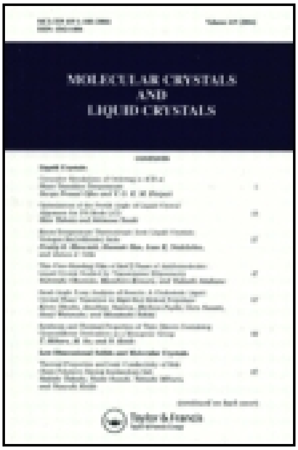

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Variable Magnetism of Layer-Structured Compounds $Cu_2(OD)_3X$ with Exchangeable Anion X: Magnetic Local Structure and Magnetic Interactions Determined by Solid-State High-Resolution Deuterium NMR

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Version of record first published: 27 Oct 2006

To cite this article: Sadamu Takeda, Masahiro Arai, Goro Maruta & Kizashi Yamaguchi (2000): Variable Magnetism of Layer-Structured Compounds $Cu_2(OD)_3X$

with Exchangeable Anion X: Magnetic Local Structure and Magnetic Interactions Determined by Solid-State High-Resolution Deuterium NMR, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 369-376

To link to this article: http://dx.doi.org/10.1080/10587250008026168

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 369-376
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Variable Magnetism of Layer-Structured Compounds $Cu_2(OD)_3X$ with Exchangeable Anion X: Magnetic Local Structure and Magnetic Interactions Determined by Solid-State High-Resolution Deuterium NMR

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(In final form July 6, 1999)

The microscopic magnetic local structure of Botallackite-type layer-structured compounds $Cu_2(OD)_3X$ ($X = C_6H_5COO^-$) exhibiting a nonequilateral planar triangular copper lattice was determined by the solid-state high-resolution deuterium NMR above 190 K. The magnetic interaction in a copper layer was probed by the isotropic NMR shifts of OD^- groups and could be approximated by a sum of 1D-Heisenberg chains in the high temperature region. Two copper chains with different exchange interactions $J = -54 \pm 4$ and -92 ± 3 K were found for $Cu_2(OD)_3C_6H_5COO$ from the temperature dependence of the three distinct NMR signals. The derived values of J almost reproduced the high temperature behavior of the magnetic susceptibility $\chi_A T$ vs. T. The magnetic susceptibility of isotopic analogue $Cu_2(OH)_3C_6D_5COO$ showed ferromagnetic interaction below 50 K. Electron spin distribution in a phenyl ring of a benzoate anion is governed by spin polarization mechanism and it's magnitude is very small. Magnetic interaction between the layers through the benzoate anion is very weak.

Keywords: layer-structured copper compounds; magnetic local structure; magnetic interaction; solid-state high-resolution deuterium NMR

INTRODUCTION

Botallackite-type compounds $Cu_2(OH)_3X$ (X = exchangeable anion) exhibit layered structures, in which a nonequilateral planar triangular lattice of copper ions is constructed as shown in Fig. 1 (i)[1,2]. The copper ions are bridged by hydroxide ions and exchangeable anions 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. 1 (iii). A variety of anions X can be incorporated and the bulk magnetism of $Cu_2(OH)_3X$ is controlled by the property of X[3-6]. In this paper, we present the solid-state high-resolution deuterium NMR (D-NMR) study of $Cu_2(OD)_3C_6H_5COO$ and it's isotopic analogue $Cu_2(OH)_3C_6D_5COO$ to elucidate the magnetic interaction in a microscopic viewpoint.

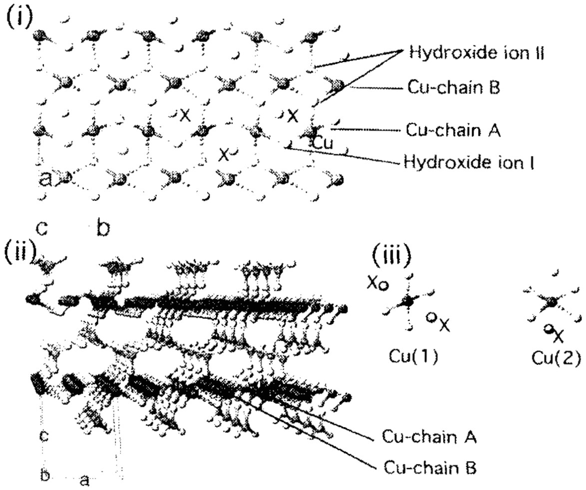

FIGURE 1 Layer structure of $Cu_2(OH)_3NO_3$; (i) viewed along **c** axis perpendicular to the layer, (ii) along **b** axis parallel to the layer. Tow chemically distinct hydroxide ions **I** and **II** are indicated in (i) and two distinct copper ions Cu(1) and Cu(2) in (iii) which form Cu-chains A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

METHOD AND EXPERIMENT

Since a hydroxide ion mediates super exchange and/or direct exchange interactions among the copper ions, the paramagnetic NMR shift of the OD^- ion, 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 technique (MAS) averages the quadrupole interaction of deuteron and the dipole interaction between deuteron and electron 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,

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

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

The coefficient A_{D} is the hyperfine coupling constant of the nucleus D in Hz[7,8], which consists of Fermi and pseudo contact terms. Since the anisotropy of the g-tensor is not large for copper complexes, the contribution of the pseudo contact to A_{D} is estimated to be *ca.* 0.2 MHz for a OD^- ion near from copper ion[2, 9, 10]. The magnetic interaction can be determined from the temperature dependence of F/k_BT. Evaluation of the factor F is described in the discussion.

The compound $Cu_2(OD)_3C_6H_5COO$ with hydroxide ions 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. 11 and $Cu_2(OH)_3C_6D_5COO$ was prepared similarly in normal water. Precise structure of the present material is not known. However, powder X-ray diffraction showed strong $(00l)$ lines $(l \leq 4)$, indicating that the layer structure was maintained and the basal spacing was enlarged to 15.3 Å by anion exchange reaction for both isotopic analogues.

D-MAS NMR spectra were measured by a similar method described in ref. 12 at the resonance frequency of 46.1 MHz and at the magic angle spinning speed of ~10 kHz with Bruker DSX300 spectrometer between 193K and 303K. The thermometer of the MAS probe and an effect of spinning speed were carefully calibrated[12]. Uncertainty of the temperature measurement after the calibration was 4K. All D-NMR shifts were measured from the external second reference of CD_3OH (3.35 ppm). Direct current magnetic susceptibility was measured with SQUID magnetometer (MPMS 5) at the external magnetic field of 1 T. Diamagnetic contributions were subtracted.

RESULTS AND DISCUSSION

There are two chemically different hydroxide ions **I** and **II**: the hydroxide ion **I** bridges three copper ions Cu(1)Cu(1)Cu(2), whereas the hydroxide ion **II** bridges another combination of copper ions Cu(1)Cu(2)Cu(2). The two hydroxide ions **II** in the unit cell are crystallographically nonequivalent for several compounds of $Cu_2(OH)_3X$[2] and three distinct NMR signals may be observed. The D-MAS NMR spectrum of $Cu_2(OD)_3C_6H_5COO$ showed two sharp and one broad signals. The intensity ratio of the NMR signals with including spinning side bands, which are spread over ± 4000 ppm is about 1:1:1, although the broad signal is difficult to be accurately integrated. The copper ions (1) are linked by the hydroxide ion **I** and by one of oxygen atoms of the anion X to form a infinite chain **A**, while Cu(2)'s are doubly linked by the hydroxide ions **II** for a chain **B**. The magnetic local structure around the hydroxide ion **I** varies largely in comparison with **II** when the anion X is exchanged, as we previously demonstrated for X = NO_3^- and $HCOO^-$[10] This behavior suggests that an one-dimensional character is strong for the dominant magnetic interaction among copper ions. Therefore we assumed one-dimensional spin-1/2 Heisenberg model. In this case, the factor F in Eq. 2 can be approximated by a Padé expansion series[13],

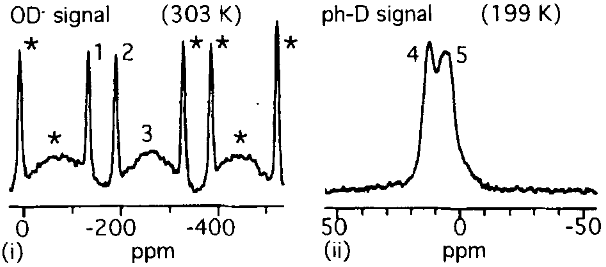

FIGURE 2 Magic angle spinning deuterium NMR spectrum. Spinning speed was 9 kHz. Asterisks indicate the spinning side bands

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

where $K=J/(2k_BT)$. The above function is not applicable for $K \le -0.5$. However, it can be used for ferro- and antiferromagnetic interactions and is convenient for analyzing a variety of compounds. Least-squared fittings of the observed temperature dependence of the isotropic NMR shifts of OD^- ions gave best fitting curves shown in Fig. 3 (i), where we fixed the diamagnetic shift δ_{dia} of the hydroxide ions to 10 ppm which was found for many diamagnetic compounds. The derived values of J and the hyperfine coupling constants are listed in Table I. A change of δ_{dia} from 5 to 15 ppm gave a change of $\pm 3 \sim \pm 4$ K for the J values. The values of J determined from the NMR signals 1 and 2 are quite similar to each other, indicating that they are included within the same magnetic chain and are assigned to the hydroxide ion II. NMR signal 3 is assigned to the hydroxide ion I. The copper chain A is largely antiferromagnetic for X = $C_6H_5COO^-$, whereas it is ferromagnetic for X = NO_3^- and $HCOO^-$ as we reported previously[10]. The Cu-OH-Cu magnetic interaction is known to be very sensitive to its angle, varying between ferromagnetic and antiferromagnetic one around 98° in the case of dinuclear copper complexes[14,15]. Although it is not established whether the same relation holds for infinite copper chains or not, similar angles were found for $Cu_2(OH)_3NO_3$[21].

The magnetic interaction within the copper chain A seems to vary largely 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.

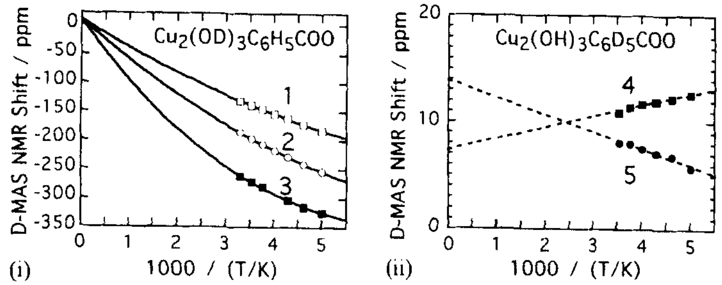

FIGURE 3 Temperature dependence of the paramagnetic shift of deuterium NMR: (i) OD⁻ signal of $Cu_2(OD)_3C_6H_5COO$ and (ii) phenyl signal of $Cu_2(OH)_3C_6D_5COO$.

Values of exchange interaction J determined by the D-MAS NMR reproduced the high temperature behavior of the magnetic susceptibility $\chi_A T$ vs. T, which was calculated with the same model of a sum of 1D-Heisenberg chains as did for the D-NMR shifts. The relation $\chi_A T = (0.335/2)\{F(J = -54\mathrm{K}) + F(J = -92\mathrm{K})\}$ was used and the function F is given in Eq. 3. The high temperature behavior of the macroscopic magnetism of the Botallackite-type layer-structured compounds can be understood by a competition among the magnetic chains with different exchange interactions. To investigate the magnetic interaction between the layers through spin-polarizable benzoate anions, electron spin distribution of phenyl group was determined by D-MAS NMR for isotopic analogue $Cu_2(OH)_3C_6D_5COO$. Plus and minus signs of slopes of the temperature dependence of isotropic D-NMR shifts were observed as depicted in Fig. 2 (ii). This result indicates that electron spins of the phenyl group are induced by Cu^{2+} ion by spin polarization mechanism. The spin density estimated by a linear fitting is very small and the magnetic interaction between the layers through benzoate anions is very weak.

The isotopic analogue $Cu_2(OH)_3C_6D_5COO$ exhibited a ferromagnetic interaction below 50 K in contrast to $Cu_2(OD)_3C_6H_5COO$ as shown in Fig. 4. This interesting phenomenon seems to be based on a sensitive change of the magnetic interaction by a very small variation of coordination structure of the benzoate anion and hydroxide anion.

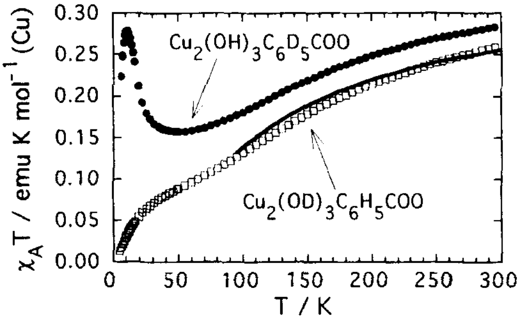

FIGURE 4 Temperature behavior of the magnetic susceptibility of $Cu_2(OD)_3C_6H_5COO$ and $Cu_2(OH)_3C_6D_5COO$. Symbols ● and ☐ are experimental data. Solid curve was calculated by a sum of one dimensional magnetic chains A and B with exchange interactions determined by D-NMR.

TABLE I Hyperfine coupling constant A_D and exchange interaction J

compound	NMR signal[a]	Hyperfine coupling A_D / MHz	Exchange interaction J / K	Cu chain
$Cu_2(OD)_3C_6H_5COO$	1	− 1.00 ± 0.15	− 51 ± 4 } − 54	B
	2	− 1.43 ± 0.09	− 57 ± 3	B
	3	− 2.26 ± 0.03	− 92 ± 3	A
$Cu_2(OH)_3C_6D_5COO$	4	(+ 2.1 ± 0.2) × 10^{-2}	—	
	5	(− 3.1 ± 0.3) × 10^{-2}	—	
$Cu_2(OD)_3NO_3$[b]		− 0.91 ± 0.05	+ 19 ± 11	A
		− 0.93 ± 0.05	− 21 ± 3	B
$Cu_2(OD)_3HCOO$[b]		− 1.28 ± 0.06	+ 13 ± 7	A
		− 1.00 ± 0.05	− 18 ± 5 } − 13	B
		− 0.74 ± 0.05	− 8 ± 5	B

a) Figures 2 and 3, b) Reference 10.

ACKNOWLEDGMENTS

We thank Dr. W. Fujita and Prof. K. Awaga of The University of Tokyo for discussions. A part of this work has been performed at the Venture Business Laboratory in Gunma University. This research was supported by grant-in-aid for Scientific Research on Priority Areas (A) "Creation of Delocarized Electronic Systems" (No. 11133213) and on (C) (No. 09640681) from the Ministry of Education, Science, Culture and Sports of Japan.

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