

## Structure and magnetism of an exchange coupled system: An NMR approach

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**Abstract.** A binuclear copper(II) complex  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  has been synthesized and characterized by X-ray crystallography and  $^1\text{H-NMR}$  studies. The crystal structure shows that the bridging angles between  $\text{Cu}(1)\text{--O}(1)\text{--Cu}(2)$  and  $\text{Cu}(1)\text{--O}(2)\text{--Cu}(2)$  are  $98.9(2)^\circ$  and  $102.2(2)^\circ$  respectively. The  $\text{Cu}(1)\text{--Cu}(2)$  distance is  $3.0097(12)\text{Å}$ . This indicates that the interaction between the two copper atoms is antiferromagnetic in nature. The geometry around  $\text{Cu}(1)$  is distorted square-pyramid with one water molecule occupying the axial fifth position, whereas, the geometry around  $\text{Cu}(2)$  is distorted square-planar with weak interactions of one of the perchlorate anion. There are eight molecules present in the unit cell. There is an interdimer interaction between the dimers. The temperature-dependent  $^1\text{H-NMR}$  chemical shift studies have been performed on six different protons of this complex which reveals that the exchange coupling constant ( $-2J$ ) is same for all protons ( $208 \pm 1\text{ cm}^{-1}$ ). However, the hyperfine coupling constant ( $A'$ ) was found to be different in magnitude as well as in sign. We also report solvent dependent NMR properties.

**Keywords.** Antiferromagnetic; intra and interdimer interaction;  $^1\text{H-NMR}$ ; chemical shift; exchange coupling; hyperfine coupling.

### 1. Introduction

Interest in binuclear centres has focused primarily on magnetic exchange (spin-spin) interaction between two paramagnetic ( $s = 1/2$ ) cupric ions (Hatfield 1975; Hodgson 1975; Pierpont *et al* 1977). Such interactions in biomolecules have received increased focus since the time binuclear copper centres were proposed (Malkin and Malstrom 1970; Mason 1976) to be part of the active site of several multi-copper containing proteins. The "type3" copper in Laccase consists of a pair of antiferromagnetically coupled copper(II) ions (Malkin and Malstrom 1970) which are capable of acting as a two electron oxidant. Mason (1976) has reviewed the evidence for binuclear copper centres in a variety of proteins.

Magnetic exchange interaction between the electrons of the two metal ions, which are weakly coupled, leads to low-lying excited states of different spin multiplicities, which can be populated at thermal energies ( $\leq 1000\text{ cm}^{-1}$ ). The resulting magnetic behaviour will be antiferromagnetic or ferromagnetic depending on whether the low-spin (spin-paired) or high-spin (spin-parallel) state is the ground state, respectively. These interactions are often termed super-exchange because of the large distances involved ( $3\text{--}5\text{ Å}$ ) between the metal ions. There has been a systematic observation of

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such interactions even in early sixties and seventies (Kato *et al* 1964; Martin 1968; Ball 1969; Ginsperg 1971; Gray 1971). Super-exchange mechanism occurs via ligand entities that bridge the two metal centres (Willett 1985; Hendrickson 1985). Both single atom and multi-atom bridges are known to propagate exchange with the magnitude of the exchange interaction being dependent upon the bridge identity, its length, the angle subtended at the bridge, the metal-bridge ligand bond lengths, the metal ion stereochemistry, etc. Most of the theoretical works for the understanding of the exchange mechanism are based on the works of Kramers (1934), Anderson (1950), Goodenough (1955) and Kanamori (1959). Extensive theoretical work has come from groups of Hay *et al* (1975), Bencini and Gatteschi (1978), de Loth *et al* (1981) and Comarmond *et al* (1982). Recently, diagrammatic valence bond theory (Ramasesha and Rao 1991; Mandal *et al* 1992; Mandal and Manoharan 1993) has been used for the understanding of exchange mechanism.

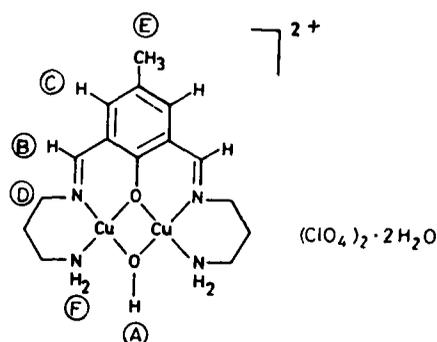
Although, different techniques such as magnetic susceptibility, EPR etc., have been used to derive the details of exchange interactions in solids, detailed studies of exchange interactions in solution have been rather few (Maekawa *et al* 1989; Mandal and Manoharan 1995). Exchange interactions in solutions are not easy to measure. This difficulty arises due to the loss of solid state packing. However, even if the integrity of metal cluster is not disturbed in solution a general application of a methodology becomes difficult due to other reasons such as the sign and magnitude of exchange interaction. This makes most methods inapplicable.

Nuclear magnetic resonance spectroscopy is in principle a powerful tool for investigating the exchange interactions in solution with its own built-in restrictions such as the effects due to electron relaxation and population of non-zero spin states. However, high resolution NMR of some nuclei can be successfully used to determine such couplings if relaxation process permits. It is known that some antiferromagnetically coupled binuclear Cu(II) complexes are expected to give relatively narrow NMR signals (Zelonka and Baird 1972; Byers and Williams 1973; Dei *et al* 1979; Maekawa *et al* 1989; Mandal and Manoharan 1995). Due to the paramagnetic effect coupled with limited Boltzman populations at the higher electronic state, different protons in the ligand moiety can sense substantial shifts, which will be moderately to highly temperature dependent depending on the value for  $|2J|$  and the location of protons.

The NMR spectra of binuclear complexes in solution provides the information on the role of the ligands in the super-exchange pathway as well as on the electronic states of the coupled metal centres (Wicholas 1970; La Mar *et al* 1973). It can also provide information about the structure of the complexes and the distribution of the unpaired electron. It can be seen, therefore the NMR studies on binuclear complexes can be a rich source of information.

Although a larger number of Cu(II) dimer compounds exhibiting antiferromagnetic coupling have been reported in the solid state, these compounds seem to be of low solubility or to dissociate considerably in solution and are therefore unsuitable for  $^1\text{H}$ -NMR studies. However, there are still few reports that demonstrate the usefulness of NMR spectra of binuclear copper(II) complexes in solution (Kitagawa *et al* 1984; Maekawa *et al* 1989; Mandal and Manoharan 1995).

The purpose of our work is to analyse NMR spectra of some binuclear copper(II) complexes, with singlet-triplet energy gap ( $-2J$ ) range of  $150\text{--}250\text{ cm}^{-1}$ . We report here the crystal and molecular structure of an exchange coupled dimer, structural formula of which is given in figure 1, and its temperature-dependent NMR spectral



**Figure 1.** Structural formula of the macrocyclic binuclear copper(II) dimer for which the NMR chemical shifts have been measured. A, B, C, D, E and F indicate the protons referred to in the text.

characteristic in solution, in order to calculate its exchange coupling in the absence of any temperature susceptibility measurement.

## 2. Experimental

### 2.1 Preparation of the ligand (L) and complex

A methanol solution (25 ml) of 1,3-diaminopropane (2.2 mmol) was added into methanol solution (25 ml) of 2,6-diformyl-4-methyl phenol (1 mmol). The mixture was refluxed for 1 h and cooled to room temperature. After reducing the volume of the solution an orange coloured oily material was obtained. This was washed with methanol several times and kept in a vacuum desiccator for drying.

The corresponding binuclear copper(II) complex was prepared by the method as reported earlier (Mandal and Nag 1984).

### 2.2 Physical measurements

Proton NMR spectra were recorded in a JEOL, JNM-GSX 400 MHz FT-NMR machine using  $7.2 \mu\text{s}$   $90^\circ$  pulse width, 8 kHz band width and 200 transients. Chemical shifts of the complex were referred to tetramethyl silane (TMS). Experiments were carried out in the temperature region  $-40^\circ\text{C}$  to  $+50^\circ\text{C}$ . A 100% deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ) solvent was used. Temperature variation was done by a JEOL variable temperature controller.

### 2.3 X-ray crystallography

Blue crystals of  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  suitable for X-ray diffraction studies were obtained by the slow evaporation of the aqueous solution of the complex. The diffraction intensities of an approximately  $0.3 \times 0.3 \times 0.1$  mm crystal were collected using an Enraf-Nonius CAD4 single crystal diffractometer with  $\text{Mo}(\text{K}_\alpha)$  radiation ( $0.71073 \text{ \AA}$ ). The cell parameters were obtained by the method of short vectors followed by least-squares refinement of randomly chosen 25 higher order reflections. Stability of the crystal during data collection was checked by monitoring the intensities of two standard reflections after every one hour of data collection. No significant variation of intensity could be noted. The intensity data were corrected for Lorentz, polarization,

**Table 1.** Crystal and structure refinement data on compound  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

Empirical formula	$\text{C}_{15}\text{H}_{28}\text{C}_{12}\text{N}_4\text{O}_{12}$
Formula weight	654.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	$a = 9.443(1)$ Å $\alpha = 90.00(1)$ deg. $b = 17.8601(3)$ Å $\beta = 90.00(3)$ deg. $c = 29.2564(6)$ Å $\gamma = 90.00(2)$ deg.
Volume	4933.92(14) Å <sup>3</sup>
Z	8
Density (calculated)	1.762 Mg/m <sup>3</sup>
Absorption coefficient	2.006 mm <sup>-1</sup>
<i>F</i> (000)	2672
Crystal size	0.3 × 0.3 × 0.1 mm
Theta range for data collection	2 to 25 deg.
Index ranges	0 ≤ <i>h</i> ≤ 11, 0 ≤ <i>k</i> ≤ 21, 0 ≤ <i>l</i> ≤ 34
Reflections collected	4312
Independent reflections	3516
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3516/0/338
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.036
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> ( <i>F</i> ) = 0.0481, <i>wR</i> <sub>2</sub> ( <i>I</i> ) = 0.1054
Extinction coefficient	0.00000(9)
Largest difference peak and hole	0.379 and -0.465 e.Å <sup>-3</sup>

decay and absorption (psi-scan) effects using the computer program MolEn (Kay Fair 1990). A total of 4312 reflections were collected in the range  $2^\circ < 2\theta < 25^\circ$  of which 3516 reflections with  $1 > 2\sigma$  were used for the structure determination.

The structure was solved by direct methods using the computer program SHELXS-86 (Sheldrick 1986) and Fourier difference synthesis using the program SHELXL-93 (Sheldrick 1993). All hydrogen atoms could be located in the difference Fourier map. The structure was refined by full-matrix least squares technique to find residuals of *R*(*F*) and *R*<sub>w</sub>(*I*) of 0.048 and 0.105 respectively, using weights based on counting statistics

$$R(F) = \frac{\sum \|F_o\| - |F_c|}{\sum F_o},$$

$$R_w(I) = \left[ \frac{\sum [W(|F_o|^2 - |F_c|^2)]^{1/2}}{\sum (W|F_o|)^2} \right]^{1/2},$$

where

$$W = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 2.6P],$$

$$P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3.$$

The final difference map was featureless. A summary of the crystal and diffraction data is given in table 1 and atomic coordinates are given in table 2.

### 3. Results and discussion

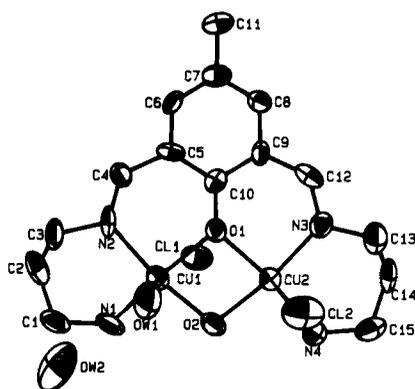
#### 3.1 Description of the structure

The ORTEP (50% probability thermal ellipsoids) representation of the  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  complex is shown in figure 2; and interatomic distances and angles

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for crystals of compound in figure 1.  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U(\text{eq})$
Cu(1)	1721(1)	4474(1)	1287(1)	39(1)
Cu(2)	-513(1)	5477(1)	882(1)	39(1)
Cl(1)	-1778(3)	3771(1)	1664(1)	62(1)
Cl(2)	1891(3)	6711(1)	225(1)	73(1)
OW1	1357(6)	58(3)	928(2)	74(2)
OW2	915(9)	831(5)	-670(2)	114(3)
O(1)	697(5)	5426(2)	1427(1)	34(1)
O(2)	561(5)	4585(2)	745(2)	44(1)
O(3)	-1539(13)	3389(5)	1268(3)	162(5)
O(4)	-2666(8)	3392(4)	1973(3)	112(3)
O(5)	-396(8)	3838(5)	1868(3)	115(3)
O(6)	-2253(8)	4524(3)	1576(3)	94(2)
OA	1571(17)	6365(9)	637(8)	131(10)
OB	3189(19)	6763(13)	46(7)	105(10)
OC	1207(20)	7411(7)	387(4)	79(6)
OD	1107(11)	6597(6)	-208(3)	113(5)
OE	3125(25)	6166(16)	176(7)	80(11)
OF	2019(31)	7478(12)	299(7)	7(10)
OG	2869(37)	7283(17)	278(9)	85(14)
OH	1219(25)	6112(14)	342(10)	117(13)
N(1)	2092(7)	3388(4)	1171(2)	53(2)
N(2)	2731(6)	4504(3)	1876(2)	39(1)
N(3)	-1460(6)	6370(3)	1109(2)	40(2)
N(4)	-1760(7)	5307(4)	338(2)	58(2)
C(1)	3367(10)	3002(4)	1365(3)	57(2)
C(2)	3598(10)	3206(4)	1863(3)	58(2)
C(3)	3952(8)	4022(4)	1941(3)	49(2)
C(4)	2311(7)	4908(3)	2211(3)	37(2)
C(5)	1182(7)	5457(3)	2238(2)	31(2)
C(6)	858(7)	5745(4)	2656(2)	35(2)
C(7)	-163(8)	6293(4)	2728(2)	42(2)
C(8)	-823(7)	6560(4)	2343(2)	36(2)
C(9)	-582(7)	6263(3)	1906(2)	32(2)
C(10)	439(7)	5696(3)	1837(2)	28(2)
C(11)	-554(11)	6585(5)	3193(2)	68(3)
C(12)	-1364(7)	6591(4)	1537(2)	37(2)
C(13)	-2287(10)	6828(4)	800(3)	63(3)
C(14)	-3354(8)	6383(4)	542(3)	54(2)
C(15)	-2694(11)	5912(6)	161(3)	73(3)

around the copper atoms are given in table 3. The structure consists of two copper centres bridged by one phenoxy and one hydroxy oxygen atoms with one imino and one amino nitrogen atoms completing the  $\text{CuN}_2\text{O}_2$  plane. The Cu-Cu separation is  $3.0097(12)\text{\AA}$  and the oxygen bridge angles from the azomethine unit Cu(1)-O(1)-Cu(2)  $98.2(2)^\circ$  and from the amino unit Cu(1)-O(2)-Cu(2)  $102.2(2)^\circ$  are slightly different. Azomethine linkages N(2)-C(4) and N(3)-C(12) (mean  $1.299\text{\AA}$ ) are essentially double bond in character, whereas the amino C-N bond lengths N(1)-C(1)  $1.499(10)\text{\AA}$  and



**Figure 2.** Structural representation of  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  with hydrogen atoms omitted (50% probability thermal ellipsoid).

**Table 3.** Selected bond distances [ $\text{\AA}$ ] and angles (deg) for  $[\text{Cu}_2(\text{L})\text{OH}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

<i>Bond distances</i>			
Cu(1)–O(2)	1.936(5)	Cu(1)–Cu(2)	3.0097(12)
Cu(1)–N(2)	1.972(6)	Cu(2)–O(2)	1.931(4)
Cu(1)–O(1)	1.998(4)	Cu(2)–N(3)	1.945(6)
Cu(1)–N(1)	1.999(6)	Cu(2)–O(1)	1.963(4)
Cu(1)–OW1#1	2.342(6)	Cu(2)–N(4)	2.004(6)
<i>Bond angles</i>			
O(2)–Cu(1)–N(2)	170.6(2)	O(2)–Cu(2)–N(3)	171.5(2)
O(2)–Cu(1)–O(1)	78.9(2)	O(2)–Cu(2)–O(1)	79.9(2)
N(2)–Cu(1)–O(1)	91.8(2)	N(3)–Cu(2)–O(1)	91.7(2)
O(2)–Cu(1)–N(1)	93.5(2)	O(2)–Cu(2)–N(4)	91.0(2)
N(2)–Cu(1)–N(1)	95.1(3)	N(3)–Cu(2)–N(4)	97.2(2)
O(1)–Cu(1)–N(1)	160.9(2)	O(1)–Cu(2)–N(4)	168.6(2)
O(2)–Cu(1)–OW1#1	91.5(2)	O(2)–Cu(2)–Cu(1)	38.96(14)
N(2)–Cu(1)–OW1#1	90.2(2)	N(3)–Cu(2)–Cu(1)	132.6(2)
O(1)–Cu(1)–OW1#1	95.0(2)	O(1)–Cu(2)–Cu(1)	41.00(12)
N(1)–Cu(1)–OW1#1	102.7(2)	N(4)–Cu(2)–Cu(1)	129.3(2)
OW1#1–Cu(1)–Cu(2)	95.8(2)	Cu(1)–O(1)–Cu(2)	98.9(2)
		Cu(1)–O(2)–Cu(2)	102.2(2)

N(4)–C(15) 1.488(10)  $\text{\AA}$  have much more single bond character. The least-squares plane calculations show that for Cu(1) donors O(1) and N(1) are displaced by  $-0.1415 \text{ \AA}$  and  $-0.1193 \text{ \AA}$  respectively on one side of the  $\text{N}_2\text{O}_2$  mean plane, whereas, donors O(2) and N(2) are displaced by  $0.1404 \text{ \AA}$  and  $0.1206 \text{ \AA}$ , respectively on the other side of the mean plane. A similar situation exists around Cu(2). Donors O(1) and N(4) are displaced by  $-0.0512 \text{ \AA}$  and  $-0.0432 \text{ \AA}$  respectively on one side of the  $\text{N}_2\text{O}_2$  mean plane, whereas donors O(2) and N(3) are displaced by  $0.0512 \text{ \AA}$  and  $0.0431 \text{ \AA}$  respectively. Least-squares plane data are given in table 4. However, it may be noted that a deviation of donor atoms of Cu(2) from the mean plane is much less when compared to the plane surrounding Cu(1). The metal atom Cu(1) is significantly out of plane with a normal distance of (0.17  $\text{\AA}$ ) from the mean plane. The deviation of metal atom Cu(2) from the

**Table 4.** Least-squares planes of the dimer  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

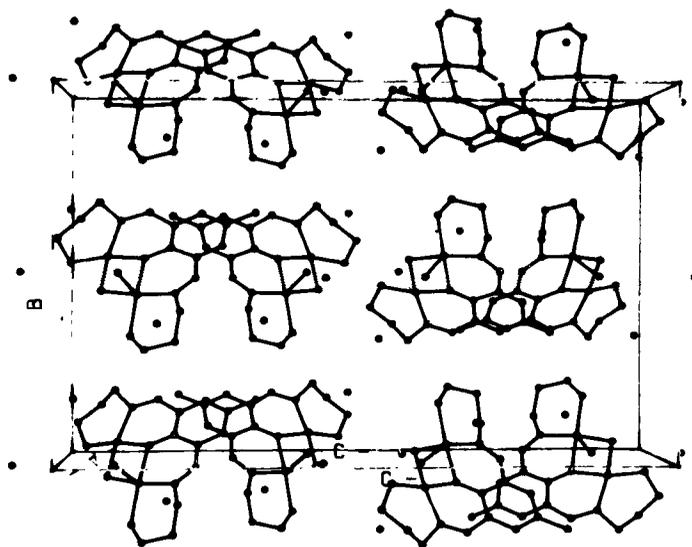
Equation of plane 1. (N1, N2, O1, O2)	
$0.7909X + 0.3801Y + -0.4795Z - 2.3431 = 0$	
Atom	Deviation from mean plane (Å)
N1	-0.1193
N2	0.1206
O1	-0.1415
O2	0.1404
Cu1	0.1744
Chi squared = 0.0	
Equation of plane 2. (N3, N4, O2, O1)	
$0.6511X + 0.5583Y + -0.5141Z - 3.7427 = 0$	
Atom	Deviation from mean plane (Å)
N3	0.0431
N2	-0.0432
O1	-0.0511
O2	0.0512
Cu2	0.0767
Chi squared = 0.0	

**Table 5.** Selected torsion angles in crystals of  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

C(1)–C(2)–C(3)–N(2)	72.7(9)	C(15)–C(14)–C(13)–N(3)	-74.9(9)
C(2)–C(3)–N(2)–Cu(1)	-56.6(7)	C(14)–C(13)–N(3)–Cu(2)	52.5(9)
C(3)–N(2)–Cu(1)–N(1)	32.5(5)	C(13)–N(3)–Cu(2)–N(4)	-23.3(6)
N(2)–Cu(1)–N(1)–C(1)	-27.3(5)	N(3)–Cu(2)–N(4)–C(15)	16.9(7)
Cu(1)–N(1)–C(1)–C(2)	44.8(8)	Cu(2)–N(4)–C(15)–C(14)	-38.0(10)
N(1)–C(1)–C(2)–C(3)	-65.0(9)	N(4)–C(15)–C(14)–C(13)	66.5(10)

mean plane (0.08 Å) is, however, much less when compared to Cu(1). The six-membered ring consisting of Cu(1), N(1), C(1), C(2), C(3) and N(2) forms a twisted half-chair conformation, whereas the six-membered ring consisting of Cu(2), N(3), C(13), C(14), C(15) and N(4) also forms a half-chair conformation but with no twisting. The torsion angles for these two ring conformations are listed in table 5. The four-membered ring formed by Cu(1), O(1), Cu(2) and O(2) does not form an ideal plane. One of the water molecules (OW1) axially coordinates with Cu(1) with a bond distance of 2.341 Å. This gives the inequalities in bond distances of Cu(1)–O(1) (1.998 Å) and Cu(1)–O(2) (1.936 Å) respectively. This yields the geometry of Cu(1) as a distorted square-pyramid. However, Cu(2) does not have any axial coordination, and surprisingly one of the perchlorate anions weakly (non-bonded) interacts with Cu(2) and gives the inequalities in bond distances of Cu(2)–O(1) (1.962 Å) and Cu(2)–O(2) (1.931 Å) respectively. This also effectively yields a distorted square-planar geometry around Cu(2) metal atom. The two water molecules are hydrogen bonded among themselves (OW(1)–OW(2) = 2.792 Å).

The shortest Cu–Cu distance between the molecules is 5.521 Å indicating weak interactions between dimers which could lead to weak interdimer exchange coupling. There are very few van der Waal contacts between the molecules. The interaction of



**Figure 3.** Packing diagram of  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  molecules in the unit cell.

molecules with anions and water molecules is responsible for crystal stability and packing forces. Figure 3 shows the packing diagram of the molecules projected onto the *bc* plane.

### 3.2 $^1\text{H}$ -NMR studies

The proton NMR spectra of the binuclear complex are shown as a function of temperature in the region 233–323 K. Though there are many peaks we are able to easily identify the change in chemical shifts as a function of temperature for six protons denoted as A, B, C, D, E and F in figure 4. This figure shows the spectra corresponding to 233 K and 323 K and reveals the gross changes in chemical shifts at extreme limits of measured temperatures. Figure 5 shows the temperature dependence of chemical shifts of only three protons, A, B and F which suffer maximal shifts. They are all quite sensitive to temperature variation. The shifts in some cases are as large as 10 ppm over the studied temperature region. It must be noted here that the NMR spectra of the pure ligand in the same solvent do not show observable shifts with temperature. It may be seen that the protons A, B, C, D and E undergo downfield shift with increase in temperature, whereas the proton F demonstrates upfield shift with increase in temperature. The line-widths of protons A, B and F increase with temperature and get completely broadened out at above 333 K. The other three protons C, D and E are least affected in terms of shift and broadening.

Though there is a reasonably strong solid-state interaction between two dimers and there are 8 molecules per unit cell, such interaction will break down in solution. However, the integrity of the dimer itself will be preserved mainly because of the fact the ligand being a macrocycle can keep the two copper(II) ions together. Thus the dimer, which could be antiferromagnetically coupled, should be responsible for the temperature dependence of the proton NMR.

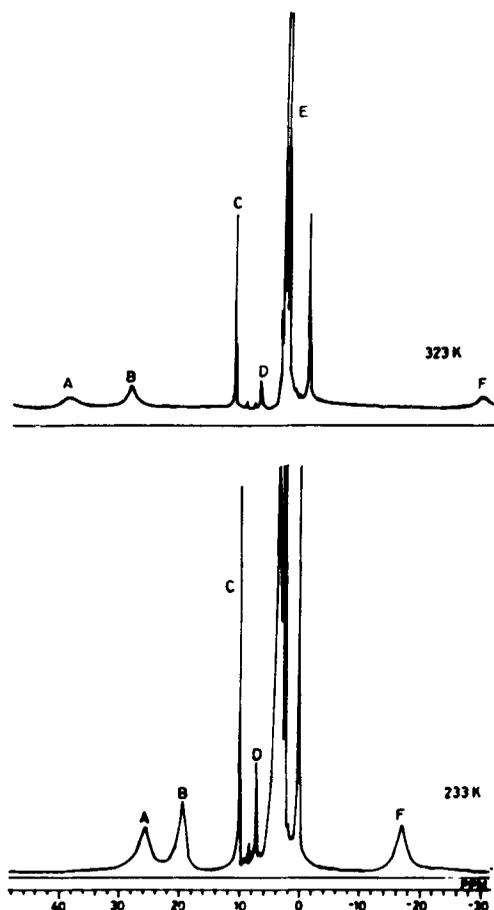


Figure 4.  $^1\text{H}$ -NMR spectra of macrocyclic binuclear Cu(II) dimer in  $\text{CD}_3\text{CN}$  solvent at two temperatures, 323 K and 233 K.

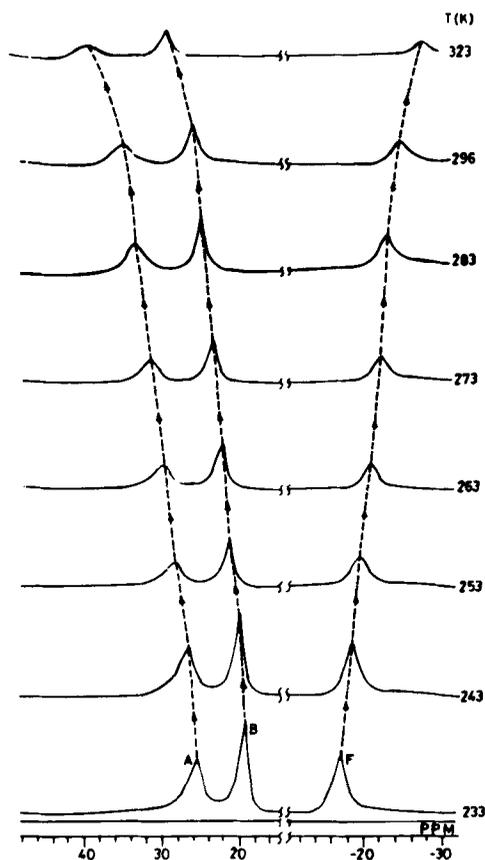
The magnetic properties of such exchange coupled systems can be explained by the simple Heisenberg Hamiltonian,

$$H = -2J \hat{s}_1 \cdot \hat{s}_2,$$

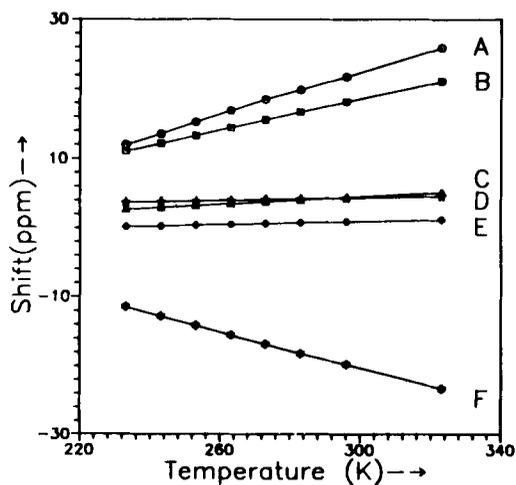
where,  $s_1 = s_2 = 1/2$ ; the temperature variation of chemical shifts could be used to calculate the exchange coupling using the expression (Byers and Williams 1973)

$$\Delta\delta_{\text{iso}} = \delta_{\text{comp}} - \delta_{\text{lig.}} = \frac{-g\beta A'}{(\gamma/2\pi)kT} [3 + \exp(-2J/kT)]^{-1} \quad (1)$$

where,  $A'$  is the hyperfine coupling due to the observed nuclei with  $S = 1$  level of the magnetically coupled dimer,  $\gamma$  is the magnetogyric ratio, and  $2J$  is the exchange coupling constant. It can be seen that the population distribution in the  $S = 0$  and  $S = 1$  states of the dimer varies with respect to temperature, and consequently the additional field (with possible changes in sign) due to unpaired electrons of the  $S = 1$  level at various nuclei causes the observed shift as presented in (1).



**Figure 5.** Observed  $^1\text{H}$ -NMR spectral shifts of protons A, B and F with temperatures.



**Figure 6.** Plot of observed  $^1\text{H}$ -NMR chemical shifts ( $\delta_{180}$ ) as a function of temperature for protons A, B, C, D, E and F shown in figure 1.

**Table 6.** Hyperfine coupling constants ( $A'$ ) for different protons and exchange coupling constants ( $-2J$ ) obtained from  $\delta_{iso}$  using (1) for  $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

Protons	$-2J$ ( $\text{cm}^{-1}$ )	$A'$ (Hz)	Protons	$-2J$ ( $\text{cm}^{-1}$ )	$A'$ (Hz)
A	208.9	$0.45 \times 10^6$	D	208.9	$0.10 \times 10^6$
B	209.0	$0.39 \times 10^6$	E	209.3	$0.13 \times 10^5$
C	209.1	$0.92 \times 10^5$	F	209.0	$-0.42 \times 10^6$

**Table 7.** Comparison of bond distances ( $\text{\AA}$ ) and bond angles (degrees) in three different antiferromagnetically coupled systems.

Compound (I) <sup>a</sup>		Compound (II) <sup>b</sup>		Compound (III) <sup>c</sup>	
<i>Bond distances</i>					
Cu(1)–N(3)	1.943	Cu(1)–N(3)	1.925	Cu(1)–N(1)	1.999
Cu(1)–N(1)	1.936	Cu(1)–N(4)	1.926	Cu(1)–N(2)	1.972
Cu(2)–N(4)	1.931	Cu(2)–N(2)	1.937	Cu(2)–N(4)	–2.004
Cu(2)–N(6)	1.961	Cu(2)–N(1)	1.961	Cu(2)–N(3)	1.945
Cu(1)–O(1)	1.933	Cu(1)–O(1)	1.986	Cu(1)–O(1)	1.998
Cu(1)–O(2)	1.952	Cu(1)–O(2)	1.898	Cu(1)–O(2)	1.936
Cu(2)–O(1)	1.943	Cu(2)–O(1)	2.007	Cu(2)–O(2)	1.963
Cu(2)–O(2)	1.897	Cu(2)–O(2)	1.915	Cu(2)–O(2)	1.931
Cu(1)–Cu(2)	3.011	Cu(1)–Cu(2)	3.018	Cu(1)–Cu(2)	3.010
<i>Bond angles</i>					
N(1)–Cu(1)–N(3)	94.5	N(4)–Cu(1)–N(3)	95.3	N(1)–Cu(1)–N(2)	95.1
N(4)–Cu(2)–N(6)	95.1	N(2)–Cu(1)–N(1)	102.1	N(3)–Cu(2)–N(4)	97.2
O(2)–Cu(1)–O(1)	77.7	O(1)–Cu(1)–O(2)	79.0	O(1)–Cu(1)–O(2)	78.9
O(2)–Cu(2)–O(1)	78.2	O(1)–Cu(2)–O(2)	77.9	O(1)–Cu(2)–O(2)	79.9
Cu(1)–O(1)–Cu(2)	101.1	Cu(1)–O(1)–Cu(2)	98.2	Cu(1)–O(1)–Cu(2)	98.9
Cu(1)–O(2)–Cu(2)	102.9	Cu(1)–O(2)–Cu(2)	104.9	Cu(1)–O(2)–Cu(2)	102.2

References: <sup>a</sup>Maekawa *et al* (1989); <sup>b</sup>Mandal and Manoharan (1995); <sup>c</sup> present study

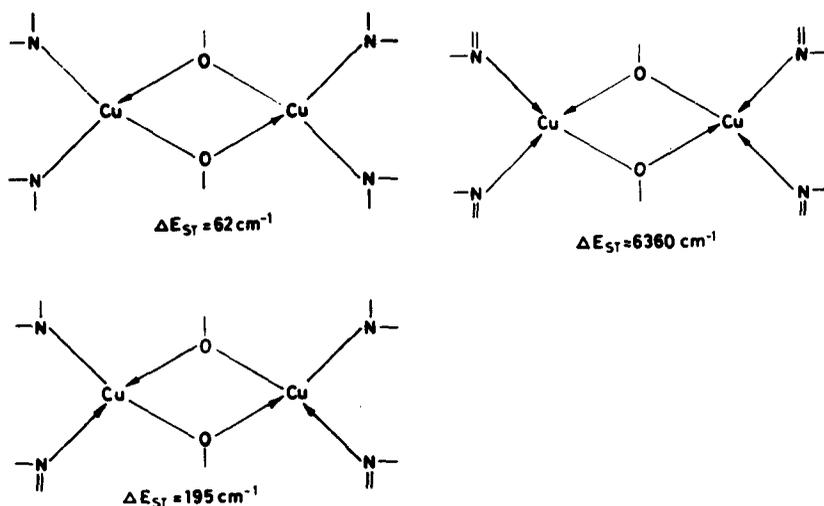
A plot of observed chemical shift against temperature is shown in figure 6. The chemical shift variations observed for each of the six protons were fitted using the above equation, which, finally yields values for the exchange coupling between the Cu(II) ions as well as the hyperfine coupling constant at each proton site. It is important to mention that  $2J$  values calculated for all protons lie in the same region  $-208 \pm 1 \text{ cm}^{-1}$ , though the hyperfine coupling is expected to be different for different protons. Table 6 gives the values for  $-2J$  and  $A'$  obtained from temperature dependent chemical shifts of different protons. It is noteworthy of mention that all proton chemical shifts yield the same value for exchange coupling, thereby suggesting that the exchange probably contributes the most to the observed temperature-dependent chemical shift as presented in (1).

At this point it is interesting to compare our results on exchange coupling of the system with two other already reported systems (Maekawa *et al* 1989; Mandal and Manoharan 1995). Although the ligands in the earlier studies and the present work are different, the coordination sphere around copper atom is similar in all the three cases.

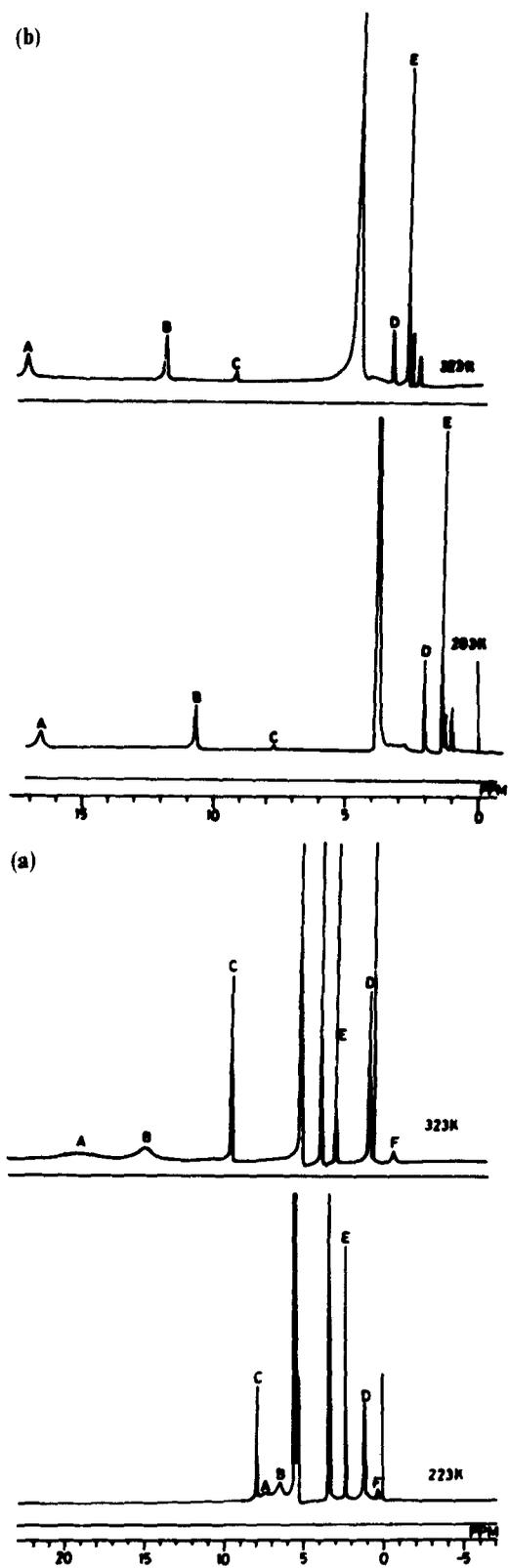
A comparison of the bond distances between copper atoms and bridging bond angles are very similar in all the cases as seen from table 7. The solid state susceptibility for the intradimer interactions of compound(I) is  $529\text{ cm}^{-1}$  (Maekawa *et al* 1989). The exchange-coupling constant ( $-2J$ ) was not derived from the isotropic chemical shift measurement in solution for the compound(I). The solid state susceptibility for the intradimer interaction of compound (II) is  $300\text{ cm}^{-1}$  (Mandal and Manoharan 1995). The solution susceptibility measurement for the same compound by Evans method and exchange coupling constant ( $-2J$ ) derived from the isotropic chemical shift measurement gives the values of  $200\text{--}225\text{ cm}^{-1}$ . The exchange coupling constant ( $-2J$ ) derived from the present study (III) of isotropic chemical shift measurement gives a value of  $208 \pm 1\text{ cm}^{-1}$ . Usually magnetic measurements obtained from the solid state do not agree with those in solution (Kitagawa *et al* 1985) because of the coordination by solvent molecules and loosening of solid state packing accompanied by loss of interdimer interactions and so on. It is pleasant, therefore, to note almost the same  $-2J$  values obtained for intradimer interactions from chemical shifts of six different protons, which is a clear indication of the correctness of this value in solution.

Additional support for the correctness of the value for exchange coupling for such a  $\text{Cu}_2\text{N}_4\text{O}_2$  cluster comes from the earlier theoretical investigations by valence bond approach (Mandal *et al* 1992). Also the experimental work based on temperature dependent NMR chemical shift using almost a similar moiety give the same value. The theoretical investigations on the three different moieties  $\text{Cu}_2\text{N}_4\text{O}_2$ , as shown in figure 7, clearly indicate that the present compound under study and the macrocyclic azo-amido complex from the work of Mandal and Manoharan (1995) point to a singlet-triplet separation of approximately  $-200\text{ cm}^{-1}$  for such a system. The maximum temperature-dependent shifts of protons A, B and F further indicate the dominance of  $\sigma$  bond effects in deciding the magnitude of antiferromagnetic exchange coupling.

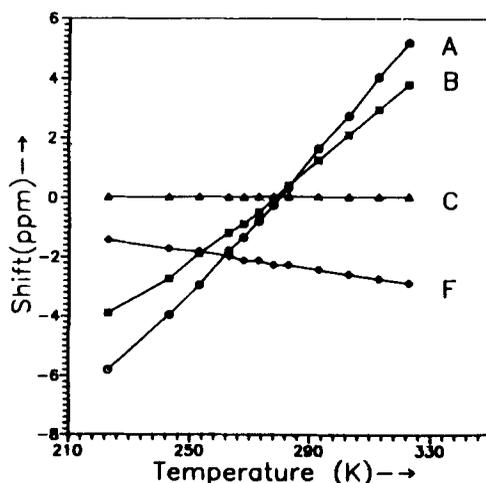
It is also interesting to note that there is a solvent dependence in the isotropic chemical shift. When  $\text{CD}_3\text{OD}$  and  $\text{D}_2\text{O}$  are used as solvents A, B and F, which suffer



**Figure 7.** Structures of  $\text{Cu}_2\text{N}_4\text{O}_2$  clusters for which exchange coupling constants have been calculated using VB approach.



**Figure 8.**  $^1\text{H-NMR}$  spectra of macrocyclic binuclear  $\text{Cu(II)}$  dimer at two temperatures, 323 K and 223 K, in (a)  $\text{CD}_3\text{OD}$  and (b)  $\text{D}_2\text{O}$  solvents.



**Figure 9.** Plot of observed  $^1\text{H-NMR}$  chemical shifts ( $\delta_{\text{iso}}$ ) as a function of temperature for protons A, B, C and F.

the maximum temperature-dependent chemical shifts in  $\text{CD}_3\text{CN}$ , continue to do so even in these solvents but the actual positions at a given temperature and also the extents of chemical shift variation over a given temperature region are different. The spectra at extreme temperatures measured in  $\text{CD}_3\text{OD}$  and  $\text{D}_2\text{O}$  solvents are given in figures 8a and b. However, the shifts versus temperature plots given in figure 9 are only for the  $\text{CD}_3\text{OD}$  solvent. It may, however, be noted that due to experimental difficulties, measurements with  $\text{D}_2\text{O}$  solvents were made only at three different temperatures and, that too, over a smaller temperature region. It is interesting to note that the calculated  $|2J|$  values for  $\text{CD}_3\text{CN}$ ,  $\text{CD}_3\text{OD}$  and  $\text{D}_2\text{O}$  using (1) are  $208(\pm 1)$ ,  $207(\pm 1)$  and  $230(\pm 2)\text{cm}^{-1}$  respectively. This possibly indicates that  $\text{D}_2\text{O}$  is providing the fifth coordination to the metal centre. This is also in agreement with our earlier theoretical finding (Mandal and Manoharan 1993).

Further detailed work on relaxation mechanism responsible for the observation of reasonably narrow signals is underway. The present system under investigation needs a thorough study by susceptibility measurement which is also in progress.

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