

Novel Co-operative Magnetic Properties of Decamethylmanganocenium 2,3-Dichloro-5,6-dicyanobenzoquinoneide, $^3[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+[\text{DDQ}]^-$

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The electron-transfer salt $^3[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+[\text{DDQ}]^-$, isomorphous to orthorhombic $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+[\text{DDQ}]^-$, has been prepared. It exhibits a complex field-dependent magnetic phase diagram at low temperatures with evidence for ferromagnetic coupling as well as a low moment state below 4 K for zero-field cooled samples.

Keywords: Decamethylmanganocenium 2,3-dichloro-5,6-dicyanobenzoquinoneide; Electron-transfer salt; Ferromagnetic coupling

Co-operative (bulk) magnetic behaviours have been observed for the $[\text{FeCp}_2]^+[\text{TCNE}]^-$ (Cp* = pentamethylcyclopentadienide; TCNE = tetracyanoethylene) and $[\text{FeCp}_2]^+[\text{TCNQ}]^-$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) electron-transfer salts.¹ The former has been characterized by powder neutron diffraction and single-crystal measurements to exhibit a spontaneous magnetization (ferromagnetic ground state) with a Curie temperature, T_C , of 4.8 K, whereas the latter is metamagnetic with a Néel temperature, T_N , of 2.55 K. The solution of a simple (one spin site) mean-field model shows that T_C is proportional to J and $S(S+1)$ where J is the exchange integral and S is the spin.² Attempts to enhance T_C by substituting the $S = 1/2$ Fe^{III} cation with the isostructural $S = 1$ Mn^{III} cation, *i.e.* $^3[\text{MnCp}_2]^+$, in the $[\text{TCNE}]^-$ salt were unsuccessful owing to decomposition arising from the chemical reactivity of the donor and acceptor.³ Recently, the expected trend has been realized with the report that the $[\text{TCNQ}]^-$ salt of $^3[\text{MnCp}_2]^+$ is ferromagnetic.⁴ The observed magnetic couplings are consistent with the expectations of the extended-McConnell configurational admixture model.⁵ With the goal of preparing additional molecular-based ferromagnets, the ferromagnetically coupled $[\text{FeCp}_2]^+[\text{DDQ}]^-$ (DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone) electron-transfer salt was characterized.⁶ As T_C is proportional to $S(S+1)$, we sought to prepare $^3[\text{MnCp}_2]^+[\text{DDQ}]^-$, anticipating that T_C might occur at temperatures accessible in our laboratories.

The salt $^3[\text{MnCp}_2]^+[\text{DDQ}]^-$ was prepared from $^3[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+[\text{PF}_6]^-$ (ref. 7) and $[\text{Et}_4\text{N}]^+[\text{DDQ}]^-$ [ref. 6(b)] at -20°C . Elemental analysis (Oneida Research Services) for $\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{MnN}_2\text{O}_2$ calc. (obs.): C, 60.88, (60.39); H, 5.47 (5.32); N, 5.07% (5.49%). Infrared spectra (Nujol): ν_{max} 2205 cm^{-1} (C≡N) (*cf.* 2206 cm^{-1} for $[\text{FeCp}_2]^+[\text{DDQ}]^-$).⁶ Room temperature Guinier powder diffraction analysis was used to determine the unit-cell lattice parameters ($a = 14.48 \text{ \AA}$, $b = 17.00 \text{ \AA}$, $c = 10.69 \text{ \AA}$, and $V = 2631.5 \text{ \AA}^3$) which are isomorphous to the Fe^{III} analogue ($a = 14.497 \text{ \AA}$, $b = 17.027 \text{ \AA}$, $c = 10.616 \text{ \AA}$, and $V = 2620 \text{ \AA}^3$).^{6a} Thus, although crystals suitable for single-crystal X-ray analysis are not available, powder diffraction data supports the assumption that $[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+[\text{DDQ}]^-$ possesses the $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+[\text{DDQ}]^-$ structure comprising parallel in- and out-of-register $\cdots\text{D}^+\text{A}^-\text{D}^+\text{A}^-\cdots$ chains.^{6a}

The 2–300 K Faraday balance⁸ magnetic susceptibility of $[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+[\text{DDQ}]^-$ can be fit by the Curie–Weiss expression, $\chi_M = C/(T - \theta)$. The effective moment, $\mu_{\text{eff}} [\equiv (8\chi T)^{1/2}]$, and θ values for five independently prepared samples are 4.22, 4.25, 4.30, 4.13, and 4.13 μ_B and +25.5, 25.8, 27.1, 28.8, and 31.9 K, and average 4.21 μ_B and 27.8 K, respectively. The moment is greater than expected from a randomly oriented sample based on $\langle g \rangle$ (*i.e.* 3.11 μ_B for $\langle g \rangle = 2.20^\dagger$), but less than expected for a sample oriented with the C_5 axis parallel to the magnetic field (*i.e.* 4.71 μ_B for $g_{\parallel} = 3.33$). Thus, owing to the orientational variability of polycrystalline samples, the observed effective moments are consistent with $S = 1/2$ and $S = 1$ ions per formula unit. The Curie–Weiss θ value of +26.8 K suggests significant ferromagnetic interactions. Hysteretic magnetic-field-dependent behaviour was observed below *ca.* 7 K. The 150–2000 G magnetic field dependence of the magnetization for a zero-field cooled sample previously aligned by 19.5 kG magnetic field is presented for increasing and decreasing magnetic fields in Fig. 1. Above *ca.* 3.8 K the magnetization exceeds the expectation calculated from the Brillouin function for fully aligned $S = 1$ and $S = 1/2$ spins. Thus, the data imply a complex magnetic phase diagram at low temperature. Assuming complete alignment of the crystals with the magnetic field parallel to the C_5 molecular axis, the expected saturation magnetization, M_s , of 24 200 emu G mol^{-1} is realized. This is consistent with ferromagnetic coupling. At *ca.* 4 K the magnetization abruptly drops by more than an order of magnitude depending on the applied field to a value lower than calculated from the Brillouin function, Fig. 1. At high temperature there is a field-dependent cross-over from a low to a high magnetization state. This is suggestive of the presence of perhaps both a spin–Peierls and metamagnetic transitions. However, since spin–Peierls transitions occur only in antiferromagnetic states, complex magnetic behaviours must be operative for the material. Details of the phase diagram consistent with both the low- and high-field cooling for DDQ as well as the other dihalo-DDQ salts will be reported later.

[†] $g_{\parallel} = 3.33$, $g_{\perp} = 1.64$ and $\langle g \rangle = 2.20$ were observed for neutral MnCp_2^+ at 4 K in methyltetrahydrofuran. Under similar conditions attempts to determine the EPR of $[\text{MnCp}_2]^+[\text{PF}_6]^-$ were unsuccessful.

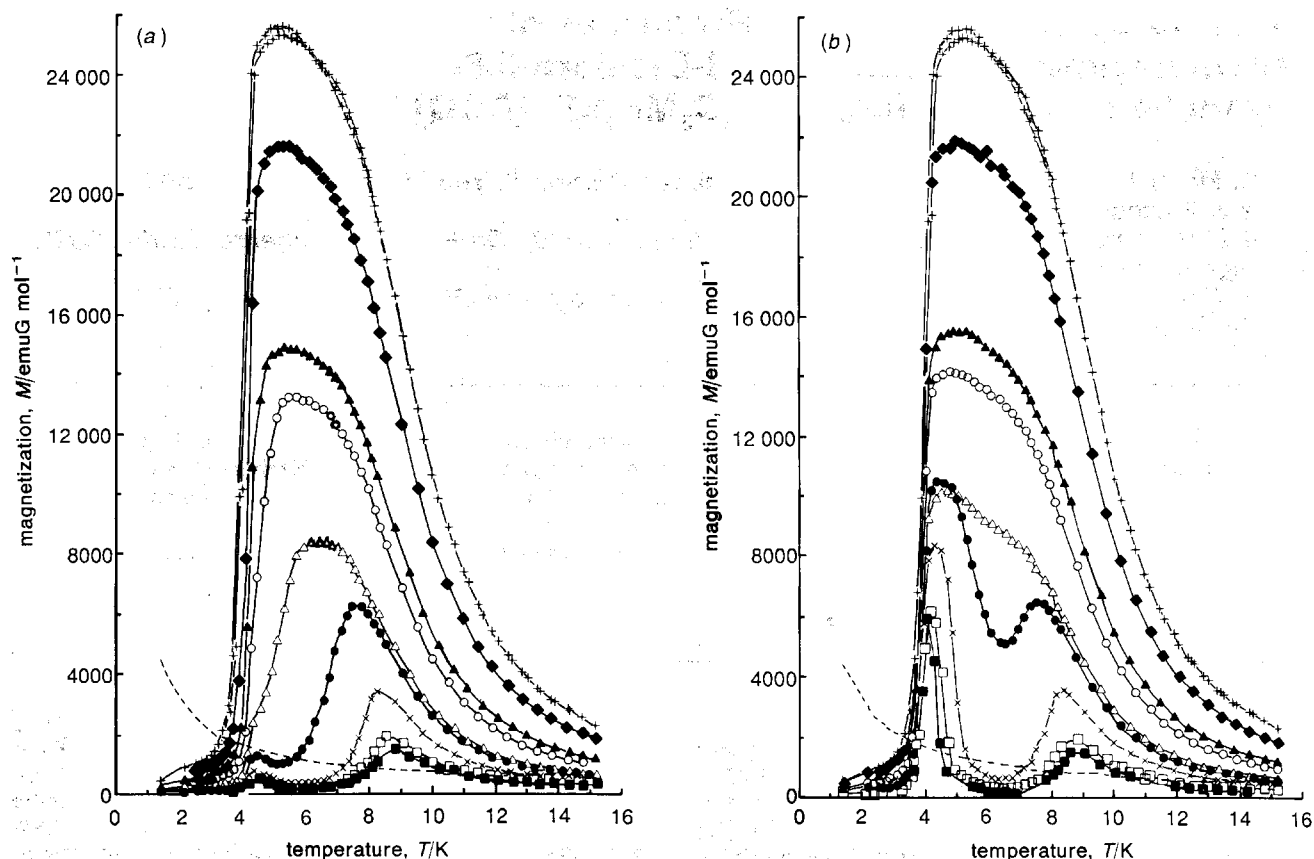


Fig. 1 Molar magnetization, M , as a function of temperature, T , for a zero-field cooled polycrystalline sample of $[\text{MnCP}_2]^+[\text{DDQ}]^-$ previous aligned in 19.5 kG at 150 (■), 200 (□), 300 (x), 400 (●), 500 (△), 750 (○), 1000 (▲), 1500 (○), and 2000 (+) G magnetic fields applied at each temperature value in an (a) increasing and (b) decreasing manner. The magnetization calculated from the Brillouin function for fully aligned $S=1$ and $S=1/2$ spins at 2000 G (---). (The actual field application sequence was 150, 300, 500, 1000, 2000, 1500, 750, 400, and 200 G prior to annealing at 25 K in zero field for 30 min and then applying 200, 400, 750, 1500, 2000, 1000, 500, 300, and 150 G fields)

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