RELATION BETWEEN MAGNETIC PROPERTIES AND STRUCTURAL CHANGES IN NEW BINUCLEAR COMPLEXES WITH MULTIATOMIC BRIDGES

SUMMARY OF THE THESIS SUBMITTED TO
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SUMMARY

The study of magnetic exchange interaction propagated by multi-atom bridges has received a lot of attention [1-3]. The interest in this area stems from attempts to mimic the structural and functional properties of biological systems and to design molecular based magnets [4-6].

The extent of spin exchange between two copper (II) centers depends on the energy of the interacting orbitals and the symmetry of the metal environment. All factors that can affect these two parameters can modify the extent of spin exchange. Various studies have shown the dependence of spin exchange on the variation in geometrical parameters such as metal – ligand bond length, M-L-M bridging angle, dihedral angle between the metal coordination planes and the degree of planarity of the bridging unit [7-10]. Variation in the bridging ligand can directly affect the nature of the bridging molecular orbital participating in the exchange where as change in the non bridging part of the ligands, the symmetry of π-orbitals and their ability to delocalize electron density can play important role in mediating the magnetic exchange in the complexes with multiatomic bridges. In most cases this type of exchange through multi atomic bridges has been shown to take place through the orbitals of the bridging ligand. However, it has also been suggested that the σ – orbitals can participate in the super exchange over a long distance in multiatomic bridges and lead to a spin exchange yet such interactions are very weak [11-15].

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

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

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

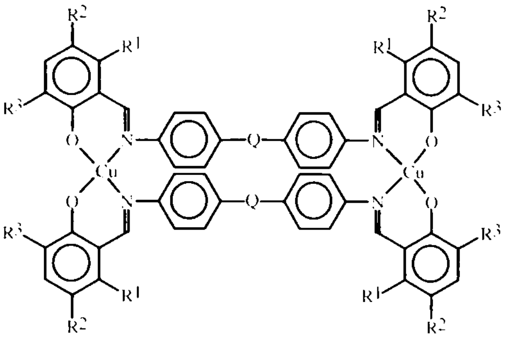
1. π-delocalized bi-bridged binuclear complexes.
2. Ternary binuclear complexes.
3. Binuclear complexes with σ-bonded bridged
4. Ternary binuclear complexes with planar bridged.

A brief introduction to the world of binucleating ligands and their classification, binuclear complexes and historical developments and recent developments in the field of molecular magnetic materials is followed by systematic presentation of the synthesis and characterization of new binucleating ligands and complexes, study of their magnetic property and biological activity and magneto - structural correlations.

The synthesis and characterization of bi-bridged binuclear complexes with ligands having extensive π-delocalization is presented in chapter 2.

Ten new biphenyl based binucleating ligands, (H_2SB) have been synthesized by condensation of 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenylsulphone or 3,3'-diaminodiphenylsulphone with o-hydroxy carbonyl compounds, namely, 2-hydroxybenzaldehyde, 2-hydroxynaphthaldehyde, 2-hydroxy-3-methoxybenzaldehyde or 5-bromo-2-hydroxybenzaldehyde. The ligands have been characterized by elemental analysis and spectroscopy.

The reactions of these ligands with cupric acetate were carried out to synthesize the following binuclear complexes-



2-I to 2-IV : $R^1 = H, R^2 = H, R^3 = H.$

2-V & 2-VI : $R^1R^2 = -(CH=CH)_2-, R^3 = H.$

2-VII & 2-VIII : $R^1 = H, R^2 = H, R^3 = -OCH_3.$

2-IX & 2-X : $R^1 = H, R^2 = Br, R^3 = H.$

2-I, 2-V, 2-VII, 2-IX : $Q = -CH_2-.$

2-II : $Q = -O-.$

2-III, 2-IV, 2-VI, 2-VIII, 2- X : $Q = -SO_2-$

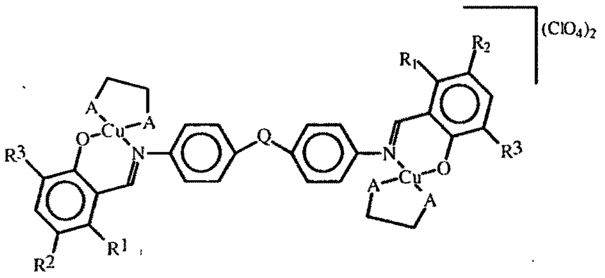
(Binuclear complexes **2-I** to **2-X**)

The complexes were characterized by elemental analysis, UV-VIS, FTIR spectroscopy and thermal analysis. Complex, **2-IX** was characterized by ESR and mass spectrometry. The peaks corresponding to $[Cu_2(SB)_2]^+$, $[Cu_2(SB)_2]^{2+}$ and $[(SB)]^+$ along with other species confirmed the formation of binuclear complexes. Magnetic properties of the complexes, **2-I, 2-II, 2-III, 2-IV, 2-V, 2-VII** and **2-IX** were studied at various temperatures from liq. N_2 to RT. The exchange parameters have been calculated and have been correlated with the structural parameters such as tortional angle.

Mixed ligand complexes play an important role in biological processes as exemplified by many instances in which enzymes are known to be activated by metal ions [16]. Copper (II) complexes have great variety of biological properties ranging from anticancer [17], antibacterial [18] and antiviral [19] activity. Copper (II) complexes containing polypyridine ligands like 2,2'-bipyridine and 1,10-phenanthroline are shown to be useful as photophysical and chemical probes of DNA in view of their relevance to various biochemical and biomedical application [20]. The binuclear complexes based on the ternary complex systems can have all these features combined with them. The single atomic bridge without any steric constraints can orient as per the structure of ternary metal coordination and thus the spin exchange in such complexes is expected to depend more on the ligands directly coordinating with the metal ions.

With this point of view new ternary binuclear complexes having multiatomic bridges with π-delocalization have been synthesized in chapter 3 and chapter 5.

Ternary complexes possessing a tertiary diimine, 2,2'-bipyridine or 1,10-phenanthroline, and another bidentate aldehyde namely, 2-hydroxybenzaldehyde, 2-hydroxynaphthaldehyde or 2-hydroxy-3-methoxybenzaldehyde have been synthesized. These mononuclear complexes have been used as precursors to synthesize ternary binuclear complexes as schematized below by condensation with 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenylsulphone or 3,3'-diaminodiphenylsulphone. The study of these ternary binuclear complexes is described in chapter 3.



3-I, 3-II, 3-III, 3-IV: R^1 = H, R^2 =H, R^3 = H.

3-V, 3-VI, 3-VII, 3-VIII, 3-IX, 3-X, 3-XI: R^1R^2 = -$(CH{=}CH)_2$-, R^3 = H.

3-XII, 3-XIII, 3-XIV, 3-XV, 3-XVI, 3-XVII, 3-VIII, 3-XIX: R^1 = H, R^2 =H, R^3 = -OCH_3.

3-I, 3-II, 3-V, 3-VI, 3-VII, 3-VIII, 3-XII, 3-XIII, 3-XIV, 3-XV: AA = 1,10-phen.

3-III, 3-IV, 3-IX, 3-X, 3-XI, 3-XVI, 3-XVII, 3-XVIII, 3-XIX: AA = 2,2'-bipy.

3-I, 3-III, 3-V, 3-IX, 3-XII, 3-XVI: Q = methane.

3-II, 3-IV, 3-VI, 3-X, 3-XIII, 3-XVII: Q = ether.

3-VII, 3-XIV, 3-XVIII: Q = 4-sulphone.

3-VIII, 3-XI, 3-XV, 3-XIX: Q = 3-sulphone.

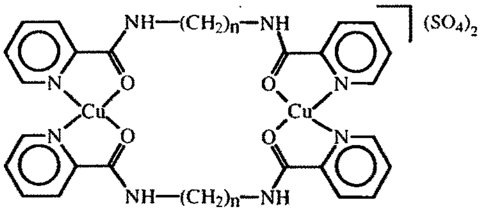
(Ternary binuclear complexes, **3-I** to **3-XIX**)

The complexes were analyzed by elemental analysis, UV-Vis, FTIR and conductivity. Molar conductance values between 130 – 160 ($\Omega^{-1}M^{-1}cm^2$) correspond to 1:2 electrolyte, confirming the presence and ionic character of $2ClO_4^-$. ESR spectra of the complexes **3-I, 3-II, 3-III, 3-IV, 3-IX, 3-XVI, 3-XVIII** and **3-XIX** were recorded. Complexes **3-III, 3-IX** and **3-XIX** were analyzed by mass spectrometry. The appearance of peaks corresponding to the mono and dications of species $[Cu_2(AA)_2SB]$, $[Cu_2(AA)SB]$, [SB], [CuAA] etc. with greater relative abundance confirmed the formation of binuclear complexes as well as the suggested formula.

Magnetic properties of the complexes were studied from LNT to RT. The values of exchange constants indicated that the two metal centers are coupled and undergo weak antiferromagnetic to ferromagnetic exchange.

Chapter 4 illustrates the synthesis of binucleating ligands N,N'-bis(2-pyridylcarbonyl)-1,4-diaminobutane and N,N'-bis(2-pyridylcarbonyl)-1,6-diaminohexane by condensation reaction between ethyl-2-pyridinecarboxylate and diaminoalkanes namely 1,4-diaminobutane or 1,6-diaminohexane. Purity of ligands were checked by M.P., elemental analysis and FTIR. ^1H NMR of the hexane based ligand, confirmed its structure.

Symmetrical bi-bridged binuclear complexes have been prepared by reaction of cupric acetate monohydrate with above two ligands.



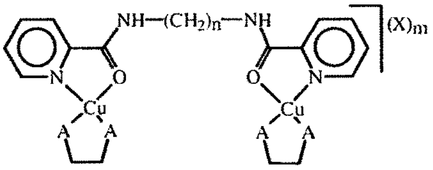
4-I : n = 4.

4-II : n = 6.

(Binuclear complexes, **4-I** and **4-II**).

Mono-bridged binuclear complexes have been synthesized by addition of bidentate ligands namely, 2,2'-bipyridine, 1,10-phenanthroline, 2-hydroxybenzoic acid or 5-bromo-2-hydroxybenzoic acid into the solution of cupric acetate and binucleating ligand.

The complexes were characterized by elemental analysis, thermal analysis, UV-VIS and FTIR. Conductivity of the complexes **4-III, 4-IV, 4-V** and **4-VI** were studied. The conductivity values conform the 1:3 and 1:4 electrolyte type of the complexes. Representative complexes were analyzed by ESR and mass spectrometry, which revealed the formation of binuclear complexes. Detailed magnetic property of the complexes **4-III, 4-V** and **4-VII** were studied from LNT to RT. The complexes are observed to undergo a weak to moderate ferromagnetic coupling between two copper (II) ions with positive J values up to 100 cm^{-1}.

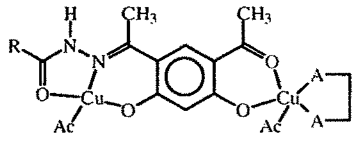


4-III : AA = phen, n = 4, X = ClO_4^-, m = 4.
4-IV : AA = phen, n = 6, X = ($3ClO_4^-$, $CH_3CO_2^-$), m = 4.
4-V : AA = bipy, n = 4, X = ClO_4^-, m = 4.
4-VI : AA = bipy, n = 6, X = ($3ClO_4^-$, $CH_3CO_2^-$), m = 4.
4-VII : AA = 2-hydroxybenzoic acid, n = 4, X = 0.
4-VIII : AA = 2-hydroxybenzoic acid, n = 6, X = 0.
4-IX : AA = 5-bromo-2-hydroxybenzoic acid, n = 4, X = 0.
4-X : AA = 5-bromo-2-hydroxybenzoic acid, n = 6, X = 0.

(Binuclear complexes, **4-III** to **4-X**).

In chapter 5, 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone (DAR) has been synthesized and characterized by elemental analysis and spectral technique. It is allowed to condense with one equivalent of benzoyl hydrazine, phenylacetyl hydrazine, nicotinoyl hydrazine or isonicotinoyl hydrazine to get binucleating ligands, N-benzoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine, (H_2drBz), N-phenylacetyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine, (H_2drPAz), N-nicotinoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine, (H_2drNz) or N-isonicotinoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine (H_2drINz). The ligands were characterized by elemental analysis and FTIR spectroscopy. Representative ligand was analyzed by ^{13}C and ^{1}H NMR to confirm the structure of the ligands.

Ternary binuclear complexes were synthesized by slow addition of bidentate ligands, namely, 2,2'-bipyridine, 1,10-phenanthroline, 2-hydroxybenzoic acid or 5-bromo-2-hydroxybenzoic acid and cupric acetate monohydrate into the complexes of cupric acetate with binucleating ligands.



Complexes **5-I**, **5-II**, **5-III** and **5-IV** : drBz
Complexes **5-V**, **5-VI** and **5V-II** : drPAZ
Complexes **5-VIII** and **5-IX** : drNZ
Complexes **5-X and 5-IX** : drINZ
5-I, **5-V**, **5-VIII** and **5-X** : AA = bipy
5-II, **5-VI**, **5-IX** and **5-XI** : AA = phen
5-III and 5-VII : AA = 2-hydroxybenzoic acid
5-IV : AA = 5-bromo-2-hydroxybenzoic acid
5-III, **5-IV** and **5-VII** : Ac (acetate ion) = 0
5-I, **5-II**, **5-V**, **5-VI**, **5-VIII**, **5-IX**, **5-X** and **5-XI** : Ac (acetate ion) = 2

(Complexes, **5-I** to **5-XI**)

Complexes were characterized by elemental analysis, TGA, molar conductivity, UV-VIS, and FTIR spectroscopy. Thermogravimetric analysis has revealed the nature of water molecules. Molar conductivity values are < 0.01 ($\Omega^{-1}M^{-1}cm^{2}$) in complexes **5-I**, **5-II** **5-V** and **5-VI**, indicating that two acetates are weakly coordinated to the metal ions. Room temperature magnetic moment values have indicated that except complex **5-IV** which is weakly antiferromagnetically coupled, all other complexes were ferromagnetically coupled. The ESR as well as mass spectrometry of the complex, **5-V** i.e. $[Cu_2(bip)(drPAZ)Ac_2].H_2O$ has been studied.

Antibacterial activity: Antibacterial activity of these ligands and complexes have been studied also found out against *S. aureus, B. megaterium* (gram positive) and *S. typhi, S. marsescens, P. vulgaris* (gram negative) strains. It was observed that the complexes were more effective than the corresponding ligands.

Conclusion:

The present work has been carried out with the aim to synthesize new magnetic systems in mild condition, with specific magnetic and molecular properties that might be suitable for future applications and is to provide the theoretical underpinning for designing such structures.

The present work is therefore encouraging and stimulating the underlying research, trying in particular to respond to the great need for a much stronger fundamental science base to underpin the development of materials suitable for practical devices and useful applications in the future.

One of the great attractions of the whole field is the potential to build compounds that behave as classical solid-state magnets while exhibiting completely new properties, such as a wide range of magnetic ordering temperatures so that the relationship between magnetism and temperature can be precisely controlled.

The present study is expected to add to the understanding of magnetic exchange phenomenon in multinuclear systems. The electronic and geometrical parameters related to the bridging and non-bridging parts of the complex molecules have been studied. Especially the effect of π geometrical parameters, torsional angle between metal coordination planes in mediating the exchange process has been investigated in detail.

It has been observed that

1. The variation in functional groups on the non bridging part of the ligand as well as a minor variation in the bridging group can affect the molecular geometry and hence can have significant effect on the extent of spin exchange between paramagnetic centers through long multiatomic bridges. It is observed that small variation in bridging functionality from $-CH_2-$, $-SO_2-$, and –O- have significant effect on the magnetic property.

As the deviation in torsional angle between the metal coordination planes increases from planarity in the order,

$[Cu_2(salDPM)_2] < [Cu_2(sal4\text{-}DPS)_2] < [Cu_2(salDPE)_2]$

the value of J also increase in the same order.

2. The systematic variation in the non bridging part of the ligands in binuclear complexes can modulate the extent of magnetic exchange. The variation in these groups can be used to change the tortional angle and there by tune the magnetic property to any desired value from ferromagnetism to antiferromagnetism.

It has been observed that on varying the non bridging ligand, the deviation in the torsional angle increases in the order $[Cu_2(salDPM)_2] < [Cu_2(naphDPM)_2] < [Cu_2(vanDPM)_2] < [Cu_2(BrsalDPM)_2]$ and the value of J also increase indicating increase in ferromagnetism with increase in non planarity.

3. In complexes with σ-bonding bridges, the results show that the bulkier and more π-bonding ligands can distort the metal coordination planes to a greater extent and hence lead to stronger ferromagnetism. At the same time it promises their use as molecular ferromagnets.

4. The examination of biological activity showed that the complexes have much better activity than the corresponding ligands. The antibacterial activity showed by the

ligands and their complexes is either comparable or slightly mediocre as compared to biological activity against known antibiotics, commonly used in clinical practice.

The fuller understanding of the effect of structural parameters which affect the spin/electron exchange in these systems can lead to "Tailor making" of the molecular magnetic materials and further in the development of multi-metallic catalysts to suit the needs for specific industrial applications. A comparison with the theoretical models will be a step towards "outside the laboratory" design of molecules having desired magnetic, redox or catalytic properties

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