

## A Comprehensive Study of Exchange Coupling in a Macrocyclic Binuclear Copper(II) Complex in the Solid and Solution States

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The exchange-coupled magnetic behavior of a macrocyclic copper(II) aza-amido complex has been studied by a variety of methods both in the solid and solution states. Differences in magnetic interactions in these states have been observed. The solution state studies have been performed using temperature-dependent <sup>1</sup>H NMR chemical shifts caused by the antiferromagnetic nature of the complex. The resulting exchange coupling constants have been compared with the theoretically calculated results. Temperature dependent spin-lattice relaxation time ( $T_1$ ) measured by the inversion recovery method indicates that the relaxation rate is found to be dominated by electron nuclear dipolar coupling modulated by exchange.

### Introduction

The study of metal-metal interactions has been an important area of research for chemists and physicists because of their potential impact on materials science, catalysis, inorganic, and bioinorganic chemistry. In the case of binuclear metal complexes the coupling between the electrons of the two metal ions leads to low-lying states of different spin multiplicities. The resulting antiferromagnetic or ferromagnetic interactions often explained by superexchange mechanism involving metal ions through the bridging atoms have been observed in a variety of macrocyclic ligand-bridged binuclear complexes. These explanations are also applicable not only to dimeric but also polynuclear complexes, an area of wide research in superconductivity, molecular ferromagnets, etc. Most of the theoretical works for the understanding of the exchange mechanism are based on the works of Kramers,<sup>1</sup> Anderson,<sup>2</sup> Goodenough,<sup>3</sup> and Kanamori.<sup>4</sup> Extensive theoretical work has come from different groups, *i.e.* Hay *et al.*,<sup>5</sup> Bencini *et al.*,<sup>6</sup> Comarmond *et al.*,<sup>7</sup> and de Loth *et al.*<sup>8</sup> Recently, diagrammatic valence bond theory<sup>9-11</sup> has been used for the understanding of exchange mechanism.

In the solid state, in addition to the intradimer interactions, various interdimer interactions complicate the experimentally observed susceptibility data for these types of dimeric moiety mainly due to complex modes of packing. Such complexities have been observed and explained using the more complex magnetic Hamiltonian in for example chloro(2-(diethylamino)-ethanolato)copper(II)<sup>12</sup> and bis(tetra-*n*-butylammonium) bis(4-

(dicyanomethylene)-1,2-dimercaptocyclopent-1-ene-3,5-dionato-*S,S'*)cuprate(II).<sup>13</sup> In the latter work, different techniques have been used to derive the details of exchange interactions in the solid state of the compound though it is a mononuclear species in solution. Hence, such complicated exchange interactions can be made to disappear in solution because of the loss of solid state packing. Though solid state magnetism can be quite easily experimentally studied by a group of techniques such as susceptibility, EPR, optical spectroscopy, etc., the leftover exchange interactions, if any, in solutions are generally not so easy to measure. Despite the loss of interdimer interactions of the clusters in solution due to removal of packing effects the retention of the intradimer interactions will depend on the nature of the ligand. If a macrocyclic ligand can hold two or more metal centers even in solution only a few experimental procedures can help in deciding the nature and magnitude of such coupling. Thus far, little attention has been paid to the understanding of difference in magnetic interactions in solid state as well as in solution.

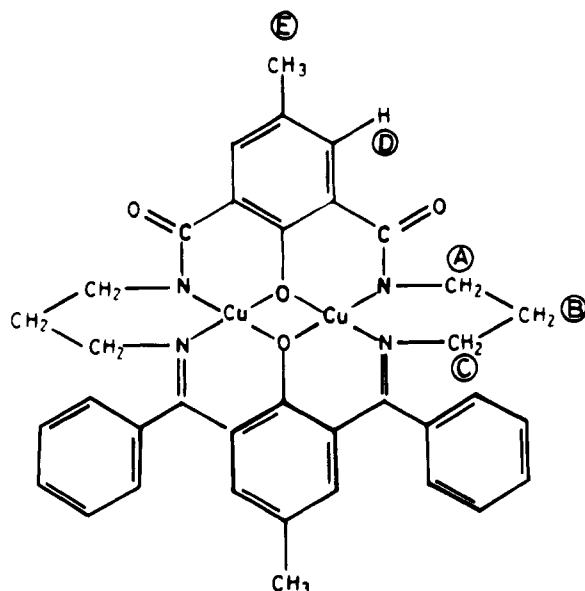
Though Mossbauer spectroscopy has been successfully used for dimeric iron complexes<sup>14</sup> and EPR for understanding coupling of very small magnitude,<sup>15</sup> high resolution NMR of some nuclei can be successfully used to determine such couplings if relaxation process permits. It is known that some binuclear complexes with antiferromagnetic interactions may give NMR lines in contrast to the corresponding mononuclear complexes. Due to the paramagnetic effect coupled with limited Boltzman populations at the higher electronic state, different protons in the moiety can sense substantial shifts which are temperature dependent. This helps in extraction of informations like the sign and magnitude of intradimer interactions, spin density distribution on different sites etc. Though such work have been done in the past, the reports are few in number.<sup>16-18</sup>

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**Figure 1.** Structural formula of the macrocyclic aza-amido binuclear copper(II) dimer for which the susceptibility and NMR chemical shifts and relaxation times have been measured. A, B, C, D, and E indicate the protons referred throughout the text.

Here, we report the magnetic properties of such a dimer in solution using NMR technique effectively which again demonstrates the usefulness of this methodology to get further insight into the solution vs solid state magnetic interactions.

The modified Evans method<sup>19</sup> is quite helpful for exploring magnetic susceptibility of binuclear copper(II) complexes in solution and it has also been shown by Kitagawa *et al.*<sup>20,21</sup> that the magnetic moment measurement in solution of a series of dimeric copper complexes clearly indicates the extent of interactions between the interacting metal centers.

We have done similar type work on a macrocyclic aza-amido dinuclear Cu(II) complex<sup>22</sup> shown in Figure 1. This exemplifies a good case of differing solid state and solution state magnetic interactions. Hence, we report here some variations in exchange interactions of this compound in the solid and solution states. In the solid state, the exchange coupling is dominated by the nature of packing which includes interdimer and intradimer exchanges while in solution the exchange is purely of intradimeric nature. While we have studied the solid susceptibility using a superconducting quantum interference device (SQUID) down to 4.2 K, we have used the variable temperature NMR studies for different protons on the dimeric moiety to understand the exchange interactions in solution. The parameters extracted from NMR studies like intradimer coupling constant have been correlated with the same from SQUID measurement as well as to our earlier theoretically calculated interaction in similar model systems. We have extended this experimental NMR chemical shift studies by also interacting with a ligand which can axially coordinate.

Nuclear relaxation has been used to characterize structure and dynamics of the molecules. Particularly, in the case of paramagnetic molecules, determination of coordination number and correlation times have been inferred from the investigation of paramagnetic relaxation.<sup>23</sup> However, the relaxation mecha-

nisms are modified when there is exchange interaction between the electron spins of the metal ions present in the moiety. Understanding of the effect of magnetic coupling on the nuclear relaxation parameters is relevant to several biological systems where such couplings are known (iron-sulfur, cytochrome oxidase) to occur. Efforts have been made by Bertini and co-workers<sup>24,25</sup> to study the relaxational ( $T_1$ ) properties of systems with weak exchange coupling. The present report includes detailed relaxation measurements of different protons of this macrocyclic Cu(II) aza-amido dimer. Various parameters associated with molecular motions have been highlighted.

## Experimental Section

(i) **Preparation of Compounds.** The free macrocyclic aza-amido ligand and its binuclear Cu(II) complex were prepared by the method of Nag and co-workers<sup>22</sup> and recrystallized from  $\text{CHCl}_3$  solution for further studies. Some amounts of these samples were received from Prof. Nag of the Indian Association for the Cultivation of Science, Calcutta, India, for initial investigation.

(ii) **Proton NMR Spectroscopy.** Proton NMR spectra were recorded in a JEOL JNM-GSX 400 MHz FT NMR machine using 7.2  $\mu\text{s}$  90° pulse width, 8 kHz band width and 200 transients. Chemical shifts of the complex were referenced to tetramethylsilane (TMS). Experiments were carried out in the temperature region 223–323 K. A 100% deuterated chloroform solvent was used. Temperature variation was done by a JEOL variable temperature controller.

(iii) **Magnetic Susceptibility Measurements.** Magnetic susceptibility measurement was carried out on powder sample at a field of 0.1 T using SQUID in the temperature range 4.2–350 K. The error in the temperature was  $\pm 0.2$  K, and the susceptibility was within 1%. The magnetic susceptibility was corrected for underlying diamagnetism using Pascal's constant.

(iv) **Solution Susceptibility Measurement.** Susceptibility of the sample was measured by the modified Evans<sup>19</sup> method. Coaxial NMR tube was used with *tert*-butyl alcohol as an internal reference. The inner tube contains only *tert*-butyl alcohol while the outer tube contains both *tert*-butyl alcohol and copper(II) complex solution. The presence of copper(II) dimer in the outer tube makes the bulk susceptibility different from that of the inner tube. The methyl proton signals from *tert*-butyl alcohol in these two inner and outer tubes were recorded and the separation of the two signals ( $\Delta\nu$ ) was monitored and it is considered as paramagnetic shift. Mass susceptibility ( $\chi_p$ ) is correlated to the above mentioned paramagnetic shift as follows:

$$\chi_p = \chi_0 + \frac{3000\Delta\nu}{4\pi\nu_0 cM} \quad (1)$$

where  $c$  is the concentration of the solute in mol/L,  $M$  is the molecular weight of the complex,  $\nu_0$  is the operating rf frequency of the spectrometer, and  $\chi_0$  is the susceptibility of pure solvent. Molar susceptibility ( $\chi_M$ ) can then be calculated by multiplying  $\chi_p$  with molecular weight,  $M$ .

(v) **Relaxation Measurement.** Longitudinal relaxation time ( $T_1$ ) was measured by the inversion recovery technique, and it consists of the following train of pulse sequence:

$$(180^\circ \dots \tau \dots 90^\circ \dots AQ \dots D)_n$$

where AQ is the acquisition time and  $D$  is the delay to allow equilibrium to be reached. The value of magnetization (which is directly related to NMR signal intensity) varies from  $-M_z(\infty)$  when  $\tau$  is zero to  $M_z(\infty)$  when  $\tau$  is five times higher than  $T_1$  and  $\tau$  is the variable time delay between the two pulses. It is possible to relate the magnetization to the  $T_1$  value by the following equation:

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$$M_z(\tau) = M_z(\infty)(1 - 2 \exp(-\tau/T_1)) \quad (2)$$

$T_1$  therefore can be calculated by least square fit analysis of the experimental data as a function of  $\tau$ .

## Results and Discussion

**Solid State Susceptibility.** The temperature-dependent solid state molar susceptibility of macrocyclic aza-amido binuclear copper(II) complex (Figure 1) corrected for diamagnetism,  $\chi_M$ , shown in Figure 2 reveals a minimum at about 94 K and increases with temperature indicating that the interaction in the binuclear species is of antiferromagnetic nature. The Heisenberg spin Hamiltonian

$$\mathcal{H} = -\sum_{ij} 2J_{ij} \hat{S}_i \cdot \hat{S}_j$$

can be used to explain the magnetic interactions of coupled spins in the moiety where such  $J_{ij}$  is the exchange interaction between the  $i$ th and  $j$ th spins. An earlier report on the crystal structure of this compound<sup>22</sup> reveals that dimer units are linked to each other by an oxygen atom showing a alternating chain of dimers. A closer scrutiny of the structure shows the presence of a tetranuclear unit in which the two dimer units are related to each other by a center of inversion and the interdimer distance is calculated to be 5.77 Å. The overall representation of the tetranuclear structure is shown in Figure 3 along with bond distances between various Cu(II) centers. The two dioxo-bridged dimers are further connected to each other by means of oxygen of apical water on the Cu<sub>2</sub>O<sub>2</sub>N<sub>2</sub> coordination. Furthermore, the tetranuclear units, the adjacent once being separated at 7.7 Å distances form a chain or one could define the structure as an alternating chain of dimers with 5.77 and 7.7 Å separations. However, as shown below, the strong exchange in the solid state seems to be restricted to the tetrameric unit with an intradimer and interdimer interacting distances being at 3.7 and 5.77 Å, respectively. We have found that the magnetism was not restricted to the dimer unit alone as explained by the simple Heisenberg Hamiltonian.

Hence the exchange interactions in the tetrameric unit represented by Figure 3 may be explained by the Hamiltonian

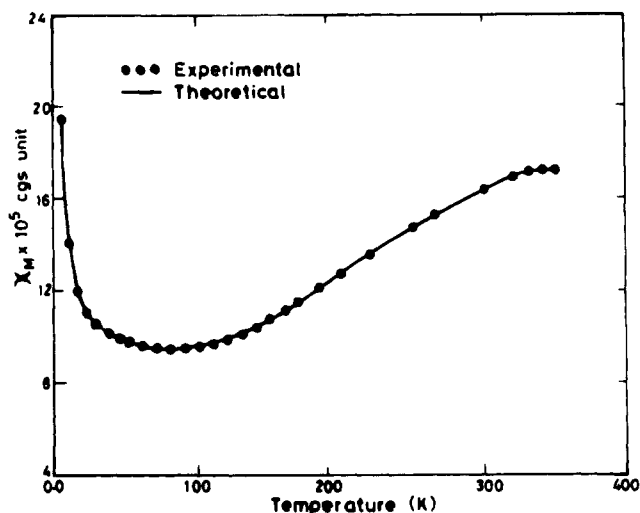
$$\mathcal{H} = -2[J_{12} \hat{S}_1 \cdot \hat{S}_2 + J_{34} \hat{S}_3 \cdot \hat{S}_4 + J_{14} \hat{S}_1 \cdot \hat{S}_4 + J_{23} \hat{S}_2 \cdot \hat{S}_3 + J_{24} \hat{S}_2 \cdot \hat{S}_4 + J_{13} \hat{S}_1 \cdot \hat{S}_3] \quad (3)$$

where  $J_{12}$  and  $J_{34}$  are the intradimer interactions and  $J_{13}$ ,  $J_{24}$ ,  $J_{14}$ , and  $J_{23}$  are the various interdimer interactions. The presence of inversion center simplifies the Hamiltonian to the following form:

$$\mathcal{H} = -2[2J_1 \hat{S}_1 \cdot \hat{S}_2 + 2J_2 \hat{S}_2 \cdot \hat{S}_3 + J_3 \hat{S}_1 \cdot \hat{S}_3 + J_4 \hat{S}_2 \cdot \hat{S}_4] \quad (4)$$

with  $J_{12} = J_{34} = J_1$ ,  $J_{14} = J_{23} = J_2$ ,  $J_{13} = J_3$ , and  $J_{24} = J_4$ . In this four-spin interactive system, we have 16 spin functions and diagonalization of the  $16 \times 16$  energy matrix produces one quintet, three triplets, and two singlets. Analytic expression of different energy levels were calculated from a mathematical package MACSYMA,<sup>26</sup> and thus obtained different energy levels are given as follows:

$$E_Q = -1/2[J_4 + J_3 + 2J_2 + 2J_1]$$



**Figure 2.** Experimental (●) and calculated (—) magnetic susceptibility measurements of macrocyclic aza-amido binuclear copper(II) dimer in the temperature region 4–350 K. Experiments were performed on a SQUID set up, and calculated results were obtained using eq 6.

$$E_{T_1} = 1/2[-J_4 - J_3 + 2J_2 + 2J_1]$$

$$E_{T_2} = 1/2[J_4 + J_3 + 2\{(J_1 - J_2)^2 + (J_3 - J_4)^2\}^{1/2}]$$

$$E_{T_3} = 1/2[J_4 + J_3 - 2\{(J_1 - J_2)^2 + (J_3 - J_4)^2\}^{1/2}]$$

$$E_{S_1} = 1/2[J_4 + J_3 + 2J_2 + 2J_1 + 2\{(J_4 + J_3 - J_1 - J_2)^2 + 3(J_3 - J_4)^2\}^{1/2}]$$

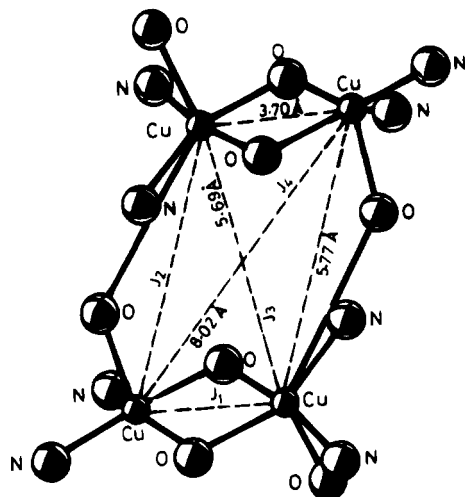
$$E_{S_2} = 1/2[J_4 + J_3 + 2J_2 - 2J_1 + 2\{(J_4 + J_3 - J_1 - J_2)^2 + 3(J_3 - J_4)^2\}^{1/2}] \quad (5)$$

For these spin levels, the general susceptibility expression is given as

$$\chi_M = \frac{2Ng^2\beta^2}{KT} \{ [5 \exp(-E_Q/kT) + \exp(-E_{T_1}/kT) + \exp(-E_{T_2}/kT) + \exp(-E_{T_3}/kT)] / [5 \exp(-E_Q/kT) + 3 \exp(-E_{T_2}/kT) + 3 \exp(-E_{T_3}/kT) + 3 \exp(-E_{T_1}/kT) + \exp(-E_{S_1}/kT) + \exp(-E_{S_2}/kT)] \} + p \frac{Ng^2\beta^2}{4kT} + N\alpha \quad (6)$$

where  $p$  is the fraction of possible paramagnetic monomeric Cu(II) impurity and  $N\alpha$  is the temperature-independent paramagnetism. The different-parameters fit of eq 6 was calculated by a nonlinear least square analysis, and the results are given in Table 1. The fit obtained by us for a tetrameric unit is a lot better than the earlier fit by Nag *et al.*<sup>22</sup> However, it is important to note that in the 4-parameter exchange interactions, the intradimer interaction is of much larger magnitude (and, of course, antiferromagnetic in character) as compared to all other binuclear exchange interactions. Among the three minor interactions, one interaction connecting the coppers along an alternating chain is of ferromagnetic origin. This probably also explains the increase in lower temperature susceptibility region, particularly when the monomeric impurity is less than 0.09% and  $N\alpha$  has a low value of  $1.06 \times 10^{-6}$ . It is important to mention that the earlier reported value<sup>22</sup> of  $-816 \text{ cm}^{-1}$  for  $2J$  seems to be too high for observing temperature-dependent chemical shift studies by NMR (*vide infra*).

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**Figure 3.** ORTEP view of the tetrameric unit of macrocyclic aza-amido binuclear copper(II) dimer.

**Table 1.** Exchange Coupling Constants for the Macrocyclic Aza-Amido Complex in the Solid State by the Fitting of SQUID Susceptibility Measurements Using Eq 6

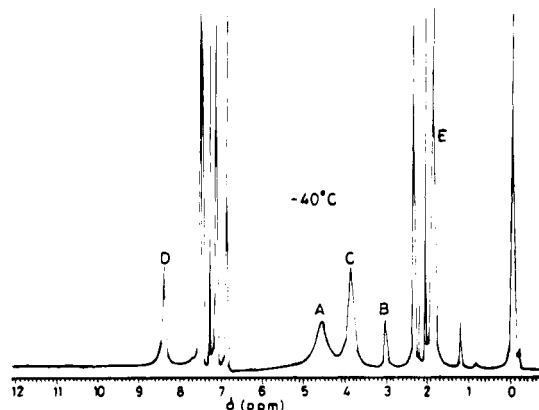
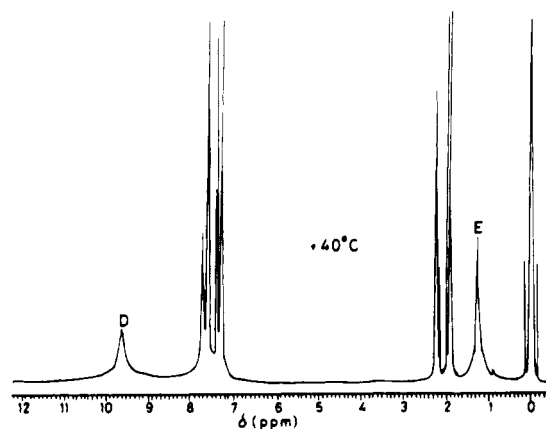
params	value (cm <sup>-1</sup> )	params	value (cm <sup>-1</sup> )
$J_1$	-300	$J_3$	-75.5
$J_2$	37.2	$J_4$	-68.4

**Solution Susceptibility.** Since the dimers are connected in the solid state only through oxygen of H<sub>2</sub>O molecule, the tetranuclear unit shown in Figure 3 is expected to break up leaving the strongly correlated binuclear species intact. Hence, we have measured the susceptibility in solution using the modified Evans method,<sup>19</sup> considered to be a sensitive experiment though our experiment has been restricted only to a small range of temperature (unlike in the solid state) due to higher freezing and low boiling point of *tert*-butyl alcohol as an internal standard.  $\chi_p$  calculated from frequency shift as a function of temperature using eq 1 is then converted into molar susceptibility  $\chi_M$  after the usual correction to  $\chi_M$  is applied.<sup>27</sup>  $\Delta\nu$ ,  $\chi_p$ , and  $\chi_M$  were obtained as a function of temperature. This molar susceptibility is then used to calculate the intradimer exchange coupling ( $-2J$ ) using the Bleaney-Bower expression:

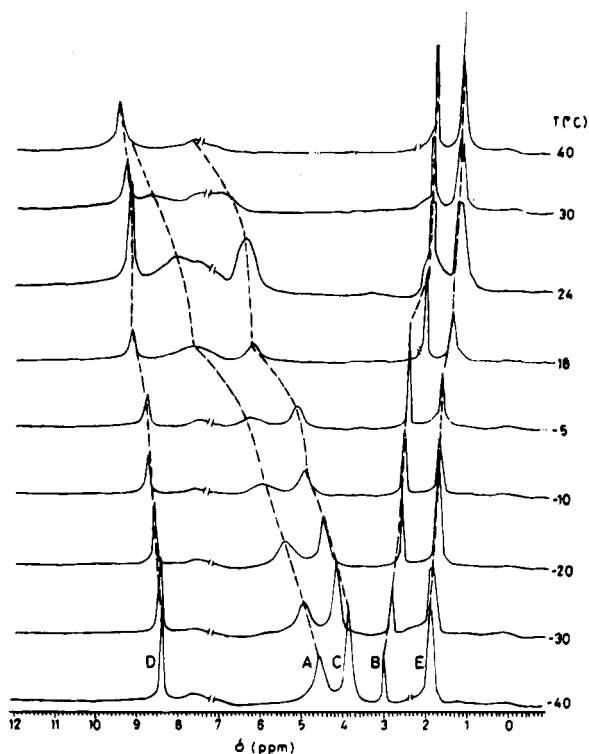
$$\chi_M = \frac{2Ng^2\beta^2}{3kT} [1 + \exp(-2J/kT)]^{-1} \quad (7)$$

The  $2J$  obtained from a nonlinear least square fit of the susceptibility as a function of temperature was found to be  $-225 \text{ cm}^{-1}$ , the magnitude of  $2J$  being less than that in the solid state. This solution value is further corroborated by NMR chemical shift measurements over a wider temperature region.

**Proton NMR Chemical Shift.** Proton NMR spectra of the ligand at room temperature and those of the metal complex, shown in Figure 4, generally gave rise to narrow signals. The spectra of the binuclear complex are shown as a function of temperature in the region  $-40$  to  $+40$  °C. Though there are many peaks, we are able to easily identify the change in chemical shifts as a function of temperature for five protons denoted as A, B, C, D, and E of Figure 1. Figures 5–7 show the temperature dependence of such observed shifts and their line widths. They are all quite sensitive to temperature, the shifts in some cases being as large as 5 ppm over the studied temperature region. It must be noted here that the NMR spectra



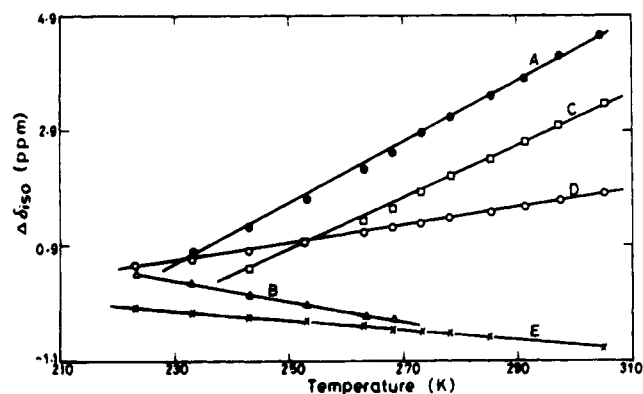
**Figure 4.** <sup>1</sup>H NMR spectra of macrocyclic aza-amido binuclear copper(II) dimer in CDCl<sub>3</sub> at two temperatures, 40 and  $-40$  °C.



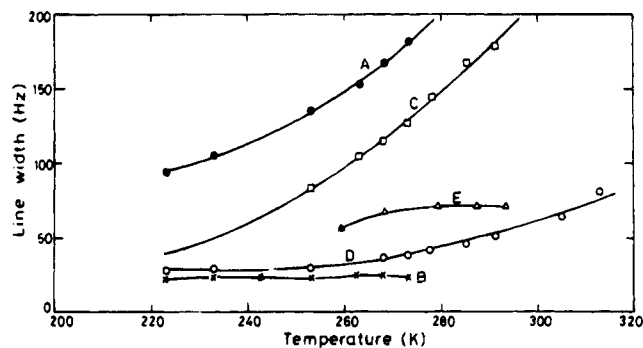
**Figure 5.** Observed <sup>1</sup>H NMR peak positions of different protons (A, B, C, D, and E of Figure 1) with temperature.

of the pure ligand in the same solvent do not show observable shift with temperature. It may be seen that the protons A, C, and D undergo downfield shift with increase in temperature while the other two protons B and E demonstrate upfield shift. The line widths of protons A and C increases with temperature

(27) Carlin, R. L. In *Magnetochemistry*; Springer-Verlag: New York, 1986; p 3.



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



**Figure 7.** Plot of the line widths of different protons (A, C, and D) vs temperature.

and completely broadened out around 303 K while the other three protons were found to be little less sensitive to broadening effects. As was the case with the published work of Maekawa and co-workers,<sup>21</sup> the  $-\text{CH}_2$  group protons adjacent to the coordinated nitrogen ligands seems to broaden quite considerably due to quadrupolar effect from  $^{14}\text{N}$ , *i.e.* protons A and C in our case. They also seem to suffer the maximum temperature-dependent shift indicating the dominance of  $\sigma$  bond effects in exchange coupling. In other words the superexchange occurs via the  $\sigma$  moiety. Our earlier theoretical calculations of exchange coupling constants indicate<sup>10</sup> that  $\sigma$ -bonding is the dominating route for exchange coupling. The antiferromagnetic systems with large couplings of magnitude  $\geq 200 \text{ cm}^{-1}$  give rise to narrowed line width of the order of 100 Hz particularly in the absence of other effects such as that due to quadrupolar relaxation, while the once with smaller coupling may give rise to large line width. If the various contributing factors to the line widths can be separated, the measure of precise line width itself could be used to calculate the magnitude of exchange coupling (*vide infra*).

In solution, the magnetism of the exchange coupled system can be explained by the simple Heisenberg Hamiltonian

$$\mathcal{H} = -2J\hat{S}_1\hat{S}_2$$

with  $S_1 = S_2 = 1/2$ ; the temperature variation of chemical shifts could be used to calculate the exchange coupling using the expression.<sup>16</sup>

$$\Delta\delta_{\text{iso}} = \delta_{\text{complex}} - \delta_{\text{ligand}} = -\frac{g\beta A'}{(\gamma/2\pi)kT} [3 + \exp(-2J/kT)]^{-1} \quad (8)$$

where  $A'$  is the hyperfine coupling due to the observed nuclei with  $S = 1$  level of the magnetically coupled dimer,  $\gamma$  is the gyromagnetic ratio, and  $2J$  is the exchange coupling constant.

**Table 2.** Hyperfine Coupling Constants ( $A'$ ) for Different Protons and Exchange Coupling Constants Obtained from  $\delta_{\text{iso}}$  Using Eq 8 for the Dimer and the Axially Interacted Dimer with Pyridine

protons	dimer		dimer + pyridine	
	$A'$ (Hz)	$-2J$ ( $\text{cm}^{-1}$ )	$A'$ (Hz)	$-2J$ ( $\text{cm}^{-1}$ )
A	63 700	201.2	89 300	206
B	-45 270	206.0		
C	60 330	205.5	54 800	200
D	30 530	200.0	39 600	210
E	-12 240	199.2	-20 300	209

**Table 3.** Exchange Coupling Constants for the Intradimer Interactions Derived from Various Experimental and Theoretical Studies

method	$-2J$ ( $\text{cm}^{-1}$ )
SQUID measurement (solid)	300
susceptibility measurement from Evans method (dimer)	225
isotropic chem shift measurement for the dimer	$202 \pm 3$
isotropic chem shift measurement for the dimer + py	$206 \pm 4$
theoretical calculation from VB studies for the dimer <sup>a</sup>	195
theoretical calculation from VB studies for the dimer + axial N <sup>b</sup>	212
Hatfield empirical formulation <sup>c</sup>	257

<sup>a</sup> Reference 10. <sup>b</sup> Reference 11. <sup>c</sup> Reference 28.

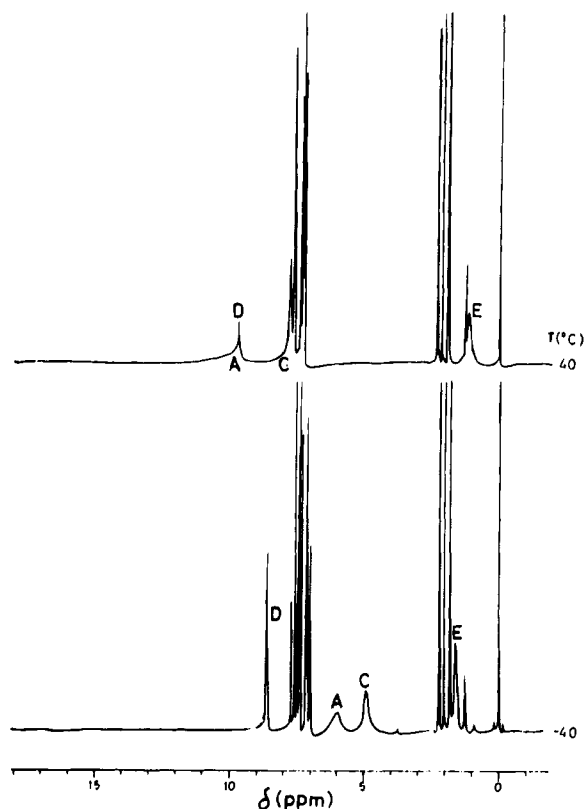
It can be seen that the population distribution in the  $S = 0$  and  $S = 1$  states of the dimer will vary with temperature, and consequently the additional field (with possible changes in sign) due to unpaired electrons of the  $S = 1$  level at various nuclei causes the observed shift as presented by eq 8.

The chemical shift variations observed for each of the five protons were fitted using the above equation which finally yields values for the exchange coupling between the Cu(II) ions as well as hyperfine coupling at each proton site. It is noteworthy to mention that  $2J$  values calculated for all protons lie in the same region  $-202 \pm 3 \text{ cm}^{-1}$  though, of course, the hyperfine coupling is expected to be different for different protons. Table 2 summarizes the values for  $2J$  and  $A'$  obtained from temperature-dependent chemical shifts of different protons. It is highly gratifying to note that all proton chemical shifts yield the same value for exchange coupling, thereby proving that the exchange is the single most contribution to the observed temperature shift as presented in eq 8.

At this point, it is interesting to compare the results on exchange coupling obtained from different methods as summarized in Table 3. While the solid state susceptibility for the intradimer interaction is  $300 \text{ cm}^{-1}$ , the solution susceptibility measurements by both methods give a value of  $200\text{--}225 \text{ cm}^{-1}$ . Usually the magnetic measurements obtained from solid state do not agree with those in solution<sup>20</sup> because of coordination by solvent molecules and loosening of solid state packing accompanied by loss of interdimer interactions and so on. Furthermore, it is pleasant to note that nearly the same  $-2J$  values obtained for intradimer interactions from chemical shifts of five different protons is a clear indication of the correctness of this value in solution. It is further quite interesting to note that the VB methodology based exchange coupling<sup>10</sup> on this system turns out to be  $195 \text{ cm}^{-1}$  in very good agreement with the experimental value which is further corroborated by the simple Hatfield empirical formulation.<sup>28</sup>

We report the effect of a ligand which can axially coordinate to the Cu(II) sites of the dimer. We have carried out the complete temperature-dependent NMR measurements by adding

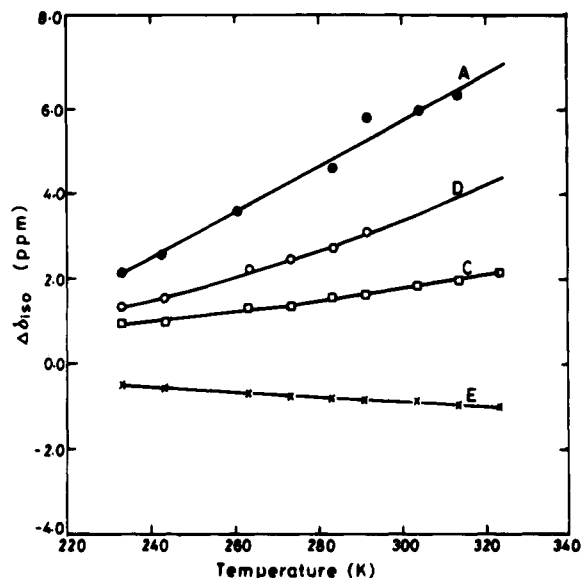
(28) Hatfield, W. E. In *Magneto-structural correlation in Exchange coupled system*; NATO ASI Ser. C; Reidel: Dordrecht, The Netherlands, 1985; Vol. 140, pp 555–602.



**Figure 8.**  $^1\text{H}$  NMR spectra of macrocyclic aza-amido binuclear copper(II) dimer + pyridine (1:2 molar ratio) in  $\text{CDCl}_3$  at two temperatures, 40 and  $-40^\circ\text{C}$ .

deuterated pyridine to the same dimer in  $\text{CDCl}_3$  in the molar ratio 2:1 to monitor the effect of axial coordination and hence its effect on the exchange coupling and spin densities. That axial coordination is effected and noted by two observations: (i) Less than 1% nondeuterated pyridine present in the deuterated sample shows minor shifts. (ii) The A, B, C, D, and E protons of the dimer undergo temperature-dependent shifts, but the absolute chemical shift positions at any given temperature for these protons are much different from those for the pure dimer as revealed in Figure 8 (cf. Figure 4 for pure dimer) shown for  $-40$  and  $+40^\circ\text{C}$ . However, we found it difficult to identify the chemical shift position of B proton at most temperatures. The shifts of all other protons as a function of temperature is shown in Figure 9. A fit using eq 8 indicates that the exchange coupling has now increased only by a small extent to  $206 \pm 4$ . This is in agreement with our theoretical finding by diagrammatic VB approach<sup>11</sup> that there is only a small increase in exchange coupling by axial interaction since the d-orbital involved in such exchange coupling is the in-plane  $d_{x^2-y^2}$ . This minor perturbation, however, will change the spin density at the coordinating sites and hence the change in the absolute positions of the chemical shift of these protons as compared to that of a pure dimer. All results are found in Tables 2 and 3.

A comment on the origin of different hyperfine couplings on protons A, B, C, D, and E will be in order. This electron-nucleus hyperfine interactions constant  $A'_i$  can have contributions from either contact or dipolar interaction or both. Contact shift due to spin transmittal through the  $\sigma$  bonds predicts negative spin densities at B and E protons and positive spin densities at the protons A, C, and D as it is assigned now and hence the  $A'_i$ 's with their respective signs. Also, the magnitude of spin densities due to contact shift will steadily decrease as a function of bonds away from the first coordination sphere of the metal atom in which the Cu-N and Cu-O have positive spins from the excited triplet states. If we use this rationale, A and C will



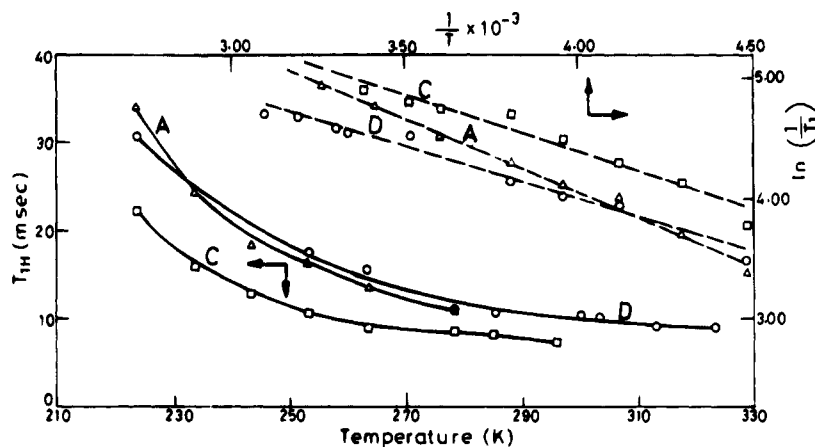
**Figure 9.** Plot of observed  $^1\text{H}$  NMR chemical shifts ( $\delta_{\text{iso}}$ ) for different protons (A, C, D, and E) with temperature of macrocyclic aza-amido binuclear copper(II) dimer with pyridine (1:2 molar ratio) as a function of temperature.

have the largest positive spin densities, D will have the next largest positive spin densities (due to a combination of transmittal of spins through the same number of bonds from two coordinating atoms, namely, N and O), and the proton B will then have a negative spin density smaller in magnitude than those on A and C. All this is in agreement with the experimental findings but the prediction of positive sign for the spin density in the proton E, is contrary to the experimental findings which could be attributed to contributions from the dipolar part which could be larger in magnitude than the contact part and of opposite sign. We, however, have no way to confirm it since the calculation a priori of these quantities or separation of the values into the two components can not be done easily for this molecule.<sup>29</sup> So it is summarized that at least for four protons A, C, D, and B the origin of the shifts may be mainly due to isotropic contact shift while for the proton E both processes may have contributed. This is particularly so since the unpaired electron originates from  $d_{x^2-y^2}$  orbitals of Cu(II) centers with the spin density getting delocalized and reaching the various protons through  $\sigma$  bonds. In view of this no special efforts were made to separate out the isotropic and dipolar contributions since the later may not have contributed to more than 10% of the total shift.

**Relaxation Mechanism.** We have investigated the NMR proton relaxation in this bimetallic exchange coupled system since in principle the understanding of nuclear relaxation induced by paramagnetic metal ions can provide information on the structure and, more so, on the time-dependent phenomena or the mechanism of it concerning the resonating nucleus. We could study through the inversion recovery method the temperature dependence of  $T_1$ .

The effect of two isolated metal atoms on a nucleus at a distance  $d_1$  and  $d_2$  from two metals is the sum of two separate relaxing effects. When the metal ions are magnetically coupled through isotropic exchange ( $2J\mathbf{S}_1\cdot\mathbf{S}_2$ ) the effect on the same nucleus would be the sum of the effect of two ions modulated by the resulting wave functions. In this type of interactive

(29) Bertini, I.; Drago, R. S. In *ESR and NMR of Paramagnetic Species in Biological and Related Systems*; Reidel Publishing Co.: Dordrecht, The Netherlands, 1980; pp 55-87.



**Figure 10.** Plot of relaxation time ( $T_1$ ) vs temperature ( $T$ ) and also a plot of  $\ln(1/T_1)$  vs  $1/T$  for protons A, C, and D of macrocyclic aza-amido binuclear copper(II) dimer as shown in Figure 1.

system the resulting Hamiltonian is represented as follows:<sup>30-33</sup>

$$\mathcal{H} = \beta B(S_{1z\beta_1} + S_{2z\beta_2}) - 2J[S_{1z}S_{2z} + 0.5(S_{1+}S_{2-} + S_{1-}S_{2+})] \quad (9)$$

Hence Bertini and co-workers<sup>30-33</sup> have derived the corresponding relaxation rates for high temperature limit as

$$T_{1M}^{-1} = K/20 \left[ 3(1 + C_1^2 + C_2^2 - 2C_1C_2) \frac{\tau_c}{1 + \omega_I^2 \tau_c^2} + 6C_1C_2 \left( \frac{\tau_c}{1 + (\omega_I + \omega_{2,3})^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_I - \omega_{2,3})^2 \tau_c^2} \right) + 6C_1 \left( \frac{\tau_c}{1 + (\omega_I + \omega_{1,3})^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_I + \omega_{2,4})^2 \tau_c^2} \right) + 6C_2 \left( \frac{\tau_c}{1 + (\omega_I + \omega_{1,2})^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_I + \omega_{3,4})^2 \tau_c^2} \right) + C_1 \left( \frac{\tau_c}{1 + (\omega_I + \omega_{1,3})^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_I - \omega_{2,4})^2 \tau_c^2} \right) + C_2 \left( \frac{\tau_c}{1 + (\omega_I - \omega_{1,2})^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_I - \omega_{3,4})^2 \tau_c^2} \right) \right] \quad (10)$$

where  $C_1 = 0.5(1 + Z_2/R)$ ,  $C_2 = 0.5(1 - Z_2/R)$ ,  $\omega_{1,3} = z_1 - J + R$ ,  $\omega_{2,3} = 2R$ ,  $\omega_{1,2} = z_1 - J + R$ ,  $\omega_{2,4} = z_1 - J + R$ ,  $\omega_{3,4} = z_1 + J - R$ ,  $z_1 = 1/2\hbar(g_1 + g_2)\beta B$ ,  $z_2 = 1/2\hbar(g_1 - g_2)\beta B$ ,  $K = \gamma_N^2 \beta^2 g^2 r^{-6}$ ,  $R = 1/\hbar \sqrt{z^2 + J^2}$ , and  $\omega_I = 2\pi\nu_0$ .  $\nu_0$  corresponds to spectrometer frequency, and  $\tau_c$  is the correlation time. All others are well-known parameters. It is important to note that susceptibility increases with temperature for antiferromagnetically coupled systems. As the susceptibility increases the protons relax fast due to paramagnetic effect. The above eq 10 is applicable to cases where  $|2J| < kT$ . Though in case of our bimetallic system  $|2J| \leq kT$  in the studied temperature region, we have applied the equation with a certain amount of caution because it is felt that  $T_1$  here is dominated by electron-nuclear dipolar coupling modulated by exchange. This is

(30) (a) Bertini, I.; Luchinat, C.; Mancini, M.; Spina, G. In *Magneto-structural correlation in Exchange coupled system*; NATO ASI Ser. C; Reidel: Dordrecht; The Netherlands, 1985; Vol. 140, pp 421-462. (b) Bertini, I.; Luchinat, C.; Mancini, M.; Spina, G. *J. Magn. Reson.* **1985**, *63*, 56.

(31) Bertini, I.; Lanini, G.; Luchinat, C. *Inorg. Chem.* **1984**, *23*, 2730.

(32) Bertini, I.; Owens, C.; Luchinat, C.; Drago, R. S. *J. Am. Chem. Soc.* **1987**, *109*, 5208.

(33) Banci, L.; Bertini, I.; Luchinat, C. *Struct. Bonding* **1990**, *72*, 113.

**Table 4.** Variation of Correlation Time for Different Protons at Various Temperatures

temp (K)	correlation time ( $\tau_c$ ) $\times 10^8$ s		
	A	C	D
223	1.217	0.519	0.281
233	0.873	0.369	
243	0.652	0.3536	0.172
253	0.586	0.306	0.155
263	0.487	0.246	0.136
278		0.201	0.081
285		0.193	0.081
300			0.079
313			0.060

obvious from the fact that the most important quantity in eq 10 is  $K$ , which represents the electron-nuclear dipolar coupling. Hence  $T_{1M}^{-1}$  should automatically be related to the hyperfine coupling measured from temperature dependent chemical shift. As a result, the protons A, C, and D are expected to be drastically affected by relaxation rate. Hence, we have measured the relaxation time  $T_1$  only for the protons A, C, and D. Furthermore, the signals of the other protons overlap considerably on the resonances of other protons and hence no attempt has been made to measure  $T_1$  for B and E protons.

The temperature dependence of  $T_1$  for these protons are shown in Figure 10. Also shown in the same Figure 10 is the plot of  $\ln(1/T_1)$  vs  $1/T(K)$  to get an insight into activation energies of the processes controlling nuclear relaxation. The activation energies for these protons A, C, and D have been estimated from the latter plot as 10.2, 9.79, and 7.26 kJ/mol. The order of these for the exchange-coupled systems under study seems to be reasonable as similar values have been derived for such exchange-coupled systems.<sup>33</sup> This probably indicates that eq 10 can be employed with reasonable expectation, if not with great accuracy, for cases of  $|2J| \leq kT$ . Furthermore,  $\tau_c$  values calculated from eq 10 are found in Table 4. The values obtained here are in reasonable agreement with similar values reported for some exchange-coupled systems.<sup>32</sup> In addition, the observation  $\tau_c(A) > \tau_c(B) > \tau_c(D)$  for any given temperature can be understood if we note (i) the protons are closer to a carbonyl group and hence amenable to weak hydrogen-bonding as compared to the other electronically similar C protons and (ii) the D protons are attached to the freely rotating C-H bond. Also, the correlation times calculated for these protons are in tune with the general broadening features observed in the temperature-dependent NMR spectra, thereby lending support to the derivation of  $\tau_c$  using eq 10 though not under perfect high temperature limit condition. It may be necessary to make

another comment on the temperature dependence of the correlation time for these nuclei. The correlation time for nuclear relaxation at room temperature is more likely to be dominated by the rotational correlation time while, lowering the temperature, it becomes determined by the electron relaxation of copper.

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