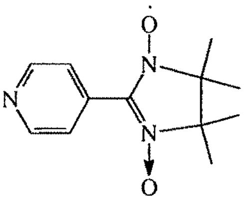
1.3.7a



1.3.7b



1.3.7c



1.3.7d

The coordination geometry around each copper (II) ion is distorted square pyramidal. The distance between metal centers are very close in each complexes. Yet the interactions between spin centers arising in these types of heterospin complexes were found to be affected upon by the coordination with nitronyl nitroxide radicals directly or indirectly. The intramolecular magnetic interactions in these complexes are summarized below-

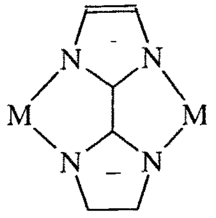
Compounds	J (cm^{-1})	Cu-Cu, A°
$[Cu_2(oxen)(o\text{-}PYNN)]^{2+}$	-150.5	5.473
$[Cu_2(oxen)(m\text{-}PYNN)]^{2+}$	-191.7	5.193
$[Cu_2(oxen)(p\text{-}PYNN)]^{2+}$	-183.5	5.235

It was shown that the exchange between Cu (II) ions through oxamido bridge was strongly antiferromagnetic while the net magnetic exchange between the heterospins, viz. Cu (II) and nitroxide radical, was found to be weakly ferromagnetic.

1.3.3c N-Hetrocycles and Aromatic amines as bridging groups:

An imidazolate bridge was suggested as a pathway for the strong antiferromagnetic interaction [148-150]. The general bridging arrangement for an imidazolate bridge (**1.3.8a**) and for a biimidazolate bridge (**1.3.8b**) can be depicted as follows:

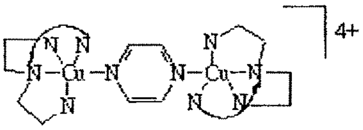
1.3.8a



1.3.8b

A number of binuclear copper (II) complexes having imidazolate or biimidazolate bridging units have been reported [151-153]. The intramolecular exchange interaction in these complexes is antiferromagnetic with J ranging from essentially 0 to –88 cm^{-1}. The copper (II) ground states have included d_{x2-y2} and d_z^2 states. There was interest in determining whether σ – or π – type molecular orbitals of the imidazolate ions are most effective in propagating the superexchange interaction. The evidence was sought in the appreciably antiferromagnetic interaction with J = -38 cm^{-1} in $[Cu_2(tren)_2(Im)](PF_6)_3$. The main lobes of the d_z^2 unpaired - electron orbitals in this complex point directly at the nitrogen atom lone pairs of the bridge. Thus, to the first approximation there is a σ – type of interaction in these complexes [151, 152].

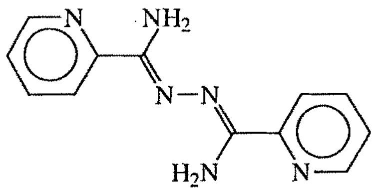
Pyrazine has been employed as a bridge in a few polymeric copper (II) complexes [154, 155]. Hoffmann and coworkers [156] employed the extended Huckel molecular orbital approach to predict that pyrazine would be very effective in supporting antiferromagnetic interactions with a σ – type of exchange path way (**1.3.9**). In response to this prediction, Haddad et al [157] prepared $[Cu_2(tren)_2(pyz)](ClO_4)_4$ and the two analogous compounds with the composition $[Cu_2(tren)_2(X)](BPh_4)_4$, where the X is either 4,4'-bipyridine or 1,2-bis(4-pyridyl)ethylene.



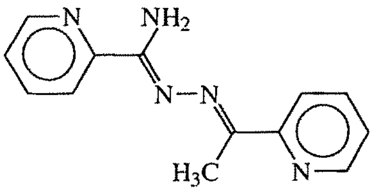
1.3.9

Polyfunctional ligands containing the diazine moiety, such as pyrazole [158 -162], phthalazine [163], pyridizine [164] and 1,2,4-triazoles have attracted attention as they contain the delocalized π – systems. In the binuclear complexes of these ligands, the antiferromagnetic coupling was generally found to be stronger via pyridazine bridge than via a phthalazine bridge [163]. Amongst the five membered ring diazine systems, pyrazolate [158 -162] has the capacity to propagate the antiferromagnetic exchange more efficiently than 1,2,4-triazole or 1,2,4-triazolate bridge due to the presence of third electronegative N in the later. Study of the imidazolate bridged dicopper (II) complexes indicated that the π – orbitals of the imidazolate ligand do not involve in coupling and the extent of spin exchange depends on the Cu-N-N angle [165 - 168], the dihedral angle and the elevation of Cu(II) with respect to the coordination plane.

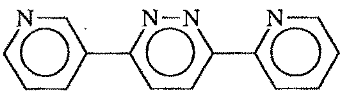
L. K. Thompson et al [169-171] extensively studied a series of copper (II) complexes with bridging (N-N) diazine ligands, (**1.3.10a** to **1.3.10d**)



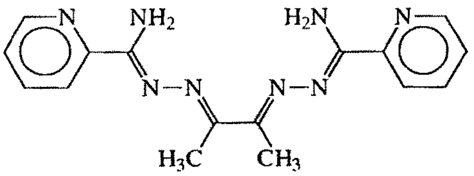
1.3.10a pahap



1.3.10b pmhap



1.3.10c dppn



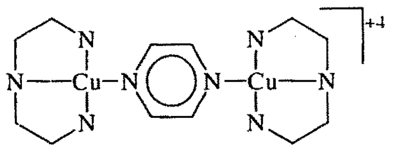
1.3.10d bdpah

1.3.10 Open chain diazine ligands.

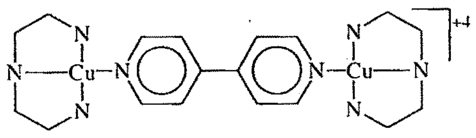
They have [169] reported that the spin exchange in these complexes depends on – (a) strict orthogonality between the copper magnetic orbitals, or accidental orthogonality resulting from the critical twist angle around N-N bond. (b) Rotation of the copper-magnetic planes about a single N-N bond at larger angles, due to additional bridging and hydrogen bonding or steric interactions and the exchange coupling becomes antiferromagnetic. The extent of magnetic exchange in these complexes is summarized below:

Compounds	J (cm^{-1})
$[\mathrm{Cu_2(pahap)_2(NO_3)(H_2O)][NO_3]_3.H_2O}$	-1.1
$[\mathrm{Cu_2(pmhap)_2(NO_3)][NO_3]_2.3H_2O}$	-
$[\mathrm{Cu_2(pahap)(dppn)(NO_3)(H_2O)][NO_3)}$	-16.2
$[\mathrm{Cu_2(pahap)(C_2O_4)].0.5H_2O}$	-2.2
$[\mathrm{Cu_2(pahap)(acac)_2(H_2O)_2][NO_3]_2.H_2O}$	-34.8
$[\mathrm{Cu_2(pahap\text{-}H)(dpa)_2]_2[(NO_3]_4.4H_2O}$	-93.2
$[\mathrm{Cu_2(bdpah\text{-}H)(NO_3)_2].[NO_3)}$	-56.0

Dinuclear copper (II) complexes bridged by pyrazine [172, 173] and 4,4'-bipyridine were extensively studied [172, 174], values of J at variable temperatures indicated that the extent of spin exchange depends on the good matching of molecular orbitals of bridging ligand and paramagnetic orbitals of metal centers. It was also shown that the J is greater for pyrazine bridge [172] (**1.3.11a**) than 4,4'-bipyridine bridge (**1.3.11b**).



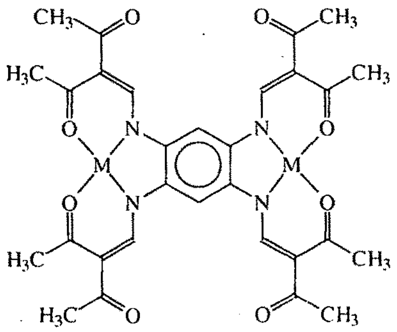
1.3.11a



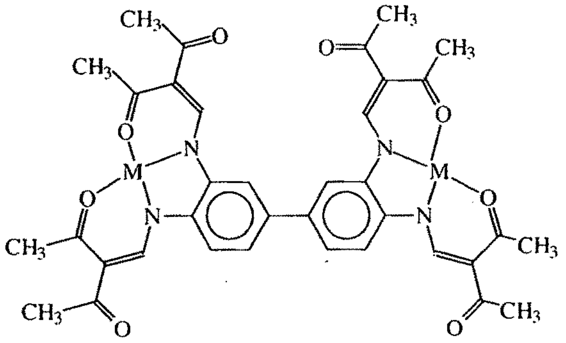
1.3.11b

Hendrickson et al reported magnetic exchange of binuclear copper (II) complexes of the type, **1.3.12a** and **1.3.12b**, in which both metal centers are connected through phenyl or substituted biphenyl ring [175]. An intramolecular antiferromagnetic exchange interaction is observed in complex, **1.3.12a** where J = -12 cm^{-1}. The Cu-Cu distance in this complex is 7.5 A°. There was no evidence for a magnetic exchange interaction in the magnetic susceptibility data for complex, **1.3.12b** measured to 4.2 °K. The intramolecular nature of the interaction seen for the complex (**1.3.12a**) was substantiated by the appearance of the copper hyperfine coupling in the EPR spectrum for a doped sample of this complex.

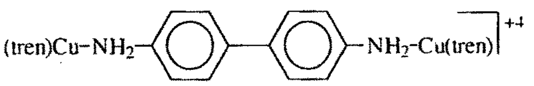
In view of the large Cu-Cu distance in excess of 12 A°, that an antiferromagnetic interaction with J = -3 cm^{-1} was reported [166] for copper (II) complex (**1.3.12c**).



1.3.12a



1.3.12b



1.3.12c

The X- ray structure was determined for the NO_3^- salt. Each copper (II) ion has trigonal bipyramidal coordination geometry. There are two crystallographically different, but similar binuclear NO_3^- salts. The biphenyl moieties in the two complexes have non – zero dihedral angle of 13.8° and 22.5°. Furthermore, the central C-C bond of each biphenyl bridge is a single bond. If there is an intramolecular interaction in these complexes, the exchange interaction is, to first order, propagated by a sigma interaction.

The dinuclear complexes with phthalate bridges have also been extensively studied [176 - 179]. Both ferromagnetic and antiferromagnetic interaction have been observed in these complexes. The terephthalato dianion has been proved to be an appropriate bridging unit to design magnetic systems with a longer, about 10 – 12 A° separation between two magnetic centers [172, 176, 180 - 183]. The intramolecular magnetic interactions in most of these complexes were observed to be negligibly small.

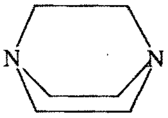
Intra chain ferromagnetic and inter chain antiferromagnetic spin exchange was observed through terephthalate bridges in [(μ-terephthalato)(ethylenediamine)] diaquacopper (II) chains have been observed [183].

An unexpected strong antiferromagnetic exchange, $J = -25.9\ cm^{-1}$, was observed through terephthalato bridged copper (II) dimers, $[Cu(\mu\text{-}TPHA)(bipy)_2(H_2O)](ClO_4)_2$ [176].

Later, another terephthalato bridged complex, $[L_2Cu_2(OH)_2(\mu\text{-}terephthalato)](ClO_4)_2$ was observed to have moderately strong intradimer magnetic exchange [184] , emphasizing the need for matching of geometrical parameters in the molecule rather than the type of bridging group.

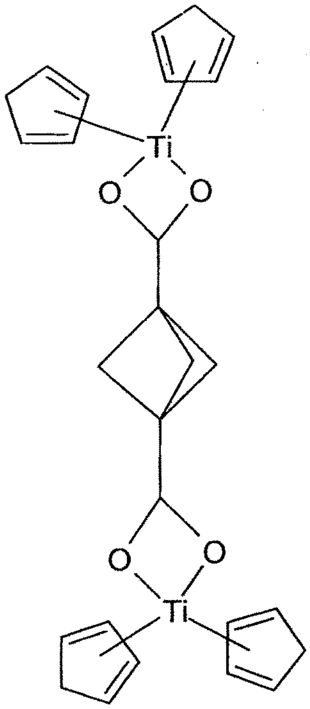
1.3.3d Metal complexes with saturated bridges:

Hoffmann et al [185] suggested that the through-bond coupling in dabco (**1.3.13a**) would provide an effective σ – type of exchange pathway. However, there is no evidence of an exchange interaction in $[Cu_2(tren)_2(dabco)](ClO_4)_4$ down to 4.2 °K [157].



1.3.13a dabco

Hendrickson and his coworkers[186] synthesized sixteen binuclear Ti (III) complexes with saturated bridges and six unsaturated bridges. Structure of the complex (**1.3.13b**) was analyzed by X- ray technique.



1.3.13b

Titanium hyperfine observed in the solution – state EPR spectra for several complexes confirmed the presence of intramolecular magnetic exchange interaction between the two Ti (III) ions. An interaction with J >> 0.001 cm^{-1} can be propagated by a saturated –C-C-C- linkage. Antiferromagnetic exchange interactions (J = -0.8 to –3.0) were observed for several other binuclear complexes in the solid state.

1.3.3e Magnetic exchange through Paramagnetic Ligands and H-bonds:

The role of nitroxyl radical in spin exchange interaction with transition metal ion has been extensively studied by K. Wieghardt and coworkers [187-189]. Eaton et al [190, 191] have made a number of observations where the nature of the molecular linkage between the nitroxyl radical and a paramagnetic metal ion affects the magnetic exchange interaction. They determined J values for the interaction of spin – labeled pyridines coordinated to copper bis (hexafluoroacetylacetone) and two vanadyl complexes [170]. The nitroxyl radical was attached to the pyridine ring by either an amide (-NH-CO-) or urea (-NH-CO-NH-) linkage. It was found that J is larger for a ligand with an urea linkage between pyridine ring and nitroxyl ring than for a ligand with an amide linkage. The addition of a -CH_2- group between the pyridine ring and the amide or urea linkage led to a decrease in the value of J.

Hydrogen bonds between H_2O molecules coordinated to nearest neighbor transition metal ions have been shown to be the magnetic exchange propagating pathways in a number of hydrated metal salts [191]. Bertrand reported [192, 193] an unusually large antiferromagnetic interaction with J = - 94 cm^{-1} for a dimeric copper (II) complex with Cu-Cu = 4.979 A°. Each copper (II) ion is coordinated by the dianion of the ligand that results from condensing two molecules of 2 – aminoethanol with 2,4-pentanedione. The dimeric association results from a hydrogen bonding between such units. It has been recognized that the H – bonds play a major role in the transmission of ferromagnetic interaction in organic ferromagnets [194].

Bis-(μ-methoxo)dichromium (III) complexes with 2,2'-selenobis(4,6-ditert-butylphenol) have been shown to undergo exchange coupling which can be tuned by the presence of H-bonds [195].

R. K. H. Singh and colleagues [196] studied copper (II) binuclear complexes of 1-phenylamidino-O-alkylurea (alkyl = n- and iso-butyl) with 1,3-diaminopropane or ethylenediamine, evaluated the isotropic exchange interaction constant J on the basis of temperature dependence of the EPR signal intensity. It appears that long range ferromagnetic exchange between two interacting spins of binuclear complexes is mediated through hydrogen bonding between copper (II) ions.

Several other reports have appeared on the magnetic interactions involving paramagnetic ligands or H-bonds. However these, these will not be discussed here as they have little relevance to the present work.

Hypothesis of the present work:

In the binuclear transition metal complexes the metal ions are held together in a molecule by multidentate ligands and except in the M-M bonded systems, they are bridged by either monoatomic or multiatomic bridges. The type (antiferromagnetic or ferromagnetic) and extent of magnetic exchange interaction between the orbitals of the coupled paramagnetic metal ions and the orbitals of the bridging atom can lead to the spin coupling and a ground state with different multiplicity.

The extent of spin exchange is sensitive to minor changes [76-78, 197-205] like-

(i) The energy of interacting orbitals.
(ii) The variation in geometrical parameters

These are further affected by

(a) The metal - ligand bond length.
(b) The M-L-M bridging angle (ϕ), **Fig. 1.11a**
(c) The dihedral angle between metal coordination planes, θ.
(d) The torsional angle Γ, **Fig. 1.11b**
(e) The degree of planarity of the bridging unit.

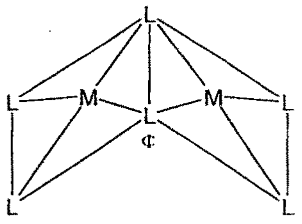


Fig. 1.11a

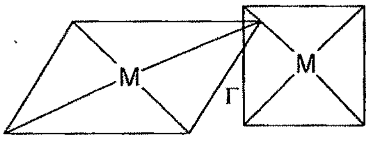


Fig. 1.11b

Thus, the low spin – high spin energy gap directly depends on the extent of overlap of the two magnetic orbitals with the bridging atom orbital in case of the complexes with monoatomic bridges. In case of the complexes involving multiatomic bridging units the low spin – high spin energy gap depends on the relative disposition of the magnetic orbitals. Also, it has a possible dependence on the energy of the magnetic orbitals and various molecular orbitals with appropriate symmetry.

In most cases this type of exchange through multi atomic bridges has been shown to take place through the π -symmetry orbitals of the bridging ligand. However, it has also been suggested [166, 184] that the σ – orbitals can participate in the super exchange over a long distance in multiatomic bridges and lead to a spin exchange, yet, such interactions may be very weak.

A complete understanding of the electron and spin exchange phenomenon can also help in achieving sequential electron transfer. This can be helpful in tuning the redox potential of the catalysts used in redox reactions to suit the substrate and thus can be helpful in developing catalytic materials also.

Variation in the bridging ligand can directly affect the nature of the bridging molecular orbital participating in the exchange where as change in the non-bridging part of the ligands, the symmetry of π-orbitals and their ability to delocalize electron density can also play important role in mediating the magnetic exchange in the complexes with multiatomic bridges.

As mentioned above, a number of parameters affecting the magnetic exchange have been identified. However, the areas such as the modification of energy of ligand and metal orbitals by presence of distant groups on the ligands, the effect of non bridging ligands on the spin exchange, the deviation from planarity of the bridging system on the magnetic exchange have still remained not fully understood.

Objective of the work:

In order to understand the role of some of these parameters in moderating / enhancing the spin exchange, we have selected four main types of binuclear complexes.

1. π - delocalized bi-bridge binuclear complexes.
2. Ternary binuclear complexes.
3. Binuclear complexes with σ-bonded bridges.
4. Ternary binuclear complexes with planar bridges.

The main objective of the present work is to study the effect of structural changes in the ligands and the change in nucleophilicity of the coordinating atoms by virtue of change in the substiuents present over the ligand on the magnetic exchange in the binuclear transition metal compounds.

The substitutions over the ligands have a significant effect on the electron density on the two paramagnetic metal centers and hence on the extent of the super exchange interaction. An electron withdrawing group on the ligand reduces the electron density on the metal ion, whereas, an electron releasing group increases the electron density, with consequent increase and decrease, respectively, of the spin exchange interaction between the two metal centers. The work was executed in the following steps to achieve the goal.

1. π - delocalized bi-bridge binuclear complexes:

Ten new biphenyl based binucleating ligands have been synthesized by condensation of 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenylsulphone or 3,3'-diaminodiphenylsulphone with o-hydroxy carbonyl compounds, namely, 2-hydroxybenzaldehyde, 2-hydroxynaphthaldehyde, 2-hydroxy-3-methoxybenzaldehyde or 5-bromo-2-hydroxybenzaldehyde. Symmetrical dicopper (II) complexes with these ligands have been synthesized. In this case change in bridging diamine can affect the coplanarity of the magnetic orbitals where as variations in the M-L bond strength can be achieved by change in carbonyl part.

2. Ternary binuclear complexes:

Ternary binuclear complexes containing the above mentioned ligands and tertiary diamines namely, 2,2'-bipyridine or 1,10-phenanthroline, have been synthesized by reactions of corresponding mononuclear copper (II) with the aromatic diamines. The presence of a π – acidic tertiary diamine is expected to affect the coordination geometry and the energy of metal centers while the presence of a single bridging group can provide more flexibility to the molecule to achieve greater stability.

3. Binuclear complexes with σ – bonded bridges:

As mentioned earlier, the σ – bonded bridges can propagate weak exchange interactions, however, their role is not fully understood. In order to understand this, two new binucleating diamides, bis(picolinoyl)butane diamine and bis(picolinoyl)hexane diamine, have been synthesized. The symmetrical binuclear complexes and ternary binuclear complexes involving these diamides and tertiary diamines 2,2'-bipyridine or 1,10-phenanthroline or derivatives of 2-hydroxybenzoic acid have been synthesized.

4. Ternary binuclear complexes with planar bridges:

New binucleating ligands based on 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone have been synthesized by condensation with benzoyl hydrazine, phenylacetyl hydrazine, nicotinoyl hydrazine and isonicotinoyl hydrazine. Ternary binuclear complexes of copper (II) possessing these binucleating hydrazones and tertiary diamines or derivatives of 2-hydroxybenzoic acid have been synthesized.

All the ligands have been characterized by analysis and various spectral techniques. The complexes have analyzed by elemental analysis, UV-VIS, FTIR and conductivity. ESR and FAB-mass spectra of the representative complexes have been recorded. The magnetic property of the complexes has been studied from LNT to RT and the values of coupling constant J have been evaluated. A correlation between the J values and the type of ligands and geometrical parameters has been attempted.

Antibacterial activity: Mixed ligand complexes play an important role in biological processes as exemplified by many instances in which enzymes are known to be activated by metal ions [206]. Copper (II) complexes have great variety of biological properties ranging from anticancer [207], antibacterial [208] and antiviral [209] activity. Copper (II) complexes containing polypyridine ligand like 2,2'-bipyridine and 1,10-phenanthroline have shown to be useful as photophysical and chemical probes of DNA in view of their relevance to various biochemical and biomedical application [210]. The binucleating ligands used in the last chapter have functional groups, viz. phenolate, hydrazone, carbonyl which are known to have important biological activity. The complexes of the non bridging ligands used also have potent biological activity hence it was thought of interest to examine the activity of these compounds and verify the effect of metal coordination. Antibacterial activity of these ligands and complexes have been also found out against, *S. aureus, B. megaterium* (gram positive) and *S. typhi, S. marsescens, P. vulgaris* (gram negative) strain.

The details of the work are presented in the following chapters.

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