CHAPTER 1

1.1 General Introduction
1.2 Hypothesis and Objectives of the present work
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1. Introduction

With the advent and spread of information technology, the demand for more efficient devices for information storage and processing is increasing and hence is the demand for magnetic devices and novel magnetic materials. Molecular magnets[1] are of great interest in this respect. They belong to a field which is still at an early stage of development. Molecular magnets are the systems where a permanent magnetization and magnetic hysteresis can be achieved (although usually at extremely low temperatures) not through a three-dimensional magnetic ordering, but as a purely one-molecule phenomenon. The engineering of molecular magnetic systems requires the search for high-spin components, which are usually available with transition metal coordination centres,[2-4] and their arrangement in sutaible molecular/supramolecular architectures so as to induce spin coupling and alignment. Of special interest is the search for ferromagnetism towards which significant progress has been made.[1,3-10]

Though it has begun in 1951 with the study of a binuclear complex, copper acetate,[11] it was only in the 1980s that the first molecular – based solids exhibited spontaneous magnetization below their Curie temperature.[12] The observations provided a strong impetus for the study of bi- and multimetallic systems. 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 1970's 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 neighbouring metals were expected to "cooperate" in promoting reactions, and electronic interactions between metals which 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,[13,14] 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.

Amongst the numerous multimetallic proteins, those with Type 3 copper site are some of the most significant and structurally well characterised. Tyrosinase, an important enzyme with both oxidase and oxygenase acitivity and hemocyanin, the molluscan oxygen carrier, both contain coupled binuclear copper active site. Cytochrome C oxidase, the terminal respiratory enzyme contains up to 12 subunits[15,16]. Subunits I, II, III (encoded by the mitochondrial genome) are thought to form the core of a functional enzyme. Within this core reside the redox active metal centres. The site of dioxygen reduction is a binuclear metal centre comprised of cytochrome a_3 and Cu_8. The multicopper oxydases, laccase, ascorbate oxidase and ceruloplasmin, catalyzing four electron reduction of dioxygen to water[17,18] consist of a combination of Type 1, Type 2 and Type 3 active sites, which undergo superexchange interaction through endogenous bridging OR^- within the binuclear centre. The active site in laccase and ascorbate oxidase is shown to be essentially trinuclear.

There are several ligands in the biological systems, which possess more than one, coordination centres. In the presence of excess of metal ions, they can quite easily form homo or hetero binuclear or polynuclear complexes.[19-27] 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 the metalloproteins whose biological functions are associated with metal centres in pairs.[28-31] 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.

Much effort have been spent on the synthesis of mono-, bi-, and trinuclear copper complexes as functional and structural models of multicopper enzymes.[32-34] Apart from the biological significance, polynuclear metal complexes and complex assemblies are of great interest from the magneto-chemical point of view.[35] Although the field of copper(II) complexes has been extensively studied with respect to binuclear systems,[1] only comparatively few examples of complexes containing more than two Cu centres have been reported. One approach for the synthesis of discrete polynuclear complexes is the introduction of compartmental ligands capable of holding together two or more metal ions.[36] Another way toward polynuclear complexes is the use of bi- or tridentate terminal ligands[37] and multiatomic bridging ligands such as carboxylate groups.[38] In trinuclear complexes, the metal atoms are arranged in either a triangular[39-40] or a linear fashion,[41-43] with the later case being less common. Polydentate ligands with flexible linker groups positioned between terminal donor units can coordinate in a variety of ways leading to helicate structures,[44-45] and self assembled clusters and grids,[46-55] depending on the relative orientation of the terminal donor sets. The predominant magnetic interaction between the metal centres in the most of the known polynuclear copper(II) complexes is antiferromagnetic, which is in accordance with the antiferromagnetically coupled metal centres in the active sites of a multicopper enzymes. Whereas, cases of a ferromagnetic interaction in polynuclear copper(II) complexes are comparatively rare.

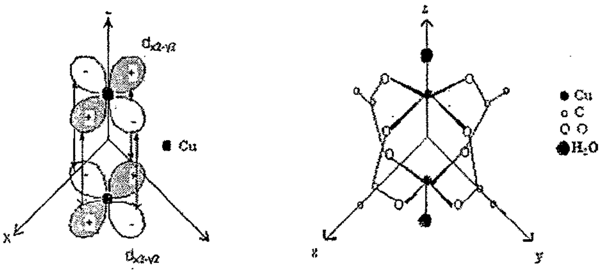
Mechanism of magnetic exchange

The magnetic interaction in 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 centres within the same molecules, leading to short range ordering. These two types can be called inter- and intramolecular magnetic exchange, respectively. Obviously, the binuclear transition metal complexes belong to the later type.

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

Direct metal – metal interaction

In this type of interaction, the spin exchange results by direct overlap of the orbitals of the paramagnetic metal centres containing the unpaired electrons. Figgis and Martin[11] 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.1.1**. 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.[54] 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 centres, resulting in diamagnetism.



(a) (b)

Fig.1.1 (a) An illustration of the δ-bonding in and (b) the structure of copper(II) acetate monohydrate after Figgis and Martin (Ref.11).

Super exchange interaction

The idea of "super-exchange"[56-58] was originally put forth by Anderson.[57] This involves an exchange of the spins over two paramagnetic centres 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.1.2**

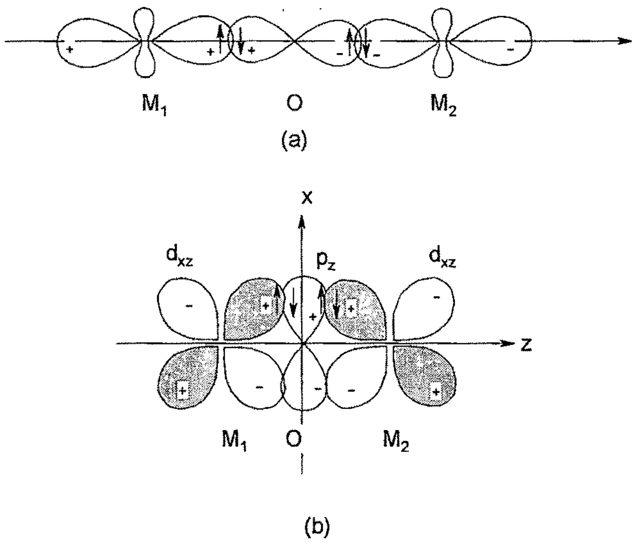
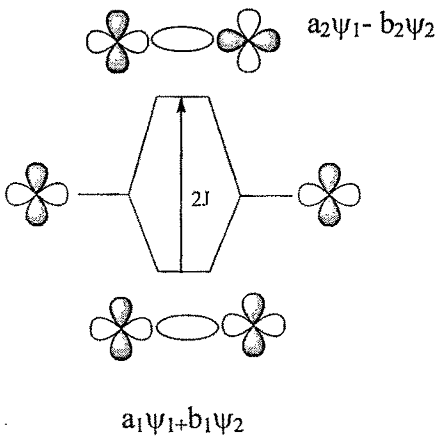


Fig.1.2 Superexchange in a linear M-O-M system. An example of superexchange via (a) σ–bonding, and (b) π–bonding.

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.1.2a** and **Fig.1.2b**, respectively. Spin polarization through the intervening bridging atom orbital induces opposite spins in the neighbouring paramagnetic centres, resulting in antiferromagnetism.

Although, the main interest was in the O bridged binuclear copper(II) complexes, various complexes with halide or S bridge have been studied.[59] It has been pointed out that S or Br bridging in copper dimers should lead to stronger antiferromagnetism than O or Cl bridging, respectively.[60] 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) centres 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.



Considerable knowledge has been gained in understanding the magneto-structural relationships in symmetrical dibridged dinuclear metal complexes, in particular, the dihydroxo-bridged copper(II) complexes. A good linear correlation between the singlet–triplet energy gap (J) and the Cu-O-Cu bridging angle in the range 95-105° was first observed by Hodgson and Hartfield.[61-68] 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.[69-76]

Binuclear first-row transition metal complexes containing the μ-oxo-di(μ-carboxylato)-dimetal(III) core have received a great deal of attention because this structural motif appears in the active site of a number of iron and manganese containing non-haem metalloproteins.[77,78] One of the most intriguing aspects of this core from an inorganic chemist's point of view is the observation of intramolecular spin exchange coupling between the unpaired electrons at both metal ions via super exchange mechanism mediated by a strong bent μ-oxobridge, (M-O-M $\approx$120°).

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. Kahn *et al*[29] and Sinn *et al*[79] 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, ϕ being 0. Any distortion of the binuclear core structure from planarity, resulting in increase in dihedral angle, ϕ, 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.[80]

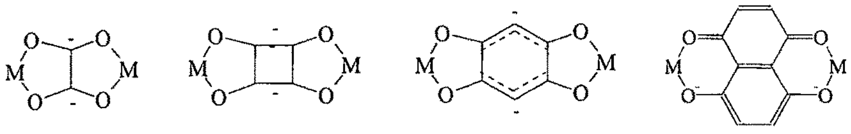
An interesting observation was made by Hendrickson and coworkers[81] in case of the transition metal complexes of a binucleating ligand formed by the condensation of 2,6-diformyl-4-methyl phenol and 1,3-diaminopropane, the net antiferromagnetic interaction decreases monotonically in the series Cu^{II} ($J = -294$ 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 copper(II) to manganese(II).

Magnetic exchange interactions propagated by multiatom bridges (Long range interactions)

Apart from the two kinds of interactions mentioned above, magnetic exchange interactions have been observed to be taking place between metal centres bridged by more than one atom.[82] The magnetic exchange in such complexes is believed to be taking place through a suitable molecular orbital of the bridging ligand, matching in symmetry and energy of the paramagnetic orbitals.

Study of long range magnetic exchange is also important to understand the mechanism of the thermal electron transfer between paramagnetic centres well separated by large organic molecules[83], and also biological electron transport over large distances.[84-86] Several studies have been carried out to determine the criteria for strongest magnetic exchange through multiatomic 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.[87] 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 centres or the number of the bridging atoms. In a series of binuclear complexes bridged by oxalate,[88-94] squarate[88,95] and the dianion of 2,5-dihydroxybenzoquinone[96] as shown in **1.3a to 1.3d** , 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.[88,97]



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

(Fig.1.3a to **1.3d)**

Amongst several other studies reported is the comparison between the magnetic exchange via squarate, naphthazarin, quinizarin,[98] 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 IN Table **1.1**.

A general conclusion can be drawn from these studies. As pointed out earlier by Hendrickson[98], the magnetic exchange through multiatomic bridges does not depend on the distance between the paramagnetic centres, it depends more on the symmetry and energy of the exchange propagating orbitals.

Table 1.1

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

The extent of spin exchange can be tuned or modified by changing the factors such as, metal-ligand bond length, M-L-M bridging angle, dihedral angle between the metal coordination planes and degree of planarity of the bridging unit.[21-24] Variation in the bridging ligand can directly affect the nature of the bridging molecular orbital participating in the exchange whereas change in the nonbridging parts of the ligands can affect the enrgy and symmetry of the paramagnetic orbitals. The symmetry of π-orbitals and their ability to delocalize electron density can play important role in mediating the magnetic exchange in the complexes with multiatomic bridges. In most cases, this type of spin exchange through multiatomic bridges has been shown to take place through the π-orbitals of the bridging ligand. However, it has also been suggested that the σ-orbiatls can participate in the super exchange over a long distance in mutiatomic bridges and lead to spin exchange yet such interactions are very weak.[25, 26, 99]

In last two decades, the study of magnetic exchange interactions propogated by multiatomic bridges has been extensively studied.[100-102] The interest in this area will elaborate the structural and functional properties of biological systems and help to design molecular magnets.[103-105]

The strategy of design and sythesis of binuclear and multimetallic complexes is based on two principles:

(1) Simple supramolecular assembly of metal ions and small ligands acting as exogenous bridging groups,

(2) Use of specially designed ligands capable of holding two or more metal ions.

The later are more robust with tailor made designs and have better control on the organization of metal ions. The simplest of these capable of simultaneously binding two metal ions were first termed as 'binucleating ligands' by Robson in

1970. There has been continuous increase in the number of types of such ligands synthesized. There are mainly two classes of the binucleating ligands as follows,

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

A summery of various types of ligands falling in these two classes is representaed in **Plate 1** to **Plate 3**.

Study of magnetic exchange through a variety of bridging groups has been reported so far and magneto-structural correlations have been established in several cases. Summary of some important reports, classified according to the bridge types is presented below.

Diazine Bridges

The N_2 diazine bridges found in some conjugated aromatic heterocyclic ligands can bring two copper(II) centres in close proximity and generate moderate to strong antiferromagnetic intermolecular exchange between the two copper centres via the π-orbital system (σ pathway) of the heterocyclic ligand. This varies with the nature of the diazine ligand. Extensive studies have revealed that for dinuclear copper(II) complexes containing two essentially planar bis-(N_4) ligands in which the magnetic orbital is $d_{X^2-Y^2}$, the 2J values are in the order pyridazine > pthalazine (450-550 cm^{-1})[106-110] > pyrazolate (200-430 cm^{-1})[111-112] >triazole (200-240 cm^{-1})[113,114] > 4-iminotriazole (<220cm^{-1}).[115-116] The N_2 diazine linkages in open chain systems with N-N single bonds are much more flexible compared to the diazine moiety in heterocyclic ring systems.[117] Previous studies[118-122] have shown that such open chain diazine ligands present several possible mononucleating and dinucleating coordination modes due to the flexibility of the ligand around the N-N single bond. In combination with other donors such open chain diazine ligands can form several types of copper(II) complex e.g. mononuclear,[122-125] dinuclear, [126-132] trinuclear[133] and tetranuclear[134-135] and series of novel open chain diazine ligands have been shown to coordinate to two copper

Plate 1

Compartmental Ligands

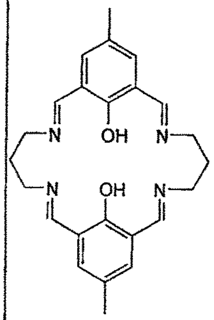


Fig.1.4 (a) Ref. 140,141

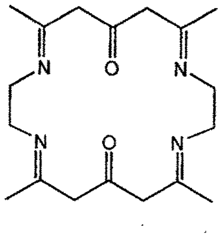


Fig.1.4 (b) Ref. 142

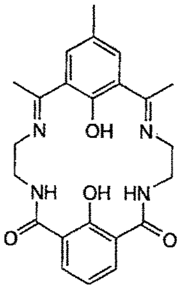


Fig.1.4 (c) Ref. 143

"End-off" acyclic compartmental ligands

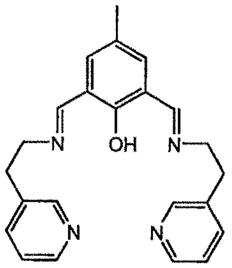


Fig.1.5 (a) Ref. 144

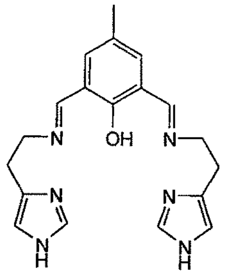
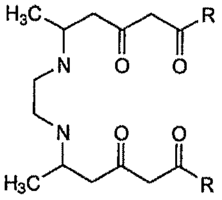


Fig.1.5 (b) Ref. 145

"Side-off" acyclic compartmental ligands



R = CH_3, C_6H_4-, tBu-

Fig.1.6 (a) Ref. 146,147,140

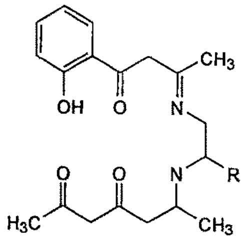
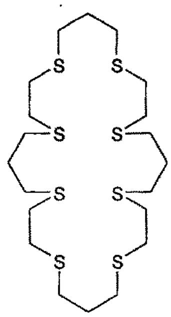
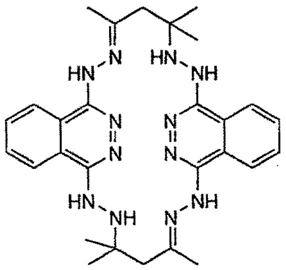


Fig.1.6 (b) Ref. 141

Plate 2
Ligands with Isolated donor sets

Extendable macrocycles and related systems





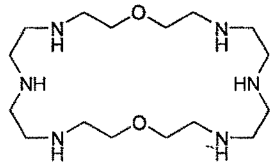


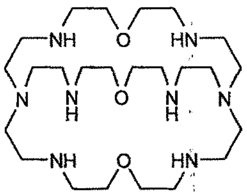
Fig.1.7 (a) Ref. 142

Fig.1.7 (b) Ref. 143

Fig.1.7 (c) R 144

Axial macrobicycles

Lateral macrobicycles



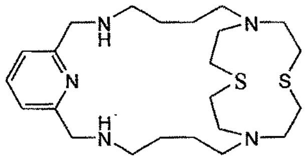
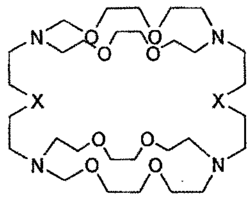


Fig.1.8 Ref. 145

Fig.1.8 (b) Ref. 148

Extended macrotricycles and related systems

Cylindrical macrobicycles



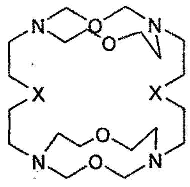
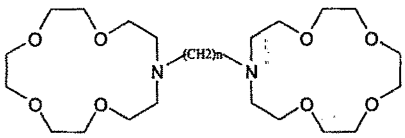


Fig.1.9 (a) Ref. 149

Fig.1.9 (b) Ref. 150(a)

Bis-macrocycles



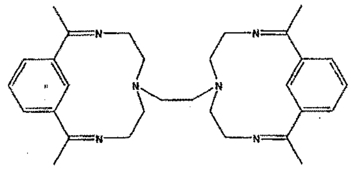


Fig.1.10 (a) Ref.150(b)

Fig.1.10 (b) Ref. 150(c)

Plate 3

Isolated donor sets within extandable macrocycles and macrobicycles.

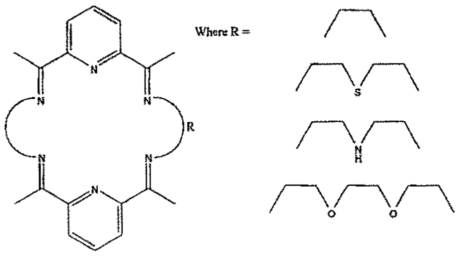


Fig.1.11 (a) **Ref. 151-155**

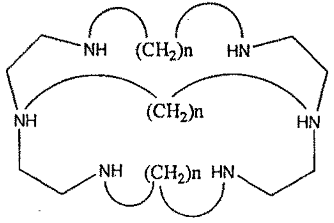


Fig.1.11 (b) **Ref. 156**

Macrotricycles and Bis-macrocycles.

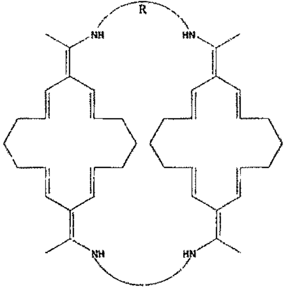


Fig.1.12 (a) **Ref. 156,** R = m-xylyl

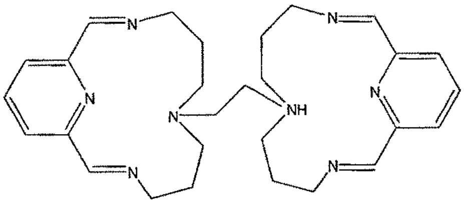


Fig.1.12 (b) **Ref. 157**

"Wish-bone" polypode and aromatic bridged closed compartments.

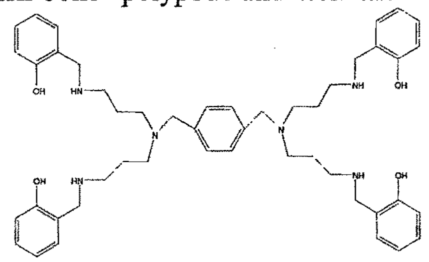


Fig.1.13 (a) **Ref. 158**

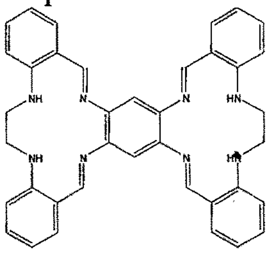


Fig.1.13 (b) **Ref. 159**

Linked open compartments and linked open chains.

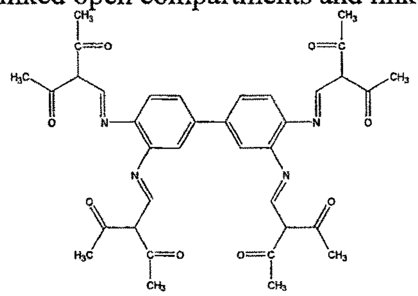


Fig.1.14 (a) **Ref. 160**

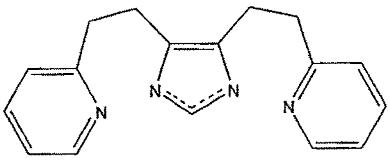


Fig.1.14 (b) **Ref. 161**

centres as N_4 or N_5 donors with a variety of geometrical arrangements, which depend on co-ligands and reaction conditions.[136,137] These flexible geometrical arrangements result from the ability of the diazine fragment to undergo free rotation around N-N bond. A linear relation has been found between the rotation angle and the exchange integral over a 105° range for such dicopper(II) systems. When the rotation angle is less than 80°, ferromagnetic exchange prevails.[138,139]

Azide and Cyanate bridges

The μ-azido ligand has been investigated as a very efficient superexchange pathway for propagating magnetic interactions between paramagnetic centres. This versatile ligand has been widely used to design molecular magnets,[162-164] because its diverse binding modes lead to variation in the magnetic properties that depend on its orientation with respect to magnetic centres.[165] The structural variety of azido complexes includes dinuclear,[166] tetranuclear,[167] cubane,[168] 1-D,[169] 2-D,[170] and 3-D[171] compounds. In general, the coordination modes observed for the bridging azido group are end-to-end[172-173] with antiferromagnetic interaction and end-on with ferromagnetic interaction.[174-177] Moreover, the magnetic properties of end-on bridged metal complexes are also dependant on the M-N-M angle.[178-182] For the copper(II) system, it is observed that when this angle is less than 108°, the complex shows ferromagnetic property; when it is larger than 108°, the magnetic interaction between the paramagnetic centres is anti-ferromagnetic in nature.

After outstanding research on azido-bridged binuclear transition metal complexes[136] from 1980's, the magnetochemical research is presently concerntrated mainly on multinuclear mono- and multidimensional systems. Still there are only five azido-bridged uniform and alternating chains reported for copper(II) and nickel(II) metal ions.[165,183-186] From all the previously reported azido-bridged complexes it is observed that single end-to-end azido bridging mode is quite common[186] but whenever an azide bridges two metals in end-on fashion, it is always associated with another bridging moity (Type-1)[187] (**Fig.1.5a**). This shows that, only a single azide flanked between two metals in end-on fashion is still lacking. A 1-D copper(II) chain with homopiperazine, i.e. [Cu-(homopiperazine)(μ-1,3-N_3)]$_n$ with alternate single end-on and single end-to-end azido bridging, has a new mode of coordination (Type-2) (**Fig.1.5b**) and a very high M-N-M bond angle (129.98°) for end-on azido bridging mode; this is very rare because only one example is reported [187b] to date with such a bond angle, larger than 125°. Magnetic measurement shows a regular alternation of two different types of antiferromagnetic interactions.[188]

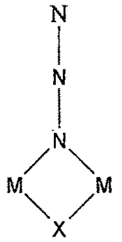


Fig.1.15a Type-1

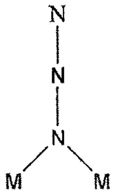


Fig.1.15b Type-2

(Where X = N_3^-, HO^-, CH_3COO^- etc)

The cyanate ion, like the most widely studied azide, can act as a bridging ligand between two metal atoms in an end-to-end or an end-on fashion. In cyanate-bridged polynuclear copper(II) compounds the end-on coordination mode is usually found. Indeed, all reported dinuclear copper(II) cyanate–bridged compounds exhibit end-on coordination,[189] three structural examples have been reported of two dimensional end-to-end cyanate-bridged copper(II) compounds[190] and only one structural example of a one dimensional end to end cyanate-bridged compound has been reported, $[\{Cu(NCO)_2(ampy)_2\text{-}(H_2O)\}_n]$[12] (ampy = 3-aminopyridine), which comprises an alternating $[Cu(ampy)_2(H_2O)_2\text{-}NCO\text{-}Cu(ampy)_2(NCO)_2\text{-}OCN\text{-}]_n$ chain.

Dicyanamide bridges

The first report on coordination compounds with the pseudo halide dicyanamide anion [dca, $N(CN)_2^-$] was published by Madelung and Kern in 1922,[191] and its coordinating ability towards 3d transition metal ions was explored by Kohler and coworkers in the 1960s and 1980s.[192] However, the homoleptic dca-containing complexes have been a subject of intensive research in the last decade due to the capability of dca in designing extended networks with a great diversity of magnetic properties.[193-196] In particular, long-range magnetic ordering was observed in the rutile-like homoleptic M(dca) compounds, where M is a six-coordinated first-row transition metal ion. The versatility of dca as a ligand is well illustrated by its five structurally characterized coordination modes[193-200] like, monodentate bridging through a nitrile nitrogen atom (a), bis-monodentate bridging through one nitrile and amide nitrogen atoms (b), end-to-end bridging through the two nitrile nitrogen atoms (c), tris-monodentate bridging of three metal atoms (d) and rarer μ_4 coordination where one of the two nitrile nitrogen atoms is coordinated to two metal ions (e). The structures and magnetic properties of the coordination polymers of dca can be strongly modified by the introduction of coligands.

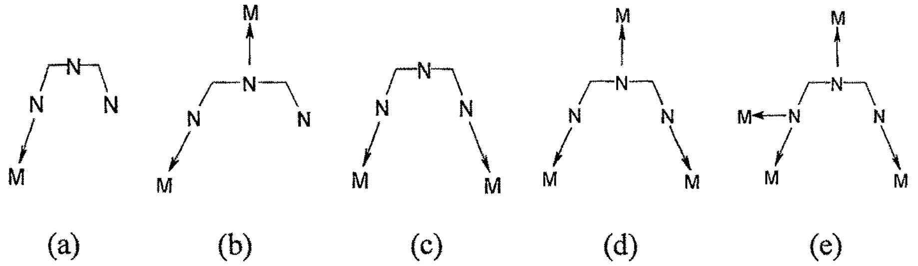


Fig.1.16

Carboxylate bridged Complexes

Caroboxylate is a versatile anion which can bridge metal ion in mono [201-206] or tri-atomic including syn-syn,[207] syn-anti,[208-213] and anti-anti [214] and mono and bi-dentate[215] modes. As expected on the basis of their, respective geometries, the mono- and tri-atomic syn-syn conformations usually favour the formation of dinuclear complexes while the anti-anti and syn-anti tri-atomic conformations generally correspond to chain or layer compounds.[210-213]

The magnetic properties resulting from their various structures is the most fascinating aspect of the chemistry of μ-carboxylato-copper(II) complexes. Although, varieties of these complexes have been structurally and magnetically characterized, there are rare examples of two-dimensional sheet like copper(II) polymers, in which the carboxylate group presents the novel bridging mode,[215] (μ_3-carboxylate-O,O') containing not only monoatomic but also triatomic syn-anti and anti-anti types.

Using 3,5-pyridinedicarboxylate bridges (Fig 1.22), a novel tetranuclear complex

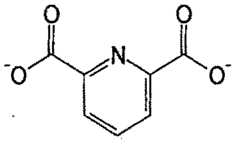


Fig.1.22

was synthesized and analysed by X-ray diffraction analysis. A mononuclear Cu-bipy complex was used as precursor to self assembly the tetranuclear complex.[216]

Imidazolate, Benzimidazolate, Biimidazolate and Bibenzimidazolate bridges

The interaction of imidazole and benzimidazole or their derivatives with transition-metal ions is believed to be important in determining the activity of many biologically important molecules and metalloproteins.[217] In 1970's, the interest in imidazolate (Im-) bridged transition-metal ions was increased due to the involvement of imidazolate ion as a bridging ligand between copper(II) and zinc(II) ions in the enzyme superoxide dismutase (SOD).[218-221] X-ray crystallographic studies[218] have indicated that the Cu^{2+} and Zn^{2+} ions exist in distorted square-planar and tetrahedral coordination environments, respectively. In the case of the 4-Cu^{2+} SOD protein, it was also found that the two Cu^{2+} ions in each subunit are antiferromagnetically coupled with a singlet-triplet separation (2J) of approximately -52 cm^{-1}.[219] Imidazolate ions are known to bridge metal ions in polymeric materials with the composition $M(Im)_2$.[217] Imidazolate bridges between copper(II) ions are present in polymeric $Cu(ImH)_2$-(Im)Cl[222] and in the semipolymeric material, $Cu_3(ImH)_8$-$(Im)_2(ClO_4)_4$.[223] The first reported *nonpolymeric* complex with imidazolate bridging between copper(II) ions is the tetramer $[Cu_2(bpim)(Im)]_2(NO_3).4H_2O$,[220] where bpim is 4,5-bis[2-(2-pyridyl)ethyliminomethyl]imidazolate. Very recently, two imidazolate-bridged binuclear copper(II) complexes have been characterized.[221] Magnetic susceptibility measurements for all three of these nonpolymeric copper(II) complexes revealed that the copper(II) ions are involved in antiferromagnetic exchange interactions propagated by the Im^- bridge.

Not only are there few complexes with benzimidazolate ion ($BzIm^-$) as a bridging ligand but there are only a limited number of transition-metal complexes containing BzIm- as a ligand.[217] No discrete dimers are known, however, the capability of $BzIm^-$ to bridge two metal ions is indicated by the isolation of $M(BzIm)_2$ complexes where M = cobalt(II),[224] palladium(II),[225] and copper(II).[217] The dianions of 2,2'-biimidazole ($BiImH_2$) and 2,2'-bibenzimidazole ($BiBzImH_2$) can function as bis-bidentate ligands, bridging between two transition-metal ions. Two papers have appeared describing the preparation and X-ray crystallographic characterization of the first complexes incorporating $BiIm^{2-}$ as a bridging ligand between metal ions. The complexes are $M_2(COD)_2(BiIm)$[226] and $M_4(CO)_8(BiIm)_2$,[227] where M = Rh(I) and Ir(I) and COD is 1,5-cyclooctadiene. The compounds $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$ and $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiBzIm)$ have been reported.[228] The $BiIm^{2-}$ and $BiBzIm^{2-}$ ions bridge between two $(Cp)_2Ti^{III}$ ($Cp = \eta^5\text{-}C_5H_5$) moieties in these complexes, an antiferromagnetic exchange interaction between two d^1 ions is present in each molecule. The reaction of $CuCl_2$, with $BiBzImH_2$ in acetone has been reported to be complex, yielding a series of products that are thought to be polymeric.[229]

Oxalate, Oxime, and Related Bridges

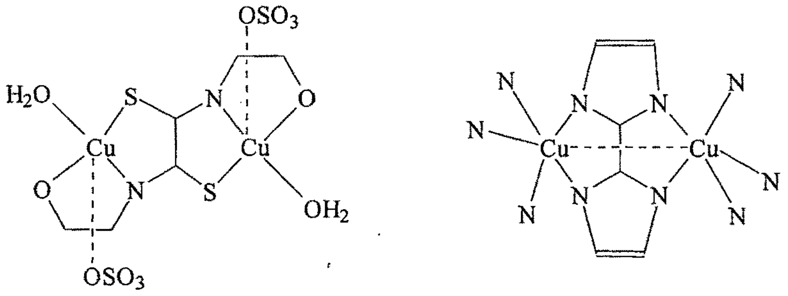
Extensive studies have been carried out by Kahn and coworkers,[230] and other groups,[231] on oxalate bridged complexes. Kahn and coworkers could 'tune' the magnetic exchange in these complexes by varying the non bridging ligands.[232] These observations paved a way for designing the binuclear complexes with desired magnetic properties. Several complexes of ligands derived from oxalate, 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,[233]

oxalato < oxamato < oxamidato

The magnetic exchange could be tuned in the μ-oxamido complexes also by varying the nature of the ligand.[234]

M. Julve *et al* [235-237] reported heterobimetallic oxalato-bridged M^{II}rhenium(IV) complexes, (M = copper, manganese, iron, cobalt). A very weak antiferromagnetic coupling between copper(II) - rhenium(IV) and manganese(II) - rhenium(IV) occurs, whereas a significant ferromagnetic interaction between rhenium(IV) - iron, rhenium(IV) - cobalt was observed. Orthogonality between magnetic orbitals in these binuclear complexes leads to ferromagnetic coupling and distortion in the coordination geometry introduces 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. $[Cu_2S_2C_2(N(CH)_2 OH_2) (H_2O)_2]SO_4$ (**Fig.1.23a**) the bridging of the dithiooxamide ligand results in very strong antiferromagnetic coupling (J = -523 cm^{-1}), despite the Cu-Cu distance of 5.65 Å[238] 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. $[Cu_2(Me_5dien)_2(biim)](BPh_4)_2$ (**Fig.1.23b**) results in zero exchange coupling (J ~ 0.5 cm^{-1}) between the copper (II) atoms separated by 5.49 Å[239] Several other scientists have studied the extent of magnetic exchange in binuclear complexes of oximato and related bridging groups.[234, 240-242.]



(a) (b)

Fig.1.23 (a) $[Cu\ S_2C_2(N(CH_2)_2OH_2)(H_2O)_2]SO_4$
(b) $[Cu_2(Me_5dien)_2(biim)](BPh_4)_2$

Yoshino and Nowacki[243] reported the structure of $[Cu_2\ (DMAEO)\ (NCS)_2\ (DMF)_2]$, where DMF is N, N' – dimethylformide and DMAEO is (**Fig.1.24**)

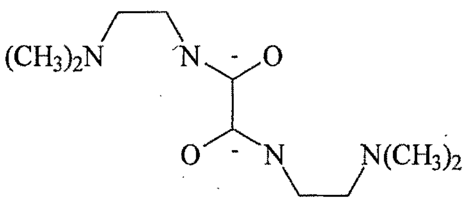


Fig. 1.24

Each copper(II) ion has square – pyramidal coordination geometry with an axial DMF ligand and one NCS^- ligand completing the square plane,[244] and 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 Å.

Kahn and coworkers[238] studied the antiferromagnetic exchange in two isomeric binuclear copper (II) complexes bridged by the following dithiooxamide **(Fig.1.25)**

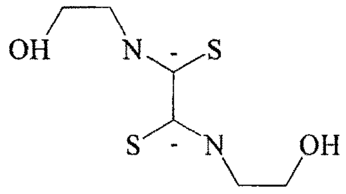


Fig. 1.25

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.

The oxamide dianion acts as a bidentate ligand and, like the oxalate dianion, is also capable of coordinating as a bridging ligand to give many kinds of binuclear complexes. The binuclear copper(II) complexes formed by the oxamide dianion are more stable than those formed by the oxalate dianion, owing to the high extent of magnetic interaction between two metal ions, especially in the N,N'-bis(coordinating group substituted)oxamides. It is hoped that the binuclear complexes formed by the N,N'-bis(coordinating group substituted) oxamides will lead to the development of a new field of coordination chemistry. Two reviews, one on "Coordination Properties of Amide Bond" and another on copper(II) complexes with N, N'-bis(alkylaminoalkyl)-oxamides and related ligands have been published in 1982[245] and 1988[246], respectively.

D. Zhang *et al* [247] studied trans-oxamido bridged copper (II) binuclear units $[Cu(oxen)(PYNN)]^{2+}$, **(Fig.1.26a)** forming helical chains. The ligands used were oxen = N,N-bis(2-aminoethyl)oxamide] and pyridine-substituted nitronyl nitroxide radicals (o-, m- and p-). (**Fig.1.26b** to **1.26d**)

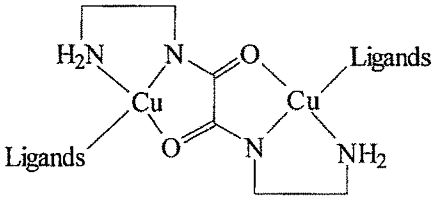
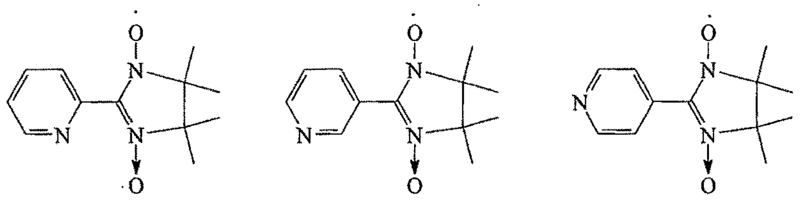


Fig.1.26 (a)



(b) (c) (d)

Fig.1.26

The coordination geometry around each copper(II) ion is distorted square pyramidal. The distance between metal centres are very close in each complex. Yet the interactions between spin centres 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 copper(II) ions through oxamido bridge was strongly antiferromagnetic while the net magnetic exchange between the heterospins, viz. copper(II) and nitroxide radical, was found to be weakly ferromagnetic.

Besides the usefulness as molecular magnets binuclear complexes have found a variety of other applications.

Copper complexes of sterically demanding tris(pyrazolyl)-hydroborate ligands have found applications as synthetic analogs for cuproprotein active sites.[248] Placement of groups such as tert-butyl or isopropyl at the 3-position of the pyrazolyl rings is a key to the success of these systems, because the presence of the substituents inhibits formation of coordinatively saturated $M(ligand)_2^{n+}$ complexes and allows for control over redox behavior.[249] The most effective model to date for the dioxygen transport protein, hemocyanin (Hc),[250] utilizes the ligand tris[1-(3,5-diisopropylpyrazolyl)]hydroborate (Tp^{ipr2}), which forms a peroxo-dicopper(II) complex with spectroscopic and physiochemical properties that are strikingly similar to those of the protein.[251]

It has been showed that copper DNA interaction is site specific with copper binding[252] with the base part of DNA, while Sn complexes prefer to bind to the phosphate backbone of the DNA helix.[253] Thus bimetallic complexes containing copper(II) and tin(IV) ions enhance the chemotherapeutic action many-fold as they provide a dual mode of binding at the molecular target site and also exhibit novelty due to preferential selectivity inside the cells.[254] Previous studies of copper(II) and copper(II)-tin(IV) complexes have shown interesting results against various cancer cell lines (HeLa cells, T47D, HT29).[255] It has been demonstrated that these complexes induce apoptosis via mitochondrial pathway.

Currently much effort is devoted to develop useful catalytic systems for mild and selective oxidations with the aid of molecular oxygen.[256] Furthermore, it is of great interest to elucidate the factors that determine the (reversible) binding and activation of O_2 in various natural oxygen transport systems and mono- and dioxygenases and to mimic their activity.[257, 258] Guided by nature, intriguing model systems[259-271] for copper-containing enzymes such as hemocyanin[272-277] have been developed. Considerable progress has been made in order to establish the active species in cytochrome P450 and related oxygenases.[278] Contrary to the successful development of oxidation catalysts based on metalloporphyrins,[279-284] synthetically useful catalysts based on copper complexes that act as mimics for copper-containing monooxygenases (e.g. tyrosinase and dopamine-β-hydroxylase[285] have hardly found. This is even more surprising if one realizes that selective oxidations of organic substrates mediated by copper-amine complexes have been known for a century.[286-289] The Glaser oxidative coupling of acetylenes,[289] the oxidative dimerization of napthols as observed by Havinga and Brackman,[290] and the formation of poly(phenylene ethers) from 2,6-disubstituted phenols as discovered by Hay[291] are all based on copper-amine complex and molecular oxygen. Numerous studies have dealt with these oxidations[292] and useful extensions to γ-oxidations of enones,[293] asymmetric phenol oxidations[294] and cis,cis-muconic acid synthesis[295] as well as improvements on poly(1,4-phenylene ether) formation have been found.[296,297] Stochiometric arene hydroxylation has been observed,[298-300] during studies of the reactivity of O_2 at copper centres in binuclear complexes designed to mimic certain oxygenases.

The multicopper centres in copper oxydases known as "blue oxydases" (ascorbate oxidase, laccase, and ceruloplasmin)[301-302] have generated interest in the synthesis of angular non-linear tricopper clusters and their physical and chemical properties. Now it is very welknown that in these copper oxydases Type-2 (normal single copper) and Type-3 (EPR-silent coupled copper atoms) centres together form a unique trimetal active site for the binding and multi-electron reduction of dioxygen. The fully oxydised active site of ascorbate oxidase has a triangular arranmgement of copper(II) atoms with Cu-Cu separations in the range 3.6-3.9Å, with an hydroxide or oxo group acting as a bridge between the two Type-3 copper atoms.[303,302a,b] Thus it is interesting to synthesize and study the trinuclear copper complexes to get the relevance towards the metalloenzymes. Further, the contribution of the various bridging ligands, to form the trinuclear complexes as well as the multinucleating ligands to hold the three metal ions have been discussed. The active site of pMMO (particulate methylmonooxygenase) was found to have ferromagnetically coupled trinuclear copper(II) centres with S = 3/2 ground state.[304] In the extensive study of copper(II) chemistry, there are only four examples of ferromagnetic trinuclear complexes, one linear, two angular and one triangular.[305] A majority of the reported trinuclear copper(II) complexes have, however, a linear geometry of the metal ions or a $Cu_3(\mu_3\text{-}X)$ unit (X = Cl, OH)[306,307]

As said earlier for trinuclear copper(II) complexes, the metal atoms are arranged in either a triangular[39, 40] or a linear fashion.[41-43] A trinuclear assembly can be formed with the help of exogeneous bridging ligands, like, -oxo, -hydoxo, -cyano, -thiocyanato, carboxylato, oxalato and some heteroatomic bridges like oxime, diazine, triazole, imidazole, benzimidazole, biimidazolate, bibenzimidazolate and dicyanamide bridges, the dinuclear complexes of which have been reviewed in the earlier section. Fluorinated acetylacetonato ligands have been widely used in the synthesis of various mononuclear and polynuclear metal complexes.[308,309-316] However, despite their potential applications, the reactivity and stability of metal complexes with fluorinated acetylacetonato ligands have not been well examined.

In the past decade a great attention has been devoted to the design and synthesis of Schiff bases with enhanced ability to severely encapsulate given metal ions.[317-322] In particular, macrocyclic and acyclic Schiff bases have successfully been proposed as excellent systems in the formation of mono-, homo- and hetero-polynuclear lanthanide complexes.[319-321] Detailed investigations of their stereo chemical, electronic, magnetic and catalytic properties have allowed the proposal of new, highly efficient molecular devices or probes for a number of specific applications.[322,323] Furthermore, they have been used as conventional precursors in the formation of the modified surfaces or otherwise not accessible mixed oxides.[324] A trinuclear copper(II) complex with Schiff base of 6-amino-6-deoxygucopyranoside has been structurally elucidated and characterized for magnetic interactions by Vigato et al. These complexes show an unusual moderate antiferromagnetic coupling, and this has been supported by the theoretical invesitigations, which show a symmetric doublet ground state.[325]

A number of functionalized macrocyclic ligands have now been reported, and most of them contain as pendant donors aliphatic amines,[326] pyridyl groups,[327] carboxylic acids,[328] alcohols and phenols,[329] nitrils,[330] and other donor groups.[331] Only recently, attempts to functionalize macrocycles with biomimetic donors have succeeded, the ligands so far reported being a bisadenine derivatives of 4, 13-diaza-18-crown-6,[332] a monopyrazole of 3,7,11,17-tetraazabicyclo heptadeca-1(17), 13, 15-triene,[333] and a mono imidazole of cyclam.[334] A trimacrocyclic ligand 1,3,5-tris(1,4,7-triazacyclonon-1-ylmethyl)-benzene was synthesized and characterized. Trinuclear complex of this ligand was yielded with copper(II) salt and above pH 9.2 the same complex diomerised to form a hexanuclear complex. An antiferomagnetically coupled pair is observed with $J = -24\ \text{cm}^{-1}$ and with $J = -61$ and $-29\ \text{cm}^{-1}$ in case of the hexanuclear complex.[335]

It is well-known that the substituted 1,2,4-triazole ligands can bridge metal ion through the N1,N2-coordination mode to afford polynuclear compounds.[336] Particularly, two series of compounds, one of dimers with a planar double-triazole bridge[337] and another of linear trinuclear compounds, mostly with a triple triazole bridge,[338,339] have been widely described. Several studies dealing with magnetostructural correlations for the dinuclear copper(II) systems[340] and with interesting spin-crossover behavior in the case of the linear trinuclear iron^{II} compounds[341] have been carried out.

Examples of cyclic trinuclear complexes obtained with 1,2,4-triazole derivatives are, however, very rare.[342] cyclic trinuclear and chain of cyclic trinuclear copper(II) complexes containing pyramidal $Cu_3O(H)$ core structure have been reported[343]. The crystal structure and magnetic properties of the copper(II) complexes, $[Cu_3(\mu_3\text{-}OH)$(3-acetylamino-5-amino-1,2,4-triazolate$)_3$ $H_2O)_3](NO_3).H_2O$ and $\{[Cu_3(\mu_3\text{-}OH)$(3-acetylamino-1,2,4-triazolate$)_3(\mu_3\text{-}SO_4)]$. $6H_2O\}$with cases of spin-frustrated systems are of particular interest.[343]

Derivatives of oxalate, oxamate and oxamide being efficient mediators of spin exchange have found lot of attention in the synthesis of trinuclear complexes also. A series of trinuclear complexes incorporating the [1,3-propanediylbis(oxamato)]cuprate(II) complex as a bridging unit between two terminal complexes have been investigated.[344] The solid state structures of the complexes show the Cu---Cu distance to be nearly the same, but that the magnitudes of the magnetic interactions vary over a large range (J = - 400 to – 80 cm^{-1}). The results of this study demonstrate that by choosing the appropriate terminal ligands it is possible to tune the exchange interaction between the copper(II) ions within the trinuclear complexes. This stresses the fact that the mechanism of the exchange interaction is governed by the magnitude of the overlap between the metal orbitals, with the Cu---Cu separation being only the secondary parameter.

Trinuclear complexes of copper(II) with oxamato bridges were synthesized and characterized with the trinucleating ligands, 2,2'-dimethyl-1,3-propylenebis(oxamato) (**Fig. 1 27**) and N,N,N',N'-tetramethylethylenediamine.

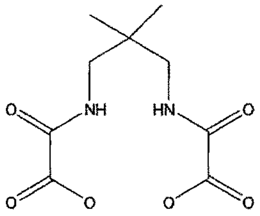


Fig. 1.27

With the previous ligand, the trinuclear complex forms a supramolecular one dimensional array with the help of hydrogen bonds. With the later ligand, the trinuclear complex of copper(II) ion, forms a hexanuclear complex with the help of hydrogen bonds and the water molecules associated with the central copper(II) ions. J_1 values vary from -125 to -386cm^{-1} and J_2 values from 0.85 to 1.94cm^{-1}.[345]

Oxamato bridged homotrinuclear complexes of nickel(II) and copper(II) have been reported and the magnetic interactions in these complexes have been studied. 2,3-napthalene-bis(oxamato) ligands **(Fig. 1.28)**, form complexes with $NiCl_2$ and $CuNO_3$ which exhibit strong antiferromagnetic interactions.

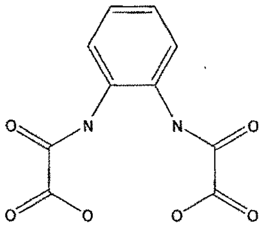


Fig. 1.28 (a)

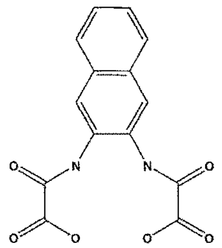
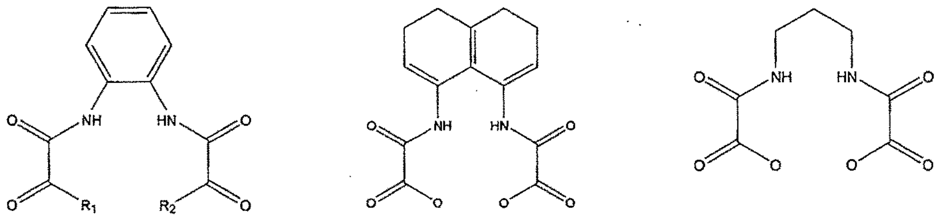


Fig. 1.28 (b)

The co-ordination chemistry of high-oxidation-state transition metal complexes is an area of considerable importance, because of their biological significance as models for redox enzymes and their potentially useful properties as catalytic oxidants, although limited in scope owing to the small number of suitable ligands.[245,346,347] One of them is the well known oxamide dianion $C_2O_2N_2H_2^{2-}$ which acts as a bidentate ligand through its strong electron-donating amide nitrogen atoms and is able to stabilize high oxidation states, as has been shown by Steggerda and co-workers[348] for copper(III) and nickel(III). The ability of this class of ligands to stabilize high oxidation states has been demonstrated by Lloret and co-workers.[349] N,N'-o-phenylenebis(oxamate) (R_1, R_2 = O) and its methylamide (R_1 = O, R_2 = NMe) and bis(methylamide), (R_1 = NMe, R_2 = NMe) (**Fig. 1.29**a), N,N'-napthalene-1,8-diylbis(oxamate) (**Fig. 1.29**b), and N,N'-trimethylene bis(oxamate) (**Fig. 1.29**c) have been found to form mononuclear complex with copper and stabilize copper(III) ion.[350]



(a) (b) (c)

Fig. 1.29

In continuation of copper(III) stabilization studies, recently, tetraaza pseudo-macrocyclic oxime-and-hydrazide ligands **(Fig. 1.30)** with adjustable cavity size have been reported with mononuclear and polynuclear copper systems.[351]

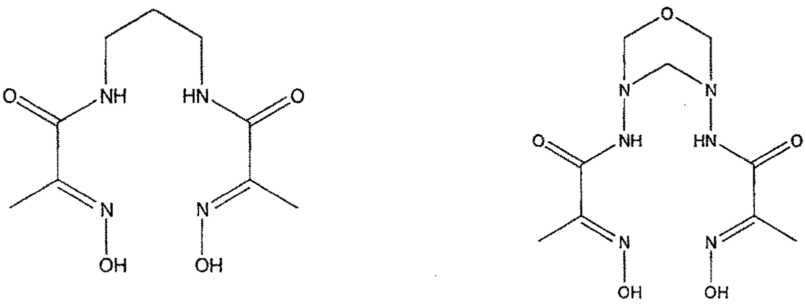


Fig. 1.30

Although the oxamide dianion itself coordinates only in a strongly alkaline solution, stable mixed-ligand complexes may be formed in the presence of suitable additional ligands in a remarkably low pH range.[352] As discussed earlier, oxamido bridges have been studied as exchange interaction mediators, with change in the substituents. A simple binuclear complex of copper(II) with trans-μ-oxamido-N,N'-diethanoato ligand **(Fig. 1.31)** is structurally characterized with dihydrate molecule at trans position.[353]

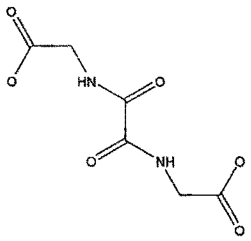


Fig. 1.31

A copper(II) binuclear complex with N,N'-bis(3-aminopropyl)oxamide **(Fig. 1.32)**,

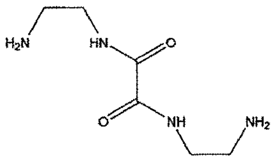


Fig. 1.32

has been reported with imidazole coordination at trans position.[354] In a similar way, trans-binuclear copper(II) complex with the ligand,

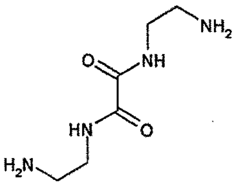


Fig. 1.33

bis(3-aminopropyl)oxamodato (**Fig. 1.33**), is found in the literature.[355] Alkyl substituted oxamide oxime metal complex of Ni^{II} was reported by Absen et al[356]. The ligand coordinates the metal ion in ML_2 fashion. The ligand is shown below.

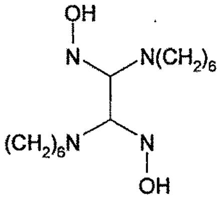


Fig. 1.34

This metal complex forms a tubular channel assembly through the supramolecular structures. Similar ligand N,N'disubstituted carboxylic acid (**Fig. 1.35**), was exmined for the complex formation with copper(II) and nickel(II) ions.

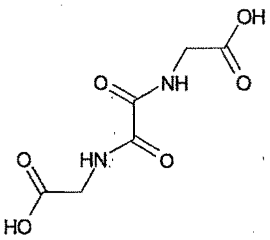
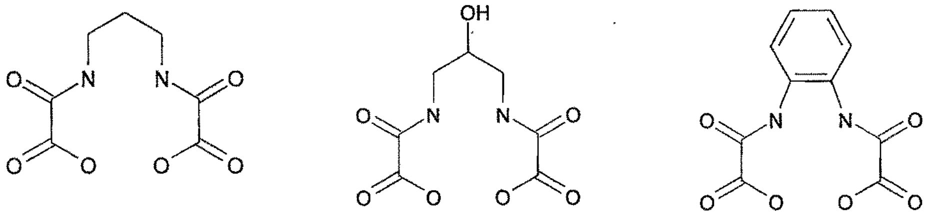


Fig. 1.35

Copper atom is situated at a mirror plane in a distorted square-pyramidal environment and nickel(II) is in distorted octahedral geometry. The copper(II) complex follows Curie law while the nickel(II) complex undergoes antiferromagnetic interaction with J = - 25 cm^{-1}.[240]

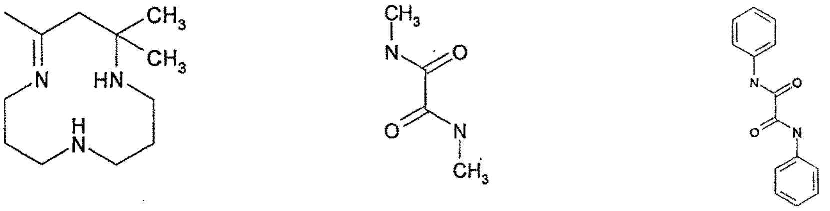
Homotrinuclear complexes of copper(II) ions with trinucleating ligands, N,N'-propylenebis(oxamate), 2-hydroxy-N,N'-trimethylenebis(oxamate), N,N'-ophenelenebis(oxamate) (**Fig. 1.36a-c**) and N,N,N',N'-tetramethylethylenediamine ligands have been reported[355]. In all of these complexes, the copper atoms reside with square planar, or square pyramidal environments. The magnetic interaction is found to be antiferromagnetic.[355]



(a) (b) (c)

Fig. 1.36

The structures of oxamidate bridged nickel(II) complexes with the ligands, 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, N,N'-dimethyloxamidate and N,N'-diphenyloxamidate have been reported **(Fig. 1.37)**.

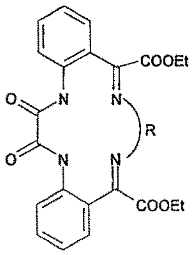


(a) (b) (c)

Fig. 1.37

Antiferromagnetic coupling with J = -57, -38 and -30 cm^{-1} found in these complexes was supported by theoretical treatment with hybrid B3LYP and broken-symmetry treatement, for calculating the coupling constants.[357]

First tetranuclear iron(III) and copper(II) complexes with macrocyclic 2,3-dioxo-5,6:13,14-dibenzo-7,12-bis(ethoxycarbonyl)-1,4,8,11-tetrazacyclotetradeca-7,11-diene, 2,3-dioxo-5,6,13,14-dibenzo-9-methyl-7,12-bis(ethoxycarbonyl)-1,4,8,11-tetraaza cyclotetradeca-7,11-diene and 2,3-dioxo-5,6:14,15-dibenzo-7,13-bis (ethoxy carbonyl)-1,4,8,12 tetraazacyclotetradeca-7,12-diene (**Fig. 1.38**), and with oxamido bridges have been reported.



With

R = $-CH_2-CH_2-$

$-CH(CH_3)CH_2-$

$-(CH_2)_3-$

$-C_6H_4-$

Fig. 1.38

In these macrocyclic complexes, copper(II) and iron(III) ions interact with each other antiferromagnetically with J = -30 and -28 cm^{-1}.[358] The tetranuclear copper(II) complexes with tetrakis(N-salicylidene)ethanetetracarboxylicacid) tetraazide ligand (**Fig. 1.39**), shows antiferromagnetic interaction with -213 and -203cm^{-1} with ONO anion. When chloride was used as counter anion, the coupling constant was found to be -472 cm^{-1}. The prediction of dimerization through phenolic oxygen bridges was explained on the basis of J values.[359]

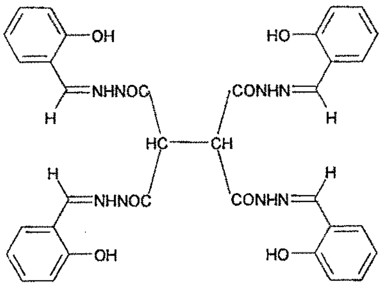


Fig. 1.39

Asymmetric central bis(oxamato) ligand, o-benzyl-bis(oxamato) (**Fig. 1.40**), was used to synthesize homotrinuclear copper(II) complexs, with the help of N,N,N''N''-pentamethylenetriamine, N,N,N',N'-tetramethylethylene diamine and dimethyl formamide as cappnig ligands. Two of the complexes, show antiferromagnetic coupling with J = -111 and -363 cm^{-1}.

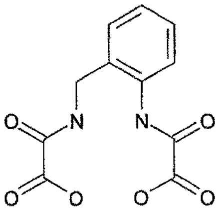


Fig. 1.40

These complexes are the first, reported with N_{aryl}, N'_{alkyl} bridge prepared to date.[360] Complex bridged heterotrinuclear complexes were reported with the bridging complex [M(bis(2-pyridylcarbonyl)amine], the other two parts of the trinuclear complexes being [M(bis(2-pyridylcarbonyl)amine)$_2${M'(hexafluoroacetylacetone)}$_2$] **(Fig.1.41).**[361]

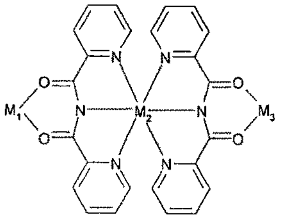


Fig. 1.41

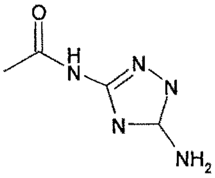


Fig. 1.42(a)

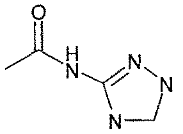


Fig. 1.42 (b)

Trinuclear and chain of cyclic trinuclear copper(II) complexes were synthesized using 3-acetylamino-5-amino-1,2,4-triazolate and 3-acetylamino-1,2,4-triazoleate ligands (**Fig. 1.42**) and were found to be containing pyramidal $Cu_3O(H)$ core. These complexes showed antiferromagnetic interactions with J = -194 and -185 cm^{-1}.[362] A copper(II) trinuclear complex with a ligand (**Fig. 1.43**) having L-histidine residues was synthesized and was found to be effective in enantio-differentiating catalytic oxidation.

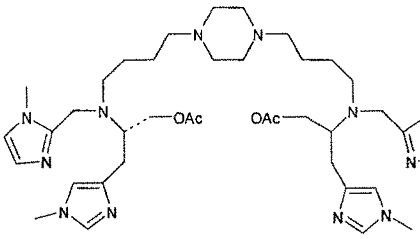


Fig. 1.43

The trinuclear complex of this ligand was found to bind stronger to L- than D-aminoacids and the difference in binding strength is particularly large between L-Tyr and D-Tyr.[363] As discussed earlier in this chapter, diazine ligands are well studied for their complexation studies as well as for electrochemical and magnetic properties.

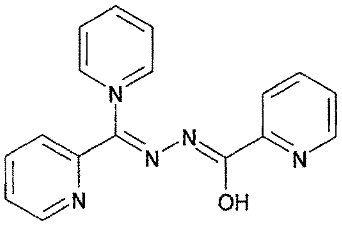


Fig. 1.44(a)

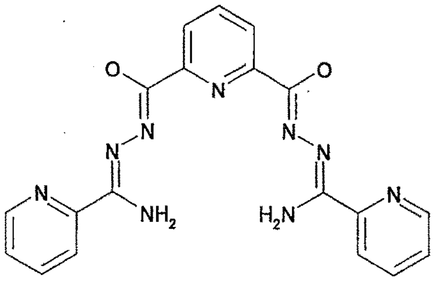
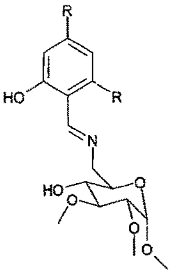


Fig. 1.44 (b)

The trinucleating ligands containing the diazine moieties, shown above (**Fig. 1.44**), were synthesized and the structural and magnetic studies of their complexes have been reported. In these complexes, copper is having a linear arrangement of metal ions, linked by a trans arrangement of N-N single bonds. Each metal ion is assigned a $d_{X^2-Y^2}$ magnetic ground state, and the trans diazine bridging arrangement leads to weak antiferromagnetic coupling with J = -42 to -63 cm^{-1}.[364]

Schiff base ligands are very important part of the trinuclear metal complexes due to their versatile bonding and easy to carry approach for the electrons. Schiff base ligands based on 6-amino-6-deoxyglucopyranoside (**Fig. 1.45**) was reported by Plass et al[365].



where R = H or t-But

Fig. 1.45

The synthesized complexes show a supramolecular structure. Both the complexes are best described as paramagnetic systems with three independent copper(II) centres at high temperatures, whereas at very low temperature, the system is antiferromagnetically coupled with a doublet ground state, which is further confirmed by the DFT calculations.

N,N'-tetracarboxyethyloxamide, a ligand synthesized from L-aspartic acid and diethyl oxalate, was found to form binuclear complexes of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) metal ions. These complexes show antimicrobial activity against gram (+)ve as well as gram (–)ve bacteria.[366]

The biological activity and enzymatic studies of copper containing binuclear complexes have been reported in the literature, as discussed earlier, and it has been revealed in the that the copper(II) ion binds to the N_7 position of guanine in the DNA helix.[367] In continuation of this study, A chiral trinuclear complex of copper [bis(aquodiaminotryptophanato) copper(II)-tin$_2$(IV)]chloride was studied with calfthymus DNA. The voltametric studies of the complex in the absence and in the presence of DNA exhibit a shift in the formal potential, E^0, and ratio of cathodic to anodic peak currents indicates strong binding of the complex to DNA. Also viscosity of DNA decreases with increasing concentration of the complex, suggesting that the complex binds to DNA by electrostatic association.[368] In further studies, F. Arjmand et al. synthesized new trinuclear complexes of copper(II), with tin(IV) zirconnium(II) and zinc(II) ions.

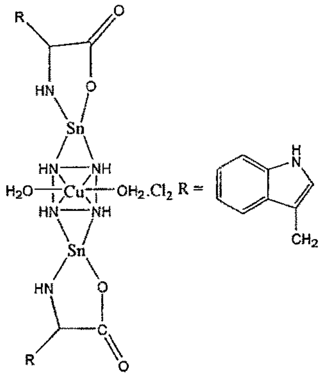


Fig. 1.46

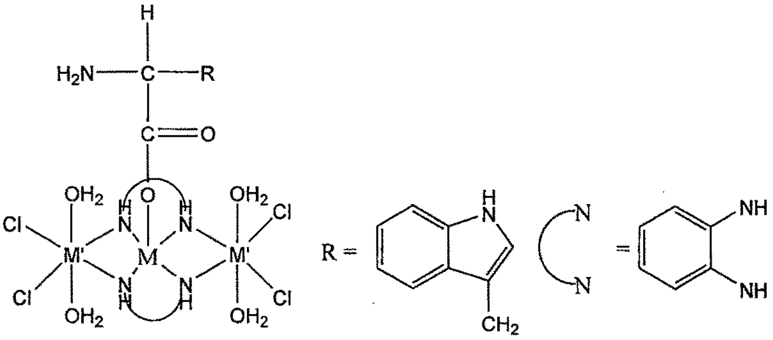
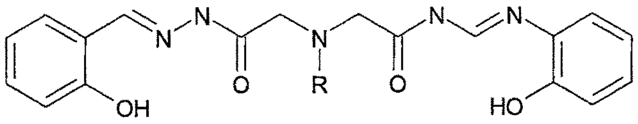


Fig. 1.47

In a comparative study, the complex with copper(II) and tin(IV) was found to have greater activity than the complex with copper(II) and zirconium(IV). In vitro studies with the trinuclear Cu-Sn_2 complex on human neuroblastoma cells have indicated that this complex exhibits significant antiproliferative activity indicative of apoptosis.[369]

Aminocarboxylate anion or its parent acid coordinates to a cobalt(III) ion as a unidentate[370] or a bidentate[371] and in some cases also as a tridentate ligand such as aspartate[372] and histidinate.[373] This type of complexes with cobalt and aminoacids were studied by Shimura *et al.*[374] Mononuclear copper complex with aroyl hydrazone of the Gly-His-Lys[375] was found to be active in the growth inhibition of a fibrosarcoma in mice. The detailed literature on the multinuclear complexes of this type of ligands will be discussed in Chapter 4.

A nonadentate bis(acylhydrazone ligand, namely bis(salicyldehyde) methylimino diacetyl hydrazone (**Fig. 1.48**), was synthesized. Its trinuclear copper(II) complexes with chloride, nitrate and sulfate as a counter anion, were synthesized and characterized. The ligand was found to be flexible and polytopic. This ligand forms a linear trimetallic unit structure depending on the anion. The complexes showed dominant antiferromagnetic coupling between the diazine bridged copper ions.



where, R = H or CH_3.[376]
Fig. 1.48

Various coordination modes of a chiral schiff base, N-(S)-2-(6-methoxynapthyl) propanoyl-N'-(2-hydroxybenzylidene) hydrazine, (**Fig. 1.49**), have been studied.

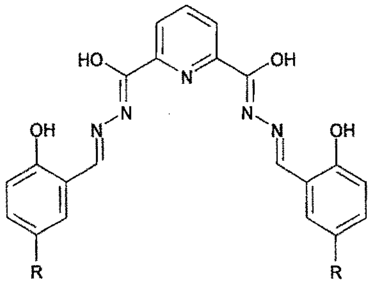


Fig. 1.49

With copper it was observed to be form infinite one-dimensional chain structure. The strong intramolecular hydrogen bonds between the >C=N- and –OH make the predominance of E-configuration. This result was supported by its X-ray crystal structure.

A multisite coordinating Tris-hydrazone ligand (**Fig. 1.51**), is an efficient ligand

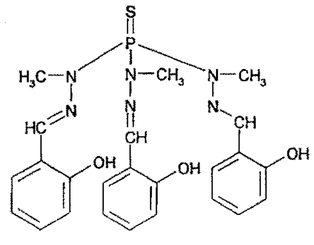


Fig. 1.51

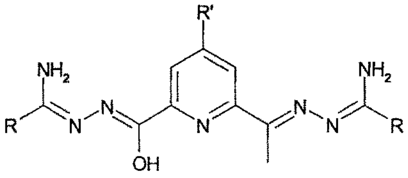
for the formation of a trinuclear complex, supported by phosporus. Depending on the transition metal ion embedded, the ligand can efficiently facilitate both antiferro- and ferromagnetic superexchange between neighbouring metal centres.[377]

Research has, recently, focused on the ability to control the construction of coordination supramolecular arrays based on covalent interactions or hydrogen bonding for the rational design of functional materials.[378] The pathways used to obtain these species are mainly based on the following synthetic schemes: (a) the self assembled method; (b) the use of polynucleating ligands; (c) the use of complexes as ligands. Species are held together by relatively weak intermolecular forces which include hydrogen bonding, van der Waals interactions, hydrophobic/hydrophilic interations, ionic forces and relatively labile metal ion-ligand coordination interactions of a largly electrostatic nature. Metal ligand interactions are generally quite labile, and the structures formed are the theromodynamically most stable products. A helicate (the term first used by Lehn and co-workers in 1987)[379, 380] is a polynuclear helical complex composed of either two or three ligand strands or two or more metal ions. Such helicates involve two or three acyclic ligands each having two or more metal binding sites. The ligands organize themselves around the metal ions, forming the classical interwinning structures of double or triple helicates. Many previous studies of helicates have involved double and triple helical structures based on Cu^+, Ag^+ and Ni^{2+} with bipyridine and terpyridine-derived ligands, in nonaqueous solvents, although helicates based on catechol binding sites and other planar nitrogen heterocyclic ligands have also been studied in nonaqueous and aqueous solvents.

There are three known homonuclear helicates involving lanthanide ions[381] and three heterotrinuclear helicates involving both, d and f element ions.[382] Supramolecular coordination chemistry in aqueous system was studied lsing lanthanide ion[383]. The helical structures of the complexes were confirmed by CD spectroscopy and the Quantum mechanical calculations.[383] Following the same methods, supramolecular architectures have been reported with oxamidates [384] and oxamates.[385,386] Simple mononuclear bis(oxamato)copper(II) complexes can give supramolecular architectures.[387] Several oxamidato-copper(II) dinuclear complexes also give supramolecular structures through hydrogen bonds,[388] carboxylato ligands,[389] N-donor spacers,[390] or small inorganic bridges (NO_2^-,N_3^-).[391] With oxamidato-nickel(II)-copper(II) entities, tetranuclear systems with SCN^- bridging ligands,[392] one-dimensional complexes in which the heterodinuclear entities are linked by the nitrite groups,[393] and very recently a supramolecular structure, in which the Cu-Ni entities are linked by hydrogen bond and behave as molecule-based magnet, have been reported.[394] So far the number of supramolecular systems derived from trinuclear copper(II)-copper(II)-copper(II) entities is very limited; with oxamidato ligand only one Cu_3 supramolecular structure has been reported.[395] Efforts are being made to link trinuclear copper(II) complexes derived from bis(oxamato)copper(II) systems in a supramolecular manner[396].

It is now well established that the self assembly processes may generate well- defined architecture in a spontaneous and direct manner[397] which are dependent upon numerous factors, such as the nature of the coordination site, the structure of the bridging ligand, the geometric preferences of the metal ions, and weaker non-covalent interactions. The application of metal-ligand interactions has proved particularly faithful, and a considerable variety of frequently predesigned molecular architectures have all been assembled.[398-400]

Among them, macrocyclic compounds formed by self assembly of transition metals introduce many special functional properties such as luminescence,[401] redox activity,[402] and magnetism[403] in to the structure apart from their particular structural features. Supramolecular structures can be formed by the grid formation. Thomson et al. reported a self assembled M_9 maganese(II), iron(III), zinc(II) and $M_5 [M_3]_2$ lead(II) complexes. A tritopic ligand 2poap **(Fig. 1.52)**, self assembles to give [3X3] nonanuclear grids with zinc(II) and iron(III).



where R = 2'-pyridyl; R' = H.

Fig. 1.52

Cl_2poap, where, R = 2'-pyridyl; R' = Cl and Cl_2poapz, where R = 2'-pyrazinyl; R' = Cl, form Mn_9 square grids. The lead(II) complex, with a trinuclear subunit structure, clearly indicates that the metal ion radius is an important factor in the self assembly out-come and that despite the large coordination pocket sizes observed in the M_9 systems in general, large cations such as lead(II) cannot be accommodated in a gridlike arrangement. These entire grid like systems incorporate paramagnetic metal centres with short range bridging connections and the presence of intramolecular spin-spin exchange interactions. Antiferromagnetic coupling occurs for all the systems, an agreement with the presence of M-O-M bridges with large (125-135°) bridge angles and direct magnetic orbital overlap, but magnetic orbital orthogonality in the copper(II) case leads to ferromagnetic exchange.[404] In continous studies of self assembled systems, Thomson *et al* reported flexible poydentated dihydrazone ligands, based on pyridine-2,6-dipicolinic, oxalic and malonic subunits. It forms polynuclear manganese(II), cobalt(II/III), nickel(II) complexes. In these clusters, magnetic interactions are found to be very weak due to very well separated, remote coordination pockets.[405]

The ability of the **oxamidato** group to transmit efficiently magnetic coupling has been well documented.[406] The oxamidato-bridged gadolinium(III)-copper(II) complexes have been investigated magnetically since the pioneering research by Gatteschi et al, who first found that the gadolinium(III)-copper(II) exchange is ferromagnetic.[407] Since the discovery of a ferromagnetic interaction in Cu_2Gd complexes in 1985,[407] the exchange coupling between a 4f ion and a spin carrier, 3d ion or organic radical, has been studied for both its fundamental aspects, with the aim to elaborate an accurate theoretical model of the interaction, and its applications especially in the building of molecule-based magnets.[408-411] A four-coordinate macrocyclic oxamidato-copper(II) complex has been used as "the complex ligand" to successfully construct polynuclear Cu_6Nd_2 complexes.[408] In recent work, a 2D heterometallic chromium(III)-copper(II)-gadolinium(III) complex, containing cyano and oxamidato bridges have been reported as a first structurally characterized 2D heterotrimetallic complex with three different spin carriers with ferromagnetic interaction.[412] Then in recent years, the first, molecular compounds exhibiting a magnetic coupling between 3d and 5f ions have been isolated.[413-416]

The magnetic behavior of the trinuclear complexes $[\{CuL^i(py)_x\}_2U]$ in which the central uranium(IV) ions, by means of a hexadentate Schiff base ligand [N,N'-bis(3-hydroxysalicyldene)-R], appeared to depend on the nature of the diimino chain R; the Cu-U interaction was found to be antiferromagnetic for R = 2-methyl-1,2-propanediamine (i = 2) and ferromagnetic for R = 1,3-propanediamine (i = 6) and dimethyl-1,3-propanediamine (i = 7).[415,416] These results revealed that the Cu-U interaction, like the 3d-4f and organic radical -4f interactions, is very sensitive to slight variations in the structure of the complexes. The most significant structural features to which the sign of the Cu-U coupling could be related concern the copper(II) ion coordination and the Cu-U separation. To continue this study, recently, a series of trinuclear Schiff base complexes of 5f (U^{IV}, Th^{IV}) and 3d (copper(II), zinc(II)) ions were synthesized and well characterized by Salmon et al.[417] A heterometallic system, M(II)-manganese$(III)_2$-M(II) with copper(II) and nickel(II) containing mangnese(III) salen type dinuclear core, was reported by Miyasaka et al[418]. They have shown how the SMM properties can be controlled using chemical modifications of a known system. This chemical flexibility is one of the most important advantages found in the bottom-up approach to designed magnetic materials; however, such examples are rare.

Hypothesis and Objective of the present work

The design of molecular magnets is based on tuning of spin exchange interaction between the neighbouring paramnganetic centres in a bi- or polynuclear transition metal complex or a radical containing species, through a variety of bridging groups. This needs complete understanding of the magnetic exchange phenomenon and the role of bridging as well as non bridging parts of the molecule. Extensive studies of binuclear complexes have indicated that, such interactions depend mainly on favourable or unfavourable interaction between the paramagnetic orbitals of the bridging groups. The extent of such an interaction depends on i) the energy of paramagnetic orbitals and their relative orientation with respect to each other and ii) the presence of exchange propagating orbitals in the bridging ligands and their energy.

For a favourable interaction the energy and symmetry of the paramagnetic orbitals and suitable bridging ligand orbitals have to match. Also, π-symmetry bridging orbitals with continuous delocalization of π-electron density are found to be more efficient mediators of spin exchange. A variety of parameters affecting the extent of spin exchange have been identified,

(a) The metal - ligand bond length.

(b) The M-L-M bridging angle (ϕ), **Fig. 1.53a**

(c) The dihedral angle between metal coordination planes, θ.

(d) The torsional angle Γ, **Fig. 1.53b**

(e) The degree of planarity of the bridging unit.

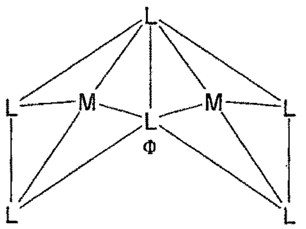


Fig. 1.53 a

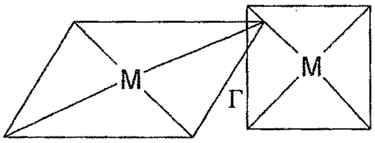


Fig. 1.53 b

In the multimetal systems the interaction between all metal centres is important than mearly the exchange between neighbouring spins. Thus it becomes important to identify the factors governing spin exchange/communication between the distant metal ions which may be separated by additional paramagnetic centres along with the bridging ligand i.e. in a linear trinuclear M-M-M arrangement, the interaction between the pairs between the first and second as well as the second and third metal centres is obvious. However, the interaction between the first and third metal ion can be affected by several other parameters. In such cases the complemetarity or counter complementarity of these interactions is also important as the overall magnetic property is a result of combination of all such interactions. In a triangular trimetallic arrangement, the interaction between each pair can be equally significant. The study of trinuclear complexes becomes important as they are a link between binuclear and polynuclear species and the understanding of parameters affecting the spin exchange in these systems can give important insights in to designing of tailor-made molecular magnets with improved tunning of magnetic exchange becoming possible with variations in the design of the molecule.

There are few less explored areas such as, the effect of distant groups on the bridging ligands, nature of the non bridging ligands and the ligand affected distortions in the molecular geometry. Spin and electron delocalization can also lead to interesting redox and physical properties. As the magnetism and redox in the coupled systems largly depends on the molecular structures, a comparision of the redox property with magnetism is also thought to be interesting. These multimetal systems can also lead to the formation of interesting super structures.

The objective of the present work is to design new trinucleating ligands capable of holding three metal ions and also proving variable electronic and geometrical environment. The bridging groups with π-delocalization can be efficient mediators of spin exchange. Hence, the trinucleating ligands with oxalate or aromatic bridging moieties become more important. The main emphasis in the present work is on the oxamide, aromatic dihydroxy phenyl and ferrocinyl bridging groups.

Oxamide ligands have versatile bonding mode with metal ions, which makes it possible to design tunable molecular materials with extended structures. They can facilitate electron and spin exchange and also have biological relevance. There have been recent efforts to achieve stabilization of unusual high oxidation states of transition metal ions and tune their properties by amide substitution. For this versatility of oxamide bridging groups exhibited in their binuclear complexes, these have been our choice for designing most of the trinuclear complexes reported in this work. Following types of bi- and trinuclear complexes of copper(II), have been synthesized characterized and an attempt is made to establish structure, magnetism and redox property relationships.

1. Binuclear complexes with σ-bonded bis(oxamide) bridges,
2. Trinuclear complexes of bis(oxamido) hydrazones with aromatic amino acids as capping ligands,
3. Angular trinuclear complexes with bis(oxalo)dihydrazones formed with aromatic aldehydes and glyoxal,
4. Linear trinuclear complexes with, aromatic dihydroxy phenyl bridging groups,
5. Heterotrinuclear Cu_2Fe complexes with a Ferrocyl ligand as a spacer. And
6. A new area of metallogels having three dimensional supramolecular structures has been explored with myo-inositol as a backbone.

1 Binuclear complexes with σ-bonded bis(oxamide) bridges: Three trinucleating ligands have been synthesized by condensation of diethyl oxamate with aliphatic diamines namely en, 2pn and 3pn. The ligands form binuclear complexes in acidic media in presence of bipy and phen. Six newly synthesized binuclear complexes have been characterized by various analytical and spectral methods including ^{1}H NMR (ligand), ESR and Mass specral analysis in addition to the UV-visible and IR spectroscopy. The complexes undergo quasireversible, stepwise redox from copper(II)-copper(II) to copper(I)-copper(I) state. Evaluation of the magnetic properties between liq. N_2 to RT indicates the presence of strong ferromagnetic interactin between copper(II) centres with the values of J ranging between 40 to 150cm^{-1}. Geometry of the ligands has been optimized using ab-initio quantum mechanical calculation using 6-31G basis set and universal force field, respectively. The calculated geometrical parameters have been correlated with the electrochemical and the magnetic properties.

2 Complexes of bis(oxamido) hydrazones with amino acids: A trinucleating ligand with combined amide-imine coordinating sites and a central site forming 6-5-6 membered chelate rings has been synthesized by converting ethyl oxamate into oxamidohydrazide and then condensing with glyoxal (**oxd**). Five trinuclear complexes have been synthesized by reacting **oxd** with cupric acetate and aromatic amino acids, namely, L-phenylalanine, L-histidine, L–tryptophan, L-tyrosine and anthranilic acid. The complexes have been characterized. Their magnetic and electrochemical properties studied in detail and have been correlated with the calculated geometrical parameters.

3 Angular Trinuclear Complexes with bis(oxalo)dihydrazones with aromatic aldehydes: To study the combination of chelate ring size, π-delocalization in the bridging ligand and electronic and geometrical influence exerted by the presence of various functional groups on the ligands, six complexes of new trinucleating ligands with substituted aromatic aldehydes have been synthesized. The *ab initio* quantum mechanical claculations have shown that the ligands have highly delocalized π-cloud, which mediates strong antiferromagnetic exchange between the copper centres. The complexes undergo reversible redox to $Cu^{I}Cu^{I}$ state at potentials affected by the nature of bidentate capping ligands.

4 Linear trinuclear complexes with aromatic bridges: In order to examine the efficacy of the aromatic bridging groups coupled with a central paramagnetic ion, three new trinucleating ligands have been synthesized by condensing *2,4*-diacetyl resorcinol with *1,2*-diamino ethane, *1,2*-diamino propane and *1,3*-diamino propane. Trinuclear complexes of copper have been prepared using 1,10-phenanthroline and 2,2'-bipyridine as capping ligands.

These ligands have extensive π-delocalization as shown by the quamtum mechanical calculation. As a result, the metal ions undergo a very strong antiferromagnetic exchange with J values between -200 to $-500 cm^{-1}$. The magnetic and redox properties have been correlated with structural parameters.

5 Trimetallic Cu_2Fe complexes with a Ferrocenoyl ligand: Disuccinoyl ferrocene (dsf) is capable of holding two metal ions and thus can form trimetallic M_2Fe type of species. Disuccinoyl ferrocene forms two different types of trimetallic species in presence of bidentate ligand 1,10-phenanthroline, 2,2'-bipyridine, 8-hydroxyquinoline, dibenzoyl methane and bis(2-pyridyl ketone). The complexes have been characterized and electrochemistry has been studied by cyclic-voltammetry.

6 Trinuclear copper(II) complex with inositol: A low molecular weight complex hydrgelator:

The ability of myo inositol as a trinucleating ligand has been explored. It has been observed that *myo*-inositol forms trinuclear complexes of copper with water molecules occupying free coordination postions around the metal ions. In presence of bipy, a trinuclear complex [Cu_3ins(bipy)$_3$] is formed, which forms a two component metallogel at high pH. The trinuclear complexes of *myo*-inositol and gel has been characterized by various analytical and spetctral methods. The SEM images of gel have shown the formation of fibrous super structures. The presnec of π– π interactions and hydrogen bonding are thought to be the forces leading to the formation of supramolecular assembly. This is the first example of a discrete trinuclear metal complex as a hydrogelator.

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

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Ligands and abbreviations

en = 1,2-diaminoethane

2pn = 1,2-diaminopropane

3pn = 1,3-diaminopropane

bipy = 2,2'-bipyridine

phen = 1,10-phenanthroline

Ac = acetate ion

ox = diethyl oxamate

glx = glyoxal

anthr = anthranilate

phe = phenylalaninate

his = L-hystidinate

trp = L-tryptophanate

tyr = tyrosinate

oxd = oxalodihydrazide

sal = anion of 2-hydroxybenzaldehyde

van = anion of o-vaniline

naph = anion of 2-hydroxynapthaldehyde

brsal = anion of 5-bromo-2-hydroxybenzaldehyde

3m2hacph = anion of 3-methyl-2-hydroxy acetophenone

dsf = 1,1'-bis-(3-carboxypropynoyl)-cyclopentadienyl)-iron

acac = acetyl acetone

8hq = 8-hydroxy quinolinate

dpk = dipyridyl ketone

dbm = dibenzoyl methane

ins = *myo* inositol