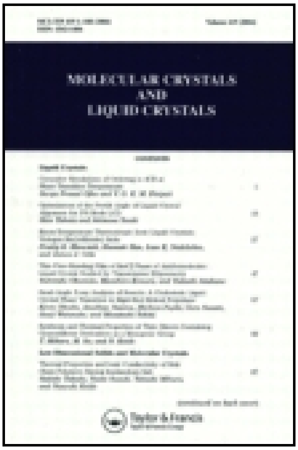

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Magnetic Phase Transition of Copper Complexes Containing Dmit or TCNQ Anion

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Magnetic Phase Transition of Copper Complexes Containing Dmit or TCNQ Anion

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Magnetic phase transitions were observed at 6 and 10 K for $(Me_4N)_2[Cu\text{-}(dmit)_2]$ ($dmit^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate) and Cu-TCNQ salts (TCNQ = tetracyanoquino dimethane), respectively.

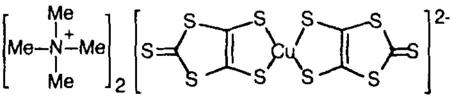
Keywords: copper complexes; copper salts; TCNQ; dmit; phase transition; weak ferromagnet

INTRODUCTION

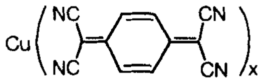
The $Ni(dmit)_2$ complexes ($dmit^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate) have been extensively studied for development of conducting and superconducting materials[1]. Underhill and co-workers reported a molecular ferromagnet, $NH_4Ni(mnt)_2{\cdot}H_2O$ (mnt = maleonitriledithiolate)[2]. On the other hand, the corresponding Cu complexes have been scarcely studied. We examined the conducting and magnetic properties of $(R_4N)_2[Cu(dmit)_2]$ (R = H, Me, Et, Bu), and will report in this paper an antiferromagnetic phase transition with spin canting in $(Me_4N)_2[Cu(dmit)_2]$.

We have also investigated molecular magnetic materials having organic π-conjugated bridging ligands, and reported the pyrimidine-bridged polymeric complexes showing ferro- or antiferromagnetic interaction[3]. Radical anion species can also be served as π-conjugated ligands; for example, in $TCNE^{\cdot-}$

complexes (TCNE = tetracyanoethylene) it was clarified that the 1/2-spin of the anion radical participated in the bulk magnetism[4]. The DCNQI-copper complexes are extensively studied for conducting materials (DCNQI = *N,N'*-dicyanoquinonediimine)[5]. An electrical bistability of Cu-TCNQ was reported[6] (TCNQ = tetracyanoquinodimethane). In the course of our magnetic study on Cu-TCNQ salts, we have found a magnetic phase transition, which will also be reported in this paper.



$(Me_4N)_2[Cu(dmit)_2]$



Cu-TCNQ salt

RESULTS AND DISCUSSION

Copper-dmit complexes

According to Steimecke's method for the synthesis of $(Bu_4N)_2[Ni(dmit)_2]$[7], we obtained the crystal of $(Me_4N)_2[Cu(dmit)_2]$ by using $CuCl_2$ and Me_4NBr in place of $NiCl_2$ and Bu_4NBr. The sample was purified by recrystallization from methanol [black plates, mp. >175°C(dec)].

The static magnetic susceptibility (χ_{mol}) was measured on a SQUID magnetometer down to 1.8 K at 5 kOe. FIGURE 1a shows the temperature dependence of χ_{mol} and the product $\chi_{mol}T$. The $\chi_{mol}T$ curve decreased with decreasing temperature down to 10 K but showed a small peak at around 8 K. Above 10 K, the $\chi_{mol}T$ curve could be analyzed by a dimer model with a ground singlet state, giving $g = 2$ and $2J/k_B = -110$ K with 12 % paramagnetic contribution. However, the fit is not so good and the peak at around 8 K could not be explained by this analysis.

In order to clarify the nature of this anomaly, we measured the field-cooled magnetization (FCM), remnant magnetization (RM), and zero-field cooled magnetization (ZFCM). The FCM (10 Oe) showed an upsurge at 7 K on cooling, and, after removal of the applied field at 1.8 K, the RM completely disappeared at 7 K on heating. The ZFCM (10 Oe) increased with increasing

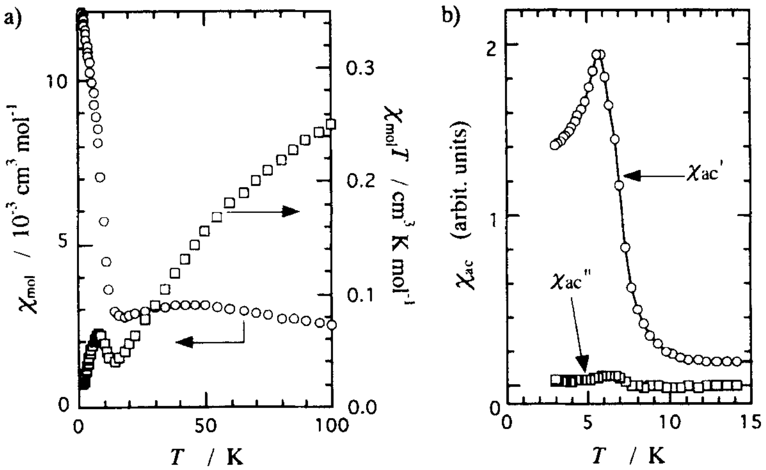


FIGURE 1 a) Temperature dependence of the static magnetic susceptibility (χ_{mol}) and the product $\chi_{mol}T$ of $(Me_4N)_2[Cu(dmit)_2]$. b) Temperature dependence of the ac magnetic susceptibilities χ_{ac}' and χ_{ac}'' of $(Me_4N)_2[Cu(dmit)_2]$.

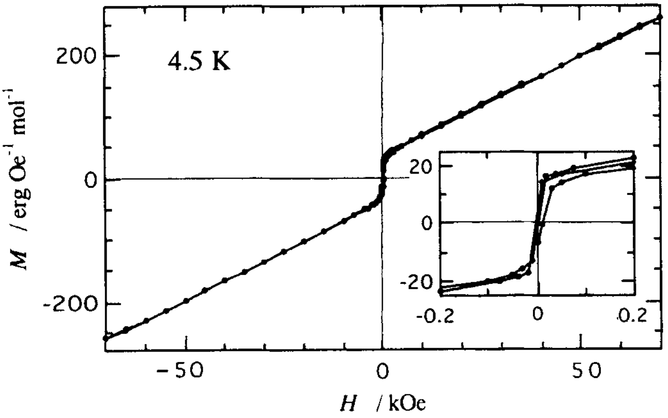


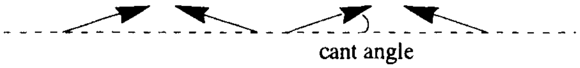
FIGURE 2 Magnetization curve of $(Me_4N)_2[Cu(dmit)_2]$ measured at 4.5 K.

temperature, exhibited a peak at 5.2 K, and then decreased to follow nearly the FCM curve.

The ac susceptibility measurement of $(Me_4N)_2[Cu(dmit)_2]$ revealed a clear magnetic phase transition. FIGURE 1b shows the temperature dependence of the χ_{ac}' (in-phase component) and χ_{ac}'' (out-of-phase component) at an applied field of 1 Oe with 10^4 Hz. A sharp peak of the χ_{ac}' at 6 K, which we define as a transition temperature, and a small hump of the χ_{ac}'' around 7 K were observed.

FIGURE 2 shows the *M-H* curve of $(Me_4N)_2[Cu(dmit)_2]$ measured at 4.5 K (below the magnetic phase transition temperature). A hysteresis loop was observed with a small coercive field of 5 Oe, indicating that the specimen has a very soft character. The magnetization varied linearly up to 7×10^4 Oe owing to rather strong antiferromagnetic interaction. The spontaneous magnetization estimated by extrapolation to $H \rightarrow 0$ was 30 erg Oe^{-1} mol^{-1} at 4.5 K, which is only 0.54% of a theoretical value of $g = 2.0$ and $S = 1/2$.

One of possible explanations for the magnetic behavior is a bulk phase transition to a canted antiferromagnet ("weak ferromagnet")[8]. Assuming that the spontaneous magnetization is attributed to the residual moment from the spin canting, the canting angle is estimated to be 0.3° at 4.5 K (SCHEME 1).



SCHEME 1

Another explanation is that the magnetization curve arises from a superposition of paramagnetic and (weak) ferromagnetic contributions; almost all paramagnetic spins are antiferromagnetically correlated, and only a small portion (0.54%) of the spins forms a (weak) ferromagnet with $T_C = 6$ K. However, the reproducibility of the magnitude of the spontaneous magnetization strongly suggested that $(Me_4N)_2[Cu(dmit)_2]$ is a canted antiferromagnet. The heat capacity measurement of $(Me_4N)_2[Cu(dmit)_2]$ is now underway in order to determine the amount of ordered spins.

Copper-TCNQ salts

Copper-TCNQ complexes were obtained from various chemical reactions: 1) The reaction of CuI and neutral TCNQ was conducted on the analogy to the preparation of NaTCNQ[9], and black powder was obtained. A slow diffusion method gave dark brown crystals. 2) The reaction of $CuSO_4$•$5H_2O$ and 2 equivalent of LiTCNQ gave $CuTCNQ_2$ as described in the literature[10]. Dark green powder was obtained. 3) The electrochemical crystallization was done in an H-shaped cell under modified conditions reported by England[11]. Polycrystals with dark violet metallic luster was obtained. 4) The reaction of copper metal with neutral TCNQ also gave the salts as black powder. The elemental analysis of these Cu-TCNQ salts indicated that the composition TCNQ/Cu varied from 1 to 2, depending on the synthetic methods.

Melby and co-workers[10] originally reported that the paramagnetic susceptibility of $Cu(TCNQ)_2$ was smaller than the nominal value expected for one S = 1/2 species. This result was explained by the following resonance contribution due to an electron transfer [Eq. (1)]. Our result agreed with theirs, but we have found another magnetic anomaly of Cu-TCNQ salts in a low temperature region. With decreasing temperature the $\chi_{\mathrm{mol}}T$ value decreased down to 12 K owing to antiferromagnetic interaction, and then increased to give a very small peak at 8 K. Below 8 K the $\chi_{\mathrm{mol}}T$ value decreased again down to 1.8 K.

$$2[Cu^{2+}(TCNQ^{-})_2] \longleftrightarrow Cu^{+}{}_2(TCNQ^{-})_2(TCNQ)_2 \longleftrightarrow Cu^{+}{}_2(TCNQ^{2-})(TCNQ)_3 \qquad (1)$$

The detailed magnetic measurements of these specimens revealed that all of the specimens exhibited a magnetic transition at around 10 K. For example, FIGURE 3a shows the results of FCM (3 Oe), RM, and ZFCM (3 Oe) measurements for the Cu-TCNQ salt which was prepared from 2LiTCNQ and $CuSO_4$ according to Melby's method[10]. The FCM curve exhibited an upsurge at 10 K on cooling the sample. Then, the applied field was removed at 1.8 K, and on heating the RM disappeared at 10 K. These findings indicate that a magnetic transition occurred at 10 K.

Similar magnetic transitions were observed for the specimens from various synthetic methods. The temperature dependence of the ac susceptibility (χ_{ac}') of Cu-TCNQ salts is shown in FIGURE 3b. For the powder samples the χ_{ac}' only showed a small ramp. On the other hand, the χ_{ac}' exhibited a peak for the crystalline samples prepared by slow diffusion and by electrochemical crystallization. These peaks are rather broad probably because of poor quality of the crystal and also because of a low content of the magnets, as described below. The magnitude of dc and ac susceptibilities was dependent on samples, but the transition temperature was the same (10 K) for all of the specimens. Thus, the component showing the magnetic phase transition should be single.

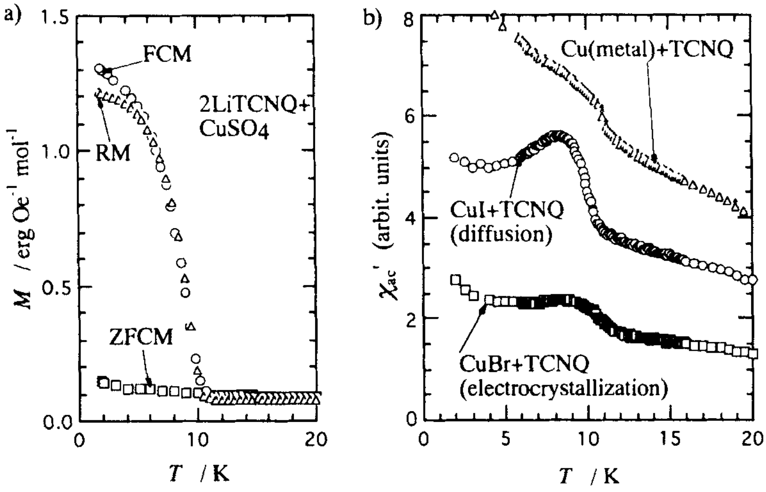


FIGURE 3 Magnetic phase transition of Cu-TCNQ salts. The preparation methods are indicated. a) FCM, RM, and ZFCM of the Cu-TCNQ salt. FCM and ZFCM were measured at an applied field of 3 Oe. b) Ac susceptibility (χ_{ac}') of the Cu-TCNQ salts at an applied field of 10 Oe with a frequency of 10^4 Hz.

The magnetization curves were obtained at 4.5 K (below the phase transition temperature). The field was applied up to $1.5\text{x}10^4$ Oe and the magnetization increased almost linearly. In a low field region, a small contribution of saturation magnetization was observed. After the field was removed, the remnant magnetization was obtained. FIGURE 4 shows a part of measured magnetization curves with hysteresis for selected four specimens. All of the Cu-TCNQ salts prepared by various methods showed hysteresis, but the magnitude was dependent on the preparation methods. The crystalline samples have a smaller coercive field (200 - 300 Oe) and larger spontaneous magnetization (0.10 - 0.14 erg Oe^{-1} g^{-1}) than the powder samples have. This hysteresis behavior seems to be affected by the quality of the crystal.

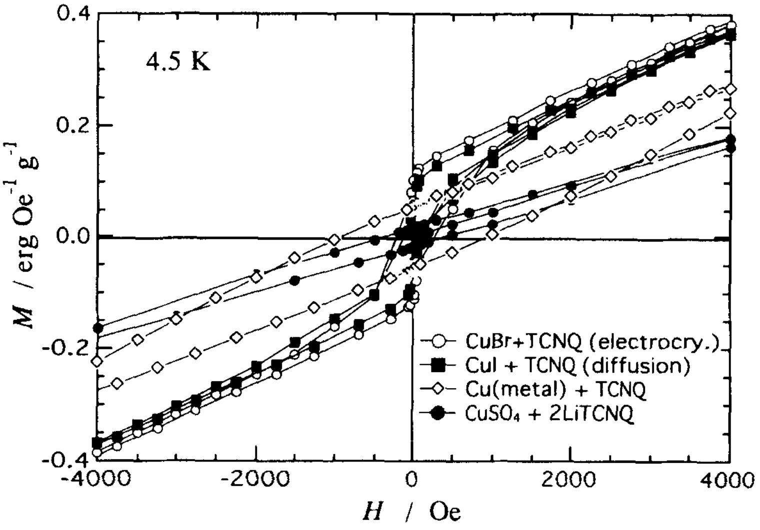


FIGURE 4 Magnetization curves of Cu-TCNQ salts. The preparation methods are indicated.

The spontaneous magnetizations were very small (0.14 - 0.02 erg Oe^{-1} g^{-1}), which correspond to only <0.7 % against the nominal value. This behavior seems to be a weak ferromagnet with a canted spin, similar to that of LiF$_4$TCNQ reported by Sugimoto *et al*[12]. However, in the present case, the observation of various magnitudes of the spontaneous magnetization indicates that this magnetic behavior can be attributed to a mixture of paramagnetic and (weak) ferromagnetic portions.

The IR spectra of neutral TCNQ and monoanionic LiTCNQ showed ν_{CN} at 2225 and 2209 cm^{-1}, respectively. In the spectra of the Cu-TCNQ salts the main bands of ν_{CN} fell between 2208 and 2212 cm^{-1} under the same conditions. Thus, the TCNQ's in these specimens are concluded to be monoanions. A neutral TCNQ band was also found in the case of $CuTCNQ_x$ $(x > 1)$.

The XPS in the Cu2p region was measured by use of a MgKα radiation. The samples prepared from Cu(0) + TCNQ and CuI + TCNQ showed typical Cu(I) signals at 953 and 933 eV. The sample prepared from Cu(II) + 2LiTCNQ showed slightly shifted signals at 956 and 937 eV. There is no shake-up satellite peak in any spectra. These measurements suggest that the Cu ions in these specimens are monocations, in good agreement with the results previously reported[13]. Therefore, the $CuTCNQ_x$ $(x>1)$ salts can be described as $Cu^+TCNQ^-TCNQ^0{}_{x-1}$.

The electrical conductivity was measured by a 4-probe method. The sample prepared from electrochemical crystallization was a semiconductor with an activation energy of 0.17 eV (100-120 K) and 0.082 eV (120-260 K). The compacted pellet of the sample prepared from LiTCNQ and $CuSO_4$ was also a semiconductor with an activation energy of 0.12 eV (80-300 K).

The electrical conductivity of the Cu-TCNQ salts was not so high as England *et al.* pointed out[11]. The canonical forms shown in Eq. (2) were proposed for CuTCNQ[11], and a mixed valence character shown in Eq. (3) was suggested for $CuTCNQ_2$[13]. They may be operative for electrical conductivity.

$$Cu^{2+}TCNQ^{2-} \longleftrightarrow Cu^{+}TCNQ^{-} \longleftrightarrow Cu^{0}TCNQ^{0} \qquad (2)$$

$$Cu^{2+}(TCNQ^{-})_2 \longleftrightarrow Cu^{+}TCNQ^{-}TCNQ^{0} \qquad (3)$$

If the above assumption is correct, this system can be regarded as an electron delocalized and/or mixed valence system like the DCNQI-Cu salts[5]. These canonical forms may be operative also for magnetic ordering.

The Cu(I) ion is diamagnetic, and TCNQ$^-$ is ready to form an antiferromagnetically coupled dimer[14]. The question that arises here is what is a spin source. The observed properties and data in elemental analysis, IR, and XPS should be attributed to a dominant portion to be diamagnetic or paramagnetic; the magnet portion of interest is not reflected on these analyses, owing to its small content. Although details of the magnet are not clarified yet, a fraction of secondary canonical forms and/or crystal defects seem to provide a spin source of this magnetic behavior.

SUMMARY

The magnetic phase transitions were observed at around 6 K and 10 K for the copper complexes, $(Me_4N)_2[Cu(dmit)_2]$ and Cu-TCNQ$_x$ ($1 \leq x \leq 2$), respectively. The former can be analyzed as a weak ferromagnet. On the other hand, the latter is supposed to be a mixture of a paramagnet and (weak) ferromagnet.

Acknowledgments

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