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Synthesis, Structure, and Magnetic Characterization of a Hysteretic Charge-Transfer Salt Metamagnet, Decamethylferrocenium 2,3-Dicyano-1,4-Naphthoquinonide, $[Fe(Cp^*)_2][DCNQ]$

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The synthesis and single-crystal structure of a new one-to-one charge-transfer salt, derived from decamethylferrocene and 2,3-dicyano-1,4-naphthoquinone, are described. $[Fe(Cp^*)_2][DCNQ]$ crystallizes in the orthorhombic space group *Pbca*, with $a = 17.3149(5)$ Å, $b = 14.6862(4)$ Å, $c = 21.0507(6)$ Å, and $Z = 8$. Magnetization vs temperature data obtained in 100 G suggest that the compound exhibits dominant one-dimensional ferromagnetic coupling and that it subsequently undergoes an antiferromagnetic phase transition below $T_N \approx 4$ K. Results of magnetization vs applied field experiments show that the compound is a metamagnet with a critical field of approximately 3 kG at 1.8 K. In the nominally antiferromagnetic state, apparent canting of the moments gives rise to a small amount of hysteresis. This picture is supported by ac susceptibility data. The ^{57}Fe Mössbauer spectrum exhibits the expected decamethylferrocenium unresolved quadrupole doublet ($\delta = 0.53$ mm/s) at 77 K and magnetic hyperfine splitting, $H_{int} = 37.9$ T, corresponding to long-range magnetic order at 1.63 K.

Introduction

The synthesis of one-to-one charge-transfer (CT) salts, built from first-row decamethylmetallocenes and organic one-electron acceptors, represents one very successful strategy for the synthesis of systematically related magnetic solids that exhibit cooperative interactions. The best-studied example of ferromagnetism in this class of solids is decamethylferrocenium tetracyanoethenide, $[Fe(Cp^*)_2][TCNE]$, which orders below 4.8 K.[1]

Although a phase transition to an antiferromagnetically ordered state is relatively uncommon in this structural class,[2] metamagnetism has been documented for several CT salts including $[Fe(Cp^*)_2][TCNQ]$ (TCNQ = dicyanoquinodimethane),[3] $[Mn(Cp^*)_2][DDQ]$ (DDQ = 2,3-dichloro-5,6-dicyanoquinone),[4] and $[Mn(Cp^*)_2][DEtDCF]$, (DEtDCF = diethyl dicyanofumarate).[5] Metamagnetism is characterized by an antiferromagnetically ordered ground state in zero applied magnetic field that switches to ferromagnet-like ordering above a certain critical field. For each of the compounds above, ferromagnetic coupling within the donor−acceptor stacks and a competition between ferromagnetic and antiferromagnetic coupling between the stacks give rise to the observed properties.

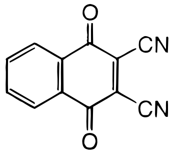

Figure 1. 2,3-Dicyano-1,4-naphthoquinone.

We have recently focused on identifying new acceptors for magnetism research by examining the extensive electrically conducting organic CT salt literature.[6] For both disciplines, candidate acceptors must possess stable radical anionic states and extended π orbitals for facilitating stacking, as well as exhibit reversible electrochemistry at appropriate potentials. One such acceptor that has been investigated in the context of conductivity[7] but that has not been previously reacted with a decamethylmetallocene is 2,3-dicyano-1,4-naphthoquinone, DCNQ, (Figure 1). This compound can be synthesized from 2,3-dichloro-1,4-naphthoquinone by published procedures.[8]

We have found that the reaction of DCNQ with decamethylferrocene, $Fe(Cp^*)_2$, gives a one-to-one salt, $[Fe(Cp^*)_2]$-$[DCNQ]$, **1**, that adopts a mixed stack geometry possessing both in-registry and out-of-registry donor−acceptor interactions. Magnetic measurements on this compound reveal it to be a new metamagnet but with an interesting modification not previously reported for CT salts: there appears to be slight canting of the

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magnetic moments in the nominally antiferromagnetic state, giving rise to a small amount of hysteresis.

Experimental Section

All reagents were purchased from Aldrich and were used as received. Elemental analyses were performed by Desert Analytics, Tucson, AZ. 2,3-Dicyano-1,4-naphthoquinone was synthesized by literature procedures.[8]

Decamethylferrocenium Dicyanonaphthoquinonide, [Fe(Cp*)$_2$]-[DCNQ], 1. 2,3-Dicyano-1,4-naphthoquinone (75 mg, 0.36 mmol) is dissolved in 30 mL of CH_2Cl_2 at −70 °C. Likewise, decamethylferrocene (120 mg, 0.37 mmol) is dissolved in 15 mL of CH_2Cl_2 at −70 °C. The solutions are mixed, whereupon a red microcrystalline solid forms immediately. The reaction mixture is held at −70 °C for 5 min and then diluted with 15 mL of hexane. The precipitate is collected by vacuum filtration on a prechilled glass frit and washed with additional cold hexane. Yield: 162 mg (84%). Anal. Calcd for $C_{32}H_{34}FeN_2O_2$: C, 71.91; H, 6.41; N, 5.24. Found: C, 71.51; H, 6.29; N, 5.09. IR (Nujol): ν_{CN} 2190 cm^{-1}.

X-ray Crystallography. X-ray diffraction was performed on a Siemens SMART CCD diffractometer equipped with a locally modified LT-2A low-temperature apparatus. A crystal suitable for X-ray diffraction was grown by slow diffusion of hexane into a CH_2Cl_2 solution at room temperature. 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 7121 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. Data above 0.75 Å were discarded because of poor intensity statistics. Structure solution via direct methods in the centrosymmetric space group *Pbca* revealed the non-hydrogen structure. Hydrogens were placed at calculated geometries and freely refined in subsequent cycles of least-squares refinement. There was no disorder, and the final residual density map was essentially flat.

Physical Measurements. Magnetic measurements were performed on Quantum Design MPMS 5S and 7 superconducting quantum interference device (SQUID) magnetometers as previously described.[9] A correction was applied to the 100 G magnetization vs temperature data to account for a small ferromagnetic impurity equivalent to 9 ppm saturated iron. The amplitude of the ac field was 5 G, and the measurements were performed with zero dc bias. ^{57}Fe Mössbauer spectroscopy measurements were made with a conventional constant acceleration spectrometer in zero applied field. The samples consisted of approximately 50 mg of crystalline material packed into cylindrical 12 mm diameter nylon holders, sealed in 5 min epoxy.

Results and Discussion

Bryce and co-workers have previously reported studies of DCNQ and [DCNQ]$^{\bullet/-}$.[7] They found that DCNQ exhibits a reversible one-electron reduction at approximately 0.2 V vs SCE, making it a somewhat stronger acceptor than TCNQ and somewhat weaker than DDQ. The radical anion, [DCNQ]$^{\bullet/-}$, was prepared by them via the lithium iodide reduction of 2-dicyanomethyleneindan-1,3-dione. The magnetic properties of several salts containing [DCNQ]$^{\bullet/-}$ were determined including, for example, M[DCNQ] where M = Li, Na, Rb, and Cs. In most instances, the unpaired electrons on adjacent [DCNQ]$^{\bullet/-}$ anions were found to couple antiferromagnetically to give essentially diamagnetic solids. However, the case where M = tetrabutylammonium was reported to be paramagnetic, indicating the presence of discrete $S = {}^1/_2$ radical anions, though no structure was determined. This result suggests that DCNQ might be a viable candidate building block for the construction of a molecule-based magnet provided one can avoid dimerization of the anions.

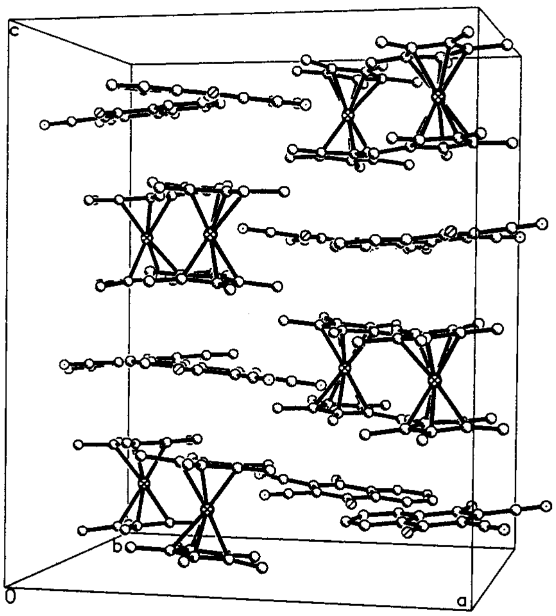

Figure 2. Packing diagram for [Fe(Cp*)$_2$][DCNQ].

Table 1. Crystallographic Data for Decamethylferrocenium 2,3-Dicyano-1,4-naphthoquinonide^a

chemical formula = $C_{32}H_{34}FeN_2O_2$	fw = 534.46
a = 17.3149(5) Å	space group = *Pbca* (no. 61)
b = 14.6862(4) Å	T = 144(2) K
c = 21.0507(6) Å	λ = 0.710 73 Å (Mo Kα)
α = 90°	ρ_{calc} = 1.326 g cm^{-3}
β = 90°	μ = 5.95 cm^{-1}
γ = 90°	R1(F) = 0.0594 [$I > 2\sigma(I)$]
V = 5353.0(3) Å^3	wR2(F^2) = 0. 0.1170 (all data)
Z = 8	

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

We have prepared **1** by reacting the neutral donor and acceptor in dichloromethane. The compound crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell (Figure 2 and Table 1). The structure consists of mixed stacks of donors and acceptors possessing in-registry and out-of-registry interstack interactions common to related compounds.[1] The symmetry and bond lengths of the radical anion indicate that the unpaired electron is highly delocalized, as expected. Bryce and co-workers have reported one crystal structure of the anion,[7] but weak dimerization in the solid state in their structure makes detailed comparisons to the present structure meaningless. Because of the possibility of polymorphism in CT salts, we have used X-ray powder diffraction data to ensure that the polycrystalline samples used for magnetic measurements possess the same structure as the large crystal for which we have solved the structure. No evidence of second phases has been found.

Utilizing a SQUID magnetometer, we have measured the properties of polycrystalline **1**. The plot of χT vs T measured at 100 G exhibits a significant increase in χT as the temperature is lowered, rising from a value of 1.3 emu K mol^{-1} at 50 K to over 7 emu K mol^{-1} below 5 K (Figure 3). The plot of χ^{-1} vs T above 10 K is linear and gives a Curie−Weiss θ of 4 K. These results indicate the presence of ferromagnetic coupling, presumably within the donor−acceptor stacks. From the value

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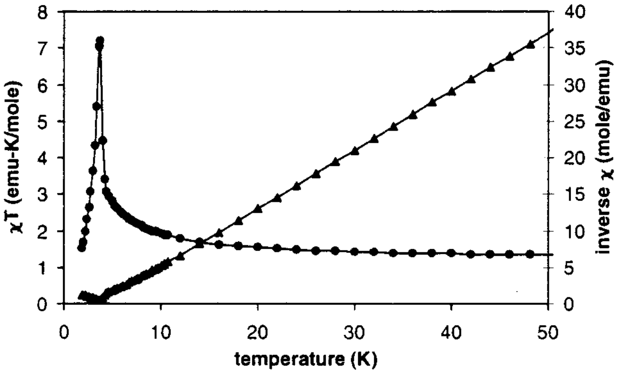

Figure 3. Plot of χT vs T and χ^{-1} vs T for [Fe(Cp*)$_2$][DCNQ] measured at 100 G.

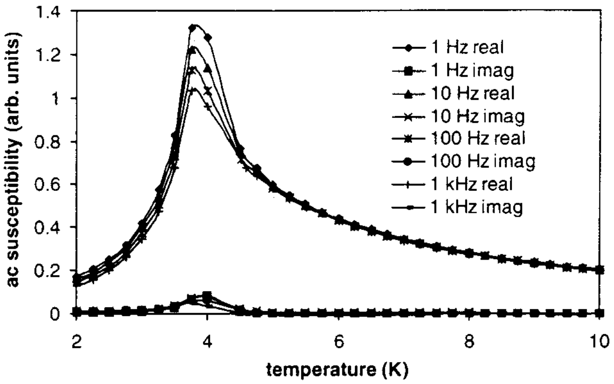

Figure 4. Plot of ac susceptibility for [Fe(Cp*)$_2$][DCNQ].

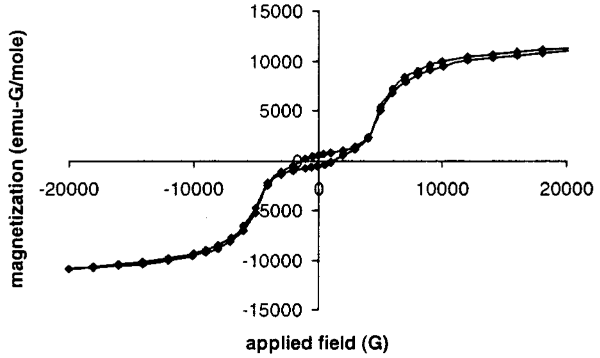

Figure 5. Plot of M vs T at 1.8 K for [Fe(Cp*)$_2$][DCNQ].

of the Curie constant, C, and assuming $g = 2.0$ for the organic acceptor, we calculate $g = 3.0 \pm 0.1$ for [Fe(Cp*)$_2$]$^+$, a value consistent with previous reports on this cation[1] and indicating a significant orbital contribution from the ^{2}E ground state.

As the temperature is decreased below approximately 4 K, a peak in χ vs T (and consequently χT vs T) at T_N is observed, indicating an apparent antiferromagnetic phase transition. However, ac susceptibility data obtained in zero dc bias (Figure 4), while supporting the existence of a phase transition, is not consistent with normal antiferromagnetism. The peak in χ' is accompanied by the onset of a small nonzero χ'' component. This imaginary component to the susceptibility is associated with the presence of hysteresis, not characteristic of an uncanted (collinear) antiferromagnet.

The plot of magnetization vs applied field, determined at 1.8 K, provides resolution to this apparent contradiction (Figure 5). It has a double "S" shape indicative of a metamagnet, a compound that switches from an antiferromagnetic ground state to a ferromagnetic-like state upon the application of a sufficiently large field. The critical field, H_{crit}, at this temperature is approximately 3 kG. An unusual property of **1** is the presence of hysteresis at 1.8 K in the nominally antiferromagnetically ordered state. At this temperature, the compound exhibits approximately 1200 G of coercive field and 500 emu G mol^{-1} of remanence. This result is quite reproducible in samples derived from separate synthetic procedures. These data suggest that that below 3 kG, in the antiferromagnetic state of **1**, the moments are canted slightly, producing a so-called weak ferromagnet. It is this condition that gives rise to hysteresis and a nonzero out-of-phase component to the ac susceptibility. This phenomenon has been observed previously in extended solids such as the one-dimensional-chain compound, cyclohexylammonium copper(II) trichloride.[10] It is important to note that among metamagnets, hysteresis due to canting, as seen here, is different from the hysteresis sometimes observed around the antiferromagnetic-to-ferromagnet-like phase transition. In the latter, the sample does not switch back reversibly from ferromagnet-like to antiferromagnetic order as the field is decreased from a high value through H_{crit}.[5] We have associated this behavior with glassiness of the spin state.

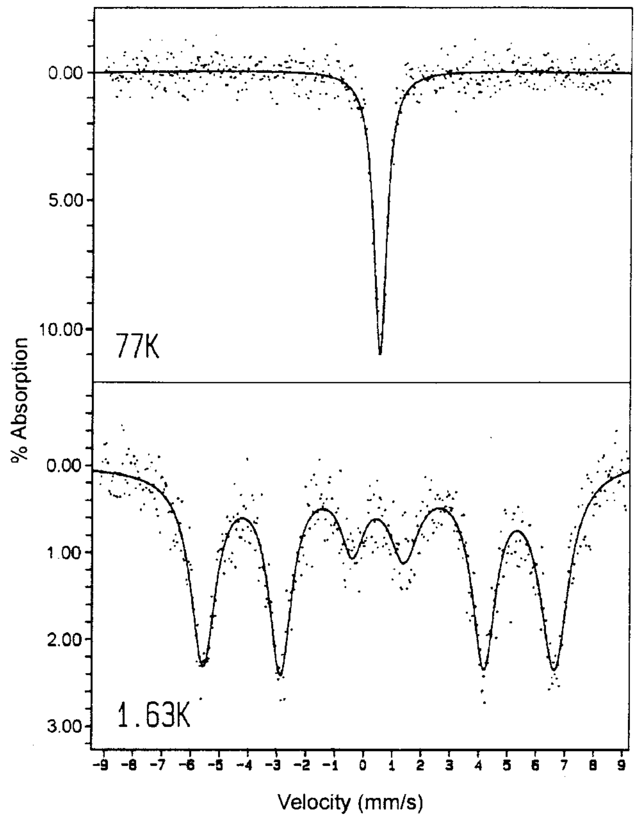

Figure 6. ^{57}Fe Mössbauer spectra measured at 77 and 1.63 K. Velocities are reported relative to that of natural iron foil.

At 20 kG, the magnetization is approximately 11 000 emu G mol^{-1}, approaching the expected value (14 000 emu G mol^{-1}, using $g = 3.0$ for the decamethylferrocenium cation) consistent with ferromagnetic coupling of the unpaired electrons (Figure 5). The low value of the saturation magnetization might indicate canting in the ferromagnet-like state as well.

Zero applied field ^{57}Fe Mössbauer spectroscopy (Figure 6) has been used to examine **1** both above and below the transition temperature. The data have been modeled by unconstrained

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Lorentzian fits. At 77 K, the typical $[Fe(Cp^*)_2]^+$ unresolved quadrupole doublet ($\Gamma = 0.33$ mm/s) with an isomer shift of 0.45 mm/s (relative to natural iron) and quadrupole splitting of 0.17 mm/s is observed, parameters typical of the ferrocenium cation. This establishes the low-spin nature of the cation. At 4.2 K (not shown), this resonance is significantly broadened, which is likely due to some degree of slow paramagnetic relaxation above T_N. Both spin−lattice (due to the low temperature and lessening of lattice phonon effects) and spin−spin relaxation times (smallest Fe−Fe distance = 8.78 Å)[11] are lengthened relative to those at 77 K.

Finally, at 1.63 K, well below T_N, one sees resolved magnetic hyperfine splitting corresponding to long-range magnetic order. These data can be fit to yield an isomer shift of 0.50 mm/s, a small quadrupolar shift of 0.35 mm/s, and an internal hyperfine field (H_{int}) of 37.9 T (379 kG). This large value of H_{int} is fairly common for slowly relaxing or magnetically ordered decamethylferrocenium systems and has, as its origin, the local g factor anisotropy that leads to significant orbital contributions to the internal field.

The absence of any other signal is evidence that only one magnetic phase is present in the sample. The observation that the ratio of peaks is not the usual 3:2:1:1:2:3 can be rationalized by noting that this expectation assumes that the sample is composed of a perfectly randomly oriented powder. However, because of suspected air and water sensitivity, the sample was not ground and instead consists of partially oriented microcrystals such as those used for the magnetic measurements. The latter leads to magnetic texture in the Zeeman spectrum. The line width broadening at 1.63 K is somewhat greater than expected for a magnetically ordered compound. We ascribe this to relaxation broadening effects that commence above T_N but that persist to temperatures below T_N until the sample is fully ordered and magnetically saturated on a Mössbauer spectroscopy time scale. This phenomenon has previously been observed in the study of $Fe(NH_4)(SO_4)_2\cdot 12H_2O$ and to a lesser extent $K_3Fe(CN)_6$.[12]

Conclusion

The magnetic properties of decamethylferrocenium 2,3-dicyano-1,4-naphthoquinonide, $[Fe(Cp^*)_2][DCNQ]$, have been measured and interpreted in the context of an unusual metamagnet. In the nominally antiferromagnetic state, apparent slight canting of the moments gives rise to hysteresis centered about $H = 0$ G. This interesting result, on a compound that utilizes a previously overlooked one-electron acceptor, suggests that other related building blocks should be examined for the construction of charge-transfer salt magnets. Future work will include an examination of the decamethylmanganocene and decamethylchromocene analogues of this compound.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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