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Three Phases of $[Fe(C_5Me_5)_2]^+[TCNQ]^-$: Ferromagnetism in a New Structural Phase

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The report of metamagnetic behavior in the organometallic charge-transfer (CT) salt $[Fe(C_5Me_5)_2]^+[TCNQ]^-$ in 1979 was a landmark in the search for ferromagnetically ordered, molecular-based charge-transfer (CT) salts.[1] Since then, five other decamethylmetallocene-based CT salts, $[M(C_5Me_5)_2]^+[TCNE]^-$ (M = Fe,[2] Mn,[3] Cr[4]) and $[M(C_5Me_5)_2]^+[TCNQ]^-$ (M = Mn,[5] Cr[6]), have been identified as bulk ferromagnets. The magnetic coupling mechanism in these materials continues to be of interest and controversy,[2−7] and in order to gain further insight into the coupling mechanism we undertook to investigate a series of binary solid solutions of the composition $[Mn_{1-x}Fe_x(C_5Me_5)_2]^+[TCNQ]^-$ ($0 \leq x \leq 1$). Unusual magnetic behavior was expected for intermediate compositions due to the fundamentally different bulk magnetic ordering behavior reported for the two pure phases, the ferromagnetic $[Mn(C_5Me_5)_2]^+[TCNQ]^-$ ($x = 0$) and the metamagnetic $[Fe(C_5Me_5)_2]^+[TCNQ]^-$ ($x = 1$). However, only ferromagnetic behavior was observed, even for compositions closely approaching the pure Fe phase, $x \sim 0.8-0.9$. This apparent anomaly led us to reinvestigate the pure $[Fe(C_5Me_5)_2]^+[TCNQ]^-$ phase. We find that, in addition to paramagnetic[8] and metamagnetic[1] phases previously reported, $[Fe(C_5Me_5)_2]^+[TCNQ]^-$ crystallizes in yet a *third* crystallographically distinct phase that gives rise to *bulk 3-D ferromagnetic* behavior with a critical temperature (T_c) of 3.0 K. This is a rare example of a single compound giving rise to three distinctly different magnetic phenomena, and it underscores the importance of subtle structural changes and their effects on magnetic ordering. We report here results of structural and magnetic studies of the ferromagnetic phase of $[Fe(C_5Me_5)_2]^+[TCNQ]^-$ (**1**).

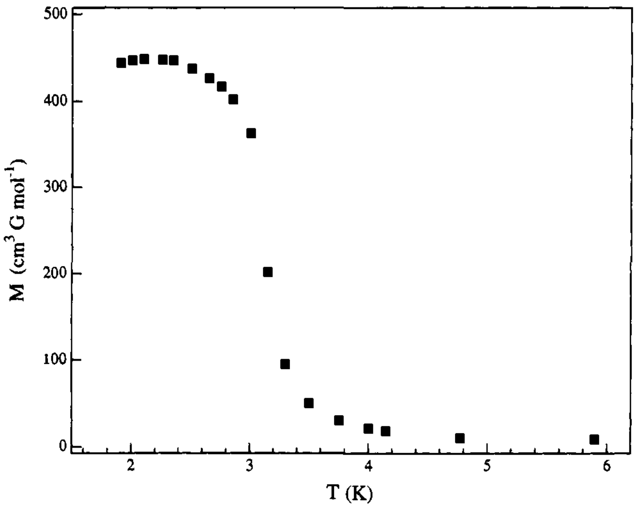

Figure 1. Field-cooled magnetization, *M*, of polycrystalline **1**-III recorded in an external field of 15 G.

Bulk **1** (which may contain a mixture of the various phases) was prepared by adding a THF solution (50 mL) of $Fe(C_5Me_5)_2$ (1.0 g, 3.0 mmol) to a THF solution (50 mL) of TCNQ (0.62 g, 3.0 mmol), cooling to −78 °C, and filtering, yielding 1.48 g of dark green microcrystalline material (91%). The ferromagnetic phase of **1** was obtained by recrystallization of the bulk material from CH_3CN at −20 °C.[9] The product crystallizes as purple parallelepipeds and upon close inspection is distinctly different from the paramagnetic and metamagnetic phases of **1**, which crystallize as purple platelets and green chunks, respectively.[10] The metamagnetic phase of **1** was obtained by recrystallization from warm CH_3CN as described previously.[10] The paramagnetic and metamagnetic phases of **1** are referred to as phases I and II, respectively, in the literature;[1b,8] thus the ferromagnetic phase of **1** will be referred to as phase III. Phase III, like phase II, is air sensitive and must be stored and manipulated anaerobically.

The complex ac susceptibility and dc magnetization, *M*, of phase **1**-III were measured with a LakeShore Model 7110 AC susceptometer and a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer, respectively. Field-cooled magnetization data for **1**-III recorded from 300 to 1.9 K at 5000 G can be fitted to the Curie−Weiss law, $\chi_{cw} = C/(T - \theta)$, above ca. 50 K with $\theta = +3.8$ K and $C = 1.26$ cm^3 K mol^{-1}. These values are similar to those reported for the metamagnetic phase of **1** ($\theta = +3$ K and $C = 1.25$ cm^3 K mol^{-1}),[1a,11] and the positive θ suggests that the dominant spin coupling in **1**-III is ferromagnetic. The occurrence of a ferromagnetic phase transition was established by measuring the magnetization as a function of temperature and field in the ranges 1.9−6 K and 0−50 000 G. As **1**-III is cooled in a low field (15 G), its magnetization shows a sharp transition, increasing abruptly between 3.5 and 3 K; below 3 K the magnetization approaches saturation, as expected for a bulk ferromagnet (Figure 1). The transition temperature, defined here as the temperature for which the slope, d*M*/d*T*, is a maximum, is $T_c = 3.1$ K. The field dependence of the magnetization at 2 K (Figure 2) is also characteristic of a polycrystalline 3-D ferromagnet, showing a steep rise to a value of $\sim 7.5 \times 10^3$ cm^3 G mol^{-1} at an applied field of only 1000 G, followed by a gradual increase to a value of 11.6×10^3 cm^3 G mol^{-1} at 50 000 G. This value is very close to the saturation magnetiza-

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(1) (a) Candela, G. A.; Swartzendruber, L. J.; Miller, J. S.; Rice, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2755. (b) Miller, J. S.; Reis, A. H., Jr.; Gebert, E.; Ritsko, J. J.; Salaneck, W. R.; Kovnat, L.; Cape, T. W.; Van Duyne, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 7111.

(2) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

(3) Yee, G. T.; Manriquez, J. M.; Dixon, D. A.; McLean, R. S.; Groski, D. M.; Flippen, R. B.; Narayan, K. S.; Epstein, A. J.; Miller, J. S. *Adv. Mater.* **1991**, *3*, 309.

(4) (a) Eichhorn, D. M.; Skee, D. C.; Broderick, W. E.; Hoffman, B. M. *Inorg. Chem.* **1993**, *32*, 491. (b) Miller, J. S.; McLean, R. S.; Vazquez, C.; Calabrese, J. C.; Zuo, F.; Epstein, A. J. *J. Mater. Chem.* **1993**, *3*, 215.

(5) Broderick, W. E.; Thompson, J. A.; Day, E. P.; Hoffman, B. M. *Science* **1990**, *249*, 401.

(6) Broderick, W. E.; Hoffman, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 6334.

(7) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40. (c) Kollmar, C.; Kahn, O. *Acc. Chem. Res.* **1993**, *26*, 259. Kollmar, C.; Kahn, O. *J. Chem. Phys.* **1992**, *96*, 2988. Kollmar, C.; Couty, M.; Kahn, O. *J. Am. Chem. Soc.* **1991**, *113*, 7995. (d) Buchachenko, A. L. *Russ. Chem. Rev.* **1990**, *59*, 307.

(8) Reis, A. H., Jr.; Preston, L. D.; Williams, J. M.; Peterson, S. W.; Candela, G. A.; Swartzendruber, L. J.; Miller, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 2756.

(9) Anal. Calcd for $C_{32}H_{34}N_4Fe$: C, 72.45; H, 6.46; N, 10.56. Found: C, 72.10; H, 6.27; N, 10.32.

(10) Miller, J. S.; Zhang, J. H.; Reiff, W. M.; Dixon, D. A.; Preston, L. D.; Reis, A. H., Jr.; Gebert, E.; Extine, M.; Troup, J.; Epstein, A. J.; Ward, M. D. *J. Phys. Chem.* **1987**, *91*, 4344.

(11) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Isr. J. Chem.* **1986**, *27*, 363.

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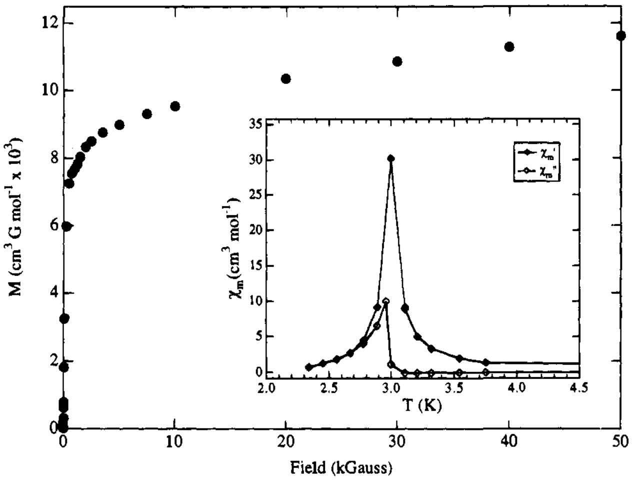

Figure 2. Field dependence of the magnetization for polycrystalline **1**-III recorded at 2 K. Inset: Temperature dependence of the real, χ', and imaginary, χ'', components of the ac susceptibility for polycrystalline **1**-III recorded at 1 G and 175 Hz.

tion of $M_{sat} = N\beta[g_D S(D^+) + g_A S(A^-)] = 12.1 \times 10^3$ cm^3 G mol^{-1} expected for a ferromagnet with $S(D^+) = S(A^-) = {}^1/_2$, $g_D = 2.33$,[12] and $g_A = 2$. This behavior is contrasted with that of the metamagnetic phase, **1**-II, in which there is a gradual increase in the magnetization as a function of $H < 1500$ G (M at 1000 G $\sim 0.85 \times 10^3$ cm^3 G mol^{-1}) followed by an abrupt transition to ferromagnetic behavior at fields $H > 1500$ G. No hysteresis in the field dependence of the magnetization for **1**-III was observed at temperatures as low as 2 K. The ferromagnetic phase transition in **1**-III was corroborated by observation of the sharp maxima expected in the real, χ', and imaginary, χ'', components of the ac magnetic susceptibility at the critical temperature (Figure 2, inset). The maxima in χ' and χ'' both occur at $T_c = 3.0$ K, slightly less than the T_c obtained from the dc magnetization measurements (3.1 K); the apparent discrepancy reflects the lower static measuring field of the ac technique (the earth's magnetic field). Taken together, the results presented here indicate that **1**-III is a bulk ferromagnet with $T_c = 3.0$ K. Magnetic studies on **1**-II prepared as described above verified that the material was metamagnetic with $T_N = 2.55$ K, as previously reported.

The structure of **1**-III, as determined by single-crystal X-ray crystallography,[13] consists of ...D^+A^-... chains in which $[Fe(C_5Me_5)_2]^+$ (D^+) cations and TCNQ$^-$ (A^-) anions alternate along the a axis (Figure 3). This ...D^+A^-... chain arrangement is similar to that found in other decamethylmetallocenium CT salts, and in particular, **1**-III is isomorphous to the Mn analog.[5,14] The structure reported for the true metamagnetic phase, **1**-II (triclinic),[10] is similar to **1**-III in that both structures contain ..$D^+A^-D^+A^-$... chains,[15] but is not isomorphous. An obvious difference between the structures of **1**-III and **1**-II (triclinic) lies in the conformation of the C_5Me_5 rings of the cations; in **1**-III, the C_5Me_5 rings adopt an eclipsed conformation, whereas in **1**-II the C_5Me_5 rings are found in a staggered conformation. There are also subtle differences in the interstack arrangment in **1**-III and **1**-II. The TCNQ$^-$ anions of **1**-II are all arranged in the same direction, while in **1**-III they form a zigzag pattern in the b direction.

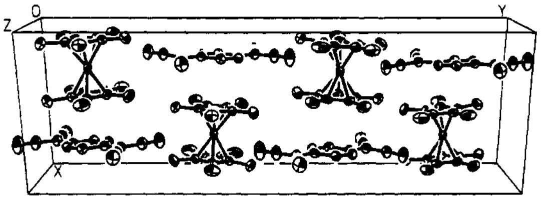

Figure 3. Packing diagram of **1**-III showing a perspective view of the ...D^+A^-... stacking arrangement along the crystallographic a-axis.

The reaction of $Fe(C_5Me_5)_2$ and TCNQ thus produces three distinct 1:1 charge-transfer salts: a ferromagnet, a metamagnet, and a paramagnet. The availability of high-quality structures for all three provides a unique opportunity for magnetostructural correlations. We are currently engaged in a detailed analysis of the structures of **1**-II and **1**-III to identify the interchain effects that influence the overall mode of bulk magnetic ordering in these materials.

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Supplementary Material Available: Tables of fractional coordinates, bond lengths, bond angles, and isotropic and anisotropic thermal parameters for **1**-III (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[12] Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955.

[13] Crystallographic data for **1**-III: monoclinic, $P2_1/n$, $a = 10.837(2)$ Å, $b = 31.356(7)$ Å, $c = 8.609(1)$ Å, $\beta = 103.09(2)°$, $V = 2849.2(10)$ Å^3, $Z = 4$. Full matrix least-squares refinement yielded the final agreement factors, $R(F) = 0.0489$ and $R_w(F) = 0.0498$ for 3170 reflections [with $|F_o| \geq 6\sigma(|F_o|)$] measured between $3 \leq 2\theta \leq 50$ at ambient temperature (Mo Kα radiation, $\lambda = 0.710\,69$ Å). For $[Mn(C_5(CH_3)_5)_2]^+[TCNQ]^-$: monoclinic, $P2_1/n$, $a = 10.829(2)$ Å, $b = 31.014(4)$ Å, $c = 8.544(1)$ Å, $\beta = 103.39(2)°$, $V = 2792(1)$ Å^3, $Z = 4$ (from ref 5).

[14] **1**-III is also isomorphous with the first structure reported for the metamagnetic phase, **1**-II. However, the structure of **1**-II was for a crystal that had been exposed to air for an extended period, causing the TCNQ$^-$ anions to undergo a solid-state reaction to produce the diamagnetic α,α-dicyano-*p*-toluoyl cyanide anion (ref 1b).

[15] We have redetermined and confirmed the structure of **1**-II.