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Synthesis, Structure, and Magnetic Properties of the Charge-Transfer Salt Ferromagnet Decamethylchromocenium Dimethyl Dicyanofumarate, $T_{\mathrm{Curie}} = 5.7$ K

Bharat B. Kaul, Roger D. Sommer, Bruce C. Noll, and Gordon T. Yee*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

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Introduction

The synthesis of one-to-one charge-transfer (CT) salts represents one very successful strategy for the synthesis of systematically related magnetic solids. Working independently, the research groups of Miller, Hoffman, and others have shown that electron-rich, first-row decamethylmetallocenes, $M(Cp^*)_2$ where M = Cr, Mn, Fe, Co, and Ni, can be paired with a palette of one-electron acceptors such as tetracyanoethylene, TCNE,[1−5] tetracyanoquinodimethane, TCNQ,[6−9] 2,5-dimethyl-*N*,*N*′-dicyanoquinodiimine, DMDCNQI,[10] and 2,3-dichloro-5,6-dicyanoquinone, DDQ,[11] to form CT salts exhibiting a range of phenomena including paramagnetism, ferromagnetism, antiferromagnetism and metamagnetism.

One limitation to this approach is the difficulty identifying and synthesizing suitable new acceptor building blocks. Candidates must possess stable radical anionic states and π orbitals for facilitating stacking and magnetic exchange, as well as exhibit reversible electrochemistry at suitable potentials. Many examples, such as those mentioned above, are derivatives of *p*-benzoquinone, but we have addressed this challenge in a novel way by targeting organic molecules structurally related to the olefinic acceptor TCNE (Figure 1). In molecule-based magnetism, TCNE is, by far, the most common acceptor and is known to play that role in at least three large families of magnetically ordering solids, including (a) charge-transfer salts, such as decamethylferrocenium tetracyanoethenide, $[Fe(Cp^*)_2][TCNE]$;[2] (b) one-dimensional coordination polymer ferrimagnets such as manganese(III) tetraphenylporphyrin bridged by $TCNE^{\bullet/-}$, MnTPP[μ-TCNE];[12] (c) three-dimensional coordination polymer ferrimagnets such as $V[TCNE]_2 \cdot 1/2CH_2Cl_2$.[13]

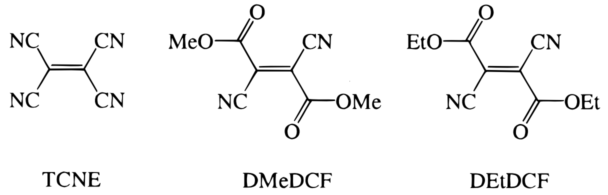

Figure 1. Tetracyanoethylene, dimethyl dicyanofumarate, and diethyl dicyanofumarate.

The reasons for the versatility of TCNE are unknown, but this observation suggests that olefinic acceptors might be more suited to the task of supporting magnetism.

In a previous paper, we conjectured that replacing two trans nitriles on TCNE with other organic functional groups capable of resonance stabilization of negative charge gives a blueprint for the synthesis of tunable and versatile one-electron acceptor building blocks useful in the construction of CT salt ferromagnets.[14] This idea was partially illustrated by the synthesis of dimethyl dicyanofumarate, DMeDCF, and diethyl dicyanofumarate, DEtDCF (Figure 1), and by examination of their reactions with decamethylmanganocene. The product of the former, $[Mn(Cp^*)_2][DMeDCF]$, exhibits a transition to a ferromagnetic state at a Curie temperature of 10.5 K.[14] This represents an improvement in T_{Curie} over that of its TCNE analogue. The latter, a somewhat more sterically demanding acceptor, gives $[Mn(Cp^*)_2][DEtDCF]$, a complex, metamagnetic spin glass. The compound exhibits both field-dependent magnetization indicative of metamagnetism and, in a lower temperature regime, frequency-dependent ac susceptibility indicative of a hysteretic spin glass state.

We have now turned to pairing DMeDCF with another one-electron donor, decamethylchromocene, $Cr(Cp^*)_2$, and report the properties of $[Cr(Cp^*)_2][DMeDCF]$ herein. We also contrast its structural and magnetic properties with those of its TCNE analogue, $[Cr(Cp^*)_2][TCNE]$, to provide a possible explanation for the slightly higher Curie temperature observed for the title compound.

Experimental Section

Preparations of air-sensitive compounds were carried out in a nitrogen-filled Braun glovebox maintained at less than 5 ppm O_2. Decamethylchromocene was purchased from Strem Chemicals. All other reagents were purchased from Aldrich and were used as delivered except as noted below. Dichloromethane was dried and distilled from P_2O_5, acetonitrile from CaH_2, and diethyl ether from Na/benzophenone. All solvents were degassed with glovebox N_2 prior to use. Dimethyl dicyanofumarate was synthesized by a previously published method.[15] Elemental analyses were performed by Desert Analytics, Tucson, AZ. Magnetic measurements were performed on Quantum Design MPMS 5S and 7 SQUID magnetometers in sample holders previously

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described.[16] M vs T measurements were made in a 100 G applied field. The amplitude of the oscillating magnetic field used for ac susceptibility measurements was 5 G with zero dc bias field. Diamagnetic corrections were applied based on Pascal's constants. A correction was applied to the M vs T data to account for the presence of a small ferromagnetic impurity equivalent to 7 ppm saturated iron. In our hands, all decamethylchromocenium-based CT salts possess some degree of ferromagnetic impurity.

X-ray Data Collection and Structure Refinement. X-ray diffraction structure determination was performed on a Siemens SMART CCD diffractometer equipped with a locally modified LT-2A low-temperature apparatus. Crystals were grown by slow diffusion of ether into an acetonitrile solution of the compound. A sample of crystals was selected in the glovebox and placed under light hydrocarbon oil in a small Petri dish. Cell dimensions were determined after harvesting reflections from a series of three orthogonal sets of 20 0.3° ω scans. Data collection covered an arbitrary hemisphere of space to 0.68 Å. Final cell parameters were determined using 7598 reflections with $I \geq 10\sigma(I)$ harvested from the complete data set. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using equivalent reflections. Structure solution via direct methods in the centrosymmetric space group *Pnma* revealed the non-hydrogen structure. Hydrogens were placed at calculated geometries and allowed to ride on the parent atom. There was no disorder, and the final residual density map was essentially flat.

Decamethylchromocenium Dimethyl Dicyanofumarate, [Cr(Cp*)$_2$][DMeDCF] 1. Decamethylchromocene (100 mg, 3.1×10^{-4} mol) was dissolved in 2 mL of CH_2Cl_2. To this solution was added a solution of dimethyl dicyanofumarate (70 mg, 3.6×10^{-4} mol) in 5 mL of CH_2Cl_2. Immediately, the color of the solution turned from yellow to red-brown. After the solution was stirred for 0.5 h at room temperature, 15 mL of ether was added slowly to precipitate a fluffy, air-sensitive, ochre solid. This solid was filtered, washed with ether, and dried in vacuo. Yield: 130 mg (81%). The complex was recrystallized from CH_2Cl_2/Et_2O at −2 °C, giving fine needles. IR (Fluorolube): ν(CN), 2167 cm^{-1} (sharp), ν(CO), 1657 cm^{-1} (sharp). Anal. Calcd for $C_{28}H_{36}CrN_2O_4$: C, 65.10; H, 7.02; N, 5.42. Found C, 65.51; H, 6.78; N, 5.55.

Results and Discussion

Two decamethylchromocenium-based ferromagnets have previously been prepared, [Cr(Cp*)$_2$][TCNE][4,5] and [Cr(Cp*)$_2$][TCNQ].[6] These exhibit Curie temperatures of 2.1 and 3.1 K, respectively, as determined by the maximum in dM/dT.[17] The properties of both of these compounds are consistent with ferromagnetic coupling of three unpaired electrons on the donor and one on the acceptor.

The title compound, [Cr(Cp*)$_2$][DMeDCF] (**1**), can be synthesized in a straightforward manner by mixing the reactants in dichloromethane at room temperature. However, unlike its manganese congener,[14] this new compound is stable in solution at room temperature, permitting its crystallization and structural characterization.

Structure. The charge-transfer salt **1** crystallizes in the space group *Pnma* with four donor−acceptor pairs per unit cell (Table 1 and Figure 2). Although the unit cell of analogous [Cr(Cp*)$_2$][TCNE] is monoclinic,[5] the structure similarly consists of $D^+A^-D^+A^-$ stacks possessing one in-registry and two out-of-registry interstack interactions. The decamethylchromocenium cation has an eclipsed conformation, resulting in gross D_{5h} symmetry. Its geometry is essentially the same as that previously reported for [Cr(Cp*)$_2$][TCNE]. The distances between chromium centers are 10.691 Å (within a stack), 9.103 Å (for the in-registry stack), 9.545 Å (for the nearest out-of-registry stack), and 11.156 Å (for the next-nearest out-of-registry stack). While two of these distances are comparable, the in-registry and next-nearest out-of-registry separations are considerably longer than those seen in [Cr(Cp*)$_2$][TCNE] (Table 2). This result is not surprising given the larger size of DMeDCF.

Table 1[a]

chemical formula = $C_{28}H_{36}CrN_2O_4$
a = 16.0414(4) Å
b = 10.6907(3) Å
c = 15.6571(4) Å
α = 90°
β = 90°
γ = 90°
V = 2685.10(12) Å^3
Z = 4
fw = 516.59
space group = *Pnma* (No. 53)
T = 141(2) K
λ = 0.710 73 Å (Mo Kα)
ρ_{calc} = 1.278 g cm^{-3}
μ = 4.61 cm^{-1}
R1(F) = 0.0459 [$I > 2\sigma(I)$]
wR2 (F^2) = 0.1083 (all data)

[a] R1 = $\sum||F_o| - |F_c||/(\sum|F_o|)$; wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. GOF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(M - N)\}^{1/2}$, where where M is the number of reflections and N is the number of parameters refined.

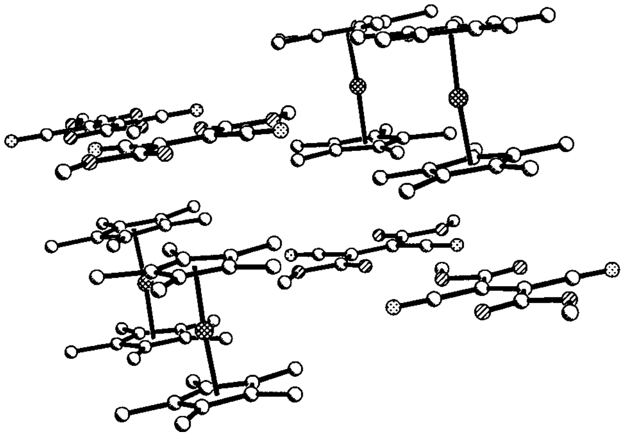

Figure 2. Packing diagram for [Cr(Cp*)$_2$][DMeDCF].

Table 2

	Cr−Cr separation	
	[Cr(Cp*)$_2$][TCNE]	[Cr(Cp*)$_2$][DMeDCF]
intrastack	10.953	10.691
interstack in-registry	8.002	9.103
nearest out-of-registry	9.459 9.459	9.545
next-nearest out-of-registry	9.709 9.872	11.156

The structure of the DMeDCF radical anion has not been previously characterized. In the present structure, it is located on a mirror plane and is thus rigorously flat, if the hydrogen atoms are disregarded. The relevant bond lengths for [DMeDCF]$^{\bullet/-}$ can be compared to those of the previously reported structure of the neutral parent.[18] Reduction to the radical anion results in no lowering of symmetry and only modest bond length increases over the whole molecule. Comparing the radical anion to the neutral parent, respectively, the most significant changes appear in the olefinic C═C (1.413(4) vs 1.344(8) Å) and the ester C−O bonds (1.360(4) vs 1.315(7) Å). This result is consistent with the related changes observed for TCNE vs [TCNE]$^{\bullet/-}$, a consequence of the expected high delocalization of the added charge.[19] Unlike the TCNE analogue, no disorder is found on the anion sites.

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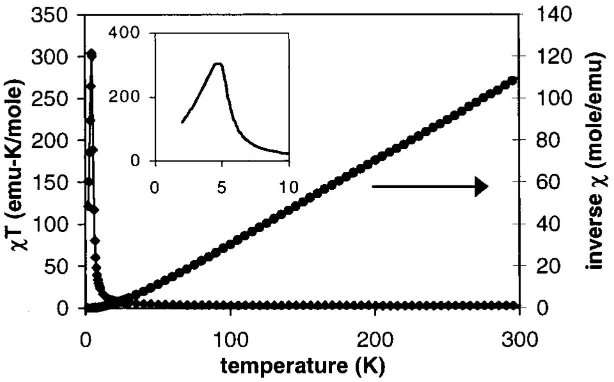

Figure 3. Plots of χT vs T (◆) and inverse χ vs T (●) for [Cr(Cp*)$_2$][DMeDCF] measured in 100 G. Inset: expansion of 0−10 K region.

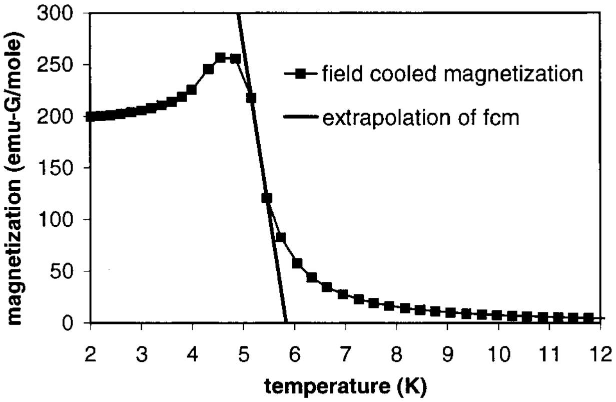

Figure 4. Plot of magnetization vs temperature in 2 G applied field for [Cr(Cp*)$_2$][DMeDCF].

Magnetic Properties. We have collected magnetic data on three independently synthesized samples of **1** including an ensemble of the crystals from which we chose a crystal large enough for X-ray diffraction analysis. X-ray powder diffraction confirms that we selected a crystal representative of the bulk. Figure 3, a representative plot of χT vs T measured at 100 G, exhibits a dramatic rise in χT as the temperature is lowered, from 2.72 emu K/mol at room temperature to a value of 300 emu K/mol below 10 K. Above 50 K, the data obey the Curie−Weiss law, giving $C = 2.53$ emu K/mol and $\theta = +23$ K. The value of C is close to the expected value (2.24 emu K/mol), and the value of θ is quite comparable to that observed by Miller et al. for the TCNE analogue (+24 K).[5] This suggests that ferromagnetic intrastack couplings in these two compounds are of similar magnitude and sign. The value of the Curie−Weiss θ is a reflection of this dominant interaction in this class of compounds.

Unfortunately, θ for [Cr(Cp*)$_2$][TCNE] has not been unambiguously identified. A second report for [Cr(Cp*)$_2$][TCNE] by Eichhorn et al.[4] and a report for [Cr(Cp*)$_2$][TCNQ] by Broderick et al.[6] both find $\theta \approx +12$ K. Our own examination of [Cr(Cp*)$_2$][TCNE] gives $\theta = +15$ K, which would then seem to indicate that at least part of the difference in T_{Curie} between this compound and **1** can be ascribed to stronger intrastack coupling in the latter.

The Curie temperature was determined from the measurement of magnetization as a function of temperature in a 2 G applied field. Extrapolation of the steepest part of field-cooled data gives a T_{Curie} of 5.7 ± 0.1 K (Figure 4). Alternatively defining it by the midpoint of the transition or the maximum in dM/dT gives 5.3 ± 0.1 K. By either measure, this is higher than that of any previously measured decamethylchromocene-based magnet.

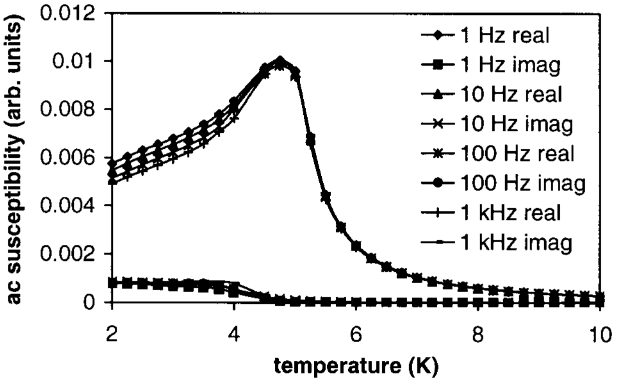

Figure 5. Plot of ac susceptibility at several frequencies for [Cr(Cp*)$_2$][DMeDCF].

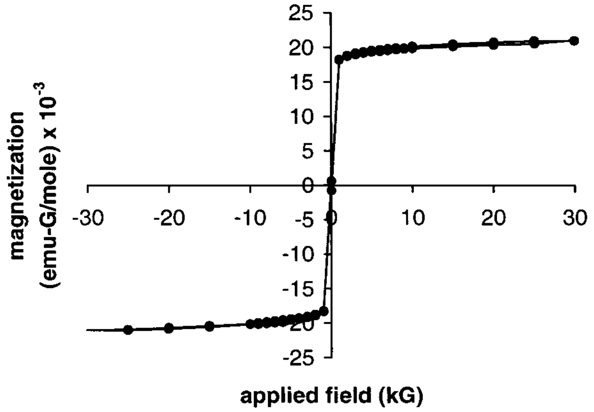

Figure 6. Plot of magnetization vs applied field at 1.8 K for [Cr(Cp*)$_2$][DMeDCF].

While the apparently stronger intrastack ferromagnetic interactions favor this result, the slightly greater interstack distances could also be playing a role. As suggested by Wynn et al.,[20] the interstack interactions are possibly a convolution of the effects of several mechanisms that gives rise to a competition between ferromagnetic and antiferromagnetic coupling. Exchange coupling, due to the overlap of partially occupied orbitals, falls off very strongly with distance and often leads to antiferromagnetic coupling.[21] Thus, higher T_{Curie} for [Cr(Cp*)$_2$][DMeDCF] could also be the result of a decreased antiferromagnetic contribution due to greater separation between the stacks relative to [Cr(Cp*)$_2$][TCNE].

Measurement of the ac susceptibility supports the existence of a ferromagnetic phase transition. A peak in χ' at 4.8 K is accompanied by the presence of nonzero χ'' (Figure 5). Unlike manganese analogue, these data are nearly frequency-independent, indicating little glassiness in the ordered state. We have previously noted the correlation between frequency-dependent ac susceptibility and the presence of hysteresis in this class of compounds.[14]

The plot of M vs H determined at 1.8 K indicates that **1** is a soft ferromagnet; the coercivity at this temperature is less than 50 G (Figure 6). The value of the saturation magnetization, M_{sat}, approximately 22 000 emu G/mol, is approaching the expected

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value calculated for three unpaired electrons on the donor and one on the acceptor (22 340 emu G/mol if $g = 2$ for both species).

Conclusion

We have synthesized and structurally characterized a new one-to-one charge-transfer salt ferromagnet constructed from decamethylchromocene and dimethyl dicyanofumarate. The compound exhibits $T_{\mathrm{Curie}} = 5.6$ K, higher than other chromocenium-based magnets, and negligible coercivity at 1.8 K. The structure of the DMeDCF radical anion is not significantly different from that of the neutral molecule, indicating a high degree of delocalization of the added negative charge. The Curie−Weiss θ for $[\mathrm{Cr(Cp^*)_2}][\mathrm{DMeDCF}]$ is apparently higher than for its TCNE analogue, reflective of stronger intrastack interactions in the former, which could explain part of the difference in T_{Curie}. The chromium−chromium interstack separations in $[\mathrm{Cr(Cp^*)_2}][\mathrm{DMeDCF}]$ are, for the most part, greater than for its TCNE analogue, and T_{Curie} for the former compound is slightly higher, consistent with weakening of an antiferromagnetic contribution to the interstack interactions due to decreased overlap between partially occupied orbitals in adjacent stacks.

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Supporting Information Available: Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center (reference number CCDC 132188). This information is also available free of charge via the Internet at http://pubs.acs.org.

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