Dialkyldicyanofumarate Diesters: Tunable Building Blocks for Molecule-Based Ferromagnets

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Abstract: Dicyanofumarate diesters have been discovered to be viable and versatile alternatives to tetracyanoethylene as building blocks for the synthesis of molecule-based magnets. The reaction of decamethylmanganocene, Mn(Cp*)$_2$, and dimethyldicyanofumarate, DMeDCF, in methylene chloride at −50 °C gives a one-to-one charge-transfer salt ferromagnet, [Mn(Cp*)$_2$][DMeDCF], that possesses one of the highest Curie temperatures, 10.6 ± 0.1 K, ever observed in this class of compounds. At 1.8 K, this compound exhibits hysteresis with $H_{coer} \sim 7$ kG. Measurement of ac susceptibility suggests some glassiness in the ferromagnetic state, similar to that seen for the tetracyanoethylene analogue, [Mn(Cp*)$_2$][TCNE]. Diethyldicyanofumarate, DEtDCF, reacts with decamethylmanganocene to give the homologous salt, [Mn(Cp*)$_2$][DEtDCF]. In contrast to the dimethyl ester, the magnetic properties of this compound are those of a glassy, hysteretic metamagnet that exhibits coercivity of around 10 kG at 1.8 K.

Introduction

This report describes our continuing effort to study the chemistry and physics of new charge-transfer (CT) molecule-based magnets. One facet of this investigation is a search for alternatives to tetracyanoethylene: sterically and electronically tunable, electron-poor, ethylene derivatives that can be easily reduced to give stable radical anionic states. Dicyanofumarate diesters nicely satisfy these criteria and we have now discovered that they support molecule-based magnetism. Specifically, dimethyldicyanofumarate, DMeDCF (Figure 1), reacts with decamethylmanganocene to give [Mn(Cp*)$_2$][DMeDCF], which exhibits ferromagnetism at 10.6 ± 0.1 K. The diethyl ester homolog, [Mn(Cp*)$_2$][DEtDCF] (Figure 1), exhibits more complex behavior, best described as that of a hysteretic, metamagnetic spin glass. Importantly, we believe these data show dicyanofumarate diesters to be promising new, *tunable*, building blocks for molecule-based magnetism research.

Background

Tetracyanoethylene, TCNE, is a versatile building block for the synthesis of molecule-based ferromagnets. In particular, it reacts with decamethylferrocene to form [Fe(Cp*)$_2$][TCNE], a charge-transfer salt possessing a single unpaired electron on each donor and acceptor.[1] This compound orders ferromagnetically below 4.8 K and represents the first such compound to exhibit hysteresis. The decamethylmanganocene and decamethylchromocene analogues, [Mn(Cp*)$_2$][TCNE] and [Cr(Cp*)$_2$][TCNE], which order at $T_{Curie} = 8.8$ K[2] and 3.65 K,[3] respectively (as determined by extrapolation of the steepest portion of the *M* vs
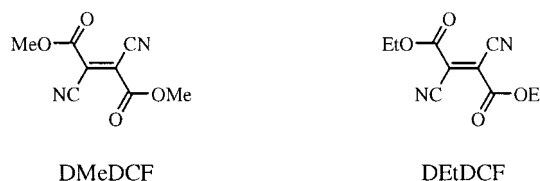

Figure 1. Fumarate esters: tunable alternative to TCNE.

T plot), illustrate the utility of TCNE and a strength of this synthetic approach: a single acceptor may be reacted with several donors to yield a family of systematically related magnets. In this case, the number of unpaired electrons on the donor varies from 1 (Fe) to 3 (Cr) while the acceptor is not changed. This ability has been important in the effort to understand the underlying mechanism of ferromagnetic coupling in molecule-based systems.

The near ubiquity of TCNE is illustrated by other large families of magnetic CT compounds that utilize the acceptor including M(TCNE)$_x$, where M = V, Mn, Fe, Co, Ni, and Mn-(porphyrin)(μ-TCNE).[4] In both of these classes of compounds, TCNE serves a dual role: it accepts an electron to form a radical anion and it also serves as a bridging ligand to very effectively mediate spin communication between the spin-containing transition metal centers.

Experimental Section

General Considerations. Preparations of air-sensitive compounds were carried out in a nitrogen-filled Braun glovebox maintained at less than 5 ppm O$_2$ and by utilizing standard Schlenk techniques. Low temperatures were maintained by Flexi-Cool immersion cooler, FTS Systems. Mn(Cp*)$_2$ was purchased from Strem Chemicals. All other

† Buffalo State College.
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(1) 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*, 769−781.
(2) 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*, 309−311.

(3) (a) Miller, J. S.; McLean, R. S.; Vazquez, C.; Calabrese, J. C.; Zuo, F.; Epstein, A. J. *J. Mater. Chem.* **1993**, *3*, 215−218. (b) Hoffman et al. have independently reported this compound and determined T_{Curie} to be 2.1 K based on the maximum in d*M*/d*T*. See: Eichhorn, D. A.; Skee, D. C.; Broderick, W. E.; Hoffman, B. M. *Inorg. Chem.* **1993**, *32*, 491−492.
(4) Miller, J. S.; Epstein, A. J. *Chem. Commun.* **1998**, 1319−1325 and references therein.

reagents were purchased from Aldrich. Reagents were used as purchased except as noted below. Methylene chloride was distilled from P_2O_5. THF and diethyl ether were distilled from Na/benzophenone. All solvents were degassed with glovebox N_2 prior to use. Dimethyldicyanofumarate and diethyldicyanofumarate were synthesized by a previously published route.[7] Elemental analyses were performed by NuMega Resonance Labs, Inc., San Diego, CA.

Magnetic Measurements. All the magnetic measurements were performed on a 5 or 7 T Quantum Design MPMS SQUID magnetometer. Measurements of magnetization as a function of temperature were performed from 1.8 to 275 K and in 100 G field. Samples were prepared as previously described.[5] The amplitude of the oscillating magnetic field used for ac susceptometry measurements was 5 G with zero dc bias field. Diamagnetic corrections were applied based on Pascal's constants.

Decamethylmanganocene Dimethyldicyanofumarate, [Mn(Cp*)₂]- [DMeDCF]. $Mn(Cp^*)_2$ (60 mg, 1.8×10^{-4} mol) was dissolved in 6 mL of CH_2Cl_2, and the solution cooled to -50 °C. To this was added a solution of DMeDCF (40 mg, 2.1×10^{-4} mol) in 6 mL of CH_2Cl_2, dropwise, while maintaining the temperature of the solution at -50 °C. The solution turned red-brown. After the mixture was stirred for 0.5 h, 5 mL of ether was added slowly (not allowing the temperature to get above -45 °C) to yield a microcrystalline red-brown solid. After the solution was stirred for an additional 10 min, the precipitate was transferred to a Schlenk frit, which was previously cooled to -50 °C, and filtered under vacuum. The solid on the frit was washed with 5 mL of cold ether, initially dried under vacuum for 0.5 h keeping the frit temperature ca. -45 °C, and finally dried at room temperature for 2 h. Yield: 80 mg (86%). IR (Fluorolube); $\nu(CN)$ 2168 cm^{-1} (sharp); $\nu(CO)$ 1656 cm^{-1} (sharp). Anal. Calcd for $C_{28}H_{36}N_2O_4Mn$: C, 64.73; H, 6.90; N, 5.40. Found: C, 64.42; H, 6.55; N, 5.50.

Decamethylmanganocene Diethyldicyanofumarate, [Mn(Cp*)₂]- [DEtDCF]. $Mn(Cp^*)_2$ (60 mg, 1.8×10^{-4} mol) was dissolved in 6 mL of CH_2Cl_2, and the solution cooled to -50 °C. To this was added, dropwise, a solution of DEtDCF (45 mg, 2.0×10^{-4} mol) in 4 mL of CH_2Cl_2, maintaining the temperature of the mixture at -50 °C. The color of the solution turned dark and after 5 min, a greenish brown solid precipitated. After the solution was stirred for 0.5 h at -50 °C, the precipitate was transferred onto a Schlenk frit, which was previously cooled to -50 °C, and filtered under vacuum. The solid on the frit was washed with 5 mL of cold ether, initially dried under vacuum for 0.5 h keeping the frit temperature ca. -45 °C, and finally dried at room temperature for 2 h. Yield: 85 mg. (86%) IR (Fluorolube): $\nu(CN)$ 2165 cm^{-1} (sharp); $\nu(CO)$ 1650 cm^{-1} (sharp). Anal. Calcd for $C_{30}H_{40}N_2O_4Mn$: C, 65.80; H, 7.36; N, 5.10. Found: C, 65.85; H, 7.03; N, 4.99.

To provide references for IR spectra of the radical anions, we prepared sodium salts, Na[DMeDCF] and Na[DEtDCF], by reacting the neutral dicyanofumarate diesters with sodium naphthalide in THF. IR data for the deep blue salts are as follows: Na(DMeDCF), $\nu(CN)$ 2191 and 2167 cm^{-1} (sharp); $\nu(CO)$ 1621 cm^{-1} (sharp). Na(DEtDCF), $\nu(CN)$ 2188 and 2169 cm^{-1} (sharp); $\nu(CO)$ 1622 cm^{-1} (sharp).

Results and Discussion

Hammett σ^-. To find tunable TCNE analogues, we have chosen to direct our efforts toward electron-poor ethylene derivatives, and in trying to identify new synthetic targets, we hypothesize that a guiding criterion for the design of new acceptors is the Hammett σ^- value for a particular functional group.[6] This parameter reflects the ability of the group to remove charge, via inductive and resonance effects, from a reaction transition state that becomes electron-rich, and should be an indicator of the ability of a group to stabilize charge in the radical anion. Mulvaney et al. have previously noted this correlation.[8] As expected, the value for CN is high (Table 1).

(5) Sellers, S. P.; Korte, B. J.; Fitzgerald, J. P.; Reiff, W. M.; Yee, G. T. *J. Am. Chem. Soc.* **1998**, *120*, 4662−4670.

(6) Gordon, A. J.; Ford, R. A. *The Chemist's Companion, A Handbook of Practical Data, Techniques, and References*; John Wiley & Sons: New York, 1972; p 152.

Table 1. Hammett σ^- Values for Candidate Functional Groups

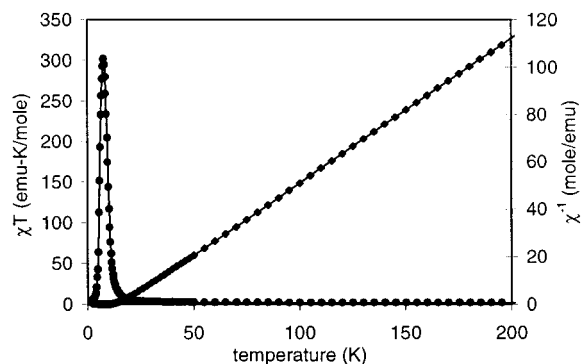| functional group	σ^-	functional group	σ^-
CHO	1.13	CO_2CH_3	0.68
CN	0.89	$CO_2CH_2CH_3$	0.68
$COCH_3$	0.85	$CONH_2$	0.62
CO_2H	0.728		

Figure 2. Plot of χT vs T (●) and χ^{-1} vs T (◆) for [Mn(Cp*)₂]- [DMeDCF] measured in 100 G.

However, several other functional groups demonstrate comparable values and could be used to form new acceptors.

Dicyanofumarate Diesters. We chose first to examine the known dicyanofumarate diesters.[7] These compounds have previously been shown to exhibit reversible one-electron reductions at approximately 0.4 V negative of TCNE.[8] Hammett σ^- values for esters suggest that these compounds should be weaker electron acceptors than TCNE, necessitating reacting them with stronger donors.[9] We observe the 0/−1 couples at approximately −0.25 V vs SCE and as expected: neither the methyl nor ethyl compound is reduced by decamethylferrocene.

(a) Dimethyldicyanofumarate. The dimethyl ester, DMe-DCF, is easily prepared from methylcyanoacetate in good yield. Subsequent reaction of this acceptor with decamethylmanganocene in methylene chloride at -50 °C gives a red-brown, somewhat air-sensitive, solid. This compound has been characterized by elemental analysis and IR spectroscopy as a 1:1 complex containing [DMeDCF]$^{-\bullet}$ radical anions. Although a large single crystal of this compound is not available because of its instability in solution at room temperature, powder diffraction analysis of a polycrystalline sample indicates it is isostructural with its chromium homolog, [Cr(Cp*)₂][DMeDCF], for which a single-crystal structure has been solved.[10] The compound adopts the familiar mixed-stack structure of other CT salt magnets, possessing both in-registry and out-of-registry chains.[1]

The magnetic properties of [Mn(Cp*)₂][DMeDCF] show it to be a new ferromagnet. The plot of χT vs T shows a sharp peak at 8 K that rises to over 300 emu·G/mol (Figure 2). The corresponding plot of χ^{-1} vs T shows excellent linear behavior that extrapolates to a Curie−Weiss θ of 16.0 K (Figure 2). From the room-temperature data, we calculate $\chi T = 1.77$ emu·K/mol, corresponding to a $g = 2.36$ for [Mn(Cp*)₂]$^+$ (assuming $g = 2.00$ for the organic anion). This value of g is consistent with that reported for other [Mn(Cp*)₂]$^+$ containing salts.[2,11]

(7) Ireland, C. J.; Jones, K.; Pizey, J. S.; Johnson, S. *Synth. Commun.* **1976**, *3*, 185−191.

(8) Mulvaney, J. E.; Cramer, R. J.; Hall, H. K., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 309−314.

(9) Ward, M. D. *Electroanal. Chem.* **1986**, *16*, 181−313.

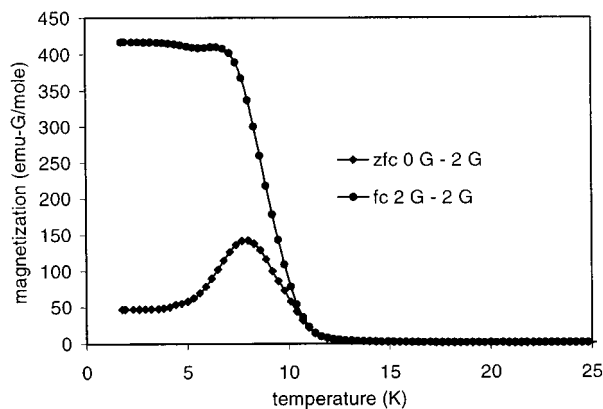(10) Kaul, B. B.; Sommer, R. D.; Noll, B. C.; Yee, G. T. Manuscript in preparation.

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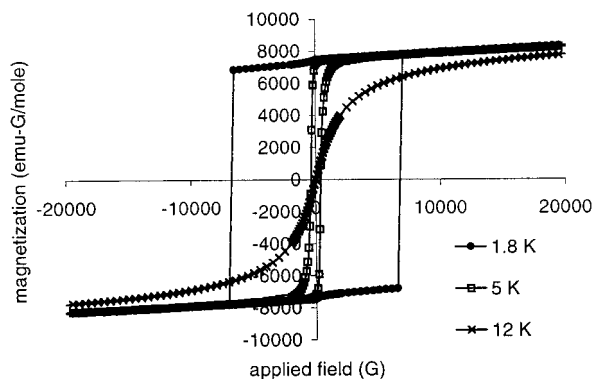**Figure 3.** Field cooled (fc) and zero-field cooled (zfc) magnetization for [Mn(Cp*)$_2$][DMeDCF].

Figure 4. Magnetization vs applied field at 1.8, 5, and 12 K for [Mn-(Cp*)$_2$][DMeDCF].

An extrapolation of the steepest part of the field-cooled magnetization data obtained at 2 G suggests a Curie temperature of 10.6 ± 0.1 K (Figure 3). The Curie temperature, as alternatively determined by the midpoint of the transition, is 9.6 ± 0.1 K. These represent an incremental improvement in T_{Curie} over the analogous TCNE compound, [Mn(Cp*)$_2$]-[TCNE][2], and the highest observed for a metallocene-based magnet.

The plots of *M* vs *H* show the evolution of a hard ferromagnet to a soft ferromagnet as the temperature is raised (Figure 4). The large coercive field is slightly sample dependent, but the data in Figure 4 are representative at almost 7 kG at 1.8 K. The magnitude of the remanence and the saturation magnetization are somewhat lower than expected (8×10^3 emu·G/mol) assuming ferromagnetic coupling. This may indicate canting of the moments in the ordered state.

Somewhat surprisingly, measurement of the ac susceptibility on [Mn(Cp*)$_2$][DMeDCF] (Figure 5) suggests that it may not be a true ferromagnet, but instead should be described as a spin glass. Frequency-dependent ac susceptibility at these low frequencies is not characteristic of true ferromagnetism.[12] The sensitivity of the χ_{real} peak position to frequency, given by $\Delta T_f/T_f\Delta\log\omega$, is approximately 0.03, where T_f is the position of the peak at drive frequency ω. This value places the compound in the canonical spin glass regime.[12] We have previously reported very similar ac susceptibility data for [Mn(Cp*)$_2$][TCNE] that suggest that it too may not be a true ferromagnet.[13]

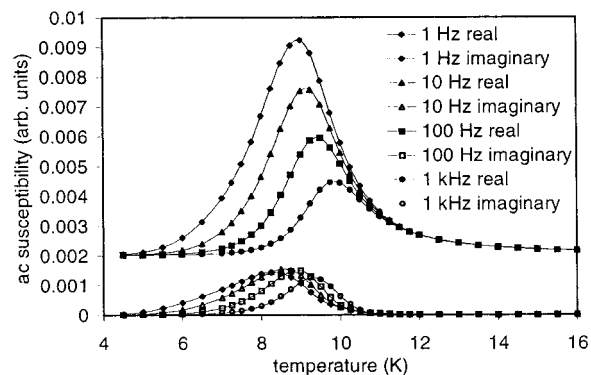(11) (a) Miller, J. S.; McLean, R. S.; Vazquez, C.; Yee, G. T.; Narayan, K. S.; Epstein, A. J. *J. Mater. Chem.* **1991**, *1*, 479−480. (b) Nayaran, K. S.; Heres, O.; Epstein, A. J.; Miller, J. S. *J. Magn. Magn. Mater.* **1992**, *110*, L6−L10.

(12) Mydosh, J. A. *Spin Glasses An Experimental Introduction*; Taylor & Francis: London, 1993; p 67.

Figure 5. Plot of real and imaginary ac χ vs *T* at several frequencies for [Mn(Cp*)$_2$][DMeDCF] (real and imaginary data are offset for clarity).

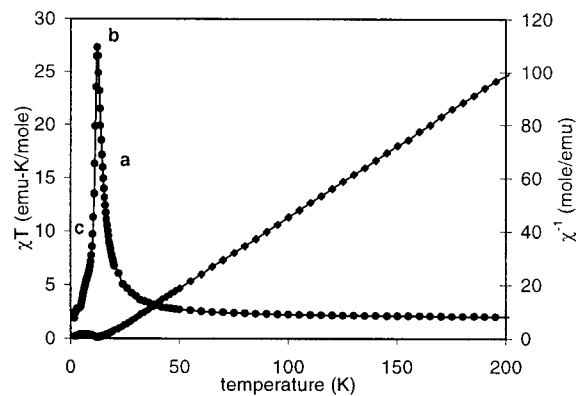**Figure 6.** Plot of χT vs *T* (●) and χ^{-1} vs *T* (◆) for [Mn(Cp*)$_2$]-[DEtDCF] measured in 100 G.

(b) Diethyldicyanofumarate. A strength of the dicyanofumarate diesters over TCNE is that the former may be tuned, both sterically and electronically, by varying the ester alkyl group. To illustrate this point, we have prepared the homologous diethyl dicyanofumarate, DEtDCF, and reacted it with Mn(Cp*)$_2$ to give a second new 1:1 CT salt, [Mn(Cp*)$_2$][DEtDCF]. This compound exhibits very different and unusual properties, best described as those of a metamagnetic hysteretic spin glass. As may be seen below in the plot of χT vs *T*, the compound appears to possess ferromagnetic coupling in one dimension above 12 K as evidenced by the strong upturn in region **a** (Figure 6). The data exhibit excellent Curie−Weiss behavior with θ for this compound equal to 15.5 K. At room temperature $\chi T = 2.00$ emu·K/mol, corresponding to $g = 2.55$ for [Mn(Cp*)$_2$]$^+$.

[Mn(Cp*)$_2$][DEtDCF] then appears to undergo an antiferromagnetic phase transition around 12 K (Figure 6, region **b**) as evidenced by a peak in χ and consequently in χT. This assignment is supported by the ac susceptibility data that show a frequency-independent peak in the in-phase component and no out-of-phase component (Figure 7).

One of the more intriguing aspects of this compound is that the phase transition at 12 K is not simply one from a paramagnet to an antiferromagnet. This is shown by the magnetization vs applied field curve at 9 K, which has the shape indicative of metamagnetism (Figure 8). This behavior is characterized by an antiferromagnetic state that switches to a ferromagnetic state upon application of a sufficiently large applied field, H_c, in this case, about 500 G. As expected, the critical field goes to zero

(13) Sommer, R. D.; Korte, B. J.; Sellers S. P.; Yee, G. T. In *Proceedings of the Fall 1997 Meeting of the Materials Research Society*; Reynolds, J. R., Jen, A. K-J., Rubner, M. F., Chiang, L. Y., Dalton, L. R., Eds.; Vol. 488, pp 471−476.
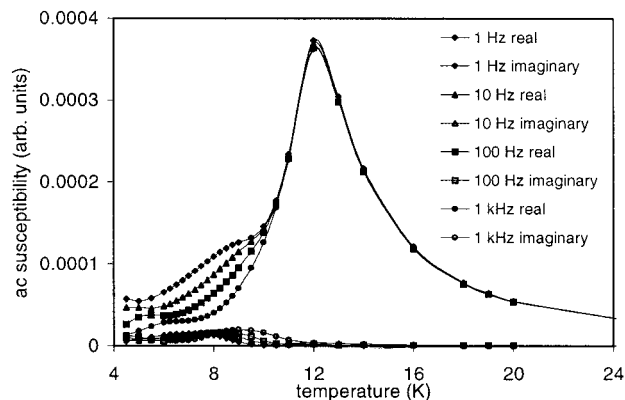
Dialkyldicyanofumarate Diesters

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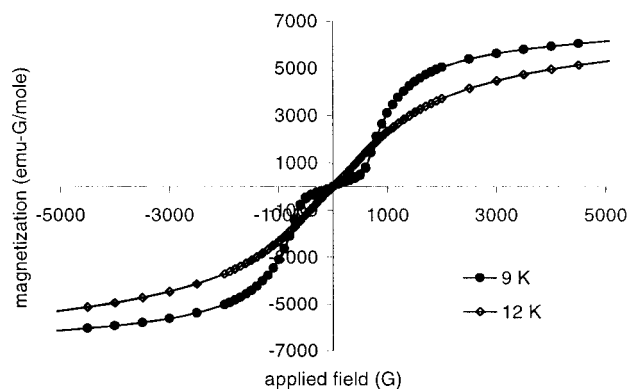**Figure 7.** Plot of real and imaginary ac χ vs T at several frequencies for [Mn(Cp*)$_2$][DEtDCF].

Figure 8. Plot of magnetization vs applied field at 9 and 12 K for [Mn(Cp*)$_2$][DEtDCF].

as the sample is warmed, resulting in an apparent soft ferromagnetic state at 12 K at all applied fields (Figure 8). Metamagnetism has been previously observed in several other charge-transfer salt magnets.[11,14,15] Though we presently do not have a single crystal structure, for a usual mixed stack, which we presume adequately describes this compound, Hoffman et al. have ascribed the metamagnetic behavior to strong intrastack magnetic coupling and weak interstack interactions.[15] Consistent with this model, we would have predicted that the ethyl homologue was more likely to be metamagnetic because its longer side chains should decrease interstack communication without necessarily compromising intrastack interactions. The comparable values of the Curie−Weiss θ should be reflective of the latter.

Below 10.5 K, [Mn(Cp*)$_2$][DEtDCF] appears to undergo a second phase transition (Figure 6, region **c**). This second transition is notable for its frequency-dependent ac susceptibility (Figure 7) and bifurcation in the field cooled magnetization vs zero-field cooled magnetization (Figure 9) suggesting a spin glass state in this temperature regime. This explains the origin of the extremely large hysteresis observed at 1.8 K (vide infra): magnetic viscosity gives rise to slow relaxation of the spins. Only Nagai et al. have reported higher coercivity among molecule-based systems. Their compound, MnTEtOPP-TCNE, where TEtOPPP is tetra(ethoxyphenyl)porphyrin, is also metamagnetic and exhibits coercivity of 20 kG.[16]

(14) Candela, G. A.; Swartzendruber, L. J.; Miller, J. S.; Rice, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2755−2756.

(15) Broderick, W. E.; Thompson, J. A.; Hoffman, B. M. *Inorg. Chem.* **1991**, *30*, 2958−2960.

(16) Nagai, K.; Jiang, L.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Thin Solid Films* **1998**, *331*, 165−169.
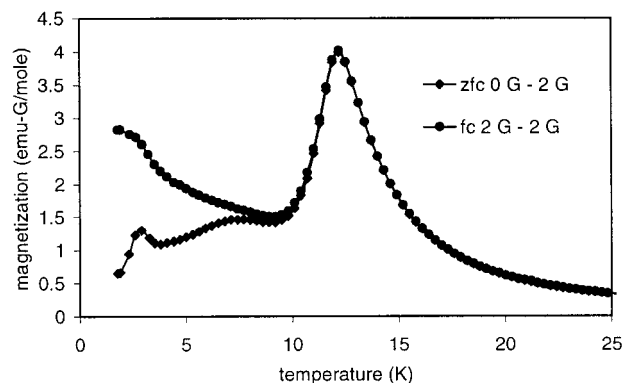

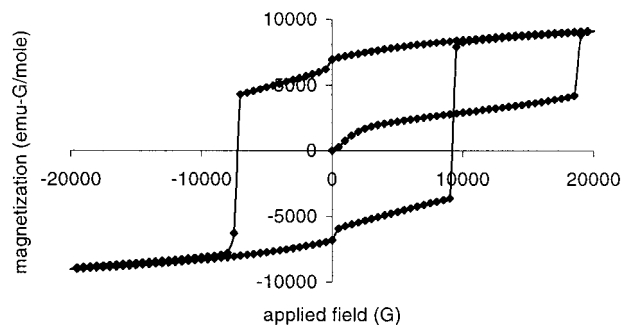**Figure 9.** Field cooled (fc) and zero-field cooled (zfc) magnetization for [Mn(Cp*)$_2$][DEtDCF].

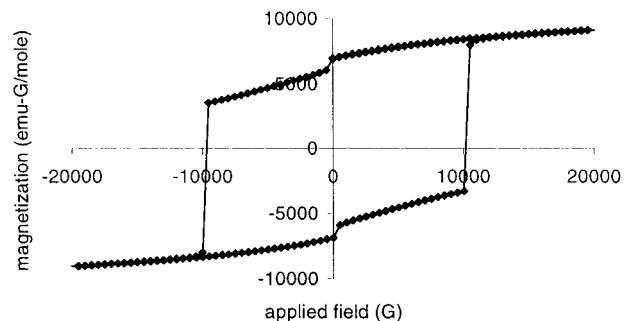**Figure 10.** Plot of magnetization vs applied field at 1.8 K for [Mn-(Cp*)$_2$][DEtDCF] zero-field cooled.

Figure 11. Plot of magnetization vs applied field at 1.8 K for [Mn-(Cp*)$_2$][DEtDCF] field cooled in 40 kG.

The plot of magnetization vs applied field at 1.8 K is displayed in Figure 10 for a sample cooled in zero applied field. At that temperature, the metamagnetic critical field increases to nearly 20 kG. Above this field, the sample abruptly switches to being nearly saturated. Note that the hysteresis loop is not symmetrically centered around zero applied field. This property has previously been observed for dilute spin glasses and supposedly results from locking in of the orientation of some of the spins as the result of cooling the sample in an applied field.[17] We observe that even cooling this molecular spin glass in nominal zero field (as evidenced by the first data point at zero applied field and zero magnetization) appears to produce significant asymmetry.

Cooling the sample in a field removes the metamagnetic behavior, leaving the compound in a long-lived "ferromagnetic" state that we ascribe to a viscous spin glass as described above. Now, *a nearly unprecedented level of coercivity* is observed, nearly 10 kG (Figure 11), larger than that observed for any other charge-transfer salt magnet. Such a metastable ferromagnetic

(17) Mydosh, J. A. *Spin Glasses An Experimental Introduction*; Taylor & Francis: London, 1993; p 91.

state has previously been reported in at least one other CT salt metamagnet, [Mn(Cp*)$_2$][DDQ], where DDQ is dichlorodicyanoquinone.[11]

Conclusions

These data show that dicyanofumarate diesters are versatile, tunable, building blocks for molecule-based magnets. In particular, we have reported a new CT salt ferromagnet with T_{Curie} = 10.6 ± 0.1 K and another that exhibits complex metamagnetic properties including nearly unprecedented coercivity. Some of the results described here obviously require further investigation, including heat capacity measurements both in zero and nonzero applied magnetic field to clarify the nature of the phase transitions. Future work will also involve transesterification with other alcohols for the purpose of discerning structure−property relationships and redox−pK_a (of the alcohol) correlations. The general usefulness of these new acceptors will be explored by pairing them with other donors.

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