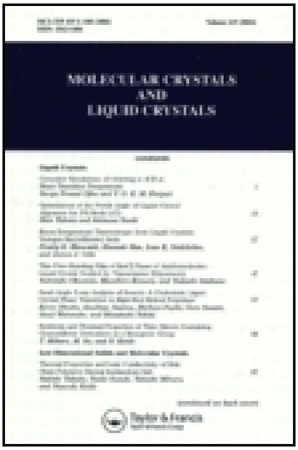

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Local Magnetic Structure of Layered Compounds $Cu_2(OD)_3X$ with Exchangeable Acid Anion X Studied by Solid State High Resolution Deuterium NMR

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The microscopic magnetic local structure of Botallackite-type layer structured compounds $Cu_2(OD)_3X$ ($X = NO_3^-$ and $HCOO^-$) exhibiting a nonequilateral planar triangular magnetic lattice was determined by the solid-state high resolution deuterium NMR of deuterated hydroxy groups in the high temperature region above 190 K. The magnetic interactions in a copper ion layer were probed by the paramagnetic NMR shifts of the two chemically distinct hydroxy groups. Isotropic NMR shift of each hydroxy group showed different temperature dependence, suggesting non-uniform magnetic interaction. The magnetic interaction in the copper layer could be decomposed into a sum of 1D-Heisenberg ferro- and antiferromagnetic chains in the high temperature region. Two distinct copper chains with ferro- and antiferromagnetic exchange interactions $J = +19 \pm 11$ and -21 ± 3 K were found for $x = NO_3^-$ from the temperature dependence of the two distinct NMR signals, while $J = +13 \pm 7$ and -13 ± 5 K for $x = HCOO^-$. The derived values of J almost reproduced the temperature behavior of the magnetic susceptibility $\chi_A T$ vs. T.

Keywords: magnetic local structure; magnetic interaction; Botallackite-type copper compounds; solid state high resolution NMR; nonequilateral planar triangular magnetic lattice

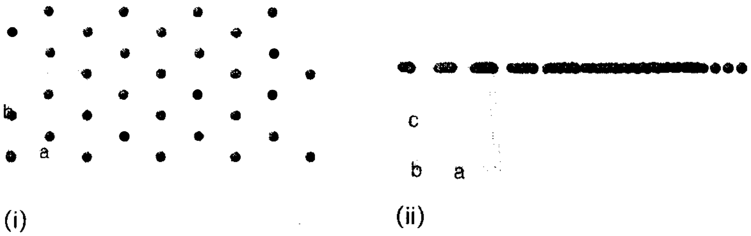

FIGURE 1 Nonequilateral planer triangular magnetic lattice structure of copper ions of $Cu_2(OH)_3NO_3$: (i) viewed along the axis perpendicular to and (ii) parallel to the **ab**-plane.

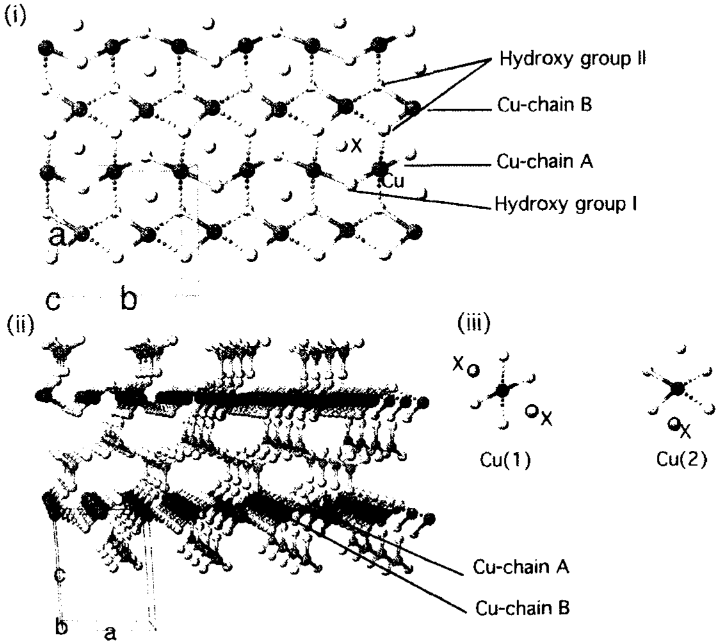

FIGURE 2 Layer structure of $Cu_2(OH)_3NO_3$; (i) viewed along **c** axis perpendicular to the layer, (ii) along **b** axis parallel to the layer. Tow chemically distinct hydroxy groups **I** and **II** are indicated in (i) together with two distinct copper ions Cu(1) and Cu(2) in (iii) which form Cu-chains A and B shown in (i), respectively.

INTRODUCTION

Botallackite-type compounds $Cu_2(OH)_3X$ (X = exchangeable anion) exhibit layered structures, in which a nonequilateral planar triangular magnetic lattice of copper ions is constructed as shown in Fig. 1[1,2]. The copper ions are bridged by hydroxy groups and an atom of exchangeable anion X to form infinite layers. Two chemically distinct copper ions lie in different distorted-octahedral coordination environments: $Cu[(OH)_4X_2]$ and $Cu[(OH)_4X(OH)]$ as depicted in Fig. 2 (iii). A variety of anions X can be incorporated and the bulk magnetism of $Cu_2(OH)_3X$ largely depends on the property of the anions X[3-5]. It has been desired to clarify in a microscopic viewpoint how the macroscopic magnetism of $Cu_2(OH)_3X$ is controlled by the X. In this paper, we present the solid-state high resolution deuterium NMR (D-NMR) study of the magnetic local structures and the magnetic interactions of Botallackite-type compounds $Cu_2(OD)_3X$: X = NO_3^- and $HCOO^-$. Particular attention was paid to the relation between the microscopic magnetic local structures determined by the NMR and the macroscopic magnetic susceptibility.

SOLID-STATE HIGH RESOLUTION DEUTERIUM NMR OF PARAMAGNETIC COMPOUNDS

Since a hydroxy group bridges three copper ions in the layer as depicted in Fig. 2 (i) and since it mediates super exchange and/or direct exchange interactions among the copper ions, the paramagnetic NMR shift of the hydroxy deuterium (D-NMR), which is induced by the hyperfine coupling between deuteron and copper spins, must be an excellent probe for elucidating the local magnetic structures and the local magnetic interactions. Magic angle spinning (MAS) averages the quadrupole interaction of deuteron and the dipole interaction between deuteron and copper spins to provide the isotropic shift of the D-

NMR absorption line. The observed isotropic shift in ppm consists of the Fermi contact term, the pseudo contact term and the temperature independent diamagnetic term as follows,

$$\delta_{\rm iso} = \delta_{\rm Fermi} + \delta_{\rm Pseudo} + \delta_{\rm dia} \tag{1}$$

$$\delta_{\rm Fermi} = \frac{\mu_{\rm B}}{3k_{\rm B}T} \cdot \frac{A_{\rm Fermi}}{\gamma_{\rm D}/2\pi} \cdot \left(\frac{g_{xx} + g_{yy} + g_{zz}}{3} \right) \cdot S(S+1) \cdot F\,, \tag{2}$$

$$\begin{aligned}\delta_{\rm pseudo} = \frac{\mu_B^2}{18k_BTr^3} \cdot S(S+1) \cdot F \cdot \{[2g_{zz}^2 - (g_{xx}^2 + g_{yy}^2)](3\cos^2\theta - 1) \\ -3(g_{yy}^2 - g_{xx}^2)\sin^2\theta\cos 2\Omega\}\end{aligned} \tag{3}$$

where $A_{\rm Fermi}$ is the Fermi contact coupling constant of the nucleus D in Hz[6,7]. The Fermi and pseudo contact terms show a similar temperature dependence and the experimentally determined hyperfine coupling constant $A_{\rm D}$ consists of the two terms. The anisotropy of the g-tensor is not large for copper complexes. Using a g-tensor with axial asymmetry ($g_{yy}^2 - g_{xx}^2 = 0$) as often assumed for most copper complexes, $g^2 - g_{\perp}^2 \approx 1.5$,[8] the contribution of the pseudo contact to the hyperfine coupling constant $A_{\rm D}$ is estimated to be *ca.* 0.2 MHz for $Cu_2(OH)_3NO_3$[2]. The magnetic interaction can be determined from the temperature dependence of F / k_BT. Evaluation of the factor F is described in the discussion.

EXPERIMENTAL

The compound $Cu_2(OD)_3HCOO$ with hydroxy groups deuterated more than 99% was prepared by anion exchange reaction in heavy water from the parent material of basic copper acetate according to a similar procedure reported in ref. 9. The compound of X = NO_3^- with *ca.* 60% deuteration was synthesized hydrothermally by using heavy water as solvent[2]. The content of the deuterium in the products was estimated from the ratio of H and D in the reactants. The obtained compounds were identified to exhibit the Botallackite structure by powder X-ray diffraction[2,3]. Each specimen showed strong (001) diffraction corresponding to the layer structure: the basal spacing was 6.93 and 6.99 Å for the green crystals of $Cu_2(OD)_3NO_3$ and light-bluish-green crystals of $Cu_2(OD)_3HCOO$, respectively.

D-MAS NMR spectra were measured by a single pulse method at the resonance frequency of 46.1MHz and at the magic angle spinning speed of 5~10 kHz with Bruker DSX300 spectrometer and a 4mm CP/MAS probe between 190K and 300K: The $\pi/2$ pulse length was 2μs and the repetition time 0.5s. A conventional zirconia rotor (4mm) with boron nitride cap was used. The specimen (*ca.* ~50mg) was carefully packed at the center of the rotor (~ 4 mm long) to achieve homogeneous temperature at the sample position and Teflon powder was used as spacers. The thermometer of the MAS probe was carefully calibrated against the isotropic chemical shift of ^{207}Pb-MAS NMR spectrum of $Pb(NO_3)_2$[10] and brittle-plastic phase transition temperatures of several kinds of orientationally disordered crystals[11] probed by proton MAS NMR. Temperature raise of the sample as the spinning speed increased was also examined and calibrated. Uncertainty of the temperature measurement after the calibration was 4K and temperature fluctuation during accumulation was within 2 K. An error of reading the shift value of the D-MAS NMR spectrum was ± 2 ppm. All D-NMR shifts were measured from the external second reference of acetone-d_6 (2.05 ppm).

RESULTS AND DISCUSSION

Figure 3 shows the D-MAS NMR spectra of the two compounds measured at room temperature. Two chemically distinct copper ions lie in different distorted-octahedral coordination environments: $Cu[(OH)_4X_2]$ and $Cu[(OH)_4X(OH)]$ designated as Cu(1) and Cu(2), respectively in Fig. 2 (iii).

There are two chemically different hydroxy groups **I** and **II**: the hydroxy group **I** bridges three copper ions Cu(1)Cu(1)Cu(2), whereas the hydroxy group **II** bridges another combination of copper ions Cu(1)Cu(2)Cu(2). The two hydroxy groups **II** in the unit formula are crystallographically nonequivalent for $Cu_2(OD)_3\,NO_3$[2] and three different NMR signals are expected. However, only two signals with almost 2:1 relative intensity were observed. The intensity ratio of the couple of isotropic signals holds for all of the couples of spinning side bands. The spinning side bands were easily identified by employing different spinning speeds. The signal with larger intensity was assigned to the hydroxy group **II**. Two crystallographically nonequivalent hydroxy groups **II** sit at the very similar magnetic environment. The compound of X = $HCOO^-$, which is isomorphous to NO_3^- compound,[3] showed three different NMR signals as depicted in the same figure, indicating a larger distortion of the magnetic local structure of this compound compared with X = NO_3^-.

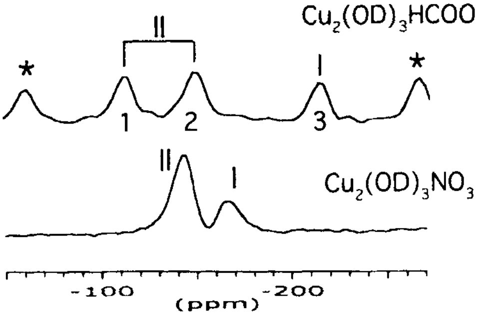

FIGURE 3 Magic angle spinning deuterium NMR spectrum at 294 K. Spinning speed was 7 kHz. Asterisks indicate the spinning side bands.

Particularly interesting is the peak 3, which was largely shifted by substitution of the anion X and was assigned to the hydroxy group **I**. The magnetic local structure of the hydroxy group **I** varies sensitively when the anion X changed.

This behavior was more clearly found for halide compounds[12], suggesting an one-dimensional character of the dominant magnetic interaction. The copper ions (1) are linked by the hydroxy group **I** and by one of the atoms of the anion X to form a infinite chain, while Cu(2)'s are doubly linked by the hydroxy groups **II**.

Assuming no magnetic interaction among copper ions, which is equivalent to put the factor $F = 1$ in Eqs. 2 and 3, a fit of the experimental values of the temperature dependence of the isotropic shift to Eqs. 1 through 3 gave a large scatter of diamagnetic shifts and apparent hyperfine coupling constants as shown in Table 1. The diamagnetic shift of the hydroxy groups is usually found in the range 5 ~ 15 ppm for many compounds. The result indicates that the magnetic interaction among the copper ions must be taken into account. Since one dimensional character of the magnetic interaction among the copper ions in the layer was suggested above, one-dimensional spin-1/2 Heisenberg model was assumed. Then the factor F in Eqs. 2 and 3 can be approximated by a Padé expansion series[13],

$$\begin{aligned} F = [(1 &+ 5.7979916K + 16.902653K^2 + 29.376885K^3 \\ &+ 29.832959K^4 + 14.036918K^5)/(1 + 2.7979916K \quad , \\ &+ 7.0086780K^2 + 8.6538644K^3 + 4.5743114K^4)]^{2/3} \end{aligned} \tag{4}$$

where $K = J/(2k_BT)$. The above function is not applicable for $K \leq -0.5$. Equation 5, however, can be used for ferro- and antiferromagnetic interactions in the present case. Least-squared fittings of the observed temperature dependence of the isotropic shifts gave the curves shown in Fig. 4. The derived values of J and the hyperfine coupling constant are listed in Table 1. The magnetic interaction in the chain of Cu(1) ions (chain A) is ferromagnetic, while the chain of Cu(2) ions (chain B) exhibits antiferromagnetic one. The Cu-OH-Cu magnetic interaction is known to be quite sensitive to its angle, varying between ferromagnetic and antiferromagnetic one around 98° in the case of dinuclear copper complexes[14]. A theoretical study of a similar behavior has also reported[15]. Although it is not established whether the same relation holds for infinite copper chains or not, similar angles were found for $Cu_2(OH)_3NO_3$: 104.05° for Cu(1)-OH-Cu(1), 78.54° for Cu(1)-O(NO_2)-Cu(1), 99.24 and 99.71° for Cu(2)-OH-Cu(2)[2]. The magnetic interaction in the chain of Cu(1) ions is expected to vary by exchanging the anion X, since the angle of Cu(1)-OH-Cu(1) and the magnetic coupling through Cu(1)-X-Cu(1) are sensitively affected by the property of the anion X.

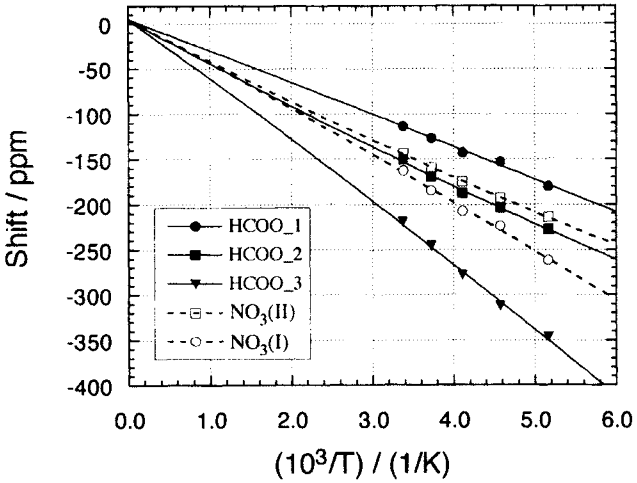

FIGURE 4 Temperature dependence of the paramagnetic shift of deuterium NMR of $Cu_2(OD)_3NO_3$ (open symbols) and $Cu_2(OD)_3HCOO$ (closed symbols).

Magnetic susceptibility is a macroscopic character of the magnetic materials. It is interesting to compare the exchange interactions *J* estimated from the D-NMR measurement with the temperature behavior of the magnetic susceptibility of the same compound. The Weiss constant of $Cu_2(OH)_3HCOO$ evaluated from the magnetic susceptibility data in the high temperature region is + 4 K, showing predominance of the ferromagnetic interaction[4], while the estimate for $Cu_2(OH)_3NO_3$ is - 1 K, suggesting slightly antiferromagnetic one[16,17]. We tried to calculate the high temperature behavior of the magnetic susceptibility $\chi_A T$ vs. T by using the same model of simple sum of 1D-Heisenberg chains with ferro- and antiferromagnetic interactions as for the D-NMR shifts. The calculation using J values that are consistent with the NMR measurement reproduced the temperature behavior of $\chi_A T$ above 50 and 30 K for X = NO_3^- and $HCOO^-$, respectively. The relation $\chi_A T = 0.218\{F(J=+19\text{K})+F(J=-24\text{K})\}$ was used for X = NO_3^- and $\chi_A T = 0.220\{F(J=+15\text{K})+F(J=-12\text{K})\}$ for X = $HCOO^-$. The function F is given in Eq. 4. The high temperature behavior of the macroscopic magnetism of the Botallackite-type layer structured compounds can be understood by a competition among the different magnetic chains of copper ions.

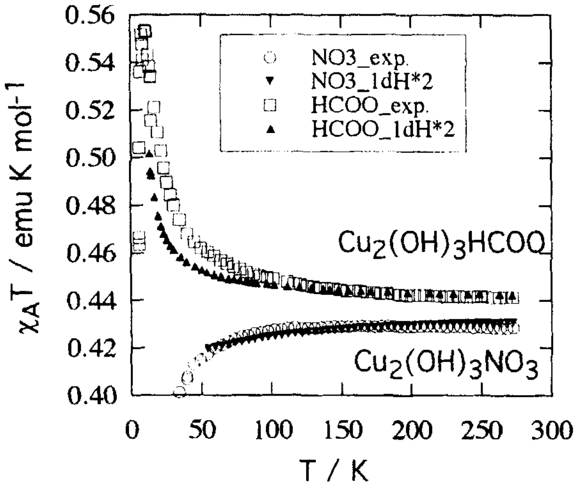

FIGURE 5 Temperature behavior of the magnetic susceptibility of $Cu_2(OH)_3HCOO$ and $Cu_2(OH)_3NO_3$. Open symbols are experimental data[4,16]. Filled triangles are calculated from the sum of one dimensional ferro- and antiferromagnetic chains with exchange interactions that are compatible with the local magnetic structure determined by D-NMR. See the last column of Table 1.

TABLE I Magnetic interactions in $Cu_2(OD)_3X$ deduced from the D-MAS NMR.

compound, T_{max} b) and basal spacing	hydroxy group c)	linear fitting A_D(ap.) / MHz	 δ_{dia} / ppm	1D Heisenberg chains a) A_D / MHz	 Cu-chain	 exchange interaction J / K d) (D-NMR)	 J / K ($\chi_A T$)
NO_3^- (10.5K) 6.93 Å	I	-1.00	+ 16	- 0.91 ± 0.05	A	+ 19 ± 11	+ 19
	II & II'	-0.77	- 12	- 0.93 ± 0.05	B	- 21 ± 3	- 24
HCOO$^-$ (8K) 6.99 Å	I (3)	-1.40	+ 21	- 1.28 ± 0.06	A	+ 13 ± 7	+15
	II (2)	-0.82	- 11	- 1.00 ± 0.05	B	- 18 ± 5 } -13	- 12
	II' (1)	-0.70	+ 8	- 0.74 ± 0.05	B	- 8 ± 5	

a) Diamagnetic shift was assumed to be +5 and +10 ppm for X = NO_3^- and HCOO$^-$, respectively. b) Temperature of a maximum of magnetic susceptibility χ_A is shown in parentheses: NO_3^-, refs. 15 and 16; HCOO$^-$, refs 4. The inter-layer distances shown were determined in the present study. c) see text. d) Values at the right hand side of the brace are averaged one for the same magnetic chain.

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