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Different Magnetic Properties of Charge-Transfer Complexes and Cation Radical Salts of Tetrathiafulvalene Derivatives Substituted with Imino Pyrolidine- and Piperidine-1-oxyls

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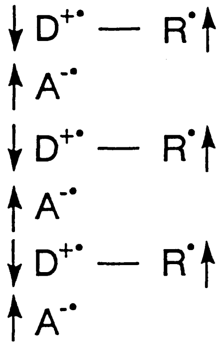
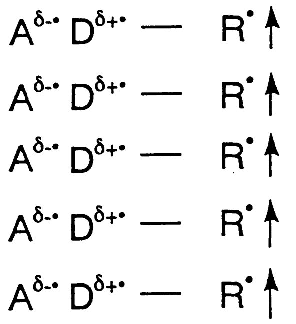
The magnetic properties of charge-transfer (CT) complexes and cation radical salts of tetrathiafulvalene (TTF) derivatives bearing two different radical substituents were investigated. Preferential spin interactions occurred between TTF cation radical ($TTF^{+\cdot}$) and an acceptor anion radical for the CT complexes, and between two $TTF^{+\cdot}$'s for the cation radical salts, respectively. In addition, the magnitude was markedly different by the kind of radical substituent, which behaved as an isolated spin.

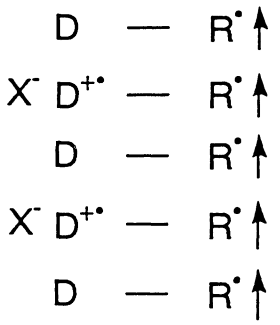
The both charge-transfer (CT) complexes and cation radical salts made of donors bearing a radical substituent ($\mathbf{R}^{\cdot}$) ($\mathbf{D}$-$\mathbf{R}^{\cdot}$) tend to align the spins of $\mathbf{R}^{\cdot}$'s by virtue of antiferromagnetic interaction between the donor cation radical ($\mathbf{D}^{+\cdot}$-$\mathbf{R}^{\cdot}$) and an acceptor anion radical ($\mathbf{A}^{-\cdot}$) through: (A) the alternate CT stack; (B) the interaction with an itinerant electron in a segregated CT stack; or (C) cation radical salts in a mixed-valence state.[1)] If spin alignment could be extended from one dimension as above to a three dimension by an interchain ferromagnetic interaction between $\mathbf{R}^{\cdot}$'s, purely organic ferrimagnets and ferromagnetic "metals" might be achieved. Several attempts have been unsuccessfully made.[2)] In this paper we report the magnetic properties of CT complexes and cation radical salts of tetrathiafulvalene (TTF) derivatives substituted with imino pyrolidine-



(A)



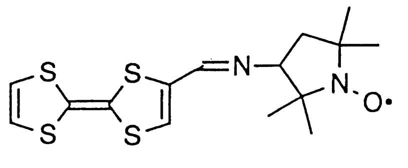
(B)



(C)

(**1**) and piperidine-1-oxyls (**2**) as a **D-R**$^{\cdot}$; and discuss the spin alignment of **R**$^{\cdot}$'s in the CT complex and cation radical salt as well as the spin-spin interactions between the TTF cation radical (TTF$^{+\cdot}$) and **A**$^{-\cdot}$ in the CT complex, and between the TTF$^{+\cdot}$'s in the cation radical salt, respectively.

D — R$^{\bullet}$ =



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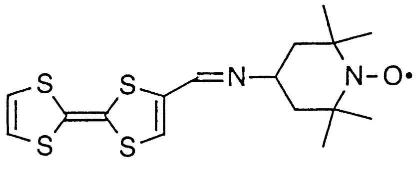

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The CT complexes of **1** and **2** with tetrafluorotetracyanoquinodimethane (TCNQF4) (**1**·TCNQF4 and **2**·TCNQF4[2a)]) were obtained in respective yields of 71 and 78% by mixing chlorobenzene solutions of **1** or **2** and TCNQF4 in an equal molar concentration. The elemental analyses of the CT complexes showed a 1:1 composition of donor and acceptor.[3)] The CN stretching bands in the IR spectra appeared at 2195 and 2177 cm^{-1} for **1**·TCNQF4, and at 2196, 2191, 2177 and 2171 cm^{-1} for **2**·TCNQF4, respectively. These values are very close to those of tetra(*n*-butyl)ammonium salt of TCNQF4 anion radical (TCNQF4$^{-\cdot}$) (2195 and 2173 cm^{-1}), suggesting a complete one-electron transfer from **1** or **2** to TCNQF4 in the complexes. In use of a weaker acceptor, TCNQ, there was no CT complex formation. On the other hand, when **1** and **2** were treated with an excess of iodine in chlorobenzene, the iodide salts of **1**$^{+\cdot}$ and **2**$^{+\cdot}$ (**1**$^{+\cdot}\cdot I_3^-$ and **2**$^{+\cdot}\cdot I_3^-$) were precipitated in quantitative yields.[4)]

The magnetic susceptibilities of the CT complexes and cation radical salts were measured in the temperature range of 4 to 300 K by SQUID magnetometer. The paramagnetic susceptibility (χ_p) was obtained by subtracting the diamagnetic contribution from the observed one. Figure 1 shows the temperature (T) dependence of χ_p x T for the CT complexes. The curve of χ_p x T *vs.* T of **2**·TCNQF4 behaves similarily to that obtained previously by Sugano et al.[2a)] Thus, the χ_p x T value (ca. 0.37 emu·K/mol) is constant between 20 and 220 K, and above 220 K there is a gradual increase, while below 20 K a small decrease occurs. This can be reasonably interpreted by considering that the substituent radical spins are isolated from one another, while the two spins of TTF$^{+\cdot}$ and TCNQF4$^{-\cdot}$ interact to form a singlet ground-state biradical in each CT molecule. For **1**·TCNQF4 the similar χ_p x T vs. T behavior was observed except for a remarkable increase in the higher temperature region. The different χ_p x T vs. T behavior between both CT complexes was against our expectation, because the radical substituent is too remote from a TTF moiety to exert influence on contact with a TCNQF4 molecule. Now, the energy difference (ΔE) between the singlet ground-state and its thermally-accessible triplet state was estimated by using a Bleaney-Bowers equation: $\chi p = Ng^2\mu_B{}^2\cdot 1(1+1)/3k_BT\{1+1/3\exp(\Delta E/k_BT)\}$, where N is the amonut of biradical, g is the g factor, μ_B is Bohr magneton, and k_B is Boltzmann constant.[5)] The values were 610 cal/mol for **1**·TCNQF4 and 2090 cal/mol for **2**·TCNQF4, respectively.[6)] On the other hand, the χ_p x T vs. T behaviors of the cation radical salts are shown in Fig. 2. For **1**$^{+\cdot}\cdot I_3^-$ the χ_p x T value (ca. 0.36 emu·K/mol) is almost constant in the whole temperature range measured, while there is a marked increase of the χ_p x T value with a raising temperature for **2**$^{+\cdot}\cdot I_3^-$. These results can be also understood based on a spin system composed of an isolated substituent radical and an interacting TTF$^{+\cdot}$ pair. The analysis as above gave the ΔE values of 324 cal/mol for **1**$^{+\cdot}\cdot I_3^-$ and >3000 cal/mol for **2**$^{+\cdot}\cdot I_3^-$, respectively.[6)]

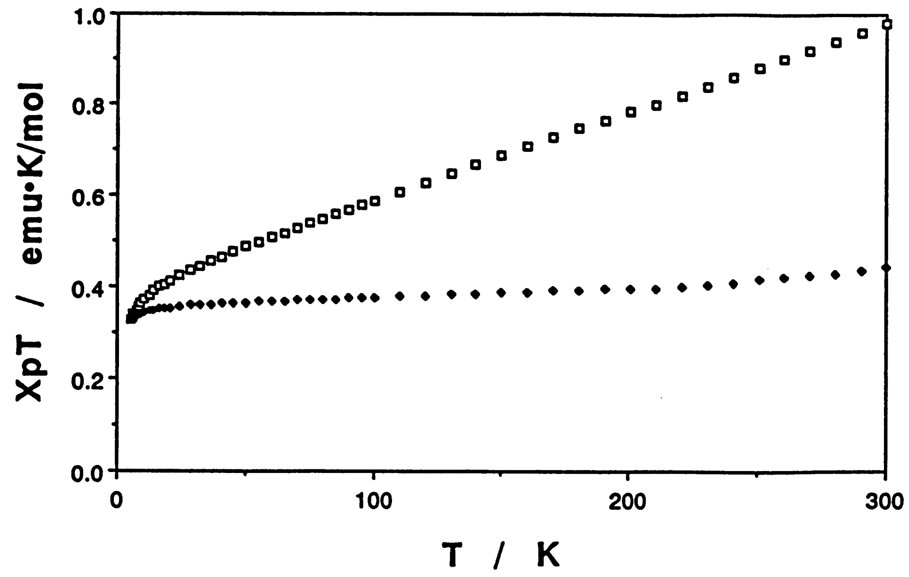

Fig. 1. The temperature (T) dependence of the paramagnetic susceptibility (χ_p) x T for **1**·TCNQF4 (□) and **2**·TCNQF4 (◆) in the temperature range of 4 to 300 K, respectively.

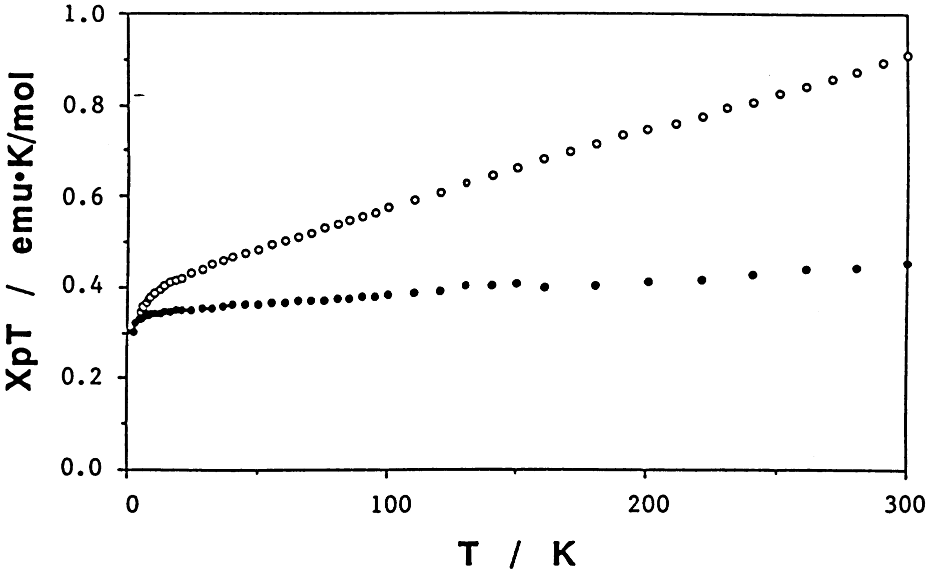

Fig. 2. The temperature (T) dependence of the paramagnetic susceptibility (χ_p) x T for **1**$^{+\cdot}\cdot I_3^-$ (●) and **2**$^{+\cdot}\cdot I_3^-$ (o) in the temperature range of 4 to 300 K, respectively.

Eventually, even the short-range spin alignment of $\mathbf{R}^{\cdot}$'s could not be achieved in the CT complexes of **1**·$TCNQF_4$ and **2**·$TCNQF_4$ or in the iodide salts of the cation radicals. It is conceivable as the main reason that the spin-spin interactions between $TTF^{+\cdot}$ and $TCNQF_4^{-\cdot}$, and between $TTF^{+\cdot}$'s are much stronger compared with that between $TTF^{+\cdot}$ and $\mathbf{R}^{\cdot}$ (the ΔE value: 30 cal/mol), which leads to isolate $\mathbf{R}^{\cdot}$ from the spin assemblies of $\mathbf{R}^{\cdot}$-$TTF^{+\cdot}$-$TCNQF_4^{-\cdot}$ and $\mathbf{R}^{\cdot}$-$TTF^{+\cdot}$-$TTF^{+\cdot}$-$\mathbf{R}^{\cdot}$, respectively. The present results also indicate marked steric influence of $\mathbf{R}^{\cdot}$ to the contact interaction between $TTF^{+\cdot}$ and $TCNQF_4^{-\cdot}$ or between two $TTF^{+\cdot}$'s. This needs to be taken into account in molecular design for new donors capable of spin alignment in CT complexes and cation radical salts.

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3) Anal. Found: C, 49.53; H, 3.07; N, 12.85%. Calcd for $C_{27}H_{19}N_6OS_4F_4$ (**1**·$TCNQF_4$): C, 50.07; H, 2.96; N, 12.97%. Found: C, 50.57; H, 3.01; N, 12.06%. Calcd for $C_{28}H_{21}N_6OS_4F_4$ (**2**·$TCNQF_4$): C, 50.82; H, 3.20; N, 12.70%.

4) T. Sugimoto, S. Yamaga, M. Nakai, K. Ohmori, M. Tsujii, H. Nakatsuji, H. Fujita, and J. Yamauchi, *Chem. Lett.*, **1993**, 1361.

5) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London*, **A214**, 451 (1952).

6) The $\chi_p \times T$ *vs.* T plot based on the Bleaney-Bowers equation should show a sigmoidal curve. However, almost a linear increase with a raising temperature was observed experimentally. This discrepancy can be understood by considering that several sigmoidal curves are superimposed, which possess different ΔE values due to different interaction between $TTF^{+\cdot}$ and $TCNQF_4^{-\cdot}$, or between $TTF^{+\cdot}$'s in the CT complexes or cation radical salts, respectively. Accordingly, the ΔE values obtained are considered to be averaged.

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