Proton ENDOR Studies on Zinc-Doped Copper(II) Acetate Monohydrate Single Crystal

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The proton ENDOR spectra of the zinc-doped copper(II) acetate monohydrate single crystal were measured at 20 K. Hyperfine coupling tensors have been determined for the two protons of the water molecule at the axial position of the paramagnetic copper ion and a proton of the water forming the hydrogen bond with carboxylate oxygen at the equatorial plane of the copper ion. The axial water protons have small positive isotropic hyperfine couplings owing to the pseudo-contact interaction, and the equatorial water proton has a small negative one due to the spin polarization effect of the positive spin on the acetate oxygen through the hydrogen bond. The anisotropic hyperfine tensors of the former protons are interpreted by the dipolar interaction with the unpaired spin on the copper $d_{x^2-y^2}$ orbital. The anisotropic interaction of the latter protons indicates that the spin delocalizes onto the oxygen atoms of the acetate bridges. Based on these observed hyperfine interactions, the mechanism of the spin–spin interaction in the dimer complex is discussed.

Magnetic exchange interactions in metal dimer complexes continue to be a subject of much interest among chemists.[1] Copper(II) acetate monohydrate involving an antiferromagnetic coupled dimer has been widely studied, resulting in a long controversy concerning the exchange pathway in the dimer. Figgis and Martin initially proposed that the antiferromagnetic interaction is due to the existence of a δ-bond between the copper(II) ions.[2] Forster and Ballhausen employed a molecular orbital treatment, showing the importance of the copper–copper σ-bond.[3] Later, Hansen and Ballhausen used a weakly coupled chromophore model which included no direct copper–copper interaction to explain the antiferromagnetism.[4] Goodgame et al. considered that the direct metal–metal bond is not important for the antiferromagnetism and that the spin coupling occurs by a superexchange via the carboxylate bridge.[5] Since then, the superexchange mechanism has been favored by most authors. Much current research is being directed toward the development of a more complete understanding of the exchange mechanism; various physical methods (EPR,[6a] NMR,[6b] NQR,[6c] etc.) have been employed.

Revealing the spin distribution in the dimer would be useful in clarifying the mechanism of the antiferromagnetism. Copper(II) acetate monohydrate doped with zinc(II) ions shows paramagnetism with $S=1/2$ of the Cu–Zn dimer at a temperature below 50 K, since the host Cu–Cu dimer becomes completely diamagnetic. An unpaired electron occupies one of the so-called "magnetic orbitals" which is centered on a copper atom. Kokoszka et al. investigated a zinc-doped copper acetate monohydrate single crystal by EPR.[7] They found that the unpaired electron on the copper $d_{x^2-y^2}$ orbital interacts weakly with the zinc ion. Since the superexchange interaction appears to occur through the ligand orbitals, the ligand hyperfine (hf) couplings provide useful information concerning the mechanism of the antiferromagnetic interaction. The EPR spectra show a well-resolved copper hf structure, which lacks resolution of the ligand hf splittings.

In this paper we report on the proton ENDOR of single crystal of zinc-doped copper(II) acetate monohydrate. The observed proton hf coupling tensors are compared to those of the other monomeric copper(II) complexes and the exchange interaction mechanisms are discussed.

Experimental

Single crystals of zinc-doped copper(II) acetate monohydrate were obtained in the same manner as that described in a reference.[7] Isotope-enriched ^{63}Cu acetate (99%) was used to simplify the EPR and ENDOR spectra. A copper acetate monohydrate crystal is monoclinic with a space group $C2/c$, containing four dimeric molecules in a unit cell. There are two independent intermolecular hydrogen bonds between the hydrogen atom of the water and oxygen atom of the acetate bridge, as shown in Fig. 1.[8]

The EPR spectra were recorded on a Varian E112 X-band EPR spectrometer. The magnetic fields and microwave frequencies were measured by an Echo Electronic EFM 2000 NMR field meter and a Takedariken TR 5204 frequency counter, respectively. The ENDOR spectra were recorded on an EPR spectrometer equipped with a Varian E1700 ENDOR unit and an ENI 550L RF power amplifier. These measurements were carried out at 20 K using an Oxford ESR 9 cryostat. At this temperature the host copper-copper dimers became completely diamagnetic ($S=0$) and the only copper–zinc dimers ($S=1/2$) were observed in the EPR spectra.

Results

The angular dependence of the proton ENDOR spectra observed for the magnetic field in the bc^* plane are shown in Fig. 2. A large number of proton ENDOR signals were observed, and some ENDOR signals were split into doublet lines by nuclear spin–spin couplings at

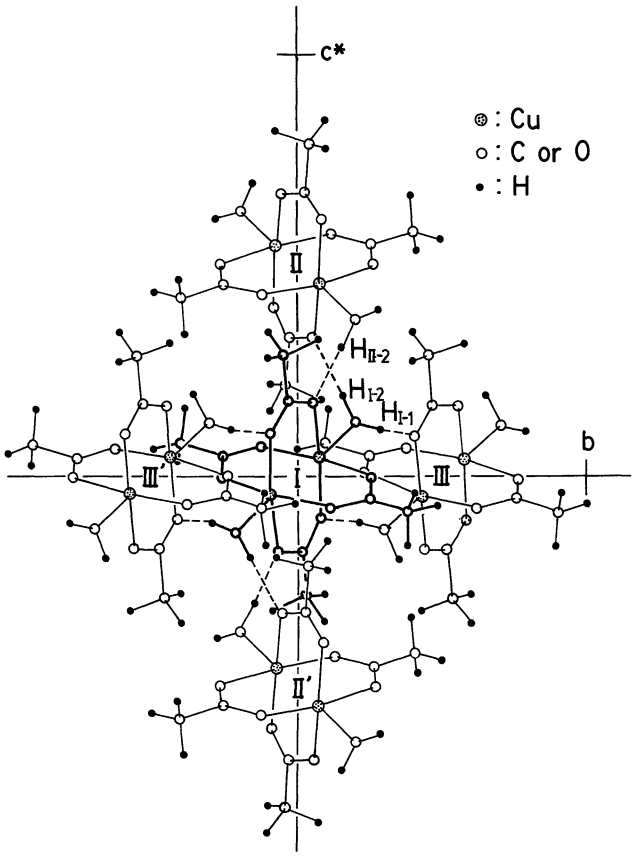

Fig. 1. Crystal structure of copper(II) acetate monohydrate projected onto the *bc** plane.

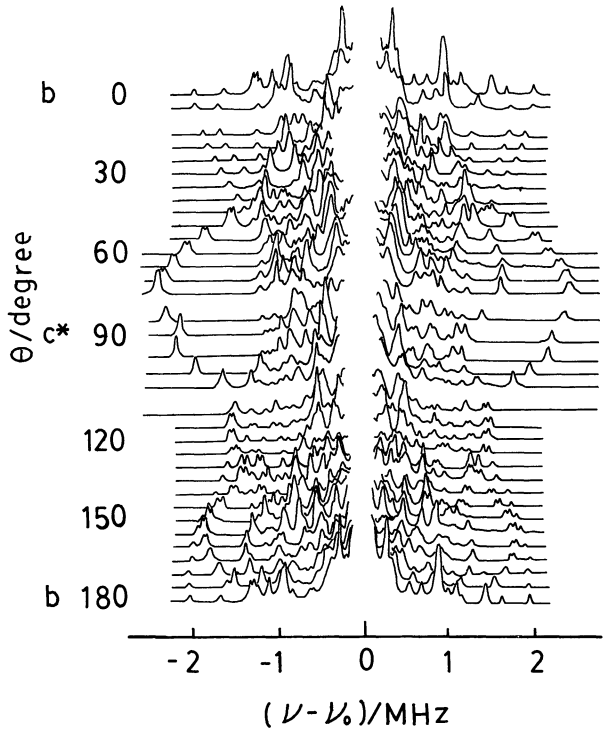

Fig. 2. Angular-dependence of ^{1}H ENDOR signals when the magnetic fields are in the *bc** plane.

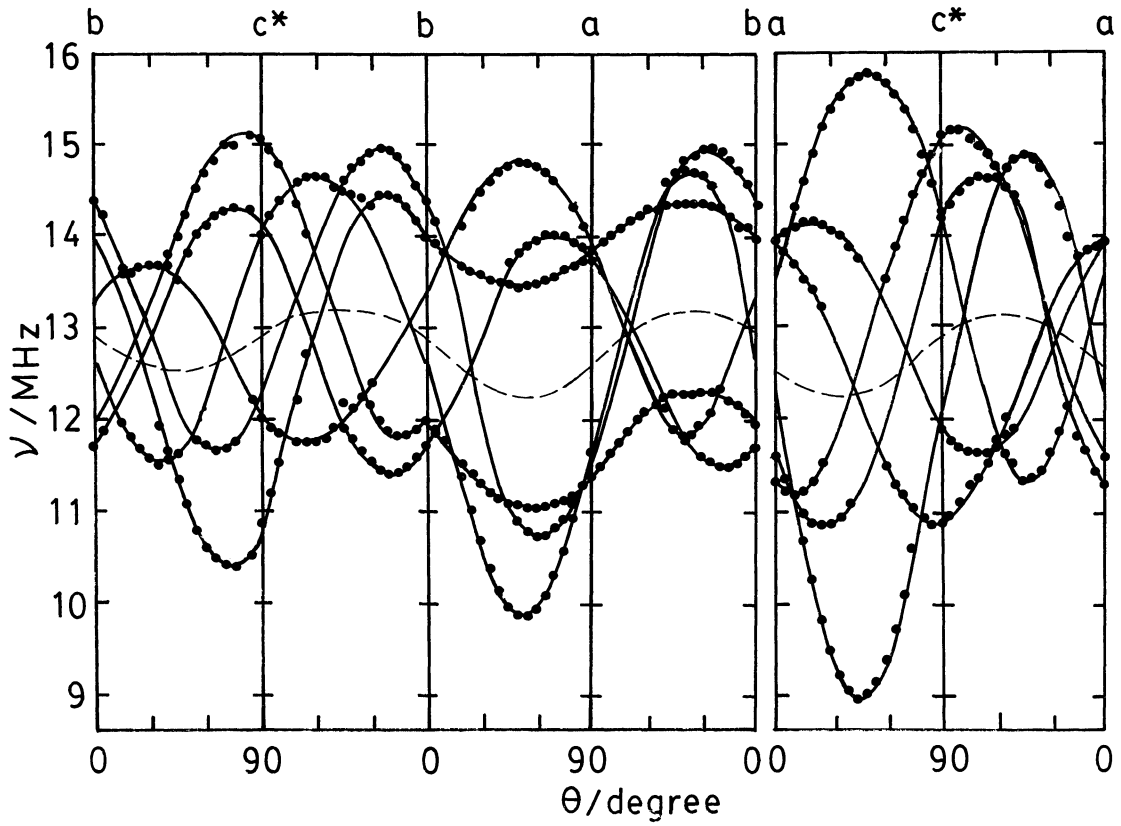

Fig. 3. Angular-dependence of ^{1}H ENDOR frequencies for rotations around the *a*-, *c**-, and *b*-axis. The broken line indicates the free proton frequency; the solid lines were calculated using the tensors of Table 1 and Eq. 1.

some crystal orientations. The ENDOR frequencies are given by

$$h\nu^{H}(M_s)=K^{H}(M_s)+h\nu(\text{2nd})+h\nu(\text{dipole}). \quad (1)$$

Although a full expression of each term was given in our previous paper,[9] it must be noted that $h\nu$(2nd) denotes a second order correction of the ENDOR frequencies due to an indirect coupling with the copper nuclei;[10] the $h\nu$(dipole) is the effect of nuclear spin–spin coupling between protons. This last term was not expressly included in the present analysis for the angular dependence of the ENDOR frequencies; however, the frequency of the center of the doublet splitting by the spin–spin coupling was used. Figure 3 shows the observed ENDOR frequencies for rotation about the *a*-, *c**-, and *b*-axis and the angular-dependent ENDOR frequencies computed by Eq. 1 and the parameters in Table 1. The signs of the hf couplings are not determinable from the conventional ENDOR technique and, hence, an assumption was made that the largest anisotropic hf principal value must be positive, since the anisotropic part of the proton hf coupling would be dominated by the dipole interaction with the spin on the metal ion. The assignment of the observed proton hf couplings to the proton positions was made by comparing their direction cosines with those of the Cu–H vectors calculated from the crystallographic data, since the principal axes of the proton hf couplings are considered to orient along the respective Cu–H directions. Three proton hf couplings could be assigned. Two of them were assigned to the protons of the water molecule coordinated to the copper ion (I-1 and I-2); the other was assigned to the proton of the water molecule which is coordinated to the neighboring complex and is involved in the hydrogen bond with the acetate oxygen (II-2). The agreement between the direction cosines of the hf coupling tensors and the crystallographic Cu–H vectors is satisfactory. The Cu–H distances calculated from the anisotropic dipolar couplings by the use of the point-dipole approximation also agree with those from the crystallographic data.

Discussion

Isotropic hf Coupling. The protons at I-1 and I-2 positions have small positive isotropic hf coupling constants, whereas the II-2 proton has a small negative one (Table 2). Similar results have been reported for $[Cu(H_2O)_6]^{2+}$ in the zinc Tutton salt by Atherton and Horsewill.[10] They found that the protons of the axial waters in $[Cu(H_2O)_6]^{2+}$ have small positive isotropic hf couplings (mean value a_{av}=0.15 MHz), and the protons of the equatorial one have negative couplings (mean value a_{av}= −0.9 MHz).

The observed hf coupling matrix ($\boldsymbol{A}$) is the sum of three contributions,

$$\boldsymbol{A}=a\boldsymbol{E}+\boldsymbol{A}^{\circ}+\boldsymbol{A}^{L}, \quad (2)$$

where the first term is the Fermi contact coupling, the second the anisotropic dipolar interaction between the electron spin and the nucleus and the third the orbital contribution to the hf couplings. Although the anisotropic spin-only coupling matrix ($\boldsymbol{A}^{\circ}$) is traceless, its orbital counterpart ($\boldsymbol{A}^{L}$) is not. The isotropic part of $\boldsymbol{A}^{L}$ is usually called the pseudo-contact interaction. Atherton and Horsewill interpreted the negative hf couplings of the equatorial protons as being the result of

Table 1. Proton Hyperfine Coupling Parameters of Zinc Doped Copper Acetate Monohydrate Single Crystal

Position[a]		Coupling constants/MHz[b]		Direction cosines			Distances/Å	
Molecule	Proton	Isotropic	Traceless	l_a	l_b	l_c*	ENDOR	X-ray
			6.15	0.727	0.591	0.350		
I	1	0.24	−2.65	−0.686	0.624	0.373	3.1	2.9
			−3.49	0.002	−0.511	0.859		
			7.61	0.677	0.296	0.674		
I	2	0.36	−3.48	0.509	0.423	−0.719	2.9	2.7
			−4.13	−0.509	0.830	0.169		
			4.81	−0.073	0.259	0.963		
II	2	−0.18	−2.36	0.998	−0.113	0.105	3.4	3.3
			−2.44	0.136	0.959	0.373		

a) Positions are indicated in Fig. 1 and the EPR active copper is the one coordinated by H_2O(I). b) Estimated error is ±0.03 MHz.

Table 2. Estimated Fermi and Pseudo-Contact Hyperfine Couplings

Proton	Experimental/MHz	Fermi/MHz	Pseudo-contact/MHz
I-1	0.24	−0.04	0.28
I-2	0.36	0.04	0.32
II-2	−0.18	−0.19	0.01

spin polarization through the OH bond by unpaired spin delocalized on the water nonbonding orbital due to an overlap with the copper unpaired spin orbital; the positive coupling of the axial protons was interpreted as arising mainly from a pseudo-contact hf interaction. In the present case the small negative spin density ($\rho_H = -0.00013$) at proton II-2 may be attributed to a spin polarization effect through the hydrogen bond due to the positive spin on the acetate oxygen, which is introduced by an overlap with the singly occupied copper 3d-orbital; this is similar to the case of protons 3 and 3′ in copper-doped zinc(II) acetate dihydrate.[11] On the other hand, the spin densities at the protons in the axial water molecule are nearly zero, indicating that neither spin delocalization nor spin polarization effects exist at the axial water molecule.

Anisotropic Coupling. The anisotropic parts of the hf tensors arise from dipolar interactions between the electron spin centered on the copper ion and the nuclear spin of the protons. However, a conventional point-dipole approximation used to evaluate the anisotropic hf tensor is not suitable for the case in which the metal-ligand distance is less than about 0.3 nm. In such a case, it is necessary to calculate the following matrix element:[12]

$$A_{\text{aniso}} = \langle \psi \mid H_{\text{dipole}} \mid \psi \rangle ; \quad (3)$$

here, H_{dipole} denotes the dipole–dipole interaction Hamiltonian and ψ is the unpaired electron orbital. Taking the $d_{x^2-y^2}$ or d_{z^2} orbital for ψ, three principal values of the tensor can be expressed in a first-order approximation as follows:

$$A_{\xi\xi} = 2PR^{-3}[1 - ((12/7)\cos^2\theta - (6/7)\sin^2\theta)R^{-2}\langle r^2\rangle_{3d}]$$

$$A_{\eta\eta} = -PR^{-3}[1 - ((12/7)\cos^2\theta - (9/7)\sin^2\theta)R^{-2}\langle r^2\rangle_{3d}] \quad (3)$$

$$A_{\zeta\zeta} = -PR^{-3}[1 - ((12/7)\cos^2\theta - (3/7)\sin^2\theta)R^{-2}\langle r^2\rangle_{3d}],$$

for $d_{x^2-y^2}$, and

$$A_{\xi\xi} = 2PR^{-3}[1 + ((6/7)\cos^2\theta - (3/7)\sin^2\theta)R^{-2}\langle r^2\rangle_{3d}]$$

$$A_{\eta\eta} = -PR^{-3}[1 + ((6/7)\cos^2\theta - (9/14)\sin^2\theta)R^{-2}\langle r^2\rangle_{3d}] \quad (4)$$

$$A_{\zeta\zeta} = -PR^{-3}[1 + ((6/7)\cos^2\theta - (3/14)\sin^2\theta)R^{-2}\langle r^2\rangle_{3d}],$$

for d_{z^2}. The principal axes ($\xi\eta\zeta$) are shown in Fig. 4, $P = g\beta_e g_n \beta_n$, R is the metal-proton distance, and θ is the angle between the z-axis and the metal-proton direction. If $R^2 \gg \langle r^2\rangle_{3d}$, the term $R^{-2}\langle r^2\rangle_{3d}$ may be ignored and Eqs. 3 and 4 are reduced to the point-dipole approximation. The anisotropic hf tensors shown in Table 3 were obtained by using $\langle r^2\rangle_{3d} = 2.88\times10^{-3}$ nm^2 for Cu^{2+} reported by Freeman et al.[13] For the protons of the I-1 and I-2 positions, the agreement between the tensors derived from the $d_{x^2-y^2}$ configuration and the experimentally determinations are satisfactory, but the

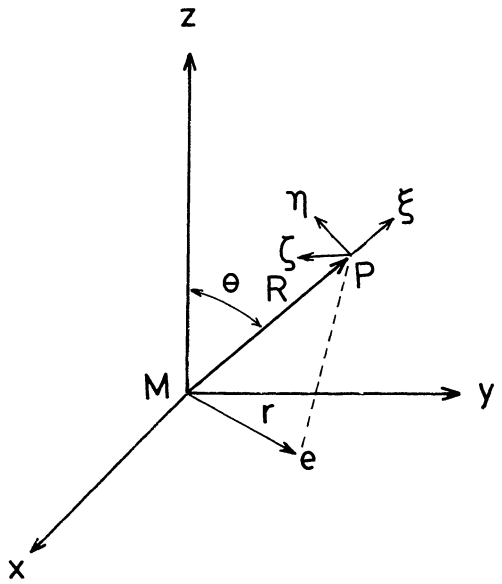

Fig. 4. Coordinate systems used for calculating the dipolar interaction between the electron spin (e) on the metal ion (M) and the nuclear spin of the proton (P). The (xyz) Cartesian coordinate system is the molecular axes of the metal complex. The (ξ, η, ζ) Cartesian coordinate system is the principal axes of the dipolar coupling tensor determined by taking the ξ-axis to be along the M–P direction and η to be in the $z\xi$ plane.

Table 3. Observed and Calculated Anisotropic hf Tensors

Position		Principal values/MHz			Direction cosines of the largest principal value					
Molecule	Proton	A_i[a]	A_i[b]	A_i[c]	l_a[a]	l_b[a]	l_c[a]	l_a[b,c]	l_b[b,c]	l_c[b,c]
I	1	6.15 −2.65 −3.49	6.11 −3.05 −3.06	6.65 −3.33 −3.33	0.727	0.591	0.350	0.766	0.575	0.287
I	2	7.61 −3.48 −4.13	7.52 −3.75 −3.77	8.14 −4.06 −4.07	0.677	0.296	0.674	0.676	0.238	0.699
II	2	4.81 −2.36 −2.44	4.53 −2.24 −2.29	4.46 −2.22 −2.24	−0.073	0.259	0.963	−0.172	0.194	0.966

a) Observed tensor. b) Calculated for the $d_{x^2-y^2}$ configuration. c) Calculated for the d_{z^2} configuration.

d_{z^2} configuration derives large hf tensors. The calculated hf tensors with both configurations for the proton II-2 are smaller than the observed hf tensor, suggesting the presence of a significant spin delocalization on the acetate oxygen.

Spin Distribution and Exchange Mechanism. In the copper(II) acetate monohydrate, two singly occupied electrons on each Cu atom interact with each other, making the triplet state energy become higher by 284 cm^{-1} than that of the singlet state.[2] In Cu–Zn dimers one unpaired electron centered on the copper atom is present. Since the unpaired electron orbital of the Cu–Zn dimer corresponds to the magnetic orbital of Cu–Cu dimer, the spin distribution of Cu–Zn dimer provides useful information concerning the magnetic orbital. The ground state configuration was initially assigned to $d_{x^2-y^2}$ by Figgis and Martin[2] and Ross;[14] they suggested that the antiferromagnetisum can be ascribed to a Cu–Cu interaction through the δ-bond; in the sustained by Forster and Ballhausen,[3] however, a Cu–Cu interaction through the σ-bond were proposed, based on the d_{z^2} ground state configuration. The isotropic proton hf couplings of the axial water molecule indicate that the spin density on the axial water molecule expected for the d_{z^2} configuration is not substantial, and that the anisotropic hf couplings of the protons are in favor of the $d_{x^2-y^2}$ ground state. Also, the isotropic and anisotropic hf coupling of the proton II-2 indicates the presence of a significant spin delocallization onto the acetate oxygen atoms from the copper $d_{x^2-y^2}$ orbital, and the spin polarization effect of the acetate ligands in the Cu–Zn dimer leads to a double-spin polarization contribution in the Cu–Cu dimer.[15] The results of the proton ENDOR study strongly support a superexchange interaction propagated by acetate bridges.

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