# SYNTHESIS AND CHARACTERIZATION OF TERNARY BINUCLEAR COPPER (II) COMPLEXES WITH LONG DIPHENYL ETHER BRIDGING GROUP: PHYSICOCHEMICAL AND MAGNETIC STUDIES

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

[1]*Applied Chemistry Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara,Gujarat India*
[2]*Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India*
*Corresponding author: rbyadavmsu@gmail.com*

## ABSTRACT

Binuclear complexes of have been synthesized by the reaction of aromatic diamine with 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). Copper (II) complexes have been characterized using various physicochemical and various spectroscopic methods (IR, ESR and mass spectrometry). The variable temperature magnetic susceptibility (90Kto300K) measurements showed weak antiferromagnetic to ferromagnetic exchange between the proximate Cu (II) ions in a complex. Molecular modeling has been used to acquire various geometrical parameters of the complex and correlated with the magnetic property.

**Keywords:** Copper (II) Complexes, Binuclear complexes, Schiff bases, Binucleating ligands, Magnetic susceptibility.

## 1. INTRODUCTION

Continued interest in the study of binuclear metal complexes is due to their specific important role played as metalloenzyme [1-3]. The binuclear copper (II) complexes have successfully been used as enzyme catalyst in several biochemical reactions [4]. In addition to the catalysis by complexes of copper, study of magnetic susceptibility (at variable temperature) is also significant to understand the type of magnetic interaction involved between two metal centers of a binuclear metal complex [5-7]. Activity of these binuclear complexes can be governed by their redox and magnetic characteristics. Therefore, it is worth exploring factors that affect the electron transfer or spin exchange between two metal centers. Unlike complexes with single atom bridge where direct super exchange can take place, polyatomic bridging units may result novel exchanges responsible for unknown geometrical architecture. Study of complexes with different geometries around the metal ion and with binucleating ligands possessing σ and π-orbitals revealed that extent of spin exchange can be dependent on the energy of the magnetic orbitals and the symmetry of the metal environment [8-11]. These factors can be affected by change in nucleophilicity and the geometry of the ligand. The coordination geometry, energy of the metal ions and resultant magnetic exchange can be affected by the non-bridging part of the ligands.

Binuclear complexes with chlorine [12], hydroxido [8] oxalate [13], squarate [13], dihydroxybenzoquinone [14], naphthazarin [15] and quinizarin bridge have been reported. 2,5-Penta and hexa coordinated complexes of the last two ligands do not undergo any magnetic exchange interaction due to the absence of ligand orbitals with an appropriate symmetry [15,16]. Copper (II) complexes of binucleating ligands with two bidentate sites separated by aromatic rings have been reported [17]. In such complexes, spin exchange between two metal centers propagated through π delocalized bridge. However, no work has been carried out on binuclear complexes with binucleating Schiff base ligand forming a bridge with metal ions (coordinated by π acidic ligand). In the present study an attempt has been made to synthesize binuclear complexes of copper (II) and further explore magnetic exchange at variable temperature through long aromatic bridging groups. Simultaneously studies are also performed on the change of electronic environment around the metal centers by the change of electronic environment caused by changing the non-coordinating

part of the ligand. Molecular modeling, by force field calculation has been used to work out the geometrical parameters/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 bases (conjugated π- system) have been performed. The Schiff bases are the condensation products of different combinations of 2-hydroxybenzaldehyde or 2-hydroxyna-phathaldeyde or 2-hydroxyl-3-methoxy-benzaldehyde and aromatic diamine, 4,4'-diamino-diphenylether.

## 2. MATERIAL AND METHODS

### 2.1. Chemicals

2-Hydroxynaphthaldehyde (Fluka), 2-Hydroxybenzal-dehyde, 4, 4'-diaminodiphenylether, 2,2'-bipyridine, 1, 10-phenanthroline, cupric acetate monohydrate and sodium perchlorate were used from Merck. 2-hydroxy-3-methoxybaenzaldehyde (o-vanillin) was procured from local manufacturers. All of these were of A. R. grade and were used as received. All solvents were distilled twice before use. All ternary complexes were prepared by the reported method [18].

### 2.2. Synthesis of binuclear complex, [Cu₂ (phen)₂,salEthSB](ClO4)₂

0.4218 gms (0.09 mmol) of ternary complex of [Cu(phen),sal](ClO₄) was dissolved in 20 ml of methanol and to this 0.0910 gms (0.45 mmol) of 4,4'-diaminodiphenyl ether solution in 20 ml of methanol

was added drop wise in 30 minutes . The flask was equipped with a water condenser and a magnetic stirrer. The reaction mixture was refluxed for 11 hours. Consumption of 4,4'-diaminodiphenyl ether was monitored by TLC. After reflux, brown coloured compound was separated, cooled and the solid obtained was washed thoroughly with 25 ml methanol in 5-6 portions and dried in bulb oven (Fig. 1).
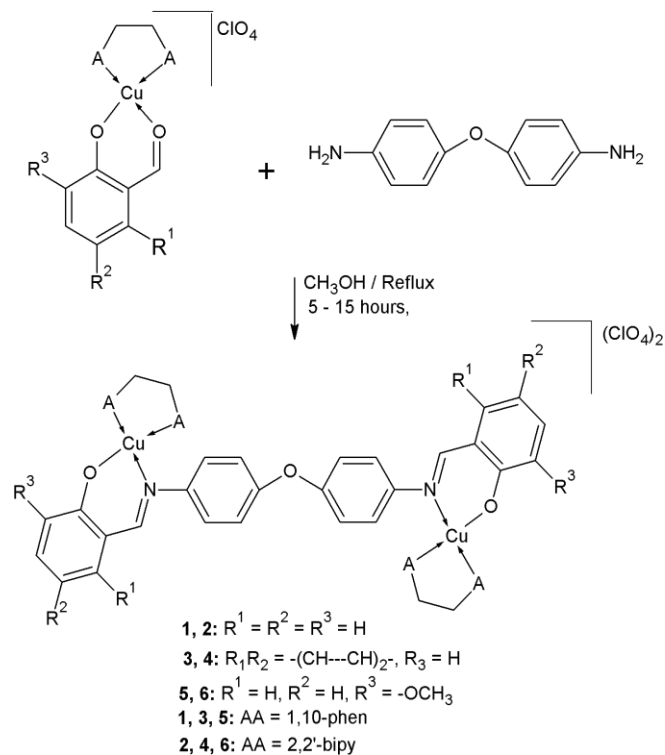


**Fig. 1: Synthesis of Binuclear complexes**

**Table 1: Elemental analysis, refluxtion time and yields and of the ternary binuclear complexes.**

| Comp. No. | Complexes | Found (Calcd[a]) (%) | | | Reflux Time (hours) | Yields (%) | Molar conductivity[b] ($\Omega^{-1}M^{-1}cm^2$) |
|---|---|---|---|---|---|---|---|
| | | C | H | N | | | |
| 1 | [Cu₂(phen)₂,salEthSB](ClO4)₂ C₅₀H₃₄O₁₁N₆Cl₂Cu₂ | 54.76 (54.94) | 3.09 (3.11) | 7.64 (7.69) | 11 | 83 | 140.14 |
| 2 | [Cu₂(bipy)₂,salEthSB](ClO4)₂ C₄₆H₃₄O₁₁N₆Cl₂Cu₂ | 52.78 (52.87) | 3.13 (3.25) | 7.87 (8.04) | 15 | 64 | 140.14 |
| 3 | [Cu₂(phen)₂,naphEthSB](ClO4)₂.2H₂O C₅₈H₄₂O₁₃N₆Cl₂Cu₂ | 56.49 (56.67) | 3.03 (3.42) | 6.00 (6.83) | 15 | 65 | 160.0 |
| 4 | [Cu₂(bipy)₂,naphEthSB](ClO4)₂.2H₂O C₅₄H₄₂O₁₃N₆Cl₂Cu₂ | 55.54 (54.91) | 3.19 (3.55) | 6.63 (7.11) | 15 | 60 | 140.14 |
| 5 | [Cu₂(phen)2,vanEthSB](ClO4)₂.2H₂O C₅₂H₄₂O₁₅N₆Cl₂Cu₂ | 52.93 (52.52) | 3.11 (3.53) | 6.60 (7.07) | 6 | 79 | 135.01 |
| 6 | [Cu₂(bipy)2,vanEthSB](ClO4)₂ C₄₈H₃₈O₁₃N₆Cl₂Cu₂ | 52.29 (52.17) | 3.23 (3.44) | 7.23 (7.60) | 5 | 90 | 130.13 |

[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.*

Complexes (**2-6**) were synthesized by using the above procedure and appropriate quantity of ternary complexes and 4,4'-diaminodiphenyl ether. The results of the C, H and N analyses, refluxtion time, yield and conductivity measurements for each complex have been given in table -1.

## 2.3. Physical measurements

Carbon, Hydrogen and Nitrogen analysis were performed on Perkin Elamer Model-2400 CHN/S analyzer. Specific conductivity of all complexes in DMF solution having 1.0 mmolar concentration was measured using a Toshniwal conductivity bridge. IR spectra (as KBr pellets) were recorded on Perkin Elamer FT-IR, spectrum RXI. The ESR spectra of complexes, 1 and 2 were recorded at room temperature on a Brucker instrument. The ESI-MS spectrum of Complex, 2 was recorded on a THERMO Finnign LCQ Advantage max ion trap mass spectrometer in acetonitrile solution.

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

The setup 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 $\pm 0.1 \mu g$ accuracy and $0.1 \mu g$, readability. The temperature inside the sample enclosure was maintainned with the help of OMEGA CYC 3200, Auto-tunning

Temperature Controller has 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 [19, 20]

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

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 $N\alpha$ is temperature independent paramagnetism i.e. 60 emu/mole, per copper ion.

## 3. RESULTS AND DISCUSSION

The values of elemental analysis of binuclear complexes given in Table 1 were 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 $130-160 (\Omega^{-1} M^{-1} cm^2)$ corresponds to 1:2 electrolyte, indicating that two perchlorates are outside of coordination sphere. Complexes 3, 4 and 5 show presence of two water molecules in C, H and N analysis. But thermal analyses of complexes were not carried out for the confirmation of nature of water molecule because of presence of perchlorates ion. Water molecule is confirmed by IR spectra only.

## 3.1. Infra red Spectra

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 1608-1616 cm$^{-1}$. These are at lower energies compared to the free organic molecule, which is 1630-1690 cm$^{-1}$.

**Table 2: IR absorptions (cm⁻¹) of ternary binuclear complexes**

| Complexes No. | $\nu(ClO_4)$ (cm⁻¹) | $\nu(>C=N)$ (cm⁻¹) | Aromatic stretching $\nu(-C-H)$ (cm⁻¹) | Miscellaneous frequencies (cm⁻¹) |
|---|---|---|---|---|
| 1 | 1108 | 1610 | 3064 | $\nu_{as}(-O-)$ 1245 |
| 2 | 1090 | 1616 | 3080 | $\nu_{as}(-O-)$ 1250 |
| 3 | 1091 | 1601 | 3060 | $\nu_{as}(-O-)$ 1243, $\nu(H_2O)$ 3436 |
| 4 | 1108 | 1603 | 3060 | $\nu_{as}(-O-)$ 1243, $\nu(H_2O)$ 3438 |
| 5 | 1108 | 1608 | 3060 | $\nu_{as}(-O-)$ 1240, $\nu(H_2O)$ 3438, $\nu_s(C-O-CH_3)$ 1032 |
| 6 | 1091 | 1608 | 3067 | $\nu_{as}(-O-)$ 1240, $\nu_s(C-O-CH_3)$ 1032 |

The shift in the $\upsilon_{>C=N}$ (imine) towards lower energy in the complexes indicate that the imine nitrogen is involved in coordination with the Cu (II) ion. Complexes 3, 4 and 5 show a broad band at 3436, 3438 and 3438 cm$^{-1}$ respectively, which can be assigned for the presence of water molecules. The IR spectra of the complexes exhibit the broad and strong band about 1086-1108 cm$^{-1}$ without any splitting corresponds to the characteristics vibration of non-coordinated $ClO_4^-$ group [21].

Moreover all complexes exhibiting asymmetric stretching frequency around 1250 cm$^{-1}$ indicating the presence of-O- group. Absorption frequencies about 1250 cm$^{-1}$ for -O-groups supported about bridging group. All the complexes exhibit absorption frequency 3064-3084 cm$^{-1}$ for aromatic stretching. Important bands in the complexes are given in Table 2.

### 3.2. Mass spectra

ESI mass spectra of the complex, [Cu$_2$(bipy)$_2$salEthSB] (ClO4)$_2$ was recorded in acetonitrile. The complex, [Cu$_2$(bipy)$_2$salEthSB](ClO4)$_2$ lost an anion and exhibit parent binuclear monocation peak at m/z 944 with relative abundance values of 88%. Parent ion peak loses the fragments another anion, a copper ion and two bipyridyl and giving the paek at m/z 470 (7%). Peak at m/z 470 loses the fragment [Cu]$^+$ showing the peak at m/z 409 (100%) which is correspond to [SB-H]$^+$. Moreover Cu(II) ion associated with one and two bipyridyl exhibiting the peaks at m/z 375 and 219 with relative abundance 7% and 17%. Bipyridyl get associated with a hydrogen ion and showing peak at m/z 157 with relative abundance values of 54%. (Fig. 2 and 3, Table 3).

**Table 3: Fragmentation pattern in the positive ion in ESI–MS of binuclear complex, [Cu$_2$ (bipy)$_2$,salEthSB](ClO$_4$)$_2$ in acetonitrile**

| m/z (% relative abundance) | Molecular formula of the fragment |
|---|---|
| 944 (8%) | [C$_{46}$H$_{34}$O$_7$N$_6$ClCu]$^+$ |
| 470 (7%) | [C$_{26}$H$_{19}$O$_3$N$_2$Cu]$^+$ |
| 409 (100%) | [C$_{26}$H$_{21}$O$_3$N$_2$]$^+$ (SB-H) |
| 375 (7%) | [C$_{20}$H$_{16}$N$_4$OCu]$^+$ |
| 219 (17%) | [C$_{10}$H$_8$N$_2$Cu]$^+$ |
| 157 (54%) | [C$_7$H$_6$NO]$^+$ |

Al these peaks assigned in the above complex strongly supported the formation of binuclear complexes with suggested molecular formulae.
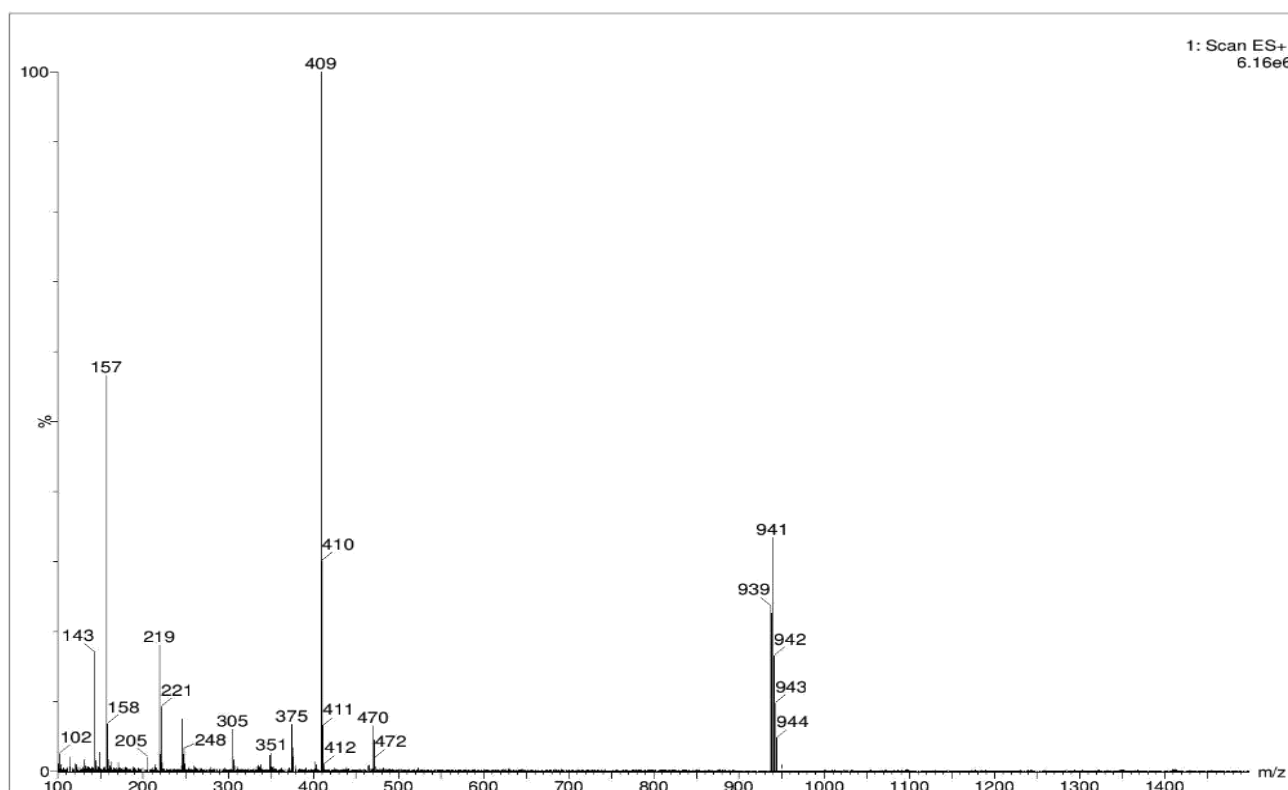


**Fig. 2: ESI–Mass spectra of binuclear complex,[Cu$_2$(bipy)$_2$salEthSB](ClO4)$_2$].**
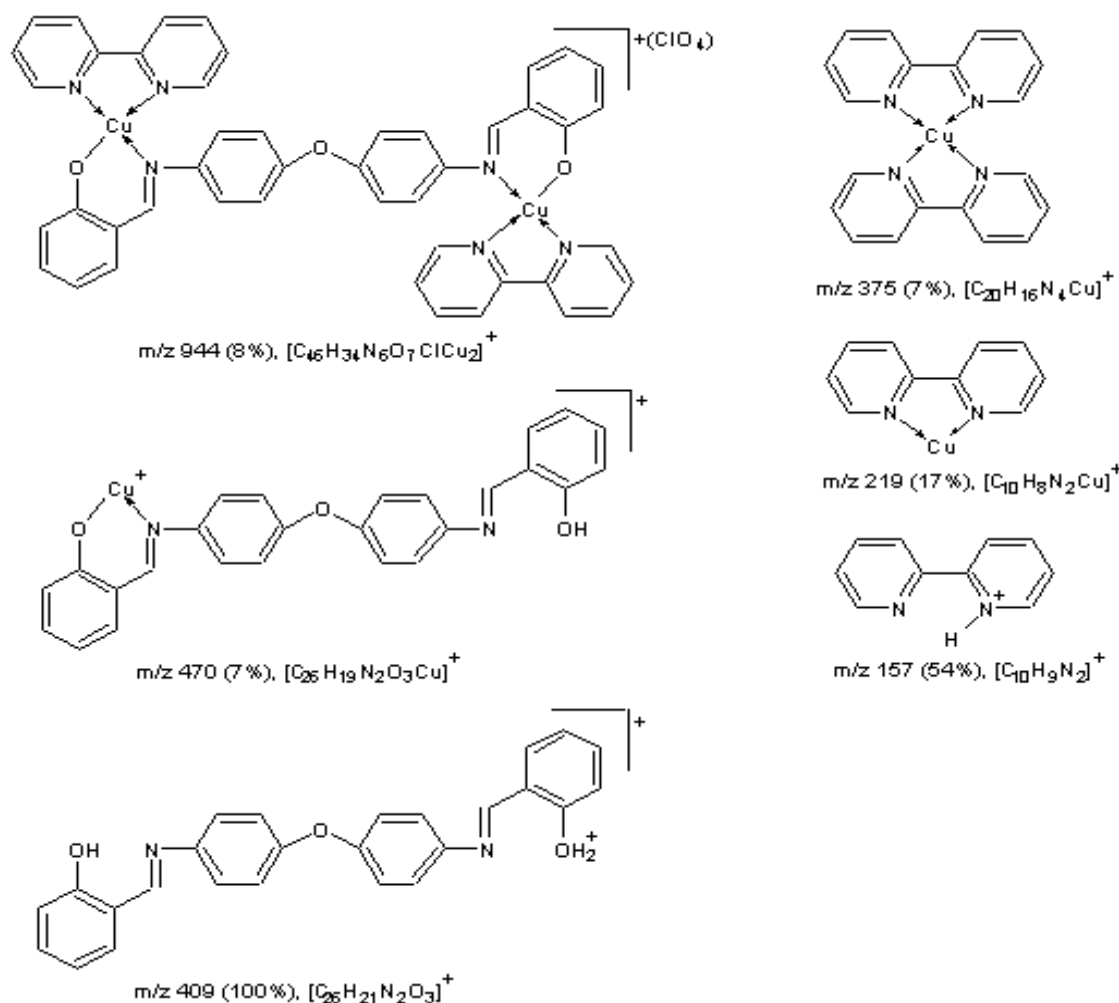
**Fig. 3: Possible structure of the complex, [Cu₂(bipy)₂salEthSB](ClO₄)₂] and corresponding fragments in ESI-Mass spectrum**

### 3.3. ESR spectral studies

The ESR spectra of polycrystalline complexes, 1 and 2 were recorded at room temperature (Table 4). Complexes have typical axial ESR with well separated g∥ and g⊥components. The observed g∥ and g⊥values are nearly matched with reported for Cu$^{2+}$ in near square planar or compressed tetrahedral geometry [22, 23].

**Table 4: ESR parameters of some complexes**

| Complexes | Room temperature | |
|---|---|---|
| | g∥ | g⊥ |
| [Cu₂(phen)₂salEthSB](ClO4)₂ | 2.2067 | 2.0677 |
| [Cu₂(bipy)₂salEthSB](ClO4)₂ | 2.2148 | 2.0694 |

### 3.4. Magnetic properties

Complexes studied here have a single bridging group and the other non-bridging sites around the metal ion occupied by π-bonding ligands. The single bridging group can allow a lot of flexibility in the structure while the π-bonding ligands and the functional groups, over the bridging ligand, can modulate the strength of M-L binding and the resultant coordination geometry. Thus a lot of variation is expected in the geometrical parameters which can affect the spin exchange interaction. The least square fitting of the magnetic susceptibility data in Bleaney – Bower's equation for complexes, 2, 3, 4, and 6, yields J values ranging between -3.39 to 68.03 cm$^{-1}$ (Fig. 4-7).

In order to evaluate the geometrical parameters, the geometries of the complexes were optimized using universal force field [24-31]. Optimized geometry of complexes are shown in fig. 9-12. The torsional angles Γ (between the metal coordination planes) have been determined. These Γvalues are correlated with the experimentally determined J values (table 5). Plots of J vs torsional angle Γ are shown in fig. 8. Fig. 8 shows

maxima for complexes with the bridging moiety but different substitutions on non bridging π-bonding ligands. As the torsional angle deviates, the metal coordination is no longer remains coplanar. This results in the mismatch of orbitals with molecular orbitals of the bridging ligand and leads to ferromagnetic interaction. The variation in geometry and in the J values is a result of change in the nature of non-bridging ligand. D. Zhang *et al.* and A Ghosh *et al.* have observed similar dependence of the extent of magnetic exchange on the non bridging ligands in the complexes [8, 32].

Thus, it can be concluded 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 tune the torsional angle and thereby control on magnetic property (from ferromagnetism to antiferromagnetism).

**Table 5: J and torsional angle of ternary binuclear complexes**

| Complexes | $J$ (cm$^{-1}$) | Torsional angle |
|---|---|---|
| [Cu$_2$(phen)$_2$,naphEthSB](ClO$_4$)$_2$.2H$_2$O | -3.39 | 91.16 |
| [Cu$_2$(bipy)$_2$,salEthSB](ClO$_4$)$_2$ | 27.13 | 111.07 |
| [Cu$_2$(bipy)$_2$,naphEthSB](ClO$_4$)$_2$.2H$_2$O | 68.03 | 116.62 |
| [Cu$_2$(bipy)$_2$,vanEthSB](ClO$_4$)$_2$ | 59.21 | 101.7 |



Fig. 5: Dependence of magnetic susceptibility on temperature in complex, 3.



Fig. 6: Dependence of magnetic susceptibility on temperature in complex, 4.
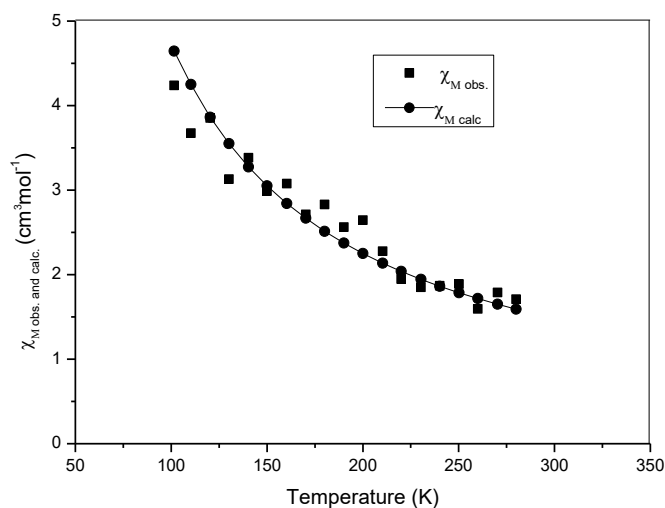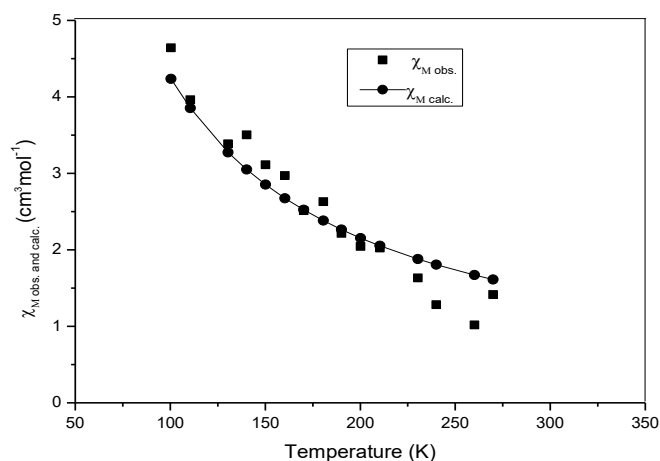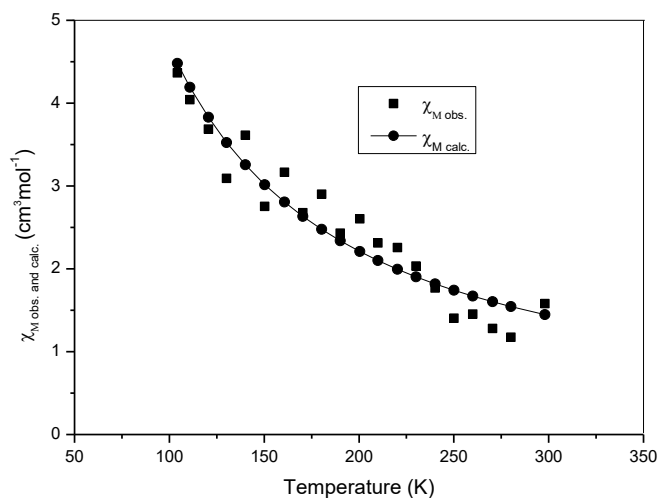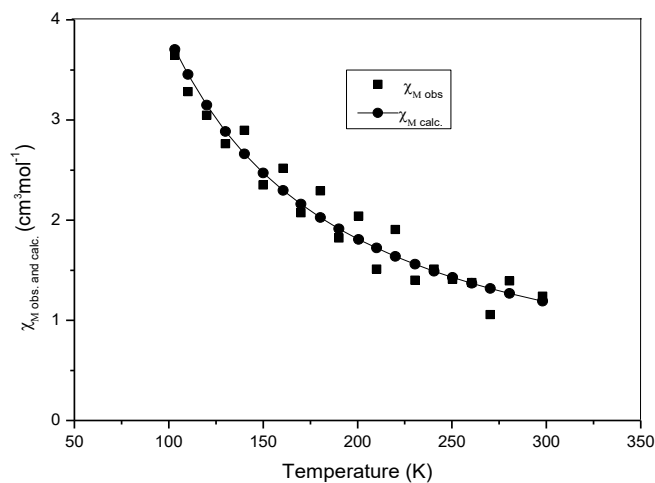


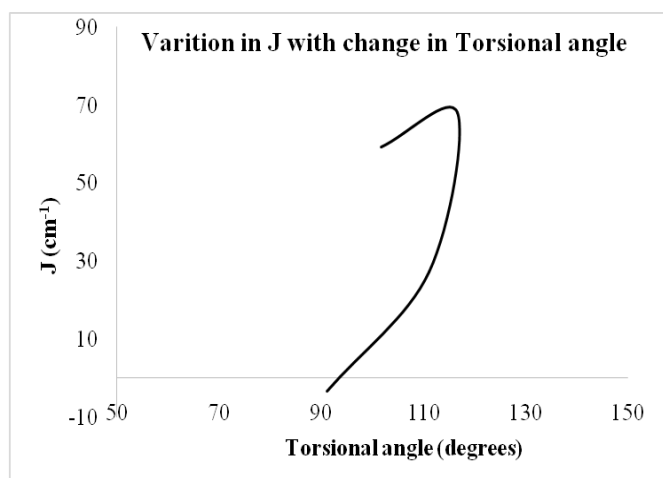Fig. 4: Dependence of magnetic susceptibility on temperature in complex, 2.



Fig. 7: Dependence of magnetic susceptibility on temperature in complex, 6.

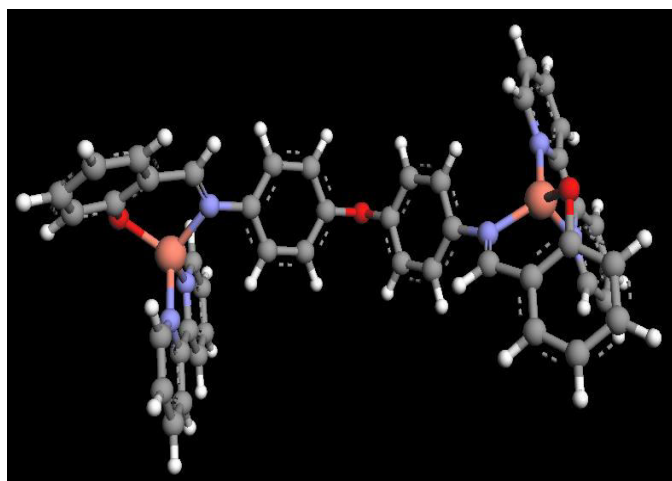**Fig. 8: Plot of J vsTortional angle in binuclear complexes.**



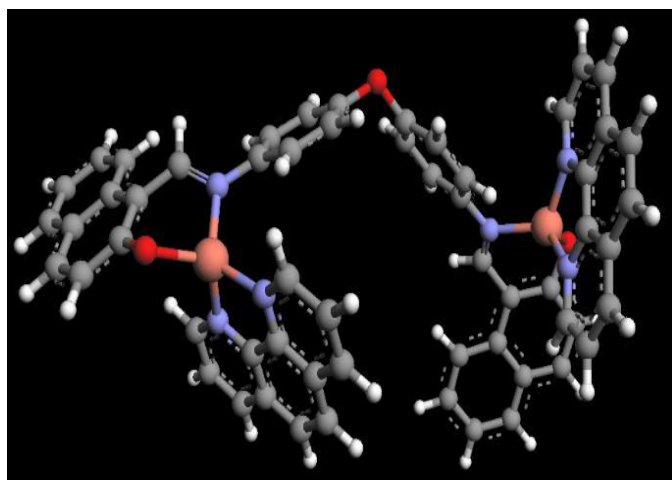**Fig. 11: Optimized geometry of the binuclear complex, 4.**



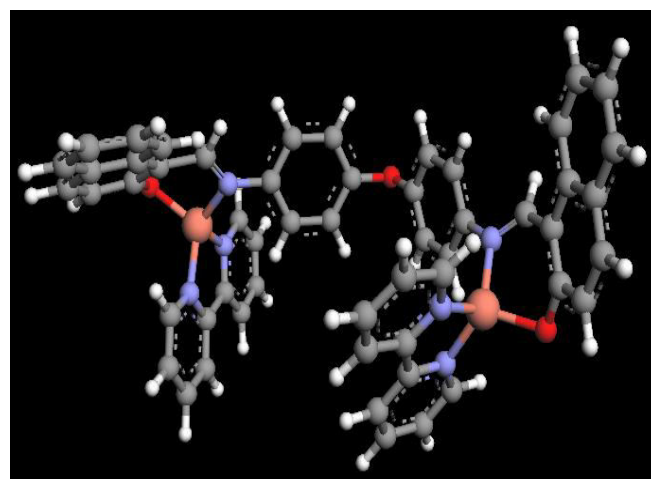**Fig. 9: Optimized geometry of the binuclear complex, 2**.



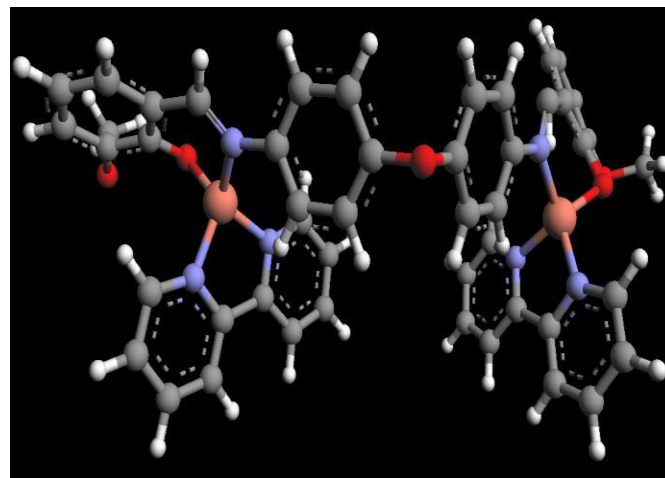**Fig. 12: Optimized geometry of the binuclear complex, 6.**

## 5.  REFERENCES

1. Linder MC, Goode CA. Biochemistry of Copper. Plenum: New York; 1991.
2. Tremolieres M, Bieth JB. *Phytochemistry,* 1984; **23 Suppl 3:**501-505.
3. Solomon EI, Penfield KW, Wilcox DE. Structure Bonding.  Berlin: 1983.
4. Osorio REHMB,  Peralta RA, Bortoluzzi AJ, deal meida VR et al. *Inorg Chem.* 2012; **51 Suppl 3:**1569-1589.



**Fig. 10: Optimized geometry of the binuclear complex, 3.**

5. Sorai M, Nakazawa Y, Nakano M, Miyazaki Y. *Chem. Rev.* 2013; **113 Suppl 1:**41-122.

6. Banerjee A, Sarkar S, Chopra D, Colacio E, Rajak KK. *InorgChem,* 2008; **47 Supl 10:**4023-4031.

7. Agnes E, Thorarinsdottir, Harris TD. *Chem. Rev.* https://dx.doi.org/10.1021/acs.chemrev.9b 00666

8. Biswas A, Das LK, Drew MGB, Diaz C, Ghosh A. *Inorg Chem,* 2012; **51 Supl 19:**10111-10121.

9. Diego V, Daniel A, Evgenia S, Eliseo R, Santiago A. *Coord Chem Rev,* 2010; **254 Supl 17–18:**2086-2095.

10. Stylianou M, Drouza C, Viskadourakis Z, Giapintzakis J, Keramidas AD. *Dalton Trans,* 2008; **44:**6188-6204.

11. Ruiz E, Alemany P, Alvarez S, Cano J. *InorgChem,* 1997; **36 Supl 17**:3683-3688.

12. Fink K, Wang C, Staemmler V. *InorgChem,* 1999; **38 Supl 17:**3847-3856

13. Felthouse TR, Laskowski EJ, Hendrickson DN. *Inorg Chem,* 1977; **16 Supl 5:**1077-1089.

14. Pierpont CG, Francesconi LC, Hendrickson DN. *InorgChem,* 1977; **16 Supl 9:**2367-2376.

15. Pierpont CG, Francesconi LC, Hendrickson DN. *InorgChem,* 1978; **17 Supl 12:**3470-3476.

16. Tsipis CA, Sigalas MP, Parageorgiou VP, Bakola-Cristianopoulou MN. *Can J Chem,* 1983; **61 Supl 7:**1500-1504.

17. Zeyrek CT, Elmali A, Elerman Y, Svoboda I. *Z Naturforsch,* 2005; **60b:**143-148.

18. Kulkarni ND, Bhattcharya PK, *Can J Chem*, 1987; **65 Supl 2:**348-352.

19. Bleany B, Bowers KD. *Proc Roy Soc (London)*, 1952; **A214:**451-465.

20. Bleany B, Bowers KD, *Phil Mag,* 1952; **43:**372-374.

21. Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B, 5th Eds, Wiley – Interscience New York; 1997.

22. Hathaway BJ. Comprehensive Coord. Chem. Vol. 5, Eds., Wilkinson G, Gillard RD, McCleverty JA. Pergamon press: Oxford; 1987.

23. Bencini A, Gatteschi D. Inorganic Electronic Structural and Spectroscopy. Vol. 1. *Eds.,* Solomon EI, Lever ABP. Wiley-Interscience: New York; 1999.

24. Thompson MA, Zerner MC. *J Am ChemSoc,* 1991; **113:**8210-8215.

25. Thompson MA, Glendening ED, Feller D. *J Phys Chem,* 1994; **98:**10465-10476.

26. Thompson MA, Schenter GK. *J PhysChem,* 1995; **99:**6374-6386.

27. Thompson MA. *J PhysChem,* 1996; **100:**14492-14507.

28. Rappe AK, Casewit CJ, Colwell KS, Goddard III WA, Skiff WM. *J Am ChemSoc,*1992; **114:**10024-10035.

29. Casewit CJ, Colwell KS, Rappe AK. *J Am ChemSoc,* 1992; **114:**10035-10046.

30. Casewit CJ, Colwell KS, Rappe AK. *J Am ChemSoc,* 1992; **114:**10046-10053.

31. Rappe AK, Colwell KS, Casewit CJ. *Inorg Chem,* 1993; **32:**3438-3450.

32. Liu X, Lu Z, Zhang D, Jiang Z, et al. *InorgChem,* 2004; **43:** 6620-6627