Interest in the synthesis of binuclear copper(II) complexes is mainly due to their applications in bioinorganic chemistry, magnetochemistry and homogeneous catalysis[1]. The main objective of bioinorganic chemistry of these compounds is to understanding the functional and structural properties of binuclear active site by developing small dicopper complex models for the metalloproteins[2]. The diazido, diphenoxido-dicopper(II) complexes having a five-coordinate geometry around each copper ion have been investigated frequently because of the interest in new inorganic materials showing molecular ferro- or antiferromagnetic interactions[3]. The metal-azido complexes deserve special mention because of their fascinating structural diversities, their importance in understanding magneto-structural correlations, and their promising potential applications in functional materials[4]. The diphenoxido-dicopper(II) complexes also show interesting non-magnetic properties such as catechol oxidase activity [5], fluorescent sensors [6], heterogeneouscatalysis [7] and also useful in metal extraction in hydrometallurgy [8].

1.1 Structure of copper(II) complexes

The most common oxidation state of copper exists in biological systems is +2. Because of its d⁹ orbital configuration, Cu(II) provides a typical example of Jahn-Teller effect. Copper centers in the complexes have a variety of distortions, which have attracted the attention of chemists for a few decades[9]. It is considered hard, and easily to coordinates with N and O. The coordination number is mainly four, five or six. When Cu(II) is four
coordinated, the geometry of the metal center is square planar. When Cu(II) is five coordinated, the geometry of the metal center is distorted square pyramidal or trigonal bipyramidal. When Cu(II) is six coordinated, the geometry of the metal center is elongated octahedron. Cu(II) may also have intermediate structures between square pyramidal and trigonal bipyramidal geometry when it is five coordinated. The judgment on the five coordinated geometry between square pyramid and trigonal bipyramid can be made based on the $\tau$ value, which was introduced by Reedijk and co-workers[10] It is defined as $\tau = (\beta-\alpha)/60$, which is the ratio differences between two in-plane angles, that are larger than 90º (Figure 1). Normally, the $\tau$ value is between 0 and 1. The absolute number 0 represents the perfect square pyramid ($C_{4v}$) and 1 represents the ideal trigonal bipyramidal ($D_{3h}$). The ideal situation is seldom[11] seen. This definition has been widely used to compare the structure of five coordinate Cu(II) complexes[12]. A few examples are given in Table 1

![Figure 1 A diagram showing the definition of $\tau$](image)
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\tau$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cu}_2(\text{D,L-Sala})_2(\text{H}_2\text{O})_2]$</td>
<td>0.01</td>
<td>[13]</td>
</tr>
<tr>
<td>Cu(cyclops)(CN)</td>
<td>0.06</td>
<td>[14]</td>
</tr>
<tr>
<td>$[\text{Cu}_2(\text{Sala})_2(\text{H}_2\text{O})]$</td>
<td>0.10 for Cu, 10.21 for Cu$_2$</td>
<td>[15]</td>
</tr>
<tr>
<td>$[\text{Cu}_2(\text{Strp})_2(\text{H}_2\text{O})]$</td>
<td>0.10 for Cu, 10.05 for Cu$_2$</td>
<td>[13]</td>
</tr>
<tr>
<td>$[\text{Cu}(\text{Sala})\text{phen}]$</td>
<td>0.13</td>
<td>[16]</td>
</tr>
<tr>
<td>$[[\text{Cu}(\text{bipy})_2\text{Cl}][\text{BPh}_4]]$</td>
<td>0.19</td>
<td>[17]</td>
</tr>
<tr>
<td>$[(\text{phen})\text{Cu(}\mu\text{-Sgly})\text{Cu(phen)}_2]^{2+}$</td>
<td>0.30 for Cu, 10.72 for Cu$_2$</td>
<td>[18]</td>
</tr>
<tr>
<td>$[\text{Cu}_2(\text{Sbal})(\text{phen})_3]^{2+}$</td>
<td>0.14 for Cu, 10.58 for Cu$_2$</td>
<td>[19]</td>
</tr>
<tr>
<td>$[\text{Cu}(\text{Sab}_4)(\text{phen})(\text{H}_2\text{O})]$</td>
<td>0.13</td>
<td>[17]</td>
</tr>
<tr>
<td>$[\text{Cu}_2(\text{Sab}_4)(\text{phen})_3]^{2+}$</td>
<td>0.15</td>
<td>[17]</td>
</tr>
<tr>
<td>$[\text{Cu}_2(\text{MeSgly})_2(\text{H}_2\text{O})_2]$</td>
<td>0.03</td>
<td>[20]</td>
</tr>
<tr>
<td>$[\text{Cu}_2(\text{Sval})(\text{H}_2\text{O})]$</td>
<td>0.07 for Cu, 10.25 for Cu$_2$</td>
<td>[21]</td>
</tr>
<tr>
<td>$[\text{Cu}(\text{bipy})_2(\text{O}_2\text{CR})]^{+}$</td>
<td>0.50</td>
<td>[21]</td>
</tr>
<tr>
<td>$[\text{Cu(phen)}_2\text{Br}][\text{ClO}_4]$</td>
<td>0.86</td>
<td>[22]</td>
</tr>
<tr>
<td>$[\text{Cu}(\text{bipy})_2\text{Cl}][\text{PF}_6]$</td>
<td>1.00</td>
<td>[14]</td>
</tr>
<tr>
<td>$[\text{CuCl}_5]^{3-}$</td>
<td>1.00</td>
<td>[23]</td>
</tr>
</tbody>
</table>
1.2 Binucleating ligands

The term binucleating ligand was introduced in 1970 for a series of polydentate ligands capable of simultaneous securing of two metal ions. Since 1970 there has been a continuous increase in the synthesis of binucleating ligands and related complexes and several reviews has been published on this subject.

In the design of suitable binucleating ligands capable of accommodating two metal atoms to form binuclear complexes, there involves three main structural principles:

1. The nature of the coordination site (N, O, P, S etc.) on which the selection of the complexed cations, their redox and substrate binding dependence of properties.

2. The properties of the binucleating subunits such as the number and arrangement of coordination site which determine the coordinative unsaturation and the geometry of the coordination shell of the cations. The ligand architecture which defines the framework holding the structure and establishes that the way in which subunits are built into final structure.

3. Depending on the nature of the subunit used as building blocks and the number of connecting bridges used for their construction, a variety of binucleating ligand structures may be envisaged.

The complexes obtained by these ligands have been divided into two classes:

1. Complexes with metals sharing at least one donor atom of the ligands containing adjacent sites in which the central metal ion provides a bridge.

2. Complexes in which the donor atoms are not shared by the two metal ions. These complexes are derived from ligands having isolated donor sets.
1.3 Synthesis of copper(II) complexes using Mannich base ligands

The Mannich base ligands will give useful information to biological reactions and helps to investigate the hidden characters of the ligand[24]. These ligands offers more flexible and non-planar conformation. These two important features, imparted to the Mannich bases, offer variety of conformations and provide an opportunity to form interesting coordination compounds. It was found that some of the Schiff base products are not stable[25]. The stability of Schiff base compounds depends on the pH, solvent and temperature. In most cases in order to overcome the problems of isolating the Schiff base ligands, they were stabilized by employing the suitable metal ions and obtained as metal complexes[26]. However, problems of isolation and ligand instability can be overcome by reducing the C=N bond of the Schiff base to give an amine and this approach presents interesting possibilities[16]. Our research group has been interested in the coordination chemistry of multidentate Mannich base ligands, [N-(2-{dimethylamino}ethyl-N’-methyl)aminomethyl]phenol formed between reaction of phenol with trialkylethylenediamine and formaldehyde (1:1:1) for the following reasons:

(1) Easy and straight forward synthesis from cheaply available starting materials.

(2) The Mannich bases, compared to the Schiff bases, are more stable.

(3) These tridentate ligands are capable of forming conformationally flexible five or six membered rings upon complexation which is important for catalytic modeling studies.

(4) In addition, these ligands offer potential hydrogen bond donor and acceptor functionalities required for the supramolecular self-assembly leading to interesting hydrogen bonded networks.
Further, they can also afford the choice of coordination environments that determine the nature of metal ions that can be bound within the closest proximity resulting in the dinuclear complexes.

The use of natural amino acids in synthesizing the ligand makes the induction of chirality in the complex easier and cheaper.

The presence of a phenolate donor is expected to give a strong charge-transfer (CT) transition to metal complexes. The presence of a strong CT transition is one of the requirements for second-order nonlinear optical materials.

The presence of amino acids will help the metal complexes to dissolve in aqueous solution for environmentally benign applications.

### 1.4 Azido bridged dinuclear copper(II) complexes

The metal-azido complexes deserve special mention because of their fascinating structural diversities, their importance in understanding magneto-structural correlations, and their promising potential applications in functional materials[27]. Basically the diazido-dicopper(II) complexes forms two types of coordination modes; (i) end-to-end ($\mu_{1,3}$-N$_3$, EE) and (ii) end-on ($\mu_{1,1}$-N$_3$, EO). When the azido bridges are exclusively end-to-end or end-on it does not mean that all bridges are structurally and crystallographically identical[28].

![Symmetric double end-to-end mode](a); asymmetric double end-to-end mode (b).

**Figure 2** Symmetric double end-to-end mode (a); asymmetric double end-to-end mode (b).
The type and the magnitude of the magnetic exchange interaction depends on the bridge identity, the metal–metal separation, the bond angles subtended to the bridging atoms, the dihedral angles between the planes containing the metal ions, the metal bridging ligand bond lengths, and the metal ion stereochemistries[29]. In general, EE diazido bridges propagate antiferromagnetic interactions[30]. But the EO coordination mode is associated with ferromagnetic coupling[31]. The EE-azido-bridged dicopper(II) complexes conform symmetrical and asymmetrical double $\mu_{2,1,3}$-azido bridges i.e (i) having four M–N(azide) short distances ($\leq 2.10\text{Å}$) [symmetrical double $\mu_{2,1,3}$-azido bridges] which are strongly antiferromagnetically coupled[32] and ii) having two M–N(azide) short ($\leq 2.10\text{Å}$) and two M–N(azide) long distances ($\geq 2.20 \text{Å}$) [asymmetrical $\mu_{2,1,3}$azido bridges] which are weakly antiferro/or ferromagnetically coupled[33]. Double EO azido bridging coordination modes are of two types: (i) symmetric double end-on azido bridges and (ii) asymmetric double end-on azido bridges. In general the symmetric double end-on azido bridged dinuclear complexes having a [Cu$_2$(μ$_1$1,1-N$_3$)$_2$]$^{2+}$ core with Cu–N$_3$–Cu angle close to $\leq 104^\circ$ and are ferromagnetically coupled. The $J$ value varies within a broad range (2.5–230cm$^{-1}$). The magnetic and structural data of asymmetric double Bridging ($\mu_{1,3}$-N$_3$) azido copper(II) complexes with antiferromagnetic coupling are illustrated in

Figure 3 Ortep diagram of dicopper(II) complex $[\text{Cu(L}_4)(\text{N}_3)]_2$ [34]
There are three structural parameters may impose significant influences on the magnetic interaction: (i) the Cu–N–Cu angle ($\theta$), (ii) the Cu–N bond distances and (iii) the distortion of the coordination geometry. The Cu–Cu distance is not an independent factor and depends on $\theta$ and Cu–N distances. The weakest ferromagnetic coupling is observed in $[\text{Cu}_2(\mu-\text{N}_3)_2(\text{tacn})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}[34]$. while the strongest ferromagnetic coupling is observed in complex $[\text{Cu}_2(\mu-\text{N}_3)_2(4-\text{Etpy})_4(\mu-\text{NO}_3)_2][35]$ due to Cu–N–Cu angle is large than 108°. It is easy to understand that longer Cu–N distance should lead to weaker coupling. Cu(II) geometry in these complexes is square pyramid with severe distortion towards TBP. This distortion is not conducive to the efficient delocalization of the $d_{x^2-y^2}$ type magnetic orbital towards the equatorial bridging ligands and hence the interaction is reduced. In general the end-on (EO) and end-to-end (EE) azido copper(II) complexes give ferromagnetic and antiferromagnetic coupling, but these rules do not apply under certain specific circumstances. When the azido bridges are exclusively end-to-end or end-on it does not mean that all bridges are structurally and crystallographically identical. Within the same system two or more different structural bridges may present, owing to different distances and/or angles found in the structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau$</th>
<th>$J$ (cm$^{-1}$)</th>
<th>$\Delta$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cu(Medpt)}(\mu-\text{N}_3)_2(\text{ClO}_4)_2$</td>
<td>0.23</td>
<td>-105</td>
<td>11.3</td>
<td>[36]</td>
</tr>
<tr>
<td>$[\text{Cu(Et5dien)}(\mu-\text{N}_3)_2(\text{ClO}_4)_2$</td>
<td>0.43</td>
<td>-28</td>
<td>15.7</td>
<td>[37]</td>
</tr>
<tr>
<td>$[\text{Cu(Me5dien)}(\mu-\text{N}_3)_2(\text{BPh}_4)_2$</td>
<td>0.29</td>
<td>-13</td>
<td>_</td>
<td>[38]</td>
</tr>
<tr>
<td>$[\text{Cu(Me5dien)}(\mu-\text{N}_3)_2(\text{ClO}_4)_2$</td>
<td>0.23</td>
<td>-7.5</td>
<td>15.7</td>
<td>[37]</td>
</tr>
<tr>
<td>$[\text{Cu(L}^{19}(\mu-\text{N}_3)_2(\text{ClO}_4)_2$</td>
<td>0.16</td>
<td>-3.4</td>
<td>_</td>
<td>[39]</td>
</tr>
</tbody>
</table>

$R = M-\text{Nazido(basal)}\AA$
Table 3  Selected structural and magnetic interaction parameters for asymmetric double Bridging ($\mu_{1,3}$-N$_3$) azido copper(II) complexes with ferromagnetic coupling.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau$</th>
<th>$J$ (cm$^{-1}$)</th>
<th>$\Delta$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(N$_3$)(tmen)(µ-N$_3$)]$_2$</td>
<td>0.20</td>
<td>0</td>
<td>_</td>
<td>[39]</td>
</tr>
<tr>
<td>[Cu(L$^{20}$)(µ-N$_3$)]$_2$(ClO$_4$)$_2$</td>
<td>_</td>
<td>2.4</td>
<td>38.1</td>
<td>[40]</td>
</tr>
<tr>
<td>[Cu(Et$_3$dien)(µ-N$_3$)]$_2$(ClO$_4$)$_2$</td>
<td>0.20</td>
<td>9</td>
<td>35.8</td>
<td>[36]</td>
</tr>
<tr>
<td>[Cu(L$^{21}$)(µ-N$_3$)]$_2$(ClO$_4$)$_2$</td>
<td>0.08</td>
<td>90.7</td>
<td>_</td>
<td>[41]</td>
</tr>
<tr>
<td>[Cu(L$^{22}$)(µ-N$_3$)]$_2$</td>
<td>_</td>
<td>13.6</td>
<td>_</td>
<td>[42]</td>
</tr>
<tr>
<td>[{Cu(phen)N$_3$)$_2$}(4,4'bpy)] (ClO$_4$)$_2$</td>
<td>_</td>
<td>5.52</td>
<td>_</td>
<td>[43]</td>
</tr>
<tr>
<td>[Cu(L$^{23}$)(µ-N$_3$)]$_2$</td>
<td>0.18</td>
<td>7.96</td>
<td>29</td>
<td>[44]</td>
</tr>
</tbody>
</table>

Table 4  Structural and magnetic parameters for symmetric double end-on($\mu_{2,1,1}$-N$_3$) azido bridged dimeric complexes.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Cu–Cu (Å)</th>
<th>Cu–N (Å)</th>
<th>Cu–N–Cu (°)</th>
<th>$J$(m$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu$_2$(N$_3$)$_2$(4-Etpy)$_4$(µ-NO$_3$)$_2$]</td>
<td>3.024</td>
<td>2.004, 1.99</td>
<td>98.2</td>
<td>230.1</td>
<td>[45]</td>
</tr>
<tr>
<td>[Cu$_2$(4-pya)$_2$(N$_3$)$_2$ (DMF)$_2$]</td>
<td>3.123</td>
<td>2.00, 2.01</td>
<td>102.1</td>
<td>145</td>
<td>[56]</td>
</tr>
<tr>
<td>[Cu$_2$(N$_3$)$_2$(t-Bupy)$_4$] (ClO$_4$)$_2$</td>
<td>3.045</td>
<td>1.99, 1.97</td>
<td>100.5</td>
<td>105</td>
<td>[47]</td>
</tr>
<tr>
<td><a href="PF$_6$">Cu$_4$(N$_3$)$_4$(Dur)</a>$_4$·4H$_2$O·6CH$_3$CN</td>
<td>-</td>
<td>2.030, 1.970</td>
<td>98.1, 96.6</td>
<td>94</td>
<td>[48]</td>
</tr>
<tr>
<td>[Cu$_2$(DMPTD)$_2$(µ -N$_3$)$_2$(N$_3$)$_2$]</td>
<td>3.076</td>
<td>2.043, 1.995</td>
<td>98.3, 101.9</td>
<td>85</td>
<td>[49]</td>
</tr>
<tr>
<td>[Cu$_2$(N$_3$)$_2$(N$_3$)$_2$(N$_2$O$_6$)]·H$_2$O</td>
<td>3.162</td>
<td>2.043, 1.990</td>
<td>101.7, 105.4</td>
<td>70</td>
<td>[50]</td>
</tr>
<tr>
<td>[Cu$_2$(N$_3$)$_2$(O$_2$CCH$_3$)$_2$(dpyam)$_2$]</td>
<td>3.20</td>
<td>2.00, 2.14</td>
<td>101.2</td>
<td>64</td>
<td>[51]</td>
</tr>
<tr>
<td>[Cu$_2$(N$_3$)$_2$(N$_3$)$_2$(phprpy)$_2$]</td>
<td>-</td>
<td>1.99, 2.14</td>
<td>101.9</td>
<td>25.6</td>
<td>[52]</td>
</tr>
<tr>
<td>[Cu$_2$(N$_3$)$_2$(N$_3$)$_2$(tbz)$_2$]·2CH$_3$OH</td>
<td>-</td>
<td>2.059, 2.037</td>
<td>104.7</td>
<td>23</td>
<td>[53]</td>
</tr>
<tr>
<td><a href="ClO$_4$">Cu$_2$(N$_3$)$_2$(tacn)$_2$</a>$_2$·CH$_3$OH</td>
<td>-</td>
<td>2.007, 1.997</td>
<td>99.9</td>
<td>25</td>
<td>[54]</td>
</tr>
</tbody>
</table>

9
our present state of understanding it is impossible to predict which coordination mode will be adopted during synthesis. The magnetic and structural data for asymmetric double Bridging ($\mu_{1,3}$-N$_3$) azido copper(II) complexes with ferromagnetic coupling are illustrated in above Table 3.

1.5 Phenoxy bridged dinuclear copper(II) complexes

Phenoxy ligands have been receiving intense attention in the synthesis of various complexes with different transition metals, among which the most frequent ones are those of copper(II). These copper(II) complexes also show remarkable non-magnetic properties, making them useful in metal extraction in hydrometallurgy [55], fluorescent sensors [56], heterogeneous catalysis [57], and show catechol oxidase activity [58]. For many years, all the phenoxy-bridged copper(II) complexes reported exhibited a relatively strong antiferromagnetic coupling. However, some strongly ferromagnetically coupled complexes have been obtained recently [59]. The magnetic properties of bridged dinuclear copper(II) complexes have been extensively studied, since the copper(II) ions have an $S = 1/2$ spin, which makes them easier to deal with, from both the experimental and theoretical points of view [60]. Bleaney and Bowers derived a theoretical expression for the magnetic susceptibility of dinuclear copper(II) systems [61], making it possible to extract the exchange coupling constant (J) for each complex from the magnetic susceptibility curves. The wealth of available coupling constants allows the study of their relationship with structural parameters, in search for some trends that could lead to a rational design of new complexes with improved magnetic properties. For the related bis(hydroxo) [62] and bis(alkoxy) [63] bridged copper(II) complexes, linear relationships
between the Cu–O–Cu bond angle and the J values obtained from a fitting of the experimental magnetic susceptibility data have been reported. For instance, in the case of hydroxo complexes, a transition from antiferromagnetism to ferromagnetism is observed for Cu–O–Cu angles smaller than 97° [62]. This phenomenon is attributed to an “accidental orthogonality” of the orbitals bearing the unpaired electrons. Thus, to minimize electronic repulsions, the system adopts the high spin state that corresponds in this case to a triplet. From a molecular orbital point of view, Hoffmann [64] and Kahn [65-66] gave consistent explanations within the extended Hückel framework. More recently, the use of theoretical methods based on density functional theory (DFT) has made it possible to obtain remarkably good quantitative estimates of the J values for this kind of complexes, in spite of the small energy differences associated to these interactions. Ruiz et al.[67] have earlier applied such an approach to the study of magnetostructural correlations in hydroxo- and alkoxobridged copper(II) complexes [68]. The results indicate that several structural parameters affect the J value, but the Cu–O–Cu angle (α), correlated with the phenyl out-of-plane shift angle (τ), plays a key role (see Figure 3).

![Figure 3](image)

**Figure 3** Distortion representation of phenoxo bridged copper(II) complexes with the phenyl out-of-plane
Among other structural parameters, a special mention the bending of the Cu$_2$O$_2$ framework around the O· · ·O hinge, that can also play an important role if it is sufficiently large. All dinuclear bis(phenoxo) bridged CuII complexes belong to one of two general types, having two chelate ligands spanning terminal and bridging positions (Figure 4(a)) or with the phenoxo groups incorporated into a multidentate macrocyclic ligand (Figure 4(b)). The second family, known as Robson complexes, has been studied by Thompson et al. [69], who showed that the exchange coupling constant is correlated to the Cu–O–Cu bond angle. An important feature of the Robson-type macrocycles is that they are generally constrained to adopt a planar configuration. Thompson et al. (Figure 4) also analyzed the effect of different electron withdrawing substituents on the value of the coupling constant. Theoretical studies of the different electronic effects of substituents on

![Figure 4 Possible molecular structure in Phenoxo bridged copper(II) complexes with different electron withdrawing substituents.](image)

the magnetic exchange interaction between substituted dialkoxo Cu(II) systems and substituted carboxylate Cu(II) complexes were later published by Rodríguez-Fortea et
al.[70]. The effects reported in those two publications correspond to substituents only one or two bonds away from the bridging oxygen atoms. The goal of the present work is to study the influence of different structural parameters on the nature and magnitude of the magnetic exchange interactions in dinuclear bis(phenoxo)-bridged Cu(II) complexes (Figure 3), as well as the long range effect of different para substituents on the phenyl rings characterized by their Hammett parameter [71]. We put special emphasis in unravelling the structural features that favour the presence of weak antiferromagnetism in a few members of the dinuclear bis(phenoxo) bridged Cu(II) family.

1.6 Theory of magnetic exchange interactions

The magnetic properties of the coupled bi-and polynuclear transitions metal complexes are affected by the magnetic exchange interaction between the neighbouring paramagnetic ions. The exchange interaction occurs between the spins of the neighbouring paramagnetic ions, when the paramagnetic centers are close enough for direct or indirect orbital overlap[72]. If the exchange interaction is greater than KT, a cooperative phenomenon of ferromagnetism or antiferromagnetism Based on the magnetic behaviour, the complexes are divided into three types based on the extent of interaction between the metal centers[73].

(1) Weakly interacting type: In complexes with intermetallic distances ranging from 3 to 6 Å, mixing of the metal magnetic orbitals is happening through a filled intervening ligand orbital. Such an interaction is always weak and produced low energy molecular states with different multiplicity (2J < 1000 cm⁻¹).
Non-interacting type: The magnetic property of the complexes is unchanged from the monomer. Binuclear complexes with intermetallic distance more than 6 Å or if the two copper containing planes are orthogonal to each other will display this type of behaviour.

Strongly interacting type: The complexes will be diamagnetic due to direct interaction between the copper atoms. Binuclear complexes with intermetallic distance less than 2 Å are generally diamagnetic.

The magnetic properties of dicopper(II) complexes with weak interaction between the partially filled metal magnetic orbitals containing the unpaired electron through the completely filled intervening ligand orbital, often termed as super exchange interaction, results interesting magnetic properties depending upon the spin of the ground state $S = 1$ (ferromagnetic) or $S = 0$ (antiferromagnetic) [74].

The exchange interaction in copper dimer is explained based on orbital model proposed by Hay and Coworkers which is grounded on the basis of magnetic orbitals and overlap density between the magnetic orbitals[75]. For a dimer of the type A-B, where A (or B) symbolizes the metallic ion surrounded by ligands, the magnetic orbitals of A and B is given by $\phi_A$ and $\phi_B$ respectively. Assuming that there is only one electron around A and B the interaction between A and B leads to molecular states of spin $S = 0$ and $S = 1$ separated by $J$. If the grouped state is $S = 0$ then the interaction will be antiferromagnetic and the interaction will be ferromagnetic when $S = 1$. In this model the singlet-triplet energy gap $J$, characterized the nature and the magnitude of exchange interaction results
from the competition between two driving forces, one favours the singlet ground state \( J_{AF} \) and another favours the triplet ground state \( J_F \). The \( S = 1 \) and \( S = 0 \) states can best be explained by Heitler London wave function built from magnetic orbital and energy for the metal-metal charge transfer configuration is very high than the ground state configuration of A-B, the \( J \) can be explained by the combination of the antiferromagnetic \( (J_{AF}) \) and ferromagnetic \( (J_F) \) components

\[
J = J_{AF} + J_F
\]  
(1)

where \( J_{AF} = -2S (\Delta^2 - \delta^2)^{1/2} \)  
(2)

\[J_F = 2j\]  
(3)

In which \( S \) is the overlap integral between the magnetic orbitals and \( j \) is the two electron exchange integral. The overlap density between the magnetic orbitals is given by

\[
\rho_{(i)} = \phi_{(A)}(i)\phi_{(B)}(i)
\]  
(4)

Then \( S \) and \( j \) are given as

\[
S = \iiint f \rho_{(i)} dt_1
\]  
(5)

\[
J = \iiint f \rho_{(i)} \rho_{(j)} / r_{ij} dt_i dt_j
\]  
(6)

\( \Delta \) is the energy gap between the two molecular orbitals in the dimer and \( \delta \) is the energy gap between the magnetic orbitals as shown in the following Figure 5

![Figure 5](image-url)  

**Figure 5** The model representation of energy gap between the two molecular and the magnetic orbitals.
Based on this model the following cases can be explained

If A = B in the dimer then δ will be zero and $J_{AF}$ reduced to $J_{AF} = -2\Delta S J_{AF}$ in absolute value depends on the overlap integral S between the magnetic orbitals and the energy gap $(\Delta^2 - \delta^2)^{1/2}$. If the magnetic orbitals are unfavorable for interaction then ρ is negligible, and then S and J will be zero at any point of the space. Under this circumstance the magnetic property of the dimer will be sum of what is expected for the two fragments. Another relatively simpler situation is the case where $\rho \neq 0$ and $S = 0$. Here the antiferromagnetic component vanishes and the dimer will be ferromagnetic. This situation corresponds to the orthogonality of the magnetic orbitals. When A = B in the dimmers, the orthogonality of the magnetic orbitals results ρ =0.

The most frequently encountered situation is the one where the antiferromagnetic interaction predominates, due to the stabilization of the singlet ground with respect to the triplet excited state and the pure Heitler- London wave function is no longer valid to describe the $S = 0$ and $S = 1$ states. Under this situation $2\Delta J$ becomes ρ. For experimental convenience, the magnetic interaction between the spins $S_A$ and $S_B$ for atom A and B respectively is given in the form suggested by Heisenberg[76], Dirac[77] and van Vleck[78], $H = -2J S_A S_B$ where J is the coupling constant, which is positive when the spins are parallel and negative when the spins are antiparallel. If $|S_A| = |S_B|$ then the total number of possible molecular states is equal to $S_A$ with total spin $S = 0, 1, \ldots, 2S_A$ and the energy difference between the states $S$ and $S-1$ is given by

$$E(S) - E(S-1) = -2JS$$

(7)

In the case of $S_A = \frac{1}{2}$, the triplet-singlet energy gap
E(1) – E(0) = -2J  \hspace{1cm} (8)

In practice the extent of magnetic interaction in dicopper complexes is determined by performing variable temperature magnetic susceptibility measurements and fitting the experimental susceptibility values to the theoretical values defined by Bleaney-Bowers equation[79].

\[ \chi_M = \left\{ N g^2 \beta^2 / kT \right\} \left[ 3 + \exp \left( -2J/kT \right) \right] (1-p) + \frac{(N g_t^2 \beta^2 / 4kT)P}{(1-p)} + N_\alpha \hspace{1cm} (9) \]

Theoretical, semi-empirical and magneto-structural studies on several binuclear copper(II) complexes have made it clear that the following factors affect super exchange interaction in binuclear copper complexes. Geometrical factors[80-86] such as geometry around the copper atoms, Cu-O-Cu bridge angle, dihedral angle between the X-Y plane of the complexes, etc. Electronegativity[87-89], and mode of bonding of the directly bound ligands. Chelate ring size[90-92] and electronic and steric effects induced by the groups attached to the ligands framework[93-95].

1.7 Catalytic studies

The remarkable catalytic activity of the binuclear copper(II) complexes should be closely related to the functions of type-3 copper in enzymes. The two copper ions are linked by a rigid bridge, as was observed in the synthetic binuclear copper(II) complexes so far studied[96], but they are rather likely to be connected with a flexible polyatomic chain[97]. Thus we have in this study investigated the catalytic activity of binuclear copper(II) complexes with a flexible bridge as well as less steric bulk.

To act as a catalyst the dicopper complex should possess the following properties

(1) The site must be able to accommodate the reactant in close proximity
(2) Bond formation between the reactant must occur and the newly formed species must be released to permit the repetition of the cycle. Catalytic efficiency towards the oxidation of ascorbic acid and 3, 5-di-t-butylcatechol by dicopper complexes has been studied.

The copper complexes derived from xylyl binucleating ligands have shown excellent catalytic efficiency and possess the following unique properties [98].

(1) Reversible binding with O\textsubscript{2} and CO at -78\degree C.

(2) Effects hydroxylation of inactivated aromatic C-H bond under very mild conditions. This reaction is very similar to o-hydroxylation of phenols to catechols by tyrosinase effects hydroxylation induced migration of the substituent present at the 2\textsuperscript{nd} position of the xylyl residue.

(3) The ligand should preferably contain heterocyclic nitrogen atoms, as strong $\sigma$-donors.

(4) The ligand should be flexible enough to stabilize a copper ion in both valence states (i.e. distorted tetrahedral for Cu(I) and tetragonal for Cu(II)).

(5) At the same time, a rigid coordination geometry is required to allow fast redox changes from Cu(I) to Cu(II) and vice versa.

(6) The ligand should be capable of holding two copper ions at a distance of 3-5 Å. The imetallic Cu\textsubscript{2} unit should be retained in solution.

(7) A tripodal N\textsubscript{3} or N\textsubscript{4} ligand bite should coordinate each copper ion, shielding one site of the metal ion but leaving at least one coordination site free and sterically accessible.
The ligand design should allow variation of the substitution pattern, to control electronic and steric properties towards the metal ion.

The complexes obtained by these ligands have recently been divided into two classes.

1. Complexes with metals sharing at least one donor atom of the ligands containing adjacent sites in which the central metal ion provides a bridge.

2. Complexes in which the donor atoms are not shared by the two metal ions. These complexes are derived from ligands having isolated donor sets.

### 1.8 Electron paramagnetic resonance

Electron paramagnetic resonance (EPR, often also ESR, electron spin resonance) spectroscopy was discovered on January 21, 1944 in Kazakhstan, USSR (Zavoiski, 1945).

A simplistic picture of an atom is a positively charged nucleus of protons and neutrons surrounded by a cloud of negatively charged electrons. Whereas the nucleus is small and dense, the electrons are the lightest charged particles in nature. If atoms (either of the same or of different elements) come close to each other, the electron clouds interact with each other. If this interaction is energetically favorable, the atoms bind into a molecule.

Electrons are elementary particles with a property called spin, giving rise to a magnetic moment. Usually, bonding electrons will organize themselves in pairs in such a way that the net magnetic moment associated with paired electrons is zero. If an atom or a molecule has one or more unpaired electron(s), it is called a radical (sometimes a free radical). The paramagnetism due to the unpaired electron(s) of a radical, in general, allows for its detection and analysis by electron paramagnetic resonance (EPR) spectroscopy. In EPR spectroscopy, one observes resonant absorption of energy by
unpaired electrons in the presence of a magnetic field, interacting magnetically with
unpaired electrons \textit{i.e.} electronic spin \( S > 0 \). EPR is similar to \textbf{Nuclear Magnetic}
\textbf{Resonance (NMR)} which you will get acquainted with in the Lab. The NMR technique
deals with nonzero \textbf{nuclear} spins, \( I > 0 \). The magnetic field is described by some
constants and units:

\textbf{Magnetic induction} \( \vec{B} \) in \textbf{teslas (T)}

\textbf{Magnetic flux density} \( \vec{H} \) in \textbf{amperes per metre (A/m)}

\( \vec{B} \) and \( \vec{H} \) relationship:

\( \vec{B} = \mu_0 \vec{H} \)

The \textbf{CGS unit for magnetic induction} is the \textbf{gauss (G)} which is equivalent to \( 10^{-4} \text{ T} \)

Furthermore, in describing EPR, following units are very important:

\textbf{Planck’s constant} \( h = 6.63 \times 10^{-34} \text{ J s} \)

\textbf{Boltzmann constant} \( k = 1.38 \times 10^{-23} \text{ J K}^{-1} \)

\textbf{Bohr magneton} \( \mu_B = 9.27 \times 10^{-24} \text{ J T}^{-1} \)

An X-band EPR experiment is done by applying a constant-frequency microwave
radiation field \( (\nu \sim 9.8 \text{ GHz}) \) while sweeping the magnetic field \( (B \sim 0.35 \text{ T}) \) linearly
through the resonance condition and detecting the absorption of the microwave energy as
a function of \( B \). From this, the energy difference between the ms-levels is determined. In
addition, other interactions in which the electron participates are detected through shifts
and splittings of the resonance line. For technical reasons (mainly to reduce noise), a
modulation field (typical 100 kHz) is added to the magnetic field, with the consequence
that the first derivative of the absorption signal is obtained. The modulation amplitude
has influence on the EPR signal intensity and shape, and is typically varied in the range 0.01-3 mT. In general, low modulation amplitude values result in EPR spectra with high resolution and relatively poor signal intensity, while increasing the modulation amplitude increases the signal intensity. However, the line shape at large amplitude values will eventually become distorted as compared with the unsaturated line shape.

For the discussion of the principles of EPR we start with the simple case of a two-level system for a paramagnetic centre with an electron spin $S = 1/2$. In the absence of any magnetic field the magnetic moment, associated with the electron spin, is randomly oriented and the two energy levels are degenerate. The application of an external magnetic field $B_0$ results in a splitting of the two energy levels as the electron spin $S$ can only be oriented parallel or anti-parallel to the magnetic field vector. The interaction of the electron spin with the external magnetic field yields an EPR spectrum with one single line which may be broadened due to the $g$ anisotropy. The information content of the EPR spectrum is considerably increased if nuclei with a spin quantum number $I > 0$ are found in the environment of the electron spin, as e.g. protons ($I = 1/2$) or nitrogen atoms ($I = 1$). The intrinsic spin angular momentum of these nuclei is associated with a magnetic moment. In addition to the external magnetic field $B_0$ the electron spin will now experience the local magnetic fields built up by the nuclei close to the unpaired electron. The interaction of the electron spin with these nuclear magnetic moments is called hyperfine interaction (HFI).

Knowledge of $g$ parameter gives us information about paramagnetic center electron structure. For free radicals and solid or liquid state ions, orbital electron moment is
hardlinked with environment and cannot occurs in whichever arrangement in magnetic field. This is due to orbital magnetic moment *freezing* phenomena in crystal network. Due to this phenomena $g$ parameter of EPR signal for many paramagnetic atoms in condensate state has different value ($g = 2.0023$). In the case of free ion, the $g$ parameter has isotropic properties. In crystal $g$ value is depended on external magnetic field vector. Resonance linewidths are defined in magnetic induction units $B$ and are measured along the $x$ axis, from line center to $y$ value crossing chosen point of spectrum. These defined widths are called halfwidths and possess some advantages: for asymmetric lines values of left and right half width can be given. Halfwidth $\Delta B_h$ is distance measured from center of line to the point in which *absorption* value has half of maximal absorption value in the center of resonance line. First inclination width $\Delta B_{1/2}$ is a distance from center of the line to the point of maximal absorption curve inclination. In a practical approach, full definition of linewidth is used. In the case of symmetric lines, halfwidth $\Delta B_{1/2} = 2 \Delta B_h$, and full inclination width $\Delta B_{\text{max}} = 2\Delta B_{1s}$.

### 1.8.1 Dinuclear Copper(II) Complexes

When two copper(II) ions interact, a singlet and a triplet are formed. The energy separation between the two is called the isotropic exchange constant $2J$ (Figure 6). The signals arising only from the triplet states are observed. When there is an antiferromagnetic coupling between two copper ions, the intensity of the triplet spectrum is found to decrease with decrease in temperature, since the triplet state is higher in energy, which is depopulated on cooling. A reverse effect is found in case of ferromagnetic coupling. The sign and the magnitude of the isotopic exchange constant
can be estimated by analyzing the temperature dependence of the triplet. When there is an antiferromagnetic coupling between two copper ions, the intensity of the triplet spectrum is found to decrease with decrease in temperature, since the triplet state is higher in energy, which is depopulated on cooling. A reverse effect is found in case of ferromagnetic coupling. The sign and the magnitude of the isotopic exchange constant can be estimated by analyzing the temperature dependence of the triplet spectrum. For the triplet state total spin $S=1$, the allowed values for the spin angular momentum are $-1$, $0$, and $+1$. In an axial environment, three energy levels are found, which are separated in the absence of magnetic field by the axial zero-field splitting parameter $D$ (Figure 7). In a rhombic environment, both axial-field splitting $D$ and rhombic zero-field splitting $E$ separate the energy levels in the absence of magnetic field. In an imaginary EPR experiment, in which the magnetic field is applied parallel to the $Z$-axis of the axial environment.

**Figure 6** Schematic representations of effect of the energy levels of dinuclear copper(II) complexes in presence of external magnetic field.
symmetry of a $s=1$ complex, two absorptions[99], according to the selection rule $\Delta M_s = \pm 1$ are observed ($H_{Z1}$ and $H_{Z2}$). From the forbidden $\Delta M_s = \pm 2$ transitions two additional quantum transitions ($B_{dp}$). The presence of a pair of coupled copper(II) ions is indicated by the half-field signal. In the polycrystalline powder EPR spectrum of a dinuclear complex has axial symmetry and two additional transition ($B_{XY1}$ and $B_{XY2}$) are observed. The axial zero-field splitting $D$ and the rhombic zero-field splitting $E$ can be expressed in the following way

\begin{align}
D &= D_{ZZ} - \frac{1}{2}(D_{XX} + D_{YY}) \quad (11) \\
E &= \frac{1}{2}(D_{XX} - D_{YY}) \quad (12)
\end{align}

The zero-field splitting is a symmetric traceless tensor ($D_{XX} + D_{YY} + D_{ZZ} = 0$) for an axial $s = 1$ system, $E = 0$ so $D = 3/2 D_{zz}$. From the separation between the two axial signals ($B_{Z1}$

**Figure 7** Energy diagram for an axial $s = 1$ system of dinuclear Cu(II) complexes
and $B_{Z2}$, the magnitude of the axial field-splitting parameter $D_{ZZ}$ can be estimated and $D$ can be calculated \[100\]

\[
\frac{2}{3}D = D_{ZZ} = \frac{g\beta B_{Z2} - g\beta B_{Z1}}{2}
\]

(13)

The zero-field splitting $D$ in a dinuclear Cu(II) complex is determined by two main contributions.\[101-102\] A direct magnetic dipolar exchange interaction denoted as $D_{\text{dip}}$ between the unpaired electron spins and an anisotropic exchange interaction denoted as $D^{\text{ex}}$. The dipolar contribution $D_{\text{dip}}$ can be calculated in the approximation of magnetic dipoles (A & B) centered on the two metal ions[103-104] separated by the distance ($r$).

The magnetic dipoles of the two spins are given by

\[
\mu_i = -\beta g_i S_i
\]

(14)

where $i = A, B$

$g_i = g$-tensor of the individual metal centers.

The dipolar interaction between the two spins is given by the Hamiltonian

\[
B_{\text{dip}} = S_A \cdot J_{AB}^{\text{dip}} \cdot S_B
\]

(15)

Where $J_{AB}^{\text{dip}}$ ⇒ the magnetic dipolar interaction of the form

\[
J_{AB}^{\text{dip}} \Rightarrow \beta^2 \frac{g_A g_B}{r_{AB}^3} - 3\beta^2 \frac{g_A r_{AB} (r_{AB} g_B)}{r_{AB}^5}
\]

(16)

$g_A$ and $g_B$ ⇒ $g$ matrices for the spins $S_A$ & $S_B$

$r_{AB} \Rightarrow$ is a column vector of the direction cosines, directed parallel to the A-B vector

$g_x$, $g_y$ and $g_z$ are components of the $g$-tensor and can be estimated from the polycrystalline powder spectrum or determined from a single-crystal EPR study. The parameter $r_{AB}$ can be obtained from a crystal structure determination. By the substitution of the parameters in equation (16), the matrix elements of the $J_{AB}^{\text{dip}}$ matrix can be calculated. Upon diagonalisation, the magnitude of $D_{\text{dip}}$ is obtained[104]. The
exchange contribution to the axial zero-field splitting may be calculated by subtracting
the dipolar contribution from the experimentally determined D values

\[ D^{ax} = D - D^{dip} \]

Since the dinuclear molecule are separated by dilution in a diamagnetic host lattice, or in
a frozen solution, copper nuclear hyperfine splitting might be observed. Some of the
absorptions are split into seven lines \((2nI+1)\) due to hyperfine splitting. But actually

copper nuclear hyperfine splitting in an axial spectrum of a dinuclear complex containing
nitrogen ligands is observed superimposed on the axial absorption and on the half-field
lines.

### 1.9 Superoxide dismutase-mimetic activity

The mechanism proposed for the dismutation of superoxide anions by both SOD and the
metal complex is thought to involve redox cycling of copper(II) ions

\[
\begin{align*}
\text{Cu(II)} + \text{O}_2^- & \rightleftharpoons \text{Cu(I)} + \text{O}_2 \\
\text{Cu(I)} + \text{O}_2^- + 2\text{H} & \rightleftharpoons \text{Cu(II)} + \text{H}_2\text{O}_2
\end{align*}
\]

It has been proposed that electron transfer between copper(II) and superoxide anion
radicals occurs through direct binding. The axial site of copper(II) complex is the likely
attachment point for \(\text{O}_2^-\). Other dimeric complexes have weakly bonded axial ligands
which are dissociated to provide sites on Cu(II) for \(\text{O}_2^-\) bonding. The copper(II)
arrangement facilitates the interaction with the radical and their dissociation to oxygen
and hydrogen peroxide. The fast exchange of axial solvent molecules and a limited steric
hindrance to the approach of the \(\text{O}_2^-\) in those complexes give rise to better SOD mimics[105].
The superoxide dismutase-mimetic activity of the complexes was measured using the xanthine/xanthine-oxidase/NBT assay system[106]. NBT acts as superoxide detecting agent through its reduction to methyl formazan (MF⁺). The color changes from yellow to violet and it is associated with an increase in the absorption at 560 nm in the electronic spectrum. When a chemical inhibitor is added the reduction reaction proceeds slowly or is totally inhibited. In this instance, the solution remains yellow and the rate of absorption increment is reduced with increasing concentration of the complex. In order to determine the complex concentration required yielding a 50% (IC₅₀) inhibition of the reaction, percentage of inhibition as a function of the logarithm of the metal concentration was plotted (Figure 77). The 100% of superoxide dismutase activity corresponds to an assay performed in the absence of the complex. It was found that Cu(II) concentration of native-SOD of 8.5 X 10⁻⁸ M is required to produce a 50% an inhibition of the reaction[107]. Copper concentration higher than 10⁻³ M interferes in SOD activity measurements.
1.10 Scope of the present investigation

The goal of the research described in this thesis is to investigate magnetic exchange interactions of homo binuclear end-to-end diazido and diphenoxido bridged complexes by crystallographically, single crystal EPR technique. In literature there are nine reports on asymmetrical $\mu_{2,1,3}$azido bridges[36]. The results of the structural and magnetic interaction parameters (Addison parameter($\tau$), $\Delta$=$M$-$N$-$N$-$M$ torsion angle) and magnetic coupling constant($J$) are not same for all the complexes[37]. The variation in ferromagnetic/antiferromagnetic interaction of the similar dinuclear copper(II) complexes are not fully understood. The ferromagnetic/antiferromagnetic interactions may probably arise due to Addison parameter($\tau$) (or/and) torsion angle($\Delta$) (or/and) end to end azido ligands (or) all of these contributes. By EPR spectral analysis, we hope to understand the exchange interaction of asymmetrical $\mu_{2,1,3}$azido bridges and diphenoxido (coordination of monodentate anions exist in cis form) dicopper(II)compounds. The spin Hamiltonian parameters obtained in EPR may be furnish useful clues about interactions between two copper ions.

Further, very limited number of diphenoxido dicopper(II) complexes with cis arrangement of monodentate anions are reported[77]. The major concern is to understand the structural, magnetic interactions and EPR triplet transition of dimeric systems. To achieve the above mentioned goals, the primary task has been to design appropriate binucleating ligands and their complexes with phenolate exogeneous donor are usually prepared by Mannich base condensation of appropriate substituted phenols with secondary amines and formaldehyde. Their spectral, magnetic, epr studies and few samples for catalytic activity are studied. The results are presented and discussed here.
1.11 References:


12) C. O'Sullivan, G. Murphy, B. Murphy, B. Hathaway, J. Chem. Soc., Dalton
13) C. T. Yang, M. Vetrichelvan, X. Yang, B. Moubaraki, K. S. Murray, J. J. Vittal, 


3498.

16) L. L. Koh, J. D. Ranford, W. T. Robinson, J. O. Svenson, A. L. C. Tan, D. Wu, 

(1997) 2645.


22) C. O. Sullivan, G. Murphy, B. Murphy, B. J. Hathaway, J. Chem. Soc., Dalton 


25) A. Meister, Biochemistry of the Amino Acids, 1&2, Academic Press, New York, 
1965


27) M.L. Bonnet, C. Aronica, G. Chastanet, G. Pilet, D. Luneau, C. Mathoniere, R.


35


114) D. Sharma, B. Narasimhan, P. Kumar, V. Judge, R. Narang, E. De Clercq, J. Balzarini, European Journal of Medicinal Chemistry. 44 (2009) 2347


