Synthesis, Structure, Magnetic Properties, and ^{1}H NMR Studies of a Moderately Antiferromagnetically Coupled Binuclear Copper(II) Complex

Anbanandam Asokan, Babu Varghese, and Periakaruppan T. Manoharan*,†

Department of Chemistry and Regional Sophisticated Instrumentation Centre,
Indian Institute of Technology Madras, Chennai 600036, India

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A binuclear Cu(II) complex of $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$ (HAP = 3-amino-1-propanol; IPA = 2-hydroxy-5-methylisophthalaldehyde) has been synthesized and characterized by X-ray crystallography, by solid state magnetic susceptibility, and in solution by ^{1}H NMR studies. The binuclear copper(II) complex crystallizes in the orthorhombic system, space group *Pbcn*, $a = 27.9972(9)$ Å, $b = 8.8713(3)$ Å, $c = 19.5939(6)$ Å, and $Z = 8$. The two copper(II) atoms in this binuclear Cu(II) complex are bridged by the oxygen atoms of the phenolate and hydroxy groups. The axial position at one Cu atom is occupied by a water molecule while another Cu has weak interaction with a perchlorate group. The coordination geometries around the two Cu atoms are distorted square pyramid and square planar. The solid state magnetic susceptibility measurement reveals a moderate antiferromagnetic exchange interaction between the two Cu atoms with a $-2J$ value of 113 ± 9 cm^{-1}. The variable-temperature ^{1}H NMR studies in CD_3CN solution show that the observed relatively sharp hyperfine shifted signals follow a Curie behavior. The exchange coupling constant ($-2J$) obtained in solution by using chemical shift as a function of temperature also reveals a moderate antiferromagnetic exchange interaction between two Cu(II) ions. An analysis of the relaxation data shows that the reorientational correlation time (τ_c) is dominated probably by a combination of electronic relaxation time τ_s and rotational correlation time (τ_r) due to an exchange-modulated dipolar mechanism for this moderately antiferromagnetically coupled binuclear copper(II) system.

Introduction

Copper(II) complexes with amino alcohol ligands were investigated initially in the 1960s.[1,2] Most of the investigations then focused on the correlation of structural features with magnetism, especially through spin−spin exchange mechanisms.[3−6] Recently there has been a renewed research interest in copper(II) complexes with amino alcohol as ligands,[7,8] prompted by possible applications to biochemistry and material chemistry.[9]

In addition to single-crystal X-ray structural information and solid state magnetic susceptibility studies, the characterization of binuclear Cu(II) complexes in solution is of significance. Although NMR spectroscopy has been successfully used to investigate the structural and bonding properties of metal complexes,[10] NMR studies of paramagnetic copper(II) complexes are fewer due to their inherent slow electronic relaxation time, leading to broadened signals.[11] On the other hand, antiferromagnetically coupled copper(II) complexes are expected to give relatively narrow NMR signals.[12−15] However, there are still few reports that demonstrate the usefulness of NMR spectra of binuclear Cu(II) complexes in solution.[16−19]

Recently we have drawn our attention to the study of interactions between paramagnetic metal ions in coupled systems by using ^{1}H NMR spectroscopy.[17] ^{1}H NMR spectroscopy has recently been employed as a tool for the determination of the molecular and electronic structures of binuclear Cu(II) complexes.[18−21] It is well-known that antiferromagnetically coupled dicopper(II) centers have a singlet ($S = 0$) ground state and a triplet ($S = 1$) first excited state with an energy difference denoted by the exchange constant $-2J$.[12] The hyperfine shifted

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† E-mail: ptm@magnet.iitm.ernet.in. Fax: 91-44-2350509.

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NMR signals observed for these binuclear systems are due to the proximity of the diamagnetic ground state and the first excited paramagnetic state. Since the population distribution between these two levels is dependent upon temperature as well as the magnitude of $-2J$,[22] it follows that the temperature dependence of hyperfine shifted ^{1}H NMR signals should correlate with the magnitude of the antiferromagnetic coupling interactions between the two Cu(II) ions.[18]

The hyperfine shifted resonances and their nuclear relaxation times are very sensitive to both the distance from the proton to the paramagnetic metal ion and the orientation of the proton to the paramagnetic metal ion. Thus, a wealth of structural and magnetic information can be obtained on the local environment of the paramagnetic center. Here, we report the synthesis, structure, magnetic properties, and ^{1}H NMR studies of a binuclear Cu(II) complex with an amino alcohol ligand. On the basis of the analysis of the ^{1}H NMR spectra, the structure in solution is discussed, which is simultaneously compared with the X-ray crystallographic structure determined and reported here. We have made an attempt to compare the exchange coupling constant ($-2J$) measured both in the solid by SQUID measurement and in solution (^{1}H NMR) by chemical shifts observed as a function of temperature. We have also addressed a possible mechanism for shortening of the electronic relaxation time for this moderately antiferromagnetically coupled binuclear copper(II) system by combining the signal assignment with X-ray crystallographic results and T_1 values. Our data indicate that ^{1}H NMR spectroscopy can be used as an excellent tool to probe the binuclear Cu(II) systems in solution in line with some of the more recent work.[18,19]

Experimental Section

CAUTION! Perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

Preparation of [(Cu$_2$(HAP)$_2$IPA)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O. The title compound was prepared by the method of Mandal and Nag.[23] A mixture of 2-hydroxy-5-methylisophthalaldehyde (IPAH) (0.164 gm, 1 mmol), NaOH (0.04 gm, 1 mmol), and water (5 cm^3) was ground to a paste in a mortar. This was added with stirring to boiling water (10 mL), whereupon a clear yellow solution was obtained. A second solution of Cu(ClO$_4$)$_2$·6H$_2$O (0.93 gm, 2.5 mmol) and 3-amino-1-propanol (HAP) (0.225 gm, 3 mmol) in water (50 cm^3) was added to the first solution and boiled. The resulting deep green solution was allowed to concentrate on a hot plate. When the volume of the solution had reduced to ca. 25 cm^3, it was filtered hot. The filtrate was allowed to cool at ambient temperature and the green crystalline product collected by filtration. The product was further recrystallized from boiling water and dried over CaCl$_2$.

Physical Measurements. ^{1}H NMR. A ^{1}H NMR spectrum was recorded on a JEOL JNM-GSX 400 MHz FT-NMR machine using a 7.2 μs 90° pulse width, a 100 kHz spectral width, and a 3.2 s delay between 90° pulses. Chemical shifts (ppm) are reported with respect to tetramethylsilane (TMS). Experiments were carried out in the temperature range 238−348 K. A 99.9% deuterated acetonitrile solution with addition of a small amount of TMS was used. Temperature variation was carried out by a JEOL variable-temperature controller.

Relaxation Measurement. The longitudinal relaxation time (T_1) was measured by the inversion recovery technique, and it consists of the pulse sequence

$$(180° - \tau - 90° - \mathrm{AQ} - D)_n$$

where AQ is the acquisition time and D is the delay time to allow equilibrium to be reached. The value of magnetization varies from $-M_z(\infty)$ when τ is zero to $M_z(\infty)$ when τ is 5 times higher than T_1 and τ is the variable time delay between two pulses. It is possible to relate magnetization to the T_1 value by the expression

$$M_z(\tau) = M_z(\infty)[1 - 2\exp(-\tau/T_1)] \tag{1}$$

T_1 therefore can be calculated by least-squares fit analysis of the experimental data as a function of τ.

Solid State Susceptibility Measurement. Solid state magnetic susceptibility in the temperature range 2−260 K was obtained with a Metronique Ingegnerie MSO3 SQUID magnetometer operating with an applied magnetic field of 1 T. The data were corrected for the sample holder contribution and for the diamagnetic contribution estimated through Pascal's constant.

X-ray Crystallography. Crystal Data Collection and Refinement. Green crystals of [(Cu$_2$(HAP)$_2$IPA)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O suitable for X-ray diffraction studies were obtained by slow evaporation of an aqueous solution of the complex. The diffraction intensities of an approximately 0.3 × 0.2 × 0.2 mm crystal were collected using an Enraf-Nonius CAD4 single-crystal diffractometer with Mo Kα radiation (0.710 73 Å). The cell parameters were obtained by the method of short vectors followed by least-squares refinement of 25 randomly chosen higher angle reflections. The stability of the crystal during data collection was checked by monitoring the intensities of two standard reflections after every 1 h of data collection. No significant variation of intensity could be noted. The intensity data were corrected for Lorentz, polarization, decay, and absorption (ψ-scan) effects using the computer program MolEN.[24] A total of 3813 reflections were collected in the range $4° < 2\theta < 50°$ of which 2950 reflections with $I > 2\sigma(I)$ were used for the structure determination. The structure was solved by a direct method using the computer program SHELXS-86[25] and refined using the program SHELXL-93.[26] All hydrogen atoms were fixed through the riding model procedure of SHELXL-93. The structure was refined by a full-matrix least-squares technique. The final residual factors were $R(F) = 0.0586$, $R_w(I) = 0.1677$, respectively. The final difference map was featureless. A summary of the crystal and diffraction data are given in Table 1, and atomic coordinates are given in Table 2.

Results and Discussion

Description of the Structure of [(Cu$_2$(HAP)$_2$IPA)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O. The ZORTEP[27] (30% probability thermal ellipsoid) representation of the [(Cu$_2$(HAP)$_2$IPA)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O complex is shown in Figure 1, and selected bond distances and bond angles around the Cu atoms are given in Table 3. The structure consists of two copper centers bridged by one phenoxy atom and one hydroxy oxygen atom in a relatively symmetric fashion resulting in comparable Cu(1)−O(1), Cu(2)−O(1), Cu(1)−O(2), and Cu(2)−O(2) bond distances. These bond lengths are in close agreement with those observed in other μ-phenoxo- and μ-hydroxo-bridged dicopper(II) complexes.[17b] The presence of the bridging OH group is brought out by locating the hydrogen atom H(2) at a distance of 0.996 Å. In addition to these bridging atoms, there are one imino nitrogen atom and one alcoholic oxygen atom; both are terminal ligands completing the CuNO$_3$ plane. The Cu−Cu separation is 2.9708 (12) Å, and the oxygen bridge angles from the azomethine unit Cu(1)−O(1)−Cu(2) and from the alcoholic unit Cu(1)−O(2)−Cu(2) are slightly different: 100.1(2)° and 98.4(2)°, respectively. The relatively small observed Cu−Cu

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Table 1. Crystal Data and Structure Refinement for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$

empirical formula	$C_{15}H_{26}Cl_2N_2Cu_2O_{14}$
fw	656.36
temp	293(2) K
wavelength (λ)	0.71073 Å
cryst syst	orthorhombic
space group	*Pbcn* (No. 9)
unit cell dimens	$a = 27.9972$ (9) Å
	$b = 8.8713$ (3) Å
	$c = 19.5939$ (6) Å
	$\alpha = 90°$
	$\beta = 90°$
	$\gamma = 90°$
volume	4866.6 (3) Å^3
Z	8
density (calcd)	1.792 g cm^{-3}
abs coeff (μ)	20.38 cm^{-1}
R (F_o)[a]	R1 = 0.0586
R_w (F_o^2)[b]	wR2 = 0.1677

[a] $R(F) = \sum||F_o| - |F_c||/\sum F_o$. [b] $R_w(I) = [\sum[W[|F_o|^2 - |F_c|^2]]^2/\sum(W|F_o|^2)^2]^{1/2}$ where $W = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 2.6P]$ and $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$[a]

atom	*x*	*y*	*z*	*U*(eq)
Cu(1)	1289(1)	360(1)	7306(1)	43(1)
Cu(2)	651(1)	1842(1)	8315(1)	42(1)
Cl(1)	1466(1)	−5808(3)	6374(2)	70(1)
Cl(2)	850(6)	2227(2)	3542(1)	68(1)
O(1)	1326(2)	1642(6)	8101(3)	41(1)
OW(1)	493(3)	2713(10)	1336(5)	84(2)
OW(2)	4498(3)	906(8)	2698(4)	89(2)
O(2)	608(2)	657(6)	7463(3)	44(1)
O(3)	−34(2)	1523(7)	8515(3)	60(2)
O(4)	1158(2)	−739(6)	6461(3)	56(2)
O(5)	889(4)	3536(10)	3916(6)	141(4)
O(6)	795(3)	953(9)	3977(4)	85(2)
O(7)	1252(3)	2010(8)	3107(4)	80(2)
O(8)	424(3)	2294(11)	3104(5)	111(3)
O(9)	1486(4)	−7329(9)	6470(5)	130(4)
O(10)	1027(4)	−5316(12)	6172(10)	208(8)
O(11)	1561(5)	−5110(14)	6997(7)	163(5)
O(12)	1806(5)	−5248(15)	5950(7)	188(6)
N(1)	785(2)	2989(7)	9143(3)	43(2)
N(2)	1968(2)	−77(8)	7311(3)	49(2)
C(1)	−277(4)	1724(14)	9138(5)	72(3)
C(2)	56(4)	2187(13)	9705(4)	70(3)
C(3)	372(3)	3498(10)	9552(4)	57(2)
C(4)	1197(3)	3388(8)	9330(4)	44(2)
C(5)	1654(3)	2959(8)	9041(4)	42(2)
C(6)	2066(3)	3436(10)	9389(4)	52(2)
C(7)	2518(3)	3014(10)	9198(4)	58(2)
C(8)	2266(3)	2094(9)	8638(4)	52(2)
C(9)	2168(3)	1590(8)	8266(4)	43(2)
C(10)	1713(3)	2044(8)	8448(3)	40(2)
C(11)	2266(3)	514(9)	7722(4)	51(2)
C(12)	2138(4)	−1259(12)	6831(5)	69(3)
C(13)	1992(4)	−851(14)	6120(5)	73(3)
C(14)	1486(3)	−1227(11)	5939(4)	59(2)
C(15)	2954(4)	3563(16)	9578(6)	83(3)
H(2)	443(4)	−318(4)	7552(2)	80(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

distance and bond angles around Cu(1)−O(1)−Cu(2) and Cu(1)−O(2)−Cu(2) are comparable to those of the earlier reported binuclear Cu(II) complexes of thistype.[28]

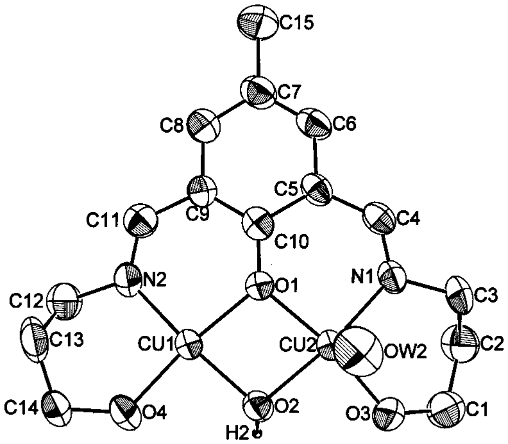

Figure 1. ZORTEP representation for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$ with hydrogen and perchlorate atoms are omitted (30% probability thermal ellipsoids).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$

	Bond Distances		
Cu1−O1	1.931(5)	Cu2−O1	1.943(5)
Cu1−O2	1.949(5)	Cu2−O2	1.976(5)
Cu1−O4	1.956(5)	Cu2−O3	1.977(6)
Cu1−N2	1.938(7)	Cu2−N1	1.953(6)
Cu1−Cu2	2.9708(12)	Cu2−OW2#1[a]	2.372(7)
O2−H2	0.996(8)		
	Bond Angles		
O2−Cu1−N2	93.5(2)	O1−Cu2−N1	92.3(2)
O1−Cu1−O2	81.1(2)	O1−Cu2−O2	80.1(2)
N2−Cu1−O2	169.9(3)	N1−Cu2−O2	172.4(2)
O1−Cu1−O4	170.4(2)	O1−Cu2−O3	166.5(2)
N2−Cu1−O4	95.1(3)	N1−Cu2−O3	95.5(2)
O2−Cu1−O4	91.0(2)	O2−Cu2−O3	91.9(2)
Cu1−O1−Cu2	100.1(2)	Cu1−O2−Cu2	98.4(2)
O2−O1−C10	175.3(5)	O1−O2−H2	125.7(6)
	Dihedral Angles		
Cu2−O2−Cu1−O1	−3.9(6)	O2−Cu1−O1−Cu2	−175.9(6)

[a] #1 $0.5 - x$, $0.5 - y$, $0.5 + z$.

Table 4. Least-Squares Planes of $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$

atom	deviation from mean plane (Å)
	Equation of Plane 1 (O1, O2, N2, O4)
	$0.1021X + 0.8262Y - 0.5540Z - 7.3272 = 0$
O1	0.1167
O2	−0.1181
N2	−0.1022
O4	0.1036
Cu1	0.0294
	Equation of Plane 2 (O1, O2, O3, N1)
	$-0.1365X + 0.8464Y - 0.5147Z - 7.3542 = 0$
O1	−0.0896
O2	0.0886
O3	−0.0767
N1	0.0777
Cu2	0.1027

The Cu(2) atom is five coordinated in a distorted square pyramid to one nitrogen and three oxygen atoms from amino alcohol, phenoxy, hydroxy, and the oxygen of water molecule occupying the apex of the pyramid. The length of the Cu(2)−O(water) bond, 2.372 Å, shows that the interaction Cu(2)−OH_2 suggests the coordination of water molecule leading to a square pyramid geometry with the Cu(2) atom being slightly out of the mean plane O(1), O(2), O(3), N(1) by 0.1027 Å (see Table 4). The Cu(1)−O(1), Cu(2)−O(1), Cu(1)−O(2), and Cu(2)−O(2) bond distances are 1.931, 1.949, 1.943, and 1.976 Å, respectively. These values are similar to the ones found in most

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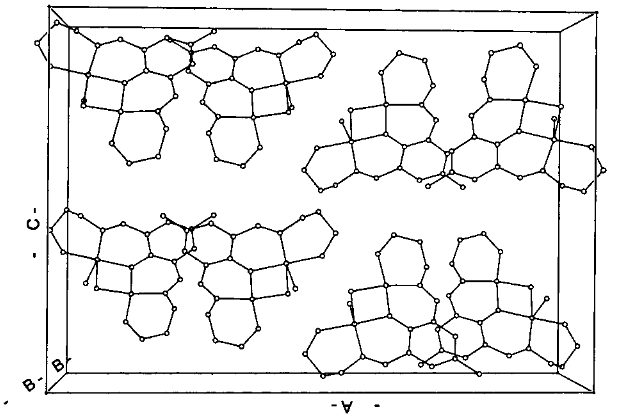

Figure 2. Unit cell packing diagram for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2{\cdot}H_2O$ along the *ac* plane.

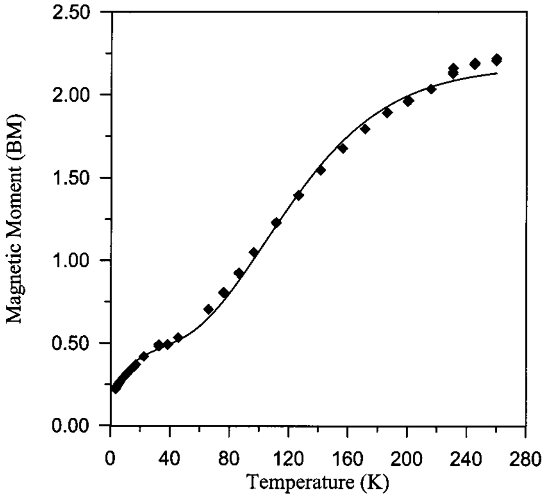

Figure 3. Plot of magnetic moment vs temperature for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)]$ $(ClO_4)_2{\cdot}H_2O$ in the solid state with (◆) representing the experimental data and the line representing the theoretical simulation using the expression in eq 2.

of the Cu(II) binuclear complexes with the Cu_2O_2 framework. The Cu(1) is four coordinated to a phenoxy oxygen, hydroxy oxygen, imino nitrogen, and alcoholic oxygen. In contrast with Cu(2), Cu(1) is located in a distorted square planar environment. The deviation of Cu(1) from the mean plane O(1), O(2), O(4), N(2) is 0.0294 Å (see Table 4). The dihedral angles Cu(2)−O(2)−Cu(1)−O(1) and O(2)−Cu(1)−O(1)−Cu(2) indicate that the Cu(II) binuclear frame Cu_2O_2 is nearly planar. The O(2)−H(2) bond is out of the Cu_2O_2 planar framework (125.7°).

The shortest Cu−Cu distance between the molecule is ∼5.6 Å, which could lead to weak interdimer interactions. There are very few van der Waal contacts between the molecules. The interaction of molecules with anions and water molecules present in the lattice are responsible for crystal stability and packing forces. Figure 2 shows the packing diagram of molecules projected along the *ac* plane.

Magnetic Properties. The variable-temperature magnetic susceptibility studies on $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2{\cdot}H_2O$ were carried out in the temperature range 2−260 K. The variable-temperature data was fitted to the modified Bleaney−Bowers equation[29] (eq 2) using the Heisenberg (isotropic)

$$\chi_m = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-\rho)+\frac{Ng^2\beta^2}{4kT}\rho + N_\alpha \quad (2)$$

exchange Hamiltonian ($H = -2JS_1{\cdot}S_2$) for two interacting $S = {}^1/_2$ centers, where $2J$ is the energy difference between the singlet and triplet states, χ_m is expressed per mole of copper atoms, N_α is the temperature independent paramagnetism, and ρ is the fraction of monomeric impurity. This procedure treats the complex as having a ground state singlet with a low-lying triplet state. A simplex curve-fitting routine[30] was used to determine the parameters g and $2J$. The best fit of the susceptibility data to the Bleaney−Bowers eq (eq 2) gave $g = 2.17$ (±0.02), $-2J = 113$ (±9.0), $N_\alpha = 120.0 \times 10^{-6}$ cgsu/mol, $\rho = 0.064$, and the least-squares error (R) is equal to 2.67×10^{-3}.

A plot of effective magnetic moment versus temperature is given in Figure 3. From this figure it is clear that the observed and calculated magnetic moment μ_{eff} decreases from a value of 2.20 μ_B at 260 K to 0.22 μ_B at 2 K, indicating a moderate intramolecular antiferromagnetic exchange interaction present in this dicopper(II) system. A small increase in the magnetic moment at 40 K is due to the presence of a small amount of monomeric impurity.

The antiferromagnetic behavior of the binuclear complexes is attributed to spin−spin interaction occurring via the superexchange pathway provided by phenoxy bridging and hydroxy bridging, rather than a direct metal−metal interaction. The Cu−Cu distance in our dicopper(II) system is estimated to be 2.97 Å. This separation generally rules out any significant amount of direct Cu−Cu interaction. The observation that hydroxo bridges and phenoxo bridges provide more pathways for spin−spin interaction has been well characterized in the dimeric Cu(II) systems studied primarily by Hatfield[31] and Hodgson.[32]

Magnetostructural Correlation. Although many factors undoubtedly influence the value of $-2J$ in compounds containing the Cu_2O_2 system, the Cu−O−Cu angle is currently regarded as being one of the most important, partly because theoretical arguments predict ferromagnetic coupling at 90° and antiferromagnetic coupling at 180°, presumably with a continuous variation in between. A considerable body of experimental evidence has been accumulated bearing this out, and indeed, for bis(μ-hydroxo) bridged complexes a linear relationship exists between exchange integral ($-2J$ increasing) and the Cu−O−Cu bridge angle (increasing). However, for single μ-hydroxo bridged species there does not appear to be any linear relationship between exchange integral and Cu−O−Cu bridge angle in the few structurally documented examples, which of course are not structurally related. Though the number of binuclear Cu(II) complexes belonging to this (system reported here) class of spin system is very small, we have made an attempt to compare the exchange coupling constant value of this binuclear system with those of a few earlier reported systems, which are given in Table 5.

The NMR Spectra and Isotropic Shift. The representative proton NMR spectrum of the binuclear copper(II) complex at room temperature (25 °C) is shown in Figure 4. This dicopper(II) complex exhibits relatively sharp hyperfine shifted signals spanning from 66 to −72 ppm. The spectrum of $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2{\cdot}H_2O$ was monitored by variable-temperature measurements (−35 to 75 °C). We have observed that some proton chemical shifts are quite sensitive to temperature;

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(29) Bleaney, B.; Bowers, K. *Proc. R. Soc. London Sect. A* **1952**, *214*, 451.

(30) Chandramouli, G. V. R.; Balagopalakrishna, C.; Rajasekaran, M. V.; Manoharan, P. T. *Comput. Chem.* **1996**, *20*, 353.

(31) Hatfield, W. E. *ACS Symp. Ser.* **1975**, *5*, 108.

(32) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173.

Table 5. Magnetic and Structural Parameters (Bond Distances, Å; Bond Angles, deg) for Binuclear Cu(II) Complexes

	compd[a]	Cu−Cu (Å)	Cu−O−Cu (deg)	−2*J* (cm^{-1})	ref
1	$[Cu_2PAP(OH)Cl_3]\cdot 1.5H_2O$	3.001	100.1	201	44
2	$[Cu_2PAP(OH)Br_3]\cdot 1.5H_2O$	3.010	101.3	191	44
3	$[Cu_2L(OH)](ClO_4)_2\cdot H_2O$	3.57	141.7	120	45
4	$[Cu(deapro)Cl]_2$	2.903	97.9	149	46
5	$[Cu(picpro)H_2O]_2\cdot 2H_2O$	2.948	98.3	128	47
6	$[Cu(OH)(eaep)]_2(ClO_4)_2$	2.917	99.2	130	48
7	$[Cu_2(HAP)_2(IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$	2.9708	98.4	113 ± 9	this work

[a] PAP = 1,4-di(2′-pyridyl)aminophthalazine; L = 30-membered N_6O_4 macrocyclic Schiff-base ligand; deapro = 1-diethylamino-2-propanolate; picpro = *N*-(picolinoyl)-3-amino-1-propanol; eaep = bis[2-(2-ethylaminoethyl)pyridine]; HAP = 3-amino-1-propanol; IPA = 2-hydroxy-5-methylisophthalaldehyde.

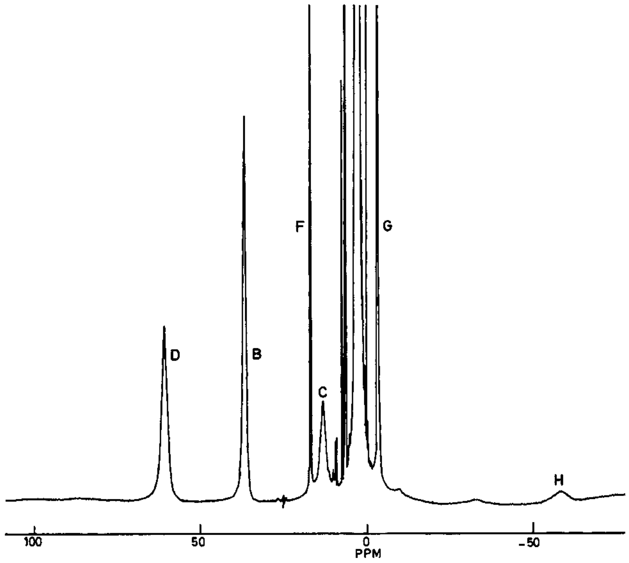

Figure 4. ^1H NMR spectrum for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$ in CD_3CN solution at room temperature.

the shift as a function of temperature for proton D is 15 ppm and for proton B is 9 ppm in the above said temperature region. All other protons reveal much lower shifts of around 5 ppm over the studied temperature region. It must be noted here that the variation of the temperature for the diamagnetic pure ligand had no effect on the proton shifts.[10,17a,33] The isotropic shifts of this dicopper(II) system follow Curie behavior. The Curie behavior of spin-coupled dicopper(II) systems has previously been shown to be a function of the magnitude of 2*J*.[18,20]

Table 6. Peak Positions, T_1 and T_2 Values, Proximity of Hydrogens to Cu, and Assignments for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2\cdot H_2O$ at Room Temperature (25 °C)

labeling	assignment	chem shift[a] (ppm)	T_1[b] (ms)	T_2[c] (Hz)	R_{Cu-H} (Å) X-ray	R_{Cu-H} (Å) soln[d]
A	O−H[e]					
B	O−CH_2	39.15	10.3	508	4.99	4.91
C	−CH_2	25.59				
D	=N−CH_2	66.47	8.5	800	4.81	4.75
E	CH=N					
F	Ar−H	17.66	25.0*	117	5.69	
G	CH_3	−3.75				
H	H_2O	−71.89				

[a] All shifts are in ppm related to TMS. [b] T_1 values are obtained using inversion recovery method. [c] The line widths are full width at half-maximum. [d] In solution, calculated $R_{Cu-H} = R_{ref}\,(T_{1i}/T_{1ref})^{1/6}$; where R_{ref} and T_{ref} are reference (*) values. [e] Observed only at 75 °C.

Signal Assignment. Signals have been assigned using[19] (i) proton longitudinal relaxation time (T_1) i.e., the majority of the protons that are close to copper will have short T_1' s in the narrow range, with broader line widths (short T_2's), while those in the periphery will have longer T_1' s and narrow line widths; the assumption here is based on the fact that protons closer to the copper centers experience stronger paramagnetic effects and hence shorter T_1's and larger shifts; another observation is that there is a good correlation between the solution determined Cu−H distances using relative T_1 values and the range found in the structure (Table 6). In fact, on the basis of these data one can assign the observed signals of protons closer to copper without any difficulty. Additionally, signals have been assigned using (ii) line widths that correlate with through-bond delocalization and (iii) the signal intensity. On the basis of the above arguments, the signals B, C, D, F, and G were assigned. Signal H is the only unassigned signal in the proton NMR spectrum. Upon addition of a small amount of D_2O, the proton signal observed at −72 ppm disappears, indicating it to be an exchangeable proton. The molecular structure of the compound discussed here consists of two exchangeable protons, i.e., OH (signal A) and axially coordinated water (H_2O) protons (signal H). The unpaired electron is present in the $d_{x^2-y^2}$ orbital which has σ bonding character, and the OH group which has the right symmetry to overlap with the $d_{x^2-y^2}$ orbital leads to direct delocalization of the unpaired electron on to the OH group and gives positive spin density on the protons. This would give a large downfield shift for the OH proton. However, we could not observe the OH proton signal at room temperature, but when we increased the temperature to 75 °C, we could observe a very broad peak appearing in the 94−130 ppm range (as it is said earlier that the isotropic shifts follow the Curie behavior). So, we can assign the signal observed at 94−130 ppm as an OH signal, whereas, in the case of axially coordinated water protons (H_2O), a spin polarization mechanism operates and gives negative spin density for the proton and correspondingly upfield shift. On the basis of these arguments the signal observed at −72 ppm can be assigned as an axially coordinated water proton signal.

It may be seen that protons B and D undergo an upfield shift with an increase in temperature while proton H demonstrates a downfield shift due to opposite shift behavior of both direct delocalization and spin polarization mechanism. They also seem to suffer the maximum temperature dependent shift next to the OH proton indicating the dominance of σ-bonding effects in exchange coupling. In other words the superexchange occurs via the σ moiety. The earlier theoretical calculations[34,35] and

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Table 7. Hyperfine Coupling Constants (A) for Different Protons and Exchange Coupling Constant ($-2J$) Obtained from $\Delta\delta_{iso}$ Using Eq 3 for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2 \cdot H_2O$

proton type	$-2J$ (cm^{-1})	A (kHz)
$=N-CH_2$	100 ± 5.3	326.189
$O-CH_2$	95 ± 5.0	191.193
H_2O	107 ± 8.6	−189.476

experimental observations[15,17] indicate that σ is the dominant route for exchange coupling operations in this type of dicopper(II) system.

Calculation of the Exchange Coupling Constant (2*J*) in Solution Using Chemical Shift. The magnitude of the antiferromagnetic coupling constant ($-2J$) can be obtained from the NMR data. Because the contact shift is proportional to paramagnetic susceptibility (χ), the temperature dependence of the shift can in principle be fit to the temperature dependence of susceptibility (χ) in an antiferromagnetic system to extract $-2J$. Two things are to be considered. First this approach assumes that the hyperfine coupling constant (A) of a particular nucleus is invariant with spin state (S') and that the dipolar component is small. In the case of antiferromagnetically coupled binuclear copper(II) complexes, only the $S' = 0$ and $S' = 1$ states need be considered in the temperature range studied. Only the latter is paramagnetic, and thus only one A value need be considered. In solution the magnetism of the exchange coupled system can be explained by the simple Heisenberg Hamiltonian

$$H = -2JS_1 \cdot S_2 \qquad (3)$$

with $S_1 = S_2 = {}^1/_2$; the temperature variation of chemical shifts could be used to calculate the exchange coupling constant using the expression[15]

$$\Delta\delta_{iso} = \frac{-g\beta A}{(\gamma/2\pi)kT}\left[3 + \exp\left(\frac{-2J}{kT}\right)\right]^{-1} \qquad (4)$$

where A is the hyperfine coupling from the proton under investigation, γ is the magnetogyric ratio, and $2J$ is the exchange coupling constant.

A suitable computer program[30] was used to fit experimental values of $\Delta\delta_{iso}$ and T for parameters A and $2J$ by using a nonlinear least-squares method. The value of g in the calculated expression for $\Delta\delta_{iso}$ was taken as 2.0023. The best fit values of A and $2J$ are given in Table 7.

Figure 5 shows the experimental points and the lines for the corresponding least-squares fit for protons B, D, and H of $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2 \cdot H_2O$. It is noteworthy to mention that $-2J$ values calculated for these protons range between 100 and 115 cm^{-1}. There is a small uncertainty in $2J$, which arises chiefly owing to the errors arising from the small variations in the observed chemical shift over the limited temperature range used. However, the hyperfine coupling constant is different for different protons (Table 7) as expected. Similar results were obtained for binuclear iron(III)[36] and binuclear copper(II)[17a] complexes. A comment on the origin of different hyperfine couplings on protons will be in order. This electron−nucleus hyperfine interaction constant (A) can have either contact or dipolar contributions or both. It is well-known that magnetic anisotropy giving rise to the dipolar shift is usually very small for copper(II) systems.[37] In our case the contact shift is the predominant one. The contact shift due to spin transmitted through σ bonds predicts positive spin densities at protons B and D and negative spin density at proton H as it is assigned now and hence the hyperfine coupling constants with their respective signs. Also the magnitude of the spin densities due to contact shift will qualitatively decrease as a function of bonds away from the first coordination sphere of the metal atom.[16]

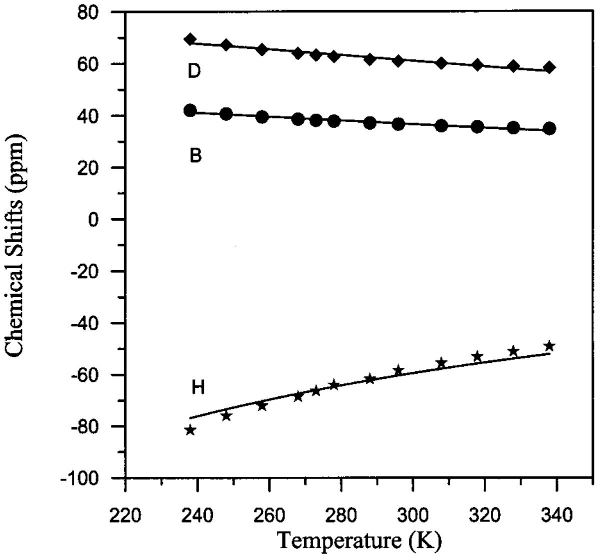

Figure 5. Plot of chemical shift vs temperature for $[(Cu_2(HAP)_2IPA)(OH)(H_2O)](ClO_4)_2 \cdot H_2O$ with (◆, ●, and ★) representing experimental data points for protons D, B, and H and the solid line representing the best fit obtained from eq 4.

At this point it is interesting to compare the results on exchange coupling obtained from both solid and solution methods. One can see good agreement between the $2J$ value obtained in the solid (by SQUID) and that obtained in solution (by the chemical shift method), indicating that the dicopper(II) ions are moderately antiferromagnetic in both solid and solution states. Also, it appears that there is not much of a structural change when the solid is brought into solution.

Relaxation Mechanism. Understanding of the effect of magnetic coupling on the nuclear relaxation parameters is relevant for several biological systems where such coupling is known or suspected to occur. In addition to this, the understanding of nuclear relaxation induced by paramagnetic metal ions can provide information on the structure and, more so, on the time-dependence phenomena or the mechanism of it concerning the resonating nucleus. With this in mind we have calculated the correlation time (τ_c) for this moderately antiferromagnetically coupled Cu^{2+} system by using the experimentally observed T_1 values.

Theory for the nuclear magnetic resonance in paramagnetic systems predicts three different contributions to nuclear longitudinal relaxation by the unpaired electrons; one arises from through-space dipolar interaction between the unpaired spin residing on the metal and the observed nucleus; another one arises from a contact interaction between the nucleus and the fraction of unpaired spin directly delocalized, or induced by spin polarization, onto s orbitals of the nucleus itself; and finally further dipolar contributions come from unpaired spin density residing on neighboring atoms. The first two contributions are described by the well-known Solomon−Bloembergen[38] equations. However, it has been recently[16b,39] shown that in exchange

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coupled systems such equations should be modified to account for the different electronic situation described by a metallic pair with total spin S'.

The equations for proton longitudinal and transverse relaxation rate enhancements due to dipolar and contact coupling to an exchange coupled system can be represented by

$$T_{1M}^{-1} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I^2 g_e^2 \mu_B^2}{r^6} \sum_i \left[C_i^2 S_i'(S_i'+1)(2S_i'+1) \exp(-E_i/kT)\left(\frac{7\tau_c}{1+\omega_s^2\tau_c^2} + \frac{3\tau_c}{1+\omega_I^2\tau_c^2}\right)\right] \Big/ \sum_i [(2S_i'+1) \exp(-E_i/kT)] \quad (5)$$

$$T_{2M}^{-1} = \frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I^2 g_e^2 \mu_B^2}{r^6} \sum_i \left[C_i^2 S_i'(S_i'+1)(2S_i'+1) \exp(-E_i/kT)\left(4\tau_c + \frac{13\tau_c}{1+\omega_s^2\tau_c^2} + \frac{3\tau_c}{1+\omega_I^2\tau_c^2}\right)\right] \Big/ \sum_i [(2S_i'+1) \exp(-E_i/kT)] \quad (6)$$

$$T_{1M}^{-1} = \frac{2}{3}\frac{A^2}{\hbar^2} \sum_i \left[C_i^2 S_i'(S_i'+1)(2S_i'+1) \exp(-E_i/kT) \frac{\tau_s}{1+\omega_s^2\tau_s^2}\right] \Big/ \sum_i [(2S_i'+1) \exp(-E_i/kT)] \quad (7)$$

$$T_{2M}^{-1} = \frac{1}{3}\frac{A^2}{\hbar^2} \sum_i \left[C_i^2 S_i'(S_i'+1)(2S_i'+1) \exp(-E_i/kT) \frac{\tau_s}{1+\omega_s^2\tau_s^2}\right] \Big/ \sum_i [(2S_i'+1) \exp(-E_i/kT)] \quad (8)$$

The nuclear relaxation rate enhancement depends on several parameters:[19] metal ion electronic configuration (S), hyperfine coupling constant (A), and the nucleus−electron reorientational correlation times τ_c and electron correlation times τ_s.

The correlation time τ_c in eq 5 is the reciprocal of rate constant τ_c^{-1}. This overall rate τ_c^{-1} is the sum of rates for three different processes,[16]

$$\tau_c^{-1} = \tau_s^{-1} + \tau_r^{-1} + \tau_m^{-1} \quad (9)$$

where τ_s^{-1} is the electron spin relaxation rate, τ_r^{-1} is the rotational correlation rate, and τ_m^{-1} is the chemical exchange rate. In the case of systems reported here τ_m is of no consequence.

So we have estimated τ_c by using eq 5. An average τ_c value of around 1.39×10^{-10} s is obtained for this complex. This value indicates that T_1 is being dominated by the rotational correlation time (τ_r) or electron relaxation time (τ_s) or a combination of both. Bertini and co-workers[40−43] have extensively studied the dimeric metal complexes that have superexchange interactions with $|2J| > kT$ and $|2J| \approx kT$. According to them, longitudinal (T_{1M}) and transverse relaxation (T_{2M}) times of copper(II) homodimers are controlled by the population distribution in the $S = 0$ and $S = 1$ states rather than by a significant decrease in an electron relaxation time (τ_s). The relatively narrow lines observed in our system may be due to appreciable population of the diamagnetic ground state. The error on the estimate of τ_r and τ_s can be anywhere between the monomeric τ_c value and $\sim 5 \times 10^{-10}$ s. Hence, no definitive conclusion on the mechanism leading to shortening of τ_s in this system can be made from these data.

Conclusion

We have synthesized a binuclear copper(II) complex with an amino alcohol. The temperature dependent ^{1}H NMR studies shows relatively sharp hyperfine shifted signals. By using the observed chemical shift as a function of temperature we have made an attempt to calculate the exchange coupling constant ($-2J$) in solution, which is further compared with the solid state susceptibility measured by SQUID. A good agreement between the solid and solution measured $-2J$ value indicates the existence of a moderate antiferromagnetic exchange interaction between two Cu atoms in both the solid and solution states. The exchangeable OH and water protons provide important chemical shifts. The relaxation process for the dicopper(II) system is mostly dominated by a dipolar mechanism. This allows T_1 values to be used as a measure of distance for any given proton residing in the dicopper(II) center complexes. Our results indicate that ^{1}H NMR spectroscopy is an excellent tool to probe the dicopper(II) systems in solution.

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Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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