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PMR Studies of Blue Form of Anhydrous Copper(II) Formate

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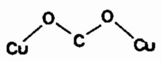
PMR spectra were recorded on the single crystals of $Cu(HCOO)_2 \cdot 4H_2O$ and the blue modification of $Cu(HCOO)_2$. The spectra exhibit paramagnetic shifts due to the hyperfine coupling and the dipole field of Cu(II) ions. The angular dependence of the PMR shifts provides the following conclusions: 1) the crystal of blue $Cu(HCOO)_2$ has a layer structure consisting of anti–anti *Cu–O–C–O–Cu bondings resembling that of the tetrahydrate, 2) the carbon atoms of the anhydride as well as of the tetrahydrate carry a negative spin density amounting to –0.025––0.030 on their p orbitals, 3) in both of the formates, the spin delocalization takes place through the p_π systems of the Cu–O–C–O–Cu bondings, and consequently 4) the superexchange interaction operates between Cu atoms through the π pathway which induces antiferromagnetic interaction in conformity with their magnetic properties.*

Introduction

Copper(II) formate tetrahydrate exhibits antiferromagnetism due to infinite *anti–anti* Cu–O–C–O–Cu links (Formula I) in two-dimensional lattices [1–3].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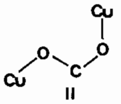
II

Anhydrous Cu(II) formate forms two magnetically different crystal modifications, *i.e.*, blue and royal blue forms [1]. The blue modification obtained by dehydrating the tetrahydrate exhibits two-dimensional antiferromagnetism, while the royal blue form prepared from a formic acid solution of the blue form shows ferromagnetic behaviors [1, 4]. The X-ray study of the royal blue form has indicated that Cu atoms form *anti–syn* Cu–O–C–O–Cu bondings (Formula II) to construct three-dimensional networks [5]. The blue form is presumed to have a layer structure consisting of *anti–anti* Cu–O–C–O–Cu arrangement found in the crystals of the tetrahydrate. The magnetically different properties of the two modifications have been explained to be due to the difference in the type of the Cu–O–C–O–Cu bonding arrangement [4, 5]. The basic Cu(II) formates Cu(OH)-(HCOO) and $Cu_3(OH)_4(HCOO)_2$ also show magnetic behaviors closely associated with the bonding arrangements [6]. These, especially anhydrous Cu(II) formates, present good examples for studying superexchange mechanisms. The earlier studies of the blue anhydride, however, were based on the presumption of its layer structure mentioned above [1, 4, 7]. In the point of view, the confirmation of the structure is important. Unfortunately, the single crystals of this modification are impossible to obtain.

In the crystals of the tetrahydrate, Cu atoms construct two-dimensional layer lattices parallel to the crystal *ab* plane, and water molecules are sandwiched between the lattices [2]. The crystals retain their external crystalline form even after losing water molecules, and the dehydrated crystals consist of sheets parallel to the *ab* plane of the original crystals. These are reasons why the layer structure of the tetrahydrate can be presumed to be retained in the blue anhydride. If this is true, the sheets are the crystal unit of the blue form, and all of them are oriented in one direction so that the dehydrated crystals can be regarded as 'quasisingle crystals' in a magnetic field applied along the plane of the sheets. Therefore, the PMR technique usually employed for single crystals can be applied to the quasisingle crystals to determine the positions of the HCOO protons. In the present investigation, we have recorded the PMR spectrum of the dehydrated crystals, in order to determine the positions of the HCOO protons in the layer lattice of the blue modification and to confirm the retention of the two-dimensional structure of the original tetrahydrate crystals.

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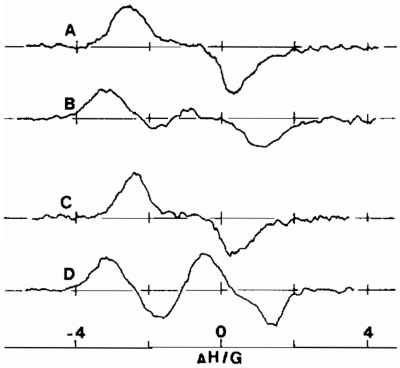

Fig. 1. Some PMR spectra of blue anhydrous Cu(II) formate (A: θ = 0°, B: θ = 30°) and Cu(II) formate tetradeuterate (C: θ = 0°, D: θ = 45°).

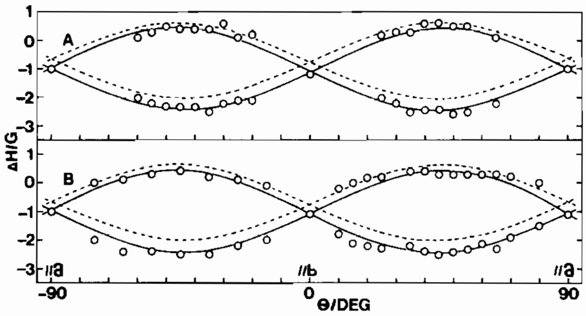

Fig. 2. Angular dependence of the PMR shifts observed for blue anhydrous Cu(II) formate (A) and Cu(II) formate tetradeuterate (B). The broken curves show shifts due to the dipole sum, and the solid curves are theoretical curves contributed from the dipole sum and the hyperfine interaction due to spin density on the HCOO carbon p orbitals.

Superexchange interaction takes place through Cu–O–C–O–Cu links in the formates. In our previous paper, we have presented an experimental evidence to it by observing the Fermi contact shift in the PMR powder spectra of the anhydrides [4]. The PMR studies of single crystals can provide more precise information about the spin delocalization closely related to superexchange interaction [8]. This is another purpose of the present investigation.

Experimental

The single crystals of $Cu(HCOO)_2 \cdot 4H_2O$ were grown by slow evaporation of an aqueous solution of Cu(II) formate tetrahydrate containing a few drops of formic acid. The obtained crystals were dehydrated gradually in air for several days. Then they were dried in a $CaCl_2$ desiccator to complete the dehydration.

The PMR spectrum was recorded by means of a JEOL JNM-MW-40 NMR spectrometer operating at 40 MHz. Hexane (isomeric mixture) was employed as an external standard. The amplitude of magnetic field modulation was equal to 0.6–0.8 G small enough compared with the width of the observed spectra.

Results

A dehydrated crystal was mounted on a glass rod so that its crystal plane corresponding to the *ab* plane of the original crystal was parallel to the external magnetic field. Figure 1 shows some typical PMR spectra recorded at 300 K and at different angles θ between the external field H_0 and the crystal axis corresponding to the a axis of the tetrahydrate crystal. Except for $H_0 \parallel a$ or b, each observed curve was resolved into two simple derivative curves each showing paramagnetic shift.

Figure 2 displays the angular dependence of the centers of the component curves. The crystal oriented as $H_0 \perp (001)$ exhibited very broad PMR spectra. This was probably due to some irregularity in the conformity of the stacking sheets or in the distance between them. The PMR spectra are insensitive to this irregularity in the crystal orientation $H_0 \parallel (001)$, but are sensitive to it when $H_0 \perp (001)$. Therefore, the spectra recorded for the former orientation were employed for the discussion, providing information sufficient enough for the present purpose.

The PMR spectra were recorded on the single crystals of $Cu(HCOO)_2 \cdot 4D_2O$ also in order to confirm the results obtained for the anhydride. Substantially the same spectra were observed for the HCOO protons of the tetradeuterate: each curve recorded for $H_0 \parallel (001)$ was made up of two component curves each exhibiting paramagnetic shift (Fig. 1). Figure 2 shows the angular dependence of the shifts.

Discussion

Figure 3 shows the network structure of $Cu(HCOO)_2 \cdot 4H_2O$ projected along the crystal c axis [2]. The positions of the hydrogen atoms have not been determined as yet. The hydrogen atom of an HCOO group is reasonably assumed to lie in the OCO plane of the formate group with the typical C–H distance 1.09 Å [9]. Therefore, the unit cell contains two magnetically nonequivalent HCOO protons in a magnetic field applied along the (001) plane at an arbitrary angle, and all HCOO protons are quivalent with one another in $H_0 \parallel a$ or b. These are consistent with the angular dependence observed for $Cu(HCOO)_2 \cdot 4D_2O$. The shift and its angular dependence of the blue anhydride closely resemble

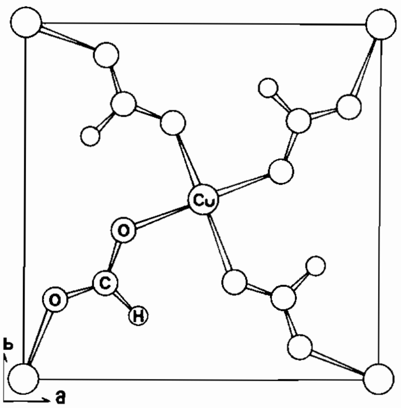

Fig. 3. Network structure of Cu(II) formate tetrahydrate.

those of the tetradeuterate. This indicates that the positions of the HCOO protons are practically unchanged on dehydration of the tetrahydrate, supporting the aforementioned presumption that the layer structure of the tetrahydrate is retained in the blue modification. Therefore, we can discuss the physical properties of the latter on the basis of the layer structure.

In paramagnetic crystals, the time-average magnetic moments of paramagnetic ions produce a local field at a given proton, *i.e.*, the so-called dipole sum H_d [8]:

$$H_d = -\frac{g^2\mu_B^2 H_0 S(S+1)}{3k(T-\Theta)} \times \sum_i \frac{3\cos^2(\theta+\theta_i)\cos^2\phi_i - 1}{|R_i|^3} \qquad (1)$$

Here, apart from obvious notations, R_i is the vector joining the ith Cu atom and the proton in question, ϕ_i is the angle between R_i and the *ab* plane, θ_i denotes the angle between the crystal *b* axis and the projection of R_i on the *ab* plane, and θ denotes the angle between *b* axis and magnetic field. The Weiss constant Θ has been determined to be equal to -124 K [4]. The *g* tensor of the Cu(II) formate has an axial symmetry, since the Cu(II) ions are surrounded by axial coordination field. The axis of $g_\parallel$ is perpendicular to the square plane consisting of four oxygen atoms from formate groups, and that of $g_\perp$ lies in the CuO_4 plane. This coordination plane is inclined from (001) by about 20°. The inclination angle is so small that *g* in equation (1) is practically isotropic and equal to $g_\perp$. The *g* values of the formates have not been determined precisely. Most of Cu(II) complexes in which Cu(II) ions are surrounded by four oxygen atoms take a $g_\perp$ value in the range of 2.05–2.10 [10]. From these informations, we can evaluate H_d for the respective formates. The broken curves in Fig. 2 show the angular dependence of H_d calculated with $g = 2.10$. They resemble the patterns of the corresponding observed angular dependences, but clearly disagree with the observed shifts in the absolute values. The employment of a *g* value equal to 2.05 yields larger disagreements. Therefore, another paramagnetic effect contributes to the PMR shifts in addition to the dipole sum.

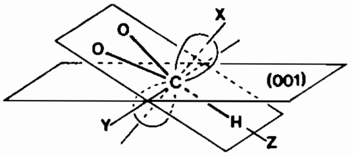

Fig. 4. Definition of the principal axes of the *Q* tensor and their relation to the crystal (001) plane in the crystals of Cu(II) formate tetrahydrate.

When unpaired electrons delocalized from Cu(II) ions onto formate groups induce spin density on the carbon atoms of the formate groups, protons bonded to the carbon atoms exhibit paramagnetic PMR shift due to the hyperfine interaction. The hyperfine-interaction field H_h at the resonant protons is given by [8]:

$$H_h = -\frac{A}{g_N\mu_N} \cdot \frac{g_e^2\mu_B^2 H_0 S(S+1)}{3k(T-\Theta)} \qquad (2)$$

Here, g_N and g_e are nuclear and electronic *g* factors, respectively, μ_N is the nuclear magneton, and *A* denotes the hyperfine coupling constant (in Gauss), which is proportional to spin density ρ_C on the carbon atom bonded to the resonant proton [8]:

$$A = Q \cdot \rho_C \qquad (3)$$

The proportionality constant *Q* is equated with the hyperfine coupling constant of a ·CH species involving one odd electron in the carbon *p* orbital. Owing to the combined effect of the isotropic Fermi contact term and the anisotropic dipolar interaction, *Q* is expressed as a tensor: the principal values have been given as $Q_x = -21$ G, $Q_y = -33$ G, and $Q_z = -10$ G [11]. The definition of the tensor axes and their relation to the crystal plane are illustrated in Fig. 4. Accordingly, *A* is anisotropic and H_h has angular dependence. The solid curves in Fig. 2 display the total shifts contributed from H_d and H_h calculated with $\rho_C = -0.025$ in agreement with the experimental data. When $g = 2.05$ is employed for the calculation of H_d, the H_h evaluated with $\rho_C = -0.030$ reproduces the same curves. The ρ_C value -0.025–-0.030 agrees well with -0.024 determined from the PMR shift of polycrystalline powders of the blue anhydride [4]. Therefore, the carbon atoms of the anhydride carry the negative spin density −0.025−−0.030 in their *p* orbitals, and the density is equal to that of the tetrahydrate. This indicates that the spin delocalization in the two formates is dominated by the same mechanism in which unpaired electrons are delocalized through the π system of the Cu–O–C–O–Cu links.

The crystalline powders of the royal blue anhydrate has a coupling constant equal to 3.9 G much larger than 0.54 G of the blue form, and the former value is too large to attribute to the spin delocalization through the π system of the formates groups. For these reasons, alternative spin-delocalization mechanism through the σ system has been proposed [4]. Unfortunately, this cannot be confirmed by the single-crystal method, because it is difficult to obtain the single crystals large enough for the PMR study. However, it is convincing that the spin-delocalization mechanism of the royal blue form is different from that of the blue form as mentioned above.

In conclusion, we have succeeded in confirming and obtaining the following conclusions in the present investigation: 1) the blue modification has network structure consisting of *anti–anti* Cu–O–C–O–Cu links, 2) the carbon atoms of the formate groups carry a negative spin density equal to −0.025−−0.030 on their *p* orbitals in the blue anhydride as well as in the tetrahydrate, and 3) the spin delocalization in the two Cu(II) formates is dominated by the π mechanism. These present convincing experimental evidence supporting the mechanism of the superexchange interaction through the p_π systems of the formate groups [4].

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