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Organometallic ferromagnets

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Some organometallic solids comprising linear chains of alternating $m_s = \frac{1}{2}$ metallocenium donors, D, and cyanocarbon acceptors, A, i.e. $\cdots D^{+\bullet}A^{-\bullet}D^{+\bullet}A^{-\bullet}\cdots$, exhibit cooperative magnetic phenomena, i.e. ferro-, antiferro-, ferri-, and metamagnetism. For $[Fe^{III}(C_5Me_5)_2]^{+\bullet}[TCNE]^{-\bullet}$ (Me = methyl; TCNE = tetracyanoethylene) bulk ferromagnetic behaviour is observed below the Curie temperature of 4.8 K. Replacement of Fe^{III} with Fe^{II}, Ni^{III} and Cr^{III} leads to complexes with dia-, antiferro- and ferrimagnetic behaviour, respectively. These results are consistent with a model of configuration mixing of the lowest charge transfer excited state with the ground state developed earlier to understand the magnetic coupling of such systems. The model predicts the magnetic coupling as a function of electron configuration and direction of charge transfer (retro or reverse) and is a useful guide to designing new organic and/or organometallic complexes with cooperative magnetic coupling. To test the model and identify new materials with ferromagnetic coupling new TCNE-based electron transfer salts were prepared.

INTRODUCTION

In the 1960s molecular and/or organic compounds exhibiting ferromagnetic behaviour were postulated and recently an example has been prepared and characterized (Miller & Epstein 1987*a*, 1989*b*; Miller *et al.* 1988*a–c*). This discovery parallels the characterization of molecular- and/or organic-based superconductors and extends the studies of cooperative phenomena in molecular or organic materials. This broad range of phenomena in the molecular or organic solid state combined with the anticipated modification of the physical properties via conventional synthetic organic chemistry as well as the ease of fabrication enjoyed by soluble materials may ultimately lead to utility in future generations of electronic and/or photonic devices.

Herein we summarize the configuration admixing of a virtual triplet excited state with the ground state for an alternating donor–acceptor, D–A, $\cdots D^{+\bullet}A^{-\bullet}D^{+\bullet}A^{-\bullet}\cdots$ one-dimensional chain model for the stabilization of ferromagnetic coupling within the formula unit and its extension to rationalize three-dimensional (bulk) ferromagnetic behaviour (Miller & Epstein 1987*a*, *b*, 1989*b*; Miller *et al.* 1988*a–c*). Reviews of the common idealized magnetic behaviours expected in materials (Miller *et al.* 1988*a*) and a more comprehensive discussion on the several additional models for ferromagnetic coupling in molecular or polymeric materials are available (Miller & Epstein 1987*a*, 1989*b*; Miller *et al.* 1988*a*).

STABILIZATION OF FERROMAGNETIC COUPLING BY CONFIGURATION MIXING

Bulk ferromagnetic behaviour requires spin alignment throughout the solid. A handful of mechanisms have been conjectured for the pairwise stabilization of ferromagnetic coupling among spins (Miller & Epstein 1987*a*, 1989*b*; Miller *et al.* 1988*a*). These models, however, are insufficient to explain three-dimensional (bulk) ferromagnetic behaviour; such a mechanism is described.

Harden M. McConnell conjectured that configuration admixing of a virtual triplet charge-transfer excited state with the ground state for a $\cdots D^{+\bullet}A^{-\bullet}D^{+\bullet}A^{-\bullet}\cdots$ chain can stabilize pairwise ferromagnetic coupling (McConnell 1967). The essence of the McConnell model is the configurational interaction of a high-spin excited state to stabilize ferromagnetic coupling. Consider $D^{+\bullet}$ with three electrons in doubly degenerate partially occupied molecular orbitals (POMO), i.e. d^3, and an $A^{-\bullet}$ with a one electron in a non-degenerate POMO, i.e. s^1. In the absence of spin interactions there are two ground states for this d^3 or s^1 $D^{+\bullet}A^{-\bullet}$ pair. The high-spin

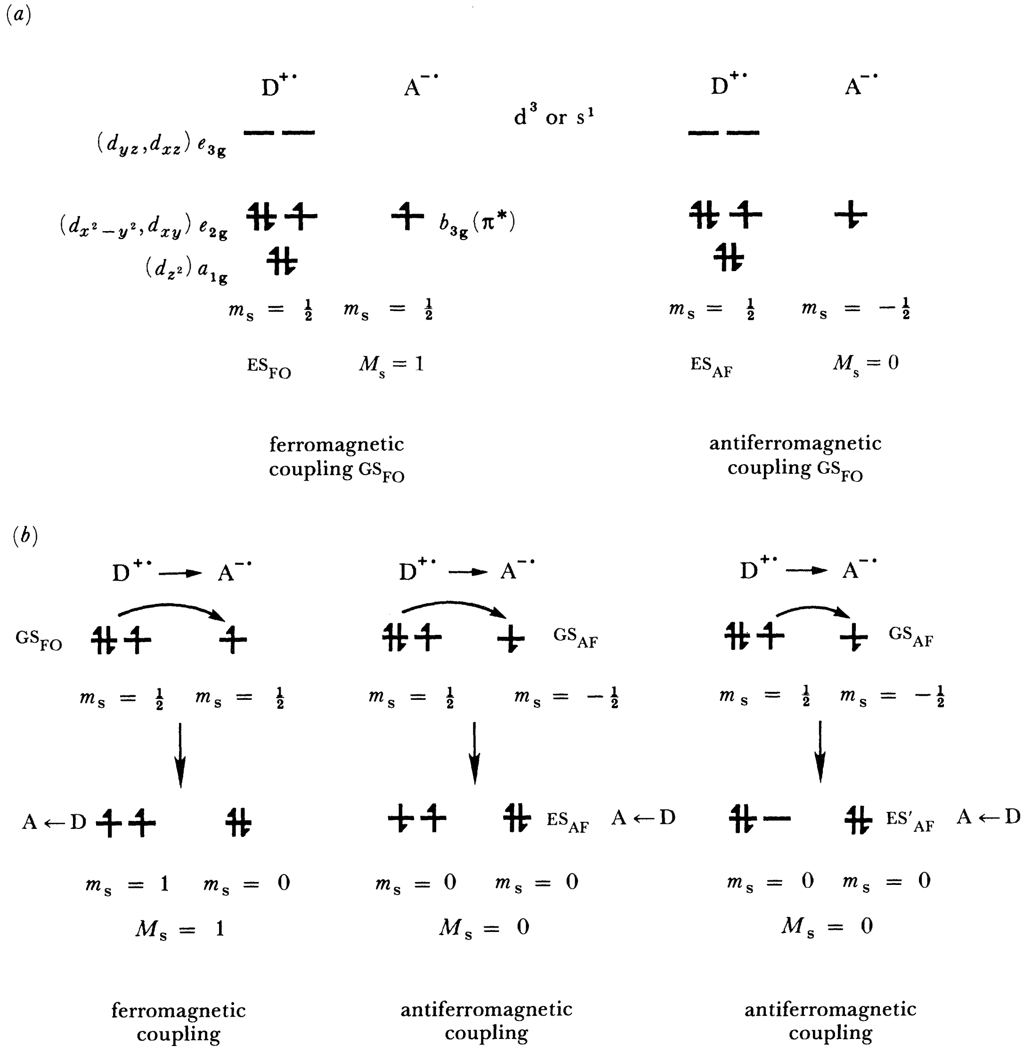

FIGURE 1. (*a*) Ferromagnetically (high-spin) and antiferromagnetically (low-spin) coupled paramagnetic ground states. (*b*) Schematic illustration of stabilization of ferromagnetic coupling via forward charge transfer from a $d^3D^{+\bullet}$ to an $s^1A^{-\bullet}$.

ferromagnetically coupled ground state ($\mathrm{GS_{FO}}$) and a low-spin antiferromagnetically coupled ground state ($\mathrm{GS_{AF}}$) – see figure 1*a* – exist at equal energy and lead to paramagnetic behaviour.

According to McConnell the ground state lowered in energy is the one with the greatest probability of configurational admixing with the lowest-energy virtual charge-transfer excited state. For each direction of virtual charge transfer Hund's rule can be used to predict the lowest charge transfer excited state. Thus cooperative magnetic coupling [ferro- (FO), ferri- (FI), or antiferromagnetic (AF)] can be predicted for a specific direction of charge transfer. For virtual forward charge transfer three excited states ($\mathrm{ES_{FO}}(\mathrm{A} \leftarrow \mathrm{D})$, $\mathrm{ES_{AF}}(\mathrm{A} \leftarrow \mathrm{D})$ and $\mathrm{ES'_{AF}}(\mathrm{A} \leftarrow \mathrm{D})$) are possible (see figure 1*b*). From Hund's rule the easiest excited $\mathrm{D}^{+\bullet}$ electron has $m_\mathrm{S} = -\frac{1}{2}$ and the lowest excited state is $\mathrm{ES_{FO}}(\mathrm{A} \leftarrow \mathrm{D})$. Thus forward charge transfer for the d^3 or s^1 electron configuration stabilizes the $\mathrm{GS_{FO}}$, which may lead to bulk ferromagnetic behaviour as observed for $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{+\bullet}[\mathrm{TCNE}]^{-\bullet}$ (see below).

Extension of the mechanism to other electron configurations possessing singly, doubly, or higher accidental or intrinsic orbital degeneracies enables the identification of configurations stabilizing ferromagnetic coupling for a specific direction of charge transfer (Miller & Epstein 1987*a*, *b*, 1989*b*; Miller *et al.* 1988*a*–*c*). The results of the evaluation of stabilization are summarized in table 1 for homospin ($m_\mathrm{S}^\mathrm{D} = m_\mathrm{S}^\mathrm{A}$) systems containing only singly and doubly degenerate orbitals (see Miller & Epstein (1987*b*, 1989*b*) and Miller *et al.* (1988*a*) for a discussion on triply degenerate orbitals and heterospin system). For heterospin systems with incomplete spin cancellation, antiferromagnetic coupling should lead to ferrimagnetic behaviour, and the FO and FI interactions can be predicted (Miller & Epstein 1987*a*, *b*, 1989*b*; Miller *et al.* 1988*a*–*c*).

TABLE 1. MAGNETIC COUPLING FOR HOMOSPIN SYSTEMS WITH SINGLY OR DOUBLY DEGENERATE HOMOS[a]

D (or A)[b]	A (or D)[b]	A ← D	D ← A	examples
s^1	s^1	AF	AF	[TMPD] [TCNQ][c], $[\mathrm{Cr(C_6H_6)_2}]$ [TTF] $[\mathrm{Pt(S_2C_4F_6)_2}]$[d], $\mathrm{V(C_6H_6)_2^{\bullet}}$
d^1	s^1	AF	FO	$[\mathrm{Ni^{III}(C_5Me_5)_2}]^{+\bullet}[\mathrm{TCNE}]^{-\bullet}$
d^3	s^1	FO	AF	$[\mathrm{Fe^{III}(C_5Me_5)_2}]^{+\bullet}[\mathrm{TCNE}]^{-\bullet}$
d^1	d^1	FO	FO	$\mathrm{Co^{II}(C_5H_5)_2^{\bullet}}$, $\mathrm{NO^{\bullet}}$
d^3	d^1	AF	AF	
d^3	d^3	FO	FO	

[a] See Miller & Epstein (1987*b*) and references therein.
[b] D and A can be interchanged.
[c] TMPD = *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine.
[d] TTF = tetrathiafulvalene.

$[\mathrm{Fe^{III}(C_5Me_5)_2}]^{+\bullet}[\mathrm{TCNE}]^{-\bullet}$ AS A MODEL SYSTEM EXHIBITING BULK FERROMAGNETIC BEHAVIOUR

Experimental evidence for ferromagnetic behaviour in a molecular compound has been limited to decamethylferrocenium tetracyanoethylenide, $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{+\bullet}[\mathrm{TCNE}]^{-\bullet}$ (Chittapeddi *et al.* 1987, 1988; Miller *et al.* 1987*a*), which possesses both the alternating $\cdots \mathrm{D}^{+\bullet}\mathrm{A}^{-\bullet}\mathrm{D}^{+\bullet}\mathrm{A}^{-\bullet} \cdots$ crystal (figure 2) and electronic structures prescribed by the configuration mixing mechanism described above (Miller *et al.* 1987*a*).

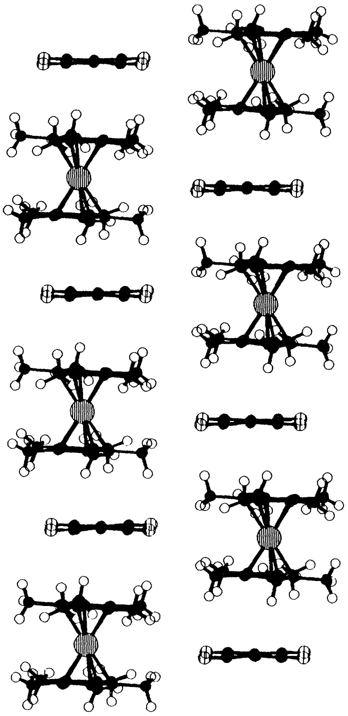

FIGURE 2. Alternating donor–acceptor, $\cdots D^{+\bullet}A^{-\bullet}\cdots$, linear chain structure of $[Fe^{III}(C_5Me_5)_2]^{+\bullet}[A]^{-\bullet}$ (A = TCNE, TCNQ), $[Fe^{II}(C_5H_5)_2]$ [TCNE], and $[Fe^{III}(C_5Me_5)_2]^{+\bullet}[C_3(CN)_5]^{-}$. The structure shows adjacent out-of-registry chains for A = TCNE.

The high-temperature susceptibility of $[Fe^{III}(C_5Me_5)_2]^{+\bullet}[TCNE]^{-\bullet}$ crystals aligned with the C_5 molecular symmetry axis parallel to the magnetic field fits the Curie–Weiss expression with $\theta_{\parallel} = +30$ K, and the effective moment (figure 3) deviates to higher moments at lower temperatures in agreement with dominant ferromagnetic interactions (Chittapeddi *et al.* 1987, 1988). For a crystal aligned perpendicular to the magnetic field $\theta_{\perp}$ is 10 K. The observed values of the susceptibility and saturation magnetization, i.e. 0.00667 mol^{-1} and 1.63 T mol^{-1} for single crystals aligned parallel to the chain axis, are in excellent agreement with those calculated for the sum of the contributions from $[Fe^{III}(C_5Me_5)_2]^{+\bullet}$ and $[TCNE]^{-\bullet}$, i.e. 0.00646 mol^{-1} at 290 K and 1.67 T mol^{-1}, respectively. A spontaneous magnetization is observed for polycrystalline samples below 4.8 K in the Earth's magnetic field (Chittapeddi *et al.* 1987). The latter is 36 % greater than iron metal on a per-iron basis and agrees with the calculated saturation moment for ferromagnetic alignment of the donor and the acceptor spins. The critical (Curie) temperature, T_C, is 4.8 K and hysteresis loops characteristic of ferromagnetic materials are observed (Miller & Epstein 1987*a*, 1989*b*; Miller *et al.* 1988*a–c*). A large coercive field of 10^{-1} T is recorded at 2 K (Chittapeddi *et al.* 1987).

The single crystal susceptibility can be compared with different physical models to aid the understanding of the microscopic spin interactions. For samples oriented parallel and perpendicular to the applied field the anisotropic susceptibility above 16 K fits a one-dimensional Heisenberg model with ferromagnetic exchange of $J_{\parallel} = 19\ cm^{-1}$ and $J_{\perp} = 5.6\ cm^{-1}$ (Chittapeddi *et al.* 1987). The difference between $J_{\parallel}$ and $J_{\perp}$ demonstrates that the ideal one-dimensional Heisenberg model, though it can fit the data, in inadequate to describe

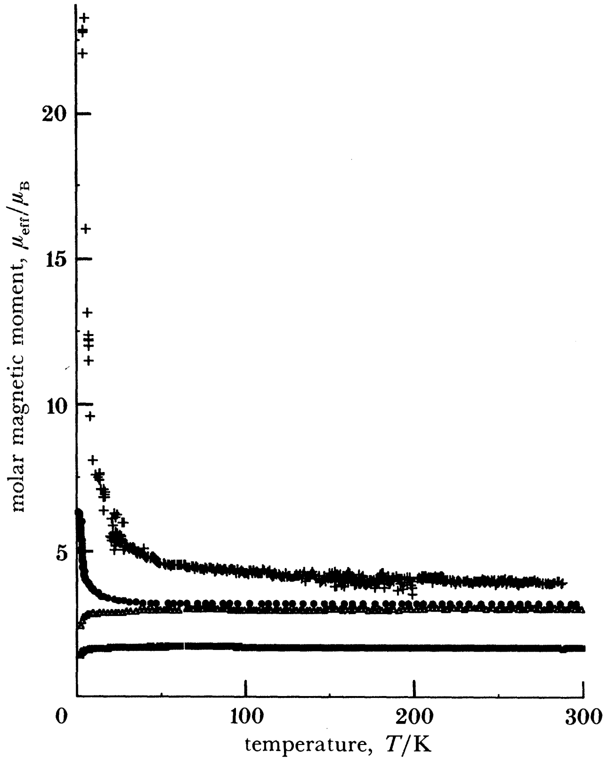

FIGURE 3. The effective moment, μ_{B}, for $[\mathrm{M^{III}(C_5Me_5)_2}]^{+}[\mathrm{TCNE}]^{-\bullet}[\mathrm{M} = \mathrm{Fe}(+), \mathrm{Co}(■)]$ and $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{+}[\mathrm{A}]^{-\bullet}[\mathrm{A} = \mathrm{TCNQ}\ (●), [\mathrm{C_3(CN)_5}]^{-}(\Delta)]$.

this system. Variation of the low-field magnetic susceptibility with temperature for a unusually broad temperature range above $T_{\mathrm{C}}[\chi \propto (T - T_{\mathrm{C}})^{-\gamma}]$, magnetization with temperature below $T_{\mathrm{C}}[M \propto (T_{\mathrm{C}} - T)^{-\beta}]$, and the magnetization with magnetic field at $T_{\mathrm{C}}(M \propto H^{1/\delta})$ enabled the estimation of the β, γ and δ critical exponents. The values of 1.2, *ca.* 0.5 and 4.4 were respectively determined for the magnetic field parallel to the chain axis. These values are consistent with a mean-field-like three-dimensional behaviour. Thus above 16 K one-dimensional nearest-neighbour spin interactions are sufficient to understand the magnetic coupling, but near T_{C} three-dimensional spin interactions are dominant (Chittapeddi *et al.* 1987).

Replacement of TCNE with TCNQ leads to the isolation of two phases of $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{+\bullet}[\mathrm{TCNQ}]^{-\bullet}$ composition (Miller *et al.* 1987*b*). The kinetic phase comprises a one-dimensional structural motif based on alternating $m_{\mathrm{S}} = \frac{1}{2}[\mathrm{Fe^{III}(C_5Me_5)_2}]^{+\bullet}$ cation donors, D, and $m_{\mathrm{S}} = \frac{1}{2}[\mathrm{TCNQ}]^{-\bullet}$ anions acceptors, A, i.e. $\cdots \mathrm{D^{+\bullet}A^{-\bullet}D^{+\bullet}A^{-\bullet}} \cdots$, as illustrated for the TCNE, electron transfer salt (figure 2). Like the TCNE electron transfer salt the effective moment, μ_{eff}, reveals a substantial deviation from the temperature-independent Curie behaviour characteristic of ferrocenium salts (figure 3) and the field-dependent magnetization reveals antiferromagnetic behaviour (with an antiferromagnetic ordering temperature, $T_{\mathrm{Neel}} \approx 2.55$ K) for H < 1.6 kG for the $[\mathrm{TCNQ}]^{-\bullet}$ salt. In contrast, for H > 1.6 kG a sharp rise and approach to magnetization saturation characteristic of ferromagnetic behaviour is observed (Candela *et al.* 1979).

This field-dependent switching from antiferromagnetic to a high-moment behaviour is consistent with metamagnetism. Ferrous chloride, $FeCl_2$, is an earlier example of a metamagnet (Stryjewski & Giordano 1977). $[Fe^{III}(C_5Me_5)_2]^{+\bullet}[TCNQ]^{-\bullet}$ is the first example where neither a one-, two- nor three-dimensional covalently bonded network structure is present, only a conventional molecular solid soluble in organic solvents.

Thus the TCNE and TCNQ electron-transfer salts of $Fe(C_5Me_5)_2$ demonstrate that high-moment, cooperative magnetic phenomena can be anticipated for molecular or organic-based compounds.

The ^{57}Fe Mossbauer spectra of the TCNE electron-transfer salt of $Fe(C_5Me_5)_2$ are informative. Atypical six-line Zeeman split spectra are observed in zero applied magnetic field at low temperature as the radical anions provide an internal dipolar field. For example, a Zeeman split spectrum with an internal field of 42.4 T (4.2 K) is observed for the $[TCNE]^{-\bullet}$ salt (Miller *et al.* 1987*a*).

The $[TCNE]^{-\bullet}$ data is in contrast with that observed for metamagnetic $[TCNQ]^{-\bullet}$ salt, which exhibits a singlet above 3.6 K. However, for the $[TCNQ]^{-\bullet}$ salt the onset of three-dimensional ordering occurs below 3.6 K with ultimate observation of a pair of six-line Zeeman split spectra in a 2:1 ratio suggesting an inequivalence of Fe^{III} sites below 4.2 K, which is not noted in the 167 K structure determination (Miller *et al.* 1987*b*). This, in conjunction with the discontinuity in the susceptibility data at 4.0 K, suggests a magnetostructural transformation perhaps accompanying the ordering process or site inequivalence in the magnetic structure of the ordered phase.

To understand the structural features necessary to stabilize bulk ferromagnetic behaviour, similarly structured electron-transfer complexes based upon TCNE and organometallic donors were investigated. These include those with substitution of the Me groups on the cyclopentadienide ring with H; increasing the ring size to six by using bis(arene)chromium, and substitution of Fe with Ru and Os.

A crucial requirement for forming ferromagnetically coupled chains is, by necessity, having stable radicals. Thus for closed-shell donors and acceptors electron transfer must occur. The solution (one-electron) reversible reduction potential, E^0, provides a means to estimate the occurrence of electron transfer for a solid. Decamethylferrocene, for example, is easier to oxidize (by 0.5 V) than ferrocene and unlike ferrocene reduces TCNE (Robbins *et al.* 1982; Rosenblum *et al.* 1964; Webster *et al.* 1962; Miller *et al.* 1989*a*; Brandon *et al.* 1966; B. Foxman, personal communication; Sullivan & Foxman 1983; Adman *et al.* 1967). The diamagnetic ferrocene analogue of $[Fe^{III}(C_5Me_5)_2]^{+\bullet}[TCNE]^{-\bullet}$, i.e. $[Fe^{II}(C_5Me_5)_2]$ [TCNE], does form and possesses the identical structural motif (see figure 3).

Attempts to prepare $[M^{III}(C_5Me_5)_2]^{+\bullet}$($M = Ru, Os$) salts of $[TCNE]^{-\bullet}$ have yet to lead to suitable compounds for comparison with the highly magnetic Fe^{III} phase (O'Hare *et al.* 1988). In addition to being more difficult to oxidize than $Fe^{II}(C_5Me_5)_2$, $[Ru^{III}(C_5Me_5)_2]^{+\bullet}$ disproportionates in solution to $Ru^{II}(C_5Me_5)_2$ and $[Ru^{IV}(C_5Me_5)_2)(C_5Me_4CH_2)]^+$ (Kolle & Grub 1985) inhibiting the formation $[Ru^{III}(C_5Me_5)_2]^{+\bullet}[TCNE]^{-\bullet}$. The Os^{III} analogue has lead to the preparation of an electron-transfer salt with TCNE; however, it has a low susceptibility and crystals unsuitable for single-crystal X-ray studies (O'Hare *et al.* 1988).

In contrast, $[Co^{III}(C_5Me_5)_2]^+[TCNE]^{-\bullet}$ {and $[Fe^{III}(C_5Me_5)_2]^{+\bullet}[C_3(CN)_5]^-$} have been prepared and exhibits essentially the Curie susceptibility anticipated for $m_S = \frac{1}{2}[TCNE]^{-\bullet}$ ($\theta \approx -1$ K) (Miller *et al.* 1987*a*). Because for the former compound the cation is diamagnetic and for the latter compound the anion is diamagnetic the electron-transfer complexes have only one spin per formula unit. Thus both the $\cdots D^{+\bullet}A^{-\bullet}D^{+\bullet}A^{-\bullet}\cdots$ structure type and $m_S \geqslant \frac{1}{2}$Ds and $m_S \geqslant \frac{1}{2}$As are necessary, but insufficient, for stabilizing cooperative highly magnetic behaviour. Replacement of Fe^{III} in $[Fe^{III}(C_5Me_5)_2]^{+\bullet}[TCNE]^{-\bullet}$ with $Ni^{III}(m_S = \frac{1}{2})$ or $Cr^{III}(m_S = \frac{3}{2})$ leads to compounds exhibiting cooperative magnetic properties (Miller & Epstein 1989*a*).

The motivation for studying the Cr^{III} and Ni^{III} complexes emanated from the aforementioned model for the stabilization of ferromagnetic coupling in molecular solids (Miller & Epstein 1987*a*, *b*, 1989*b*; Miller *et al.* 1988*a–c*). Antiferromagnetic coupling is predicted for d^1–s^1 complexes (s^1 is one electron in a non-degenerate orbital on, for example, the donor; d^1 is one electron in a doubly degenerate (or accidentally degenerate) orbital on, for example, the acceptor) with $A^{-\bullet} \leftarrow D^{+\bullet}$ charge transfer (see table 1). The $[Ni^{III}(C_5Me_5)_2]^{+\bullet}[TCNE]^{-\bullet}$ complex possesses this electronic configuration and its susceptibility obeys the Curie–Weiss expression with $\theta = -10$ K (Miller & Epstein 1989*a*). This is consistent with dominant antiferromagnetic interactions. A consequence of the model is that all half-filled POMO cases are expected to exhibit antiferromagnetic coupling.

For heterospin systems ($m_S^D \neq m_S^A$) with lower symmetry s and d POMOs only two electron configurations support ferromagnetic coupling. Illustrative systems, however, have yet to be identified for these electron configurations. Because of an accidental degeneracy of the cation's e_{2g} and a_{1g} orbitals (Robbins *et al.* 1982) $[Cr^{III}(C_5Me_5)_2]^{+\bullet}$ possesses a t^3 POMO (t^3 is three electrons in a triply degenerate (or accidentally degenerate) orbital on, for example, the donor); thus its $[TCNE]^{-\bullet}$ salt is predicted to exhibit antiferromagnetic coupling leading to ferrimagnetic behaviour (as the spin states cannot cancel) for either $A^{-\bullet} \leftarrow D^{+\bullet}$ or $D^{+\bullet} \leftarrow A^{-\bullet}$ charge transfer (Miller & Epstein 1987*a*, *b*, 1989*b*; Miller *et al.* 1988*a*, *b*, *c*). Investigation of the magnetic properties of the Cr^{III} system is in progress; the preliminary magnetization data is consistent with ferrimagnetic behaviour (Miller & Epstein 1989*a*).

To test the necessity of a ^2E ground state, the TCNE electron-transfer salt with the lower-symmetry $Fe(C_5Me_4H)_2$ donor was prepared (Miller *et al.* 1989*a*). The magnetic susceptibility can be fit by the Curie–Weiss expression, $\chi = C/(T-\theta)$, between 2.2 and 320 K and the moment is consistent with two independent spins. The susceptibility is not field-dependent and $\theta \approx 0$ K. The absence of three-dimensional ferromagnetic or antiferromagnetic ordering above 2.2 K in $[Fe(C_5Me_4H)_2]^{+\bullet}[TCNE]^{-\bullet}$ in contrast with $[Fe(C_5Me_5)_2]^{+\bullet}[TCNE]^{-\bullet}$ is in accord with the ^{57}Fe Mossbauer data which only shows nuclear quadrupole splitting for the $[Fe(C_5Me_4H)_2]^{+\bullet}$ salts and not zero-field Zeeman splitting. The lack of magnetic ordering may arise from poorer intra- and intermolecular overlap within and between the chains leading to substantially weaker magnetic coupling for $[Fe(C_5Me_4H)_2]^{+\bullet}[TCNE]^{-\bullet}$. This would suppress any spin ordering temperature. Alternatively, because of the overall C_{2v} symmetry the $[Fe(C_5Me_4H)_2]^{2+}$ charge transfer excited state may be a singlet, not a triplet as expected for $[Fe(C_5Me_5)_2]^{2+}$. The admixture of a singlet, not a triplet charge transfer excited state should lead to antiferromagnetic not ferromagnetic coupling (McConnell 1967; Miller & Epstein 1987*a*, *b*, 1989*b*; Miller *et al.* 1988*a–c*).

The TCNE electron-transfer salt of $Fe^{II}(C_5Me_5)(C_5H_5)$ was sought as the donor had C_5 symmetry and was a sufficiently strong to reduce TCNE. However, unlike the TCNE charge and electron salts of $Fe(C_5H_5)_2$ and $Fe(C_5Me_5)_2$, respectively, which possess the desired $\cdots$DADADA$\cdots$ motif in the solid state (figure 2) the simple (1:1) $[Fe(C_5Me_5)(C_5H_5)]^{+\bullet}$ salt could not be isolated and the isolated complex (2:3) salt does not have the desired ⋯DADADA⋯ one-dimensional chain structure. As the latter structural motif is the only one reported to support cooperative magnetic interactions (e.g. ferromagnetic) we were unsuccessful in using $\mathrm{Fe(C_5Me_5)(C_5H_5)}$ as a donor to prepare new materials to extend our understanding of cooperative magnetic behaviour in molecular materials. The formation of $\mathrm{[FeCpCp^*]_2[TCNE]_3THF}$ emphasizes the current inability to predict solid-state compositions let alone structure types (Miller & Glatzhofer 1989).

The infrared spectra and magnetic susceptibility of the $\mathrm{[Cr^I(C_6Me_xH_{6-x})_2]^{+\bullet}[TCNE]^{-\bullet}}$ ($x = 3, 6$) salts are consistent with two unpaired electrons per formula unit and these salts exhibit dominant ferromagnetic coupling as evidenced from a fit of the high temperature susceptibility to the Curie–Weiss expression with $\theta \approx +11.4$ K (Miller *et al.* 1989*b*). Crystals suitable for single-crystal X-ray analysis, however, have not been prepared; thus the structures of these salts are unknown. With the observation of ferromagnetic coupling in other charge-transfer salts with $\cdots \mathrm{D^{+\bullet}A^{-\bullet}D^{+\bullet}A^{-\bullet}} \cdots$ linear chains (Miller & Epstein 1987*a*, 1989*b*; Miller *et al.* 1988*a–c*) and the infrared evidence for isolated $\mathrm{[TCNE]^{-\bullet}}$ and not $\mathrm{[TCNE]_2^{2-}}$, we propose that these ferromagnetically coupled complexes also have this structural arrangement. Specific details of the intra- and interchain interactions arising from the canting and interchain registry of the chains as well as the interatomic separations must await the structural determinations.

A motivation for this study was to probe the effect of the electronic structure on the magnetic behaviour. As discussed earlier, the present understanding of the mechanism for stabilization of ferromagnetic coupling in molecular-based donor–acceptor complexes is configurational mixing of a charge-transfer excited state with the ground state. The model predicts that for excitation from the HOMO of a donor to an acceptor both with a half-filled non-degenerate HOMO, as is the case for these $\mathrm{[TCNE]^{-\bullet}}$ salts, only antiferromagnetic coupling is stabilized. Because the $\mathrm{[Cr(arene)_2]^{+\bullet}}$ cation has an $\mathrm{e_g^4a_{1g}^1}$ electronic structure and an $\mathrm{^2A_{1g}}$ ground state (Anderson & Drago 1970) antiferromagnetic behaviour is predicted. The observed ferromagnetic coupling thus suggests that the model is inadequate. The model, however, is consistent with the observed data if we consider that the $\mathrm{A^{-\bullet} \leftarrow D^{+\bullet}}$ charge-transfer excitation results from the next highest occupied molecular orbital, not the POMO of the cation, to the radical anion POMO. Thus ferromagnetic coupling that may ultimately lead to bulk ferromagnetic behaviour is achievable for systems where both the donor and acceptor have $\mathrm{^2A_g}$ ground states.

MODEL FOR THE STABILIZATION OF BULK FERROMAGNETIC BEHAVIOUR

The model for magnetic coupling by configuration admixing of a virtual triplet excited state with the ground state is limited to the repeat unit, i.e. $\mathrm{[Fe^{III}(C_5Me_5)_2]^{+\bullet}[TCNE]^{-\bullet}}$. Inter- *and* intrachain spin alignment are required for bulk ferromagnetism. Again mixing of the $\mathrm{ES_{FO}}$ with $\mathrm{GS_{FO}}$ lowers of the energy to $\mathrm{GS'_{FO}}$ (see figure 4*a*). Because the cation is essentially equidistant to a $\mathrm{[TCNE]^{-\bullet}}$ above and below it within a chain, virtual transfer of an $\mathrm{e_{2g}}$ electron forming the admixable triplet excited state with either $\mathrm{[TCNE]^{-\bullet}}$ may occur. Thus two excited states can mix with the $\mathrm{GS_{FO}}$ to further lower the energy to $\mathrm{GS''_{FO}}$ (figure 4*b*) leading to intrachain spin alignment. However, even with complete intrachain spin alignment (i.e. ferromagnetic coupled), if spins on adjacent chains correlate in the opposite sense, bulk antiferromagnetic coupling may dominate. Macroscopic ferromagnetism will not occur unless interchain spin

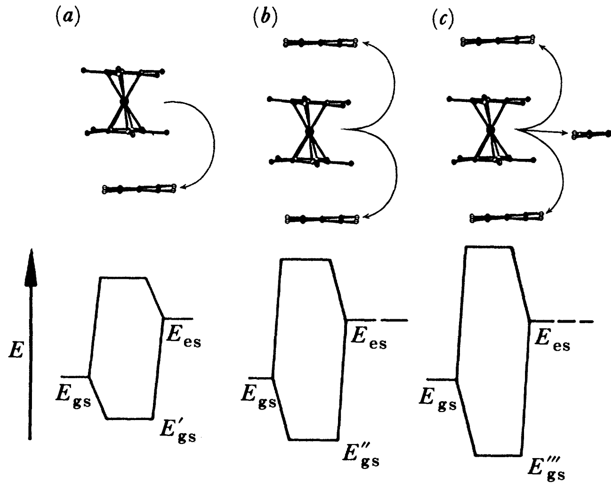

FIGURE 4. Schematic illustration of (*a*) mixing of the $\mathrm{GS}_{\mathrm{FO}}$ with $\mathrm{ES}_{\mathrm{FO}}$ to lower the energy to $\mathrm{GS}'_{\mathrm{FO}}$; (*b*) mixing of the $\mathrm{GS}_{\mathrm{FO}}$ with a pair $\mathrm{ES}_{\mathrm{FO}}$s arising from intrachain interactions to lower the energy to $\mathrm{GS}''_{\mathrm{FO}}$; (*c*) mixing of the $\mathrm{GS}_{\mathrm{FO}}$ with additional $\mathrm{ES}_{\mathrm{FO}}$s arising from interchain interactions to further lower the energy to $\mathrm{GS}'''_{\mathrm{FO}}$, which may lead to the macroscopic spin alignment necessary for bulk ferromagnetic behaviour.

alignment occurs. If adjacent chains are out-of-registry by half the chain axis length, then $[\mathrm{TCNE}]^{-\bullet}$s residing in adjacent chains may be comparably separated from $\mathrm{Fe}^{\mathrm{III}}$ sites as are the intrachain $[\mathrm{TCNE}]^{-\bullet}$s. Thus the $\mathrm{ES}_{\mathrm{FO}}$ on adjacent chains can additionally mix with $\mathrm{GS}''_{\mathrm{FO}}$ (figure 4*c*) to further lower the energy of the system to $\mathrm{ES}'''_{\mathrm{FO}}$ leading to the spin alignment throughout the bulk that is necessary for bulk ferromagnetism.

DESIGN CRITERIA FOR FERROMAGNETIC COUPLING VIA THE MCCONNELL MECHANISM

The McConnell mechanism leads to several important criteria for the design of a molecular–organic ferromagnet. Foremost is the requirement that the stable radicals possess a non-half-filled degenerate POMO. (For an electron-transfer salt, this requirement applies to either a donor or acceptor, but is not required for both.) These radicals must not have structural or electronic distortions that lower the symmetry and significantly break the degeneracies, e.g. the Jahn–Teller effect. Accidentally degenerate systems (e.g. high-spin transition, lanthanide and actinide metal coordination complexes), however, suffice. Furthermore, opposing effects (e.g. retro against forward virtual charge transfer) or magnitude of the stabilization (e.g. inversely proportional to distance and energy difference between the mixing states) may obscure the effect and lead to other phenomena. Additionally, other mechanisms (Miller & Epstein 1987*a*, 1989*b*; Miller *et al.* 1988*a*) for molecular-based ferromagnetic behaviour may be present.

CONCLUSION

The quest for s or p orbital-based ferromagnets remain the focus of intense interest worldwide. The magnetic data on $[\mathrm{Fe}(\mathrm{C_5Me_5})_2]^{+\bullet}[\mathrm{TCNE}]^{-\bullet}$ demonstrates that ferromagnetism is achievable in organic-based molecular systems. Replacement of the doublet organic acceptor with a diamagnetic acceptor, e.g. $[\mathrm{C_3(CN)_5}]^{-}$, demonstrates that the organic species is crucial for achieving bulk ferromagnetism (Miller *et al.* 1987*a*). Accidental or intrinsic orbital degeneracies, albeit rare for organic molecules, are needed for stabilization of ferromagnetic coupling by the generalized McConnell-like mechanism. Thus stable D_{2d} or C_n ($n \geqslant 3$) symmetry $m_S \geqslant \frac{1}{2}$ radicals with a degenerate POMO as well as crystal engineering to assure the necessary primary, secondary and tertiary structures appear to be required.

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Discussion

J. SILVER (*Department of Chemistry and Biological Chemistry, University of Essex, U.K.*). How close are the chains to each other in the oxidized decamethylferrocene materials? Does Dr Miller think this influences the magnetics and how?

J. S. Miller. The interchain distances are around 8 Å (1 Å = 10^{-1} nm). It is very likely this influences the magnetics, and the chains would have to get closer together to increase the ferromagnetic properties as these depend on inter- and intrachain spin alignment.

J. Silver. Has Dr Miller tried to prepare hexamethylferrocenium materials where the methyls are symmetrical on each ring. This should allow the chains to get closer together.

J. S. Miller. No, this would introduce a C_2 axis and cause the splitting of the doubly degenerate orbitals and thus not be helpful.