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Ferro- and antiferromagnetic interactions of layer-structured basic copper compounds as studied by solid-state high-resolution deuterium NMR

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Abstract

Magnetic local structure of a ferromagnetic layer-structured basic copper compound $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$ with dicaboxylate anion was examined by solid-state high-resolution deuterium NMR above 200 K. The magnetic interaction in a copper layer was probed by the isotropic D NMR shift of OD^- ions. Only one strong signal was observed for the OD^- ions of $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}$ $0.07D_2O$, while more than two signals corresponding to different magnetic chains of Cu^{2+} ions in a layer were observed for most of $Cu_2(OD)_3X$ where X was univalent anion. A ferromagnetic exchange interaction $J = +71$ K within a copper layer was estimated from the temperature dependence of the isotropic D NMR shift by assuming an one-dimensional Heisenberg model. A layer-structured compound $Cu_2(OH)_3(SCN)$ with non-oxygen atom coordination for bridging copper ions was synthesized by anion exchange reaction. The magnetic susceptibility measurement indicates that a weak ferromagnetic interaction dominates in the high temperature region and a weak antiferromagnetic interaction appears in the low temperature region.

Keywords: Layer-structured basic copper compound; Local magnetic structures; Local magnetic interactions; Hyperfine coupling of OD^- ions; Solid-state high-resolution deuterium NMR

1. Introduction

Botallackite-type basic copper compounds $Cu_2(OH)_3X$ (X = exchangeable univalent anion) exhibit a layered structure as schematically depicted in Fig. 1 [1,2]. Hydroxide ions and exchangeable anion X bridge the copper ions to form infinite layers. Two chemically distinct copper ions lie in different distorted-octahedral coordination environments, i.e., $Cu[(OH)_4X_2]$ and $Cu[(OH)_4X(OH)]$. Each copper ion forms an one-dimensional chain and the two distinct chains are alternately connected to form a layer, in which all copper ions sit on the same plane constructing a nonequilateral planar triangular arrangement in the case of a simple compound such as $Cu_2(OH)_3Br$ [1]. Various anions X can be incorporated by anion-exchange reaction by stirring the suspended powder crystals of basic copper acetate $Cu_2(OH)_3CH_3COO\cdot H_2O$ in MX aqueous solutions, where M is an alkali metal ion [3–6]. The bulk magnetism of $Cu_2(OH)_3X$ sensitively depends on X. The magnetism also varies with different intercalation structures exhibiting various interlayer distances even for the same exchangeable anion X, particularly for aliphatic mono-carboxylate $C_nH_{2n+1}COO^-$ [7]. We have demonstrated that the magnetic interactions within the copper layer could be approximated by a sum of one-dimensional magnetic chains in the high temperature region [8–11]. The copper chain A in Fig. 1 shows ferro- and antiferromagnetic interactions depending on the anion X, while the copper chain B mostly exhibits antiferromagnetic interaction. The antiferromagnetic interaction dominates the bulk magnetism for many compounds $Cu_2(OH)_3X$. It was reported, however, in recent years that a compound with dicaboxylate (*trans*-3-hexenedioate) anion showed ferromagnetic ordering at 13 K [6].

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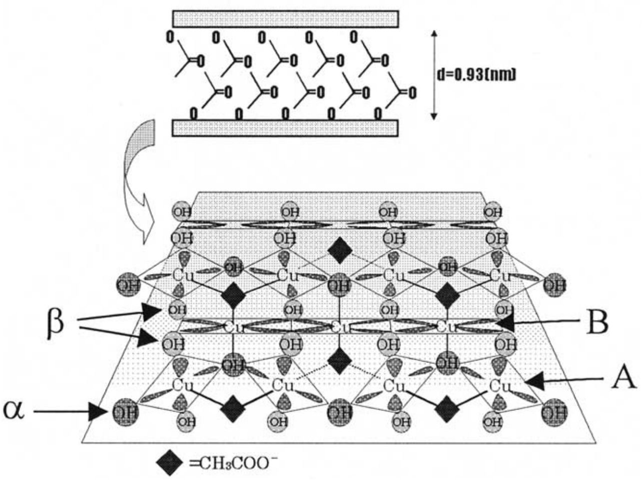

Fig. 1. Schematic view of layered structure and intra-layer structure of $Cu_2(OH)_3CH_3COO\cdot H_2O$. Two distinct copper chains **A** and **B** with different coordination structures are illustrated. Water molecules are not shown in this figure.

This led us to investigate the local magnetic structure of the deuterated analogue by means of the solid-state high-resolution deuterium NMR (D NMR) spectroscopy to elucidate the magnetic interactions within the layer in a microscopic viewpoint.

In many cases, the oxygen atoms of exchangeable anions bridge the copper ions within a layer. An effort to employ non-oxygen atoms for bridging the copper ions is interesting in a viewpoint of modifying the magnetic coupling among the copper ions [11]. Thiocyanate ion was used to form the layered structure compound $Cu_2(OH)_3(SCN)$.

2. Method and experiment

2.1. Solid-state high-resolution deuterium NMR and magnetic susceptibility measurements

Since an OD^- ion bridges copper ions and mediates exchange interactions among them, the paramagnetic D NMR shift of the OD^- ion, which is induced by the hyperfine coupling between the deuteron of OD^- and the electron spins of copper ions, is an excellent probe for elucidating the local magnetic structures and the local magnetic interactions in a microscopic view point. The high-speed magic angle spinning technique removes the quadrupole coupling of deuteron and averages the anisotropy of the dipolar interaction between deuteron and electron spins to provide an isotropic shift of the D NMR absorption line. The observed isotropic shift consists of the Fermi contact term, the dipolar interaction term (pseudo contact) and the temperature independent diamagnetic term (chemical shift) as follows [12,13]:

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

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

$$\delta_{\mathrm{Pseudo}} = \frac{\mu_{\mathrm{B}}^2}{18k_{\mathrm{B}}Tr^3}\{[2g_{zz}^2-(g_{xx}^2+g_{yy}^2)](3\cos^2\theta-1) -3(g_{yy}^2-g_{xx}^2)\sin^2\theta\cos 2\Omega\}S(S+1)F(J,T) \tag{3}$$

Electron spin induced on the deuteron by electron spins of Cu^{2+} ions causes a Fermi contact shift of the D NMR resonance line, whereas anisotropy of the g-tensor of Cu^{2+} ion gives a pseudo contact shift. Since the temperature dependence of δ_{Pseudo} is the same as that of δ_{Fermi}, Eqs. (2) and (3) can be reduced to the following formula:

$$\delta_{\mathrm{Fermi}} + \delta_{\mathrm{Pseudo}} = \frac{\mu_{\mathrm{B}}}{3k_{\mathrm{B}}T}\,\frac{A_{\mathrm{D}}}{\gamma_{\mathrm{D}}/2\pi}S(S+1)F(J,T) \tag{4}$$

The coefficient A_{D} is the hyperfine coupling constant of the nucleus D in hertz unit [14], which consists of Fermi and pseudo contact terms. The function $F(J, T)$ gauges the interactions among the $S = 1/2$ electron spins of the Cu^{2+} ions. The anisotropy of the g-tensor is often small for copper complexes. The contribution of the pseudo contact term to the hyperfine coupling constant A_{D} in Eq. (4) was estimated to be approximately 0.2 MHz for an analogous compound $Cu_2(OD)_3(NO_3)$ [8,15]. Magic angle spinning deuterium NMR (MAS D NMR) spectra were measured by a similar method described in Ref. [14] at the resonance frequency of 46.1 MHz and at the magic angle spinning speed of 8–10 kHz with a Bruker DSX300 spectrometer. The thermometer of the MAS NMR probe and an effect of spinning speed on temperature increase were carefully calibrated by using ^{207}Pb NMR shift of $Pb(NO_3)_2$ [16]. The precision of the temperature measurement after calibration was ±2 K. All D NMR shifts were measured from the external second reference of CD_3OD (CD_3: 3.35 ppm).

Direct current magnetic susceptibility was measured with SQUID magnetometer (Quantum Design MPMS 5) at an external magnetic field of 1 T.

2.2. Sample preparation

The preparation method of $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$ is similar to that of the protonated compound reported in Ref. [6]. The starting compound $Cu_2(OH)_3CH_3COO\cdot H_2O$ was synthesized by titration of copper acetate by sodium hydroxide [17]. Powder crystals of $Cu_2(OH)_3CH_3COO\cdot H_2O$ (0.5 mmol) were suspended and stirred in 15 ml of 0.25 M heavy water solution of sodium salt of *trans*-β-hydromuconic (*trans*-3-hexenedioic) acid $Na_2C_4H_6(COO)_2$ at room temperature for 1 day. Repeating once the treatment of the reaction product with a fresh solution for 2 days completed the exchange reaction. The green powder microcrystalline sample was washed by heavy water and dried in desiccator. Elemental analysis gave C: 24.14% and H(D): 2.69%, indicating a formula of $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$, which is similar to the previous report for the protonated compound [6]. The powder X-ray diffraction showed strong (0 0 *l*) lines ($l \leq 4$) as shown in Fig. 2, indicating that the layered structure was maintained and the interlayer distance was enlarged by anion exchange to 1.02 nm from 0.93 nm of starting compound.

Thiocyanate ion was incorporated in the layered structure similarly. Powdered crystals of the starting compound $Cu_2(OH)_3CH_3COO\cdot H_2O$ (2.35 mmol) were suspended and stirred in 30 ml of 1.58 M normal aqueous solution of sodium thiocyanate at room temperature. The acetate ion was gradually exchanged by thiocyanate ion while maintaining the layered structure, which was checked by powder X-ray diffraction at every 2 h as depicted in Fig. 3(a–d). The peak at $d_{0\,0\,1} = 0.93$ nm and its higher diffraction peaks of starting compound gradually disappeared and a new peak at $d_{0\,0\,1} = 1.12$ nm and its higher diffraction (0 0 *l*) with $l \leq 3$ increased until the reaction period reached 6 h. At this stage, the starting compound almost completely changed to a new layer structured compound as shown in Fig. 3(d). Elemental analysis gave C, 5.38% (Calc. 5.09); H, 1.98% (1.28); N, 6.18% (5.93) and S, 12.9% (13.58), indicating a formula $Cu_2(OH)_3SCN$. A longer reaction period induced a reduction of Cu(II) ions to form α-Cu(I)SCN and after 45 h of stirring the powder crystals almost completely transformed to α-Cu(I)SCN, which was confirmed by powder X-ray diffraction shown in Fig. 3(f) and elemental analysis, C, 9.87% (Calc. 9.88); N, 11.23% (11.52) and S, 25.14% (26.36). Therefore, the layer-structured compound $Cu_2(OH)_3SCN$ can be obtained by controlling the reaction time. The same preparation procedure was conducted with employing D_2O to obtain the deuterated analogue. However, the MAS D NMR signal was not detected at present.

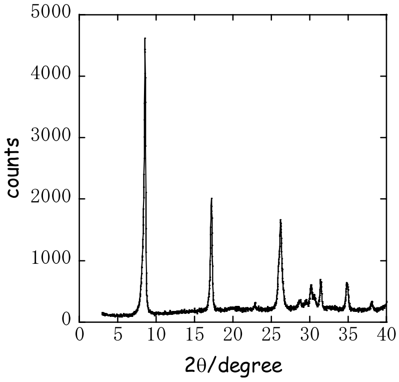

Fig. 2. Powder X-ray diffraction pattern of deuterated compound $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$ measured with Cu Kα irradiation.

3. Results and discussion

3.1. Magnetic susceptibility measurement

Fig. 4(a) shows the magnetic susceptibility χT of $Cu_2(OH)_3SCN$. A very weak ferromagnetic interaction dominates in the high temperature region and a weak antiferromagnetic interaction appears in the low temperature region. The Weiss temperature $\theta_W = +7$ K was estimated from the high temperature region of $1/\chi$ vs. T above 150 K. Strong antiferromagnetic interactions dominates in a compound $Cu_2(OD)_3(CH_3(CH_2)_6COO)$ with an interlayer distance of 2.49 nm [10] as depicted in Fig. 4(b). The Weiss temperature $\theta_W = -163$ K of this compound was estimated in the high temperature region above 150 K. On the other hand, for the complex $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$, a ferromagnetic interaction dominates the bulk magnetism as shown in Fig. 5. The Weiss temperature θ_W of this compound is +49 K. The ferromagnetic behavior is very similar to that of protonated compound reported by Hornick et al. [6]. The maximum value of χT of the present deuterated compound is approximately 1/20 times smaller than the reported value for the protonated one. The inter layer distance 1.02 nm of deuterated compound $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$ coincides with that of protonated one $Cu_2(OH)_{1.92}(C_4H_6(COO)_2)_{1.04}\cdot 0.22H_2O$ [6].

3.2. Solid-state high-resolution deuterium NMR

To investigate the local magnetic structures within a layer in a microscopic view point, solid-state high-resolution deuterium NMR spectrum was measured with high-speed magic angle spinning for $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$. Fig. 6(a) shows a whole range of the MAS D NMR spectrum measured at a spinning rate of 8 kHz at 313 K. There are many spinning side bands spread over 8000 ppm around an isotropic shift at −298 ppm. The isotropic shift was distinguished by use of different spinning speed as usual. The envelope of all the spinning side bands corresponds to the powder line shape of the hydroxide deuterium atom and the whole spectrum shape is governed by a quadrupole interaction of the hydroxide deuterium and an anisotropic dipole interaction between the deuteron and electron spins of the copper ions. Fig. 6(b) depicts a magnified region near the isotropically shifted signal.

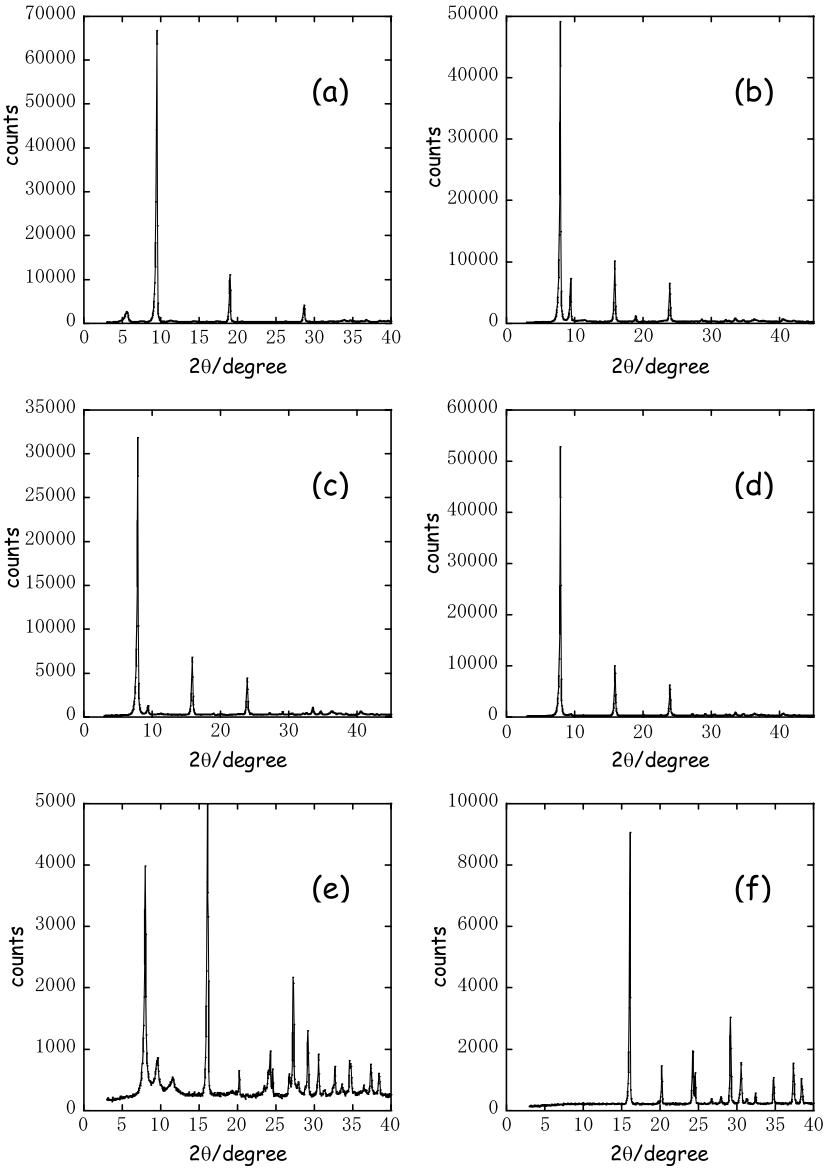

Fig. 3. Reaction time dependence of the powder X-ray diffraction pattern: (a) starting material $Cu_2(OH)_3CH_3COO \cdot H_2O$, (b) powder crystal of starting material was suspended and stirred in aqueous NaSCN solution at room temperature for 2 h, (c) 4 h, (d) 6 h, (e) 18 h and (f) 45 h. The diffraction pattern of $Cu_2(OH)_3CH_3COO \cdot H_2O$ gradually disappeared and the diffraction of $Cu_2(OH)_3SCN$ increased within 6 h as shown in (a–d). Longer reaction period induced a reduction of the Cu(II) ion to form α-Cu(I)SCN as depicted in (e) and (f).

Only one strong signal was observed for the OD^- ions of $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02} \cdot 0.07D_2O$, while more than two signals corresponding to chemically different OD^- ions, i.e., α and β depicted in Fig. 1, of different magnetic chains of Cu^{2+} ions in a layer were observed for most of the $Cu_2(OD)_3X$ compounds, where X is univalent anion. For example, four isotropically shifted signals with a relative intensity of 2:1:2:1 corresponding to β, α, β′, α′ OD^- ions of different copper chains were observed for $Cu_2(OD)_3(CH_3(CH_2)_6COO)$ with an inter layer distance of 2.49 nm as shown in Fig. 7 [10]. All the four signals showed different temperature dependencies of their shifts as depicted in Fig. 8(a). Since the hydroxide ion α is linked to the magnetic orbitals $d_{x^2-y^2}$ in Cu-chain **A**, it dominantly detects the magnetic interaction in the one-dimensional Cu-chain **A**. When the anion X is exchanged, the magnetic local structure around the hydroxide ion α varies largely in comparison with β as previously demonstrated for $X = NO_3^-$, $HCOO^-$, and $C_6H_5COO^-$ [8,9]. This behavior suggests that a one-dimensional character is strong for the dominant magnetic interaction among copper ions in the high temperature region. Thus, we assumed a one-dimensional $S = 1/2$ Heisenberg model. In this case, the term $F(J, T)$ in Eq. (4) can be approximated by a Padé expansion series [18],

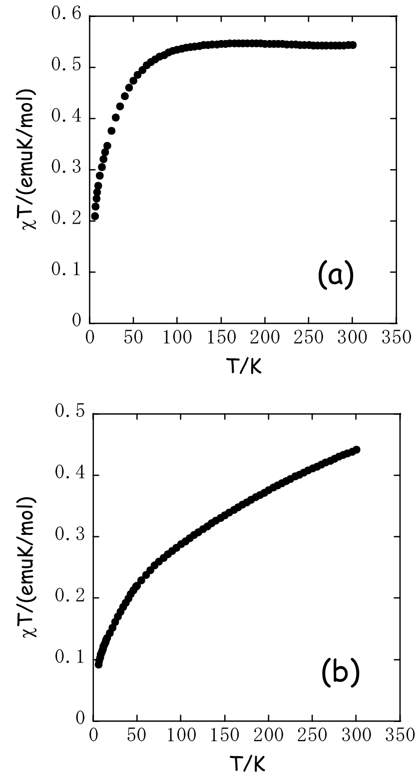

Fig. 4. Magnetic susceptibility χT of $Cu_2(OH)_3SCN$ (a) and $Cu_2(OD)_3(CH_3(CH_2)_6COO)$ (b) as a function of temperature.

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

where $K = J/(2k_BT)$. The above function can be used for ferro- and antiferromagnetic interactions and is convenient for analyzing a variety of $Cu_2(OD)_3X$ compounds. Least-squares fittings of the observed temperature dependence of the isotropic NMR shifts of OD^- ions gave the best fitting curves depicted in Fig. 8(a), where we fixed the diamagnetic shift δ_{dia} of the hydroxide ions to 10 ppm as found for many diamagnetic compounds. The derived values of the exchange interaction J and the hyperfine coupling constants A_D are listed in Table 1. A change of δ_{dia} from 5 to 15 ppm gave a change of ±2 K for J values. The Cu-chains **A** and **A′** are largely antiferromagnetic for $Cu_2(OD)_3(CH_3(CH_2)_6COO)$ as well as the Cu-chains **B** and **B′**, whereas the Cu-chain **A** is ferromagnetic for $X = NO_3^-$ and $HCOO^-$ as we reported previously [8]. The magnetic interaction of Cu–OH–Cu is known to be very sensitive to its angle, varying between ferro- and antiferromagnetic around 98° in the case of dinuclear

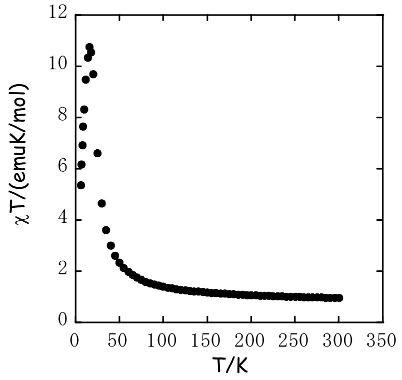

Fig. 5. Magnetic susceptibility χT of $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$ as a function of temperature.

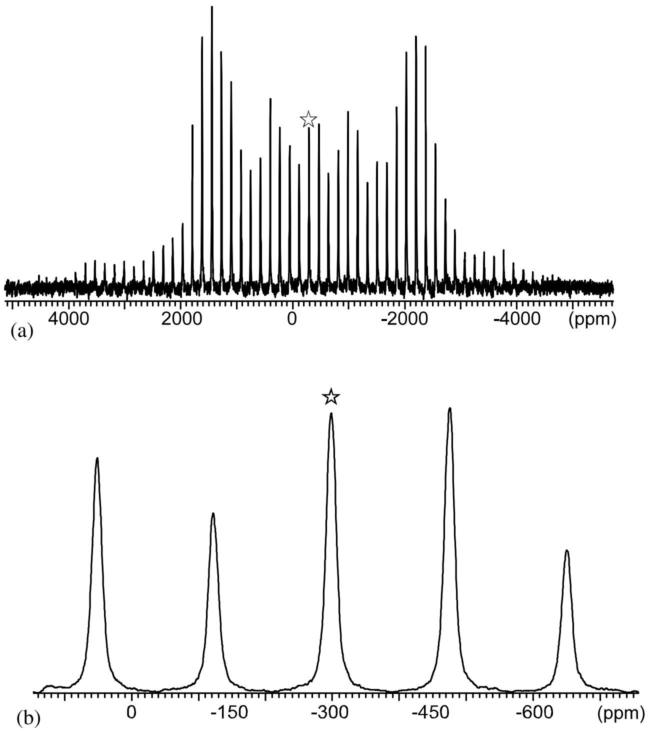

Fig. 6. MAS D NMR spectrum of $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02}\cdot 0.07D_2O$ measured at spinning speed of 8 kHz at 313 K, (a) full range spectrum covering all of the spinning side bands and (b) magnified region near the isotropically sifted signal. The isotropic shift is marked with star and all other peaks are spinning side bands.

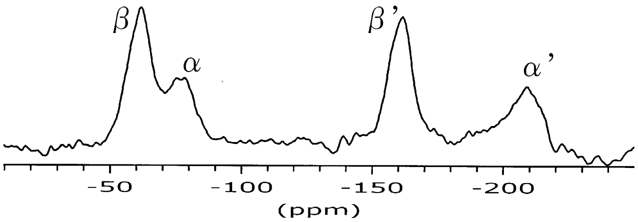

Fig. 7. Four isotropically shifted signals of MAS D NMR spectrum of $Cu_2(OD)_3(CH_3(CH_2)_6COO)$ measured at 303 K with the spinning speed of 10 kHz.

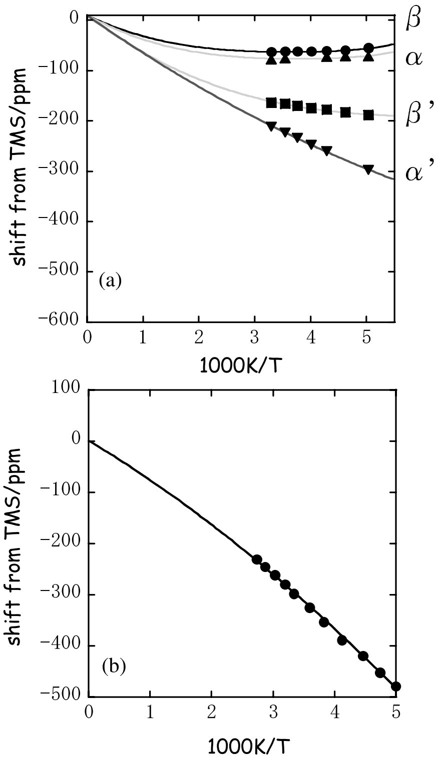

Fig. 8. Temperature dependence of isotropic shift of MAS D NMR of $Cu_2(OD)_3(CH_3(CH_2)_6COO)$ (a) and of $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02} \cdot 0.07D_2O$ (b).

copper complexes [19]. Although it is not established whether the same relation holds for the infinite copper chains, the angles around 98° were found for $Cu_2(OH)_3NO_3$ [2]. The magnetic interaction within the copper chain **A** seems to vary largely by exchanging the anion X, since the angle of Cu–OH–Cu in this chain can be sensitively affected by the property of the anion X.

For $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02} \cdot 0.07D_2O$, which shows ferromagnetic behavior as a bulk magnetism, only one signal was observed for OD^- ions. Judging from the elemental analysis, one of the three hydroxide ions of $Cu_2(OD)_3X$, where X is univalent anion, is exchanged with an oxygen atom of divalent $C_4H_6(COO^-)_2$ anion to link the upper and lower layers shown in Fig. 1. The hydroxide ion α may almost be exchanged, since one of the three coordination bonds of this hydroxide ion is axial coordination to the copper ion as depicted in Fig. 1 and this bond is weaker than the planar coordination bonds. All the three coordination bonds of X are axial coordination and therefore the anion X can be easily exchanged at first. On the other hand, all the three coordination bonds of the hydroxide ion β provide a planar coordination for the copper ions. The hydroxide ions β strongly coordinate to the copper ions and remain in the copper layer after the exchange reaction. Thus the observed signal of OD^- ion was assigned to the hydroxide ion β shown in Fig. 1. Then we assumed a one-dimensional Heisenberg model for the analysis of the temperature dependence of the shift of this signal as in the case of $Cu_2(OD)_3X$. The fitting of Eq. (4) with use of a function $F(J, T)$ of Eq. (5) is shown in Fig. 8(b). All the values of the diamagnetic shift $\delta_{dia} = 1 \pm 10$ ppm of the hydroxide ions, the exchange interaction $J = +71 \pm 20$ K and the hyperfine coupling constant $A_D = -1.40 \pm 0.13$ MHz were estimated from the least-squares fitting, indicating a ferromagnetic coupling within the copper chain **B** in the layer. When we fixed the diamagnetic shift δ_{dia} of the hydroxide ions to 10 ppm, we obtained the values of $J = +57 \pm 2$ K and $A_D = -1.50 \pm 0.01$ MHz (Table 1). This result for $Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02} \cdot 0.07D_2O$ with the divalent anion $C_4H_6(COO^-)_2$ linking the upper and the lower layers is very different from the case of $Cu_2(OD)_3X$, in which the copper chain **B** always shows an antiferromagnetic interaction for univalent acid anions X. A significant deformation of Cu–OD–Cu angle in the copper chain **B** is considered to occur in this system. The magnetic interaction in the copper chain **A** could not be determined at present, since the hydroxide ion α, which mainly probes the magnetic interaction within the copper chain **A**, was lost in this compound.

Table 1
Magnetic interactions deduced from solid-state high-resolution deuterium NMR spectrum

Compound (interlayer distance)	Hydroxide ion	HFCC A_D (MHz)	Magnetic interaction J (K)
$Cu_2(OD)_3(CH_3(CH_2)_6COO)$	β	−1.01	−209
(2.49 nm)	α	−1.15	−201
	β′	−1.62	−122
	α′	−1.51	−44
$Cu_2(OD)_{1.96}(C_4H_6(COO)_2)_{1.02} \cdot 0.07D_2O$	β	−1.40	+71
(1.02 nm)		(−1.50) [a]	(+57)[a]

[a] See the text.

Acknowledgements

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