New Ferromagnetically Coupled Dicopper (II) Complexes with σ – bonding bridge

Ran Bahadur Yadav

Applied Chemistry Department, Faculty of Technology and Engineering, Kalabhavan, The Maharaja Sayajirao University of Baroda, Vadodara-390001, INDIA

Abstract

Four ternary binuclear complexes, [Cu₂(A)₂,pichx](ClO₄)₄ (1 and 2) and [Cu₂(A₂)pichx](3 and 4) have been synthesized. In the complexes two metal centers are held together by σ - bonding bridge i.e. pichx = N,N'-bis(2-pyridylcarbonyl)-1,6-diaminohexane and A₂ is 2,2'-bipyridyl or 1,10-phenanthroline or 2-hydroxybenzoic acid or 5-bromo-2-hydroxybenzoic acid coordinated to the metal ions as non-bridging ligands. The complexes were characterized by elemental analyses, conductance, magnetic susceptibility measurement, IR and electronic spectroscopy. The ESI-mass of the complex is consistent with the binuclear formulation. The complexes are observed to undergo a weak to moderate ferromagnetic coupling between two copper (II) ions.

Keywords: Binucleating ligand, binuclear Cu (II) complexes, σ – bonding bridges and magnetic properties.

Introduction

The field of molecular magnetism has seen giant leaps since the 1980s, from the search for molecule-based magnets to the achievements of single-molecule magnets and multifunctional materials[1–6]. It is well established that the extent of exchange coupling between two copper (II) centers depends on various structural features such as the coordination geometry of the copper ions, 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[5-12]. In most cases this type of exchange through multi atomic bridges has been shown to take place through the bridging ligand, possessing π - orbitals. However, it has been suggested that the σ – orbitals[13, 14] can participate in the super exchange over a long distance in multiatomic bridges and lead to a spin exchange[15-17], yet such interactions are very weak.

In order to study magnetic exchange between paramagnetic metal centers through saturated moiety, new ternary binuclear complexes, [Cu₂(A)₂,pichx](ClO₄)₄ and [Cu₂(A)₂,pichx] have been synthesized. The ligand, pichx = N,N'-bis(2-pyridylcarbonyl)-1,6-diaminohexane (pichx) and A₂ = 2,2'-bipyridyl or 1,10-phenanthroline or 2-hydroxybenzoic acid or 5-bromo-2-hydroxybenzoic acid. The complexes have been characterized based on elemental analysis and spectral properties.

Material and Methods

Ethyl-2-pyridinecarboxylate, 1,6-diaminohexane, 2,2'-bipyridine, 1,10-phenanthroline, 2-hydroxybenzoicacid, 5-bromo-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.

Synthesis of binucleating ligand, N, N'-bis (2-pyridylcarbonyl)-1,6-diaminohexane (pichx): A solution of ethyl-2-pyridinecarboxylate (25 mmol, 3.37 ml) was placed in a flask equipped with water condenser and a magnetic stirrer. To this was added a solution of 1,6-diaminohexane (12.5 mmol, 1.45 gms). The mixture was allowed to reflux for eight hours. A pale brown solid compound separated out on cooling. The solid product obtained was crystallized from 50:50 CHCl₃ and petroleum ether. Finally, the compound was washed with 20 ml (in five portions) distilled water and 10 ml diethylether and dried in air. The yield was 3.1978 gms (40%) and mpt 98-100 °C. It was characterized by IR (KBr, cm⁻¹) 3371, 3068, 2924, 2853, 1657, 1593. Elemental analysis, calculated for formula C₁₈H₂₂N₄O₂ : Found (Calc.) C 66.26 (66.26), H 6.74 (6.47), N 17.18 (17.09) and Chemical shift values in ¹H NMR recorded in CDCl₃ solution: (δ)1.473 (t, 2H (CH₂)); 1.640 (t, 2H (CH₂)); 3.461 (m, 2H (CH₂)); 7.446 (m, H (PyH)); 7.856 (m, H (PyH); 8.089 (s, H (NH)); 8.196 (d, H (PyH); 8.545 (m, H (PyH). Chemical shift values in ¹³C NMR: (δ) 26.68 (C (CH₂); 29.56 (C (CH₂); 39.31 (C (CH₂); 122.16 (C (Py)); 126.05 (C (Py)); 137.33 (C (Py)); 148.01 (C (Py)); 149.99 (C (Py)); 164.26 (C (C=O)).

Synthesis of binuclear [Cu₂(A)₂,pichx](ClO₄)₄ type complexes, (1 and 2): Copper (II) acetate monohydrate (1.66 mmol, 0.333 gms) in 20 ml CH₃OH was taken in three neck flat bottom flask. To this was added 2,2'-bipyridine (1.66 mmol, 0.2605 gms) in 15 ml CH₃OH and pichx (0.83 mmol, 0.2716 gms) in 15 ml CH₃OH simultaneously drop wise over 1 hour.

The reaction mixture was allowed to reflux for two hours. The excess of CH₃OH was distilled out from reaction mixture, 20 ml distilled water followed by sodium perchlorate monohydrate (3.33 mmol, 0.468 gms) 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.

Complex, 2 was prepared by following similar procedure as above and using pichx (0.83 mmol, 0.2716 gms) and 1,10-phenathroline (0.3306 gm, 1.67 mmol) respectively, (Scheme 1).

Synthesis of binuclear [Cu₂(A)₂,pichx] type complexes, (3 and 4): A solution of copper (II) acetate monohydrate (0.333 gms, 1.66 mmol) in 20 ml methanol was taken in a three neck flask. Solution of 2-hydroxybenzoic acid (1.67 mmol, 0.230 gms) and pichx (0.83 mmol, 0.2716 gms), 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 (**3**).

Complexes, **4** was prepared by following similar procedure as above and using pichx (0.83 mmol, 0.2716 gms) and 5-bromo-2-hydroxybenzoic acid (1.67 mmol, 0.3616 gms). (Scheme-1).

Physical measurements: The electronic spectra of the complexes in UV-Vis region were recorded in methanolic solutions using Perkin Elmer Lambda 35, UV – Visible spectrometer. IR spectra (as KBr pellets) were recorded on Perkin Elmer FT-IR, spectrum RX1. NMR of the ligand was recorded on Brucker 400 MHZ. The ESI-MS spectrum of

Complex, [Cu₂(phen)₂,pichx](ClO₄)₄ was recorded on a THERMO Finnign LCQ Advantage max ion trap mass spectrometer in acetonitrile solution. Specific conductivity of the complexes 1 and 2 in DMF solution having 1.0 mmolar concentration was measured using a Toshniwal conductivity bridge.

Magnetic susceptibility of the complexes at room temperature was measured in the powder form using the Faraday method with magnetic field of 0.8 Tesla. Magnetic moments per atom were calculated using following formula,

$$\mu_{eff} = 2.808(\chi_m\ T \times 10^{-6}/2)^{1/2}$$

Where, χ_m = Molar magnetic susceptibility per metal atom and other terms have their usual meanings. Pascal corrections have been incorporate.

Results and Discussion

Elemental analysis of the purified ligand is agreeable with suggested empirical formula. The ^{1}H NMR and ^{13}C NMR of the ligand have all features expected for the proposed structure (figure-1a, 1b and figure-2). The binucleating ligand, bis(picolinamide) is ambidentate and can coordinate with the metal ion either (1) through the amide nitrogen or (2) the amide oxygen. In both cases, it will form five membered chelate rings with the metal ion (figure-3a and 3b). 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 (figure-4) 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 oxygen.
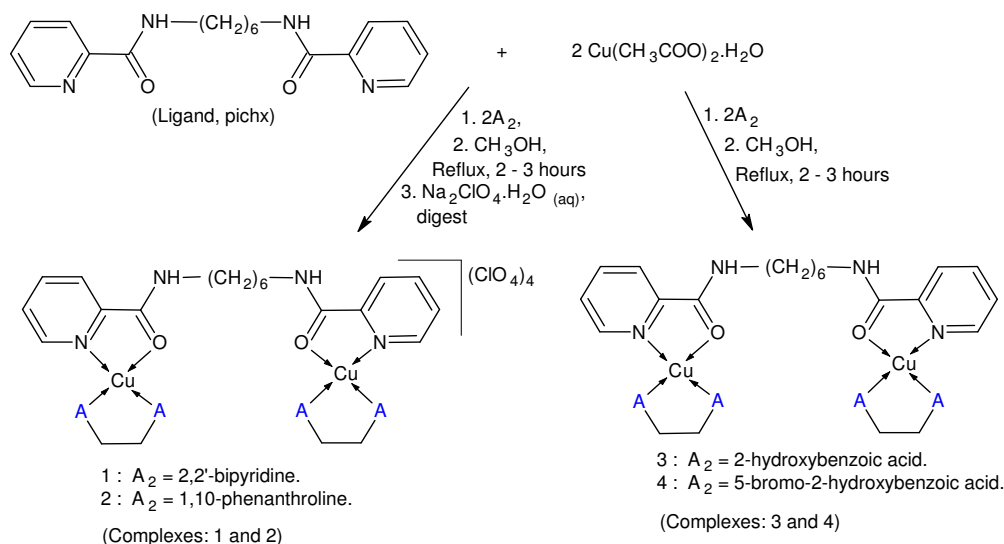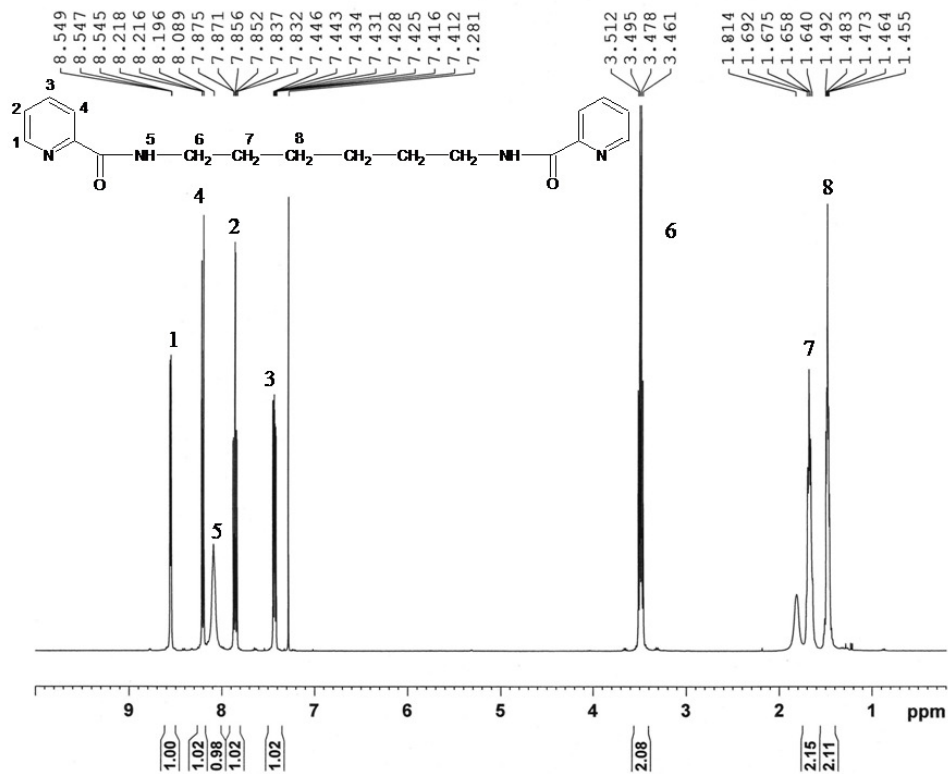

Scheme-1
Synthesis of binuclear complexes
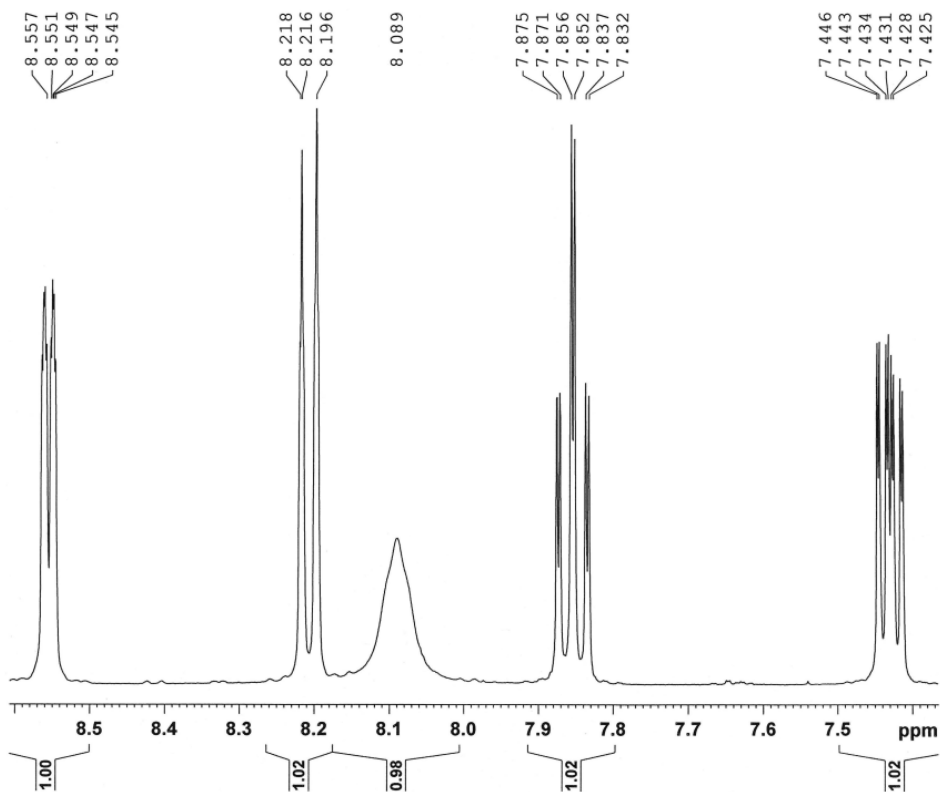
Figure-1a
^{1}H NMR of binucleating ligand, pichx in CDCl$_3$

Figure-1b
^{1}H NMR of binucleating ligand, pichx in CDCl$_3$ (expanded)
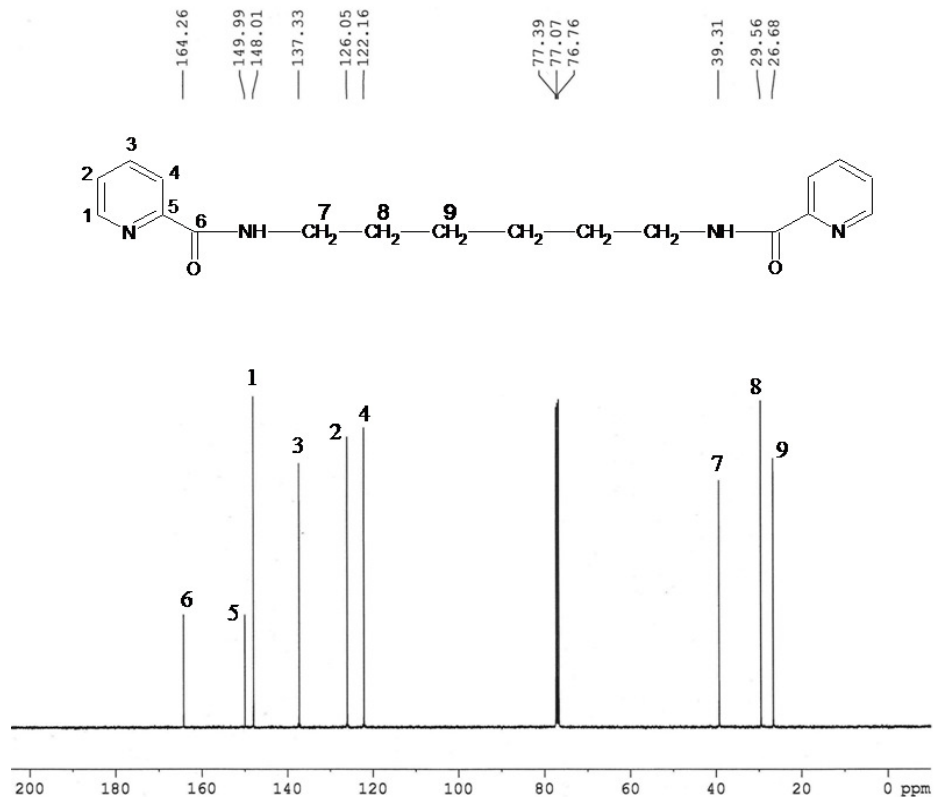
Figure-2
^{13}C NMR of binucleating ligand, pichx in CDCl$_3$
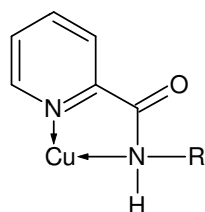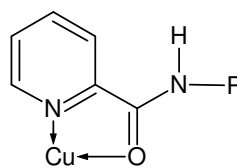

Figure-3a **Figure-3b**
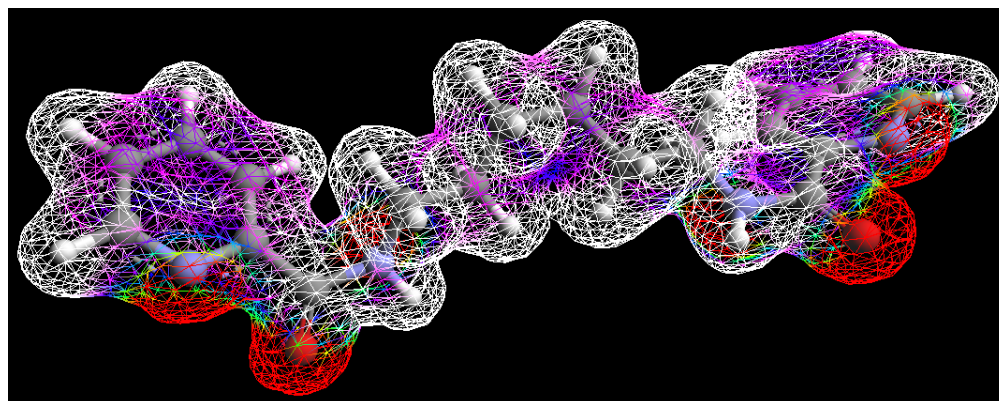**Possible mode of coordination of ligand**

Figure-4
Plot of electrostatic potential over electron densities of ligand, pichx (Red regions indicate region richer in electron densities)

As the values in table-1 reveal, the complexes 1 and 2 correspond to the general formulae $[Cu_2(A)_2, pichx] (ClO_4)_4$ and complexes 3 and 4 correspond the general formulae $[Cu_2(A)_2, pichx]$. Complexes 1 and 2 are found to be highly soluble in DMF, hence conductance studies were carried out in DMF to confirm the number of anions inside or outside the coordination sphere. Complexes show the conductance values between 290 – 300 $(\Omega^{-1}cm^2mol^{-1})$ corresponds to 1: 4 electrolyte, indicating that four anions are outside of the coordination sphere. Complexes 3 and 4 were having non-conductance nature.

Electronic Spectra: The electronic spectra of the binuclear complexes in methanolic solutions show several bands in the range of 200 – 850 nm. Intense bands observed below 350 nm are due to interligand transitions. The weak and broad band observed in each complex between 684 – 688 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 transitions are usually seen as a broad band near 600 nm in normal copper complexes (table-2). The lower energy of these transitions in complexes is indicative of significant distortion from planarity to weaken the ligand field.

Infrared spectra: The presence or absence of certain bands in the IR spectra have been, generally, utilized to illustrate the structure of the complexes. Most important bands in the complexes are listed in, table-2.

In the ligand and complexes, absorption due to stretching of the amide N-H is observed between 3233 - 3371 cm^{-1}. The absorption due to the stretching of amide >C=O is observed between 1631-1647 cm^{-1} in the binuclear complexes, 1 to 4. These are at lower energy compared to the free ligand value of 1657 cm^{-1}. The shift in the amide $\nu_{(>C=O)}$ 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[18]. In the IR spectra of the complexes, 1 and 2, ν_{as} of perchlorate is observed between 1090 – 1092 cm^{-1}. There is no splitting of the ~1090 cm^{-1} band indicating that perchlorate is tetrahedral and ionic i.e. not coordinated with the metal ions[19].

Other characteristic bands of ligand include asymmetric stretching between 2927 – 2931 cm^{-1} and symmetric stretching between 2857 – 2870 cm^{-1} due to the presence of –CH_2 groups. –C=C- stretching in aromatic ring is observed between 3067 – 3081 cm^{-1} and stretching of the >C=N (ring) appears between 1592 – 1601 cm^{-1}. Thus, the IR spectra support the suggested structures of the complexes.

Table–1
Reflux time, yields, elemental analysis, molar conductivity and magnetic moment of the binuclear complexes

Comp No.	Complexes	Reflux Time (hours)	Yield (%)	Elemental analysis Obsd. (Calc) in %			Molar conductivity $(\Omega^{-1}cm^2mol^{-1})$	Magnetic moment (B.M.)
				C	H	N		
1	$[Cu_2(bipy)_2, pichx](ClO_4)_4$ $C_{38}H_{38}N_8O_{18}Cl_4Cu_2$	4	31	38.70 (39.20)	3.89 (3.26)	10.06 (9.63)	300	1.84
2	$[Cu_2(phen)_2, pichx](ClO_4)_4$ $C_{42}H_{38}N_8O_{18}Cl_4Cu_2$	4	66	41.16 (41.62)	3.42 (3.14)	9.82 (9.25)	290	2.03
3	$[Cu_2(salac)_2, pichx]$ $C_{32}H_{30}N_4O_8Cu_2$	2	50	50.49 (50.96)	4.05 (4.13)	7.98 (7.72)	-	1.86
4	$[Cu_2(Brsalac)_2, pichx]$ $C_{32}H_{28}N_4O_8Br_2Cu_2$	3	91	43.02 (43.48)	3.71 (3.17)	6.85 (6.34)	-	2.04

The values given in parentheses are theoretical values calculated from the molecular formulae.

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

Comp. No.	Uv-visible absorption	ν(-NH) stretching	aromatic stretching ν(-C-H)	ν_{as}(-CH_2) and ν_s(-CH_2)	ν(>C=O)	ring stretching ν(-C=N)	miscellaneous frequencies
1	260, 300, 310, 684	3361	3083	2933, 2863	1647	1601	ν(ClO$_4$)1092
2	214, 300, 310, 684	3341	3071	2932, 2857	1643	1598	ν(ClO$_4$)1090
3	220, 271, 300, 315, 684	3368	3067	2931, 2862	1638	1601	-
4	238, 268, 306, 688	3233	3071	2927, 2870	1631	1592	ν(C-Br)1097

Mass Spectra: The ESI-MS spectrum of the binuclear complex, $[Cu_2(phen)_2,pichx](ClO_4)_4$ was recorded. The spectrum of complex is shown in figure-5. In the mass spectrum, peak at m/z = 1210.9 correspond to parent ion peak of the complex, $[Cu_2(A)_2,pichx](ClO_4)_4$. Subsequently, perchlorate ions and a phenantroline molecule are lost from parent ion and peak for resultant fragment, $[Cu_2(phen)pichx]^+$ is observed at m/z = 632.8. Peak corresponding to $[Cu(phen), pichx]^+$ is obtained at m/z = 568.0 with 100% relative abundance. An important peak correspond to binucleating ligand is observed at m/z = 389.2. This is formed due to protonation of the ligand molecule, $[pichx+H]^+$. Important fragments are listed in table-3.

Table–3
Fragmentation pattern in the positive ion ESI-MS of $[Cu_2(phen)_2,pichx](ClO_4)_4$.

m/z (% relative abundance)	Possible fragments
1210.9 (13%)	$[Cu_2(phen)_2,pichx](ClO_4)_4$
632.8 (15%)	$[Cu_2(phen),pichx]^+$
568.0 (100%)	$[Cu(phen),pichx]^+$
452.5 (34%)	$[Cu_2(pichx)]^+$
423.1 (70%)	$[Cu(phen)_2]^+$
389.2 (44%)	$[Cu(pichx)]^+$
327.2 (64%)	$[pichx+H]^+$
243 (14%)	$[Cu(phen)]^+$

Peaks observed at various m/z values for the complex **2** strongly elucidate the formation of binuclear complexes with suggested molecular formulae.

Magnetic Properties: The magnetic susceptibility of complexes was measured at room temperature using Faraday set up. The values of magnetic moment per atom are 1.84 – 2.04 B.M. (table-1). These higher values of magnetic moments than free copper (II) ion, indicate ferromagnetic interaction between two metal centres.

Hendrickson and coworkers[13] first time suggested that the σ – orbitals can participate in the super exchange over a long distance in multiatomic bridges. The role of σ – orbitals in superexchange interaction has been further supported by the study of spin exchange interaction in the binuclear complexes, bearing the saturated bridging moieties[20]. It is appropriate to recall at this stage that in multi atomic bridging ligands, some molecular orbital with appropriate energy and symmetry is usually available to mediate the exchange[5-12]. In order to examine this, systematic variations have been made in the non bridging ligand in the present complexes. The bridging ligand with –CH_2– group is common in all complexes while the non bridging secondary ligand changes from bipy, phen, salc and Brsalc. Results show that bulkier and more π-bonding ligands can distort the metal coordination planes to a greater extent and hence lead to stronger ferromagnetism. D. Zhang et al.[21] have observed similar dependence of the extent of magnetic exchange on the non bridging ligands in the complexes with oxalodiamide bridging groups.
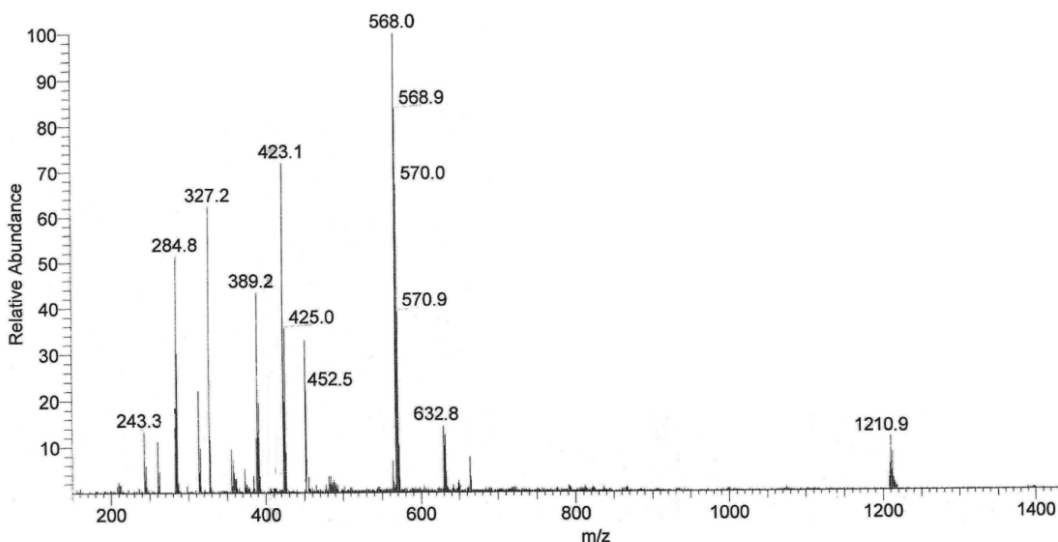

Figure - 5
ESI-MS spectra of binuclear complex, $[Cu_2(phen)_2,pichx](ClO_4)_4$.

Conclusion

In the present endeavour, binuclear complexes, possessing aliphatic bridging moiety have been synthesised and characterised. Room temperature magnetic studied revealed that a ferromagnetic interaction has been exits between the metal centers which is propagated through the σ - bonding orbitals of the aliphatic bridging moiety. Room temperature magnetic data indicated that bulkier and more π-bonding ligands can create greater mismatch of atomic orbitals with Molecular orbitals of bridging ligand. Hence, results lead towards ferromagnetism.

Acknowledgements

References

1. Coronado E., Galan-Mascaros J.R., Gomez-Garcia C.J. and Laukhin V, Coexistence of ferromagnetism and metallic conductivity in a molecule-based layered compound, *Nature,* **408,** 447–449 (**2000**)

2. Sato E., Iyoda T., Fujishima A. and Hashimoto K., Photoinduced magnetization of a cobalt-iron cyanide, *Science***, 272**, 704-705 **(1996)**

3. Miller J.S. and Drillon M., Eds, Magnetism: Molecules to Materials II. Nanosized Magnetic Materials; Wiley-VCH: Weinheim, **(2002)**

4. Gatteschi D. and Sessoli R., Quantum tunneling of magnetization and related phenomena in molecular materials, *Angew. Chem., Int. Ed.*, **42**, 268–297 **(2003)**

5. Calzado C.J., Clemente-Juan J.M., Coronado E., Gaita-Arino A. and Suaud N., Role of the electron transfer and magnetic exchange interactions in the magnetic properties of mixed-valence polyoxovanadate complexes, *Inorg. Chem.,* **47,** 5889-5901 **(2008)**

6. Sorai M., Nakazawa Y., Nakano M. and Miyazaki Y., Calorimetric Investigation of Phase Transitions Occurring in Molecule-Based Magnets, *Chem. Rev.*, **113**, 41-122 **(2013)**

7. Venegas-Yazigia D., Aravena D., Spodine E., Ruiz E. and Alvarez S., Structural and electronic effects on the exchange interactions in dinuclear bis(phenoxo)-bridged copper(II) complexes, *Coord. Chem. Rev.*, **254,** 2086-2095 **(2010)**

8. Stylianou M., Drouza C., Viskadourakis Z., Giapintzakis J. and Keramidas A.D., Synthesis, structure, magnetic properties and aqueous solution characterization of p-hydroquinone and phenol iminodiacetate copper (II)

complexes, *Dalton Trans.,* 6188-6204 **(2008)**

9. Ruiz E., Alemany P., Alvarez S. and Cano J., Structural modeling and magneto-structural correlations for hydroxo-bridged copper (II) binuclear complexes, *Inorg. Chem.,* **36**, 3683-3688 **(1997)**

10. Hatfield W.E., *Comments Inorg. Chem*, **1**, 105–121 **(1981)**

11. Melnik M., Study of the relation between the structural data and magnetic interaction in oxo-bridged binuclear copper compounds, *Coord. Chem. Rev.,* **42**, 259–293 **(1982)**

12. Kato M. and Muto Y., Factors affecting the magnetic properties of dimeric copper (II) complexes, *Coord. Chem. Rev.,* **92**, 45–83 **(1988)**

13. Felthouse T.R. and Hendrickson D.N., Magnetic exchange interactions in binuclear transition-metal complexes, 17. Benzidine and p-phenylenediamine, extended aromatic diamine bridging ligands in binuclear copper(II) 2,2',2''-triaminotriethylamine and vanadyl bis(hexafluoroacetylacetonate) complexes, *Inorg. Chem.,* **17(9),** 2636-2648 **(1978)**

14. Chaudhury P., Order K., Wieghardt K., Ghering S., Hasse W., Nuber B. and Weiss J., Moderately strong intramolecular magnetic exchange interaction between the copper (II) ions separated by 11.25.ANG. in [L$_2$Cu$_2$(OH$_2$)$_2$(.eta.-terephthalato)](ClO$_4$)$_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), *J. Am. Chem. Soc.,* **110,** 3657–3658 **(1988)**

15. Glerup J., Goodson P.A., Hodgson D.J. and Michelsen K., Magnetic Exchange through Oxalate Bridges: Synthesis and characterization of (μ-Oxalato)dimetal (II) complexes of Manganese, Iron, Cobalt, Nickel, Copper, and Zinc, *Inorg. Chem.,* **34**, 6255–6264 **(1995)**

16. Real J.A., Mollar M., Ruiz R., Faus J., Lloret F., Julve M. and Levsalles M.P., Oxamidato complexes. Part 6. Complex formation between copper (II) and N,N-bis[2-(dimethylamino)ethyl]oxamide (H$_2$ dmaeoxd). Preparation, crystal structure, and magnetic properties of [Cu$_2$ (dmaeoxd)(NCO)$_2$ (H$_2$O)$_2$], *Dalton Trans,* 1483–1488 **(1993)**

17. Calvo R., Steren C.A., Piro O.E., Rojo T., Zungia F.J. and Castellano E.E., Crystal structure and magnetic properties of diaqua(L-aspartato)copper(II), *Inorg. Chem.,* **32,** 6016–6022 **(1993)**

18. Gandhi J.B., Kulkarni N.D., Study of uranyl complexes with new binucleating ligands involving amide and imine coordinating sites, *Polyhedron*, **18**, 1735–1742 **(1999)**

19. Nakamoto K., Infrared and Raman Spectra of Inorganic and Coordination Compounds : Part B, 5th Eds, Wiley –

Interscience New York, **(1997)**

20. Clauss A.W., Wilson S.R., Buchanan R.M., Pierpont C.G. and Hendrickson D.N., Magnetic exchange interactions propagated by saturated bridges in binuclear dicyclopentadienyltitanium(III) complexes, *Inorg. Chem,* **22,** 628-636 **(1983)**

21. Liu Z., Lu Z., Zhang D., Jiang Z., Li L., Liu C. and Zhu D., New Types of Heterospin Complexes from trans-Oxamido-Bridged copper (II) binuclear units and nitronyl nitroxide radicals: Crystal structure and magnetic characterization, Inorg. Chem., **43,** 6620–6627 **(2004)**