Novel Co-operative Magnetic Properties of Decamethylmanganocenium 2,3-Dichloro-5,6-dicyanobenzoquinonide, $^{9}\text{[Mn(C_5Me_5)_2]}^+\text{[DDQ]}^-$

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The electron-transfer salt $^{9}\text{[Mn(C_5Me_5)_2]}^+\text{[DDQ]}^-$, isomorphous to orthorhombic $\text{[Fe(C_5Me_5)_2]}^+\text{[DDQ]}^-$, 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-dicyanobenzoquinonide; Electron-transfer salt, Ferromagnetic coupling

Co-operative (bulk) magnetic behaviours have been observed for the $\text{[FeCp]}^+$ and $\text{[TCNE]}^-$ salts, with $\text{[TCNE]}^-$ being pentamethylcyclopentadienide; $\text{[TCNE]}^-$ being tetracyanoethylene, and $\text{[FeCp]}^+$ being hexafluorophosphate. 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 Neel 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. Attempts to enhance $T_C$ by substituting the $S=1/2$ Fe III cation with the isostructural $S=1$ Mn III cation, i.e. $^{9}\text{[MnCp]}^+$, in the $\text{[TCNE]}^-$ salt were unsuccessful owing to decomposition arising from the chemical reactivity of the donor and acceptor. Recently, the expected trend has been realized with the report that the $\text{[TCNO]}^-$ salt of $^{3}\text{[MnCp]}^+$ is ferromagnetic. The observed magnetic couplings are consistent with the expectations of the extended-McConnell configurational admixture model.

With the goal of preparing additional molecular-based ferromagnets, the ferromagnetically coupled $\text{[FeCp]}^+$ $\text{[DDQ]}^-$ salt was characterized. As $T_C$ is proportional to $S(S+1)$, we sought to prepare $^{3}\text{[MnCp]}^+$ $\text{[DDQ]}^-$, anticipating that $T_C$ might occur at temperatures accessible in our laboratories.

The salt $^{3}\text{[MnCp]}^+$ $\text{[DDQ]}^-$ was prepared from $^{3}\text{[Mn(C_5Me_5)_2]}^+$ $\text{[PF_6]}^-$ (ref. 7) and $\text{[Et_4N]}^+$ $\text{[DDQ]}^-$ (ref. 6(b)) at $-20^\circ$ C. Elemental analysis (Oenda Research Services) for $^{3}(\text{C_5H_5})_2\text{MnN_2O_2}$ calc. (obs.): C, 60.88, (60.39); H, 5.47 (5.32); N, 5.07 (5.49%). Infrared spectra (Nujol): $V_{max}$ 2205s cm$^{-1}$ (C=N) for $\text{[FeCp]}^+$ $\text{[DDQ]}^-$, and 2206s cm$^{-1}$ (C=N) for $\text{[FeCp]}^+$ $\text{[DDQ]}^-$ $\text{[DDQ]}^-$ salt. The 2-300 K Faraday balance magnetic susceptibility of $\text{[Mn(C_5Me_5)_2]}^+$ $\text{[DDQ]}^-$ can be fit by the Curie–Weiss expression, $\chi_m = C/(T-\theta)$. The effective moment, $\mu_{eff}$ = $(8\chi T)^{1/2}$, and $\theta$ values for five independently prepared samples are 4.22, 4.25, 4.30, 4.13, and 4.13 $\mu_B$ and +25.5, 25.8, 27.1, 28.8, and 31.9 K, and average 4.21 $\mu_B$ and 27.8 K, respectively. The moment is greater than expected from a randomly oriented sample based on $(g)$ (i.e. 3.11 $\mu_B$ for $g = 2.20$), but less than expected for a sample oriented with the $C_s$ axis parallel to the magnetic field (i.e. 4.71 $\mu_B$ for $g = 3.33$). 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 $\theta$ value of +26.8 K suggests significant ferromagnetic interactions. Hysteric 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 $C_s$ molecular axis, the expected saturation magnetization, $M_s$, of 24 200 emuG 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.

$^+$ $g_{eff} = 3.33$, $g_s = 1.64$ and $\langle g \rangle = 2.20$ were observed for neutral $\text{MnCp}^+$ at 4 K in methyltetrahydrofuran. Under similar conditions attempts to determine the EPR of $\text{[MnCp]}^+$ $\text{[PF_6]}^-$ were unsuccessful.
Fig. 1 Molar magnetization, $M$, as a function of temperature, $T$, for a zero-field cooled polycrystalline sample of $[\text{MnCp}]^+\cdot[\text{DDQ}]^-$ previous aligned in 19.5 kG at 150 $\degree$C, 200 $\degree$C, 300 $\degree$C, 400 $\degree$C, 500 $\degree$C, 1000 $\degree$C, 1500 $\degree$C, and 2000 $\degree$C 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, 1500, 2000, 1000, 500, 300, and 150 G fields)

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References

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