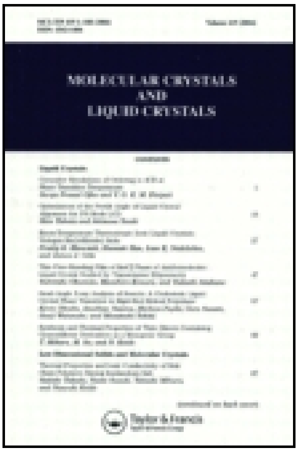

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Sadamu Takeda, Atsushi Watanabe, Goro Maruta & Takasuke Matsuo (2002): Magnetic Interactions through Short Hydrogen Bond in Hydrogen-Bonded Basic Copper (II) Salt; Cu 2 Na(D 3 O 2)(SO 4) 2, Molecular Crystals and Liquid Crystals, 376:1, 443-448

To link to this article: http://dx.doi.org/10.1080/10587250210791

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 443-448
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1058-725X/02 \$12.00 + .00

Magnetic Interactions through Short Hydrogen Bond in Hydrogen-Bonded Basic Copper (II) Salt; $Cu_2Na(D_3O_2)(SO_4)_2$

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Magnetic interactions through short hydrogen bond of Cu(II)-O··D··O-Cu(II) of Natrochalcite-type compound $Cu_2Na(D_3O_2)(SO_4)_2$ were studied by solid-state high-resolution deuterium NMR and magnetic susceptibility measurements. A positive Weiss temperature of + 9.9 K suggests a ferromagnetic interaction in a Cu(II) chain in which Cu(II) ions are linked by hydroxyl ions. Hyperfine coupling constant of deuterium in the hydrogen bond of $R_{O\cdots O} = 2.440$ Å was determined to be –1.1 MHz from temperature dependence of isotropic shift of a magic angle spinning deuterium NMR spectrum. Minus sign of the hyperfine-coupling constant indicates that negative spin is induced on the deuterium in the hydrogen bond by Cu(II) ions in both side of the O··D··O hydrogen bond. This result implies that the hydrogen bonds between the Cu(II) chains mediate a weak ferromagnetic interaction to form a two-dimensional ferromagnetically coupled Cu(II) layer. The copper layers are antiferromagnetically coupled through sodium and sulfate ions to undergo an antiferromagnetic phase transition at 3.3 K.

Keywords: hydrogen-bonded Cu(II) layer, magnetic interactions, magnetic phase transition, hyperfine coupling, solid-state high-resolution deuterium NMR

INTRODUCTION

The hydrogen-bond network controls molecular assembly in the solid state. This point has been utilized to construct novel molecule-based ferromagnets and it has been found that magnetic interaction through hydrogen bonding played an important role for mediating the intermolecular ferromagnetic interaction [1]. The magnetic interaction in the metal complex systems through hydrogen bonding has been suggested by measurements of magnetic susceptibility for binuclear complex [2]. In this paper, hyperfine-coupling constant of deuterium atom in the Cu(II)-O··D··O-Cu(II) hydrogen bond was directly observed for elucidating the magnetic interaction through hydrogen bond network in the metal complex systems.

Natrochalcite-type compound $Cu_2Na(H_3O_2)(SO_4)_2$, which exhibits hydrogen bond network, is a good candidate, since all of the hydrogen bonds are crystallographically equivalent. In this compound, Cu(II) ions are linked by hydroxyl oxygen atoms to form infinite linear chains with Cu-Cu distance of 3.094 Å. The linear chains are connected by short O··H··O hydrogen bonds to form two-dimensional layers of Cu(II) ions as depicted in Fig. 1. The hydrogen bond distance is 2.440 Å [3]. Layers are linked by SO_4^{2-} and Na^+ ions, which are not shown in this figure for simplicity.

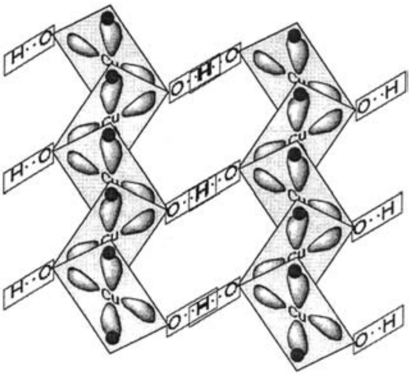

FIGURE 1 Layer structure of hydrogen bonded Cu(II) layer of Natrochalcite-type compound $Cu_2Na(H_3O_2)(SO_4)_2$. Cations of SO_4^{2+} and Na^+ are not depicted for simplicity.

METHOD AND EXPERIMENT

Paramagnetic NMR shift of deuterium in hydrogen bond must be an excellent probe for elucidating the local magnetic interaction through hydrogen bond. Magic angle spinning technique (MAS) averages the quadrupole interaction of deuteron and the dipole interaction between deuteron and electron spins to provide an isotropic shift of the D-NMR absorption line. The observed isotropic shift in ppm consists of the Fermi contact term, the pseudo contact (dipole) term and the temperature independent diamagnetic term as follows,

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

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

The coefficient A_{D} is the hyperfine-coupling constant of the nucleus D in Hz [4], 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 small [5]. Function $F(J,T)$ represents a term of exchange interaction among Cu(II) ions.

Deuterated compound $Cu_2Na(D_3O_2)(SO_4)_2$ was precipitated from heavy water solution of Na_2SO_4 and $CuSO_4$ in a molar ratio 1:4 at 343 K. Powder X-ray diffraction pattern of the sample is in excellent agreement with the reported structure [3].

A D-MAS NMR spectrum was measured by a similar method described in ref. 1 at a resonance frequency of 46.1 MHz and at a magic angle spinning speed of 8 ~10 kHz with a Bruker DSX300 spectrometer between 194K and 300K. The thermometer of the MAS probe and an effect of spinning speed were carefully calibrated [1]. 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 a SQUID magnetometer (MPMS 5) at the external magnetic field of 1 T.

RESULTS AND DISCUSSION

A plot of $\chi_A T$ as a function of temperature shown in Fig. 2 (a) and Weiss temperature of + 9.9 K obtained from a linear plot of χ_A^{-1} as a function of temperature above 100 K showed predominance of ferromagnetic interaction in the high temperature region. However, this material undergoes antiferromagnetic phase transition at 3.3 K as indicated by a cusp of magnetic susceptibility shown in Fig. 2 (b).

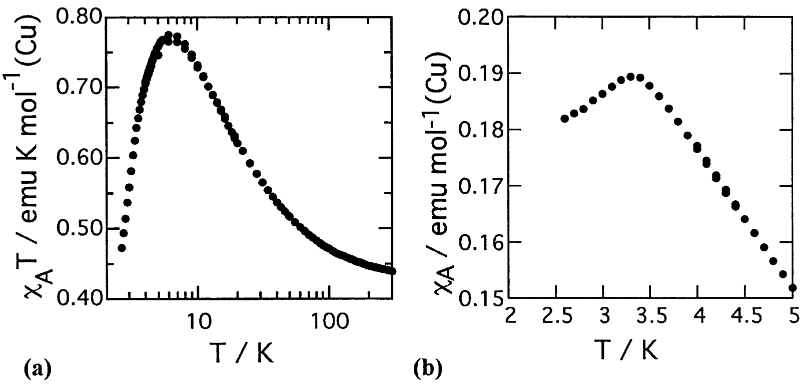

FIGURE 2 Magnetic susceptibility of $Cu_2Na(D_3O_2)(SO_4)_2$. Value of χ_A is taken for one mole of Cu(II) ion. (a) $\chi_A T$ as a function of temperature. (b) χ_A as a function of temperature near magnetic phase transition.

The solid state high-resolution deuterium NMR spectrum of this compound at 300 K is shown in Fig. 3. Many spinning side bands appeared over ±3000 ppm (±140 kHz) and two kinds of deuterium atoms were distinguished as indicated by solid and broken lines showing envelops of overlapped two powder spectra. Nuclear quadrupole interaction of deuterium atom and anisotropic dipole interactions between deuterium and electron spins determine the powder spectral line shape. The integrated intensity ratio is almost 1 : 2 for solid and broken curves. Spectrum shown by the solid curve is the signal of the deuterium in the hydrogen bond and the broken curve corresponds to two other deuterium atoms, which do not participate in the hydrogen bond as shown in the insert of Fig. 3. The assignment described above is rational, since the quadrupole coupling constant is smaller and asymmetric parameter of the quadrupole

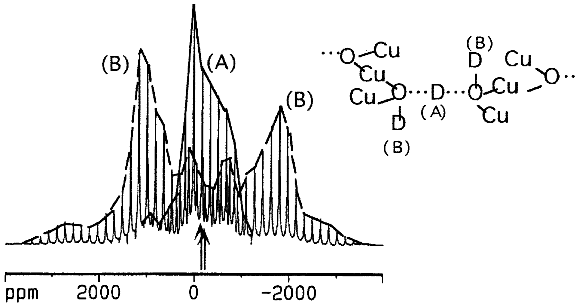

FIGURE 3 Magic angle spinning deuterium NMR of polycrystals of $Cu_2Na(D_3O_2)(SO_4)_2$. Insert is a schematic view of different two deuterium atoms around hydrogen bond.

interaction is larger for the very short hydrogen bond than hydroxyl deuterium without hydrogen bond [6]. The isotropic shifts were distinguished from spinning side bands by using different spinning speeds as usual. Two isotropic shifts at 300 K are depicted in Fig. 4 (a). Lower field peak at -158 ppm is hydrogen-bonded deuterium. Magnitude and sign of the hyperfine-coupling constant of the hydrogen-bonded deuterium were simultaneously determined to be −1.1 MHz from a linear slope of the peak position as a function of inverse temperature shown in Fig. 4 (b). It is concluded that exchange interaction J is so small as not to be precisely determined by the temperature variation of the shift measured above 194 K. Therefore, the function $F(J.T)$ in Eq. 2 is almost temperature independent and equals unity. Since anisotropy of the g-value of the Cu(II) ion is small, the observed hyperfine-coupling constant is almost proportional to the electron spin density induced by copper ions on the hydrogen-bonded deuterium. Thus, the electron spin on the deuterium in the hydrogen bond has opposite sign compared with the electron spin of Cu(II) ions in both side of O··D··O hydrogen bond as schematically shown in Fig. 4. Electron spin density waves generated by Cu(II) ions in both side of the hydrogen bond coincide in phase at the position of deuterium atom in the hydrogen bond. This result implies that the hydrogen bonds mediate the ferromagnetic interaction between the copper chains, although in this case the exchange interaction is small.

This study demonstrated that high-speed magic angle spinning deuterium

NMR is a powerful technique to elucidate the local magnetic interactions in metal complexes.

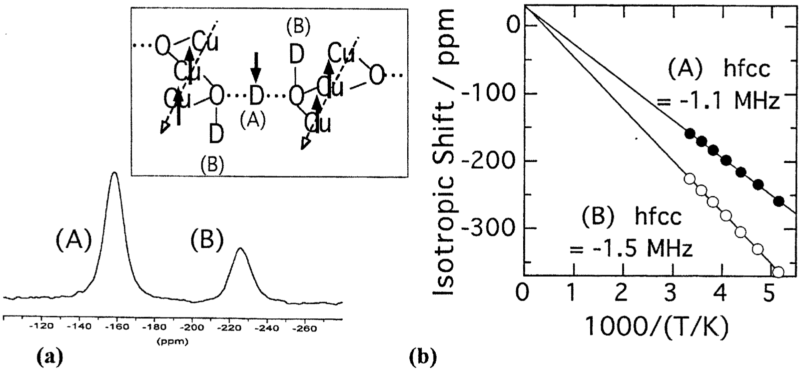

FIGURE 4 (a) Isotropic shift of the magic angle spinning deuterium NMR of polycrystals of $Cu_2Na(D_3O_2)(SO_4)_2$ at 300 K. (b) Temperature variation of two isotropic shift (A) -O··D··O- and (B) -O-D.

ACKNOWLEDGMENTS

Magnetic susceptibility measurements have been performed at the Venture Business Laboratory in Gunma University. This research was supported by The Mitsubishi Foundation, Japan Securities Scholarship Foundation and by grant-in-aid for Scientific Research on Priority Areas (A) from the Ministry of Education, Science, Culture and Sports of Japan.

REFERENCES

[1.] G. Maruta, S. Takeda, R. Imachi, T. Ishida, T. Nogami, and K. Yamaguchi, *J. Am. Chem. Soc.*, **121**, 424 (1999).
[2.] J.A. Bertrand, T.D. Black, P. Garyeller, F.T. Helm, and R. Mahmood, *Inorg. Chem.* **15**, 2965 (1976), J.A. Bertrand, E. Fujita, and D.G. VanDerveer, *Inorg. Chem.* **19**, 2022 (1980).
[3.] G. Giester and J. Zemann, *Z. Krist.*, **179**, 431 (1989), G. Giester, *Z. Krist.*, **187**, 239 (1989),
[4.] R. Kurland, B.R. McGarvey, *J. Magn. Reson.* **2**, 286 (1970).
[5.] M. Atanasov, N. Zotov, C. Friebel, K. Petrov, and D. Reinen, *J. Solid State Chem.* **108**, 37 (1994).
[6.] I.J.F. Poplett, M. Sabir, and J.A.S. Smith, *J. Chem. Soc., Faraday Trans.* 2, **44**, 1651 (1981)