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

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Version of record first published: 24 Sep 2006.

To cite this article: Masahiro Kubota , Gunzi Saito , Hiroshi Ito , Takehiko Ishiguro & Norimichi Kojima (1996): Magnetism of the Organic Superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 284:1, 367-377

To link to this article: http://dx.doi.org/10.1080/10587259608037939

Mol. Cryst. Liq. Cryst., 1996, Vol. 284, pp. 367–377
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MAGNETISM OF THE ORGANIC SUPERCONDUCTOR κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

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Abstract The magnetic anisotropy and spin structure of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl are studied. The antiferromagnetic resonance-like signals are observed.

INTRODUCTION

The organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl undergoes a transition to weak ferromagnetic phase at T_{WF} = 22 K at ambient pressure.[1] The temperature dependence of electrical resistivity shows the trace of superconducting phase below 12 K. A number of phases (metallic, semiconducting, weak ferromagnetic and superconducting

phases) are found in the T-P phase diagram even in the moderate pressure region less than ~1 kbar.[2] The existence of multiple phases at low pressure indicates that the physical properties of the title salt are subject to the subtle structural change due to, for example, ethylene conformation, isotope exchange of the outer ethylene groups, etc. We previously reported that the T_{WF} of the deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (abbreviated as D-salt) is a little higher (T_{WF} = 24 K) than that of the hydrogenated one (abbreviated as H-salt) and that the superconducting phase is not obviously mixed with the weak ferromagnetic phase in the D-salt.[3] These experimental results show that the weak ferromagnetic phase of the D-salt is more stable than that of the H-salt. In this paper we report magnetization measurements on the D-salt and ESR measurements on both the H- and D-salts at ambient pressure. We discuss the magnetic natures of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and the isotope effect on the magnetic properties.

EXPERIMENTAL

The samples of the H(or D)-salt were grown by electrochemical oxidation of BEDT-TTF-H_8 (or 98 % deuterated BEDT-TTF-D_8). Magnetization measurements were performed with a SQUID magnetometer. We present the data in which the core distributions are subtracted, using the Pascal rule. ESR measurements were performed in the range between 2.5 and 294 K, using an X-Band ESR spectrometer.

RESULTS AND DISCUSSION

Magnetization

Figure 1 shows the field dependence of the magnetization of single crystal of the D-salt at 5 K under the field applied along the b-axis (H_{ext}//b). The stepwise change at ~0.3 T indicates that a spin-flop transition occurs. The easy axis of the antiferromagnetic spins is considered to be parallel to the b-axis, which is perpendicular to the two-dimensional

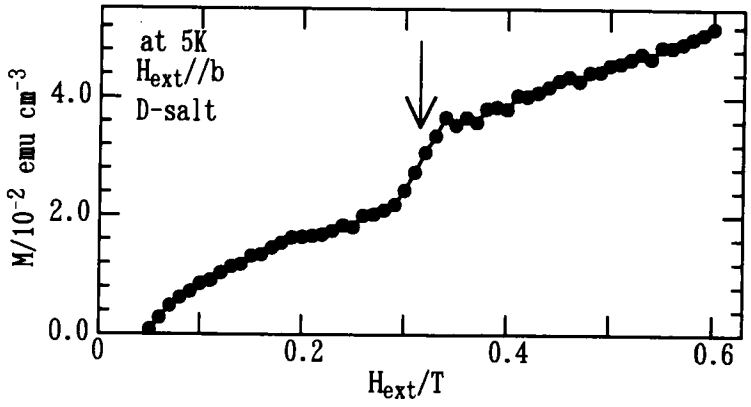

FIGURE 1 The field dependence of the magnetization of the D-salt of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl above at 5 K with H_{ext}//b. The arrow indicates the spin-flop transition.

BEDT-TTF cation layer. It was reported that a spin-flop transition occurs at H_{SF} = ~0.4 T at 5 K in the H-salt with H_{ext}//b.[4] The difference of the H_{SF} between the H- and D-salts indicates that the magnetic anisotropy of the H-salt is larger than that of the D-salt. Previously we reported that the saturation moment is ~10 $^{-3}\mu_B$ for both the H- and D-salts.[3] Furthermore, no anisotropy of the magnetization was observed in the ac-plane (conducting plane) in both the H- and D-salts.[1,5] The experimental results indicate that the spin structures of the weak ferromagnetic phase possess no significant difference between the H-and D-salts.

The exchange interaction field, H_{ex}, is estimated as 130(±9) T by using the following equation:

$$H_c \sim 2 H_{ex} \qquad (H_{ex} \gg H_a) \qquad (1)$$

where H_a is the magnetic anisotropy field and H_c is the parallel-lining field of the antiferromagnetic spins obtained from the field dependence of the magnetization of the D-salt above the H_{SF}. Using the values of the H_{ex} and H_{SF} with the following equation:

$$H_{SF} = \sqrt{2\,(H_{ex}-H_a)H_a} \cong \sqrt{2\,H_{ex}H_a} \quad (H_{ex} \gg H_a) \qquad (2)$$

the H_a can be estimated as ~10 mT. The values of the H_a and H_{ex} show that the D-salt is a Heisenberg-type antiferromagnet like ordinary organic magnetic materials. From the value

of the H_a, the value of the magnetic anisotropy energy, E_a, can be estimated as ~10^{-18} erg/unit cell.

Provided that the title salt has the orthorhombic structure at low temperature, the E_a is given by :

$$E_a = \sum_{\mu=a,b,c} \Psi_{a\mu} \alpha_\mu^2 \qquad (\alpha_\mu = \cos\theta_\mu) \qquad (3)$$

where θ_μ is the angle between the direction of the spin and μ-axis and $\Psi_{a\mu}$ is the anisotropy constant of the μ-axis. Considering only the dipole-dipole interaction, the $\Psi_{a\mu}$ is described by the following dipole-sum :

$$\Psi_{a\mu} = \frac{1}{2} g^2 \mu_B^2 \sum_{i,j} S_i S_j \frac{1}{r_{ij}^3} \left(1 - \frac{3 r_{ij\mu}^2}{r_{ij}^2}\right) \qquad (4)$$

where S_i is the i-site spin density, r_{ij} is the distance between i- and j-sites, and $r_{ij\mu}$ is the μ-coordinate of the vector ij. Assuming that the spin density is the same as the charge density obtained by the extended Hückel method based on the X-ray analysis data at 127 K [6], the dipole-sums calculated within a radius of 100 Å of a unit cell are given in Table I. It is shown that, if only the dipole-dipole interaction contributes to the E_a, the easy axis must be parallel to the a-axis. This is inconsistent with the results of the magnetization

TABLE I The value of each dipole-sum (× 10^{-19} erg/unit cell).

	μ=a	b	c
$\Psi_{a\mu}$	-5.935	4.274	1.661

measurements. Then we estimate the spin-orbit coupling, E_{asp}, by :

$$E_{asp} \sim (\Delta g)^2 J \qquad (5)$$

where Δg is the g-shift and J is the exchange interaction energy. Using J = 44(±3) K, the E_{asp} is obtained to be ~10^{-19} erg/unit cell. The evaluated E_{asp} is comparable to that of the dipole-dipole interaction in Table I. Thus we consider that both the dipole-dipole interaction and spin-orbit coupling equally contribute to the magnetic structure of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$, which is extraordinary because the spin-orbit coupling of

organic magnetic materials is generally very weak.[7]

The results of the magnetization measurements on both the H- and D-salts show that the weak ferromagnetic phase of the D-salt is less magnetically anisotropic and more stable than that of the H-salt. A probable reason of this fact is the structural difference between the H- and D-salts at low temperature. Provided that the unit cell of the D-salt is larger than that of the H-salt, the dipole-dipole interaction and the transfer integral of the D-salt can be smaller than those of the H-salt. The results of the electrical resistivity measurements on both the H- and D-salts show that the D-salt is in the inverse pressure state from the H-salt by 120~140 bar [8], consistent with our conjecture. However, the C-D bond is generally shorter than C-H bond.[9] Then the unit cell of the D-salt would be smaller than that of the H-salt, which is inconsistent with our conjecture. In order to clarify the isotope effect on the crystal structure, we are going to make the X-ray analysis for both the H- and D-salts at low temperature.

ESR in the weak ferromagnetic state

Below T_{WF}, ESR signals were not observed in the H-salt (two samples), while the signals were found in the D-salt (three samples). The ESR signals were observable in the temperature range between 2.5 and 14 K. The resonance field (H_{res}) showed stronger

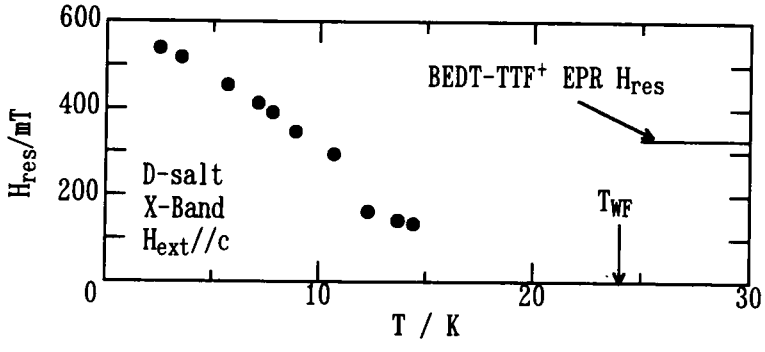

FIGURE 2 Temperature dependence of the H_{res} of the AFMR signal of the D-salt of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl in T<T_{WF}.

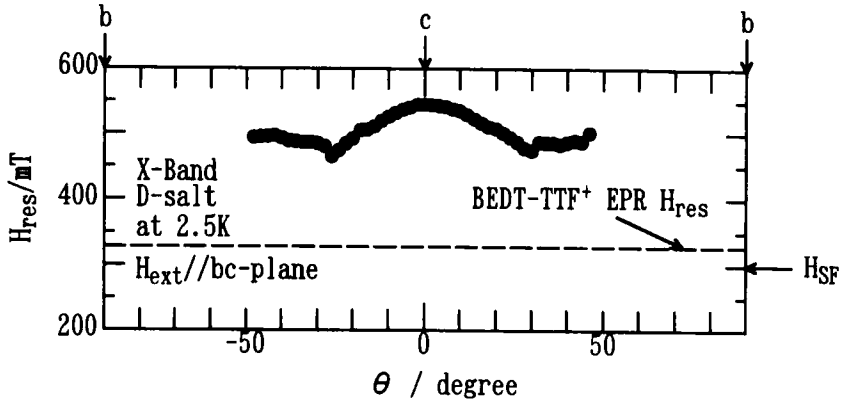

FIGURE 3 Angle dependence of the H_{res} of the AFMR signal of the D-salt of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl in T<T_{WF}.

temperature dependence than the H_{res} of the conventional BEDT-TTF cation radicals (BEDT-TTF$^+$ EPR H_{res}) as shown in Figure 2. At 2.5 K we observed no anisotropy of the H_{res} of those signals in the ac-plane. When the direction of applied field was varied from the c-axis to the b-axis at 2.5 K, the H_{res} of those signals showed stronger angle dependence than the BEDT-TTF$^+$ EPR H_{res} as shown in Figure 3. Furthermore, the absolute value of the H_{res} was larger than the BEDT-TTF$^+$ EPR H_{res} or the H_{SF} of the D-salt. Based on these facts, we ascribe the signals to the spin-flop mode of antiferromagnetic resonance (AFMR). However, we should remark that the angle dependence of the H_{res} of those signals cannot be fitted to the Nagamiya's standard AFMR theory.[10]

ESR in the paramagnetic state

Figure 4 shows the ESR data for both the H- and D-salts in the paramagnetic state. There are no significant differences between the H- and D-salts in ESR properties such as spin susceptibility (χ_{spin}), peak-to-peak linewidth ($\Delta H_{p\text{-}p}$), and g-value. In an antiferromagnet above Néel temperature, it is known that the $\Delta H_{p\text{-}p}$ of a low-dimensional system decreases with decreasing temperature, while that of a three-dimensional system increases.[11] From this fact and the comparison of the ESR properties in the paramagnetic state with those of the isostructural salt, κ-(BEDT-

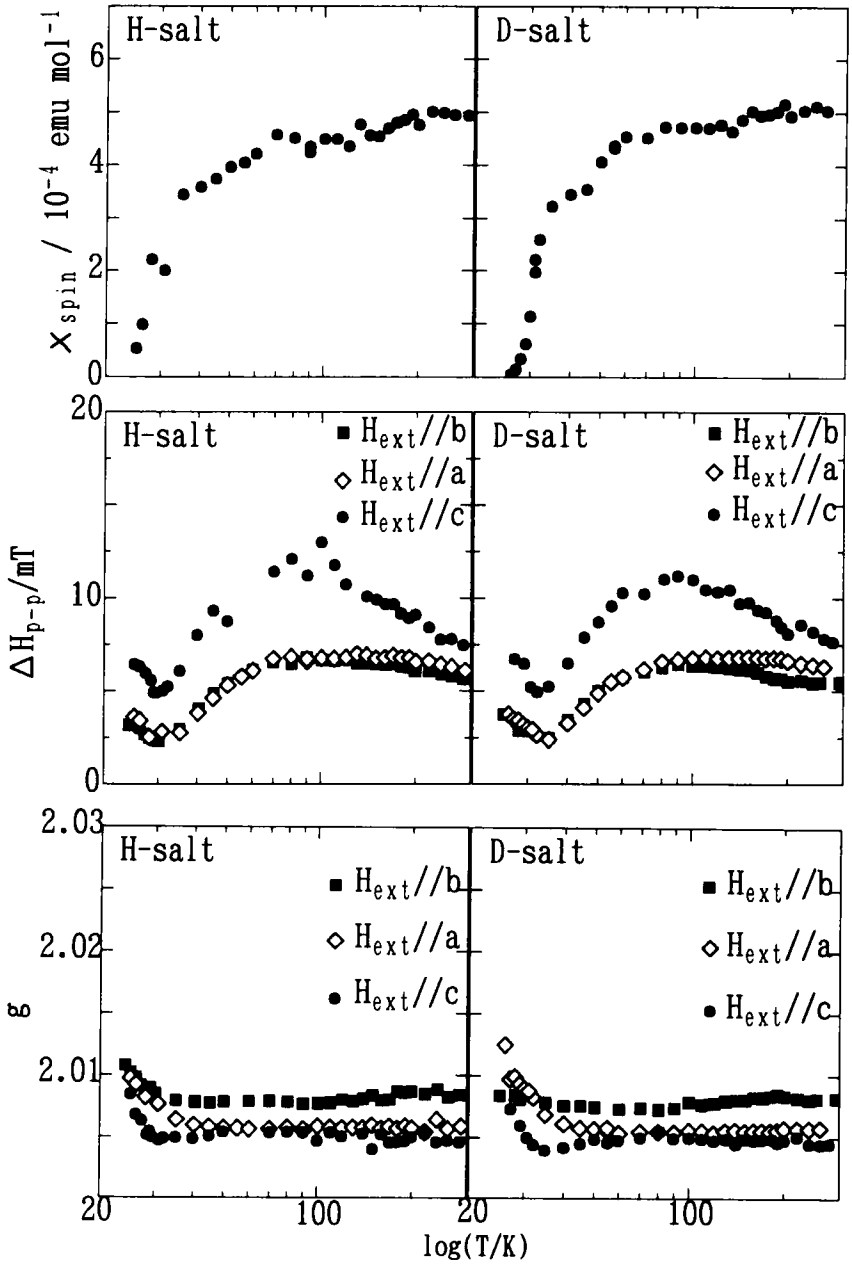

FIGURE 4 Temperature dependences of the χ_{spin}, ΔH_{p-p} and g-values of the H- and D-salts of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.

$TTF)_2Cu[N(CN)_2]Br$ (abbreviated as Br-salt)[12], the paramagnetic state is classified into three temperature regions I ~ III (I : 294~60 K, II : 60~35 K, III : 35 K~T_{WF}).

In the region I, the χ_{spin} is almost temperature independent (5.0×10^{-4} emu / mol at room temperature) down to 150~180 K and starts to decrease slightly below that temperature. The g-values are almost temperature independent. In H_{ext}//c, the ΔH_{p-p} increases monotonically from 7.5 mT at room temperature to ~11 mT around 90 K and turns to decrease below this temperature. In two other conditions (H_{ext}//a and H_{ext}//b), the similar tendencies are observed. These ESR properties are almost the same as those of the Br-salt, indicating that the electronic state of the H- and D-salts is similar to that of the Br-salt in this region.

In the region II, the χ_{spin} decreases rapidly from 4.6×10^{-4} emu/mol at 60 K to 3.5×10^{-4} emu/mol at 35 K. In H_{ext}//c, the ΔH_{p-p} decreases from ~10 mT at 60 K to ~5.2 mT at 35 K. In two other conditions (H_{ext}//a and H_{ext}//b), the similar tendencies are observed in the ΔH_{p-p}. These behaviors imply that the low-dimensional antiferromagnetic short range order grows with decreasing temperature in the region II. As for the g-values, they show anisotropic temperature dependencies. They are almost constant in H_{ext}//b, while they decrease in H_{ext}//c and increase in H_{ext}//a slightly with decreasing temperature. The ESR properties of the Br-salt in the region II were the same as those in the region I.[12]

In the region III, the χ_{spin} decreases rapidly with decreasing temperature and at last reaches zero at ~24 K. In H_{ext}//c, the ΔH_{p-p} increases divergently with decreasing temperature (~6.7 mT at 25 K). In two other conditions (H_{ext}//a and H_{ext}//b), the same tendencies in the ΔH_{p-p} are observed. These behaviors of the χ_{spin} and ΔH_{p-p} can be consistently explained by the growth of the three-dimensional antiferromagnetic short range order, though we cannot compare the ESR properties between the title salt and the Br-salt in this region because of the absence of the results on the Br-salt.[12] The g-values increase with decreasing temperature.

The results of the ^{13}C-NMR measurements on κ-$(BEDT\text{-}TTF\text{-}^{13}C)_2Cu[N(CN)_2]X$ (X=Cl, Br) where the center carbon atoms of BEDT-TTF are substituted by ^{13}C atoms were recently reported.[13] The results of these measurements show that the electronic state is the same between X=Cl and Br above 60 K and that the antiferromagnetic short range

order grows below that temperature in X=Cl but not in X=Br. This is consistent with the ESR properties of the H- and D-salts and the Br-salt in the paramagnetic state. We estimate the upper band width (W_U) and the effective on-site Coulomb repulsion (U_{eff}) of both the title salt and the Br-salt, using the value of the χ_{spin} at 127 K and the results of the tight binding band calculations with the extended Hückel method based on the X-ray analysis data at 127 K.[6] The Pauli paramagnetic susceptibility, χ_{pauli}, is described by:

$$\chi_{pauli} = \frac{\chi_{pauli}^{(0)}}{1 - U_{eff} D(E_F)} \qquad (6)$$

where $D(E_F)$ is the density of states at Fermi level and $\chi_{pauli}^{(0)}$ is the Pauli paramagnetic susceptibility for a free electron system and given as follows:

$$\chi_{pauli}^{(0)} \text{ (emu mol}^{-1}) = 3.23 \times 10^{-5} \times D(E_F) \text{ (states eV}^{-1} \text{ molecule}^{-1} \text{ spin}^{-1}) \qquad (7)$$

The results are summarized in Table II. There is no difference of the W_U between the title salt and the Br-salt, but the magnitude of the U_{eff} of the title salt is larger by 20 % than that of the Br-salt. Thus we consider that the antiferromagnetic short range order in the regions II and III is due to the strong electron correlation in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.

TABLE II The value of the experimental χ_{pauli} ($\times 10^{-4}$ emu mol^{-1}) at 127 K and the results of the calculations of $D(E_F)$ (states eV^{-1} molecule^{-1} spin^{-1}), $\chi_{pauli}^{(0)}$ ($\times 10^{-4}$ emu mol^{-1}), W_U (eV) and U_{eff} (eV) of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X based on the X-ray analysis data at 127 K [6] (a : ref.12).

X	χ_{pauli}	$D(E_F)$	$\chi_{pauli}^{(0)}$	W_U	U_{eff}
Cl	4.6~4.9	0.80	0.26	0.60	1.2
Br	~5.0[a]	0.95	0.31	0.60	1.0

Concerning the g-value, we have no idea at present to explain the behaviors in the regions II and III.

CONCLUSION

From the results of the magnetization measurements on the D-salt we estimate the values of the H_{ex} and H_a of the weak ferromagnetic phase of the D-salt and find that the D-salt is a Heisenberg type antiferromagnet. Based on the calculations on the contribution of the dipole-dipole interaction and spin-orbit coupling to the magnetic anisotropy energy in the title salt, we find that both the dipole-dipole interaction and spin-orbit coupling might equally contribute to the magnetic structure of the weak ferromagnetic phase of the title salt. The results of the magnetization measurements on the H- and D-salts show that the weak ferromagnetic phase of the D-salt is more stable and less magnetically anisotropic than that of the H-salt. This may be due to the larger unit cell of the D- than the H-salt. However, it is inconsistent with the fact that the C-D bond is generally shorter than the C-H bond. In the ESR measurements below T_{WF}, the signals ascribable to the spin-flop mode of the antiferromagnetic resonance (AFMR) were observed in the samples of the D-salt, although the properties of these signals do not obey the Nagamiya's standard AFMR theory. There are no significant differences between the H- and D-salts in ESR properties above T_{WF}. The results of the ESR measurements above T_{WF} reveal that the paramagnetic state of the title salt changes successively with three temperature regions I ~ III (I : 294~60 K, II : 60~35 K, III : 35 K~T_{WF}). We conjecture that the electronic state in the region I is almost the same as that of the isostructural organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. The behaviors of the χ_{spin} and ΔH_{p-p} show that the low-dimensional antiferromagnetic short range order grows with decreasing temperature in the region II and the three-dimensional antiferromagnetic short range order in the region III. The antiferromagnetic short range order is considered to be due to the strong electron correlation in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.

We thank Dr. T.Komatsu in University of Tokyo and Mr. J.Yamaura and Prof. T.Enoki in Tokyo Institute of Technology for useful discussions. This work was supported by a Grant-in-Aid for Scientific Research for Priority Areas from the Ministry of Education, Science, Sports and Culture of Japan.

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