

Synthesis, Spectroscopic and Magnetic Properties of New Binuclear Copper (II) Complexes Containing Isomeric Long Multiatomic Bridging Groups.

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Abstract

Seven new ternary binuclear Copper(II) complexes with a general formula, $[ACu(\mu-B)CuA](ClO_4)_2$, where $A = 2,2'$ -bipyridine or 1,10-phenanthroline and B are four binucleating Schiff base ligands derived by condensation of the 4,4'-diaminodiphenylsulphone and its isomer 3,3'-diaminodiphenylsulphone with 2-hydroxynaphthaldehyde or 2-hydroxy-3-methoxybenzaldehyde. The complexes have been synthesized and characterized using elemental analysis, conductivity and various spectroscopic techniques such as IR, electronic spectra, ESR and mass spectrometry. The variable temperature magnetic susceptibility (90K to 300K) measurements indicate the presence of weak antiferromagnetic to ferromagnetic exchange interaction between the proximate metal ions in the complexes. Molecular modeling has been used as a tool to calculate various geometrical parameters in the complexes which have been correlated with the observed magnetic property.

Key words: Copper (II) binuclear complexes, binucleating ligands, magnetic interactions.

Introduction

The synthesis, characterization and magnetic investigations of exchange – coupled transition metal complexes in which the spin coupling between the paramagnetic metals is propagated by multi-atom bridges, have been an active field of research with the aim of understanding fundamental factors, governing the magnetic properties of transition metal complexes and to obtain some useful information about designing molecular – based magnets and to mimic the active sites and function of biological substance.¹⁻⁵

Studies of complexes with different geometries around the metal ion and with binucleating ligands possessing σ – and π – orbitals have clearly indicated that the spin – spin interaction is dependent on the availability of bridge molecular orbitals with the appropriate symmetry and energy to propagate interaction between the metal orbitals in which unpaired electron present.⁶⁻⁹ Further variation in the nucleophilicity of the coordinating atom or π bonding ability can be brought by changing the substituent over the non coordinating part of the ligand. Thus the ligands are expected to provide geometrically similar but electronically different coordination environment on the two metals ions.

Binuclear complexes with oxalate¹⁰, squarate¹¹, hydroxy¹², azido¹³, phenolato¹⁴, and m-phenylenediamine¹⁵ and types of bridging ligands studied extensively. In order to understand further the magnetic behavior of this kind of complexes, binuclear complexes possessing isomeric substituted bridging ligands have been synthesized and characterized by elemental analysis, conductance, spectral and magnetic studied.

Experimental

Materials and methods

2-Hydroxynaphthaldehyde (Fluka) was used as received. 2-Hydroxy-3-methoxybenzaldehyde, 4,4'-diaminodiphenylsulphone, 3,3'-diaminodiphenylsulphone, 2,2'-bipyridine, 1,10-phenanthroline, cupric acetate monohydrate and sodium perchlorate were used from Merck. o-Vanillin was obtained procured from Aldrich. All chemicals were AR grade, used as a received. All the ternary complexes were prepared by the reported method.¹⁶

Synthesis of binuclear complexes, [Cu₂(phen)₂naph4-sulSB](ClO₄)₂:

The ternary complex [Cu(phen)₂(naph)](ClO₄) (0.5140 g, 1.0 mmol) was dissolved in methanol (25 ml) and to this 4,4'-diaminodiphenylsulphone solution (0.0991 g, 0.5 mmol) in 25 ml of methanol was added dropwise in 1 hour. The flask equipped with a water condenser and a magnetic stirrer. The reaction mixture was refluxed for 35 hours. Consumption of 4,4'-diaminodiphenylsulphone was monitored by TLC. After refluxion brown coloured compound was separated, cooled and the solid obtained was washed thoroughly with 25 ml in 5-6 portion and dried in bulb oven.

Table 1. Elemental analysis, refluxion time and yields and of the binuclear complexes.

Comp. No.	Complexes	Found ^a (Calcd.)(%)			Refluxion time (hours)	Yield (%)	Molar Conductivity ^b (Ω ⁻¹ cm ² mol ⁻¹)
		C	H	N			
1	[Cu ₂ (phen) ₂ naph4-sulSB](ClO ₄) ₂ .2H ₂ O C ₅₈ H ₄₂ O ₁₄ N ₆ Cl ₂ SCu ₂	54.65 (54.54)	2.96 (3.28)	5.61 (6.58)	35	66	160.16
2	[Cu ₂ (phen) ₂ naph3-sulSB](ClO ₄) ₂ .2H ₂ O C ₅₈ H ₄₂ O ₁₄ N ₆ Cl ₂ SCu ₂	54.18 (54.54)	3.18 (3.28)	5.39 (6.58)	50	57	160.16
3	[Cu ₂ (bipy) ₂ naph3-sulSB](ClO ₄) ₂ .2H ₂ O C ₅₄ H ₄₂ O ₁₄ N ₆ Cl ₂ SCu ₂	52.38 (52.76)	3.25 (3.47)	6.03 (6.83)	50	60	165.16
4	[Cu ₂ (phen) ₂ o-van4-sulSB](ClO ₄) ₂ .2H ₂ O C ₅₂ H ₄₂ O ₁₆ N ₆ Cl ₂ SCu ₂	49.21 (50.48)	3.24 (3.39)	5.68 (6.79)	26	60	160.01
5	[Cu ₂ (phen) ₂ o-van3-sulSB](ClO ₄) ₂ .2H ₂ O C ₅₂ H ₄₂ O ₁₆ N ₆ Cl ₂ SCu ₂	49.28 (50.48)	3.12 (3.39)	5.39 (6.79)	31	67	165.16
6	[Cu ₂ (bipy) ₂ o-van4-sulSB](ClO ₄) ₂ C ₄₈ H ₃₈ O ₁₄ N ₆ Cl ₂ SCu ₂	49.98 (49.99)	3.60 (3.29)	7.32 (7.29)	50	29	130.13
7	[Cu ₂ (bipy) ₂ o-van3-sulSB](ClO ₄) ₂ C ₄₈ H ₃₈ O ₁₄ N ₆ Cl ₂ SCu ₂	49.77 (49.99)	3.15 (3.29)	7.43 (7.29)	20	59	140.14

^aThe values in parenthesis are theoretical values calculated from the molecular formulae.

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

Complexes (**2-7**) were synthesized by using the above procedure and appropriate quantity of ternary complexes and respective diamines. The results of the C, H and N analyses, reflux time for each complexes and conductivity measurements have been given in table 1 and 2 respectively (Figure. 1).

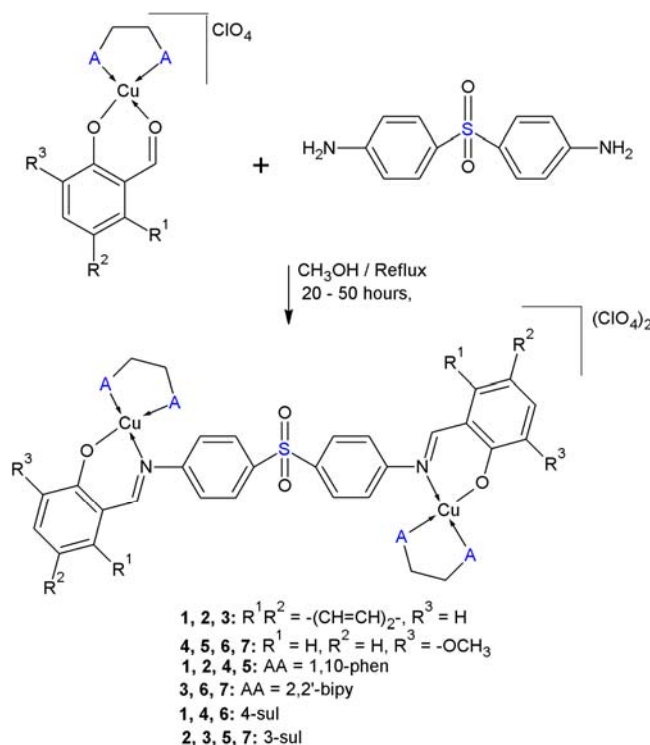


Figure1. Synthesis of ternary binuclear complexes (**1-7**)

Physical Measurements

Elemental analysis of the complexes were determined on Perkin Elmer Model-2400 CHN/S analyzer. The electronic spectra in UV-Vis region were recorded in methanolic solutions using Shimadzu UV-240 recording spectrophotometer. IR spectra (as KBr pellets) were recorded in the $4000-400\text{ cm}^{-1}$ on Perkin Elmer FT-IR, spectrum RXI. The ESR spectra of the complex $[Cu_2(bipy)_2, o\text{-van}4\text{-sulSB}](ClO_4)_2$ and $[Cu_2(bipy)_2, o\text{-van}3\text{-sulSB}](ClO_4)_2$ were recorded at RT and liquid nitrogen temperature on a Varian E-15 spectrometer. The FAB mass spectrum of the complex $[Cu_2(bipy)_2, o\text{-van}3\text{-sulSB}](ClO_4)_2$ 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 was recorded at room temperature with an accelerating voltage of 10 KV. Specific conductivity of all the complexes in DMF solution having 1.0 mmolar concentration was measured using a Toshniwal conductivity bridge. 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. Diamagnetic corrections were incorporated using Pascal's constants.

The effective magnetic moments were calculated by the formula-

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

A least-squares calculations were performed by fitting the experimentally observed values of magnetic susceptibility at various temperature to Bleaney-Bower's equation^{17,18}

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

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

Table2. IR absorptions (cm⁻¹) and energies of the charge transfer λ_{max} (nm) of the ternary binuclear complexes

Comp No.	v(ClO ₄)	v(>C=N)	aromatic stretching v(-C-H)	v _{as} (-SO ₂ -) and v _s (-SO ₂ -)	miscellaneous frequencies	Uv-Visible
1	1098	1600	3059	1338, 1144	v(H ₂ O) 3438	294, 406, 618
2	1103	1600	3058	1336, 1140	v(H ₂ O) 3436	288, 380, 617
3	1101	1602	3061	1315, 1145	v(H ₂ O) 3470	292, 388, 606
4	1098	1603	3056	1327, 1149	v(H ₂ O) 3471, v _{as} (C-O-CH ₃)1249, v _s (C-O-CH ₃) 1062	284, 400, 635
5	1112	1604	3056	1327, 1149	v(H ₂ O) 3538, v _{as} (C-O-CH ₃) 1249, v _s (C-O-CH ₃) 1062	284, 400 634,
6	1107	1604	3070	1301, 1149	v _{as} (C-O-CH ₃) 1249, v _s (C-O-CH ₃)1033	288, 400, 620
7	1095	1609	3081	1317, 1149	v _{as} (C-O-CH ₃) 1250, v _s (C-O-CH ₃) 1034	286, 396, 624

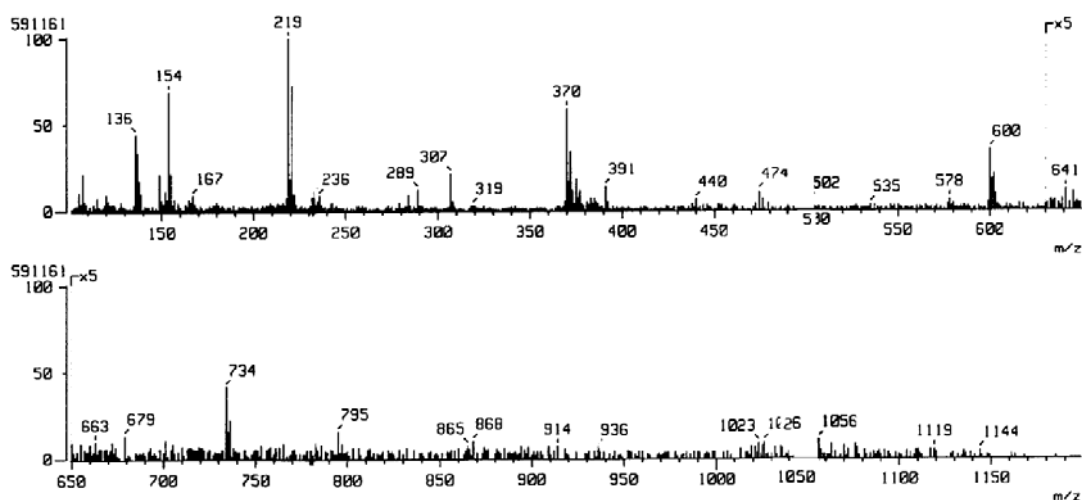


Figure2. FAB-mass spectra of binuclear complex, [Cu₂(bipy)₂O-van3-sulSB](ClO₄)₂.

Table 3. Fragmentation pattern in the positive ion in FAB – MS of $[\text{Cu}_2(\text{bipy})_2\text{o-van3-sulSB}](\text{ClO}_4)_2$ in m-nitrobenzyl alcohol.

m/z (% relative abundance)	Molecular formula of the fragment
476(8%)	$[\text{C}_{48}\text{H}_{38}\text{N}_6\text{O}_6\text{SCu}_2]^{2+}$
474 (17%)	$[\text{C}_{48}\text{H}_{34}\text{N}_6\text{O}_6\text{SCu}_2]^{2+}$ (binuclear dication)
953 (6%)	$[\text{C}_{48}\text{H}_{39}\text{N}_6\text{O}_6\text{SCu}_2]^+$ (parent ion peak)
795 (17%)	$[\text{C}_{38}\text{H}_{30}\text{N}_4\text{O}_6\text{SCu}_2]^- \text{H}]^+$
736 (24%)	$[\text{C}_{38}\text{H}_{33}\text{N}_4\text{O}_6\text{SCu}]^+$
734 (43%)	$[\text{C}_{38}\text{H}_{31}\text{N}_4\text{O}_6\text{SCu}]^+$
578 (7%)	$[\text{C}_{48}\text{H}_{44}\text{N}_6\text{O}_{14}\text{Cl}_2\text{SCu}_2]^{2+}$
578 (7%)	$[\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_6\text{SCu}]^+$, (Cu-SB)
375 (19%)	$[\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cu}]^+$
370 (61%)	$[\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_2\text{Cu}]^+$ (mononuclear complex)
219 (100%)	$[\text{C}_{10}\text{H}_8\text{N}_2\text{Cu}]^+$
167 (10%)	$[\text{C}_7\text{H}_5\text{O}_2\text{S N}]^+$
149 (22%)	$[\text{C}_8\text{H}_7\text{NO}_2]^+$

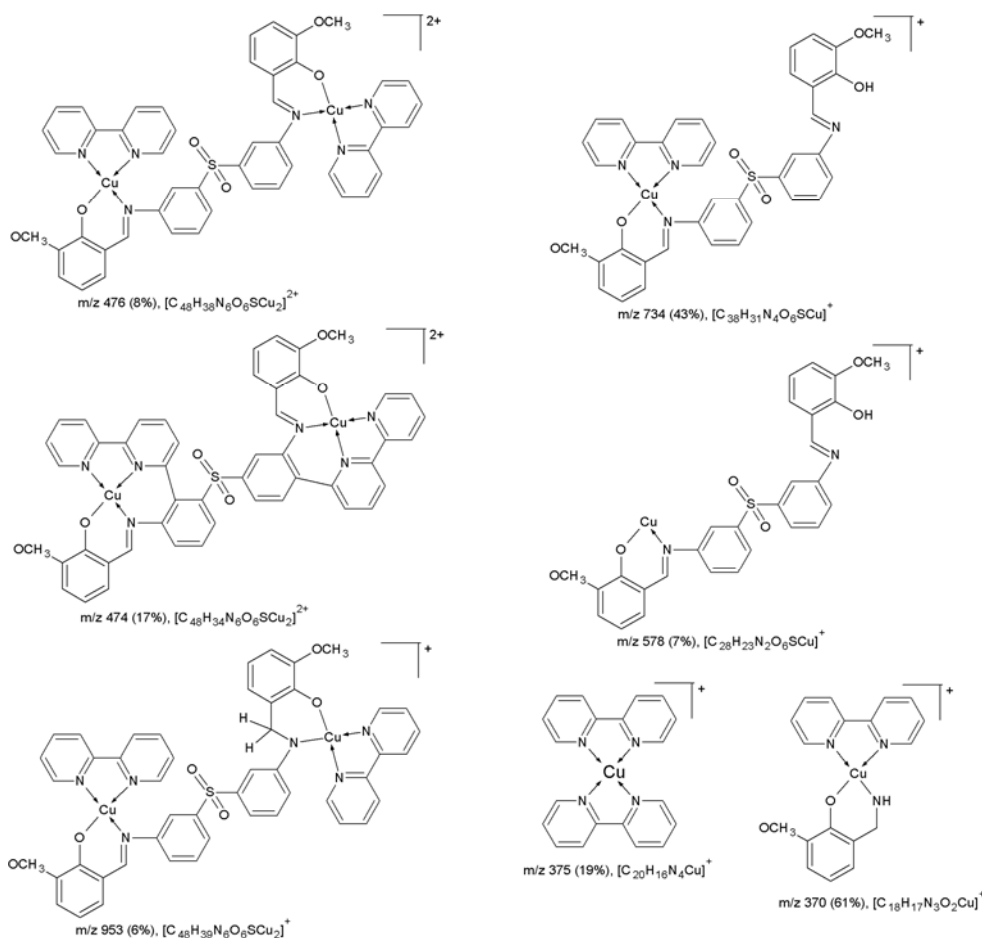


Figure 3. Possible fragmentation in the binuclear complex, $[\text{Cu}_2(\text{bipy})_2\text{o-van3-sulSB}](\text{ClO}_4)_2$.

Result and Discussion

The complexes are stable at room temperature, non hygroscopic, insoluble in CH_3OH , CHCl_3 , CH_2Cl_2 , and partly soluble in DMSO but soluble in DMF. As table 1 reveals the analytical data with suggested molecular structure in figure 1. The molar conductivity of the complexes studied in DMF solution, values falls in the range for 1:2 electrolyte.¹⁹

IR and electronic spectra

The IR spectra of the complexes in the $400 - 4000 \text{ cm}^{-1}$ region exhibit several bands corresponding to stretching and bending modes of C-C, C-H, C=N, $-\text{SO}_2-$ etc.

The $\nu(>\text{C}=\text{N})$ vibration as a strong band is observed in $1600 - 1609 \text{ cm}^{-1}$ region in all the complexes indicating the bathochromic shift relative to the free organic molecule i. e. $1650 - 1690 \text{ cm}^{-1}$. The lowering of $\nu(>\text{C}=\text{N})$ in all the complexes suggests the involvement of this group in coordination of metal ion via nitrogen atom. For the IR spectrum of the complexes $\nu(\text{ClO}_4^-)$ band is observed between $1095 - 1112 \text{ cm}^{-1}$ without any splitting indicating that perchlorate is outside of the coordination sphere²⁰. Moreover complexes exhibiting symmetric stretching $\nu(-\text{SO}_2-)$ between $1140 - 1149 \text{ cm}^{-1}$ and unsymmetrical stretching $\nu(-\text{SO}_2-)$ between $1301 - 1338 \text{ cm}^{-1}$, strongly supporting the presence of $-\text{SO}_2-$ group in the complexes. Complexes **1 - 5**, showing broad band in the $3436 - 3538 \text{ cm}^{-1}$ range due to lattice held water molecule. Aromatic stretching frequency $\nu(\text{C-H})$ occurred between $3056 - 3081 \text{ cm}^{-1}$.

Complexes **4 - 7** exhibiting symmetric frequency in $1033 - 1062 \text{ cm}^{-1}$ and asymmetric frequency at 1250 cm^{-1} for the presence of C-O- CH_3 group. The electronic spectra of the complexes (**1 - 7**) recorded in methanolic solution, exhibiting strong band between $284 - 294 \text{ nm}$ and $380 - 406 \text{ nm}$ which may be assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ interligand transition. The weak and broad band appeared between $617 - 635 \text{ nm}$ due to d - d transition, suggesting a square planar geometry, around metal center. (Table 2).

Mass spectra

In the FAB mass spectrum of the complex $[\text{Cu}_2(\text{bipy})_2\text{o-van3-sulSB}](\text{ClO}_4)_2$, the parent ion peak can be observed at $m/z = 1151$. This is formed by protonation of the complex molecule, $[\text{M}+\text{H}^+]$. The dication corresponding to $[\text{M}+2\text{H}^+]$ is observed at $m/z = 578$. The complex cation on association with one H forms the species with $m/z = 953$ (6%), (Fig. 2 and Fig. 3, Table 3). Peaks observed at m/z 953, 795, 578 and 219 strongly elucidating the formation of binuclear complex.

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 the metal complex and thus are responsible for occurrence of widely observed peak with low relative abundance.

ESR studies

The ESR spectra of complexes, **6** and **7** were recorded in the form of DMSO glass at liq. N_2 temperature. The spectra are given in figure 4 to figure 5 and results are summarized in Table 4. The ESR of **6** and **7** recorded at LNT shows clear hyperfine coupling with copper nuclear spin ($I = 3/2$) and have typical rhombic ESR with well resolved g_x , g_y and g_z components.

Table 4. ESR parameters of ternary binuclear complexes at RT and LNT.

Comp. No	Complexes	Room Temperature	LNT
6	$[\text{Cu}_2(\text{bipy})_2\text{o-van4-sulSB}](\text{ClO}_4)_2$	$g_x, 2.06336$ $g_y, 2.16299$ $g_z, 2.22606$	$g_x, 1.91981$ $g_y, 2.02464$ $A_y(\text{G}), 3.7809 \times 10^{-3} \text{ cm}^{-1}$ $g_z, 2.31336$ $A_z(\text{G}), 1.728 \times 10^{-2} \text{ cm}^{-1}$
7	$[\text{Cu}_2(\text{bipy})_2\text{o-van3-sulSB}](\text{ClO}_4)_2$	$g_x, 2.26096$ $g_y, 2.11367$ $g_z, 2.05023$	$g_x, 1.91981$ $g_y, 2.03097$ $A_y(\text{G}), 2.845 \times 10^{-3} \text{ cm}^{-1}$ $g_z, 2.24532$ $A_z(\text{G}), 1.834 \times 10^{-2} \text{ cm}^{-1}$

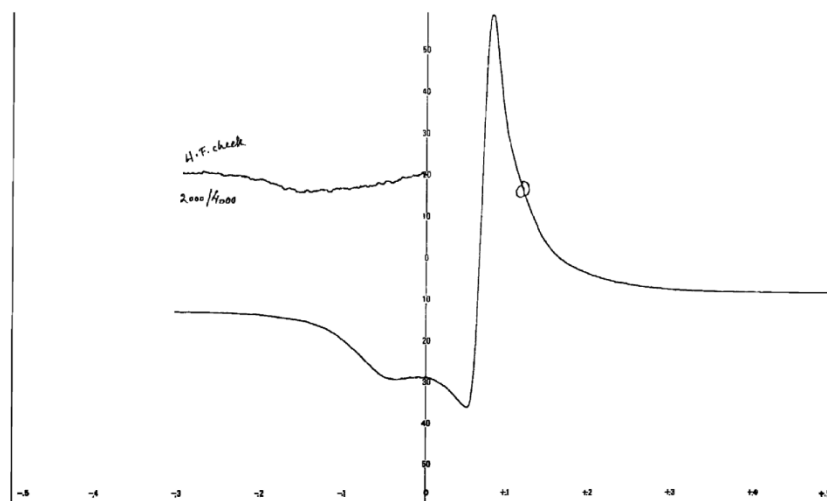


Figure 4. ESR spectra of complex $[\text{Cu}_2(\text{bipy})_2\text{o-van4-sulSB}](\text{ClO}_4)_2$ at RT.

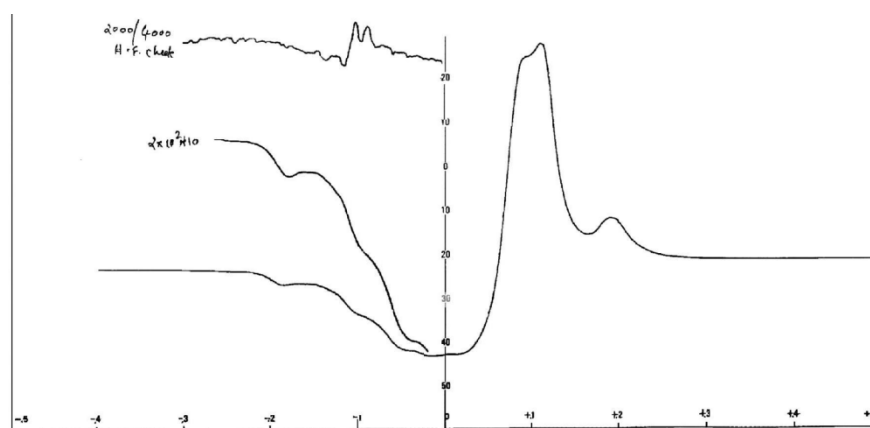


Figure 5. ESR spectra of complex, $[\text{Cu}_2(\text{bipy})_2\text{o-van4-sulSB}](\text{ClO}_4)_2$ at LNT.

The observed g_{\parallel} and g_{\perp} values are within the range of values expected and reported in the literature^{21, 22} for Cu^{2+} in near square planar or compressed tetrahedral geometry. The values of hyperfine coupling constant are, however, much lower indicating substantial delocalization of Cu^{2+} electron density over the ligand due to significant $\text{M} \rightarrow \text{C} \pi$ -interaction.

Magnetic properties

The 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 while the π -bonding ligands and the functional groups over the bridging ligand can modulate the strength of M-L binding and the coordination geometry. Thus a lot of variation is expected in the geometrical parameters which can affect the spin exchange interaction.

Table 5. J and torsional angle of the ternary binuclear complexes.

Complexes	J (cm^{-1})	Torsional angle
$[\text{Cu}_2(\text{bipy})_2\text{o-van4-sulSB}](\text{ClO}_4)_2$	55.24	92.46
$[\text{Cu}_2(\text{phen})_2\text{naph4-sulSB}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	-39.89	169.54
$[\text{Cu}_2(\text{bipy})_2\text{o-van3-sulSB}](\text{ClO}_4)_2$	-13.03	101.7
$[\text{Cu}_2(\text{phen})_2\text{naph3-sulSB}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	64.12	128.86
$[\text{Cu}_2(\text{bipy})_2\text{naph3-sulSB}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	57.35	159.43

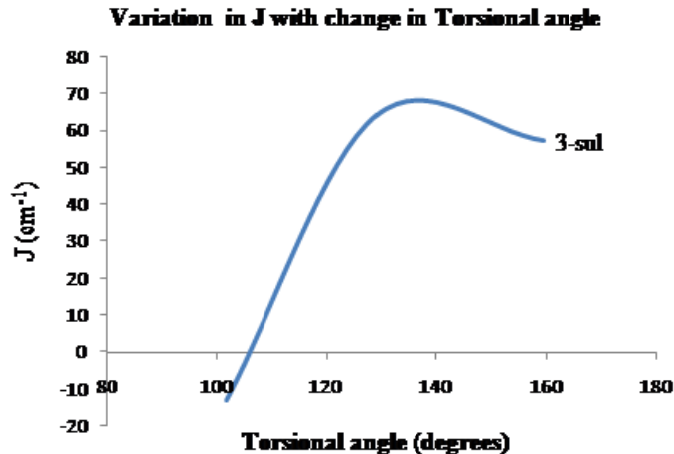


Figure 6. Plot of J vs torsional angle in binuclear complexes.

The least square fit of the magnetic susceptibility data to Bleaney – Bower's equation in complexes, 1, 2, 3, 6 and 7 yield J values ranging between -39.89 to 64.12 cm^{-1} i.e. the type of magnetic exchange varies from antiferromagnetic to ferromagnetic. Thus the magneto – structural correlations are expected to be interesting. In order to evaluate the geometrical parameters, the geometries of the complexes were optimized using universal force field²³⁻³⁰. The torsional angles Γ , between the metal coordination planes have been determined. These have been correlated with the experimentally determined J values (Table 5). Plots of J vs torsional angle Γ of 3,3'-diphenyl sulphone bridging group

have been represented in figure 6. Plots of J vs torsional angle Γ show a maximum in the series of complexes with the same bridging moiety but different substitutions on non bridging part or variation in the non bridging π -bonding ligands.

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 change the torsional angle and there by tune the magnetic property to any desired value from ferromagnetism to antiferromagnetism.

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