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FERROMAGNETIC LINEAR CHAIN OF p-NPNN•Cu(hfac)$_2$ WITH ENHANCED INTERCHAIN INTERACTION

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Abstract The complex p-NPNN•Cu(hfac)$_2$ (p-NPNN=p-nitrophenyl nitronylnitroxide and hfac=hexafluoroacetylacetonate) crystallizes into the triclinic $P\bar{1}$ space group [a=12.515(3) Å, b=12.540(2) Å, c=11.610(3) Å, α=106.18(2)°, β=119.15(2)°, γ=91.14(2)°, V=1501.7(6) Å^3, Z=2]. The structure consists of an alternating chain of p-NPNN and Cu(hfac)$_2$ in which p-NPNN bridges two nonequivalent copper ions occupying the axial positions. The chains are connected by a π-π and head-to-tail overlap of the p-NPNN molecules, resulting in a two-dimensional network. The high-temperature magnetic susceptibilities can be interpreted in terms of a ferromagnetic intrachain interaction of J/k_B=14.3 K and an antiferromagnetic interchain interaction of zJ'/k_B=-2.6 K. The observed interchain interaction which would originate in the overlap of p-NPNN is much stronger than those in the related Cu(II) materials reported so far. The low-temperature magnetic susceptibilities indicate an antiferromagnetic order at T_N=1.22 ±0.01 K, followed by an enhancement of the susceptibility below T_c=0.6 ±0.1 K, probably due to a spin canting.

Keywords: Nitronylnitroxide, Crystal structure, Magnetic properties, Magnetic transition

INTRODUCTION

The study of magnetic materials has been an important field in both physics and chemistry,[1] and the search for molecule-based magnetic materials has intensified in recent years.[2,3] In this research frontier, a stable organic radical family, nitronylnitroxide, has attracted much interest, because of potential ferromagnetic properties: various nitronylnitroxide derivatives have been found to exhibit ferromagnetic intermolecular interactions in their bulk crystals.[4-15] Among them p-NPNN (p-nitrophenyl nitronylnitroxide) is the most well-known compound as the first pure organic ferromagnet.[16,17] p-NPNN crystallized into the β form[18] shows a three-dimensional ferromagnetic order below 0.65 K.[16,17] Except this phase, p-NPNN provides three more polymorphs each of which shows different magnetic ground state.[19,20] From the structural viewpoint, it is characteristic of *p*-NPNN especially in the β form that multi-dimensional intermolecular contacts are seen in the crystals, reflecting the strong electronic polarization effects in the molecule.[17, 18]

Moreover, the nitronylnitroxide has also been known to be a ligand for various transition and rare-earth metal ions. The crystal structures and magnetic properties of such complexes have been extensively studied by the group of Gatteschi, and various interesting magnetic systems have been observed especially in the M(hfac)$_2$ (M=Cu, Mn, etc. and hfac=hexafluoroacetylacetonate) complexes of nitronylnitroxides.[21]

In order to examine the properties of *p*-NPNN as a ligand, we prepared *p*-NPNN•Cu(hfac)$_2$ and studied the crystal structure and the magnetic properties. We describe how the potentiality of *p*-NPNN yielding multi-dimensional intermolecular interactions reflects in the crystal structure and in the magnetism.

TABLE I Crystallographic data and experimental parameters for *p*-NPNN•Cu(hfac)$_2$.

Formula	$CuC_{23}N_3O_8F_{12}H_{18}$
Mol wt.	755.9380
Crystal system	*triclinic*
Space group	$P\bar{1}$
a /Å	12.515(3)
b /Å	12.540(2)
c /Å	11.610(3)
α /deg	106.18(2)
β /deg	119.15(2)
γ /deg	91.14(2)
V /Å^3	1501.7(6)
D (calcd.)/g cm^{-3}	1.672
Z	2
μ /cm^{-1}	8.91
Radiation	Mo K$_\alpha$ (λ =0.71073 Å) graphite monochromator
2θ range/deg	4.0-55.0
No.collected	7332
No.obsd.[a)]	5077
R	0.0685
R_w	0.0673

a) $|F_0| > 3.0\sigma(F_0)$

TABLE II Positional parameters (x10^4) and equivalent temperature factors (Å^2) for *p*-NPNN•Cu(hfac)$_2$.

	X	*Y*	*Z*	*B*(eq)
Cu1	0(0)	0(0)	0(0)	4.1(.0)
Cu2	5000(0)	5000(0)	0(0)	4.2(.0)
O1	-1100(3)	757(3)	548(4)	4.9(.1)
O2	754(3)	-493(3)	1637(3)	4.6(.1)
F1	-1581(6)	2725(4)	1837(7)	12.9(.4)
F2	-2949(4)	1363(4)	1050(5)	11.5(.3)
F3	-1646(5)	2034(5)	3203(5)	12.9(.3)
F4	798(5)	-1185(5)	4087(6)	12.9(.3)
F5	1983(6)	315(4)	5058(5)	14.5(.3)
F6	2242(5)	-1048(5)	3783(5)	12.9(.3)
C1	-954(4)	970(5)	1738(5)	4.8(.2)
C2	-165(5)	598(5)	2802(6)	5.6(.2)
C3	629(5)	-125(4)	2661(5)	4.6(.2)
C4	-1798(6)	1758(6)	1983(7)	7.0(.3)
C5	1439(6)	-491(5)	3902(6)	6.4(.3)
O3	3464(3)	4817(3)	-1720(3)	4.4(.1)
O4	5394(3)	3604(3)	-809(3)	4.5(.1)
F7	1572(6)	4981(5)	-3923(7)	22.4(.4)
F8	1664(5)	3651(7)	-5211(5)	15.4(.4)
F9	933(4)	3482(7)	-4151(6)	17.9(.4)
F10	4933(5)	1515(4)	-3686(4)	10.6(.3)
F11	6414(3)	1970(3)	-1579(5)	8.9(.2)
F12	4682(4)	1054(3)	-2239(5)	9.3(.3)
C6	3062(4)	4008(4)	-2815(5)	4.4(.2)
C7	3609(5)	3087(4)	-3064(5)	5.1(.2)
C8	4727(5)	2962(4)	-2028(5)	4.5(.2)
C9	1824(5)	4052(5)	-4026(6)	5.8(.2)
C10	5218(5)	1881(5)	-2396(6)	5.6(.2)
O5	1465(3)	1768(3)	1626(4)	4.6(.1)
O6	3558(3)	3810(4)	339(5)	6.6(.2)
O7	-3134(4)	4157(5)	-2407(6)	9.7(.3)
O8	-2434(5)	4421(7)	-3613(6)	12.4(.4)
N1	2332(3)	2254(3)	1552(4)	3.9(.2)
N2	3324(3)	3195(3)	920(4)	4.4(.2)
N3	-2338(4)	4150(4)	-2670(5)	6.5(.2)
C11	2197(4)	2905(4)	758(5)	3.8(.2)
C12	3682(4)	2255(4)	2526(5)	4.4(.2)
C13	4259(4)	2548(5)	1723(6)	4.9(.2)
C14	3818(5)	1123(5)	2750(7)	6.2(.3)
C15	4056(5)	3204(6)	3891(6)	6.4(.3)
C16	5542(5)	3252(6)	2587(8)	7.0(.3)
C17	4186(6)	1505(6)	601(7)	6.9(.3)
C18	1037(4)	3234(4)	-119(5)	3.9(.2)
C19	868(5)	3536(5)	-1246(6)	5.7(.3)
C20	-233(5)	3834(6)	-2075(6)	6.1(.3)
C21	-1151(4)	3832(4)	-1764(6)	4.9(.2)
C22	-1013(4)	3560(5)	-650(6)	5.0(.2)
C23	87(4)	3253(4)	182(6)	4.6(.2)

EXPERIMENTAL

p-NPNN was prepared according to the literature method.[22] The complex, *p*-NPNN•Cu(hfac)$_2$ was obtained by the reaction of stoichometric amounts of the components in hot cyclohexane. The green needle crystals were grown by slow evaporation of the solvent. The results of the elemental analyses were satisfactory for the 1:1 adduct (Calcd for $C_{23}H_{18}N_3O_8F_{12}Cu$: C, 36.54; H, 2.40; N, 5.56. Found: C, 36.65; H, 2.51; N, 5.62).

X-ray diffraction data were collected on a RIGAKU AFC-5 automatic four-circle diffractometer with graphite-monochromatized Mo K_α radiation (λ=0.71073Å). Unit cell dimensions were obtained by a least-squares refinement using 25 reflections with $20^\circ < 2\theta < 25^\circ$. During data collection, the intensities of three representative reflections were measured as a check on crystal stability, and no loss was shown. No absorption correction was carried out, because the influence of the absorption was negligibly small. The Patterson map revealed the positions of the copper atoms and the positions of the other non-hydrogen atoms were obtained by successive Fourier syntheses (SHELX-86).[23] With anisotropic thermal parameters for all non-hydrogen atoms, block-diagonal least-squares refinement was employed (UNICS III).[24] The positions of hydrogen atoms were found by differential Fourier methods, and were refined with isotropic thermal parameters. Details of the crystallographic parameters are given in Table I. Final positional parameters are listed in Table II.

The dc magnetic susceptibility was measured in the temperature range of 3-280 K in the field of 1 T on a Faraday balance.[25] The paramagnetic susceptibility, χ_p, was calculated from the dc susceptibility, subtracting the diamagnetic susceptibility of χ_d= -7.2×10^{-4} emu mol^{-1}, which was obtained, assuming that χ_p follows the Curie law at high temperatures. The ac susceptibility, χ_{ac}, in the temperature range of 2.7-30 K was measured on a magnetosusceptometer of Lake Shore ACS 7121 in the field of 0.5 mT (125 Hz) and that in the range of 0.03-4.2 K was done on a home-made susceptometer of usual mutual inductance method with a dilution refrigerator in the field of 0.1 mT (525 Hz). Polycrystalline samples were used for both the dc and ac magnetic susceptibility measurements.

CRYSTAL STRUCTURE

The complex crystallizes in the triclinic $P\bar{1}$ space group in which one unit of *p*-NPNN•Cu(hfac)$_2$ is crystallographically independent. Figure 1 shows ORTEP view of the asymmetric unit, where the fluorine atoms were omitted for the sake of clarity.

Figure 2 shows a projection of the structure onto the *ab* plane, where the CH_3 groups of *p*-NPNN and the CF_3 groups of Cu(hfac)$_2$ are omitted. The copper atoms are located at (0, 0, 0) and (0.5, 0.5, 0) positions with an inversion symmetry around them. They are octahedrally coordinated by four oxygens of two hfac ligands occupying the equatorial positions and two oxygens of two different *p*-NPNN in the axial positions. Selected

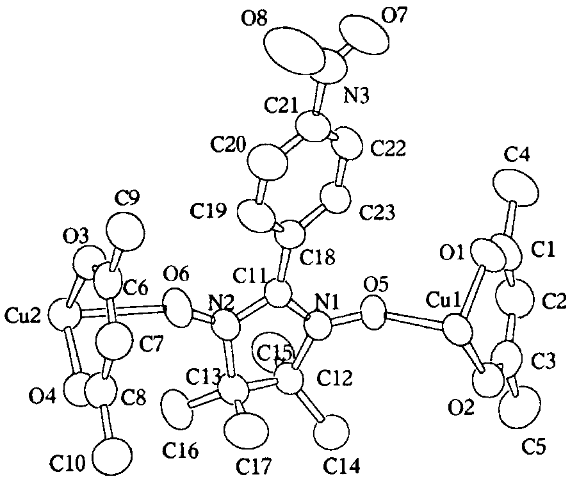

Figure 1 ORTEP view of the asymmetric unit of *p*-NPNN•Cu(hfac)$_2$. The fluorine atoms are omitted for the sake of clarity.

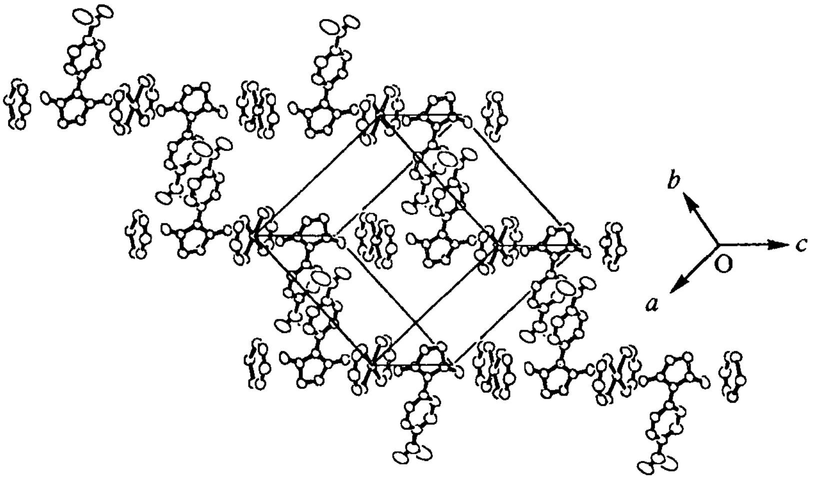

Figure 2 A projection of the structure of *p*-NPNN•Cu(hfac)$_2$ onto the *ab* plane. The CH_3 groups of *p*-NPNN and the CF_3 groups of Cu(hfac)$_2$ are omitted for the sake of clarity.

TABLE III Selected bond lengths (Å) and angles (deg) for *p* -NPNN•Cu(hfac)$_2$.

	Bond Lengths		
Cu1-O1 (eq) [a)]	1.941(4)	Cu1-O2 (eq)	1.953(4)
Cu1-O5 (ax) [a)]	2.444(4)	Cu2-O3 (eq)	1.929(4)
Cu2-O4 (eq)	1.939(4)	Cu2-O6 (ax)	2.559(5)
O5- N1	1.284(6)	O6-N2	1.269(7)
N1-C11	1.348(7)	N2-C11	1.356(8)
	Angles		
O1-Cu1-O5	82.6(2)	O2-Cu1-O5	83.8(2)
O1-Cu1-O2	91.9(2)	O4-Cu2-O6	87.9(2)
O3-Cu2-O6	81.1(2)	O3-Cu2-O4	92.6(2)
Cu1-O5-N1	127.7(3)	Cu2-O6-N2	154.2(4)

a) The equatorial and axial Cu-O distances are denoted by (eq) and (ax), respectively.

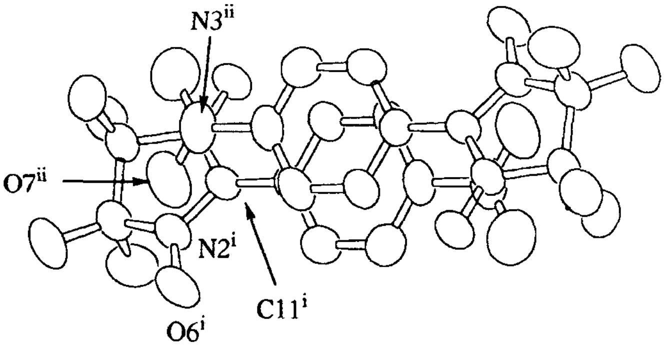

Figure 3 A top view of the intermolecular arrangement of *p*-NPNN between the chain (Symmetry operations; (i) *x, y, z* ; (ii) *-x, -y*+1, *-z*).

bond distances and angles are listed in Table III, where the equatorial and axial Cu-O bond distances are denoted by (eq) and (ax), respectively. The radical bridges the nonequivalent copper ions, resulting in an alternating stack of *p*-NPNN and Cu(hfac)$_2$ along the [110] direction. Such a one-dimensional alternation has been observed in the crystals of MeNN•Cu(hfac)$_2$ (MeNN=methylnitronylnitroxide),[26] *i*-PrNN•Cu(hfac)$_2$ (*i*-PrNN=*iso*-propylnitronylnitroxide),[27] and so on. The axial bond distances which are relevant to the exchange interaction have been reported to be 2.341(6) and 2.431(5) Å for MeNN•Cu(hfac)$_2$[26] and 2.407(6) and 2.446(8) Å for *i*-PrNN•Cu(hfac)$_2$.[27] The axial distances in *p*-NPNN•Cu(hfac)$_2$ are slightly longer than those in the related materials, presumably due to the larger substituent of the nitronylnitroxide.

The molecular axes of the *p*-NPNN molecules appearing in the chain are alternately arranged to the [$1\bar{1}0$] and [$\bar{1}10$] directions. The chains are connected by an intermolecular π-π and head-to-tail overlap of *p*-NPNN, resulting in a two-dimensional spin lattice parallel to the *ab* plane. Figure 3 shows a top view of the overlap of *p*-NPNN which include an inversion symmetry. The intramolecular dihedral angle between the nitrophenyl group and the dihydroimidazole ring is 19.8(2)°, which is typical or slightly smaller for phenyl-substituted nitronylnitroxides. The short intermolecular, interatomic distances in the arrangement are 3.230(9) Å of $O6^{i}\cdots O7^{ii}$, 3.362(9) Å of $N2^{i}\cdots O7^{ii}$ and 3.511(9) Å of $C11^{i}\cdots N3^{ii}$ (symmetry operations; (i) *x*, *y*, *z*; (ii) -*x*, -*y*+1, -*z*). Such a head-to-tail arrangement resembles to that in the α phase *p*-NPNN, although the shortest distance is observed between the oxygen atom of the NO group and the nitrogen atom of the NO$_2$ group to be 3.081 Å in it.[19] The potentiality of *p*-NPNN producing multi-dimensional structures, appears to result in the interchain contacts in the crystal of *p*-NPNN•Cu(hfac)$_2$.

MAGNETIC PROPERTIES

Figure 4 shows the temperature dependence of χ_p of *p*-NPNN•Cu(hfac)$_2$ in the range of 3-280 K, where the product χ_pT is plotted as a function of temperature in a logarithmic scale. The value of χ_pT increases with decreasing temperature from 280 K down to *ca.* 4 K, indicating a ferromagnetic intrachain interaction. However, after passing a maximum of 1.5 emu K mol^{-1} at this temperature, χ_pT shows a slight decrease. The ferromagnetic behavior would originate in either the intrachain interaction between *p*-NPNN and Cu(hfac)$_2$, or the interchain interaction between *p*-NPNNs. Since, if the ferromagnetic interaction is limited in a dimer like the interchain interaction, the value of χ_pT approaches to *ca.* 1.0 emu K mol^{-1} at the absolute zero temperature, the maximum value clearly denies the latter possibility. The intrachain interaction is ferromagnetic, and the decrease in χ_pT below 4 K would be due to an antiferromagnetic interchain interaction which originates in the intermolecular overlap of *p*-NPNN shown in Figure 3. We have proposed an empirical relation between the intermolecular arrangement of nitronylnitroxide and the magnetic coupling: a short distance between the NO groups on which the unpaired electron is concentrated leads to an antiferromagnetic coupling, while a contact between the NO group and the substituent at the α carbon (nitrophenyl ring in this case) results in a ferromagnetic coupling.[12] In fact, *p*-NPNN in the α form which includes a similar molecular arrangement, shows a ferromagnetic coupling.[19] The observed antiferromagnetic coupling for the arrangement in Figure 3, however, seems to disagree with the rule. It is speculated that penetration of the unpaired π electron into the nitrophenyl ring is not so negligible that the magnetic coupling depends rather seriously on the feature of overlapping especially in the case of face-to-face arrangement, as is demonstrated theoretically.[28, 29]

The magnetic susceptibility of the one-dimensional ferromagnetic chain[30] is given by,

$$\chi_{\mathrm{chn}} = \frac{Ng^2\mu_\mathrm{B}^2}{4k_\mathrm{B}T}\left(\frac{1+a_1x+a_2x^2+a_3x^3+a_4x^4+a_5x^5}{1+b_1x+b_2x^2+b_3x^3+b_4x^4}\right)^{\frac{2}{3}} \quad (1)$$

$$\text{with } x = \frac{J}{2k_\mathrm{B}T},$$

where N is the number of the spins (=$2N_\mathrm{A}$ (Avogadro's constant), in this case), g is the average g-factor for the two spins, μ_B is the Bohr magneton, J is the intrachain ferromagnetic coupling constant, and k_B is the Boltzmann constant. The constants, a_1-

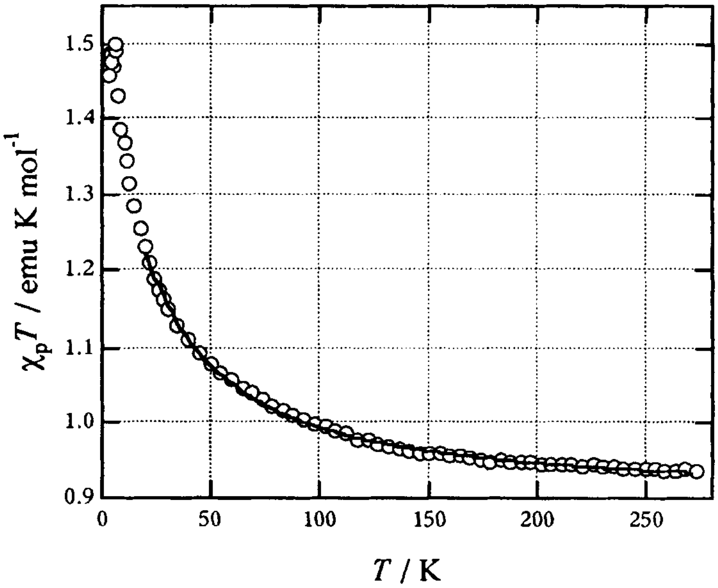

Figure 4 Temperature dependence of the paramagnetic susceptibility χ_p of *p*-NPNN•Cu(hfac)$_2$ in the range of 3-280 K. The solid curve is the theoretical one (see the text).

a_5 and b_1-b_4, are given in the literature.[30] When the interchain interactions can be taken into account with molecular field approximation, the susceptibility becomes[31]

$$\chi = \frac{\chi_{\mathrm{chn}}}{1-(zJ'/c)\chi_{\mathrm{chn}}} \tag{2}$$

where $c=Ng^2\mu_B{}^2$, J' is the interchain magnetic coupling constants, and z is the number of nearest neighbors and equals to 2 in this case. We tried to fit the data to Eq. (2), but the obtained fitting parameters were found to depend on the temperature range adopted in the analyses. In the case of MeNN•Cu(hfac)$_2$ and i-PrNN•Cu(hfac)$_2$ in which the ferromagnetic chains are well isolated from each other, their susceptibilities can be understood with Eq. (2) in the whole range of 1-300 K.[26,27] The deviation of the data of p-NPNN•Cu(hfac)$_2$ would come from the strong interchain interaction. When using

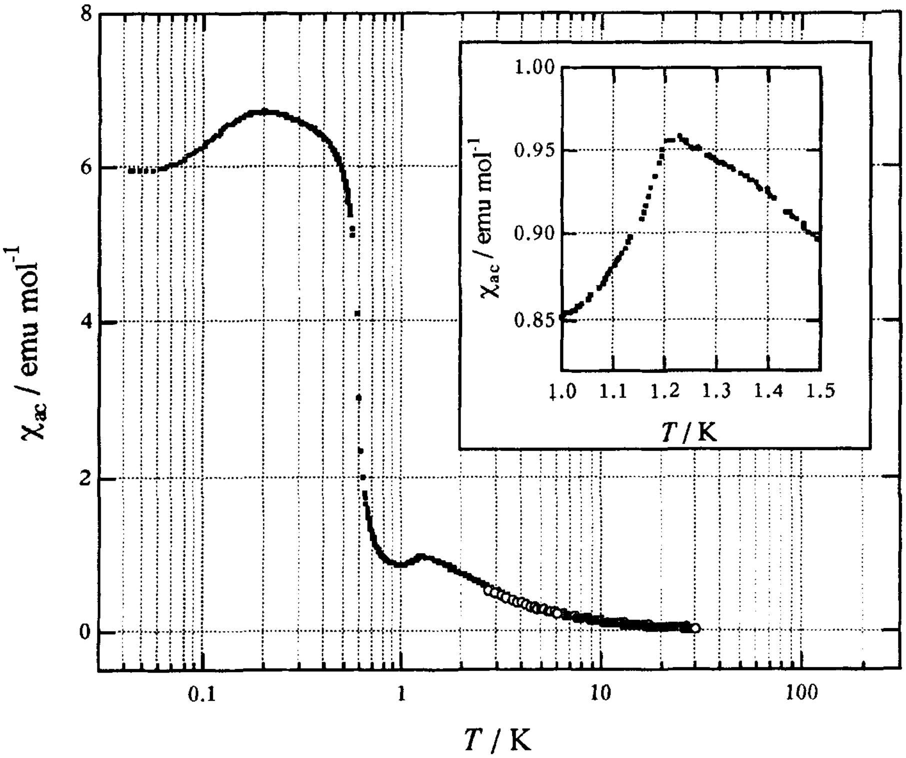

Figure 5 Temperature dependence of the ac magnetic susceptibility of χ_{ac} in the range of 0.03-30 K. The circles and dots show the results obtained on the Lake Shore susceptometer and on the home-made susceptometer with the dilution refrigerator, respectively. The inset shows the behavior in the range of 1.0-1.5 K in an enlarged scale.

the data above 20 K in which the interchain interaction is weak enough to be treated as a molecular field, the best fit is obtained with g=2.19, J/k_B=14.3 K and zJ'/k_B= -2.6 K. The solid curve in Figure 4 is the theoretical one. While the obtained J value is in the same order of magnitude as those of MeNN•Cu(hfac)$_2$ and *i*-PrNN•Cu(hfac)$_2$, the zJ' value is larger than those of them by two or three orders.[26,27] The enhancement of the interchain interaction caused by the interaction between the *p*-NPNNs is confirmed by the magnetic measurements.

The results of the χ_{ac} measurements are shown in Figure 5, where the circles show those obtained on the Lake Shore susceptometer and the dots do those on the home-made susceptometer. The diamagnetic contribution is not compensated in χ_{ac}. The inset of Figure 5 shows the behavior in the range of 1.0-1.5 K in an enlarged scale. The value of χ_{ac} increases gradually with decreasing temperature from 30 K and turns to decrease below T_N=1.22 ±0.01 K, showing a discontinuous gradient change. The behavior indicates an antiferromagnetic order which is caused by the antiferromagnetic interchain interaction operating in the two-dimensional network. Since any magnetic ordered state has not been observed in MeNN•Cu(hfac)$_2$ or *i*-PrNN•Cu(hfac)$_2$ at least down to 1 K,[26,27] the magnetic order would be caused by the intense interchain interaction in *p*-NPNN•Cu(hfac)$_2$. However, χ_{ac} jumps up suddenly by *ca.* six times below T_c=0.6 ±0.1 K (the point of the maximum gradient), suggesting some kind of ferromagnetic order with a permanent magnetic moment. Coexistence of the antiferromagnetic order at T_N=1.22 K and the permanent moment below T_c=0.6 K, strongly suggests a spin canting, although the microscopic mechanism is not identified in the spin lattice of *p*-NPNN•Cu(hfac)$_2$ at this stage. The temperature dependence of χ_{ac} below T_c could be related to freezing of the magnetic domain motions.

SUMMARY

We have prepared *p*-NPNN•Cu(hfac)$_2$ to see the performance of the first pure organic ferromagnet, *p*-NPNN, as a ligand. The crystal consists of the alternating chain of *p*-NPNN and Cu(hfac)$_2$ in which *p*-NPNN bridges two nonequivalent copper ions occupying the axial positions. In addition, *p*-NPNN interacts with that in the neighboring chain through the π-π and head-to-tail overlap. The potentiality of *p*-NPNN producing multi-dimensional structures, appears to result in the two-dimensional network. The high-temperature magnetic susceptibilities can be interpreted in terms of a one-dimensional ferromagnetic chain with an antiferromagnetic interchain interaction. The estimated interchain interaction which would originate in the overlap of *p*-NPNN, is much stronger than those in the related Cu(II) materials reported so far. The low-

temperature magnetic susceptibilities show the anomaly at T_N=1.22 K indicating an antiferromagnetic order, and also do the enhancement of the susceptibility below T_C=0.6 K. It is speculated that the anomaly at T_N=1.22 K shows a antiferromagnetic order formed by J and J', followed by a ferromagnetic order with a spin canting below T_C=0.6 K. Detail low-temperature studies are in progress to see the character of the ordered state.

DEDICATION

This paper is dedicated to Professor Yusei Maruyama on the occasion of his retirement from the Institute of Molecular Science and his start at Hosei University. One of us (KA) was introduced to nitronylnitroxides while at the low temperature center of IMS under the supervision of Maruyama-*sensei*. KA would like to express his gratitude to Maruyama-*sensei* for his supervision there and for his continued encouragement and interest after IMS. We take advantage of this opportunity to wish him good health, continued contributions to Material Science and happiness in his personal life.

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