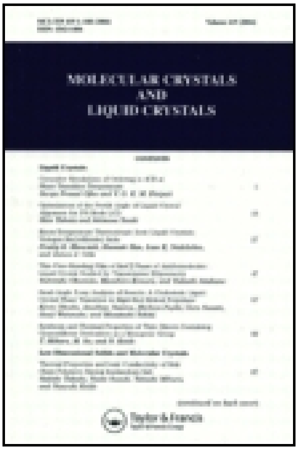

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Local Magnetic Interactions and Mechanism of the Magnetism of Layer-Structured Compound $Cu_2(OD)_3CH_3(CH_2)_6COO$ with an Interlayer-Distance of 24.9 Å

Sadamu Takeda [a], Masahiro Arai [a] & Goro Maruta [b]

[a] Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma, 376-8515, Japan

[b] Meson Science Laboratory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Oho, Tsukuba, 305-0801, Japan

To cite this article: Sadamu Takeda, Masahiro Arai & Goro Maruta (2000): Local Magnetic Interactions and Mechanism of the Magnetism of Layer-Structured Compound $Cu_2(OD)_3CH_3(CH_2)_6COO$ with an Interlayer-Distance of 24.9 Å, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 343:1, 77-82

To link to this article: http://dx.doi.org/10.1080/10587250008023506

Mol. Cryst. and Liq. Cryst., 2000, Vol. 343, pp. 77-82
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Local Magnetic Interactions and Mechanism of the Magnetism of Layer-Structured Compound $Cu_2(OD)_3CH_3(CH_2)_6COO$ with an Interlayer-Distance of 24.9 Å

SADAMU TAKEDA[a], MASAHIRO ARAI[a] and GORO MARUTA[b]

[a]*Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376–8515, Japan and* [b]*Meson Science Laboratory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Oho, Tsukuba 305–0801, Japan*

The microscopic magnetic local structure of layer-structured basic copper compounds $Cu_2(OD)_3CH_3(CH_2)_6COO$ 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^- ions and could be approximated by a sum of 1D-Heisenberg chains in the high temperature region. Four copper chains with different exchange interactions $J = -209$, -201, -122, and -44 K were found from the temperature dependence of the four distinct deuterium NMR signals. The derived values of J almost reproduced the high temperature behavior of the magnetic susceptibility $\chi_A T$ vs. T of this compound.

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

INTRODUCTION

Basic copper salt compounds $Cu_2(OH)_3X$ (X = exchangeable anion) exhibit layered structures as schematically shown in Fig. 1[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 $Cu[(OH)_4X(OH)]$. A variety of anions X can be incorporated by anion-exchange reaction with stirring the suspended powder of basic copper acetate $Cu_2(OD)_3CH_3COOH_2O$ in MX aqueous solutions, where M is an alkali metal ion[3]. The bulk magnetism of $Cu_2(OH)_3X$ sensitively depends on X and its different stacking structures particularly for $C_nH_{2n+1}COO^-$[4-6]. In this paper, we present the solid-state high-resolution deuterium NMR (D-NMR) study of $Cu_2(OD)_3CH_3(CH_2)_6COO$ with an interlayer distance of 24.9 Å to elucidate the magnetic interaction in a microscopic viewpoint and the mechanism of the magnetism of this compound.

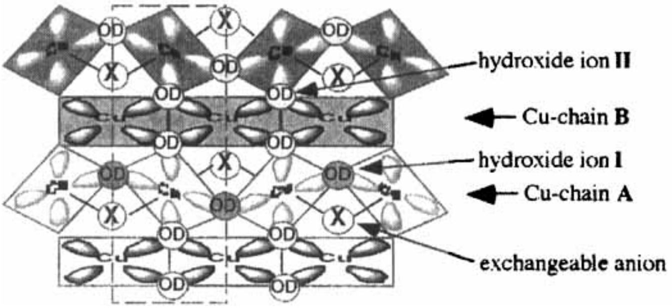

FIGURE 1 Schematic view of a layer structure of $Cu_2(OD)_3X$. Magnetic orbitals $d_{x^2-y^2}$ of unpaired electrons of Cu(II) ion are depicted to show two different bridging schemes of copper ions for Cu-chains **A** and **B**, respectively. The units of $Cu[(OH)_4X_2]$ are linked at edges of x-y planes of four-coordination to form infinite Cu-chain **A**, while the units $Cu[(OH)_4X(OH)]$ are linked by sides of the planer-coordination to form Cu-chain **B**.

METHOD AND EXPERIMENT

Since a hydroxide ion mediates exchange interaction 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 high-resolution D-NMR absorption line in the solid state. The observed isotropic shift in ppm scale consists of the Fermi contact term, the pseudo contact term and the temperature independent diamagnetic term as follows,

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

$$\delta_{\text{Fermi}} + \delta_{\text{Pseudo}} = \frac{\mu_B}{3k_B T} \cdot \frac{A_D}{\gamma_D / 2\pi} S(S+1) \cdot F(J,T) . \tag{2}$$

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 small 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 $F(J,T)/k_B T$. Evaluation of the term $F(J,T)$ is described in the discussion.

The compound $Cu_2(OD)_3CH_3(CH_2)_6COO$ with hydroxide ions deuterated more than 99% was prepared by anion exchange reaction with stirring 0.12 g of the parent material of basic copper acetate in 15 ml of 0.2 M heavy water solution of $CH_3(CH_2)_6COONa$ for 50 days at room temperature. Powder X-ray diffraction showed strong (00l) lines ($l \leq 4$), indicating that the layer structure was maintained and the interlayer distance was enlarged to 24.9 Å by the anion exchange. The distance is similar but slightly different from that of α-phase of protonated compound [6].

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. The thermometer of the MAS probe and an effect of spinning speed on the temperature of the sample were carefully calibrated[12]. Uncertainty of the temperature measurement after the calibration was 4K. The D-NMR shifts were measured from the external reference of CD_3OH (3.35 ppm). Direct current magnetic susceptibility was measured with SQUID magnetometer (MPMS 5) at the external field of 1 T.

RESULTS AND DISCUSSION

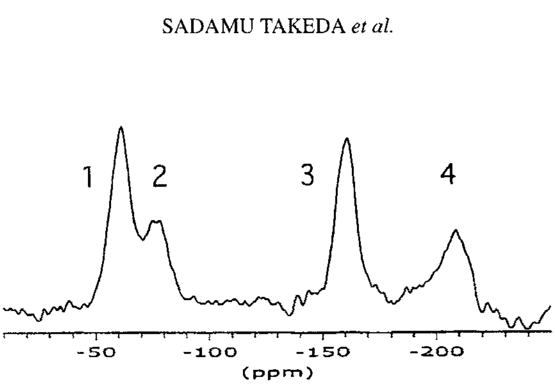

FIGURE 2 Magic angle spinning deuterium NMR spectrum measured at 303 K with the spinning speed of 10 kHz.

There are two chemically different hydroxide ions **I** and **II**, the number ratio of **I** and **II** is 1:2 as depicted in Fig. 1. The D-MAS NMR spectrum of $Cu_2(OD)_3CH_3(CH_2)_6COO$ showed four isotropic signals. The intensity ratio of the NMR signals including spinning side bands, which are spread over ± 4000 ppm, is almost 2:1:2:1 from low- to high-field signals shown in Fig. 2. Here we note that NMR signal of D_2O molecule was not found. The smaller signals were, therefore, easily assigned to the hydroxide ions **I** and the larger one to **II**. Since the hydroxide ion **I** 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 was exchanged, the magnetic local structure around the hydroxide ion **I** varied largely in comparison with **II** as previously demonstrated for X = NO_3^-, $HCOO^-$, and $C_6H_5COO^-$[10, 11] This behavior suggests that an one-dimensional character is strong for the dominant magnetic interaction among copper ions in the high temperature region. Thus we assumed one- dimensional spin-1/2 Heisenberg model. In this case, the term $F(J,T)$ in Eq. 2 can be approximated by a Padé expansion series[13],

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

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 $Cu_2(OD)_3X$. Least-squared fittings of the observed temperature dependence of the isotropic NMR shifts of OD^- ions gave best fitting curves depicted in Fig. 3, 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 A_D are listed in the right hand side of Fig. 3. A change of δ_{dia} from 5 to 15 ppm gave a change of ± 2 K for estimating J values. The Cu-chains A are largely antiferromagnetic for the present compound as well as the Cu-chines **B**, whereas the Cu-chain **A** 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]. Although it is not established whether the same relation holds for infinite copper chains or not, similar angles were found for $Cu_2(OH)_3NO_3$[2]. 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)can be sensitively affected by the property of the anion X.

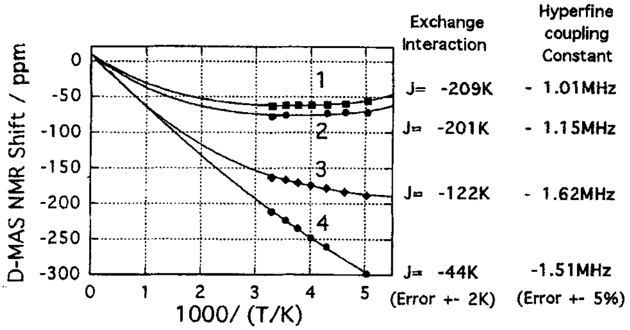

FIGURE 3 Temperature dependence of the paramagnetic shifts of deuterium NMR and the parameters of magnetic interactions.

Values of exchange interaction J determined by the D-MAS NMR almost reproduced the high temperature behavior of the magnetic susceptibility $\chi_A T$ vs. T of the deuterated compound, which was calculated with the same model of a sum of 1D-Heisenberg chains as did for the D-NMR shifts. The relation

$$\chi_A T = (0.382/4)\{F(J = -209\mathrm{K}) + F(J = -201\mathrm{K}) + F(J = -122\mathrm{K}) + F(J = -44\mathrm{K})\}$$

was used and the function $F(J,T)$ is given in Eq. 3. The high temperature behavior of the macroscopic magnetism of the layer-structured basic copper compounds $Cu_2(OH)_3X$ can be understood by a competition among the magnetic chains with different exchange interactions.

ACKNOWLEDGMENTS

This research was supported by The Japan Securities Scholarship Foundation and by grant-in-aid for Scientific Research on Priority Areas (A) (No. 11133213) from the Ministry of Education, Science, Culture and Sports of Japan.

References

[1] H.R. Oswald, Y. Iitaka, S. Locchi and A. Ludi, *Helv. Chim. Acta* **44,** 2103 (1961).

[2] H. Effenberger, *Z. Krist.* **165,** 127 (1983).

[3] S. Yamanaka, T. Sako, and M. Hattori, *Chem. Lett.* 1869 (1989).

[4] W. Fujita, K. Awaga, *Inorg. Chem.* **35,** 1915 (1996).

[5] W. Fujita and K. Awaga, *J. Am. Chem. Soc.* **119,** 4563 (1997).

[6] V. Laget, C. Hornick, P. Rabu, and M. Drillon, *J. Mater. Chem.* **9,** 169 (1999).

[7] H.M. McConnell, D.B. Chesnut, *J. Chem. Phys.* **28,** 107 (1958).

[8] R. Kurland, B.R. McGarvey, *J. Magn. Reson.* **2,** 286 (1970).

[9] M. Atanasov, N. Zotov, C. Friebel, K. Petrov, and D. Reinen, *J. Solid State Chem.* **108,** 37 (1994).

[10] S. Takeda, G. Maruta, K. Terasawa, N. Fukuda, and K. Yamaguchi, *Mol. Cryst. Liq. Cryst.* **335,** 11 (1999).

[11] S. Takeda, M. Arai, G. Maruta, and K. Yamaguchi, *Mol. Cryst. Liq. Cryst* in press.

[12] G. Maruta, S. Takeda, R. Imachi, T. Ishida, T. Nogami, and K.Yamaguchi, *J. Am. Chem. Soc.* **121,** 424 (1999).

[13] G.A. Baker, Jr., G.S. Rushbrooke, and H.E. Gilbert, *Phys Rev.* **135,** A1272 (1964).

[14] O. Kahn, *Molecular Magnetism,* VCH Publishers, Cambridge, 1993; p. 159.