Research article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

Synthesis, Characterization and Magnetic properties of New Ternary Binuclear Copper (II) Complexes with long Bridging group

[1]Ran Bahadur Yadav* and [2]N. D. Kulkarni

[1]Applied Chemistry Department, Faculty of Technology and Engineering, Kalabhavan, The Maharaja Sayajirao University of Baroda, Vadodara-390001, Gujarat, India,
Email: rbyadavmsu@gmail.com
[2]Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara-390002, Gujarat, India, Email: ndkmsu@gmail.com

ABSTRACT

Binuclear complexes of copper (II) have been synthesized by the reaction of aromatic diamines with the ternary complexes of copper (II) with 2,2'-bipyridyl or 1,10-phenanthroline (as primary ligand) and 2-hydroxybenzaldehyde or 2-hydroxynaphathaldeyde or 2-hydroxyl-3-methoxybenzaldehyde as secondary ligand. Complexes have been characterized by elemental analysis, conductometry, spectral and magnetic properties (90K to 300K temperature range). Data suggest long range spin exchange interaction between two copper centers which correlated with the variation in non bridging part of ligands.

KEY WORDS: Copper (II) Complexes, Binuclear complexes, Binucleating ligand, Magnetic interactions.

***Corresponding author**

Dr Ran Bahadur Yadav

Assistant Professor, Applied Chemistry Department,
Faculty of Technology and Engineering, Kalabhavan,
The Maharaja Sayajirao University of Baroda,
Vadodara- 390001, India.
Email: rbyadavmsu@gmail.com (M) +91 9408091499

INTRODUCTION

The growing interest in the study of binuclear copper (II) complexes is due to their role as potential models for several important biological systems, containing binuclear spin coupled sites.[1-3] These binuclear copper (II) complexes can be used similar to enzyme catalyst in several biochemical reaction.[4] The catalytic activity of these complexes attributed due to their redox and magnetic characteristics. Therefore, factors that affect the electron transfer or spin exchange between two metal centers are worth exploring. Unlike complexes with single atom bridge where direct super exchange can take place, polyatomic bridging units can function in a more noble manner. Study of complexes, with different geometries around the metal ion and with binucleating ligands possessing σ and π – orbital, indicate that extent of spin exchange in such compounds depends on the energy of the magnetic orbitals and the symmetry of the metals environment.[5-11] These factors are affected by change in nucleophilicity and the geometry of the ligands, respectively. The coordination geometry and energy of the metal ions can be affected by the non-bridging part of the ligands and hence affects the magnetic exchange.

Binuclear complexes with oxalate[12], squarate[12], dihydroxybenzoquinone[13], naphthazarin[14] and quinizarin bridge have been reported. 2,5-Penta and hexa coordinated complexes of the later two compounds were shown not to undergo any magnetic exchange interaction because of the absence of ligand orbitals with proper symmetry.[14, 15] Copper (II) complexes of binucleating ligands with two bidentate sites, separated by aromatic rings, have been studied earlier also.[16] In such complexes spin exchange between two metal centers propagated through π delocalized bridge. However, no work has been carried out on binuclear Schiff base complexes (with substituted binuclear Schiff base ligand) forming a bridge and with the metal ions coordinated to another bidentate ligand. In present study, an attempt has been made to synthesize binuclear complexes of copper (II) and to study the magnetic exchange at variable temperature through long aromatic bridging groups. Further studies have also been performed on the change of electronic environment around the metal centers by changing the non coordinating part of the ligand. Molecular modeling, by force field calculation, has been used to work out the geometrical parameters in various complexes and then correlated with geometrical property.

In order to achieve above objectives, synthesis and characterization of ternary binuclear copper (II) complexes involving, a tertiary diamine, 2,2’-bipyridine, 1,10-phenanthroline and binucleating Schiff base having conjugated π- system, have been performed. The Schiff bases used for the purpose, are the condensation products of different combination of 2-hydroxybenzaldehyde or 2-hydroxynaphathaldeyde or 2- hydroxyl-3-methoxybenzaldehyde and aromatic diamine, 4,4’-diaminodiphenylmethane.

MATERIALS AND METHOD

Chemicals

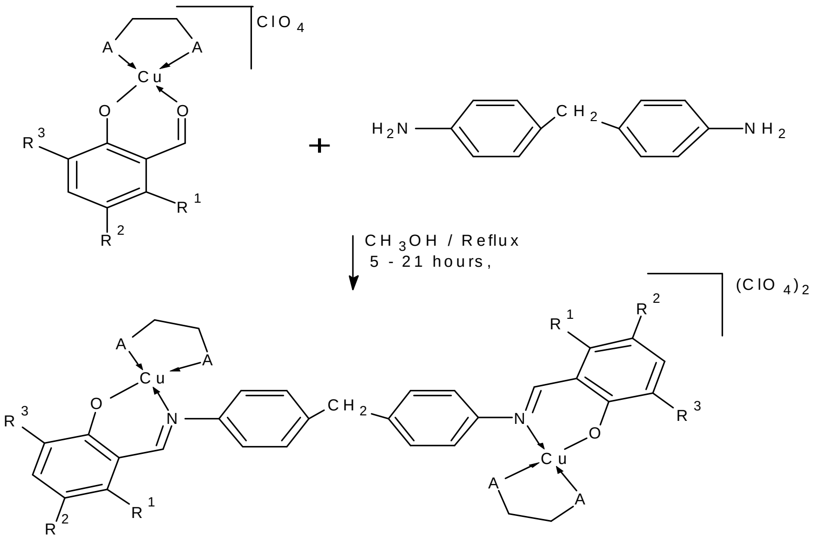
2-Hydroxynaphthaldehyde (Fluka), 2-Hydroxybenzaldehyde, 4,4’-diaminodiphenylmethane, 2,2’-bipyridine, 1,10-phenanthroline, cupric acetate monohydrate and sodium perchlorate were used from Merck. o-Vanillin (LR) was obtained from local manufacturers . All solvents were distilled twice before use.

All the ternary complexes were prepared by the reported method.[17]

Synthesis of binuclear complexes, [Cu$_2$ (Phen)$_2$,SalMeSB](ClO4)$_2$

0.8 mmol of ternary complexes of [Cu(Phen),(sal)](ClO$_4$) was dissolved in 20 ml of methanol and to this 0.4 mmol of 4,4’-diaminodiphenyl methane solution in 20 ml of methanol was added dropwise in 30 minutes. The flask equipped with a water condenser and a magnetic stirrer. The reaction mixture was refluxed for 11 hours. Consumption of 4,4’-diaminodiphenyl methane was monitored by thin layer chromatography. After refluxtion brown coloured compound was separated, cooled and the solid obtained was washed thoroughly with 25 ml in 5-6 portions and dried in bulb oven **(Figure 1).**

Complexes (2-6) were synthesized by using the above procedure and appropriate quantity of ternary complexes and 4,4’-diaminodiphenyl methane. The data of the C, H and N analyses, refluxtion time for each complexes and conductivity measurements have been given in T**able 1**.



1, 2: $R^1 = R^2 = R^3 = H$
3, 4: $R^1R^2 = -(CH=CH)_2-$, $R^3 = H$
5, 6: $R^1 = H$, $R^2 = H$, $R^3 = -OCH_3$
1, 3, 5: AA = 1,10-phen
2, 4, 6: AA = 2,2'-bipy

Figure: Synthesis of binuclear complexes, 1-6.

Table 1: “Elemental analysis, refluxtion time, yields and molar conductivity of ternary binuclear complexes”.

Comp. No.	Complexes	Found (Calc^a.) (%)			Refluxtion time (hours)	Yields (%)	Molar conductivity^b ($\Omega^{-1}M^{-1}cm^2$)
		C	H	N			
1.	[Cu$_2$(phen)$_{2,}$salMeSB](ClO4)$_2$ $C_{51}H_{36}O_{10}N_6Cl_2Cu_2$	56.34 (56.14)	3.25 (3.30)	7.75 (7.71)	11	77	140.28
2.	[Cu$_2$(bipy)$_{2,}$salMeSB](ClO4)$_2$ $C_{47}H_{36}O_{10}N_6Cl_2Cu_2$	54.38 (54.12)	3.37 (3.45)	7.92 (8.06)	11	81	140.14
3.	[Cu$_2$(phen)$_{2,}$naphMeSB](ClO4)$_2$.2H$_2$O $C_{59}H_{44}O_{12}N_6Cl_2Cu_2$	57.28 (57.74)	3.17 (3.58)	5.60 (6.85)	21	42	138.30
4.	[Cu$_2$(bipy)$_{2,}$naphMeSB](ClO4)$_2$ $C_{55}H_{40}O_{10}N_6Cl_2Cu_2$	57.82 (57.78)	3.39 (3.50)	6.91 (7.35)	15	49	135.29
5.	[Cu$_2$(phen)2,vanMeSB](ClO4)$_2$ $C_{53}H_{40}O_{12}N_6Cl_2Cu_2$	54.41 (55.30)	3.47 (3.47)	6.49 (7.30)	15	72	130.26
6.	[Cu$_2$(bipy)2,vanMeSB](ClO4)$_2$ $C_{49}H_{40}O_{12}N_6Cl_2Cu_2$	53.22 (53.35)	3.48 (3.63)	7.20 (7.62)	13	84	150.15

[a] The values in parenthesis are theoretical values calculated from the molecular formulae .

[b] The conductivity measurements were carried out with 1× 10^{-3} M solution of the complexes in DMF.

Physical measurements

Carbon, Hydrogen and Nitrogen analysis were performed on Perkin Elamer Model-2400 CHN/S analyzer. Specific conductivity of all the complexes in DMF solution having 1.0 mmolar concentration was measured using a Toshniwal conductivity bridge.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 instruments, equipped with spherical reflectance assembly using $BaSO_4$ as a reference material. IR spectra (as KBr pellets) were recorded on Perkin Elamer FT-IR, spectrum RXI. The ESR spectra of complexes [Cu$_2$(bipy)$_{2,}$naphMeSB](ClO4)$_2$ and [Cu$_2$(bipy)2,vanMeSB](ClO4)$_2$ were recorded at RT and liquid nitrogen temperature on a Varian E-15 spectrometer. The ESR spectra of complexes [Cu$_2$(phen)$_{2,}$salMeSB](ClO4)$_2$ and [Cu$_2$(bipy)$_{2,}$salMeSB](ClO4)$_2$ were recorded at room temperature on a Brucker. The FAB mass spectrum of the complex [Cu$_2$(bipy)$_{2,}$naphMeSB](ClO4)$_2$ in m-nitrobenzyl alcohol matrix was recorded on a JEOLSX 102/DA – 6000 mass spectrometer / Data system. Argon (6 KV, 10 mA) was used as a FAB gas. The spectra was recorded at room temperature with an accelerating voltage of 10 KV.

Magnetic Susceptibility measurements were carried out on solid samples in the 90–300 K temperature range with an indigenous Faraday set up. All measurements were done at a field strength of 0.8 Tesla. The sample cell was calibrated with $Hg[Co(SCN)_4]$ as calibrant. Diamagnetic corrections were incorporated using Pascal’s constants. The effective magnetic moments were calculated by the formula-

$$\mu_{eff} = (3k/N_A\mu_B)^{1/2}(\chi_A T)^{1/2}$$

A least-squares calculations were performed by fitting the experimentally observed values of magnetic susceptibility at various temperature to Bleaney-Bower’s equation [18, 19]

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

The difference $|\chi^2_{calc} - \chi^2_{obsd}|$ 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.

RESULT AND DISCUSSION

As the values of elemental analysis of binuclear complexes given in **Table 1**, analyzed on the basis of suggested molecular formulae. The complexes are found to highly soluble in DMF. Hence the conductance studies were carried out in a mmolar solution of DMF. All six complexes show molar conductance values between 130 – 150 ($\Omega^{-1}M^{-1}cm^2$) corresponds to 1:2 electrolyte, indicating that two per chlorates are out side of coordination sphere. Complex **3** show the presence two water molecules but thermal analysis was not carried out for the confirmation of nature of water molecule because of presence of per chlorates ion. Water molecule is confirmed by only IR spectra.

Electronic and IR spectra

The electronic spectra of the complexes have been recorded both in solution and in the solid state. The observations of the medium intensity band close to 290 nm and 390 nm occur due to the inter ligand charge transfer band. Data show each complex exhibit one d-d band in the visible region strongly indicating presence of four coordinated copper (II) ions in a molecule (**Table 2)**.

The IR spectra of the complexes in the region 400 – 4000 cm^{-1} are very rich. The IR spectra obtained for these complexes are in agreement with proposed structures. The absorption frequency of the imine >C=N is appeared between 1600 – 1613 cm^{-1}. These are at lower energies compared to the free organic molecule. The shift in the $\nu_{>C=N}$ (imine) towards lower energy in the complexes indicate that the imine nitrogen is involved in coordination with the Cu (II) ion. Complex **3** show a broad band at 3500 cm^{-1}, which can be assigned for the presence of water molecules. The IR spectra of the complexes exhibit the broad and strong band about 1086 – 1100 cm^{-1} without any splitting corresponds to the characteristics vibration of non – coordinated $ClO4^-$ group.[20] Moreover complexes exhibiting asymmetric stretching frequency around 2920 cm^{-1} indicate the presence of $–CH_2$- group. Presence of absorption frequency for $–CH_2$- group indicated about bridging group. All the complexes exhibit absorption frequency 3055 - 3084 cm^{-1} for aromatic stretching (**Table 2).**

Table 2: "Energies of the charge transfer (nm) and IR absorptions (cm^{-1}) of ternary binuclear complexes".

Comp. No.	Charge transfer band		ν(>C=N) (cm^{-1})	ν(ClO_4) (cm^{-1})	miscellaneous frequencies (cm^{-1})
	position λ_{max} (nm)	d-d transition (nm)			
1.	294, 392	782*	1613	1086	3063, 2923
2.	276, 390	776*	1612	1087	2920, 3084
3.	296, 388	726*	1600	1103	2922, 3062, 3500
4.	286, 404	630	1600	1098	3055, 2924
5.	282, 390	654	1610	1090	3059, 2927, 1238, 1032
6.	284, 390	634	1610	1092	3057, 2926, 1250, 1030

* The ligand field absorption are observed in d. r. s. and all other values in methanolic sol.

Mass spectra

FAB mass spectra of the complex $[Cu_2(bipy)_{2,}naphMeSB](ClO4)_2$ consist of parent binuclear monocation peak at m/z 789 with relative abundance value of 36%. Complex $[Cu_2(bipy)_{2,}naphMeSB](ClO4)_2$ lost the fragments bipyridyl with two ClO_4^- ions, showing the parent ion peak at 789 with relative abundance 36%. Parent ion peak lost a $[Cu,2H]^+$ fragment and showing the peak at m/z 724 (84%), this peak lost a $[Cu,2H]^+$ and showing the peak at m/z 659 with relative abundance 40%. $[Cu,bip]^+$ peak observed at m/z 219 with relative abundance 16%**.** All these peaks assigned strongly supported the formation of binuclear complexes with suggested molecular formulae.

The peaks corresponding to the fragments of m-nitrobenzyl alcohol and associated products are observed at m/z 136, 137, 154, 289 and 307. These fragments can get associated with various fragments of metal complexes and thus responsible for the presence of widely distributed peaks with low relative abundance (**Figure 2** and **Figure 3**).

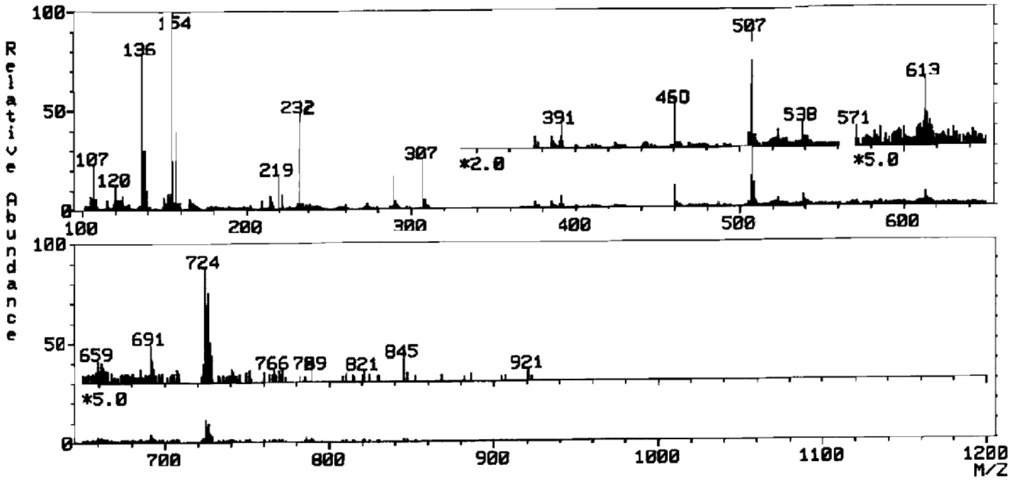
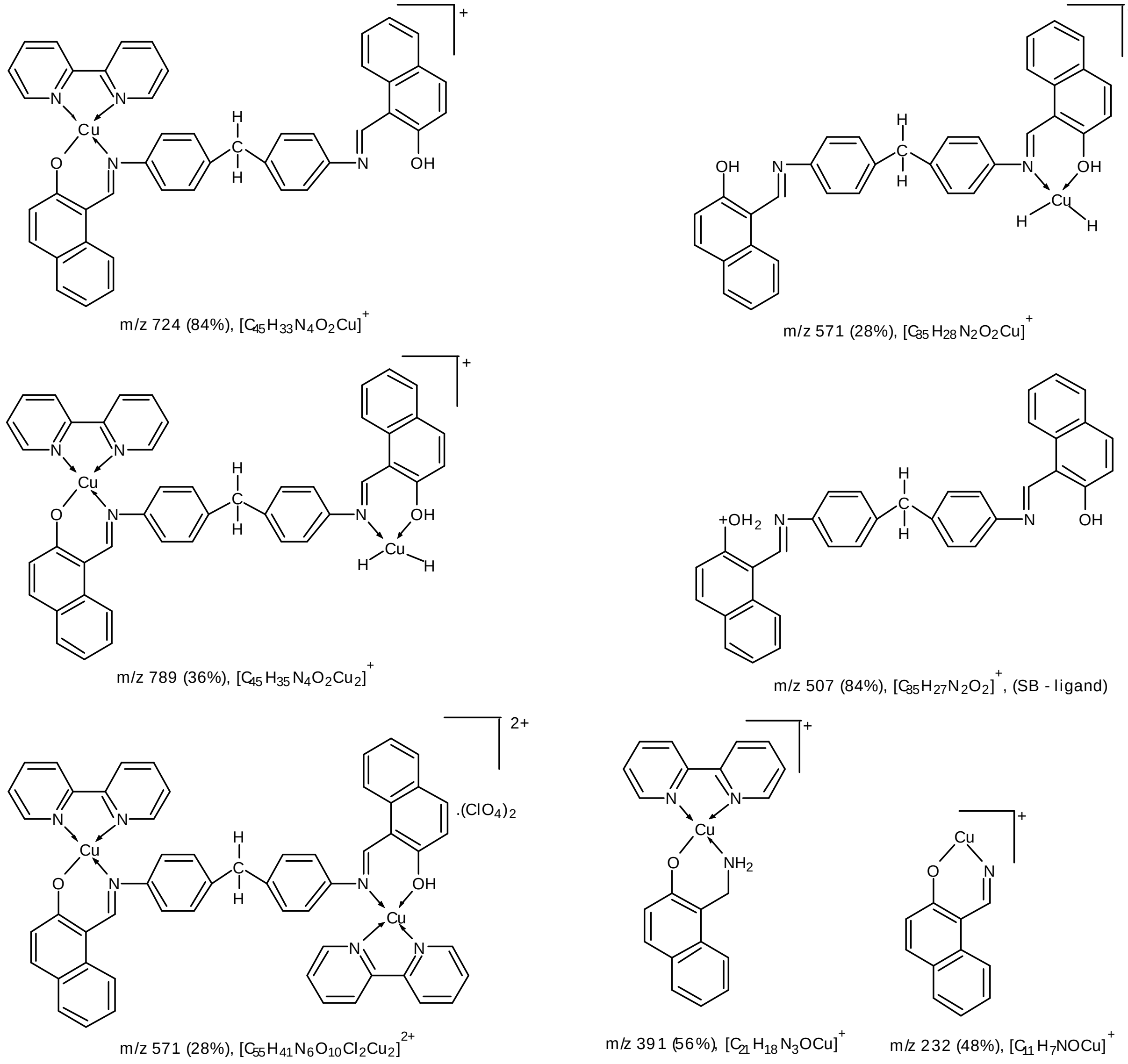


Figure 2: FAB – mass spectra of complex, $[Cu_2(bipy)_{2,}naphMeSB](ClO4)_2$.



m/z 724 (84%), $[C_{45}H_{33}N_4O_2Cu]^+$

m/z 571 (28%), $[C_{35}H_{28}N_2O_2Cu]^+$

m/z 789 (36%), $[C_{45}H_{35}N_4O_2Cu_2]^+$

m/z 507 (84%), $[C_{35}H_{27}N_2O_2]^+$, (SB - ligand)

m/z 571 (28%), $[C_{55}H_{41}N_6O_{10}Cl_2Cu_2]^{2+}$

m/z 391 (56%), $[C_{21}H_{18}N_3OCu]^+$

m/z 232 (48%), $[C_{11}H_7NOCu]^+$

Figure 3: FAB – mass spectra of complex, $[Cu_2(bipy)_2naphMeSB](ClO4)_2$.

ESR studies

The ESR spectra of polycrystalline complexes, **1** and **2** were recorded at room temperature while those of complexes **4** and **6** were recorded at RT and in the form of DMSO glass at liq. N_2 temperature. The spectra are given in **Figure 4** to **Figure 6**, and results are summarized in **Table 3.** The ESR spectra of complex **6** were recorded at RT and LNT are identical.

All complexes have typical axial ESR with well separated $g_{\|}$ and $g_{\perp}$ components. The observed $g_{\|}$ and $g_{\perp}$ values are within the range of values expected and reported in the literature for Cu^{2+} in near square planar or compressed tetrahedral geometry.[21, 22] The values of hyperfine coupling constant are, however, much lower indicating substantial delocalization of Cu^{2+} electron density over the ligand due to significant M→C π-interaction.

Table 3: “ESR parameters of some complexes”.

Complexes	Room temperature		LNT in DMSO	
	$g^{||}$	$g_{\perp}$	$g^{||}$	$g_{\perp}$
$[Cu_2(phen)_2, salMeSB](ClO4)_2$	2.2194	2.0687	-	-
$[Cu_2(bipy)_2, salMeSB](ClO4)_2$	2.2260	2.0675	-	-
$[Cu_2(bipy)_2, naphMeSB](ClO4)_2$	2.1385	2.0536	2.1492	2.0601
$[Cu_2(bipy)_2, vanMeSB](ClO4)_2$	2.1635	2.0800	2.1635	2.0800

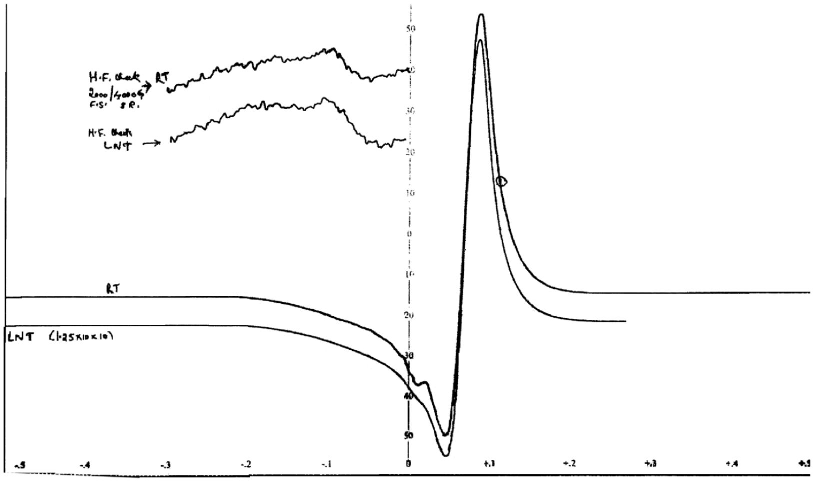


Figure 4: ESR of the binuclear complex, 4 at RT and LNT.

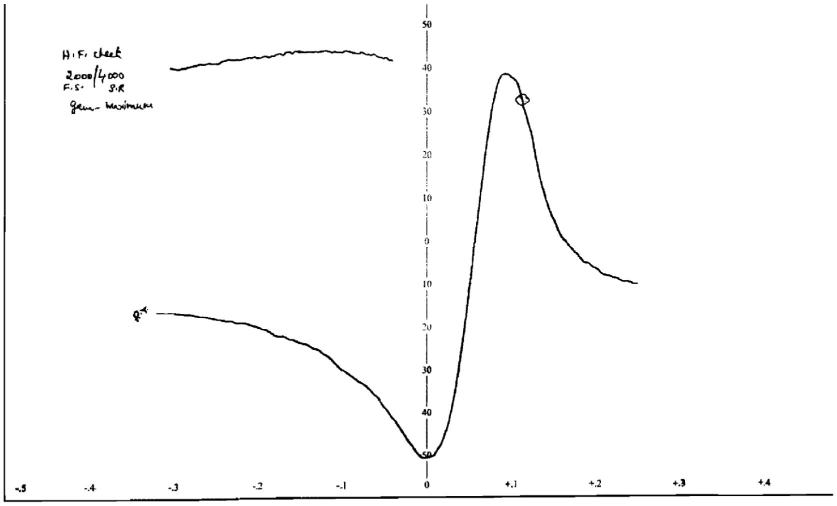


Figure 5: ESR of the binuclear complex, 6 at RT.

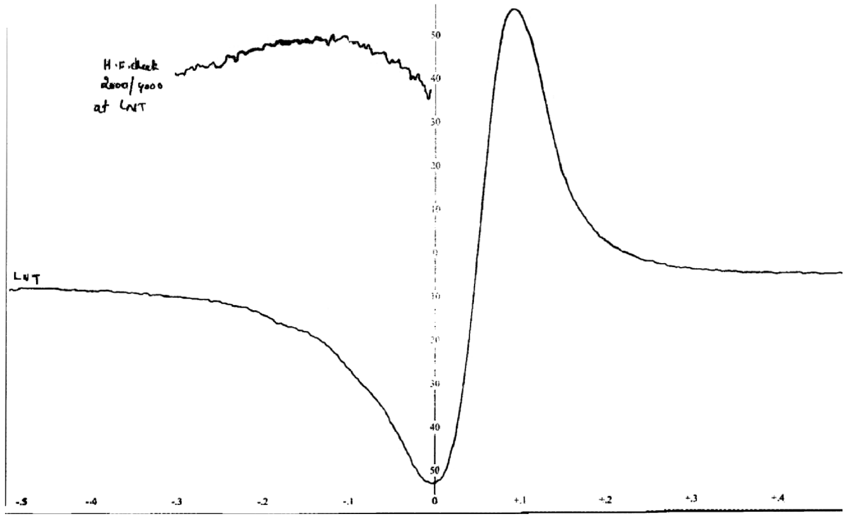


Figure 6: ESR of the binuclear complex, 6 at LNT.

Magnetic properties

Complexes studied here have a single bridging group and the other non-bridging positions around the metal ion occupied by π-bonding ligands. The single bridging group can allow a lot of flexibility in the structure. However, π-bonding ligands having functional groups, with bridging ligand can modulate the strength of M-L binding and the coordination geometry. Distinct influence is expected on the geometrical parameters with concomitant effect on the spin exchange interaction.

The least square fitting of magnetic susceptibility data, to Bleaney – Bower's equation in complexes, **2, 3, 4, 5** and **6,** yield J values ranging between -1.22 to 55.0 cm^{-1} i.e. the type of magnetic exchange varies from weak ant ferromagnetic to ferromagnetic. Therefore, magneto – structural correlations are expected to be worth exploring.

Complexes have very poor solubility in non coordinating solvents and hence determination of crystal structure was not possible. In order to evaluate the geometrical parameters, the geometries of the complexes were optimized using universal force field (**Figure 8**).[23-30] Though not so accurate as quantum mechanical calculations, it is well known that at all levels of calculations, while the absolute values of electron density, energy etc. are significantly affected, the trends and the overall geometry of the molecules remains unaltered.

Table 5: "J and tensional angle of ternary binuclear complexes".

Complexes	J (cm^{-1})	Tensional angle
$[Cu_2(bipy)_2vanDPM](ClO_4)_2$	-9.10	100.85
$[Cu_2(bipy)_2salDPM](ClO_4)_2$	55.00	136.15
$[Cu_2(phen)_2vanDPM](ClO_4)_2$	52.04	148.09
$[Cu_2(phen)_2naphDPM](ClO_4)_2.2H_2O$	29.47	164.39
$[Cu_2(bipy)_2naphDPM](ClO_4)_2$	-1.22	166.98

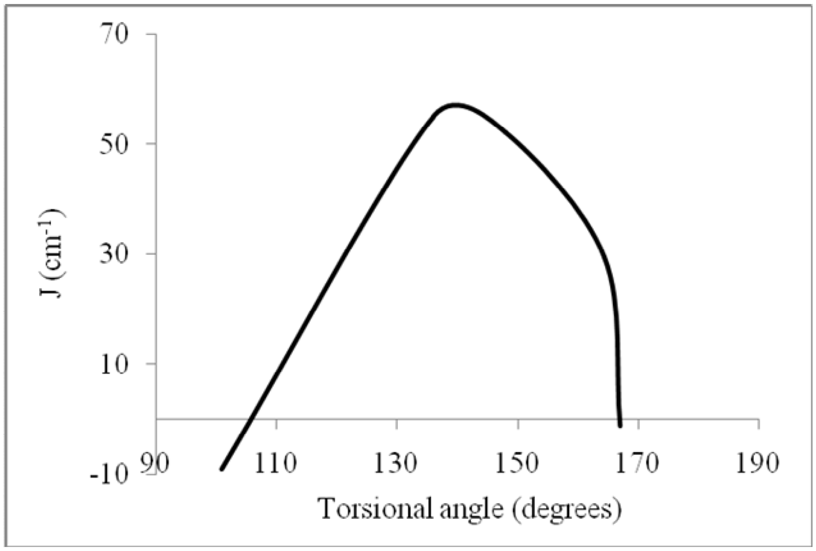


Figure 7: Plot of J *vs* tortional angle in binuclear complexes.

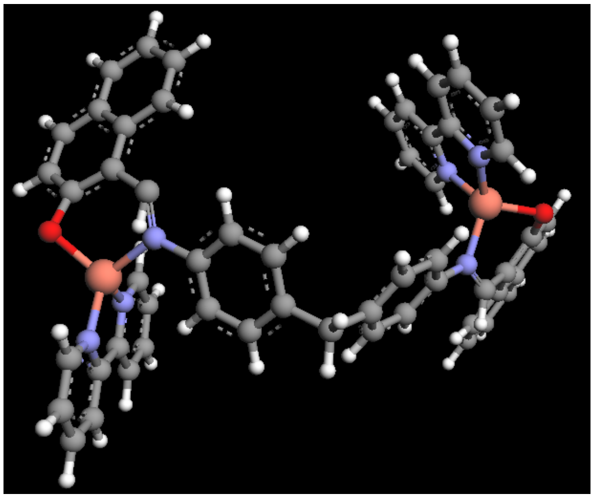


Figure 8: Optimized geometry of binuclear complex, [Cu_2(bipy)$_2$naphDPM](ClO_4)$_2$.

The torsional angles Γ between metal coordination planes have been determined. Γ data have been correlated with the experimentally determined J values (**Table 5**). Plots of J vs Γ have been depicted in **Figure 7**. The two metal centers associated with diphenyl methane bridging group and on variation in the non bridging π-bonding ligands. It has been observed that a 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 torsional angle and there by tune the magnetic property to any optimized value from ferromagnetism to antiferromagnetism. Similar dependence of the extent of magnetic exchange on the non bridging ligands in complexes has been reported earlier.[10]

ACKNOWLEDGEMENTS

Thanks are due the Department of Science and Technology, New Delhi, India for their financial support, SAIF, CDRI Lucknow for FAB mass spectra, the Director NCL Pune and the Director, SAIF, IIT Powai for providing the ESR spectra of complexes.

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