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### **Synthesis And Magneto Structural Correlations In New Binuclear Copper (II) Complexes With Conjugated Bridging Groups.**

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#### **ABSTRACT**

New binuclear complexes of Copper(II) of the type  $[Cu_2L_2]$ ,  $H_2L =$  bis(2'-hydroxybenzylidene-4-iminophenyl)methane, bis(2'-hydroxybenzylidene-4-iminophenyl)ether, bis(2'-hydroxybenzylidene-4-iminophenyl)sulphone, bis(2'-hydroxybenzylidene-3-iminophenyl)sulphone and their derivatives with substitution on hydroxyl phenyl part of ligands. Complexes have been synthesised and characterized by using various spectral techniques. The variable temperature magnetic studies are revealed about long range spin exchange interactions. The magnetic properties have been analysed on the basis of the structural parameters related to the ligands and substituents present on them.

**KEY WORDS:** Copper (II) Complexes, Binuclear complexes, Schiff bases, Binucleating ligands, Magnetic interactions.

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## INTRODUCTION

In recent years study of binuclear copper (II) complexes has been a subject of considerable interest due to structural, magnetic and ESR properties associated with them<sup>1-6</sup>. Some of these compounds can also provide a good models for bi/multinuclear active sites in metalloenzymes<sup>7-11</sup>. The catalytic activity of these binuclear centres can probably be attributed to their redox characteristics which are expected to be affected by the magnetic exchange and existence of a suitable path to mediate the spin / electronic exchange<sup>12,13</sup>. Unlike complexes with single atom bridges where direct super exchange can take place, polyatomic bridging units behave in a more complex manner. Studies of complexes with different geometries around the metal ion and with binucleating ligands possessing  $\sigma$  and  $\pi$  – orbitals have clearly demonstrated that spin – spin interaction is dependent on the availability of bridging molecular orbitals with an appropriate symmetry and energy. This propagates interaction between the metal orbital in which the unpaired electron resides<sup>14-17</sup>.

Aromatic bridging groups or the groups with highly conjugated  $\pi$  – systems have more number of closely spaced molecular orbitals to match with the paramagnetic orbitals of the metal ions. Above systems can be expected to be better mediators for magnetic exchange. Nitrogen heterocycles like pyrazolate, pyrimidine, pyrazine and various triazine as well as oxalate and hydroxido type bridging ligands have been proved as efficient mediators of spin interaction for this reason<sup>18-23</sup>. Copper (II) complexes of binucleating ligands with two bidentate sites, separated by one aromatic ring have been studied and possibility of isomeric ligands having different ability to mediate magnetic exchange was proposed<sup>24</sup>.

In present work, an attempt is made to synthesize new homo binuclear complexes of copper(II) of the type  $[\text{Cu}_2\text{L}_2]$ ,  $\text{H}_2\text{L} =$  bis(2'-hydroxybenzylidene-4-iminophenyl)methane, bis(2'-hydroxybenzylidene-4-iminophenyl)ether, bis(2'-hydroxybenzylidene-4-iminophenyl)sulphone, bis(2'-hydroxybenzylidene-3-iminophenyl)sulphone and their derivatives. Complexes are characterized by analysis and by various spectral techniques. The resulting complexes were characterised by elemental analysis and various spectral techniques (i.e. UV-VIS, IR, ESR and mass spectra). The variable temperature magnetic measurements have been carried out to get insight into long range spin exchange interaction. Molecular modelling by force field calculation has also been used to work out the geometrical parameters. The magnetic properties have been analysed on the basis of the structural parameters related to the ligands and substituents present on them.

## EXPERIMENTAL

### Reagents

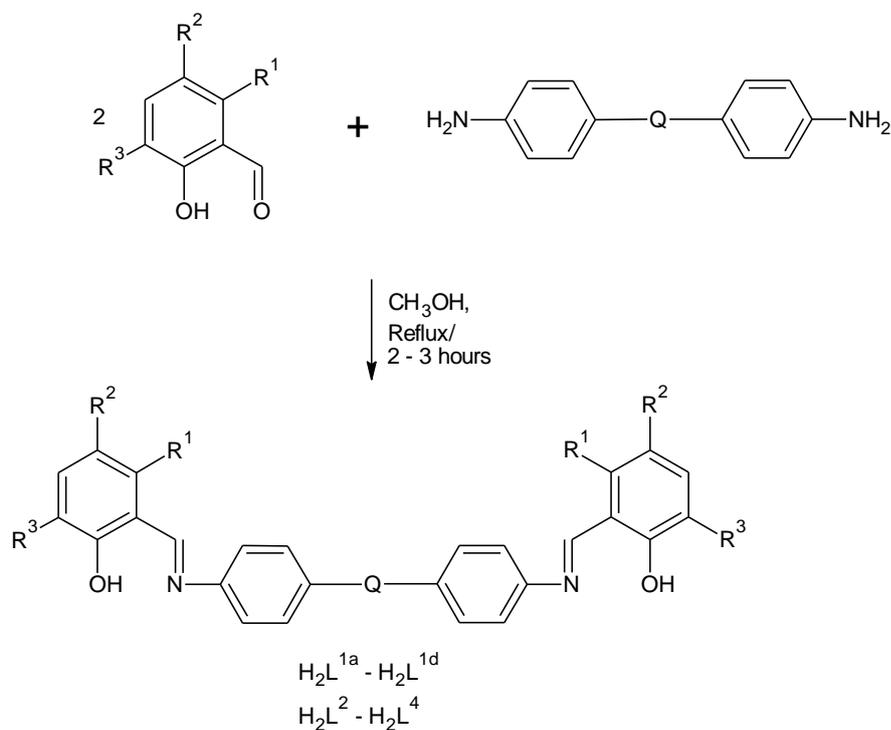
2-Hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde and 2-hydroxynaphthaldehyde were procured from Aldrich. 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenylsulphone, 3,3'-diaminodiphenylsulphone, glacial acetic acid and cupric acetate monohydrate were purchased from Merck. All these reagents were AR grade and were used as received. 2-hydroxy-3-methoxybenzaldehyde (o-Vanillin) was obtained from local manufacturers.

All solvents were distilled twice before use.

### Synthesis of binucleating Schiff base ligands, $H_2salDPM (H_2L^{1a})$

4,4'-Diaminodiphenylmethane (0.99 g, 5mmol) was dissolved in 60 ml of methanol. 2-Hydroxybenzaldehyde (1.22 g, 10 mmol) was added to the solution, followed by 2 ml of glacial acetic acid to facilitate the reaction. The reaction mixture was allowed to reflux for two hours at the end of which a bright yellow coloured compound separated. The solid obtained was filtered and washed with  $CH_3OH$  (15 ml) and dried. The compound was recrystallised from hot  $CHCl_3$ . Yield:72 %, mp. 225 °C.

Ligands  $H_2salDPE (H_2L^{1b})$ ,  $H_2sal4-DPS (H_2L^{1c})$ ,  $H_2naphDPM (H_2L^2)$ ,  $H_2vanDPM (H_2L^3)$ , and  $H_2BrsalDPM (H_2L^4)$  were prepared by similar methods as  $H_2L^{1a}$ , using equivalent quantities of respective aldehydes and amines as shown in **scheme 1**. The yields, mp and the result of elemental analysis are summarized in **Table 1**.



$$\text{H}_2\text{L}^{1b} = \text{bis}\{4-(2\text{-hydroxybenzyl})\text{iminophenyl}\}\text{ether}$$

$$\text{H}_2\text{L}^{1d} = \text{bis}\{4-(2\text{-hydroxybenzyl})\text{iminophenyl}\}\text{sulphone}$$

$$\text{H}_2\text{L}^2 = \text{bis}\{4-(2\text{-hydroxynaphthyl})\text{iminophenyl}\}\text{methane}$$

$$\text{H}_2\text{L}^3 = \text{bis}\{4-(2\text{-hydroxy-3-methoxybenzyl})\text{iminophenyl}\}\text{methane}$$

$$\text{H}_2\text{L}^4 = \text{bis}\{4-(5\text{-bromo-2-hydroxybenzyl})\text{iminophenyl}\}\text{methane}$$
**(Scheme 1)****Table No. 1:** “Preparative yields, mp and analytical data of the binucleating Schiff bases”

	Ligands	Yields (%)	Mp. (°C)	Elemental analysis Found (Calc)* %		
				C	H	N
$\text{H}_2\text{L}^{1a}$	[H <sub>2</sub> salDPM] C <sub>27</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	72	225	79.81 (79.80)	5.31 (5.42)	7.02 (7.89)
$\text{H}_2\text{L}^{1b}$	[H <sub>2</sub> salDPE] C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	64	192	77.79 (76.46)	4.66 (4.90)	7.38 (6.86)
$\text{H}_2\text{L}^{1d}$	[H <sub>2</sub> sal4-DPS] C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> S <sub>1</sub>	62	270	68.12 (68.42)	4.22 (4.38)	6.43 (6.14)
$\text{H}_2\text{L}^2$	[H <sub>2</sub> naphDPM] C <sub>35</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub>	56	262	83.01 (83.00)	5.13 (5.13)	5.59 (5.53)
$\text{H}_2\text{L}^3$	[H <sub>2</sub> vanDPM] C <sub>29</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub>	65	198	74.86 (74.67)	5.74 (5.57)	5.85 (6.00)
$\text{H}_2\text{L}^4$	[H <sub>2</sub> BrsalDPM] C <sub>27</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> Br <sub>2</sub>	96	290	57.90 (57.45)	3.80 (3.54)	4.95 (4.96)

\* Values given in parentheses are calculated from molecular formulae.

**Preparation of [Cu<sub>2</sub>(salDPM)<sub>2</sub>]**

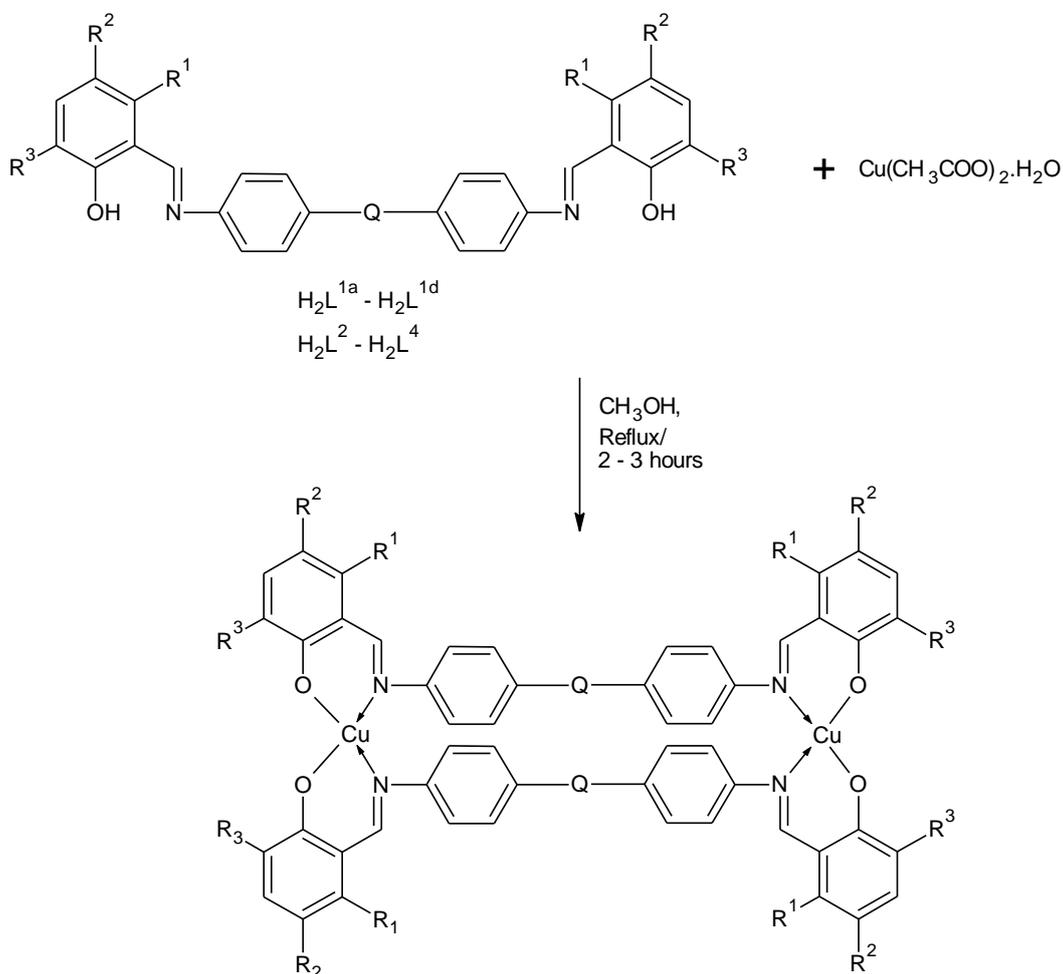
Ligand [H<sub>2</sub>salDPM] (0.507g, 1.25 mmol) was suspended in 30 ml of methanol in a 150 ml flask equipped with a reflux condenser. A solution of cupric acetate monohydrate (0.249g, 1.25 mmol) in 20 ml methanol was added slowly to the above solution. The resulting solution was stirred for three hours at 60 °C. The dark brown coloured microcrystalline solid obtained at the end of reaction was filtered and washed thoroughly with methanol till the washings were clear. The product was dried at 80 °C.

Complexes [Cu<sub>2</sub>(salDPE)<sub>2</sub>], [Cu<sub>2</sub>(sal4-DPS)<sub>2</sub>], [Cu<sub>2</sub>(vanDPM)<sub>2</sub>], [Cu<sub>2</sub>(naphDPM)<sub>2</sub>] and [Cu<sub>2</sub>(BrsalDPM)<sub>2</sub>] were synthesised using similar procedure as for [Cu<sub>2</sub>(salDPM)<sub>2</sub>] and appropriate quantities of ligands (Scheme 2).

**Preparation of the complex [Cu<sub>2</sub>(sal3-DPS)<sub>2</sub>]**

Cupric acetate monohydrate (0.499 g, 2.5 mmol) was dissolved in 30 ml methanol in a flask equipped with a reflux condenser. A solution of 2-hydroxybenzaldehyde (0.611 g, 5 mmol) in 15 ml methanol was added to this. The colour of the solution turned green on coordination of the aldehyde

with Cu (II). A solution of 3,3'-diaminodiphenylsulphone (0.621 g, 2.5 mmol) in 20 ml methanol, was added dropwise to the above solution over two hours at reflux temperature. The resulting solution was allowed to reflux for additional one hour with constant stirring. The dark brown microcrystalline solid formed was filtered, washed thoroughly with 30 ml methanol in 5-6 portions and dried.



**1 to 4:**  $R^1 = H, R^2 = H, R^3 = H.$

**5:**  $R^1R^2 = -(CH=CH)^2-, R^3 = H.$

**6:**  $R^1 = H, R^2 = H, R^3 = -OCH_3.$

**7:**  $R^1 = H, R^2 = Br, R^3 = H.$

**1, 5, 6 and 7:**  $Q = -CH_2-.$

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

**3 and 4:**  $Q = -SO_2-.$

[Scheme 2]

### Physical measurements

Carbon, Hydrogen and Nitrogen analysis were carried out on a Perkin Elmer Model-2400 CHN/S analyser. The thermogravimetric analysis of the complexes were carried out by using thermal analyser, Mettler Toledo SW 7.01 instrument in nitrogen atmosphere with a heating rate of 5 °C/min.

IR spectra were recorded in the forms of KBr pellets on Perkin Elmer FT-IR, spectrum RX1 spectrometer. The electronic spectra of the complexes in UV-VIS region were recorded in methanolic solutions using Shimadzu UV-240 recording spectrophotometer. The diffuse reflectance spectra were recorded on the same instrument, equipped with spherical reflectance assembly using BaSO<sub>4</sub> as a reference material. The ESR spectra of the complex, **7** at LNT and RT were recorded on a Varian E-15 spectrometer. The FAB mass spectrum of the complex, **7** in m-nitrobenzyl alcohol matrix was recorded on a JEOL SX 102/DA – 6000 mass spectrometer / Data system. Argon (6 KV, 10 mA) was used as a FAB gas. The spectra were recorded at room temperature with an accelerating voltage of 10 KV.

Magnetic Susceptibility of the polycrystalline sample of the complexes, **1, 2, 3, 4, 5, 6** and **7** were performed in the temperature range 90–300 K with an indigenous Faraday set up using an applied magnetic field of 0.8 T. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetic corrections were incorporated using Pascal's constants.

The set up has an electromagnet, POLYTRONIC electromagnet Model: HEM -200 with highest field strength of 1 Tesla and Faraday pole caps with a 30 mm pole gap. A METTLER ultramicro balance, Model UMX - 5 Comparator with hang down facility is used for weighing procedure. The balance has 5 mg capacity with ±0.1 µg accuracy and 0.1 µg, readability. The temperature inside the sample enclosure was maintained with the help of OMEGA CYC 3200, Auto-tuning Temperature Controller having an accuracy of 0.01°.

A least-squares calculations were performed by fitting the experimentally observed values of magnetic susceptibility at various temperature to Bleaney-Bower's equation<sup>25, 26</sup>

$$\chi = g^2 N \mu_B^2 / 3kT [1 + 1/3 \exp(-2J/kT)] + N\alpha$$

The difference  $|\chi^2_{\text{calc}} - \chi^2_{\text{obsd}}|$  was minimised to get the values of coupling constant J, which is a measure of the magnetic exchange between the copper (II) ions and Nα is temperature independent paramagnetism i.e. 60 emu/mole, per copper ion.

## RESULTS AND DISCUSSION

The binucleating Schiff base ligands except those of 3,3'-diaminodiphenylsulphone were obtained in appreciably good yields. The formation of these molecules is confirmed by the absence of  $\nu_{>C=O}$  and  $\nu_{NH}$  as in the original reactants and the appearance of  $\nu_{>C=N}$ . The IR spectra of the ligands have all other expected features.

The reactions of these ligands in equivalent amounts with cupric acetate monohydrate, as detailed in the experimental section, resulted in the formation of binuclear complexes. 3,3'-Diaminodiphenylsulphone is much less reactive as compared to the diamines used in this work. The condensation with aldehydes was very difficult. Hence, metal assisted synthesis was attempted. The reaction of 3,3'-diaminodiphenylsulphone with  $\text{Cu}(\text{sal})_2$  and related complexes with 2-hydroxyaromatic carbonyls resulted in the formation of binuclear complexes in appreciable yields.

The elemental analysis of the complexes as summarised in the **Table 2**, indicated that the complexes have general formula,  $[\text{Cu}_2\text{L}_2]$ .

**Table No. 2:** "Preparative yield and analytical data of binuclear complexes"

Comp. No.	Complexes	Yield (%)	Elemental analysis Found (Calc)*		
			C%	H%	N%
1	$[\text{Cu}_2(\text{salDPM})_2]$ $\text{C}_{54}\text{H}_{40}\text{N}_4\text{O}_4\text{Cu}_2$	93	69.86 (69.30)	4.81 (4.27)	5.72 (5.98)
2	$[\text{Cu}_2(\text{salDPE})_2]$ $\text{C}_{52}\text{H}_{36}\text{N}_4\text{O}_6\text{Cu}_2$	96	66.87 (66.45)	4.33 (3.83)	5.82 (5.96)
3	$[\text{Cu}_2(\text{sal3-DPS})_2]$ $\text{C}_{52}\text{H}_{36}\text{N}_4\text{O}_8\text{S}_2\text{Cu}_2$	83	60.35 (60.29)	3.68 (3.47)	5.22 (5.41)
4	$[\text{Cu}_2(\text{sal4-DPS})_2]$ $\text{C}_{52}\text{H}_{36}\text{N}_4\text{O}_8\text{S}_2\text{Cu}_2$	98	60.38 (60.28)	3.69 (3.47)	5.30 (5.41)
5	$[\text{Cu}_2(\text{naphDPM})_2]$ $\text{C}_{70}\text{H}_{48}\text{N}_4\text{O}_4\text{Cu}_2$	96	73.54 (74.00)	4.34 (4.23)	5.20 (4.93)
6	$[\text{Cu}_2(\text{vanDPM})_2]$ $\text{C}_{58}\text{H}_{48}\text{N}_4\text{O}_8\text{Cu}_2$	48	64.70 (64.86)	4.59 (4.65)	5.13 (5.22)
7	$[\text{Cu}_2(\text{BrsalDPM})_2]$ $\text{C}_{54}\text{H}_{36}\text{N}_4\text{O}_4\text{Br}_4\text{Cu}_2$	98	51.11 (51.81)	3.23 (2.87)	4.53 (4.47)

\*Values given in parentheses are calculated from the molecular formulae.

### Electronic spectra

The electronic spectra of the binuclear complexes in methanolic solutions show bands in the range of 276 to 404 nm. The bands in the region 276 - 404 nm is due to intraligand transitions. The bands between 380 - 430 nm can be assigned to the MLCT transition from copper (II) ion to the imine nitrogen atoms. The complex, **5** do not have appreciable solubility in methanol or any non coordinating solvent. Hence, the intra ligand charge transfer and ligand field transitions could not be seen in the solution spectra. However, the transitions are clearly observed in the diffuse reflectance spectra in the powder form recorded using  $\text{BaSO}_4$  as reference material (**Table 3**).

The diffuse reflectance spectra of the complexes exhibit the ligand field transitions between 650 to 810 nm regions. The broad bands observed in all the complexes are characteristic of  $d^9$  metal

ions in square planar geometry. The single broad band in each complex is a combination of the three possible transitions  $A_{1g} \leftarrow B_{1g}$ ,  $B_{2g} \leftarrow B_{1g}$  and  $E_{1g} \leftarrow B_{1g}$ .

**Table No. 3:** "Electronic spectral properties of binuclear complexes"

Complexes	Absorption in methanolic Solutions ( $\lambda$ in nm )	d.r.s. ( $\lambda$ in nm )
$[Cu_2(salDPM)_2]$	390 & 276	700
$[Cu_2(salDPE)_2]$	390& 298	810
$[Cu_2(sal3-DPS)_2]$	386 & 292	666
$[Cu_2(sal4-DPS)_2]$	338 & 294	670
$[Cu_2(naphDPM)_2]$	-	426 & 710
$[Cu_2(vanDPM)_2]$	508, 404& 308	720
$[Cu_2(BrsalDPM)_2]$	394 & 298	658

### IR spectra

The IR spectra of the complexes in the  $400\text{ cm}^{-1} - 4000\text{ cm}^{-1}$  region exhibit several bands corresponding to stretching and bending of  $-C-C-$ ,  $-C-H-$ ,  $>C=N-$  etc.

A strong absorption appears between  $1600\text{ cm}^{-1} - 1612\text{ cm}^{-1}$  region in all the complexes. This can be attributed to the  $>C=N-$  stretching. These vibrations occur at lower frequencies compared to the  $\nu_{>C=N-}$  in free ligands where they appear between  $1616\text{ cm}^{-1} - 1624\text{ cm}^{-1}$ . The shift towards lower energy in the complexes indicates direct involvement of the imine nitrogen in the coordination to the metal ion. The characteristic asymmetric stretchings band corresponding to  $\nu_{-CH_2-}$ ,  $\nu_{-SO_2-}$  and  $\nu_{C-O-C}$  in the ligands appear at  $2924\text{ cm}^{-1} - 2928\text{ cm}^{-1}$ ,  $1358\text{ cm}^{-1} - 1379\text{ cm}^{-1}$  and  $1027\text{ cm}^{-1}$ , respectively. Other characteristic features of the ligands observed in the IR spectra of both, the ligands and the complexes include  $-C=C-$  stretching in aromatic ring between  $1590\text{ cm}^{-1} - 1490\text{ cm}^{-1}$ , stretching of the phenolic group  $\nu_{C-O}$  between  $1260\text{ cm}^{-1} - 1180\text{ cm}^{-1}$  and  $\nu_{-OCH_3}$  at  $1238\text{ cm}^{-1}$  in the complexes derived from vanillin, the corresponding bending vibrations are observed in  $600 - 900\text{ cm}^{-1}$  region (**Table 4**).

### Mass Spectra

The FAB mass spectrum of the complex  $[Cu_2(BrsalDPM)_2]$  (**Fig. 1**), consists of a peak corresponding to the parent binuclear mono cation  $[Cu_2(BrsalDPM)_2]^+$  at  $m/z$  1250 with relative abundance value of 65%. The peak corresponding to the parent binuclear dication,  $[Cu_2(BrsalDPM)_2]^{2+}$ , is observed at  $m/z$  625 with very high relative abundance value 92%. The

presence of these peaks confirms the formation of binuclear complexes rather than polynuclear species.

**Table No.4:** “Important IR frequencies ( $\text{cm}^{-1}$ ) of the binucleating Schiff base ligands and binuclear complexes”

Complexes	* $\nu_{\text{C=N}}$ ( $\text{cm}^{-1}$ )	Miscellaneous frequencies ( $\text{cm}^{-1}$ )
[H <sub>2</sub> salDPM] [Cu <sub>2</sub> (salDPM) <sub>2</sub> ]	1619 1612	$\nu_{\text{-CH}_2}$ 2923 $\nu_{\text{-CH}_2}$ 2924
[H <sub>2</sub> salDPE] [Cu <sub>2</sub> (salDPE) <sub>2</sub> ]	1620 1609	$\nu_{\text{-O}}$ 1032 $\nu_{\text{-O}}$ 1027
[Cu <sub>2</sub> (sal3-DPS) <sub>2</sub> ]	1609	$\nu_{\text{-SO}_2}$ 1357
[H <sub>2</sub> sal4-DPS] [Cu <sub>2</sub> (sal4-DPS) <sub>2</sub> ]	1618 1609	$\nu_{\text{-SO}_2}$ 1368 $\nu_{\text{-SO}_2}$ 1357
[H <sub>2</sub> naphDPM] [Cu <sub>2</sub> (naphDPM) <sub>2</sub> ]	1624 1600	$\nu_{\text{-CH}_2}$ 2921 $\nu_{\text{-CH}_2}$ 2922
[H <sub>2</sub> vanDPM] [Cu <sub>2</sub> (vanDPM) <sub>2</sub> ]	1618 1612	$\nu_{\text{-CH}_2}$ 2924, $\nu_{\text{-C-O-CH}_3}$ 1253 $\nu_{\text{-CH}_2}$ 2928, $\nu_{\text{-C-O-CH}_3}$ 1239
[H <sub>2</sub> BrsalDPM] [Cu <sub>2</sub> (BrsalDPM) <sub>2</sub> ]	1618 1608	$\nu_{\text{-CH}_2}$ 2924, $\nu_{\text{-C-Br}}$ 628 $\nu_{\text{-CH}_2}$ 2926, $\nu_{\text{-C-Br}}$ 645

\*The shift in the  $\nu_{\text{C=N}}$  stretching towards lower energy is due to the coordination of nitrogen with Copper (II).

Some of the important fragments are noted in **Table 5**. A peak corresponding to [Cu<sub>2</sub>(BrsalDPM)]<sup>+</sup> at m/z 690 is observed with relative abundance of 45%. The existence of this fragment supports the bis-bidentate coordination mode of the ligand and hence the formation of binuclear complex. This fragment loses one Cu atom to give a peak corresponding to [Cu(BrsalDPM)<sub>2</sub>]<sup>+</sup> at m/z 627.

A peak corresponding to free binucleating Schiff base ligand [(BrsalH)<sub>2</sub>DPM]<sup>+</sup> appears at m/z 565 (60%). This species undergoes further fragmentation to give other related species.

The peak corresponding to the fragments of m-nitrobenzyl alcohol and associated products are observed at m/z 136, 137, 154, 289 and 307. These fragments get associated with various fragments of metal complexes and thus are responsible for the occurrence of widely distributed species with high masses and low abundance.

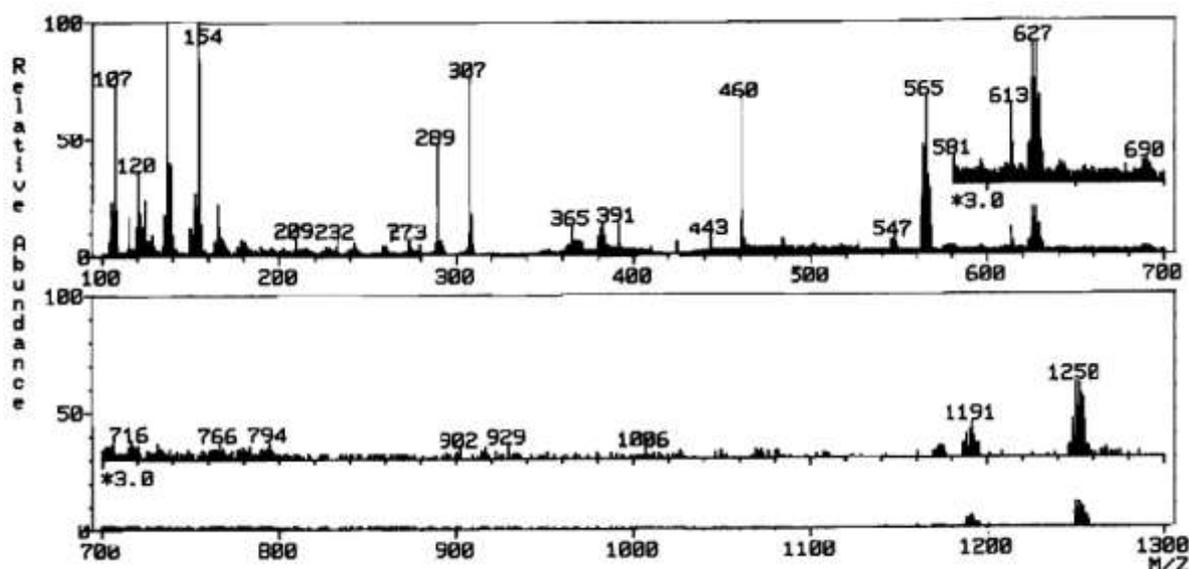


Fig. 1: FAB – Mass spectra of  $[\text{Cu}_2(\text{BrsalDPM})_2]$ .

Table No. 5: “Fragmentation pattern in the positive ion FAB-MS of  $[\text{Cu}_2(\text{BrsalDPM})_2]$  in m-nitrobenzyl alcohol”

m/z (%relative abundance)	Molecular formula
1250 (65%)	$[\text{C}_{54}\text{H}_{36}\text{O}_4\text{N}_4\text{Br}_4\text{Cu}_2]^+$
902 (44%)	$[\text{C}_{34}\text{H}_{22}\text{O}_4\text{N}_3\text{Br}_3\text{Cu}_2]^+$
690 (45%)	$[\text{C}_{27}\text{H}_{19}\text{O}_2\text{N}_2\text{Br}_2\text{Cu}_2]^+$
629 (38%)	$[\text{C}_{54}\text{H}_{40}\text{O}_4\text{N}_4\text{Br}_4\text{Cu}_2]^{2+}$
627 (92%)	$[\text{C}_{54}\text{H}_{38}\text{O}_4\text{N}_4\text{Br}_4\text{Cu}_2]^{2+}$
625 (92%)	$[\text{C}_{54}\text{H}_{36}\text{O}_4\text{N}_4\text{Br}_4\text{Cu}_2]^{2+}$
565 (60%)	$[\text{C}_{27}\text{H}_{21}\text{O}_2\text{N}_2\text{Br}_2]^+$
547 (5%)	$[\text{C}_{27}\text{H}_{19}\text{ON}_2\text{Br}_2]^+$
460 (70%)	$[\text{C}_{20}\text{H}_{16}\text{ON}_2\text{Br}_2]^+$
443 (12%)	$[\text{C}_{20}\text{H}_{15}\text{N}_2\text{Br}_2]^+$
365 (13%)	$[\text{C}_{14}\text{H}_9\text{N}_2\text{Br}_2]^+$
363 (8%)	$[\text{C}_{14}\text{H}_7\text{N}_2\text{Br}_2]^+$
120 (18%)	$[\text{C}_7\text{H}_6\text{NO}]^+$
107 (38%)	$[\text{C}_7\text{H}_7\text{O}]^+$

### ESR spectra

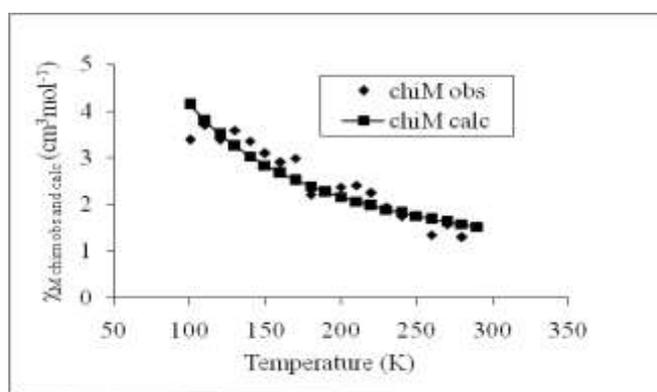
The ESR spectra of complex,  $[\text{Cu}_2(\text{BrsalDPM})_2]$  were recorded at room temperature in polycrystalline powder form and as frozen solution in DMF at LNT. The spectra at RT and LNT are both identical. They are typical axial ESR indicating tetragonal distortion / near square planar geometry around copper ion. The  $g_{\parallel}$  and  $g_{\perp}$  values recorded in **Table 6**, are typical of normal copper (II) coordination. A very weak transition at half field strength is also observed indicating the possibility of magnetic exchange between two copper (II) ions.

**Table No. 6:** ESR of the  $[\text{Cu}_2(\text{BrsalDPM})_2]$ 

	$g_{\perp}$	$g_{\parallel}$
<b>Room temperature</b>	2.06	2.23
<b>Liquid N<sub>2</sub> temperature</b>	2.06	2.21

### Magnetic Exchange

The magnetic susceptibility measurements between 90 °K – 270 °K and the subsequent least squares fit of the experimental data to the Bleaney – Bower's equation are used to evaluate the coupling constant  $J$  between the copper (II) centres in the binuclear complexes , **1, 2, 3, 4, 5, 6** and **7** . The  $\chi_M$  vs T plots with calculated and observed values are shown in **Fig. 2**. The values of  $J$  range between  $-7.24 \text{ cm}^{-1}$  to  $53.16 \text{ cm}^{-1}$  shown in **Table 7**. Data indicate that all binuclear complexes except  $[\text{Cu}_2(\text{salDPM})_2]$ , have significant ferromagnetic exchange.

**Fig. 2:** Dependence of magnetic susceptibility on temperature in complex, 1.**Table No. 7:** “ $J$  and torsional angle of complexes”

Complexes	$J \text{ (cm}^{-1}\text{)}$	Torsional angle
$[\text{Cu}_2(\text{salDPM})_2]$	-7.24	175.3
$[\text{Cu}_2(\text{sal4-DPS})_2]$	12.98	172.55
$[\text{Cu}_2(\text{salDPE})_2]$	39.02	170.0
$[\text{Cu}_2(\text{naphDPM})_2]$	27.19	172.29
$[\text{Cu}_2(\text{vanDPM})_2]$	27.07	136.48
$[\text{Cu}_2(\text{BrsalDPM})_2]$	53.16	129.08
$[\text{Cu}_2(\text{sal3-DPS})_2]$	47.33	177.79

The magnetic exchange interaction between paramagnetic metal ions depend on several parameters related to the geometry of the molecule and energies of paramagnetic orbitals. The influence of such parameters on the magnetic exchange can be understood by considering ligand mediated interaction between paramagnetic orbitals.

The multiatomic bridging ligands, specially those having conjugated  $\pi$  – systems, have a number of closely spaced molecular orbitals. Usually one of these closely spaced orbitals can have matching energy and symmetry with paramagnetic orbitals of metal atom. The interaction can lead to the formation of two metal centred molecular orbitals one of them essentially bonding and the other essentially antibonding. The paramagnetic orbitals of the metal ion being the highest occupied amongst all interacting orbitals and the resulting MOs are usually HOMO and LUMO. The occupation of these two orbitals by the two unpaired electrons over the metal ions leads to the singlet and triplet states with an energy difference of  $2J$ .

If  $-2J = kT$ , the magnetic susceptibility depends on Boltzmann population distribution, of singlet and triplet state and leads to paramagnetism. However, if  $-2J > kT$  the population of singlet state increases and ultimately the system becomes diamagnetic below certain temperature i.e. antiferromagnetism is developed.

The situation, where  $-2J < kT$  at all temperatures, can arise when there is no effective interaction between the paramagnetic orbitals or the orbital orientation forces them to remain degenerate. In such cases, the ground state is a triplet state and hence the result is ferromagnetism.

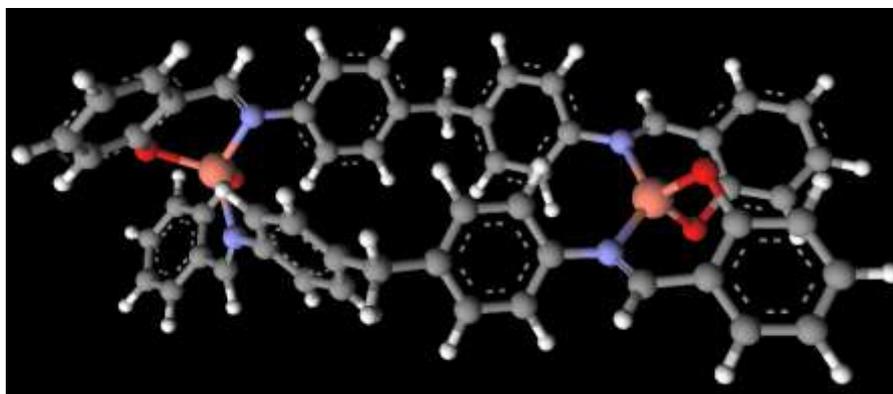
The extent of such ligand mediated exchange in binuclear complexes depends on: (i) the energy of the interacting orbitals and (ii) the variation in geometrical parameter such as metal-ligand bond length, M-L-M bridge angle ( $\phi$ ), dihedral angle between coordination planes ( $\theta$ ) and degree of planarity of the bridging unit.

Super exchange interaction in the binuclear complexes can be considered as a special case with the interacting bridged MOs being replaced by the bridging atom orbitals. Smith studied, binuclear copper (II) complexes, bridged by single alkoxy oxygen<sup>27</sup>. These complexes were shown to have a maximum Cu-O-Cu angle of  $135^\circ$ . The magnetic moment of the complex was found to be 0.6 BM per Cu (II) centre at room temperature, indicating the presence of a strong antiferromagnetic interaction. A number of studies<sup>28-35</sup> have shown that in  $\mu$ -oxo i.e.  $\mu$ -hydroxo,  $\mu$ -alkoxo, or  $\mu$ -phenoxo bridged dicopper (II) complexes the extent of antiferromagnetic exchange decrease with the decrease in the Cu-O-Cu angle  $\phi$  and becomes ferromagnetic below the angle of  $97.5^\circ$ . In addition to the optimum value of the M-L-M angle ( $\phi$ ), the planarity of the binuclear core structure is also an important requirement for the exchange interaction. Kahn et al<sup>36, 37</sup> showed dependence of the value of  $J$  on the dihedral angle ( $\theta$ ), between the two copper coordination planes in O-bridged non planar

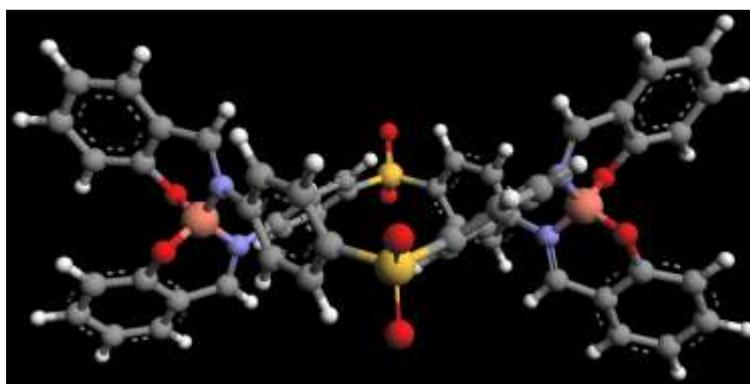
dimers. There is maximum antiferromagnetic interaction between magnetic orbitals, where dihedral angle between coordination planes ( $\theta$ ) is zero or  $180^\circ$ . Any distortion of the binuclear core structure from the planarity, results in an increase in  $\theta$ , reducing the overlap of copper (II)  $d_{x^2-y^2}$  orbitals with the bridging oxide ion orbitals. This causes exchange interaction weakening. A relationship between geometrical parameters and the extent of spin exchange may be expected in complexes with multiatomic bridging units.

A systematic variation has been made in the bridging part of the binucleating ligands. The bis-phenyl moieties are linked by etherial  $-O-$ , methylene  $-CH_2-$  or sulphonyl  $-SO_2-$ . Sulphonyl bridging at 3 or 4 position with respect to the coordinating site has been selected to get an insight into the effect of positional isomer changes. The non bridging part of the ligands have substitutions at 3, 4 and 5 positions. These are expected to bring in variations in the electron density over the coordinating atom, its  $\pi$  – bonding ability and hence the coordination geometry.

Geometry of the complexes has been optimised using Universal Force Field method<sup>38-45</sup>. The optimised geometry of the complexes is given in **Fig.3**. The torsional angle between the metal coordination planes were determined and have been correlated with the extent of spin exchange, **Table 7**.



**Fig. 3a:** Optimised geometry of complex, 1.

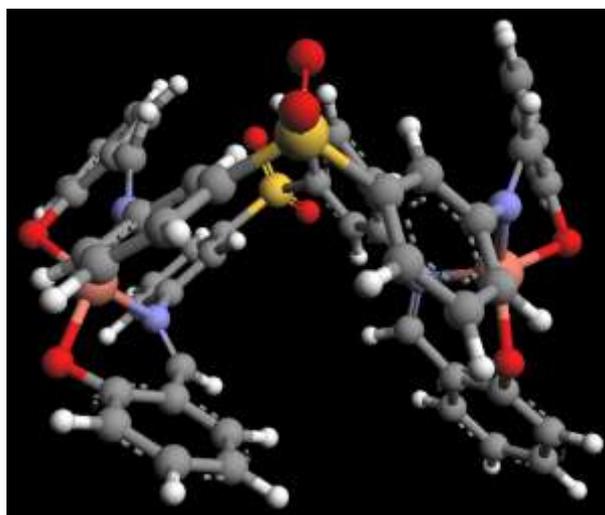


**Fig 3b:** Optimised geometry of complex, 4.

Data of **Table 7** indicate that the extent of spin exchange depends largely on the torsional angle between metal coordination planes. J values indicate about greater ferromagnetic interaction with greater deviation in torsional angle from  $180^\circ$ .

A comparison between the complexes, **1**, **2** and **4**, where the ligands differ only in the central functionality holding the bis-phenyl moieties, shows that the deviation in torsional angle increases from linearity in the order  $1 < 4 < 2$ . Consequently, complex **1** is weakly antiferromagnetic while the others are moderately ferromagnetic. However complex **2** shows distinct ferromagnetism.

The complexes, **1**, **5**, **6** and **7**, have same bridging functionality while the non-bridging part has different functional groups. The deviation in torsional angle from  $180^\circ$  increases in the order,  $1 < 5 < 6 < 7$ . The J values also increase in the order  $1 < 5 \approx 6 < 7$ . Above data show a fare relationship between J and torsional angle.



**Fig 3c:** Optimised geometry of complex, **3**.

The complex **3** appears to be an exception because the deviation in torsional angle between metal coordination planes is less i.e.  $177.79^\circ$  but J is higher. In this molecule  $-\text{SO}_2-$  group occupies meta position to the coordinating site and this has two effects: (i) the delocalization of metal electron/spin density at position three (required for propagating exchange is less) and (ii) the molecule is highly distorted (ligand orbitals with suitable energy have nodes). This hinders effective overlapping between paramagnetic orbitals of copper (II) ions and the molecular orbitals possessed by the bridging ligands. Hence, metal paramagnetic orbitals are forced to remain degenerate and results in greater ferromagnetism.

The substitutions over the ligands have a significant effect on the electron density on the two paramagnetic metal centres and hence on the extent of the super exchange interaction. An electron

withdrawing group on the ligand reduces the electron density on the metal ion whereas an electron releasing group increases the electron density. This affects spin exchange interaction between two metal centres. The substitution on the ligand may also affect the planarity of the molecule and hence the overlap of the metal orbitals with the orbitals of the bridging atoms. Extent of magnetic exchange depends upon large substituent on the ligand and results leads to ferromagnetism<sup>46</sup>.

## **CONCLUSION:**

Data allow to conclude that variation in functional group 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 centres through long multiatomic bridges.

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