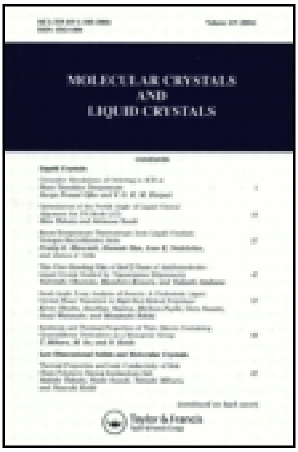

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New Charge-Transfer Complex-Based Organic Ferromagnets: Pyridinium-Substitued Imidazolin-1-Oxyl/ Tetrafluorotetracyanoquinodimethanide or Hexacyanobutadienide Salts

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NEW CHARGE-TRANSFER COMPLEX-BASED ORGANIC FERROMAGNETS: PYRIDINIUM-SUBSTITUTED IMIDAZOLIN-1-OXYL / TETRAFLUOROTETRACYANOQUINODIMETHANIDE OR HEXACYANOBUTADIENIDE SALTS

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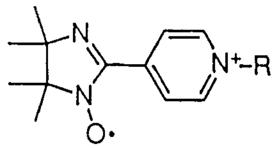
abstract The charge-transfer (CT) complexes of a series of 4,4,5,5-tetramethylimidazolin-1-oxyls substituted with 4-(*N*-alkylpyridinium) groups at the 2-position with two radical anions, tetrafluorotetracyanoquinodimethanide ($TCNQF_4^{-\bullet}$) and hexacyanobutadienide ($HCBD^{-\bullet}$) were prepared and their magnetic properties were investigated in the temperature range of 5 to 300 K. Ferromagnetic interaction was observed for the three CT complexes. Furthermore, the magnetic measurement at lower temperatures than 5 K showed that these CT complexes exhibited a ferromagnetic phase transition between 0.4 and 0.55 K. Consequently, the present CT complexes make a group of another type of organic ferromagnets without any magnetic metal elements.

INTRODUCTION

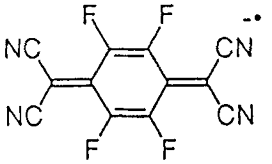
The development of molecular/organic ferromagnets exhibiting three-dimensional spin alignment in the same direction at reasonable temperatures now continues to lay a challenging subject upon chemists and physicists in several fields.[1] Since the first discovery of ferromagnetic interaction in a galvinoxyl crystal,[2] similar phenomena have also been recognized in almost 20 organic radical crystals for the last few years.[3] Very recently, a purely organic ferromagnet has at last been synthesized in a *p*-nitrophenyl nitronyl nitroxide crystal[4] and successively in several nitroxide crystals.[5-8] In contrast, there is so far almost no progress in the achievement of ferromagnetism based on two different spins of radical cation and radical anion in purely organic CT complexes, in spite of a great success in metallocene/tetracyanoethylene or tetracyanoquinodimethane CT systems,$^{9-12}$ in which metal d electrons play an essential role. Now we invetsigated the synthesis of stable and definitively characterized CT complexes and their magnetic properties till low temperatures with aim at the discovery of new purely organic ferromagnets.

SYNTHESIS OF CT COMPLEXES OF 2-[4-(*N*-ALKYL PYRIDINIUM)]IMIDAZOLIN-1-OXYLS WITH TETRAFLUOROTETRACYANOQUINODIMETHANIDE AND HEXACYANOBUTADIENIDE

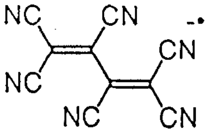
The CT complexes of a series of 4,4,5,5-tetramethylimidazolin-1-oxyls substituted with 4-[*N*-alkyl (R) pyridinium] groups (**1**(R)$^{+\bullet}$: R=Me, Et, *n*-Pr, *n*-Bu) at the 2-position with TCNQF4$^{-\bullet}$ and HCBD$^{-\bullet}$ were preapred by mixing aqueous solutions of the iodide salt of **1**(R)$^{+\bullet}$ and of the lithium salt of TCNQF4$^{-\bullet}$ or the sodium salt of HCBD$^{-\bullet}$ in equal concentrations at r.t. The CT complexes of **1**(R)$^{+\bullet}$ with TCNQF4$^{-\bullet}$ and HCBD$^{-\bullet}$ were



1(Me)$^{+\bullet}$: R=Me
1(Et)$^{+\bullet}$: R=Et
1(Pr)$^{+\bullet}$: R=*n*-Pr
1(Bu)$^{+\bullet}$: R=*n*-Bu



TCNQF4$^{-\bullet}$



HCBD$^{-\bullet}$

colored blue and blackish brown, respectively. The elemental analyses showed a 1:1 composition of the radical cation and the radical anion for all CT complexes.^{13} Of the CT complexes only **1**(Me)$^{+\bullet}$·TCNQF4$^{-\bullet}$ was obtained by recrystallization from acetone/petroleum ether as the single crystal, whose crystal structure analysis was successfully performed. The crystal structure is shown in Figure 1(a). The crystal has an alternating stacking of **1**(Me)$^{+\bullet}$ and TCNQF4$^{-\bullet}$ layers along the *b* axis direction. Within each TCNQF4$^{-\bullet}$ layer the two neighboring TCNQF4$^{-\bullet}$ molecules form a tight dimer structure as evidenced from the closer face-to-face contact (3.188 Å) than a normal π–cloud thickness (3.536 Å) as seen between the dimer units related by an inversion center. The contact between one TCNQF4$^{-\cdot}$ molecule and **1**(Me)$^{+\cdot}$ molecules in its proximity can be visualized by Figure 1(b). Thus, within each **1**(Me)$^{+\cdot}$ layer one NO group of **1**(Me)$^{+\cdot}$ molecule is connected with the NO groups by aid of the interaction with one TCNQF4$^{-\cdot}$ molecule in close proximity, resulting in a one-dimensional spin chain along the *c* axis direction. This one-diemensional spin chain also interacts with its neighboring ones by aid of the same TCNQF4$^{-\cdot}$ molecule. As a result each of the two-dimensional spin network is completed within the *b* - *c* plane and furthermore extended to the *a* axis direction through the interaction with the neighboring networks again by aid of the same TCNQF4$^{-\cdot}$ binder. It should be noted that the oxygen atom of NO group is disordered. The arrangement of oxygen atom as shown in Figure 1 has a preference for the reversed one, and the ratio is 83.7 : 16.3. This fact must be taken into consideration in understanding the magnetic properties of this CT complex and the other ones.

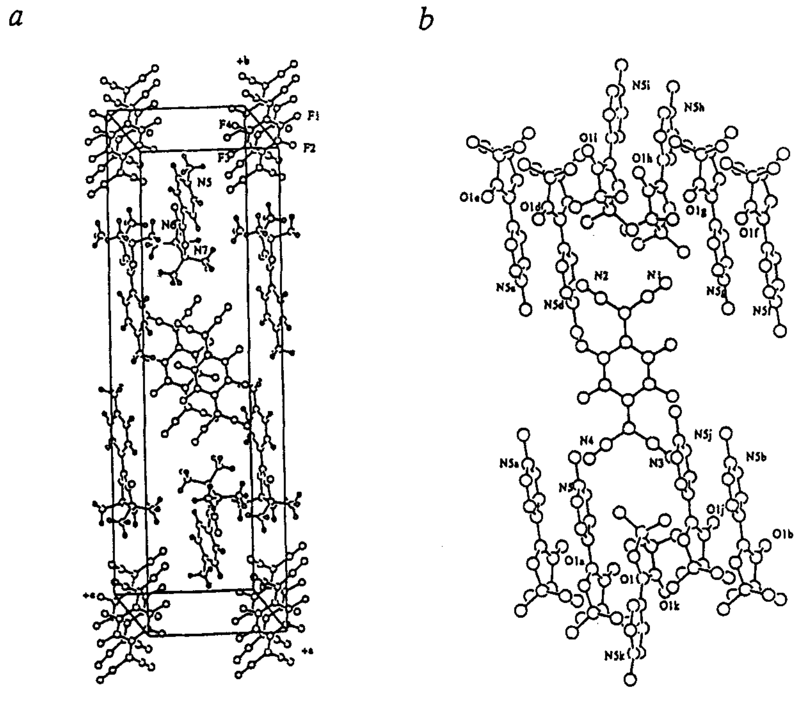


FIGURE 1 (a) The Crystal structure of **1**(Me)$^{+\cdot}$·TCNQF4$^{-\cdot}$, and (b) the view of the contact between one TCNQF4$^{-\cdot}$ molecule and **1**(Me)$^{+\cdot}$ molecules in its proximity.

SPIN INTERACTION IN THE CT COMPLEXES OF $1(R)^{+\cdot}\cdot TCNQF4^{-\cdot}$ AND $1(R)^{+\cdot}\cdot HCBD^{-\cdot}$

The situation of spin interaction in the CT complexes of **1**(R)$^{+\cdot}$·TCNQF4$^{-\cdot}$ and **1**(R)$^{+\cdot}$·HCBD$^{-\cdot}$ was shown by the magnetic measurement using a SQUID magnetometer (MPMS, Quantum Design) under an applied magnetic field of 500 G in the temperature range of 5 to 300 K. The molar paramagnetic susceptibility (χ_p) at each temperature was obtained by correcting the diamagnetic contribution calculated from Pascal's constants. The temperature dependences of the product of χ_p and temperature ($\chi_p \cdot T$) are shown in Figures 2 and 3 for the CT complexes of **1**(R)$^{+\cdot}$ with TCNQF4$^{-\cdot}$ and HCBD$^{\cdot}$, respectively. As is seen from the figures, the following characteristics can be pointed out. (1) For the three CT complexes of **1**(Me)$^{+\cdot}$·TCNQF4$^{-\cdot}$, **1**(Me)$^{+\cdot}$·HCBD$^{-\cdot}$ and **1**(Pr)$^{+\cdot}$·TCNQF4$^{-\cdot}$ there was a steep increase in the $\chi_p \cdot T$ value with a lowering temperature below ca. 10 K, suggesting the dominance of ferromagnetic interaction. This was confirmed by investigating the field (H) dependence of the magnetization (M) at 2, 5 and 10 K, respectively, as shown in Figure 4. Thus, the lower the temperature, the more rapid the M value approached to saturation. The values of saturation magnetization are estimated ca. 4,000, 4,800 and 5,200 emu·G/mol for **1**(Me)$^{+\cdot}$·TCNQF4$^{-\cdot}$, **1**(Me)$^{+\cdot}$·HCBD$^{-\cdot}$ and **1**(Pr)$^{+\cdot}$·TCNQF4$^{-\cdot}$, respectively. These corespond to 72, 87 and 94% of the value (ca. 5,500 emu·G/mol) expected for the surviving **1**(R)$^{+\cdot}$ spin entity, since the radical anion partner becomes spinless as a result of a tight dimer formation. Accordingly, there is a spin loss of ca. 5 to 25%, depending upon the kind of CT complex. As for this cause the disorder in the arrangement of NO groups in the crystal is conceivable, as seen in **1**(Me)$^{+\cdot}$·TCNQF4$^{-\cdot}$. For this CT complex the O atom of NO group is arranged at both N atoms on the imidazoline ring and the ratio is 83.7:16.3. Assumed that the preferred arrangement is reponsible of a ferromagnetic interaction between the two neighboring spins, the amount involved in the interaction might be reduced to $(0.837)^2$ x 100 = 70%, which is well consistent with the experimental result (ca. 72%). Supposedly the degree of disorder of NO group is smaller for the other CT complexes according to this consideration. The crystal structure analysis of the two remaining CT complexes is by all means necessary to confirm this argument. Furthermore it remains to be elucidated how the arrangement of NO group in the crystal is different between these CT complexes and the others which exhibited weak antiferromagnetic interaction. (2) For all CT complexes the $\chi_p \cdot T$ value tends to increase with an increasing temperature in the high temperature region. The magnitude of slope is different by the kind of CT complex. This behavior can be explained by considering the presence of a thermally-accessible triplet of the TCNQF4$^{-\cdot}$ or HCBD$^{-\cdot}$ spin pair in the

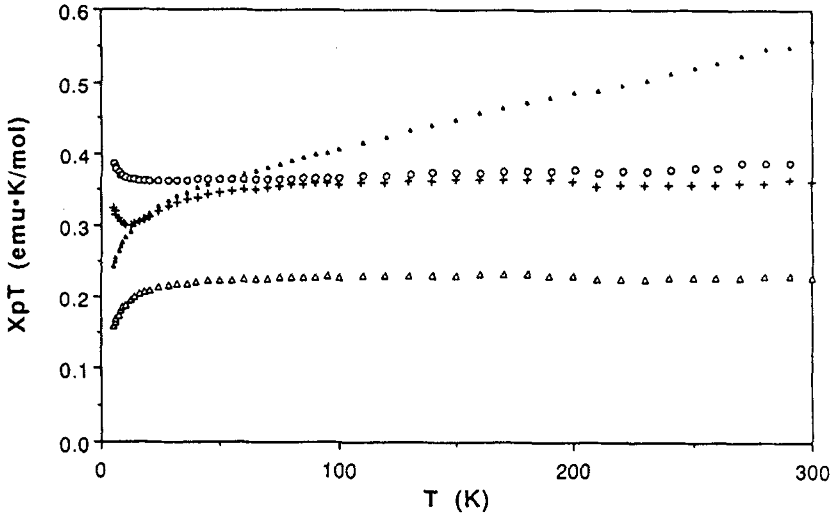


FIGURE 2 Temperature dependence of $\chi_p \cdot T$ for the CT complexes of TCNQF4$^{-\cdot}$ with **1**(Me)$^{+\cdot}$ (+), **1**(Et)$^{+\cdot}$ (▲), **1**(Pr)$^{+\cdot}$ (o) and **1**(Bu)$^{+\cdot}$ (△) in the temperature range of 5 to 300 K.

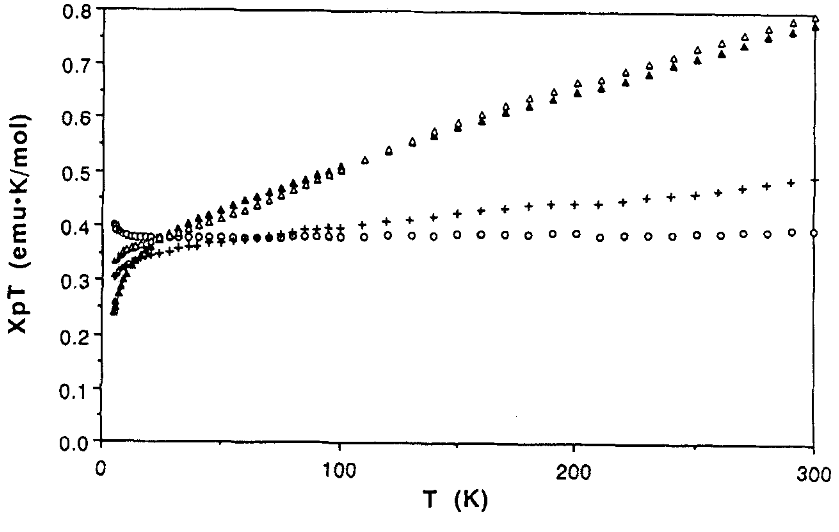


FIGURE 3 Temperature dependence of $\chi_p \cdot T$ for the CT complexes of HCBD$^{-\cdot}$ with **1**(Me)$^{+\cdot}$ (o), **1**(Et)$^{+\cdot}$ (▲), **1**(Pr)$^{+\cdot}$ (△) and **1**(Bu)$^{+\cdot}$ (+) in the temperature range of 5 to 300 K.

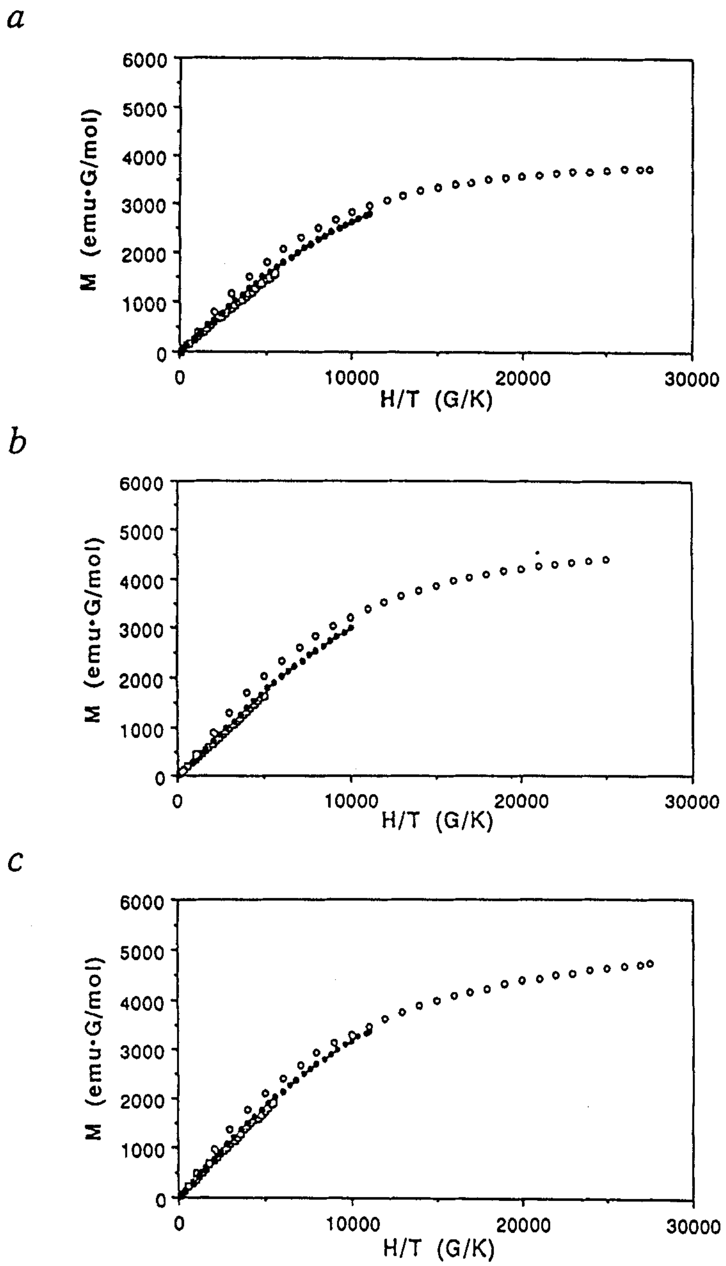


FIGURE 4 Field (H) dependence of the magnetization (M) at 2 (○), 5 (●) and 10 K (□) for (a) $\mathbf{1}(\mathrm{Me})^{+\bullet}\cdot\mathrm{TCNQF}_4^{-\bullet}$, (b) $\mathbf{1}(\mathrm{Me})^{+\bullet}\cdot\mathrm{HCBD}^{-\bullet}$ and (c) $\mathbf{1}(\mathrm{Pr})^{+\bullet}\cdot\mathrm{TCNQF}_4^{-\bullet}$.

singlet ground state, judging from the crystal structure of **1**(Me)$^{+\cdot}$·TCNQF$_4^{-\cdot}$. (3) The χ_p·T of **1**(Bu)$^{+\cdot}$·TCNQF$_4^{-\cdot}$ in the high temperature region is fairly small (ca. 0.22 emu·G/mol) as compared with the value (0.375 emu·G/mol) expected for one S=1/2 spin entity. This suggests the possibility of spin pair formation in the **1**(Bu)$^{+\cdot}$ radical cation as well as theTCNQF$_4^{-\cdot}$ radical anion. Attempt to get the single crystal is still unsuccessful, which is required for the X-ray structure analysis. (4) The powdered sample of CT complexes was used for all magnetic measurements as mentioned above. It is necessary to be checked whether there is difference in magnetic properties between the powdered and crystalline samples. Figure 5 shows the magnetic results obtained by

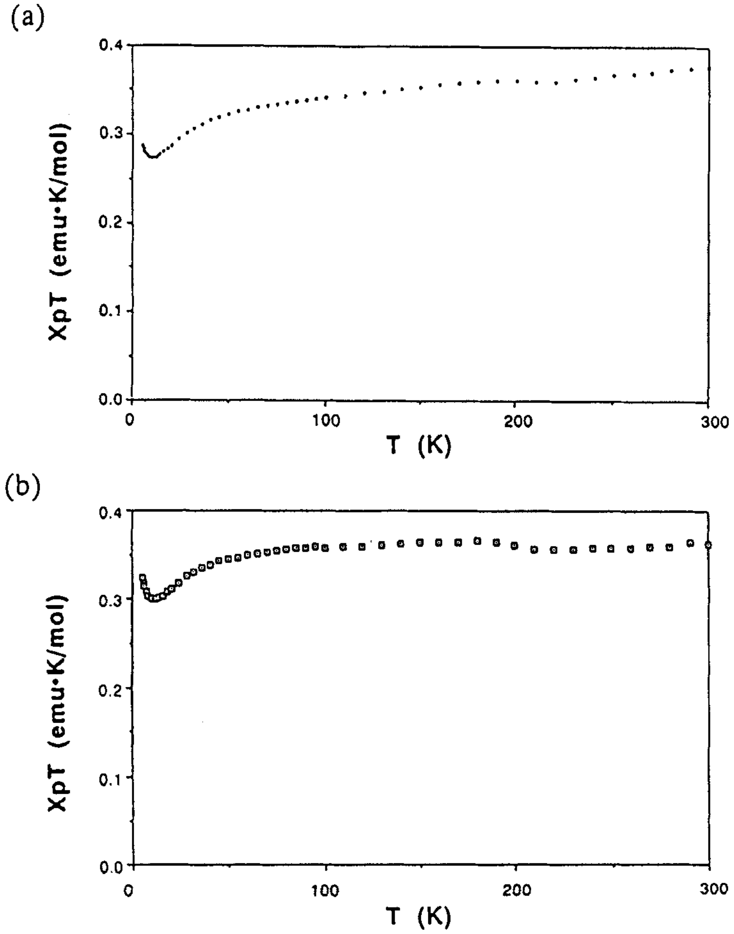
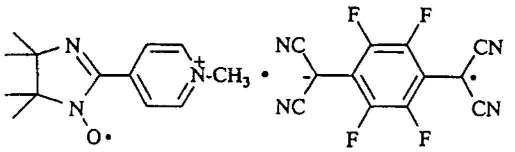


FIGURE 5 Temperature dependence of χ_p·T for (a) powdered and (b) crystalline samples of **1**(Me)$^{+\cdot}$·TCNQF$_4^{-\cdot}$ in the temperature range of 5 to 300 K.

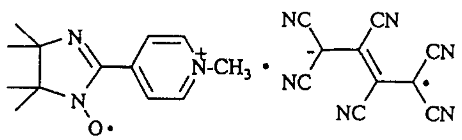
using the powdered and crystalline samples of **1**(Me)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$ under the same condition. Almost no difference was recognized between both samples, although there was a slightly larger decrease of $\chi_p \cdot T$ with a lowering temperature for the powdered one. Based on this result, the magnetic measurement of **1**(Me)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$, **1**(Me)$^{+\bullet}\cdot$HCBD$^{-\bullet}$ and **1**(Pr)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$ at lower temperatures than 5 K was performed by using their powdered samples.

FERROMAGNETIC PHASE TRANSITION AT 0.4 - 0.55 K IN 1(Me)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$, 1(Me)$^{+\bullet}\cdot$HCBD$^{-\bullet}$ AND 1(Pr)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$

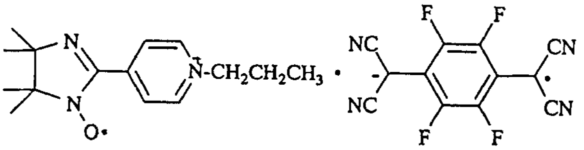
By the magnetic measurement at lower temperatures than 5 K it was found that the CT complexes exhibited a ferromagnetic phase transition between 0.4 and 0.55 K.[14] The ac magnetic susceptibility (χ_{ac}) was measured down to ca. 40 mK in a ^{3}He - ^{4}He dilution refrigerator at the ac magnetic field of ca. 4 nT (127 Hz). The plot of χ_{ac} against temperature is shown in Figure 6, in which peak maxima albeit in a slightly round shape appear at 0.22, 0.33 and 0.40 K for **1**(Me)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$, **1**(Me)$^{+\bullet}\cdot$HCBD$^{-\bullet}$ and **1**(Pr)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$, respectively. These peak temperatures should not, however, be



1(Me)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$



1(Me)$^{+\bullet}\cdot$HCBD$^{-\bullet}$



1(Pr)$^{+\bullet}\cdot$TCNQF$_4^{-\bullet}$

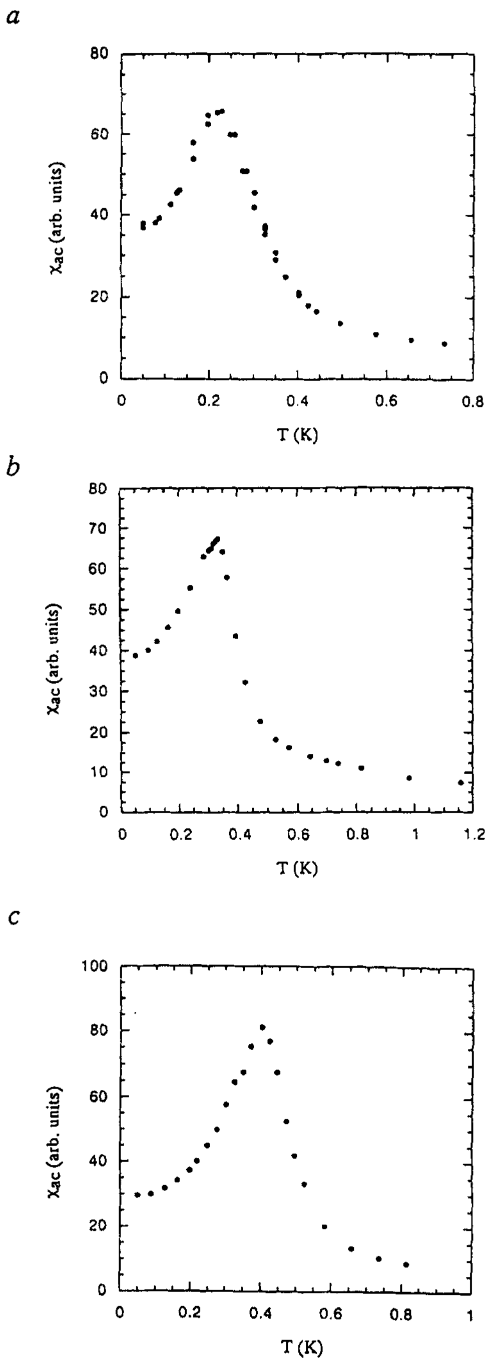


FIGURE 6 Temperature dependence of the ac magnetic susceptibility (χ_{ac}) below 0. 8 K for (a) **1**(Me)$^{+\cdot}\cdot$TCNQF$_4^{-\cdot}$, (b) **1**(Me)$^{+\cdot}\cdot$HCBD$^{-\cdot}$ and (c) **1**(Pr)$^{+\cdot}\cdot$TCNQF$_4^{-\cdot}$.

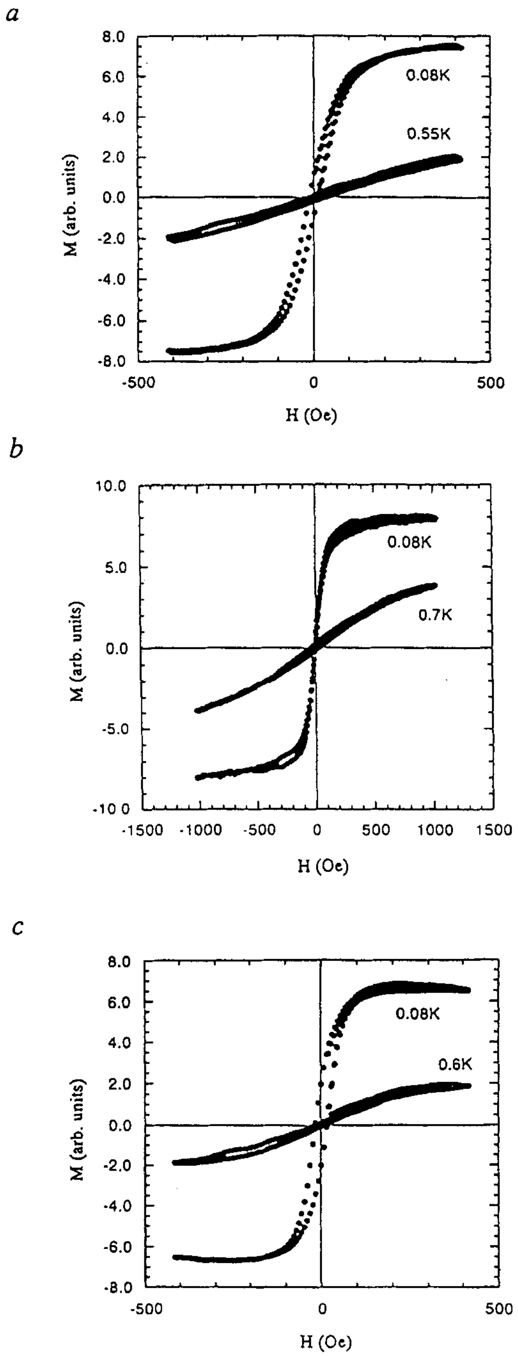


FIGURE 7 Hysteresis magnetization front and rear the ferromagnetic phase transition for (a) $\mathbf{1}(\mathrm{Me})^{+\cdot}\cdot\mathrm{TCNQF}_4^{-\cdot}$, (b) $\mathbf{1}(\mathrm{Me})^{+\cdot}\cdot\mathrm{HCBD}^{-\cdot}$ and (c) $\mathbf{1}(\mathrm{Pr})^{+\cdot}\cdot\mathrm{TCNQF}_4^{-\cdot}$.

assigned as the ferromagnetic phase transition temperatures (T_C's). Rather T_C can be defined in the present study as a temperature where χ_{ac} starts to rapidly increase. There is a slight difference (0.1 - 0.2 K) between the T_C and the peak temperature. When the M - H curves were measured above and below T_C, a typical ferromagnetic hysteresis was observed below T_C (see Figure 7). Both coercive forces ($\leq$ 20 Oe) and saturation fields are low for the three CT complexes like the other organic ferromagnets recently discovered.[4-8] It should be noted that the estimated saturation moments at the lowest temperature were ca. 0.5 μ_B/formula unit (f.u.) or less than 1 μ_B/f.u. expected for one S = 1/2 spin entity. The main cause of this reduction of the magnetic moment might be attributed to magnetic fluctuations resulting from the low-dimensional character of these CT complexes, as seen from the crystal structure of **1**(Me)$^{+\cdot}\cdot$TCNQF$_4^{-\cdot}$ (see Figure 1).

CONCLUSION

The present CT complexes make a group of another type of CT complex-based organic ferromagnets without any magnetic metal elements. The first one has been discovered in a fullerene/tetrakis(dimethylamino)ethylene CT complex (T_C = 16.1 K),[15] whose magnetic details, however, still now remain to be eleucidated because of insufficient structural characterization due to the extreme instability in air. In contrast, the present CT complex-based organic ferromagnets are quite stable in air and have a definitive 1:1 compostion of the radical cation and the radical anion. Through theoretical consideration in combination with the crystal structure data, the origin of this ferromagnetism will be continuously pursued. When this problem is cleared up, the information will serve as a reliable guiding principle for the synthesis of CT complex-based organic ferromagnets.

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