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CALORIMETRIC STUDIES ON [DMeFc][TCNE] AND [DMeFc][TCNQ]†

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Abstract Typical molecular-based magnets, decamethylferrocenium tetracyanoethenide ([DMeFc][TCNE]) and decamethylferrocenium tetracyanoquinodimethanide ([DMeFc][TCNQ]), have been studied by means of adiabatic calorimetry. The Curie temperature of [DMeFc][TCNE] was determined to be T_c = 4.74 K. The excess entropy derived from the observed heat-capacity anomaly was very close to the expected magnetic entropy, 2 R ln 2. Detailed analysis of the heat-capacity anomaly revealed that [DMeFc][TCNE] is a good one-dimensional (1D) Ising magnet. Two structural phase transitions were found for the first time at 248.7 and 281.8 K, and attributed to the orientational order-disorder character of the TCNE anion. For [DMeFc][TCNQ] an antiferromagnetic phase transition was observed at T_N = 2.54 K. The magnetic lattice anisotropy of the TCNQ salt is smaller than that of the TCNE salt.

INTRODUCTION

Molecular-based ferromagnetism has become an important subject of magnetochemistry. In this rapidly growing field a breakthrough was made in 1986 by Miller *et al.*[1] who reported the preparation of a ferromagnetic charge-transfer complex compound, decamethylferrocenium tetracyanoethenide, $[Fe(C_5Me_5)_2]^+[(NC)_2C=C(CN)_2]^-$, which is hereafter referred to as [DMeFc][TCNE]. This compound was epochmaking in the sense that it contains ferromagnetically-coupled organic radicals in contrast to other ferromagnetic molecular complexes so far known, *e.g.* manganese(II)-phthalocyanine[2,3] and iron dithiocarbamates.[4,5]

The molecular-based antiferromagnet decamethylferrocenium 7,7,8,8-tetracyano-*p*-quinodimethanide, [DMeFc][TCNQ], is isomorphous with [DMeFc][TCNE].[6] Comparison between these two compounds is, therefore, interesting as it may provide

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a clue to the magnetostructural correlation of molecular-based magnetic materials. The objective of the present paper is to elucidate the characteristics of spin-spin interaction in this interesting molecular ferromagnet [DMeFc][TCNE] in comparison to the analogous antiferromagnet [DMeFc][TCNQ]. It should be noted that we have already reported the preliminary results[7] of heat-capacity measurements for [DMeFc][TCNE] and Chakraborty *et al.*[8] have independently measured the heat capacity of this compound.

EXPERIMENTAL

Polycrystalline samples of [DMeFc][TCNE] and [DMeFc][TCNQ] were prepared by the method of Miller *et al.*[6,9] Elementary analyses showed good agreement with the calculated values.

For [DMeFc][TCNE], two series of heat-capacity measurements were carried out. In the temperature range of 1-25 K an adiabatic calorimeter utilizing a ^{3}He/^{4}He dilution refrigerator[10] was used and 4.4636 g of the polycrystalline sample was loaded in a gold-plated copper container together with 11.3 kPa of heat conduction gas (^{3}He). In the 15-320 K range another adiabatic calorimeter[11] was employed. The amount of sample used in this case was 2.2904 g.

For [DMeFc][TCNQ] heat-capacity measurements were performed only in the 1-25 K region; 2.7373 g of the sample was loaded in the container with 21 kPa of ^{3}He gas.

VERY LOW TEMPERATURE HEAT CAPACITY OF [DMeFc][TCNE]

The molar heat capacities of [DMeFc][TCNE] in the 1-25 K range are shown in FIGURE 1. A heat-capacity peak was found at 4.74 K. This transition temperature is slightly lower than that already reported, T_c = 4.8 K[1,9] and T_c = 4.82 K.[8] However, the discrepancy is not so large and may be attributable to the difference between polycrystalline and single crystal samples.

The phase transition peak has a cusp-like shape and no indication of latent heat. The transition behavior bears a resemblance to an anomaly derived from a mean field approximation. Mean field behavior was also observed in temperature dependence of the magnetization.[12] Accordingly, the critical fluctuation is not so dominant in this higher-order phase transition. This aspect coincides with the fact that in the vicinity

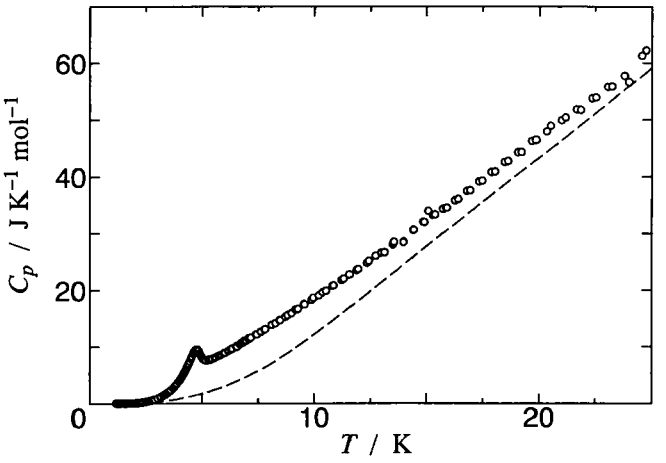

FIGURE 1 Temperature dependence of molar heat capacity of [DMeFc][TCNE]. The broken curve shows the estimated contribution from lattice vibrations.

of the phase transition the thermal relaxation time does not exhibit any remarkable elongation associated with the critical slowing down.

To separate the magnetic contribution a normal heat-capacity curve was roughly estimated by a curve-fitting method in the range of 10-25 K after subtraction of a guessed high-temperature tail of the magnetic contribution.[13] The normal heat capacity, C_p(normal), was approximated by a combination of two Debye functions. The excess heat capacity thus determined is shown in FIGURE 2. A characteristic feature is the coexistence of the phase transition peak at 4.74 K and a remarkable hump centered at 8.5 K. Obviously the hump corresponds to the strong short range order characteristic of the 1D stacking structure in [DMeFc][TCNE].

The magnetic entropy corresponding to both anomalies was determined by extrapolating the excess heat capacity to the high temperature limit. The total entropy was found to be S_{mag} = (12 $\pm$ 1) J K^{-1} mol^{-1} and the critical entropy, which is defined as the entropy gain up to the critical temperature T_c, was evaluated to be S_c = 1.46 J K^{-1} mol^{-1}. The value of S_{mag} is well approximated by 2 R ln 2 (= 11.53 J K^{-1} mol^{-1}). Therefore, we can safely conclude that the charge transfer from the donor [DMeFc] to the acceptor [TCNE] is complete and that the compound consists of

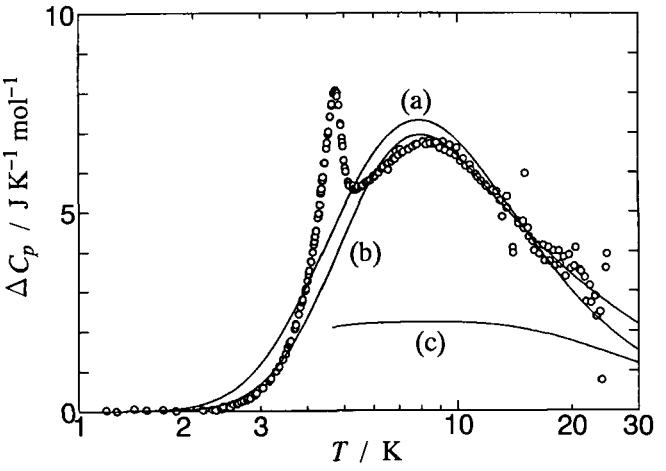

FIGURE 2 Excess heat capacities of [DMeFc][TCNE]. Theoretical curves are based on (a), pure Ising 1D ferromagnet with J / k_B = 19 K; (b), anisotropic Heisenberg 1D ferromagnet[13] with $J_\parallel / k_B$ = 25 K and $J_\perp / J_\parallel$ = 0.5; (c), Heisenberg 1D ferromagnet[14] with J / k_B = 13 K, respectively.

a spin 1/2 cation and a spin 1/2 anion. The fraction of S_c in S_{mag} is only ~0.12, which is very small in comparison to an ordinary 3D Ising magnet (0.75–0.85) or 3D Heisenberg magnet (0.6–0.7). This fact clearly demonstrates that the short range order effect is dominant above the Curie temperature.

Anisotropic Character of Intracolumnar Magnetic Interaction

Although Miller *et al.*[9,12] successfully adopted the 1D ferromagnetic Heisenberg model[14] for the analysis of their magnetic susceptibility data, the same model failed to account for the heat-capacity hump. We found that a more appropriate model is an anisotropic Heisenberg 1D ferromagnet, whose heat capacity has been numerically given by Blöte.[13] When the anisotropy of the magnetic interaction is relatively weak, the deviation of the heat-capacity curve from that of the isotropic chain, $J_\perp / J_\parallel$ = 1 (curve (c) in FIGURE 2), is pronounced. However, if the magnetic interaction has a strong Ising character, say, $J_\perp / J_\parallel < 0.5$, it is practically difficult to discriminate its heat-capacity curve from that of the pure Ising chain, $J_\perp / J_\parallel$ = 0 (curve (a) in FIGURE 2). This is the case for the present compound. Taking into account the ambiguity involved in the estimated

normal heat capacity, we can conclude that there exists a strong Ising type anisotropy of the order of $J_\perp / J_\parallel < 0.5$ in [DMeFc][TCNE]. The origin of this Ising anisotropy can be satisfactorily attributed to the anisotropic g-tensor of $[DMeFc]^+$ cation radical. This conclusion derived from the present calorimetric study coincides well with $J_\perp / J_\parallel \approx 0.30$ derived from the magnetic susceptibility for single crystals.[15]

Close examination of the magnetic elementary excitations in the ordered phase provides another evidence for the strong Ising character. The excess heat capacity obviously exhibits the exponential temperature dependence characteristic of excitation over an energy gap rather than the power-law dependence of spin wave excitation. The energy gap was estimated to be $\Delta E / k_B \approx 28$ K from the data in the range of 1-3 K and the dominant thermal excitation in [DMeFc][TCNE] is inferred to be the bound-state type inherent in the Ising magnet.

Estimation of Intercolumnar Interaction

The ferromagnetic phase transition at 4.74 K is obviously a manifestation of the exchange interaction between columns consisting of alternating cation and anion arrays, because pure 1D system cannot bring about a long range order at finite temperatures. This intercolumnar exchange interaction, J_{inter}, is much weaker than the exchange in a column, J_{intra}, as already discussed above. A rough estimation of the intercolumnar interaction was attempted by use of a mean field approximation.

According to Scalapino *et al.*[16] the intercolumnar coupling is replaced with a mean field and the resulting 1D problem can be solved. The critical temperature T_c is given by

$$1 - 2zJ_{inter}\chi_{1D}(T_c) = 0,$$

where χ_{1D} stands for the magnetic susceptibility of the 1D system under consideration, and z is the coordination number of a chain(assumed to be 6 here). The formula of magnetic susceptibility for the anisotropic Heisenberg 1D ferromagnet[17] is available,

$$\chi_{1D}(T) \approx (S^2 / k_B T)\exp[4S^2(J_\parallel^2 - J_\perp^2)^{1/2} / k_B T],$$

when the anisotropy of magnetic interaction $J_{\parallel} / J_{\perp}$ is large. If we adopt the anisotropic interactions determined from the single crystal susceptibility,[15] $J_{\parallel} / k_B$ = 27.4 K and $J_{\perp} / k_B$ = 8.1 K, we obtain zJ_{inter} / k_B = 38 mK. Because of the neglect of spin fluctuations, the mean field approximation usually underestimates the microscopic interaction strength with respect to a given critical temperature. The present estimate of zJ_{inter} is probably accurate within a factor of 2~3.

Therefore, it is concluded that [DMeFc][TCNE] has strong anisotropy in its magnetic lattice structure, $zJ_{inter} / J_{intra} \approx 0.001$, in addition to extreme Ising anisotropy of magnetic interaction, $J_{\parallel} / J_{\perp} \approx 3$.

STRUCTURAL PHASE TRANSITIONS OF [DMeFc][TCNE]

Heat-capacity measurements have also shown the existence of two phase transitions at 248.7 K and at 281.8 K. Excess heat capacities around these phase transitions are shown in FIGURE 3. The anomaly centered at 248.7 K exhibits a rather sharp peak tailing to low temperatures, while the anomaly around 281.8 K seems to be a broad cusp. The small heat-capacity anomaly around 295 K is caused by incomplete cancellation of the contribution from Apiezon H grease used for the cell sealing.

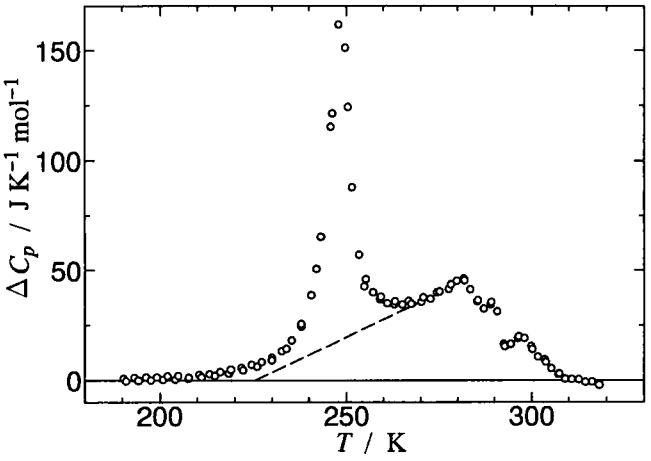

FIGURE 3 Excess heat capacities of [DMeFc][TCNE]. Two anomalies are tentatively separated by a broken line.

The excess enthalpy and entropy arising from these two anomalies were calculated to be ΔH = 3320 J mol^{-1} and ΔS = 12.8 J K^{-1} mol^{-1}, respectively. As shown in FIGURE 3 the two anomalies were tentatively separated by a straight line and the respective transition entropies were obtained as follows : $\Delta S \approx$ 5.9 J K^{-1} mol^{-1} for the low temperature anomaly and $\Delta S \approx$ 7.0 J K^{-1} mol^{-1} for the high temperature one. Both values are close to R ln 2 (= 5.76 J K^{-1} mol^{-1}), suggesting these phase transitions are of order-disorder type in nature.

An orientational order-disorder transition is the most plausible origin because a disorder in [TCNE]$^-$ anion was reported from X-ray structural analysis at room temperature and at -40 ℃.[9] Such a disorder has a potential to cause a phase transition within its ordering process. However, further investigations, especially structural analysis below 200 K, are necessary.

COMPARISON WITH THE ISOMORPHOUS METAMAGNET [DMeFc][TCNQ]

The calorimetric results for [DMeFc][TCNQ] are shown in FIGURE 4. A sharp peak centered at 2.54 K was observed. This transition temperature agrees well with the reported Neel temperature.[6] No latent heat was observed and the phase transition is considered to be of second order.

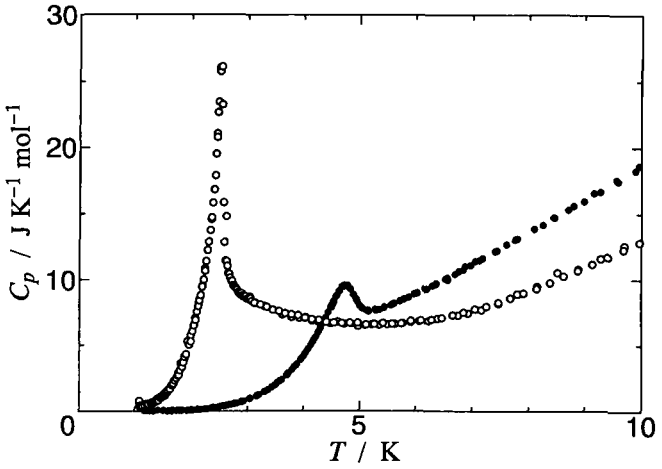

FIGURE 4 Comparison of molar heat capacities between [DMeFc][TCNE] (●) and [DMeFc][TCNQ] (○) in the 1-10 K region.

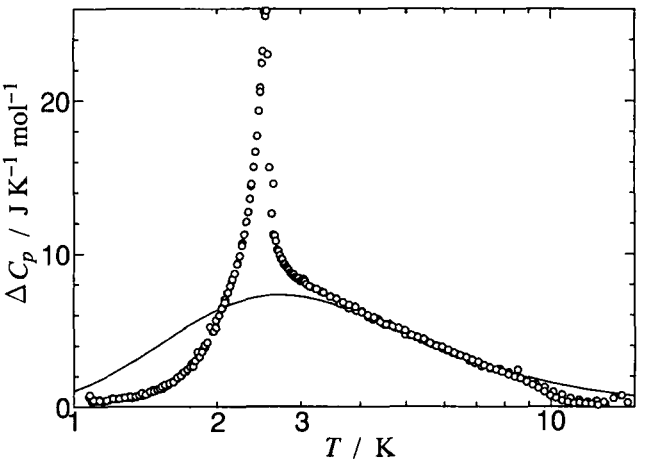

FIGURE 5. Excess heat capacities of [DMeFc][TCNQ]. The solid curve is based on 1D Ising model with J / k_B = 6.5 K.

One of the remarkable features of this heat-capacity anomaly is that the low temperature tail bears a resemblance to that of the TCNE compound. This behavior suggests the existence of an energy gap arising from the Ising nature. In fact, the energy gap was estimated to be $\Delta E / k_B \approx 6.5$ K. Hence in [DMeFc][TCNQ] the magnetic interaction has a strong Ising character as in the TCNE compound.

Based on the ^{57}Fe Mössbauer spectroscopy, which suggests some structural change associated with this phase transition, Miller *et al.*[6] pointed out that such a magnetostructural behavior is analogous to a spin Peierls transition. An energy gap is certainly expected for magnetic excitation in the spin Peierls phase. However, the spin Peierls nature is incompatible with the Ising anisotropy which stabilizes the Neel ground state rather than the spin Peierls phase. Thus, the Ising anisotropy is the more plausible origin of the observed exponential tail behavior of heat capacity.

The total excess entropy of [DMeFc][TCNQ] was determined in order to measure the extent of short range order. By tentatively adopting the normal heat capacity of [DMeFc][TCNE] as that of [DMeFc][TCNQ], a rough estimation of the total transition entropy was made. This procedure is employed because the dominant contribution of the Debye heat capacity is similar between the two compounds possessing a homologous crystal structure and nearly the same crystal density. The excess heat

TABLE I Characteristic quantities of magnetic heat-capacity anomalies.

Substance	ΔE / k_BK	S_c / S_{mag}	$z J_{inter}$ / J_{intra}
[DMeFc][TCNE]	~28	~0.12	0.001
[DMeFc][TCNQ]	~6.5	~0.4	0.2

capacity thus obtained is shown in FIGURE 5. As a result, the excess entropy was evaluated to be $\Delta S \approx 11.2$ J K^{-1} mol^{-1}, which is very close to the magnetic entropy, 2 R ln 2. On the other hand, the critical entropy was estimated to be ~4.0 J K^{-1} mol^{-1}. The fraction of the critical entropy in the total excess entropy is thus only ~0.36, showing a remarkable short range order effect inherent in low dimensional magnets. The low dimensionality in [DMeFc][TCNQ] is, however, weaker than that in the TCNE analogue. This may be attributable to the different size of the counter anion, which significantly affects the exchange paths.

Magnetically the [TCNQ]$^-$ radical behaves similarly to the [TCNE]$^-$ radical. A remarkable difference between these two radicals is their dimensions. The cyano group moieties, on which the unpaired electron is mainly distributed, are separated further in a [TCNQ]$^-$ radical, owing to intervening quinone ring, than in a [TCNE]$^-$ radical. Hence an overlap with the π-orbital of the cyclopentadienyl ring is expected to be smaller in [DMeFc][TCNQ] than in [DMeFc][TCNE]. The intracolumnar magnetic interaction is also weaker in the former than in the latter. On the other hand, the strength of the intercolumnar interaction has an opposite tendency because of the enhanced overlap of [TCNQ] orbitals between columns. In fact, magnetic susceptibility measurements[18] revealed the Curie-Weiss behavior of [DMeFc][TCNQ] with a small Weiss temperature θ = +3 K, in contrast to the large Weiss temperature θ = +30 K for [DMeFc][TCNE]. Miller *et al.*[6] have reported, about the metamagnetic behavior of [DMeFc][TCNQ], that a dominant interaction is intracolumnar ferromagnetism with a weak intercolumnar antiferromagnetism.

This magnetostructural correlation clearly reflects on several parameters obtained in the present paper. They are the energy gap of magnetic excitation, the fraction of critical entropy, and the intercolumnar/intracolumnar interaction ratio, as shown in TABLE I. The first of them is simply proportional to the intracolumnar interaction.

The second provides the measure of short range ordering effect, which closely correlates with the third parameter. These parameters provide clear evidence for the strong 1D and Ising character in [DMeFc][TCNE] and [DMeFc][TCNQ].

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REFERENCES

1. J. S. Miller, J. C. Calabrese, A. J. Epstein, R. W. Bigelow, J. H. Zhang, and W. M. Reiff, J. Chem. Soc., Chem. Commun., 1986, 1026 (1986).
2. C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, J. Chem. Phys., 53, 1638 (1970).
3. S. Mitra, A. K. Gregson, W. E. Hatfield, and R. R. Weller, Inorg. Chem., 22, 1729 (1983).
4. H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull, and F. R. Merritt, Phys. Rev., 155, 563 (1967).
5. N. Arai, M. Sorai, H. Suga, and S. Seki, J. Phys. Chem. Solids, 38, 1341 (1977).
6. J. S. Miller, J. H. Zhang, W. M. Reiff, D. A. Dixon, L. D. Preston, A. H. Reis, Jr., E. Gebert, M. Extine, J. Troup, A. J. Epstein, and M. D. Ward, J. Phys. Chem., 91, 4344 (1987).
7. M. Nakano and M. Sorai, Chem. Phys. Lett., 169, 27 (1990).
8. A. Chakraborty, A. J. Epstein, W. N. Lawless, and J. S. Miller, Phys. Rev., B40, 11422 (1989).
9. J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff and A. J. Epstein, J. Am. Chem. Soc., 109, 769 (1987).
10. S. Murakawa, T. Wakamatsu, M. Nakano, M. Sorai, and H. Suga, J. Chem. Thermodyn., 19, 1275 (1987).
11. M. Sorai, K. Kaji, and Y. Kaneko, J. Chem. Thermodyn., 24, 167 (1992).
12. S. Chittipeddi, K. R. Cromack, J. S. Miller, and A. J. Epstein, Phys. Rev. Lett., 58, 2695 (1987).
13. H. W. J. Blöte, Physica, 79B, 427 (1975).
14. G. A. Baker, Jr., G. S. Rushbrooke, and H. E. Gilbert, Phys. Rev., 135, A1272 (1964).
15. S. Chittipeddi, M. A. Selover, A. J. Epstein, D. M. O'Hare, J. Manriquez, and J. S. Miller, Synth. Met., 27, B417 (1988).
16. D. J. Scalapino, Y. Imry, and P. Pincus, Phys. Rev., B11, 2042 (1975).
17. J. D. Johnson and J. C. Bonner, Phys. Rev., B22, 251 (1980).
18. G. A. Candela, L. J. Swartzendruber, J. S. Miller, and M. J. Rice, J. Am. Chem. Soc., 101, 2755 (1979).