

# Synthesis, Characterisation and Magnetic Properties of Binuclear Copper (II) Complexes with Aliphatic Diamide Bridge

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## Abstract

New ternary binuclear complexes, with the formulae,  $[Cu_2A_2L](ClO_4)_4$  (1, 2) and  $[Cu_2A_2L]$  (3) have been synthesized. The ligand is  $L = N,N'$ -bis(2-pyridylcarbonyl)-1,4-diaminobutane and  $A = 2,2'$ -bipyridyl, 1,10-phenanthroline or 2-hydroxybenzoic acid. The ligand and complexes have been characterized by analytical and spectral methods including UV-Vis, FTIR, <sup>1</sup>H NMR and ESR. Mass spectrometric data has been used further to support the formation of binuclear complexes. Magnetic studies carried out between LNT and RT and structural parameters of the complexes have been calculated by using universal field method. The complexes are observed to undergo a weak to moderate ferromagnetic coupling between two copper (II) ions with positive  $J$  values up to  $73\text{ cm}^{-1}$ .

**Key words:** Binucleating ligand, binuclear Cu (II) complexes,  $\sigma$  – bonding bridge and magnetic properties.

## I. INTRODUCTION

Since last few decades the study of magnetic interactions in di- and polynuclear transition metal complexes is playing key role in the development of magneto-chemistry. Magnetism has been explored mainly in the field of solid-state physics for inorganic substances consisting of atoms or ions of transition elements, in which electron spins in atomic orbitals mainly contribute to the magnetism. In view of the above, traditional magnetism may be called “atom-based magnetism” [1]. However, the generalisation changed drastically with the report of bulk ferromagnetism in molecular complexes in the final two decades of last century. Because spins of unpaired electrons on delocalized molecular orbitals are responsible for the magnetism, this new magnetism has been called “molecule-based magnetism” [1-12].

The extent of spin exchange between two copper (II) centers depends on the energy of the interacting orbitals and on the variation in

geometrical parameters such as metal – ligand bond length, M-L-M bridging angle, dihedral angle between the metal coordination plane and the degree of planarity of the bridging unit [13-18]. In most of cases this type of exchange take place through multi atomic bridges possessing conjugated  $\pi$  - orbitals. However, it has been also suggested that the  $\sigma$  – orbitals [19, 20] can participate in the super exchange over a long distance in multiatomic bridges and lead to a spin exchange [21-23], yet such interactions are very weak. The present work was carried out with the intension of understanding the probable role of  $\sigma$  - bonded bridging ligand in propagating magnetic interaction in the bimetallic species.

## II. MATERIALS AND METHODS

Ethyl-2-pyridinecarboxylate, 1,4-diaminobutane, 2,2'-bipyridine, 1,10-phenanthroline, 2-hydroxybenzoic acid, cupric acetate monohydrate, and sodium perchlorate were obtained from Merck. All of these were of A. R. grade and were used as received. All solvents were distilled twice before use.

Carbon, Hydrogen and Nitrogen analysis was carried out on Perkin Elmer Model-2400 CHN/S analyzer. <sup>1</sup>H NMR of the ligand was recorded on Bruker 400 MHz. Specific conductivity of the complexes, 1 and 2 in DMF solution having 1.0 mmolar concentration was measured using a Toshniwal conductivity bridge. The electronic spectra of the complexes were recorded in methanolic solutions using Perkin Elmer Lambda 35, UV – Vis spectrometer. IR spectra (as KBr pellets) were recorded on Perkin Elmer FT-IR, spectrum RXI. The FAB mass spectrum of the complex, 3 was recorded in m-nitrobenzyl alcohol matrix 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. The ESR spectra of the complex, 3 was recorded at RT and liquid nitrogen temperature on a Varian E-15 spectrometer. 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 field strength of 0.8 Tesla. The sample cell was calibrated with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant. Diamagnetic corrections were incorporated using Pascal's constants. Least-squares calculations were performed by fitting the experimentally observed values of magnetic susceptibility at various temperature to Bleaney-Bower's equation [24, 25].

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

The difference  $|\chi_{\text{calc}}^2 - \chi_{\text{obsd}}^2|$  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.

#### A. Preparation of binucleating ligand (picbu)

A solution of ethyl-2-pyridinecarboxylate (3.779 g, 3.40 mL, 25 mmol) was placed in a flask equipped with water condenser and a magnetic stirrer. To this was added a solution of 1,4-diaminobutane (1.102 g, 1.25 mL, 12.5 mmol). The mixture was allowed to reflux for nine hours. A pale yellow solid compound separated out on cooling. The solid product obtained was crystallized from 50:50  $\text{CHCl}_3$  and petroleum ether. Finally, the compound was washed with 20 mL distilled water and 10 mL diethylether and was dried in air (Fig. 1). The yield was 2.5284 g, (40%) and mpt 107 -110 °C. It was characterized by IR (KBr,  $\text{cm}^{-1}$ ) 3358, 3066, 2945, 2856, 1657, 1593. Elemental analysis, calculated for formula  $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_2$ : Found (Calc.) C 64.66 (64.43), H 5.97 (6.04), N 18.76 (18.79) and  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ), ( $\delta$ ): 1.764 (2H ( $\text{CH}_2$ )); 3.531 (2H ( $\text{CH}_2$ )); 7.406 (t, H (PyH)); 7.825 (t, H (NH)); 7.864 (d, H (PyH)); 8.183 (H (PyH)).

#### B. Preparation of binuclear $[\text{Cu}_2\text{A}_2(\text{picbu})(\text{ClO}_4)_4]$ type complexes, (1 and 2)

Copper (II) acetate monohydrate (0.333 g, 1.66 mmol) in 20 mL  $\text{CH}_3\text{OH}$  was taken in three neck flat bottom flask. To this was added 2,2'-bipyridine (0.2605 g, 1.67 mmol) in 15 mL  $\text{CH}_3\text{OH}$  and picbu (0.248 g, 0.83 mmol) in 15 mL  $\text{CH}_3\text{OH}$  simultaneously dropwise over 1 hour. The reaction mixture was allowed to reflux for two hours. The excess of  $\text{CH}_3\text{OH}$  was distilled out from reaction mixture, 20 mL distilled water followed by sodium perchlorate monohydrate (0.468 g, 3.33 mmol) in 10 mL distilled water were added. The solution was allowed to digest for 30 minutes on water bath. Light blue coloured solid separated on cooling was filtered, washed thoroughly with 50 mL distilled water followed by 25 mL ethanol and dried in air (1).

Complex, 2 was prepared by following similar procedure as above and using picbu by 0.248 g, 0.83 mmol) and 1,10-phenathroline (0.3306 g, 1.67 mmol) respectively, (Fig. 1).

#### C. Preparation of binuclear complex, $[\text{Cu}_2\text{A}_2(\text{picbu})]$ (3)

A solution of copper (II) acetate monohydrate (0.333 g, 1.66 mmol) in 20 mL methanol was taken in a three neck flask. Solution of 0.230 g, (1.67 mmol) of 2-hydroxybenzoic acid and 0.248 g, (0.83 mmol) of picbu, each in 15 mL methanol, were added dropwise with constant stirring over 1 hour to the hot refluxing solution of copper (II) acetate. The solution was allowed to reflux for further 2 hours where upon a micro crystalline solid separated out. It was filtered, washed thoroughly with ~ 30 mL methanol and dried in air (Fig. 1).

### III. RESULTS AND DISCUSSION

The purified ligand has elemental analysis consistent with the empirical formula. The proton NMR of the ligand has all features expected for the proposed structure (Fig. 2). The assignment of lines in  $^1\text{H}$  NMR to various types of protons in the molecule is shown in Fig. 3. The binucleating ligand, bis(picolinamide) is ambidentate and can coordinate with the metal ion either through the amide nitrogen or the amide oxygen. In both cases, it forms five member chelate rings with the metal ion (Fig. 4). In order to verify the preference for coordination, the ligand geometry was optimized by semi-empirical Quantum Mechanical (PM3) calculations and the energy, electrostatic potentials and electron densities were calculated. The map of electrostatic potential over electron density shows maximum electron density (Fig. 5) over pyridine nitrogen and amide oxygen directed towards each other in a way to facilitate the coordination of a metal ion at this site and confirms the coordination through amide nitrogen.

The elemental analyses show that the composition is  $[\text{Cu}_2\text{A}_2(\text{picbu})(\text{ClO}_4)_4]$  for complexes 1 and 2 and complex 3 is consistent with molecular formulae,  $[\text{Cu}_2\text{A}_2(\text{picbu})]$ . The complexes 1 and 2 are easily soluble in DMF, hence conductance studies were carried out in DMF. Complexes 1 and 2 show the conductance values between 290 – 300 ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) corresponds to 1 : 4 electrolyte, indicating that four anions are outside of the coordination sphere.

The presence or absence of certain bands in the IR spectra have been, generally, utilized to illustrate the structure of the complexes. More important bands in the complexes are listed in, Table 2. Absorption due to stretching of the amide N-H is observed between 3328 - 3367  $\text{cm}^{-1}$  in the free ligand and complexes. The absorption due to the stretching of amide  $>\text{C}=\text{O}$  is observed between 1633-1637  $\text{cm}^{-1}$  in the binuclear complexes. These are at lower energy compared to the free ligand value of 1657  $\text{cm}^{-1}$ . The shift in the amide  $\nu_{>\text{C}=\text{O}}$  towards lower energy in the

complexes, indicates that the amide oxygen is involved in coordination with the Cu (II) ion. Also, the almost unaffected amide  $>N-H$  stretching frequency indicates that the amide nitrogen is not coordinated with the metal ion. Complexes, 1 and 2 show strong absorption bands between 1090 – 1091  $cm^{-1}$ , confirmed the presence of perchlorate ions. There is no splitting of the  $\sim 1090\text{ cm}^{-1}$  band indicating that perchlorate is tetrahedral and ionic in nature [26]. Other bands characteristic of ligands include asymmetric stretching between 2923 – 2945  $cm^{-1}$  and symmetric stretching between 2840 – 2875  $cm^{-1}$  due to the presence of  $-CH_2$  groups.  $-C=C-$  stretching in aromatic ring is observed between 3066 – 3090  $cm^{-1}$  and stretching of the  $>C=N$  (ring) appears between 1598 – 1606  $cm^{-1}$ . Thus, the IR spectra support the suggested structures of the complexes.

The electronic spectra of the binuclear complexes in methanolic solutions show several bands in the range of 215 – 714 nm. Intense bands between 215 – 271 nm are due to interligand transitions. Charge transfer is observed around 325 nm. The weak and broad band observed in each complex between 650 – 750 nm can be assigned to the Laporte forbidden ligand field transitions. In a square planar environment Cu(II), a  $d^9$  metal ion, has  $A_{1g} \leftarrow B_{1g}$ ,  $B_{2g} \leftarrow B_{1g}$  and  $E_g \leftarrow B_{1g}$  transitions, which have similar energy and hence remain merged to form a broad band.

The FAB mass spectra of the complex,  $[Cu_2(salac)_2(picbu)]$ , was recorded in *m*-nitrobenzyl alcohol, Fig. 6. In the FAB mass spectrum of the complex,  $[Cu_2(salac)_2(picbu)]$ , parent ion peak can be observed at  $m/z = 697$ . This is formed by protonation of the complex molecule,  $[M+H]^+$ . Peaks corresponds to  $[Cu_2(salac)(picbu)+H]^+$ , and  $[Cu_2(picbu)]^+$  observed at  $m/z$  560 and 423 respectively. A peak corresponding to binucleating ligand,  $[picbu+H]^+$  appears at  $m/z = 299$ . This fragment undergoes further fragmentation to give other related species at  $m/z = 141$  (7%) and  $m/z = 89$  (26%). Some important fragments with the observed  $m/z$  values are summarized in Table 3 and the fragments formed are represented in Fig. 7.

Peaks observed at various  $m/z$  values for the complex, 3 strongly elucidate the formation of binuclear complexes with general formula  $[Cu_2A_2(picbu)]$ .

The peak corresponding to the fragments of *m*-nitrobenzyl alcohol and associated products are observed at  $m/z$  136, 137, 154, 289, 307 and 614 with high relative abundance. These fragments can get associated with various fragments of the binuclear complex and thus are responsible for the occurrence

of widely distributed peak with low relative abundance.

The ESR spectrum of complex  $[Cu_2(salac)_2(picbu)]$  was recorded at room temperature in the polycrystalline solid state and at LNT in the form of frozen solution in DMF (Fig. 8). The *g* values are shown in Table 4. Both spectra are identical with *g* values supporting square planar geometry around the metal centre. A half field transition is observed at RT and at LNT in the frozen solution confirming the presence of intra molecular spin-spin interaction through the  $\sigma$  – orbitals in the bridging molecule.

#### A. Magnetic Properties

The magnetic susceptibility of complexes, 1, 2 and 3 were measured from liq.  $N_2$  to room temperature. The least squares fit of the data to Bleaney - Bower's equations yielded positive *J* values ranging between 9 to 73  $cm^{-1}$ . This indicates a weak to moderately strong ferromagnetic exchange between the metal centers in these complexes through  $\sigma$  – bonded bridging groups (Fig. 9).

Hendrickson and co-workers [19] first time suggested that the  $\sigma$  – orbitals can participate in the super exchange over a long distance in multiatomic bridges. The role of  $\sigma$  – orbitals in superexchange interaction has been further supported by the study of spin exchange interaction in the binuclear complexes, bearing the saturated bridging moieties [27]. Binuclear complexes, bearing aliphatic bridging moieties and absence of the interdimer interaction has been confirmed from the structural data obtained from the single crystal X-ray diffraction studies [23]. In these complexes, the antiferromagnetic interaction is intramolecular and is purely through the  $\sigma$  – bonding orbitals of the aliphatic bridging moieties.

Earlier, it was discussed that spin exchange between two copper (II) centers depends on the energy of the interacting orbitals and on the variation in geometrical parameters such as metal – ligand bond length, M-L-M bridging angle, dihedral angle between the metal coordination plane and the degree of planarity of the bridging unit [13-18]. In order to examine this, systematic variations have been made in the non bridging ligand in the complexes. The geometry of the complexes were optimized using universal force field [28-35]. Optimized geometry of complex, 1 is shown in Fig. 10. The torsional angle between the metal coordination planes has been calculated. The values in Table 5 indicate that the *J* values increase with increase in deviation in torsional angle from  $180^\circ$ . As the torsional angle deviates more from  $180^\circ$ , the metal coordination is no longer coplanar. This results in the mismatch of the overlapping metal ion 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 have observed similar dependence of the extent of magnetic exchange on the non bridging ligands in the complexes with oxalodiamide bridging groups [36].

#### IV. CONCLUSIONS

In the present endeavour, the bis(picolyamide) bridging ligand is common in the binuclear complexes while the non bridging secondary ligand changes from bipy to salac to phen. Results shows that to the first approximation bulkier and more  $\pi$ -bonding ligands can distort the metal coordination planes to a greater extent and hence lead to stronger ferromagnetism. Magnetic studied also revealed that ferromagnetic interaction exists between the metal centres which is propagated through  $\sigma$  – bonding orbitals of the aliphatic bridging moieties.

#### V. ACKNOWLEDGEMENTS

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## Figures

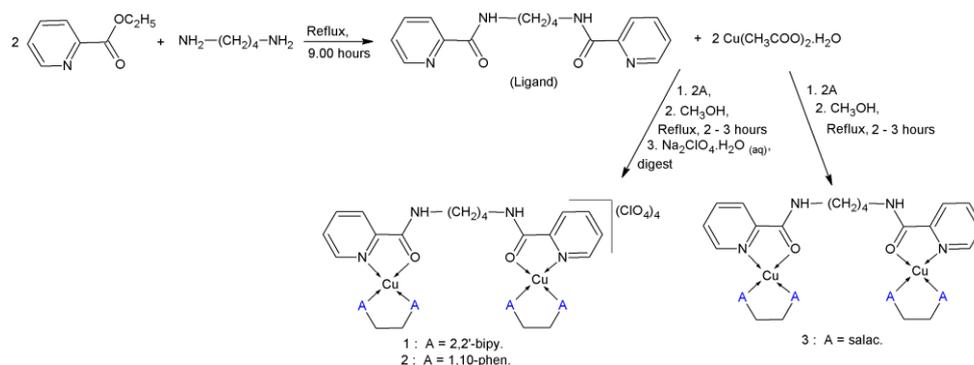


Fig. 1 - Schematic representation of the synthesis of ligand and binuclear complexes.

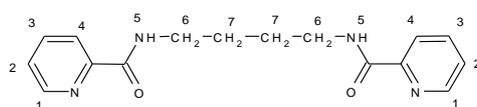


Fig. 2- Types of protons in binucleating ligand, picbu.

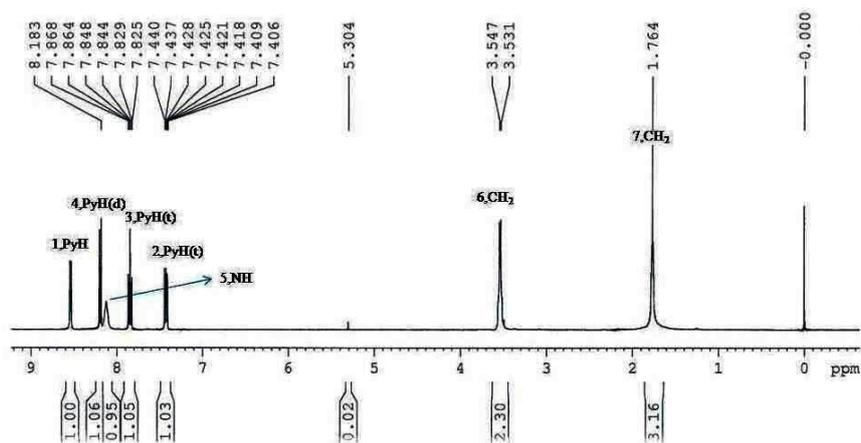


Fig. 3a - <sup>1</sup>H NMR spectrum of the ligand, picbu in CDCl<sub>3</sub>.

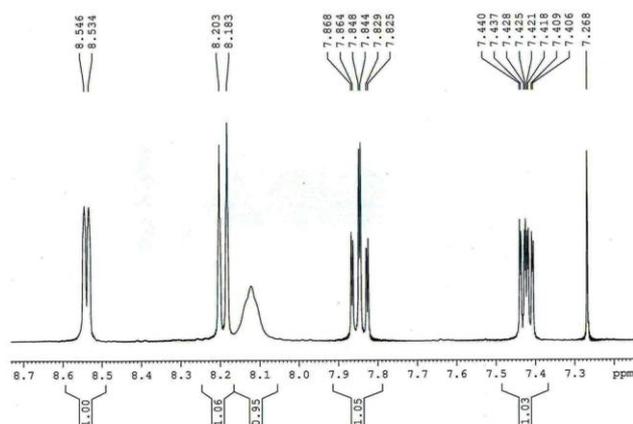


Fig. 3b-  $^1\text{H}$  NMR spectrum of the ligand, picbu in  $\text{CDCl}_3$  (expanded).



Fig.4- Mode of coordinations of ligand to the metal ion.

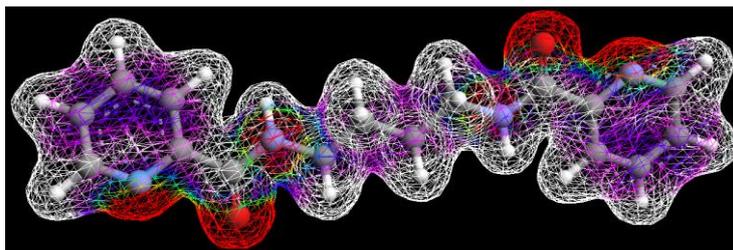


Fig. 5- Plot of electrostatic potential over electron density of ligand, picbu. (Red regions indicate region richer in electron density).

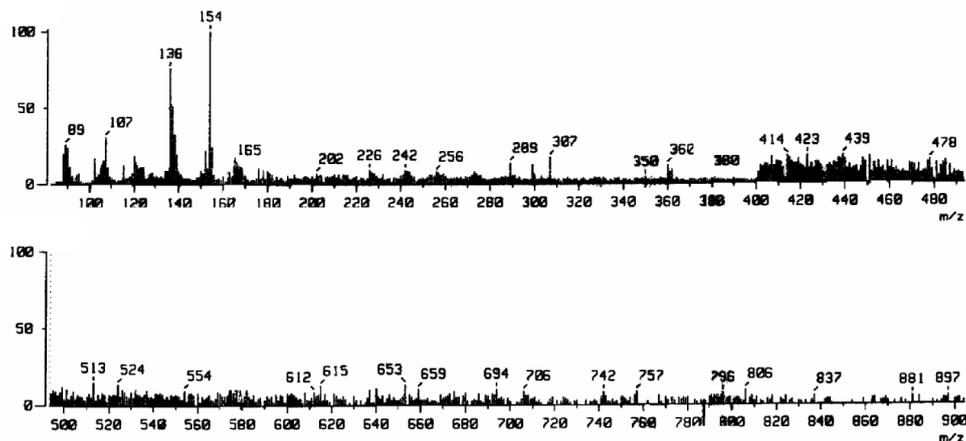


Fig. 6- FAB-Mass spectra of the binuclear complex,  $[\text{Cu}_2(\text{salac})_2(\text{picbu})]$ .

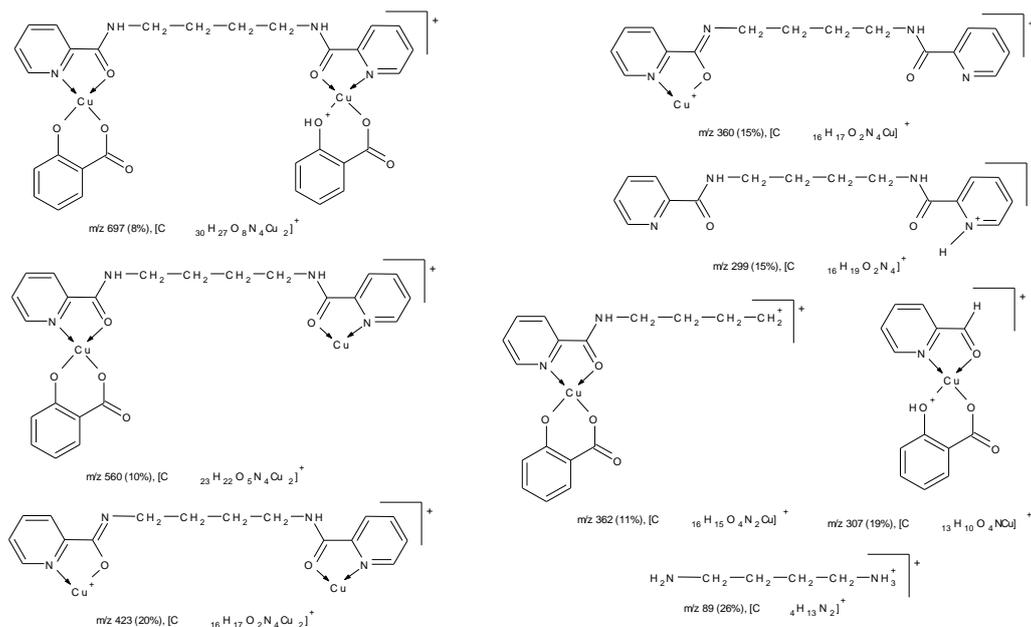


Fig. 7- Possible structure of the complex,  $[\text{Cu}_2(\text{salac})_2(\text{picbu})_2]$  and the corresponding fragments in FAB-Mass spectrum.

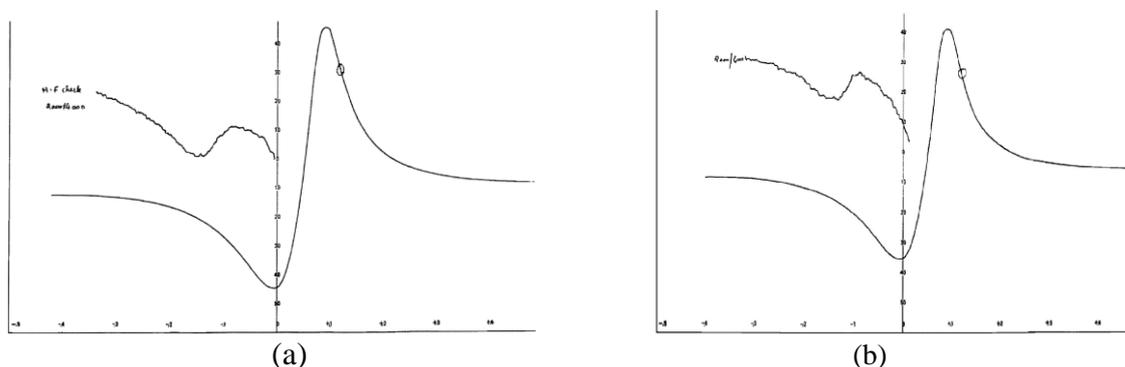


Fig. 8 - ESR of binuclear complex,  $[\text{Cu}_2(\text{salac})_2(\text{picbu})_2]$  at (a) RT and (b) LNT.

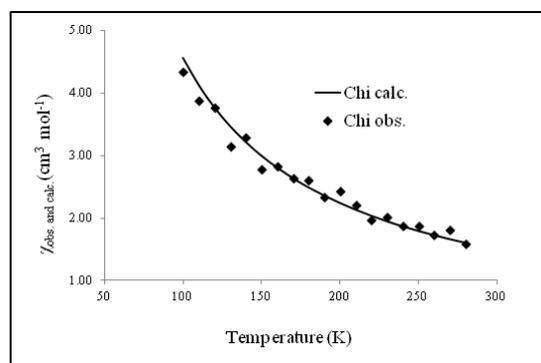


Fig. 9 - Thermal variation of the molar magnetic susceptibility (obs. and calc.) for complex,  $[\text{Cu}_2(\text{bipy})_2(\text{picbu})](\text{ClO}_4)_4$ .

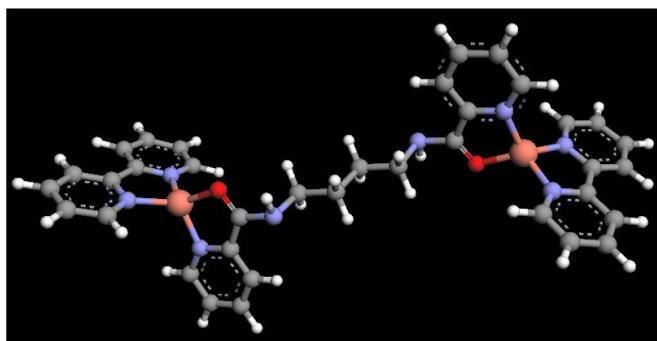


Fig. 10 - Optimized geometry of the binuclear complex,  $[\text{Cu}_2(\text{bipy})_2(\text{picbu})](\text{ClO}_4)_4$ .

Table 1 - Elemental analysis, reflux time, yields and molar conductivity of the binuclear complexes.

Comp. No.	Complexes	Found <sup>a</sup> (Calcd.) (%)			Refluxion time (hours)	Yields (%)	Molar conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )
		C	H	N			
1.	$[\text{Cu}_2(\text{bipy})_2(\text{picbu})](\text{ClO}_4)_4$	38.65	3.47	10.40	3	52	300
	$\text{C}_{36}\text{H}_{34}\text{N}_8\text{O}_{18}\text{Cl}_4\text{Cu}_2$	(38.06)	(2.99)	(9.87)			
2.	$[\text{Cu}_2(\text{phen})_2(\text{picbu})](\text{ClO}_4)_4$	41.20	3.04	9.37	4	57	290
	$\text{C}_{40}\text{H}_{34}\text{N}_8\text{O}_{18}\text{Cl}_4\text{Cu}_2$	(40.57)	(2.87)	(9.47)			
3.	$[\text{Cu}_2(\text{salac})_2(\text{picbu})]$	51.57	3.70	8.22	2	83	----
	$\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_8\text{Cu}_2$	(51.64)	(3.73)	(8.03)			

<sup>a</sup>The values in parenthesis are theoretical values calculated from the molecular formulae

Table 2 - Electronic absorptions (nm) and IR absorptions ( $\text{cm}^{-1}$ ) of the ternary binuclear complexes.

Comp. No.	Uv-visible absorption	$\nu(-\text{NH})$ stretching	aromatic stretching $\nu(-\text{C}-\text{H})$	$\nu_{\text{as}}(-\text{CH}_2)$ and $\nu_{\text{s}}(-\text{CH}_2)$	$\nu(>\text{C}=\text{O})$	ring stretching $\nu(-\text{C}=\text{N})$	$\nu(\text{ClO}_4)$
1.	215, 271, 325, 714	3367	3086	2940, 2840	1637	1604	1091
2.	226, 271, 294, 674	3341	3071	2923, 2856	1636	1606	1090
3.	232, 294, 325, 654	3228	3066	2926, 2865	1633	1600	-

Table 3- Fragmentation pattern in the positive ion FAB-MS of  $[\text{Cu}_2(\text{salac})_2(\text{picbu})]$  in m-nitrobenzyl alcohol.

m/z (% relative abundance)	Molecular formula of the fragments
697 (8%)	$[\text{C}_{30}\text{H}_{27}\text{O}_8\text{N}_4\text{Cu}_2]^+$ (parent ion, $[\text{M}+\text{H}]^+$ )
560 (10%)	$[\text{C}_{23}\text{H}_{22}\text{O}_5\text{N}_4\text{Cu}_2]^+$
423 (20%)	$[\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}_4\text{Cu}_2]^+$
360 (15%)	$[\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}_4\text{Cu}]^+$
299 (14%)	$[\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}_4]^+$ (binucleating ligand)
362 (11%)	$[\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2\text{Cu}]^+$
89 (26%)	$[\text{NH}_2-(\text{CH}_2)_4-\text{NH}_3]^+$ (amine)

Table 4 - ESR of the  $[\text{Cu}_2(\text{salac})_2(\text{picbu})]$

	Room temperature	Liquid N <sub>2</sub> temperature
$g_{\parallel}$	2.17	2.17
$g_{\perp}$	2.09	2.09

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

Complexes	J (cm <sup>-1</sup> )	Torsional angle	g
$[\text{Cu}_2(\text{bipy})_2(\text{picbu})](\text{ClO}_4)_4$	9.9	108.96	2.12
$[\text{Cu}_2(\text{salac})_2(\text{picbu})]$	23.1	119.56	1.95
$[\text{Cu}_2(\text{phen})_2(\text{picbu})](\text{ClO}_4)_4$	73.0	120.98	1.99