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Ferromagnetism in Decamethylchromocenium Tetracyanoethylenide: Configuration Mixing Does Not Explain Ferromagnetic Spin Coupling in Metallocenium Charge-Transfer Salts

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Introduction

Ferromagnetic spin–spin coupling is uncommon in molecular crystals but is often seen in integrated-stack charge-transfer (CT) D^+–A^- salts containing the $[M(C_5(CH_3)_5)_2]^+$ cation. Until recently, the prevailing explanation for ferromagnetic D^+–A^- coupling in these materials was based on McConnell's remark that it might be achieved by configuration mixing through a virtual CT state, provided that either the donor or acceptor has an orbitally degenerate ground state.[1] This mechanism would explain the observation of ferromagnetism in $[Fe(C_5(CH_3)_5)_2][TCNE]$ (**1**)[2] (TCNE = the tetracyanoethylenide anion), $[Mn(C_5(CH_3)_5)_2][TCNQ]$ (**2**)[3] (TCNQ = the tetracyano-*p*-quinodimethanide anion), and $[Mn(C_5(CH_3)_5)_2][TCNE]$ (**3**),[4] in which the cations have $S = {}^1/_2$ ($^2E_{2g}$) and $S = 1$ ($^3E_{2g}$ or $^3A_{2g}$) ground states, respectively.[5] To test this proposal, we recently prepared the related compound $[Cr(C_5(CH_3)_5)_2][TCNQ]$ (**4**).[6] Here the CT mechanism would predict antiferromagnetic coupling of the D^+ and A^- spins, as the ground-state electronic configuration of the cation ($S = {}^3/_2$, $^4A_{1g}$) is orbitally nondegenerate.[5] However, **4** not only shows ferromagnetic intrachain coupling but is also a bulk ferromagnet, with a critical temperature $T_c = 3.1$ K.[6]

Although this discovery invalidates the CT mechanism as an explanation for the ferromagnetism in the isostructural series of TCNQ salts $[M(C_5(CH_3)_5)_2][TCNQ]$ (M = Fe, Mn, Cr), preliminary references to data identifying $[Cr(C_5(CH_3)_5)_2][TCNE]$ (**5**) as a *ferri*magnet[7] cloud the issue. Ferrimagnetism would stem from *anti*ferromagnetic intrachain coupling between the $S = {}^3/_2$ $[Cr^{III}(C_5(CH_3)_5)_2]^+$ and the $S = {}^1/_2$ $TCNE^-$, resulting in a ferromagnetic alignment of the residual moments, with a spin of $S = {}^3/_2 - {}^1/_2 = 1$ per formula unit. Furthermore, recent theoretical examinations[8,9] of the CT model as a possible mechanism for ferromagnetism in metallocenium CT salts have discussed only the TCNE series $[M(C_5(CH_3)_5)_2][TCNE]$ (M = Fe, Mn, Cr, Ni) and have not considered that with TCNQ. We have therefore reexamined the properties of **5** and report that $[Cr(C_5(CH_3)_5)_2][TCNE]$ in fact displays *ferro*magnetic D^+–A^- intrachain coupling and indeed appears to be a bulk ferromagnet at low temperatures.

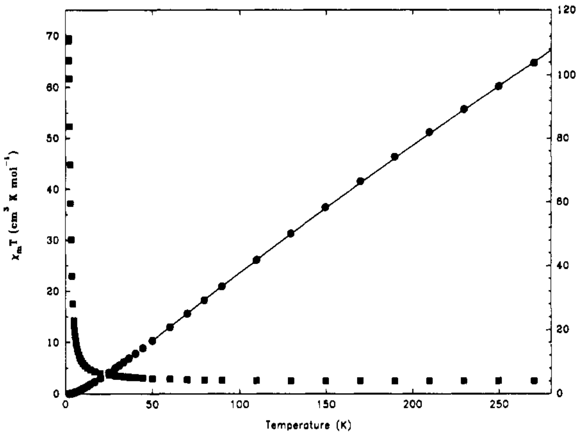

Figure 1. Temperature dependence of χ_mT (squares) and χ_m^{-1} (circles) for polycrystalline **5** at 250-G applied field. The solid line represents a fit of $\chi_m^{-1}(T)$ for $T > 50$ K as described in footnote 10. Fit parameters C and Θ are given in the text.

Experimental Section

The 1:1 CT salt **5** was prepared by combining equimolar acetonitrile solutions of $[Cr(C_5(CH_3)_5)_2]$[5] and TCNE (Aldrich) under a nitrogen atmosphere and was recrystallized from acetonitrile. The compound is very air-sensitive and must be stored and manipulated anaerobically. Elemental analysis was determined by Desert Analytics, Tucson, AZ. Anal. Found: C, 68.64; H, 6.54; N, 12.20. Calcd for $C_{26}H_{30}N_4Cr$: C, 69.31; H, 6.71; N, 12.44.

The magnetization, *M*, of polycrystalline **5** was measured with a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. The samples were contained in glass holders designed to minimize the holder correction. They consist of a uniform glass tube that incorporates a thin platform sealed across the middle. With this design only the platform contributes to the background. The sample tubes were loaded in a glovebox under a nitrogen atmosphere, packed with a glass wool plug, and sealed under vacuum.

Results and Discussion

The room-temperature value $\chi_mT = 2.60$ cm^3 K mol^{-1} for **5** corresponds to $\mu_{eff} = 4.56$ μ_B, which is close to the spin-only value (4.24 μ_B) for an uncorrelated two-spin system with $S(D^+) = {}^3/_2$ and $S(A^-) = {}^1/_2$ and $g = 2$ for both spins. Field-cooled magnetization data for **5** recorded from 280 to 1.9 K at 250 G are shown in Figure 1, plotted as χ_mT and χ_m^{-1} vs T. χ_mT is essentially constant from 280 to ~50 K, and χ_m^{-1} vs T over the same interval can be fit to the sum of a Curie–Weiss term, $\chi_{CW} = C/(T - \Theta)$, and a diamagnetic term, χ_d (Figure 1).[10] As expected, the fit gives a Curie constant, $C = 2.25$ cm^3 K mol^{-1}, that matches the value of $C = 2.27$ cm^3 K mol^{-1} predicted for one $S = {}^3/_2$ and one $S = {}^1/_2$ spin per formula weight, both with $g = 2.0$.[11] The Weiss constant is positive, $\Theta = +12.2$ K; thus, the dominant intrastack D^+–A^- spin coupling is ferromagnetic. For comparison, $\Theta = +10.5$ and $+11.6$ K for ferromagnets **2** and **4**, respectively.

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(10) Magnetization data were not corrected for sample holder or core diamagnetism; however, the data were fit to $\chi_m = C/(T - \Theta) + \chi_d$, yielding a diamagnetic correction of 8.8×10^{-4} cm^3 mol^{-1}, one-third of which can be accounted for by core diamagnetism as estimated from Pascal's constants and the rest of which can be attributed to the sample holder. This fit is indicated by the solid line in Figure 1. A more accurate measurement of the diamagnetic contribution was not performed because of the sample loading technique required by the extreme air-sensitivity of the sample.

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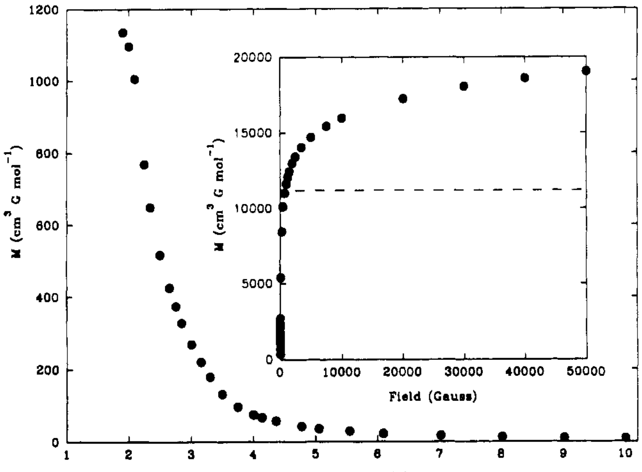

Figure 2. Field-cooled magnetization M of polycrystalline **5** at 15-G applied field. Inset: field dependence of the magnetization for polycrystalline **5** at 2 K. The dashed line represents the expected M_{sat} if **5** were a *ferri*magnet.

As the sample is cooled below $T \sim 15$ K, χ_mT increases markedly, suggesting a transition to a ferromagnetically ordered state. This possibility was examined by measuring the magnetization as a function of temperature from 10 to 1.9 K. As **5** is cooled in a low field (15 G), the abrupt increase in the magnetization expected for such a transition is apparent at $\sim$4 K (Figure 2). The transition temperature, defined here as the maximum of the slope, dM/dT, is $T_c \sim 2.1$ K, as compared to $T_c = 3.1$ K for $[Cr(C_5(CH_3)_5)_2][TCNQ]$. Definitions of T_c that involve extrapolations of low-temperature data for **5** would give higher values of T_c (up to $\sim$4 K). The field dependence of the magnetization at 2 K is shown in the inset to Figure 2. This curve is characteristic of a polycrystalline bulk ferromagnet, with its steep rise to $M \sim 17\,000$ cm³ G mol⁻¹ at an applied field of 10 000 G, followed by a shallower increase. The magnetization clearly is still rising at the highest field measured (50 000 G), indicating that saturation has not yet been reached. The magnetization at 50 000 G, $M = 1.90 \times 10^4$ cm³ G mol⁻¹, nonetheless approaches the value of $M_{\text{sat}} = N\beta[g_DS(D^+) + g_AS(A^-)] = 22\,333$ cm³ G mol⁻¹ expected for a ferromagnet with $g_D = g_A = 2$, $S(D^+) = {}^3/_2$, and $S(A^-) = {}^1/_2$. In contrast, if **5** were a ferrimagnet, the saturation magnetization would be proportional to the difference of the two spins: $M_{\text{sat}} = N\beta[g_DS(D^+) - g_AS(A^-)] = 1.12 \times 10^4$ cm³ G mol⁻¹. As this value is far exceeded (Figure 2, inset), **5** *cannot* be a ferrimagnet. This conclusion is particularly secure because the fit to the high-temperature values of χ_m^{-1} (see above) confirms that the ^4A state of $[Cr(C_5(CH_3)_5)_2]^+$ does not exhibit significant orbital contributions, which might increase M_{sat} over that expected for a $g = 2$ ferrimagnet.

The shape of the magnetization curve further rules out the possibility that **5** is a metamagnet, with weak antiferromagnetic coupling between ferromagnetically coupled chains. Metamagnetic materials show a field-dependent change from an antiferromagnetic to a ferromagnetic ground state and are characterized by M vs H plots that have a positive curvature at low fields and a negative curvature at high fields.[7a] Examples involving metallocenium CT salts include $[Fe(C_5(CH_3)_5)_2][TCNQ]$[12] and $[Mn(C_5(CH_3)_5)_2][M(tfd)_2]$ (tfd = bis(trifluoromethyl)ethylenedithiolate; M = Ni, Pd, Pt).[13] Figure 2 clearly shows that the curvature of the M vs H plot for **5** is negative even for applied fields as low as 5–50 G, which is not characteristic of a metamagnet but of a material displaying ferromagnetic interchain coupling—a bulk ferromagnet.

The combination of the abrupt rise in the field-cooled magnetization at $\sim$4 K and the large value of the saturation magnetization clearly demonstrate that the D^+–A^- coupling in $[Cr(C_5(CH_3)_5)_2][TCNE]$ is ferromagnetic and indicates that the material is a bulk ferromagnet. This result removes any uncertainty about the systematic dependence of the sign of the D^+–A^- spin coupling on the electronic structure of the $[M(C_5(CH_3)_5)_2]^+$ cation. The six CT salts $[M(C_5(CH_3)_5)][TCNE$ or $TCNQ]$ (M = Fe, Mn, Cr) all show ferromagnetic D^+–A^- intrachain coupling. This is in contrast to the predictions of the configuration mixing mechanism for intrachain D^+–A^- coupling, which requires antiferromagnetic coupling for the two salts with M = Cr.[1b] Hence this mechanism does *not* provide an appropriate framework for understanding spin–spin coupling in these charge-transfer salts.

Among the other possible mechanisms for ferromagnetic spin–spin coupling, the most attractive alternative is McConnell's proposal based on spin-polarization,[14] which was recently examined in relation to metallocenium CT salts by Kahn and coworkers.[15] In all three of the decamethylmetallocenium ions under consideration (Fe, Mn, Cr) the unpaired electron(s) reside in molecular orbitals (a_{1g} and e_{2g}) which are centered on the metal atom and orthogonal to orbitals on $C_5(CH_3)_5$. Spin polarization should lead to negative spin density on the $C_5(CH_3)_5$ ring.[16] Antiferromagnetic coupling between this negative spin density and the spin on the neighboring acceptor molecule would result in an overall *ferro*magnetic coupling of the total spin moments on the metal and the acceptor. This spin-polarization mechanism thus explains the ferromagnetism in all of the $[M(C_5(CH_3)_5)_2]^+$-containing materials in which it has been observed.

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