

Magnetic Susceptibility and PMR Spectrum of New Basic Copper(II) Formates $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$ and $\text{Cu}(\text{HCOO})(\text{OH})$

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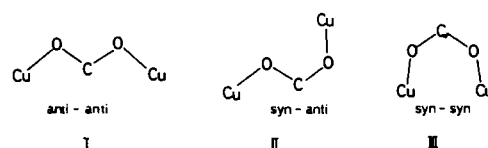
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New basic copper(II) formates $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$ and $\text{Cu}(\text{HCOO})(\text{OH})$ have been prepared and characterized by the magnetic susceptibility and PMR spectrum. The magnetic susceptibility of $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$ can be explained by the theoretical equation for linear trinuclear clusters. $\text{Cu}(\text{HCOO})(\text{OH})$ shows a phase transition to an anti-ferromagnetic ordered state accompanied by a spin-flop phenomenon at 21.3 K. Each compound exhibits PMR spectrum consisting of two components each showing the Fermi contact shift. The coupling constants are determined as $A_{\text{CH}} = 1.8 \text{ G}$ and $A_{\text{OH}} = -1.2 \text{ G}$ for $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$ and as $A_{\text{CH}} = 3.9 \text{ G}$ and $A_{\text{OH}} = -2.0 \text{ G}$ for $\text{Cu}(\text{HCOO})(\text{OH})$: the oxygen atoms in the hydroxy groups of each compound carry positive spin density and the carbon atoms of the formate groups negative spin density. The sign and magnitude of the spin exchange interaction depend markedly on the mechanism of spin delocalization onto the ligand molecules.

Introduction

Anhydrous Cu(II) formate forms two magnetically different crystal modifications, blue and royal blue forms, characterized well by various studies including X-ray analysis, magnetic susceptibility and PMR spectrum [1–4]. The blue form shows anti-ferromagnetism due to *anti-anti* bonding arrangements (Formula I) of infinite $\text{Cu}-\text{O}-\text{C}-\text{O}-\text{Cu}$ links [1, 4]. *Syn-anti* $\text{Cu}-\text{O}-\text{C}-\text{O}-\text{Cu}$ links (Formula II) are formed in the crystals of the royal blue form, which exhibits ferromagnetism [3, 4]. The PMR studies carried out on the modifications [4] have given direct experimental evidence for superex-



change interaction through formate groups: the anti-ferromagnetic interaction of the blue form takes place through the π orbitals of the formate groups whereas the ferromagnetism of the royal blue form is due to the polarization of the σ systems in the $\text{Cu}-\text{O}-\text{C}-\text{O}-\text{Cu}$ links. In the crystals of Cu(II) formate monourea [5, 6] and $[(\text{CH}_3)_4\text{N}][\text{Cu}(\text{HCOO})_2(\text{NCS})]$ [7], both of which contain dimeric units analogous to that of Cu(II) acetate monohydrate involving *syn-syn* arrangements (Formula III), anti-ferromagnetic interaction operating between copper atoms is much stronger than that in the blue form. These are good examples showing that magnetic interaction is strongly correlated to the nature of metal–ligand–metal bonding. A new type of Cu(II) formate, if it can be prepared, is expected to exhibit a novel magnetic property. In addition, it can provide valuable information about the mechanism and nature of superexchange interaction. From these points of view, we have prepared new basic salts of Cu(II) formate $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$ and $\text{Cu}(\text{HCOO})(\text{OH})$. The magnetic susceptibilities of the complexes have been determined down to 4.2 K to obtain information about the spin interaction and the type of spin aggregation. The superexchange interaction is caused by the delocalization of unpaired electrons onto ligand molecules. This phenomenon can be revealed by the contact shift in NMR spectra. Therefore, PMR spectra have been recorded for the polycrystalline powders of the new Cu(II) compounds. The mechanism of the superexchange interaction has been elucidated on the basis of the spin density distribution determined by the PMR spectra.

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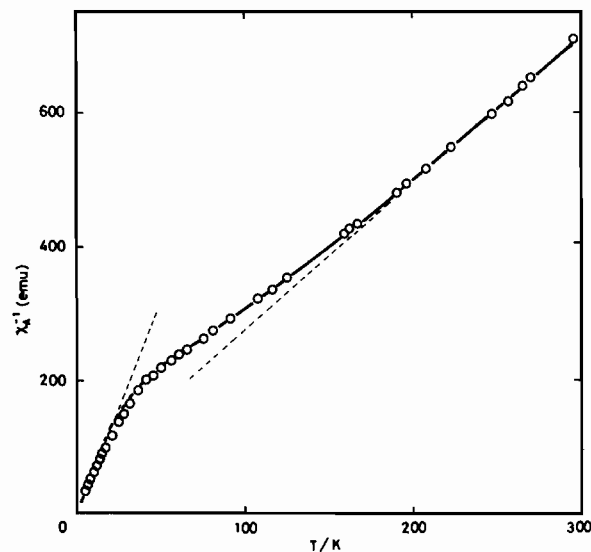


Fig. 1. Reciprocal magnetic susceptibility of $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$. The molar susceptibility is evaluated for the molecular weight corresponding to the formula $\text{Cu}(\text{HCOO})_{2/3}(\text{OH})_{4/3}$. The curve shows the susceptibility calculated for linear trinuclear clusters.

Experimental

$\text{Cu}(\text{HCOO})(\text{OH})$ was prepared by dissolving $\text{Cu}(\text{II})$ formate tetrahydrate in a minimum amount of water, followed by heating the resulting solution gently at 60–70 °C for several days. Blue prismatic crystals separated. *Anal.* Calcd. for $\text{Cu}(\text{HCOO})(\text{OH})$: Cu, 50.6; H, 1.61; C, 9.56%. Found: Cu, 50.0; H, 1.62; C, 9.70%. The effective magnetic moment showed 2.17 B.M. at 24 °C.

$\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$ was prepared by heating gently the powdered crystals of $\text{Cu}(\text{HCOO})(\text{OH})$ described above in a 1:1 mixture of water and methanol at 60–70 °C for several days. Bright green crystalline powders were obtained. *Anal.* Calcd. for $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$: Cu, 54.6; H, 1.73; C, 6.89%. Found: Cu, 54.1; H, 1.76; C, 6.96%. The effective magnetic moment was 1.83 B.M. at 25 °C.

The magnetic susceptibility [8] was determined by the Faraday method with a Cahn RH electric balance in a temperature range of 4.2–300 K. It was corrected for diamagnetic contributions (10^{-6} emu mol^{-1}) from Cu^{2+} (–11), OH^- (–12), and HCOO^- (–20) [9], and for the temperature independent paramagnetism (60×10^{-6} emu mol^{-1}).

The broad line PMR spectrum of crystalline powders was recorded by means of a JEOL JNM-MW-40 NMR spectrometer operating at 40 MHz in the temperature range 78–300 K [10].

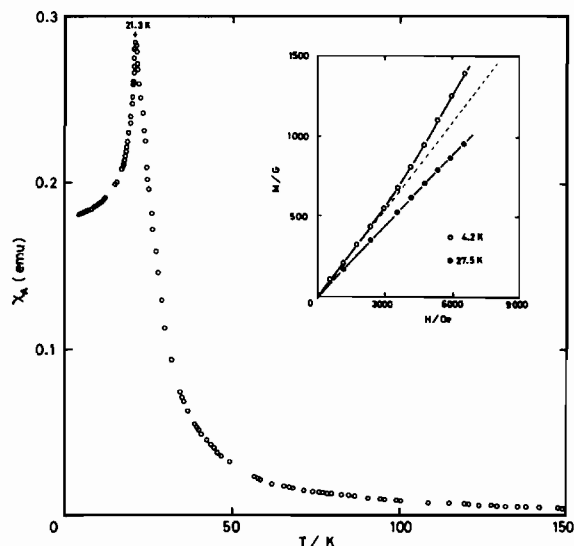


Fig. 2. Magnetic susceptibility of $\text{Cu}(\text{HCOO})(\text{OH})$. In the inset, the magnetization is plotted against applied magnetic field at different temperatures.

Results

$\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$ exhibited the temperature dependence of the magnetic susceptibility as shown in Fig. 1, which shows the reciprocal molar magnetic susceptibility corresponding to the chemical formula $\text{Cu}(\text{HCOO})_{2/3}(\text{OH})_{4/3}$. The observed susceptibility obeyed the Curie–Weiss law $1/\chi = C/(T - \theta)$ in the two temperature ranges $T \geq 160$ K and $T \leq 20$ K: the Curie and Weiss constants were determined as $C_h = 0.419$ emu K mol^{-1} and $\theta_1 = -17.3$ K for the high temperature range, and $C_h = 0.192$ emu K mol^{-1} and $\theta_1 = -0.97$ K for the low temperature range.

Figure 2 shows the molar magnetic susceptibility of $\text{Cu}(\text{HCOO})(\text{OH})$, which obeyed the Curie–Weiss law with $C = 0.520$ emu K mol^{-1} and $\theta = 43.3$ K at temperatures above 130 K. The susceptibility exhibited a sharp maximum at $T_m = 21.3$ K and a plateau below 12 K. This magnetic behavior is characteristic of antiferromagnetic materials exhibiting an ordered state. In the inset of Fig. 2, the magnetization determined at 4.2 and 27.5 K is plotted against the external field strength. The magnetization at temperatures above T_m was proportional to the applied field up to the maximum field strength (7000 G) of our equipment. Below T_m , however, the magnetization deviated from the proportional relation to the external field above its strength of 2000 G, and the susceptibility increased with increasing field strength. The susceptibility plotted in Fig. 2 was determined at field strength for which the proportional relation of magnetization held.

Figure 3 shows the typical PMR spectra recorded for the crystalline powders of $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$

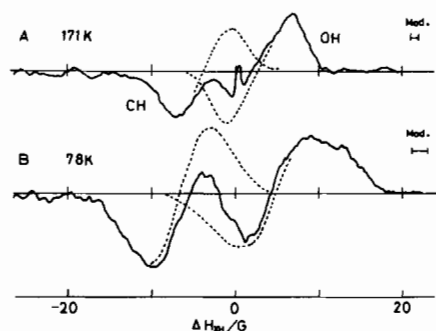


Fig. 3. PMR spectra of polycrystalline $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$. The sharp peak at the origin in the spectrum A is due to isohexane employed as an external standard. Each intrinsic spectrum can be decomposed into two simple derivative curves (broken curves) with the intensity ratio 2:1, *i.e.*, the stronger component shifted to high field and the weaker component with low field shift.

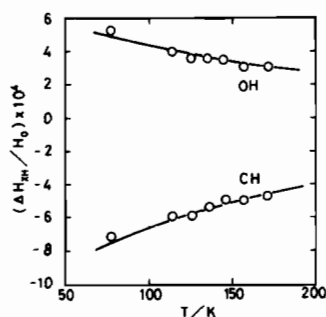


Fig. 4. Temperature dependence of the contact shifts of OH and CH protons in $\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$. The curves are calculated on the basis of equation (3) with the coupling constant 1.8 G for the CH protons and -1.2 G for the OH protons.

at different temperatures. Each observed curve can be decomposed into two simple derivative curves with the intensity ratio 2:1. The center of each component curve shifted with temperature proportionally to the magnetic susceptibility (Fig. 4). This indicates that the shifts are ascribable to the paramagnetic property.

Figure 5 shows the PMR powder spectra of $\text{Cu}(\text{HCOO})(\text{OH})$, each of which is made up of two component curves with almost the same intensity. The shift of each component changed with temperature in proportion to the magnetic susceptibility as shown in Fig. 6.

Discussion

$\text{Cu}_3(\text{HCOO})_2(\text{OH})_4$

The magnetic susceptibility obeys the Curie-Weiss law in the two temperature ranges. This magnetic behavior is characteristic of magnetic clusters involv-

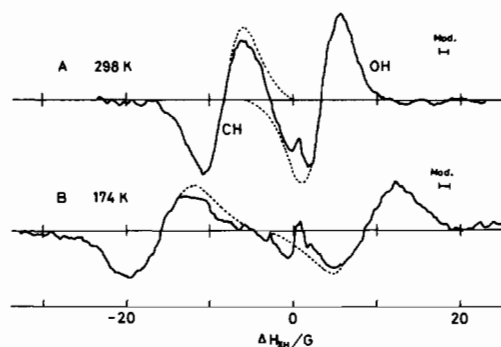


Fig. 5. PMR powder spectra of $\text{Cu}(\text{HCOO})(\text{OH})$. The sharp peak at the origin in each spectrum is due to isohexane employed as an external standard. Each intrinsic spectrum can be resolved into two component curves (broken curves) with almost the same intensity.

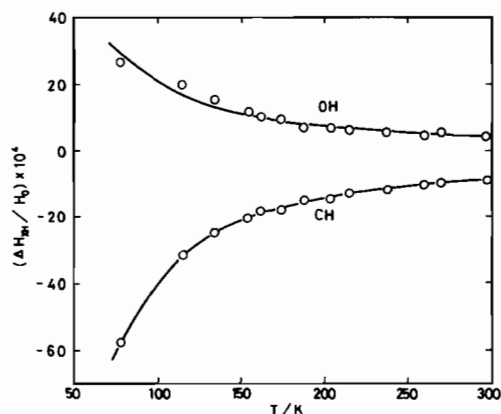


Fig. 6. Temperature dependence of the contact shifts of OH and CH protons in $\text{Cu}(\text{HCOO})(\text{OH})$. The curves are calculated on the basis of eqn. (3) with the coupling constant 3.9 G for the CH protons and -2.0 G for the OH protons.

ing odd numbers of copper atoms. The ratio $C_b/C_1 = 2.2$ suggests that trinuclear clusters form the magnetic unit. For a system of three spins $S_1-S_2-S_3$ interacting with each other, the Hamiltonian is given by

$$\mathcal{H} = -2J(S_1S_2 + S_2S_3) - 2J'S_1S_3, \quad (1)$$

where J and J' denote the exchange integrals. On the basis of the Hamiltonian, the magnetic susceptibility can be formulated as [11]

$$\chi = \frac{1 + \exp[(-2J+2J')/kT] + 10\exp[(J+2J')/kT]}{1 + \exp[(-2J+2J')/kT] + 2\exp[(J+2J')/kT]} \times \frac{Ng^2\mu_B^2}{12kT} \quad (2)$$

This equation reproduces the observed susceptibility well with $J/k = -40$ K, $J' = 0$ and $g = 2.19$ (Fig. 1). The g value agrees with 2.13 evaluated from C_h . These indicate that the crystals consist of linear trinuclear clusters.

The PMR spectrum constructed by two components suggests that the crystals involve only two magnetically different kinds of protons. Hence, it is reasonably assumed that two HCOO groups in the chemical formula are magnetically equivalent to each other and all of four OH protons also equivalent. From the intensity ratio, the stronger component is attributable to the OH protons, and the weaker one to the HCOO protons.

The paramagnetic shift arises generally from the isotropic Fermi contact interaction and the anisotropic dipolar interaction [12–14]. The contribution from the latter is negligibly small for polycrystalline powders of Cu(II) complexes [14], because they have a small g anisotropy. Accordingly, the observed shift $\Delta H_{XH}/H_0$ of XH protons can be given by the Fermi contact term [12–14]:

$$\frac{\Delta H_{XH}}{H_0} = -A_{XH} \frac{\chi}{N g_N \mu_N} \quad (3)$$

Here, A_{XH} is the contact coupling constant of resonant XH protons in Gauss. As shown in Fig. 4, the observed shifts can be reproduced well with this equation by use of the observed magnetic susceptibility: $A_{OH} = -1.2$ G and $A_{CH} = 1.8$ G. The coupling constant A_{XH} of the XH protons is proportional to the spin density ρ_X on the atom X bonded to the resonant proton [12–14]:

$$A_{XH} = Q_{XH}^H \rho_X \quad (4)$$

The proportionality constant Q_{XH}^H has been theoretically established to be negative in sign [12]. Hence, the high field PMR shift indicates the presence of positive spin density on an X atom bonded to the resonant XH proton, and the low field shift does negative spin density distributed on the neighboring X atom.

The unpaired electron of a copper ion is delocalized onto the atoms of ligand molecules coordinating to the Cu(II) ion. In this case, the atom bonded to the Cu(II) ion carries a positive spin density (or spin density with the same sign as that of the Cu(II) ion). The delocalized electron diffuses progressively over the atoms of the ligand molecules with alternation in sign. Therefore, the oxygen atom of OH groups in $Cu_3(HCOO)_2(OH)_4$ carries positive spin density, while a fractional positive spin exists on the oxygen atoms of O–CH–O groups and induces negative spin density on the neighboring carbon atom: the OH protons show high field shift whereas the HCOO protons do low field shift. This theoretical expectation is consistent with the aforementioned assignment.

TABLE I. Weiss Constants θ , Exchange Integrals J , and Contact Coupling Constants A_{XH} of $Cu_3(HCOO)_2(OH)_4$ and $Cu(HCOO)(OH)$.

Compound	θ/K	$(J/k)/K$	A_{XH}^b/G			
$Cu_3(HCOO)_2(OH)_4$	-17.3	-40	CH +1.8			
			OH -1.2			
$Cu(HCOO)(OH)$	+43.3	-	CH +3.9			
			OH -2.0			
$Cu(HCOO)_2^a$						
			Blue	-1.24	-42	CH +0.54
			Royal Blue	+17	+9.9	CH +3.9

^aRef. 4. ^bThe atom X bonded to the resonant proton carries a spin density with sign opposite to that of A_{XH} .

Unfortunately, this compound is difficult to obtain single crystals available to X-ray studies. The present investigation, however, proposes a structure involving linear trinuclear clusters as expected from the chemical composition.

$Cu(HCOO)(OH)$

Ferromagnetic interaction dominates in this compound ($\theta > 0$), and a phase transition to an antiferromagnetic ordered state takes place due to additional antiferromagnetic interaction. The susceptibility below T_m increases with increasing magnetic field strength above 2000 G. This behavior is characteristic of spin-flop phenomenon accompanying anti ferromagnetism [15]. These magnetic properties are caused by an aggregate of infinite copper atoms interacting with each other.

The PMR spectrum consisting of only two components suggests that the crystals contain only one kind of equivalent OH and of HCOO. From the same consideration as made for the PMR spectrum of $Cu_3(HCOO)_2(OH)_4$, the component showing high field shift can be assigned to the OH protons and the component of low field shift is attributable to the CH protons of the formate groups. The coupling constants are evaluated as $A_{CH} = 3.9$ G and $A_{OH} = -2.0$ G with equation (3) on the basis of the observed susceptibility.

From the requirement of the chemical composition, both of OH and HCOO groups have to act as bridging ligands. Along with this, the present investigation indicates that copper atoms are linked by infinite Cu–O–Cu and Cu–O–C–O–Cu bondings to construct either coupled chains or networks.

Spin Density and Exchange Interaction

The proportionality constant of eqn. (4) has been evaluated as $Q_{CH}^H (\pi) = -23$ G for $\cdot CH$ species in

which an unpaired electron occupies the $p\pi$ orbital of the carbon atom [12]. The contact coupling constant of the blue form of anhydrous Cu(II) formate has been determined to be equal to -0.54 G, yielding reasonable spin density $\rho_C(\pi) = -0.024$ distributed in the carbon $p\pi$ orbital by use of the aforementioned $Q_{CH}^H(\pi)$ value [4]. When the same value of $Q_{CH}^H(\pi)$ is employed for the royal blue form, the spin density localized in the $p\pi$ orbital is evaluated as $\rho_C(\pi) = -0.17$. This absolute value of the royal blue form is much larger than that of the blue form, although the magnetic interaction operates to a greater extent in the latter than in the former. When spin delocalization takes place through the σ system of the formate groups and yields spin density in the σ orbitals of the carbon atoms, $Q_{CH}^H(\sigma)$ is evaluated to be approximately equal to -170 G [4]. This value provides a reasonable spin density $\rho_C(\sigma) = -0.023$ populated in the carbon σ orbitals. The theory of superexchange interaction shows that the spin delocalization through the σ system of the formate groups yields ferromagnetic interaction between copper atoms whereas that through the π system induces antiferromagnetic interaction. This explains well the difference between the magnetic properties of the two modifications in accordance with the results of the PMR studies [4]. The spin density on the carbon atoms of $Cu_3(HCOO)_2(OH)_4$ is evaluated as either $\rho_C(\pi) = -0.08$ or $\rho_C(\sigma) = -0.01$ according to the spin delocalization mechanism π or σ , and $\rho_C(\pi) = -0.17$ or $\rho_C(\sigma) = -0.02$ for $Cu(HCOO)(OH)$. These $\rho_C(\pi)$ values seem to be too large to attribute to the spin delocalization effect, while the $\rho_C(\sigma)$ values are reasonable.

The value of Q_{OH}^H has not been established. Looyestijin *et al.* [16] have carried out ^{17}O NMR and PMR studies on $[Cu(OH)_2Cl_4]^{2-}$ complexes in which water molecules coordinate to copper atoms: the fractional spin 0.07 exists on the oxygen atoms bonded to copper atoms, and it polarizes the O-H bonds producing a spin density equal to -0.003 on the hydrogen atoms. On the basis of this experimental result, Q_{OH}^H can be evaluated as $(-0.003/0.07) \times 508 = -20$ G, where the value 508 is the coupling constant (in Gauss) of hydrogen atoms. By use of this value, the spin density on the oxygen atoms of the hydroxy groups is evaluated as 0.10 for $Cu(HCOO)(OH)$ and 0.06 for $Cu_3(HCOO)_2(OH)_4$. These values are reasonable because the unpaired electrons are delocalized directly onto the oxygen atoms of hydroxy groups from copper atoms.

Exchange interaction through Cu-OH-Cu bonding depends markedly on the bond angle [11]: the Cu-O-Cu angle nearly equal to 90° yields ferro-

magnetic interaction between copper atoms, and antiferromagnetic interaction becomes dominant with the increase of the bond angle. The Cu-O-C-O-Cu links also can provide either ferromagnetic or antiferromagnetic interaction according to the spin delocalization mechanism. The antiferromagnetic interaction of $Cu_3(HCOO)_2(OH)_4$ is due to hydroxy and/or formate bridgings. $Cu(HCOO)(OH)$ has at least two different kinds of magnetic interactions. This is obviously related to the two kinds of the Cu-L-Cu links

In addition to our previous works [4, 13, 14, 17], the present investigation has presented examples showing that spin exchange interaction is closely associated with spin delocalization. It is especially noteworthy that the Cu-O-C-O-Cu links in the Cu(II) formates have extensive spin delocalization effects and provide various types of mechanisms according to the delocalization mechanism.

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