MAGNETIC PROPERTIES IN CHARGE-TRANSFER COMPLEXES OF HIGH-SYMMETRY ORGANIC ACCEPTORS

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ABSTRACT

Tris(1,2-benzodithio)- and tris(1,2-ethylenedithio)-trimethylenemethane dication salts were synthesized for the purpose of using as an acceptor in the formation of charge-transfer (CT) complexes with some dianionic donors. In the CT complexes of these dications with hexacyanotrimethylenecyclopropane and tetrafluorotetracyanoquinodimethane dianions, in which the CT degree is albeit small, the spin-spin interaction between the cation radical and the anion radical was antiferromagnetic in the temperature range of 60-293 K, but changed to a ferromagnetic one in the lower temperature range till 15 K, the lowest temperature used in this experiment. This provides the first demonstration of ferromagnetic spin-spin interaction in purely organic/molecular CT complexes. It is conceivable that the ferromagnetic spin-spin interaction is caused by a "spin polarization" mechanism rather than a "CT configurational mixing" mechanism.

INTRODUCTION

The continuous search for bulk ferromagnetism in the organic solid state is the current interest of many synthetic chemists and physicists. Recently, with guidance from a McConnell's model ("CT configurational mixing" mechanism),[1] in which the ferromagnetic interaction can be stabilized by admixing the lowest excited CT triplet state with the ground state in alternating donor-acceptor stacking, a ferromagnetic organometallic/molecular CT solid, decamethylferrocenium tetracyanoetheyenide, was first prepared.[2] This success suggests that the McConnell model may also serve as a useful guiding principle for the production of purely organic s/p orbital-based ferromagnets.[3] Trimethylenemethane dication (1^{2+}) is worthy to be considered as an acceptor model, since the two-electron reduced species of 1^{2+}, trimethylenemethane (1), whose basic structure could participate in the excited state of the CT complex with a dianionic donor, has been shown experimentally to be a triplet in the ground state.[4] MO calculations not only support the experimental

1^{2+}: *=+
1 : *=·

2^{2+}: *=+
2 : *=·

3^{2+}: *=+
3 : *=·

4^{2+}: *=+
4 : *=·

5^{2+}: *=+
5 : *=·
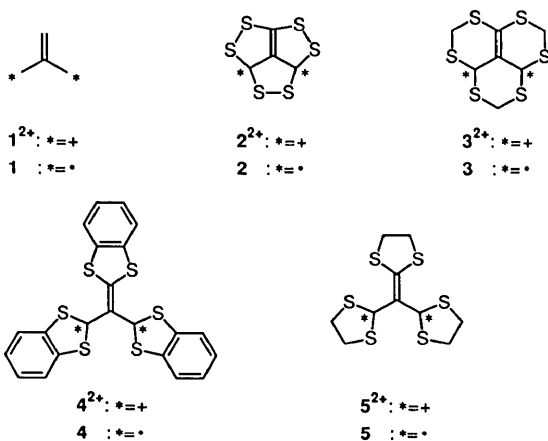
conclusion, but also predict a large energy gap of ca. 20 kcal/mol between the ground state triplet and its higher-energy singlet.[5] Of course, 1^{2+} needs to be stabilized by appropriate substitution for the present purpose. On the ground of preserving a planarity of 1^{2+}, hexathiotrimethylnemethane (2) and tris(methylnedithio)-trimethylnemethane (3) dications (2^{2+} and 3^{2+}) are most promising. However, their synthesis still remains without success.[6] The other possible candidates are trimethylenemethane dications symmetrically substituted with three 1,2-benzodithio or 1,2-ethylenedithio groups (4^{2+} and 5^{2+}). In this presentation, we disclose the synthesis of these dication salts,[7] the spin-state of the trimethylenemethanes (4 and 5) generated by electrochemical two-electron reduction of 4^{2+} and 5^{2+},[7] and the formation and magnetic properties of CT complexes between 4^{2+} or 5^{2+} and some dianions.[8]

RESULTS AND DISCUSSION

Synthesis of 4^{2+} and 5^{2+} salts

The bis(trifluoromethanesulfonate) and bis(tetrafluoroborate) salts of 4^{2+}[9] and 5^{2+}, respectively, (4^{2+}·2CF3SO3$^-$ and 5^{2+}·2BF4$^-$) were synthesized in one step as shown in Scheme 1. Thus, when a sulfolane solution of potassium tricyanomethanide and 1,2-benzenedithiol or 1,2-ethanedithiol (5 equiv.) was reacted with an excess of trifluoromethanesulfonic acid at room temperature, and then the mixture was heated at 80 °C for 23 h, 4^{2+}·2CF3SO3$^-$ (red needles from CH3NO2 - EtOAc, mp > 300 °C (dec)) and 5^{2+}·2BF4$^-$ (after counter anion exchange with HBF4·Et2O, orange needles from CH3CN - CHCl3, mp 237-238 °C (dec)) were isolated in respective yields of 57 and 55%. The ^{13}C NMR spectra of 4^{2+}·2CF3SO3$^-$ in CF3CO2D and of 5^{2+}·2BF4$^-$ in CD3CN

Scheme 1
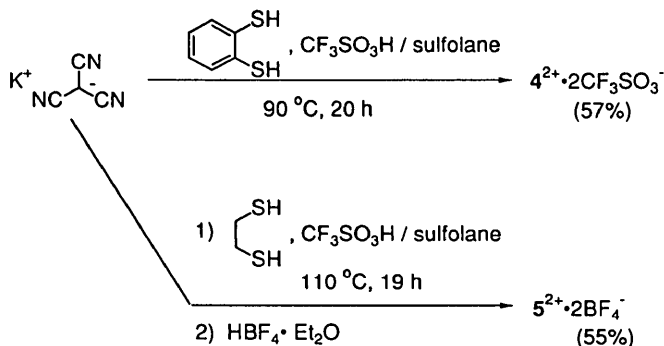
showed only five and three signals, respectively, suggesting that the molecular symmetry of 4^{2+} and 5^{2+} is C_3 or higher in solution. The chemical shifts of the central and exomethylene carbons of trimethylenemethane moiety were δ 105.1 and 184.3 for $4^{2+} \cdot 2CF_3SO_3^-$, and δ 117.8 and 210.0 for $5^{2+} \cdot 2BF_4^-$, respectively. It is inferred that the two positive charges are more localized on the trimethylenemethane moiety in 5^{2+} than in 4^{2+}, where some charge delocalization on the aromatic 1,3-dithiolium rings takes place.

In contrast with a propeller-type conformation of 4^{2+} and 5^{2+} in solution, these dications prefer to adopt a C_3 symmetry-destroyed conformation in solid state. The single crystals of $4^{2+} \cdot 2CF_3SO_3^-$ suitable for the X-ray structure analysis were obtained. The molecular structure is depicted in Figure 1. The (1,3-benzodithiol-2-ylidene)-1,3-dithiolium moiety takes almost a plane, and one more 1,3-dithiolium group is perpendicular to the plane.
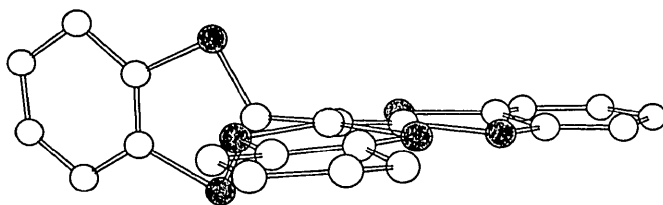

Figure 1. The molecular structure of $4^{2+} \cdot 2CF_3SO_3^-$: black circles represent sulfur atoms.

ESR spectra of electrochemically one- and two-electron reduced species of 4^{2+} and 5^{2+}

The one- and two-electron reductions of $4^{2+}\cdot 2CF_3SO_3^-$ and $5^{2+}\cdot 2BF_4^-$ were carried out and the generated cation radicals ($4^{+\cdot}$ and $5^{+\cdot}$) and diradicals (4 and 5) were investigated by ESR. In each case two pairs of reversible waves were observed in cyclic voltammetric measurement in DMF containing (n-Bu)$_4$N$^+\cdot$ClO$_4^-$ at 0 °C. The redox potentials were as follows: -0.01 and -0.24 V vs. Ag/AgCl for $4^{2+}\cdot 2CF_3SO_3^-$, and ±0.00 and -0.55 V for $5^{2+}\cdot$ 2BF$_4^-$, respectively. The degassed CH$_3$CN solution containing $4^{2+}\cdot 2CF_3SO_3^-$ and the supporting electrolyte was electrochemically reduced at -40 °C. The signal began to appear at -1.6 V (uncorrected with a reference electrode) and the intensity became stronger by gradually raising the voltage, reaching a maximum at -2.2 V. The solution was immediately frozen and the ESR spectrum was measured. Figure 2 shows the ESR spectrum at -50 °C. The
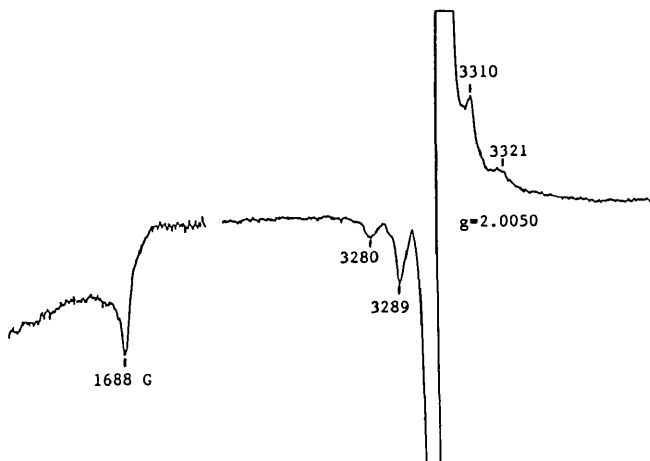

Figure 2. The ESR spectrum of 4 at -42 °C in CH$_3$CN.

strong doublet signal appeared at g = 2.0050, which is considered due to $4^{+\cdot}$. No observation of hyperfine structure in the spectrum of $4^{+\cdot}$ suggests preferential spin-distribution on the hexathiotrimethylenemethane moiety. This is also consistent to the result on the spin density distribution calculated by MO calculations. Furthermore, both four signals on both wings of the central signal and a half-field resonance signal at 1688 G were also observed, which are based on randomly oriented 4. The zero-field splitting parameters D and E are 20.6 and ~0 G, respectively. The axial symmetry of the D tensor (i.e. E ~0) indicates that the two interacting unpaired electrons of 4 delocalize with at least C3 symmetry. The smaller D value observed for 4 compared with that of 1 (D = 266 and E ~0 G) also suggests a large delocalization of the two unpaired electrons on the hexathiotrimethylenemethane moiety (see Figure 3).
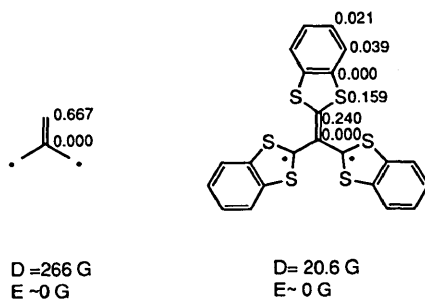
D =266 G
E ~0 G

D= 20.6 G
E~ 0 G

Figure 3. The unpaired electron density distribution and zero-field splitting parameters D and E of **1** and **4**.

The temperature dependence of the half-field resonance signal intensity obeyed a Curie law in the temperature range of -50 to -196 °C, establishing that **4** is in the ground state triplet. In the similar manner $5^{2+} \cdot 2BF_4^-$ was subjected to electrochemical reduction in degassed C_2H_5CN at -40 °C. Figure 4 shows the ESR spectrum when the intensity of signals appeared became maximum. The thirteen signals with a coupling constant of 0.9 G were observed, obviously

$A_H = 0.9$ G
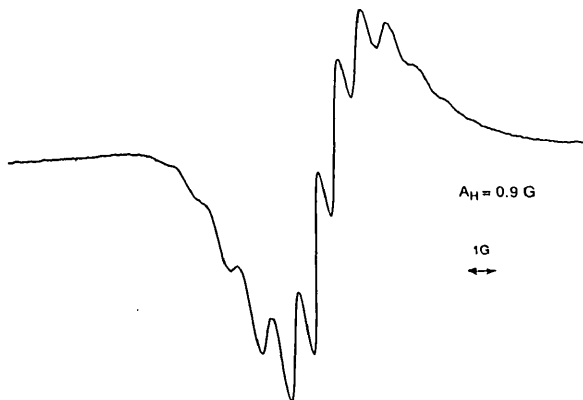
1G

Figure 4. The ESR spectrum of $5^{+\cdot}$ at -42 °C in CH_3CN.

indicating due to $5^{+\cdot}$. Although the reduction was carried out at a lower temperature of -90 °C, the triplet ESR spectrum of **5** could not be obtained. This result implies such a high reactivity as to allow a rapid ring-closure to the trimethylenecyclopropane, which was isolated from the reaction solution and identified. Presumably, alike **4** the ground state of **5** is also triplet.
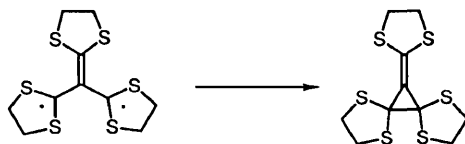
CT Complexes of 4²⁺ and 5²⁺ with some dianions

By using dianion salts of hexacyanotrimethylenecyclopropane (HCTMC),[10] tetrafluorotetracyanoquinodimethane (TCNQF4), hexacarbomethoxy-trimethylenecyclopropane (HCMTMC)[10] and dichlorodicyanobenzoquinone (DDQ), the formation of CT complexes with 4^{2+} and 5^{2+} was investigated. The CT complexes of 4^{2+} with HCTMC^{2-} and TCNQF4^{2-} (4^{2+}·HCTMC^{2-}
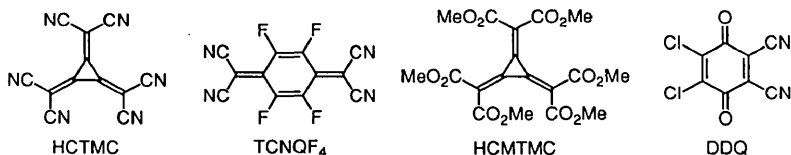

and 4^{2+}·TCNQF4^{2-}) and of 5^{2+} with HCTMC^{2-} (5^{2+}·HCTMC^{2-}) were only obtained in 67, 54 and 93% yields, respectively. In the other combinations CT complex formation was not recognized at all. Instead, in the reaction of 4^{2+}·2CF3SO3$^-$ with HCMTMC^{2-} and DDQ^{2-} salts, a dication (6^{2+}) salt was isolated, which corresponds to a coupled product of two $4^{+\cdot}$'s. In view of the first oxidation potentials of the dianions used (HCTMC^{2-}: E_1^{ox} = +0.34 V vs. Ag/AgCl; TCNQF4^{2-}: +0.06 V; HCMTMC^{2-}: -0.07 V; DDQ^{2-}: -0.13 V) and of the first reduction potentials of 4^{2+} (E_1^{red} = -0.01 V) and 5^{2+} (±0.00 V),

6^{2+} (X=HCTMC,DDQ)
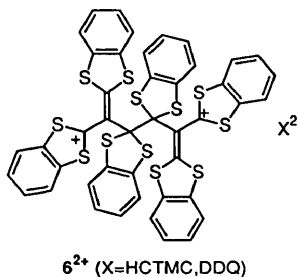
for the CT complexes obtained the CT from $HCTMC^{2-}$ or $TCNQ^{2-}$ to 4^{2+} or 5^{2+} is unfavorable in energy, resulting in small CT degree. The CN stretching frequencies of the CT complexes are very close to those of $HCTMC^{2-}$ (2181, 2164 cm^{-1}) and $TCNQF4^{2-}$ (2162, 2131 cm^{-1}) rather than of $HCTMC^{-\cdot}$ (2209, 2195 cm^{-1}) and $TCNQF4^{-\cdot}$ (2195, 2173 cm^{-1}): 2187 and 2166 cm^{-1} for $4^{2+}\cdot HCTMC^{2-}$; 2162 and 2129 cm^{-1} for $4^{2+}\cdot TCNQF4^{2-}$; 2185 and 2170 cm^{-1} for $5^{2+}\cdot HCTMC^{2-}$. The accurate CT degrees were estimated from the spin amounts measured by ESR as mentioned later. On the other hand, in the use of $HCMTMC^{2-}$ and DDQ^{2-} dianions the CT can be complete, and $4^{+\cdot}$ and $5^{+\cdot}$ are produced together with the corresponding anion radicals. Contrary to our expectation the cation radicals are not so stable as to be susceptible of radical coupling reaction, by reason of insufficient delocalization of the positive charge on the whole molecule as a result of such a preferential C3 symmetry-destroyed conformation as observed in 4^{2+}.

The spin-spin interaction between $4^{+\cdot}$ or $5^{+\cdot}$ and $HCTMC^{-\cdot}$ or $TCNQF4^{-\cdot}$ residing in the three CT complexes was investigated by ESR. The magnetic susceptibilty was also measured, but it was difficult to accurately separate the observed magnetic susceptibility into the paramagnetic and comparable diamagnetic portions, respectively. Figure 5 shows the solid ESR spectra of the CT complexes at 293 K. For the CT complexes of 4^{2+} and 5^{2+} with
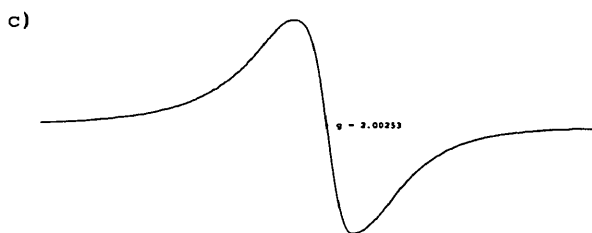
a)

g=2.00290

b)

g=2.00297

c)

$g = 2.00253$
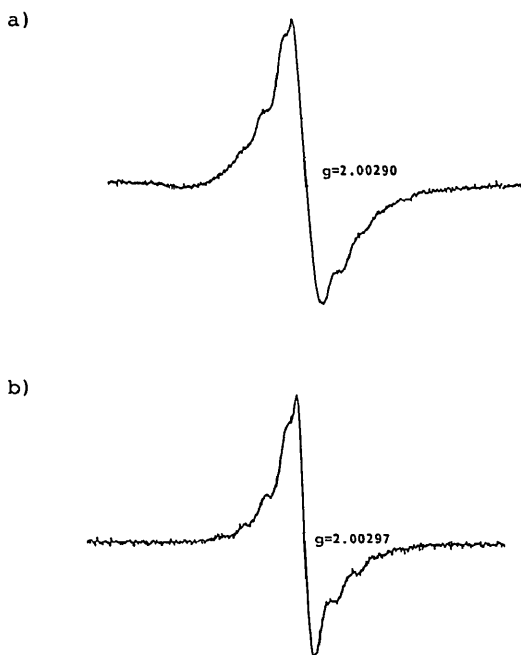
Figure 5. The solid ESR spectra of (a) $4^{2+}\cdot HCTMC^{2-}$, (b) $5^{2+}\cdot HCTMC^{2-}$ and (c) $4^{2+}\cdot TCNQF4^{2-}$ at 293 K.
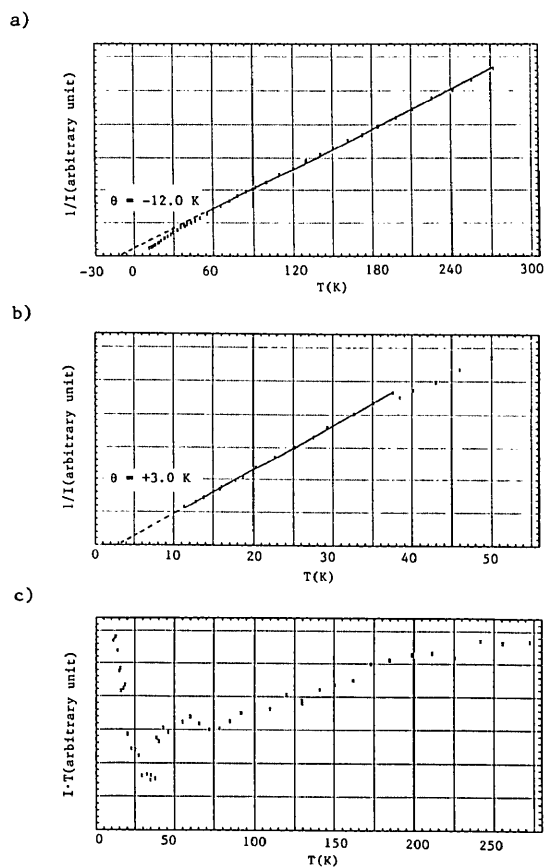
a)

$\theta = -12.0$ K

b)

$\theta = +3.0$ K

c)

Figure 6. The temperature (T) dependence of the signal intensity (I) ((a) and (b): 1/I - T; (c): I·T - T) for $4^{2+}\cdot HCTMC^{2-}$.

HCTMC^{2-} six weak signals due to the fine structure of a triplet species were observed on a doublet-like signal at g = 2.0090 and 2.0097, respectively. The zero-field splitting parameters D and E are 12.5 and 1.8 G for 4^{2+}·HCTMC^{2-}, and 11.8 and 1.7 G for 5^{2+}·HCTMC^{2-}, respectively. On the other hand, the 4^{2+}·TCNQF$_4$$^{2-}$ complex exhibited only a broad and strong doublet signal. The spin amounts of the CT complexes at 293 K were calculated from the signal intensities (I) with a reference TANOL: 1.64×10^{21}, 3.72×10^{20} and 3.55×10^{22} spins/mol for 4^{2+}·HCTMC^{2-}, 5^{2+}·HCTMC^{2-} and 4^{2+}·TCNQF$_4$$^{2-}$, which correspond to the spin contents of 0.27, 0.0062 and 5.89%, respectively. The temperature (T) dependence of I was investigated for each CT complex. The results on 1/I - T ((a) in the range of all temperature used and (b) in the range of lower temperatures) and I·T - T (c) are shown in

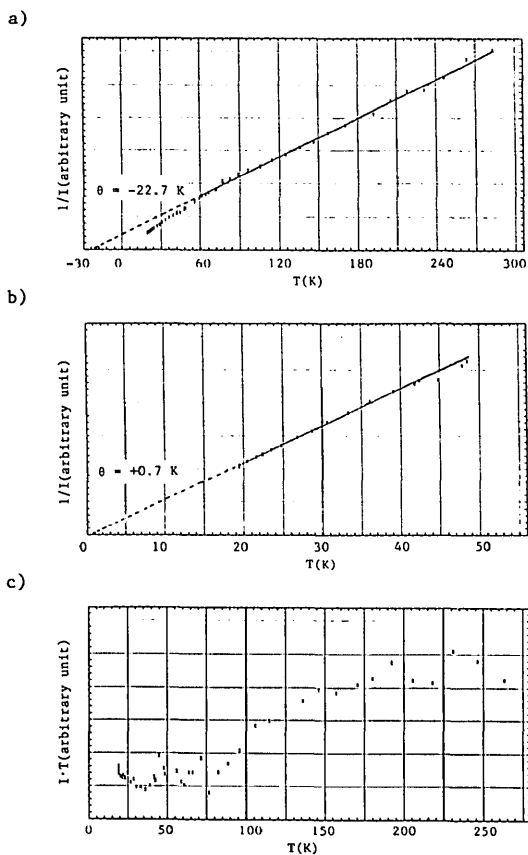Figure 7. The temperature (T) dependence of the signal intensity (I) ((a) and (b): 1/I - T; (c): I·T - T) for 5^{2+}·HCTMC^{2-}.

Figure 6 (4^{2+}·HCTMC^{2-}) , Figure 7 (5^{2+}·HCTMC^{2-}) and Figure 8 (4^{2+}·TCNQF4^{2-}). For all CT complexes antiferromagnetic spin-spin interaction occurred in the temperature range of 283 - 60 K. The Weiss temepratures (θ) are -12.0, -22.7 and -8.2 K for 4^{2+}·HCTMC^{2-},

a)

b)

c)
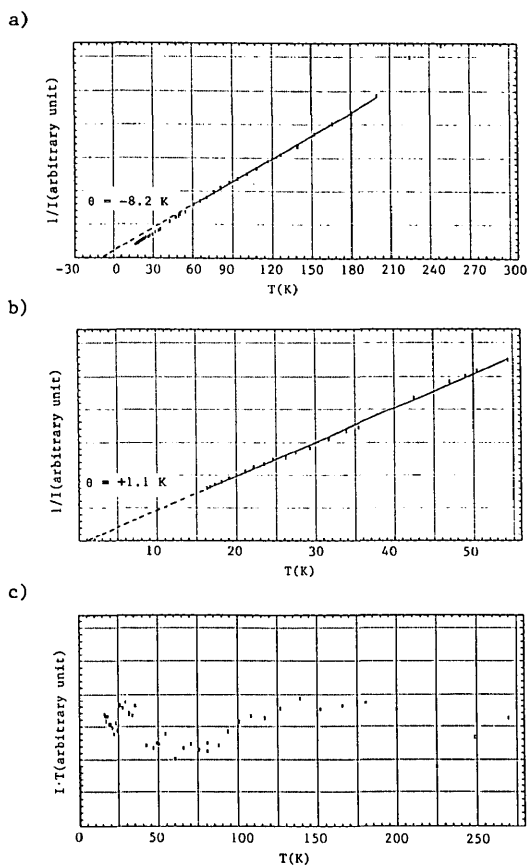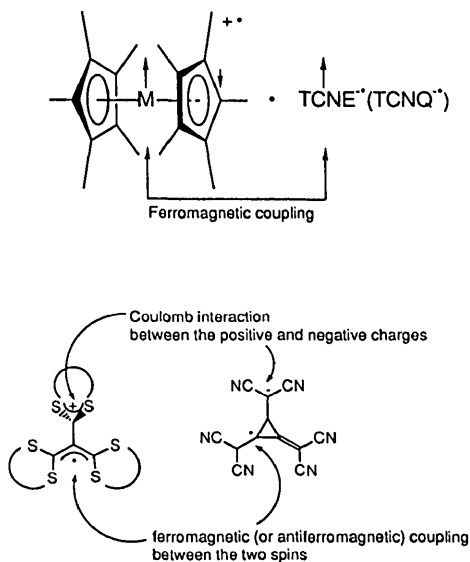

Figure 8. The temperature (T) dependence of the signal intensity (I) ((a) and (b): 1/I - T; (c) I·T - T) for 4^{2+}·TCNQF4^{2-}.

5^{2+}·HCTMC^{2-} and 4^{2+}·TCNQF4^{2-}, respectively. However, as further lowering the temperature from 60 to 15 K, the lowest temperature used in this experiment, ferromagnetic spin-spin interaction preferentially occurred, as evidenced by the positive sign in θ values: +3.0, +0.67 and +1.1 K for 4^{2+}·HCTMC^{2-}, 5^{2+}·HCTMC^{2-} and 4^{2+}·TCNQF4^{2-}, respectively. This provides a first example of ferromagnetic spin-spin interaction in a purely

organic CT complex, of course although it is already known that in a fairly number of organometallic CT complexes with metallocenes ferromagnetic spin-spin interaction is not only recognized,[11] but some of them also become ferromagnets with three-dimentional spin ordering.[12] Now that the crystal structure is still unknown in any CT complex, it cannot be discussed on the origin of ferromagnetic spin-spin interaction in the CT complexes. Nevertheless, judged from the facts that the CT complexes are almost in the dication - dianion state and that 4^{2+} (probably also 5^{2+}) prefers to adopt a C_3 symmetry-destroyed conformation in solid state, it is not probable that the spin-spin interaction occurs based on "CT configurational mixing" mechanism, in which double degeneracy in lowest unoccupied MO's of 4^{2+} and 5^{2+} plays a crucial role, contrary to our initial guiding principle, Another mechanism must be considered. Very recently, Hoffman[13] and Kahn[14] independently claimed another McConnell idea, "spin polarization" mechanism,[15] to the occurrence of a ferromagnetic spin-spin interaction in CT complexes between metallocenes and acceptors such as tetracyanoethylene and TCNQ. According to this mechanism, antiferromagnetic spin-spin interaction between negative spin density on the cyclopentadiene ring and the spin of the acceptor anion radical, results in overall ferromagnetic alignment of the metal-centered and anion radical spins. This situation might also be settled in the present purely organic CT complex. Eventually, this accidental finding could serve as a new and reliable guiding principle in creating CT complex-based purely organic/molecular ferromagnets.

Ferromagnetic coupling

Coulomb interaction between the positive and negative charges

ferromagnetic (or antiferromagnetic) coupling between the two spins

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