Ferromagnetic Molecular Charge-Transfer Complexes

JOEL S. MILLER*†

Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station, E328, Wilmington, Delaware 19898

ARTHUR J. EPSTEIN*

Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

WILLIAM M. REIFF

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

Contents

I. Overview

Some ionic molecular solids comprised of linear chains of alternating $S = \frac{1}{2}$ metallocenium donors (D) and $S = \frac{1}{2}$ planar polycyano hydrocarbon 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. The high-temperature ($T \geq 50$ K) magnetic

susceptibility can usually be fit by the Curie–Weiss expression, $\chi \propto (T - \Theta)^{-1}$, with $\Theta > 0$ for those salts with dominant ferromagnetic interactions and $\Theta < 0$ for those salts with dominant antiferromagnetic interactions. For $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$, magnetization in the absence of an applied field, i.e., spontaneous magnetization or bulk ferromagnetic behavior, is observed below the Curie temperature of 4.8 K and the magnetization exhibits a hysteresis curve with a coercive field of 1 kG. Critical exponents β, γ, and δ characteristic of bulk ferromagnetic behavior are also observed. The ^{57}Fe Mössbauer spectra show that this class of charge-transfer complexes exhibits zero applied field Zeeman-split spectra with large internal fields of 400–450 kG.

In order to understand the magnetic coupling in this class of materials, a model based on the configurational admixture of the lowest charge-transfer excited state with the ground state was developed. Ferromagnetic stabilization is consistent with forward (A←D), but not retro (D←A), charge transfer between the cation and anion for this class of compounds. The model is expanded to other electron configurations that contain singly, doubly, or triply degenerate partially occupied molecular orbitals (POMO) and offers a convenient guide to explore ferro-, antiferro-, and ferrimagnetic phenomena in molecular systems. Assuming the virtual charge transfer (retro or forward) excitation involves only the highest energy POMO, stabilization of ferromagnetic coupling via this mechanism requires that the *stable radicals possess a non-half-filled degenerate POMO* and the excited state possesses the same spin multiplicity and mixes with the ground state. Thus, the radical must possess a POMO with accidental or intrinsic (i.e., belonging to the D_{2d}, C_3, or higher point group) orbital degeneracies. Since ferromagnetism is a bulk phenomenon, ferromagnetic coupling must be present and dominate throughout the solid. A model for achieving this is discussed. Novel materials as well as more intensive experimental data and deeper theoretical insight are necessary to test these concepts and establish a salient understanding of cooperative phenomena in molecular solids. The report of bulk ferromagnetism in $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ affords the opportunity to test these concepts in real systems.
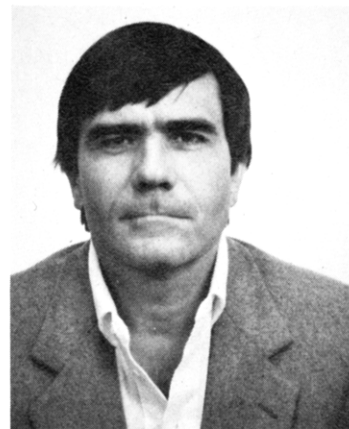
Joel S. Miller was born in Detroit, MI, and received his Bachelor of Science in Chemistry from Wayne State University in 1967 and Ph.D. from UCLA in 1971. After a postdoctoral fellowship at Stanford University, he joined the Xerox Webster Research Center in 1972 and later joined the Occidental Research Corp. (ORC) in 1978. In 1981 he was Visiting Professor of Chemistry at the University of California, Irvine, CA, and Chairman of the Southern California Section of the American Chemical Society. After the demise of ORC he joined the Central Research and Development Department at the Du Pont Co., where he is currently a Research Supervisor for solid-state chemistry. His research interests focus on the solid-state electrical, magnetic, and optical properties of molecular (organic, organometallic, and inorganic coordination) compounds and charge-transfer complexes as well as the surface modification of solids.

William M. Reiff was born in Binghamton, NY, and went on to receive his A.B. at S.U.N.Y. Binghamton in 1964 and his Ph.D. at Syracuse University in 1968. He was an NIH–PHS graduate fellow from 1966 to 1968 and an associate scientist at Brookhaven National Laboratory. He was an NSF faculty associate–postdoctoral fellow in the Departments of Chemistry and Physics at the University of Texas, Austin, from 1968 to 1970. He joined the Department of Chemistry at Northeastern University in 1970 and has been full professor since 1977. He is an active visiting scientist at the Francis Bitter National Magnet Laboratory. His current research interests include low dimensional magnetism charge-transfer complexes, ultra-low-temperature magnetism of ionic iron fluoride compounds, Mössbauer studies of gold compounds, metal ion insertion chemistry, and heterogeneous catalysis via low-valent metal clusters.

Arthur J. Epstein was born in Brooklyn, NY, and received his B.S. in Physics from the Polytechnic Institute of Brooklyn in 1966 and his Ph.D. in Physics from the University of Pennsylvania in 1971. After 13 years as a scientist at the Xerox Webster Research Center, he joined The Ohio State University in 1985 as Professor of Physics and Professor of Chemistry. He is also adjunct Professor of Physics at the University of Florida and has been a Visiting Professor at the Technion–Israel Institute of Technology and the University of Paris. His research interests include synthetic metals, molecular magnetism, conducting polymers, and ceramic superconductors.

II. Introduction

With the first reports[1] by Du Pont researchers that segregated linear-chain, 1-D, charge-transfer salts based upon TCNQ[2] may exhibit high dc electrical conductivity as well as other novel solid-state properties[3-5] and the conjecture that a high-temperature excitonic superconductor based upon a linear-chain compound might be prepared,[6] the past quarter of a century has witnessed substantial multidisciplinary efforts focused toward understanding and exploiting this fascinating class of molecular solids.[3-5] In contrast, molecular solids possessing linear chains comprised of alternating donors (D) and acceptors (A), i.e., ⋯DADADA⋯, are in general poor conductors; however, they exhibit a variety of interesting optical properties,[7] and recently special examples have been characterized to exhibit a temperature/pressure-dependent change in the degree of charge transfer, i.e., a "neutral–ionic" transition,[8] as well as cooperative magnetic phenomena,[9] e.g., bulk meta-[9,10] and ferromagnetism[9,11] as well as a spin–Pierels transition.[12] Herein after reviewing magnetic phenomena of molecular materials, we discuss the structure–function relationship of an unusual class of molecular solids which exhibit ferromagnetic behavior. Finally, models consistent with the stabilization of ferromagnetic coupling and bulk ferromagnetic behavior for this class of compounds are discussed.

III. Magnetic Phenomena

All substances exhibit a magnetic moment, M, upon application of a magnetic field, H, which is related to H by $M = \chi H$, where χ is the magnetic susceptibility.[13,14a-c] Open-shell paramagnetic compounds have their induced moment aligned parallel to the field. For noninteracting independent spins the magnetic moment is inversely proportional to temperature (T) and the susceptibility can be modeled by the Curie expression (eq 1) where $x = g\mu_B H/k_B T$ or the more general Bril-

$$\chi = C/T \qquad (1)$$

$$C = Ng^2\mu_B^2 S(S + 1)/3k_B T =$$
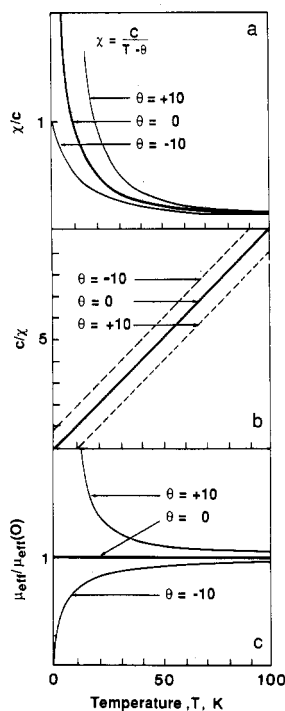$$(0.375 \text{ (emu K)}/\text{mol})(S(S + 1)g^2)/3T$$

Figure 1. Susceptibility (χ) (a), reciprocal susceptibility (χ^{-1}) extrapolated from the high-temperature region (b), and effective moment (μ_{eff}) (c) as a function of temperature for independent $g = 2$, $S = {}^1/_2$ spins as well as ferromagnetically coupled ($\Theta = 10$ K) and antiferromagnetically coupled ($\Theta = -10$ K) spins.

$$\chi = N g \mu_B J B_J(x)/H \qquad (2)$$

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh}\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \operatorname{ctnh}\left(\frac{x}{2J}\right)$$

louin (eq 2) expressions, where N is Avogadro's number, g is the Lande factor, μ_B is the Bohr magneton, $J = S + L$, $x \equiv g J \mu_B B / k_B T$, and k_B is the Boltzmann constant.[14a-c] Closed-shell diamagnetic compounds have their induced moment aligned antiparallel to the field. This latter phenomenon is temperature independent.

In some circumstances these spins experience an effective parallel (or antiparallel) exchange (molecular or Weiss) field due to the neighboring spins which leads to an increase (or decrease) in the measured susceptibility from that predicted for independent spins. The high-temperature susceptibility data often may be expressed by the Curie–Weiss[14] law (eq 3), where for ferromagnetic (parallel) and antiferromagnetic (antiparallel) interactions Θ is respectively greater or less than zero.

$$\chi = C/(T - \Theta) \qquad (3)$$

$$\mu_{eff} = (3\chi k_B/NT)^{1/2} = 2.823(\chi T)^{1/2} = \mu_B[g^2 S(S + 1)]^{1/2} \qquad (4)$$

The magnitude of χ is temperature dependent and chemists frequently report the effective moment,[14c] μ_{eff} (eq 4). The susceptibility, reciprocal susceptibility (χ^{-1}), and effective moment possess characteristic temperature dependencies. The magnetization (M) also possesses a characteristic field dependency, which enables the rapid qualitative determination of the magnetic behavior. These dependencies are illustrated for in-
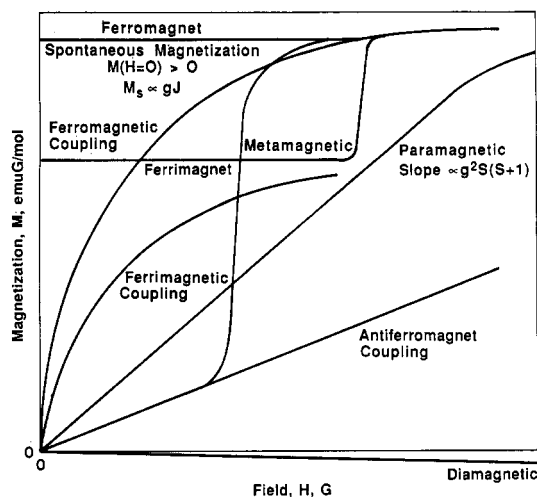

Figure 2. Schematic illustration of the magnetization (M) as a function of field (H) for several types of commonly observed magnetic behavior.

dependent spin (Curie), ferromagnetic, and antiferromagnetic behaviors in Figures 1 and 2.

At sufficiently low temperature the spins may order. If they align parallel to each other (ferromagnet), then a macroscopic spontaneous magnetization at zero applied field [i.e., $M(H_{app} = 0) > 0$] is present with a characteristic saturation moment, M_s (e.g., 1.22×10^4 (emu G)/mol for Fe),[14d] in a finite applied field. The saturation magnetization, M_s, can be calculated from eq 5. If neighboring spins are aligned antiparallel

$$M_s = N g S \mu_B \qquad (5)$$

(antiferromagnet), then there is no net macroscopic moment in zero applied field and the susceptibility is anisotropic below the Néel temperature. Ferrimagnetism occurs when the antiferromagnetically aligned spins have differing local moments resulting in incomplete cancellation of the parallel and antiparallel spin sublattices leading to a reduced, but nonzero, moment. The saturation magnetization for a ferrimagnet can be calculated from eq 6 or 7 depending if incomplete

$$M_s = N \Delta g S \mu_B \qquad (6)$$

$$M_s = N g \Delta S \mu_B \qquad (7)$$

cancellation of sublattice magnetic moments arises from differences in g or S, respectively. Application of a magnetic field to a ferromagnet leads to alignment of the ferromagnetic domains and $M(H)$ exhibits a hysteresis behavior with a characteristic coercive field (e.g., ~ 1 G for Fe)[14e] necessary to move the domain walls. Metamagnetism is the field-dependent transformation from an antiferromagnetic state to a high-moment ferromagnetic state. Like the gas/liquid critical behavior, the onset of cooperative magnetic behavior near the Curie temperature, T_c, can be scaled with critical exponents; i.e., the phenomena can be modeled by $(T - T_c)^\lambda$, where λ is the critical exponent.[15] The critical exponents can be compared against theoretical expectations to elucidate the dimensionality and anisotropy of the dominant spin interactions.

The highly magnetic ferro- (e.g., Fe, CrO_2) and ferrimagnetic (e.g., Fe_3O_4) materials frequently find utility in technological applications ranging from household

TABLE 1. Summary of Magnetic Phenomena Found in Molecular Compounds[15]

magnetic behavior	magnetic susceptibility, χ(300 K),[a] emu/mol	magnetic susceptibility χ(30 K),[a] emu/mol	effect of field and field gradient product, $H\, dH/dz$	$\chi(T)$	molecular example
diamagnetism	$\sim -10^{-4}$	$\sim -10^{-4}$	repulsive	none	$[Fe^{II}(C_5Me_5)_2][TCNE]$
paramagnetism[b]	1.25×10^{-3}	12.5×10^{-3}	attractive	$\propto T^{-1}$	$[Fe^{III}(C_5Me_5)_2]^{•+}[C_3(CN)_5]^{•+}$
antiferromagnetism[b,c]	1.19×10^{-3}	8.33×10^{-3}	attractive	complex[d]	$[Ni^{III}(C_5Me_5)_2]^{•+}[TCNE]^{•-}$
ferromagnetism[b,c]	1.32×10^{-3}	25.0×10^{-3}	attractive	complex[e]	$[Fe^{III}(C_5Me_5)_2]^{•+}[TCNE]^{•-}$
ferrimagnetism[c]	$>+10^{-3}$	complex	attractive	complex	$[Cr^{III}(C_5Me_5)_2]^{•+}[TCNE]^{•-}$
metamagnetism[c]	$>+10^{-3}$	complex	attractive	complex	$[Fe^{III}(C_5Me_5)_2]^{•+}[TCNQ]^{•-}$

[a] $\chi \equiv M/H$. [b] Assuming one $S = 1/2$, $g = 2$ unpaired electron per repeat unit. [c] Assuming $\Theta = 15$ K. [d] At higher temperature $\propto (T - \Theta)^{-1}$ with $\Theta > 0$. [e] At higher temperature $\propto (T - \Theta)^{-1}$ with $\Theta < 0$.
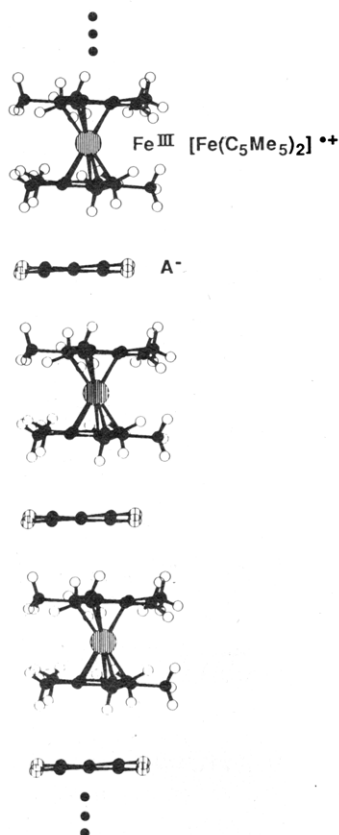

Figure 3. Alternating donor/acceptor, ···$D^{•+}A^{•-}D^{•+}A^{•-}$···, linear-chain structural motif observed for $[Fe^{III}(C_5Me_5)_2]^{•+}[A]^{•-}$ (A = TCNQ, TCNE, DDQ, $C_4(CN)_6$), $[Fe^{II}(C_5H_5)_2][TCNE]$, $[Fe^{II}(C_5Me_5)_2]^{•+}[C_3(CN)_5]^{-}$, and $[M^{III}(C_5Me_5)_2]^{+}[TCNE]^{•-}$ (M = Co, Ni). The structure shown here is for A = TCNE (open circles = H, closed circles = C, small hatched circles = N, and large hatched circles = M).

magnets to complex digital recording media and are the subject of contemporary materials research to improve their properties.[16] Table 1 summarizes the more common magnetic behaviors.

Highly magnetic materials, i.e., ferro- or ferrimagnetic, have close approach of the spin-containing moieties (i.e., covalent- or metallic-bonded 1-D, 2-D, or 3-D network structures) where the magnetic sites are d or f orbital transition, lanthanide, or actinide metal based. Examples of highly magnetic molecular-based compounds[17,18] with p or even d orbitals contributing to the cooperative magnetic properties were until recently unknown. Their discovery parallels the quest for molecular-based superconductors[20] and the exploration of cooperative phenomena in quasi-1-D materials.[4] This broad range of phenomena combined with the anticipated modulation of the physical properties via con-

ventional synthetic organic chemistry as well as the ease of fabrication enjoyed by organic materials may lead to their use in future generations of electronic and/or photonic applications.

IV. Magnetic Properties of $[Fe(C_5Me_5)_2]^{•+}[Anion]^{•-}$

Our strategy for designing molecular ferromagnets evolved from research aimed at preparing $TCNQ^2$ (**1**)-based sublimable conducting charge-transfer salts

1 **2** **3**
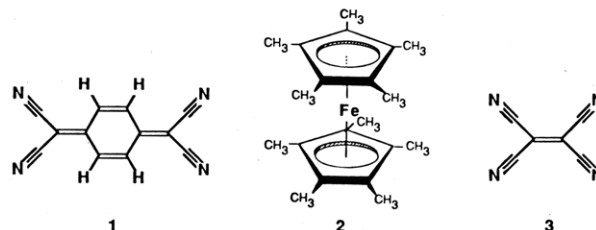
containing organometallic cations. Two 1:1 charge-transfer salts of $[Fe^{III}(C_5Me_5)_2]^{•+}[TCNQ]^{•-}$[10,21] composition have been prepared. The kinetic phase is comprised of a 1-D structural motif based on alternating $S = 1/2\,[Fe^{III}(C_5Me_5)_2]^{•+}$ (**2**) cation donors (D) and $S = 1/2\,[TCNQ]^{•-}$ anion acceptors (A), i.e., ···$D^{•+}A^{•-}D^{•+}A^{•-}$···,[21] as illustrated for the $TCNE^2$ (**3**) salt (vide infra) (Figure 3). The effective moment (μ_{eff}) reveals a substantial deviation[10] from the temperature-independent Curie behavior characteristic of ferrocenium salts[22] (Figure 4). The field-dependent magnetization reveals antiferromagnetic behavior (with an antiferromagnetic ordering temperature, $T_{Neel} \sim 2.55$ K) for $H < 1.6$ kG for the $[TCNQ]^{•-}$ salt. In contrast, for $H > 1.6$ kG a sharp rise and approach to magnetization saturation characteristic of ferromagnetic behavior are observed (Figure 5).[9,10]

This field-dependent switching from antiferromagnetic to a high-moment behavior is consistent with metamagnetism; several examples of which, e.g., $FeCl_2$, have been characterized.[23] This molecular charge-transfer complex, however, is the first example where neither a 1-, 2-, nor 3-D covalently bonded network structure is present—only a conventional organic solvent soluble molecular solid.[17,18]

With this discovery of a molecular metamagnet we sought to prepare a molecular ferromagnet. The strategy was to elucidate the structure–function relationship through modification of the radical anion, cyclopentadiene ring substituent group, and the metal to identify the combination of steric and electronic features leading to stabilization of ferromagnetic coupling as well as bulk ferromagnetic behavior. The primary
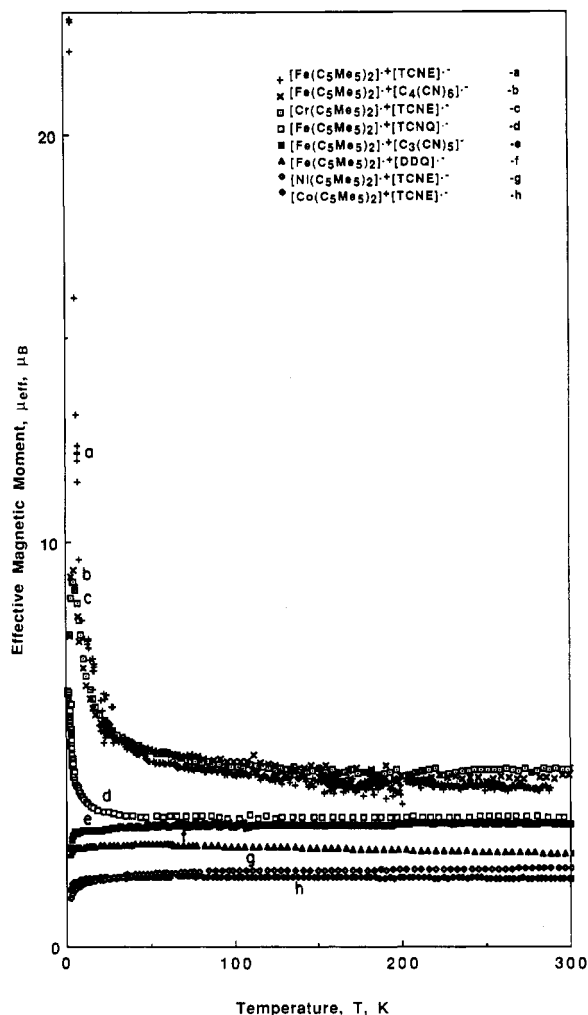
Figure 4. Effective moment (μ_{eff}) as a function of temperature for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[A]^{-}$ [A = TCNQ, TCNE, DDQ, $C_4(CN)_6$, $C_3(CN)_5$] and $[M^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (M = Co, Cr, Ni). Data are for polycrystalline samples.

Figure 6. Reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[A]^{-}$ [A = TCNQ, TCNE, DDQ, $C_4(CN)_6$, $C_3(CN)_5$] and $[M^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (M = Co, Cr, Ni). Data are for polycrystalline samples.

Figure 5. Magnetization (M) as a function of applied field (H) for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[A]^{\cdot-}$ [A = TCNQ, TCNE, $C_4(CN)_6$]. Data are for polycrystalline samples.

tactic was to use a smaller radical anion as the $[Fe-(C_5Me_5)_2]^{\cdot+}$ salt on the premise that if spin-pairing bond formation is avoided, it would have a greater spin density which could lead to greater spin interactions.
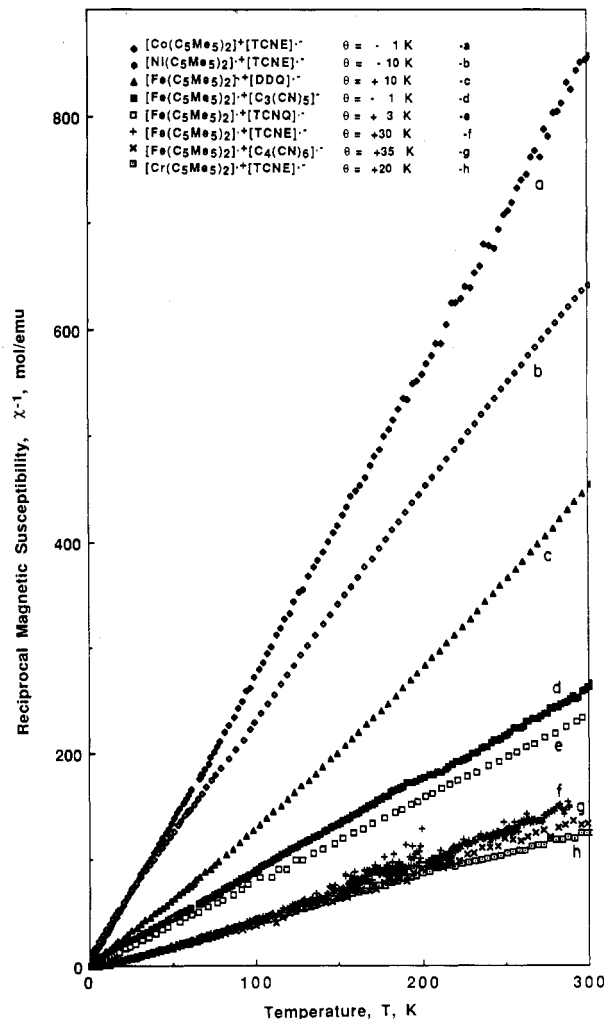
This philosophy led to the identification of $S = 1/_2$-$[TCNE]^{\cdot-2}$ (3). The structure of $[Fe(C_5Me_5)_2]^{\cdot+}$-$[TCNE]^{\cdot-}$ prepared from acetonitrile contains a molecule of solvent. Upon harvesting of the crystals[11] the solvent molecule, however, is completely lost with transformation from a monoclinic into an orthorhombic unit cell. The orthorhombic phase can be directly prepared from tetrahydrofuran. Both phases possess the $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ motif (Figure 3); however, the anion is disordered and unrefinable in the orthorhombic phase.[11b] All physical measurements were obtained on the orthorhombic phase.

The susceptibility of polycrystalline samples of $[Fe-(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ obeys the Curie–Weiss expression, $\chi = C/(T - \Theta)$, with $\Theta = +30$ K for $T > 60$ K (Figures 4 and 6), suggesting dominant ferromagnetic interactions.[11] Below 60 K a substantial departure from Curie–Weiss behavior is evident, and below 15 K the magnetization is no longer linearly proportional to the magnetic field (Figure 5). Using a modification of the Faraday technique, i.e., application of a field gradient without an external field other than the Earth's magnetic field, a spontaneous magnetization up to 8×10^3 (emu G)/mol is observed for polycrystalline samples (Figure 7).[11b]
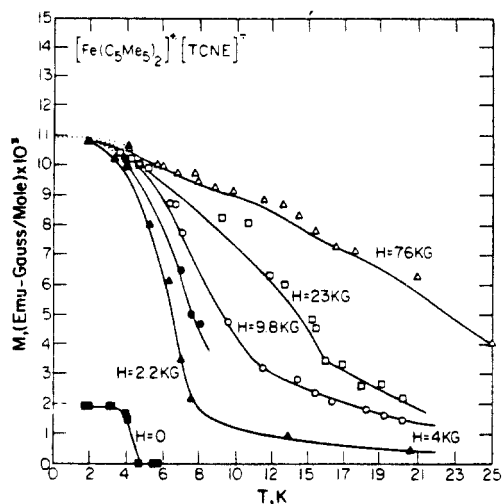
Figure 7. Magnetization (M) as a function of temperature for a polycrystalline sample of $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ at several magnetic fields. The solid lines are guides for the eye.
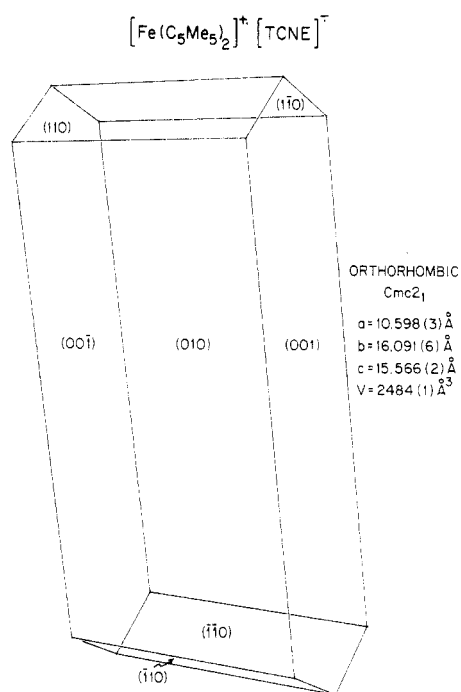
Figure 8. Habit of orthorhombic $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$. Single crystals are aligned with 001 and 010 parallel to the field.

Figure 9. Reciprocal magnetic susceptibility as a function of temperature taken for a single crystal of $Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ aligned parallel to the magnetic field.
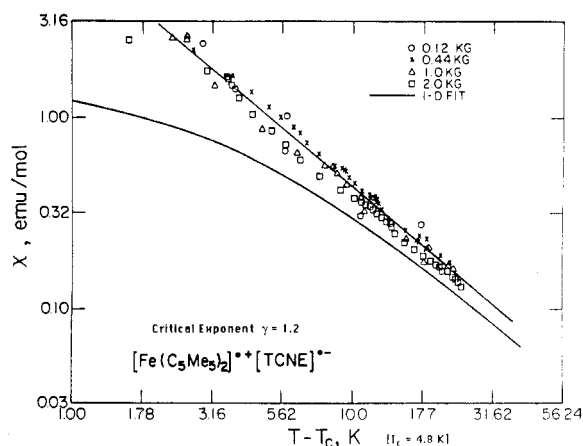
Figure 10. Magnetic susceptibility as a function of $T - T_c$, enabling the determination of the γ critical exponent. Note that the ordinate and abscissa are logarithmic.

Studies on aligned single crystals give a more detailed understanding.[24] The experimentally determined magnetic susceptibility at 290 K is 6.67×10^{-3} emu/mol, which is in good agreement with the 6.46×10^{-3} emu/mol value calculated from the sum of independent spins (eq 8) using anisotropic g values of $g_\parallel = 4$ (and

$$\chi_{total} = \chi_D + \chi_A =$$
$$[(g_\parallel^D)^2 + (g^A)^2]NS(S + 1)\mu_B^2/3k_BT \quad (8)$$

$g_\perp = 1.3$) for the cation[25a] and the nearly isotropic value of $g = 2$ for the anion.[25b] For single crystals with the chain axis (001) (Figure 8) aligned parallel to the magnetic field, below T_c the saturation moment (M_s) can similarly be calculated from the sum of independent spins (eq 9). The experimental saturation magnetiza-

$$M_s = [g_\parallel^D + g^A]NS\mu_B \quad (9)$$

tion parallel to the $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ stacking axis is 1.63×10^4 (emu G)/mol,[24] 36% greater than iron metal on a mole (not density or volume) basis and in accord with the saturation moment calculated from eq 9 of 1.675×10^4 (emu G)/mol.

From low-field $\chi(T)$ data for temperatures greater than the critical (Curie) temperature for the onset of the long-range ferromagnetic order (T_c) and from the temperature dependence of the spontaneous magnetization for $T < T_c$, the T_c was determined to be 4.8 K.

The single-crystal reciprocal susceptibility (χ^{-1}) can be fit by the Curie–Weiss expression above 60 K with $\theta = +30$ K (Figure 9). The data can be fit to a Padé series expansion[26] for the 1-D $S = \frac{1}{2}$ Heisenberg model with ferromagnetic coupling (eq 10), where $K = J/2k_BT$.

$$\frac{TX(K)}{Ng^2\mu_B^2} =$$
$$\left[\frac{1 + 5.8K + 16.90K^2 + 29.38K^3 + 29.83K^4 + 14.04K^5}{1 + 2.80K + 7.01K^2 + 8.65K^3 + 4.57K^4}\right]^{2/3}$$

$$(10)$$

A good fit is obtained for a coupling constant (J) of 27.4 K (19 cm^{-1}) despite the assumption that all the spins are identical (not alternating $g = 4$ and $g = 2$ per repeat unit).[24] The fit shown by the solid line in Figure 9

TABLE 2. Comparison of the Critical Constants for $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ with Theory

critical exponent	$[Fe(C_5Me_5)_2]^{\cdot+}$ $[TCNE]^{\cdot-}$	ising 2-D	molecular field theory	ising 3D	heisenberg 3-D	CrO_2	Fe^0	$CrBr_3$
β	0.50	0.125	0.5	0.313	0.38	0.33	0.34	0.368
γ	1.21	1.75	1.0	1.25	1.375	1.6	1.33	1.215
δ	4.42	15.0	3.0	5.2		5.79		4.28
α^a		0	0	0.2	0.14			0.17
η^b		0.25	0	0.056				0.07
ξ^c		1	0.5	0.643	0.70			0.64

^{a}Specific heat, $C(T) \propto (T - T_c)^\alpha$. ^{b}Neutron diffraction scattering intensity. ^{c}Neutron diffraction correlation length.

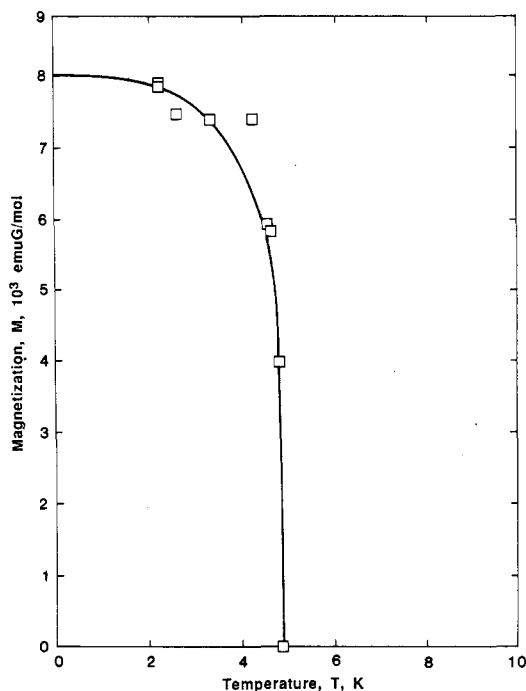**Figure 11.** Zero applied field $M(T)$ for $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$. Solid curve is a comparison to $M(T_c - T)^\beta$ with $\beta = 0.5$. The field gradient was aligned parallel to the stacking axis.
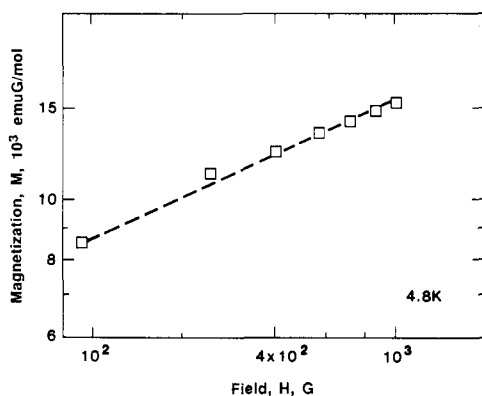

Figure 12. Fit of the $M(H)$ at T_c, enabling a determination of the δ critical exponent for a single crystal with the applied magnetic field aligned parallel to the stacking axis. Note that the ordinate and abscissa are logarithmic.

Figure 13. Field-dependent magnetization showing hysteresis of $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ for a single crystal oriented with the stacking axis parallel to the applied field. The coercive field (H_c) is 1 kG at 2.0 K and 30 G at 4.7 K.

assumes one $g = 3.9$ spin and one $g = 2$ spin. Similar fits were obtained in the study of a polycrystalline sample with $J = 30$ K (21 cm^{-1}) and a magnitude consistent with an averaging of the anisotropic g tensor for $[Fe(C_5Me_5)_2]^{\cdot+}$.[11b] Thus, above 16 K the magnetic behavior is adequately described by nearest-neighbor interchain ferromagnetic interactions.

Below 16 K the 1-D Heisenberg model breaks down.[11b,24] Examination of the variations of the low-field magnetic susceptibility with temperature above T_c [$\chi \propto (T - T_c)^{-\gamma}$] (Figure 10), spontaneous magnetization with temperature below T_c [$M \propto (T_c - T)^{-\beta}$] (Figure 11), and magnetization with magnetic field at T_c ($M \propto H^{1/\delta}$) (Figure 12) enables evaluation of the β, γ, and δ critical exponents.[26] Our results for the magnetic field parallel to the chain axis are 1.2, 0.5, and 4.5, respectively. When these values are compared with model-dependent predictions, the exponents are consistent with a 3-D behavior and there is no evidence for an intermediate 2-D regime[24] (Table 2). To further clarify the dimensionality of the system, low-temperature specific heat and neutron diffraction studies aimed at elucidating the magnetic structure as well as additional critical constants are in progress. The 30 protons lead to neutron scattering problems, and perdeuterio analogues are sought for these experiments.

The magnetization versus applied field measured for $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ exhibits hysteresis loops characteristic of ferromagnetic materials. At 4.7 K a hysteresis with coercive field of 30 G is observed, whereas at lower temperatures a well-defined remnant magnetization nearly equal to the saturation magnetization is seen. A large coercive field of 1 kG is observed at 2 K (Figure 13).[24]

The key physical properties for $[Fe(C_5Me_5)_2]^{\cdot+}[A]^{\cdot-}$ are summarized in Table 3.

TABLE 3. Summary of the Properties of [M(C₅R₅)₂][Anion] Complexes Possessing a •••DADA••• 1-D Structure

	Fe[a]	Fe[b]	Fe[a]	Fe[a]	Fe[a]	Fe[a]	Fe[a]	Co[a]	Ni[a]	Ni[a]	Fe[a]	Cr[a]
metal												
anion	[C₃(CN)₅]⁻	TCNE	TCNE	TCNE[c,d]	TCNQ	DDQ	C₄(CN)₆	TCNE	TCNE	C₄(CN)₆	TCNQI₂	TCNE
acceptor spin, S	0	0	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2
acceptor charge	1−	0	1−	1−	1−	1−	1−	1−	1−	1−	1−	1−
space group crystal system	$C2/c$ monoclinic	$P1$ triclinic	$C2/c$ monoclinic	$Cmc2_1$ orthorhombic	$P1$ triclinic	$Pbna$ orthorhombic	$P2/n$ monoclinic		ortho-rhombic[g]		$P2_1/n$ monoclinic	
$R_f(T)$, % (°C)	3.6 (−100)	14 (room temp)	5.9 (−30)	d	6.0 (−106)	5.4 (room temp)	6.2 (−106)				3.4 (−100)	
intrachain Fe–Fe, Å	10.305	9.75	10.415	10.621	10.549	10.616	10.783				11.131	
C₅Me₅–anion, Å	3.440	3.280	3.519	~3.6	3.670	3.564	~33.68 (av)				−3.9	
C₅Me₅–anion dihedral angle, deg	0		2.8		3.9	3.33	26.0				i	
in-ref Fe–Fe, Å	8.600, 9.567, 9.939	6.780, 7.700, 7.890	8.603, 8.732, 9.651	8.649, 9.618, 9.649	8.628, 9.348	8.691, 9.723, 10.030	8.719, 9.865, 10.030				8.728, 9.778	
ν(CN), Nujol, cm⁻¹	2106 s, 2207 s	2203, 2180	2144 s, 2183 m	2144 s, 2183 m	2153 s, 2179 s	2206 s	2168 m, 2185 s	2144 s, 2182 m	2144 s, 2182 m	2189 m, 2209 s	2149 w, 2180 s	2143 m, 2182 s
Mössbauer transitions, 1.4 K	1	2		6	12	6	6				6	
H_{int}, kG (1.4 K)				424	404, 449	451	449[h]				~400	
Curie–Weiss, Θ, K	−1		+30	+30	+3	+10	+35	−1	−10	−6	+95	+20
critical temp, T, K				4.82[e]	2.55[f]							
dominant magnetic behavior	para-magnetic	diamagnetic		bulk ferro-magnet	meta-magnetic	ferro-magnetic	ferro-magnetic	para-magnetic	antiferro-magnetic	antiferro-magnetic	ferro-magnetic	ferri-magnetic
ref	12	34b, 39	11, 12	12	10, 21	33	28	12	45	45	32	45

[a] R = Me. [b] R = H. [c] Loss of MeCN solvent leads to formation of the orthorhombic phase. [d] Anion is disordered and has not been refined. [e] Critical temperature. [f] Neel temperature. [g] Isomorphous to orthorhombic [Fe(C₅Me₅)₂]⁺•[TCNE]⁻•. [h] 1.68 K.
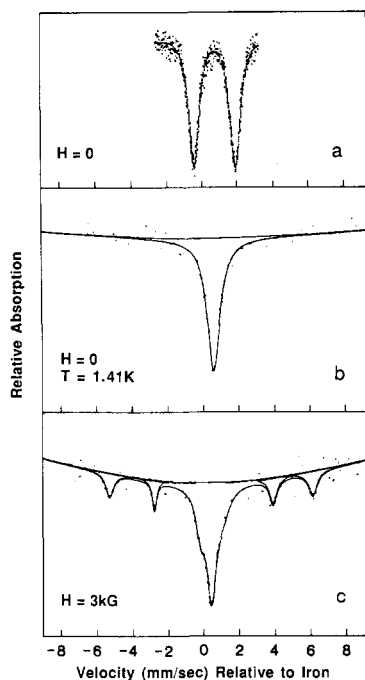
Figure 14. ^{57}Fe Mössbauer spectra at 4.2 K for (a) [Fe^{II}-(C$_5$H$_5$)$_2$][TCNE] (H_{app} = 0), (b) {[Fe^{III}(C$_5$Me$_5$)$_2$]$^{•+}$}$_2$[TCNQ]$_2{}^{2-}$ (H_{app} = 0), and (c) {[Fe^{III}(C$_5$Me$_5$)$_2$]$^{•+}$}$_2$[TCNQ]$_2{}^{2-}$ (H_{app} = 3 kG).

A. Anisotropic Magnetic Properties

Preparation of large single crystals facilitating the measurement of magnetic anisotropy has yet to be achieved. Attempts to grow large crystals of the 1-D TCNQ salt are thwarted by the formation of the thermodynamically favored dimer phase, which exhibits independent spin (Curie) magnetic behavior.[21a,27] Large needle crystals of the TCNE salt can be easily grown from acetonitrile; however, the unit cell contains a solvent molecule that is lost upon isolation of the crystals, leading to a polycrystalline sample. Thus, large crystals of the TCNE salt can only be prepared in equilibrium with its supernatant.[11] Small single crystals enabling the determination of the magnetic anisotropy of the TCNE salt can be grown from tetrahydrofuran; however, the anion cannot be refined due to disorder.[11b] Likewise, disorder of the anion in the [C$_4$(CN)$_6$]$^{•-}$ (vide infra) salt, although permitting the determination of the gross structural features, limits detailed microscopic analysis of the structural features important for understanding of the magnetic properties.[28] Nondisordered large single crystals are a high priority in order to determine the magnetic anisotropy.

B. Mössbauer Spectroscopy

The ^{57}Fe Mössbauer spectra of ferrocene and related compounds have been extensively studied.[29a-d] The Fe^{II} compounds, e.g., [Fe^{II}(C$_5$H$_5$)$_2$][TCNE],[30,31] exhibit a single, symmetrical quadrupole doublet (Figure 14a) typical of ferrocene, whereas $S = {}^1/_2$ Fe^{III} compounds, e.g., {[Fe^{III}(C$_5$Me$_5$)$_2$]$^{•+}$}$_2$[TCNQ]$_2{}^{2-}$, exhibit a singlet[21b] (Figure 14b) typical of ferrocenium. These spectra are essentially invariant with temperature. In an applied magnetic field, a six-line spectrum arising from the external field induced Zeeman splitting of the nuclear levels and corresponding to the usual transition selec-

[Fe(C$_5$Me$_5$)$_2$][TCNE]

VELOCITY (mm/sec) RELATIVE TO IRON
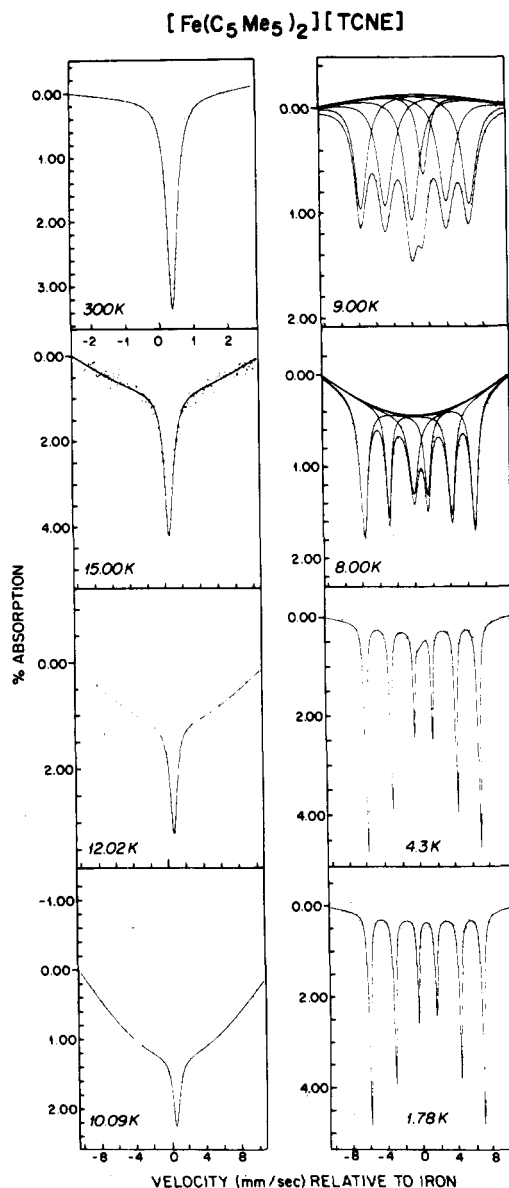
Figure 15. ^{57}Fe Mössbauer spectra as a function of temperature for [Fe^{III}(C$_5$Me$_5$)$_2$]$^{•+}$[TCNE]$^{•-}$.

tion rules[29d] is observed (Figure 14c). In contrast, for the 1:1 charge-transfer salts possessing an $S = {}^1/_2$ anion between a pair of planar $S = {}^1/_2$ cation sites, the anions provide an internal dipolar field leading to progressive slow paramagnetic relaxation broadening with decreasing temperature. This, in combination with 3-D ordering processes, results in the observation of Zeeman splitting in zero applied field.[9,11,21b,28,32,33a] Thus, as typified by [Fe^{III}(C$_5$Me$_5$)$_2$]$^{•+}$[TCNE]$^{•-}$, in the absence of an applied magnetic field, six-line Zeeman-split spectra with an internal field of 424 kG (4.3 K) are observed[11] (Figure 15). The internal field for this class of compounds varies from 400 to 450 kG (Table III), which is substantially greater than the expectation of 110 (kG/spin)/Fe[29e] assuming only the Fermi contact contribution to internal field. Clearly, a large orbital contribution to the internal field is present. Thus, the observation of unprecedentedly large hyperfine field effects in zero external field Mössbauer spectra is coincident with the identification of a rich variety of magnetic behaviors in the present class of ···
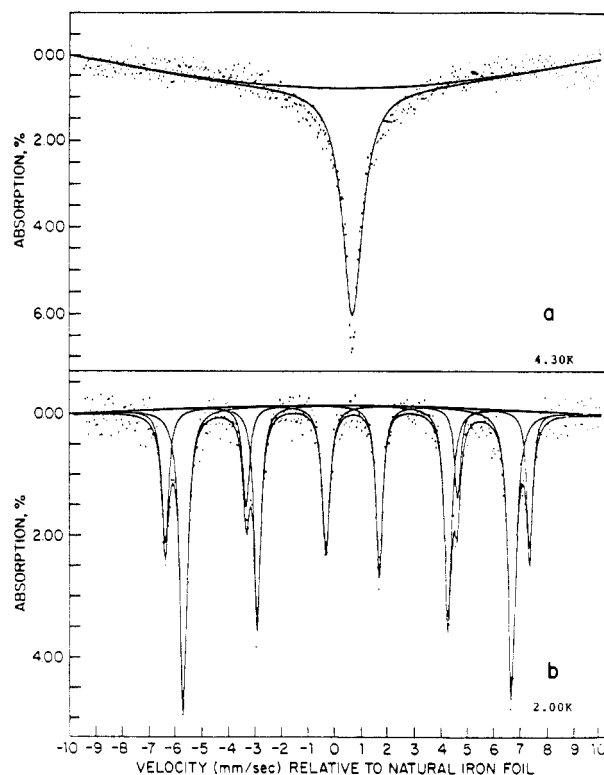
Figure 16. ^{57}Fe Mössbauer spectra as a function of temperature for $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNQ]^{\bullet-}$ at 2.0 and 4.3 K.

$D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ compounds using more conventional bulk susceptibility methods.

The metamagnetic $[TCNQ]^{\bullet-}$ salt exhibits a singlet above 3.6 K (Figure 16a). However, the onset of 3-D ordering occurs below 3.6 K with ultimate observation of a pair of six-line Zeeman-split spectra[21b] in a 2:1 ratio, suggesting an inequivalence of Fe^{III} sites below 4.2 K (Figure 16b), which is not noted in the 167 K structure determination.[21b] Heat capacity studies of this system are necessary before the nature of the transition leading to site inequivalence is fully understood. 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.

The Mössbauer spectra for S_{total} = 3, $[Fe^{III}$-$(C_5R_5)_2]^{\bullet+}[Fe^{III}X_4]^-$ (R = H, Me; X = Cl, Br), which do not possess the $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ structural motif, are more complex and are not directly comparable to those materials that belong to the $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ structure type.[34,35]

C. Structure–Function Relationship

In order to probe the structure–function relationship, with the goal of understanding the structural features necessary to stabilize bulk ferromagnetic behavior of similarly structured, i.e., $\cdots$DADADA$\cdots$, compounds, compounds based on the $M(C_5R_5)_2$ donors[36] were studied. The three synthetic variables that were modified are (1) substitution of the Me groups on the C_5 ring with H, (2) use of alternate open- and closed-shell, planar and nonplanar anions, and (3) use of other third-row as well as fourth- and fifth-row transition-metal ions.

1. Alternate Ligand Substituents

Ferrocene is more difficult to oxidize (by 0.5 V) than decamethylferrocene and is insufficient to reduce TCNE.[37-40] Nevertheless, the ferrocene analogue of $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$, i.e., $[Fe^{II}(C_5H_5)_2][TCNE]$, forms[30,38-41] and possess the identical structural motif[41] (Figure 3). In contrast to the $[Fe^{III}(C_5Me_5)_2]^{\bullet+}$ salt, this diamagnetic,[32] green, classical Mulliken charge-transfer complex[7] exhibits a broad charge-transfer absorption at ~8100 cm^{-1} (~1 eV)[39] and above 1.6 K a quadrupole doublet ^{57}Fe Mössbauer resonance characteristic of Fe^{II}.[29-31] These data suggest that complete charge transfer to form stable $S = {}^1/_2$ D's and A's is necessary to achieve stabilization of ferromagnetic behavior. Either a temperature- or pressure-induced "neutral-ionic" transition[8] might be sufficient to lead to the stabilization of ferromagnetic behavior; however, above 2 K at ambient pressure only Fe^{II} is observed via Mössbauer spectroscopy (Figure 14a), and no discontinuity is observed in the susceptibility data.[30]

In principle, more oxidizing acceptors should stabilize complete charge transfer with ferrocene. The charge-transfer $[Fe^{III}(C_5H_5)_2]^{\bullet+}[A]^{\bullet-}$ [A = $TCNQF_4$[42] and C_4-$(CN)_6$[28]] complexes were prepared and characterized to possess Fe^{III} and $[A]^{\bullet-}$ by ^{57}Fe Mössbauer and infrared spectroscopies. Both materials, however, exhibit weakly antiferromagnetic susceptibilities (i.e., $\theta \sim -3$ K) and singlet Mössbauer spectra without evidence for zero applied field Zeeman splitting characteristic of ferrocenium. The 1:1 $TCNQF_4$ salt does not possess the $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ motif[42] observed for the highly magnetic $TCNQ$,[21b,27] $TCNE$,[11] $TCNQI_2$,[32] DDQ,[33] and C_4-$(CN)_6$[28] charge-transfer salts and does not exhibit cooperative magnetic properties. This points to the importance of this structure type. Since the $[Fe^{III}$-$(C_5Me_5)_2]^{\bullet+}$ salt of $[C_4(CN)_6]^{\bullet-}$ exhibits ferromagnetic interactions[28] (vide infra), the structure of the $[Fe^{III}$-$(C_5H_5)_2]^{\bullet+}$ salt should provide important information on this point. However, crystals suitable for structure determination have yet to be prepared and this issue remains under active research. Likewise, the complex $[Fe^{III}(C_5H_5)(C_5Me_5)]^{\bullet+}[TCNE]^{\bullet-}$ has been prepared; however, preliminary susceptibility data do not suggest ferromagnetic behavior.[43]

2. Alternate Anions

Replacement of $[TCNQ]^{\bullet-}$ with $[TCNE]^{\bullet-}$,[11] $[C_4$-$(CN)_6]^{\bullet-}$,[28] $[TCNQI_2]^{\bullet-}$,[32] or $[DDQ]^{\bullet-}$[33] leads to similarly structured complexes with dominant ferromagnetic behavior as evidenced by the high-temperature susceptibility obeying the Curie–Weiss expression with $\theta \geq 10$ K (Table III). Replacement of $S = {}^1/_2[TCNE]^{\bullet-}$ with $S = 0$ $[C_3(CN)_5]^-$[11b] leads to formation of a $\cdots$ $D^{\bullet+}A^-D^{\bullet+}A^-\cdots$ structured phase which exhibits essentially Curie susceptibility ($\theta = -1.2$ K) with the concomitant lower moment characteristic of highly anisotropic ferrocenes.[21b] The nonplanar $S = {}^5/_2[Fe^{III}X_4]^-$ (X = Cl, Br) T_d anions do not form the $\cdots D^{\bullet+}A^-D^{\bullet+}A^-\cdots$ structural motif with $Fe(C_5R_5)_2$ (R = H, Me). Thus, although they exhibit a variety of interesting complex magnetic behavior,[34,35] direct comparison to the present system is not appropriate.

3. Alternate Metals

The $S = 0$ Co^{III} analogue of $[Fe^{III}(C_5Me_5)_2]^{•+}$-$[TCNE]^{•-}$ has been prepared and exhibits essentially the Curie susceptibility anticipated for $S = 1/2[TCNE]^{•-}$ ($\Theta = -1.0$ K).[11b] Attempts to prepare $[M^{III}(C_5Me_5)_2]^{•+}$ (M = Ru, Os) salts of $[TCNE]^{•-}$ have yet to lead to suitable compounds for comparison with the highly magnetic Fe^{III} phase.[43] Formation of $[Ru^{III}(C_5Me_5)_2]^{•+}$ is complicated by disproportionation to $Ru^{II}(C_5Me_5)_2$ and $[Ru^{IV}(C_5Me_5)(C_5Me_4CH_2)]^+$.[44] The Os^{III} analogue has led to the preparation of several phases with TCNE and $C_4(CN)_6$; however, differing stoichiometries, low susceptibilities, and crystals unsuitable for single-crystal X-ray studies[43] have hampered progress in this area. Replacement of Fe^{III} in $[Fe^{III}(C_5Me_5)_2]^{•+}[A]^{•-}$ [A = TCNE, $C_4(CN)_6$] with Ni^{III} ($S = 1/2$) or Cr^{III} ($S = 3/2$) leads to compounds exhibiting cooperative magnetic properties.[45] The motivation for studying these complexes emanated from the model[19] for the stabilization of ferromagnetic coupling in molecular solids, and the magnetic properties of these materials will be discussed in the section devoted to the model.

Consequently, available data suggest that the ···$D^{•+}A^{•-}D^{•+}A^{•-}$··· structure type with both $S \geq 1/2$ D's and $S \geq 1/2$ A's is necessary, but insufficient, for stabilizing cooperative highly magnetic behavior.

The key physical properties for $[M(C_5R_5)_2]^{•+}[A]^{•-}$ are summarized in Table III.

V. Models for Ferromagnetic Coupling in Molecular Solids

Ferromagnetism requires spin alignment throughout the bulk, and, though rare for a molecular solid,[18] the quest for molecular-based ferromagnets is the subject of increasing contemporary interest.[9,17,46-48] Three mechanisms have been proposed for achieving ferromagnetic coupling in a molecular solid and recent research directed toward this end has started. McConnell proposed two models, namely, Heitler–London spin exchange between positive spin density on a radical and negative spin density on another[49] and configurational admixing of a virtual triplet excited state with the ground state for a chain of alternating radical cation donors and radical anion acceptors.[50,51] Mataga[52] and Ovchinnikov[53] essentially suggested that very high spin multiplicity alternate hydrocarbon molecules may have ferromagnetic domains. Ferromagnetic superexchange has also been proposed by Soos and co-workers[54] and is discussed with the configurational mixing model for heterospin systems.

A. Heitler–London Spin Exchange

In 1963 McConnell stated[49] that radicals with "...large positive *and* negative atomic π-spin densities ... [that] pancake ... so that atoms of positive spin density are exchanged coupled ... to atoms of negative spin density in neighboring molecules ... give a ferromagnetic exchange interaction". Here ferromagnetic exchange results from the incomplete cancellation of antiferromagnetic coupled spin components. This is a mechanism for pairwise ferromagnetic exchange,[55] not bulk ferromagnetism. Ferromagnetic exchange in three dimensions is necessary for bulk ferromagnetic behavior. To achieve ferromagnetic exchange via this mechanism, routes to spin pairing, e.g., bond formation, must be avoided. Free radicals, e.g., $R^•$, readily dimerize. Stable free radicals, e.g., $[TCNE]^{•-}$[56] or $[TCNQ]^{•-}$,[21b] possess atoms with unequal positive and negative spin densities such that it is conceivable that they might form a structure that complies with McConnell's requirement. However, of the numerous structures reported, none have the overlap described by McConnell.[57] Even with these stable radicals dimerization to form diamagnetic π dimers occurs.[27] Examples of C–C σ-bond formation between $C(CN)_2$ moieties[58] on adjacent TCNQ's as well as of more complex chemical reactions[59] have also been reported. Hindered stable radicals, for example, allyl or nitroxide radicals (e.g., 4[60] and 5,[61] respectively), might be suitable. However, where evidence exists, they exhibit Curie or antiferromagnetic behavior. High spin multiplicity radicals, e.g., $S = 1$ O_2,[62] $C_6(NC_2H_4)_6$,[46,51,92] or $S = 4$ polycarbenes,[47,48,63] studied to date likewise exhibit either antiferromagnetic coupling or independent-spin Curie behavior.

4   5
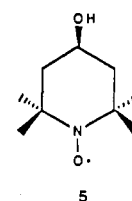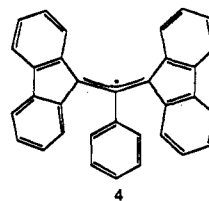
Cleverly designed stable radicals with the proper solid-state packing are sought to test this model. Recently, the spin multiplicity of dicarbenes incorporated into rigid [2.2]cyclophanes has been shown to be controlled by the overlapping modes of the spins in the aromatic C_6 rings.[64] McConnell's model[49] suggests that the singlet pseudometa isomer should possess a singlet ground state.[47,48,64] This is in contrast to the behavior of the quintet pseudoortho and pseudopara isomers of the bis(phenylmethylenyl)[2.2]cyclophanes. ESR[47,48,64] and computational data[65] on this system are consistent with these results, suggesting that ferromagnetic exchange can be achieved by this McConnell model. Preliminary results on an intermolecular system are also consistent with McConnell's model;[66] however, a bulk ferromagnet has yet to be reported.

B. High Spin Multiplicity Molecules and Polymers

With the foundation of the ground-state triplet behavior of diphenylcarbene in 1968, Mataga suggested[52] that large planar alternate hydrocarbons comprised of meta-substituted triplet diphenylcarbene moieties will have a high-spin (ferromagnetically coupled) ground state via Hund's rule. Bulk ferromagnetic behavior requires spin alignment throughout the solid (i.e., inter- as well as intramolecular ferromagnetic coupling). A mechanism for achieving intermolecular ferromagnetic coupling was not discussed. McConnell's Heitler–London spin-exchange mechanism might suffice; however, intermolecular ferromagnetic coupling may not be necessary if the high spin multiplicity radical was its

own ferromagnetic domain. Examples[47,48,52] of high spin multiplicity polymers that Mataga suggested include 6 and 7.

6

7
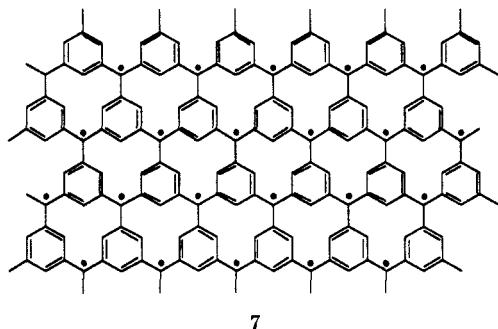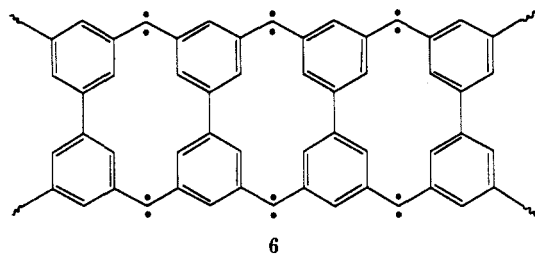
With guidance from McConnell's Heitler–London spin-exchange model, Iwamura[47,48,63,67] and co-workers recently have prepared several high-spin polycarbenes via a route that Mataga suggested, namely, the in situ photolysis of polydiazo derivatives. The best characterized compound is a nonet ($S = 4$) tetracarbene, 8, prepared via eq 11. The paramagnetic susceptibility

(11)

8
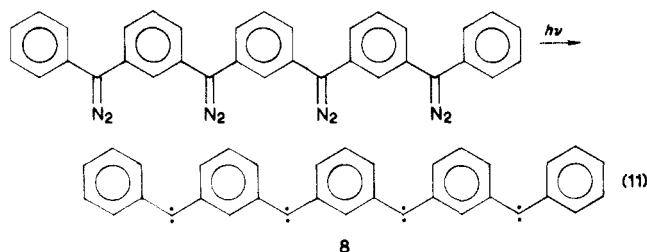
of 8 diluted in either a 2-methyltetrahydrofuran glass or a benzophenone crystal confirms the nonet ground state ($\mu_{eff} = 9.08$ μ_B vs a calculated spin only value of 8.49 μ_B); however, the temperature dependence of the susceptibility exhibits only independent-spin or antiferromagnetic behavior.[63]

Preparation of an organic ferromagnet via Mataga's prescription is problematic. Mataga notes that as the molecule becomes larger, the energy levels form bands and the bonding/high-spin nonbonding and nonbonding/antibonding band gaps become smaller. If these gaps become comparable to $k_B T$, then ferromagnetic spin alignment may no longer be feasible as thermal population of higher excited states may occur. Additionally, he states that correlation should lower the energy of the nonmagnetic states, making it more difficult to achieve ferromagnetic behavior. Stable triplet carbenes are required. Carbenes can be further stabilized via greater sp hybridization of the carbene carbon.[68] The low-temperature photolytic loss of dinitrogen, eq 11, however, leaves sp^2 carbon. Routes to linear sp $-C(N_2)-$ carbon, e.g., via addition of steric bulk, should impart greater stability to the triplet. Additionally, chemical problems that must be avoided

prior to the realization of an organic ferromagnet via Mataga's concept include minimization of bond formation prevalent with radicals or spin pairing via distortions and rehybridization; e.g.
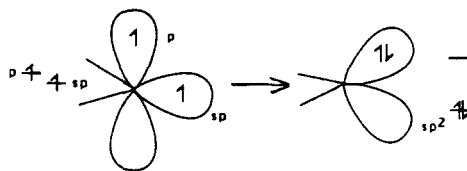

Ovchinnikov[53] stated that the spin (S) for planar alternate hydrocarbons can be calculated by eq 12,

$$S = |n^* - n|/2 \qquad (12)$$

where n is the number of nonstarred atoms and n^* is the number of starred atoms (where adjacent atoms are respectively starred and nonstarred and identically denoted atoms are not adjacent to each other). For example, trimethylenemethane[69] (9) is predicted to have

9 $S = 1$

10 $S = (R - 1)/2$

11 $S = x/2$
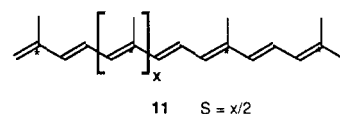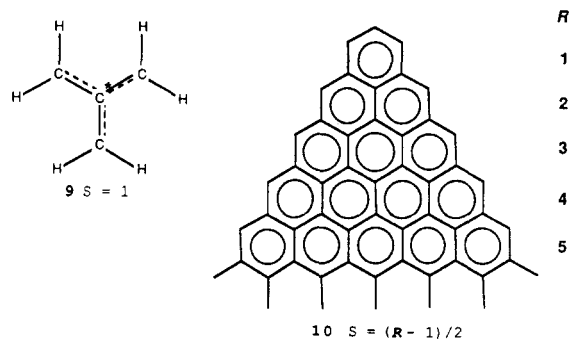
$S = 1$. Likewise, large molecules should have large S's. The ground state of fused C_6 rings (10) are also predicted to have high-spin ground states via the formula $S = (R - 1)/2$, where R is the number of rows.[53] Three and six fused rings ($R = 2$ and 3) possess $S = {}^1/_2$ and $S = 1$ ground states, respectively.[70] Polymers such as 11 are predicted to have a large value for S, i.e., $x/2$.[53,71] Boron-substituted graphite, BC$_7$ (12), is also predicted to have a high spin state.[53] Recently, BC$_3$ has been prepared;[72] however, other compositions as well as their magnetic properties have yet to be reported.

12 $S = \infty$
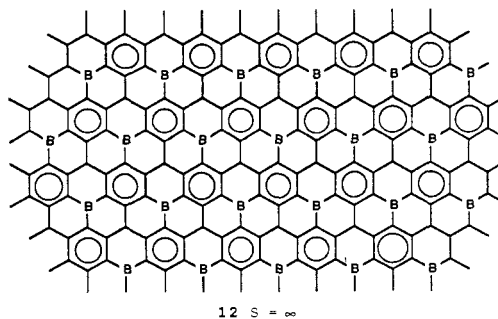
Chemical reactivity arising from the unpaired electrons on 10 and 11 ($R = 2, 3$) to form bonds suggests that stable high-spin materials are difficult to prepare. Distortions as well as intermolecular coupling which pair up electrons must also be avoided.
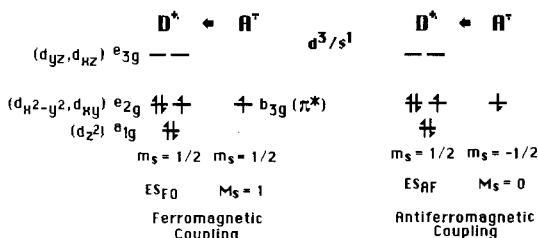
Figure 17. Ferromagnetically ($M_s = 1$) and antiferromagnetically ($M_s = 0$) coupled paramagnetic ground states.

Attempts to prepare a polymer similar to 7 based on the iodine oxidation of 1,3,5-triaminobenzene has been recently reported, although its reproducible chemical or physical characterization has not been described.[73] Additionally, attempts to prepare a ferromagnetic organic polymer via the formation of a poly(diacetylene) from a stable nitroxy biradical monomer have been reported.[74] In either case magnetization corresponding to only ~ 0.1–2% of the maximum theoretical magnetization is realized. The low value and marked variation between samples suggest that the ferromagnetic behavior is not intrinsic.

C. Configurational Mixing of an $S = 1$ Excited State To Stabilize Ferromagnetic Coupling

Experimental evidence for ferromagnetic behavior in a molecular solid has been limited to the charge-transfer salt of decamethylferrocene, $(\eta^5\text{-}C_5Me_5)_2Fe^{II}$ (2), with tetracyanoethylene, TCNE (3).[9,11,24] The mechanisms that govern the stabilization of ferromagnetism in this class of linear-chain alternating radical cation donor (D) and radical anion acceptor (A), i.e., $\cdots$ $D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$, molecular charge-transfer complexes are not firmly established; however, it is attractive to consider[9,11b,19] the admixing of a virtual triplet excited state with the ground-state model originally proposed by McConnell[50,51] as this class of complexes possesses both the crystal and electronic structures required by this model. Stabilization of pairwise ferromagnetic coupling (i.e., stabilization of a high-spin, e.g., triplet, state) does not guarantee bulk ferromagnetism in a substance; however, a mechanism to attain bulk ferromagnetism is proposed.

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 one electron in a nondegenerate POMO, i.e., s^1. In the absence of spin interactions there are two ground states for this d^3/s^1 $[D]^{\bullet+}[A]^{\bullet-}$ pair.[75] The $M_s = 1$ ferromagnetically coupled (GS_{FO}) and $M_s = 0$ antiferromagnetically coupled (GS_{AF}) states (Figure 17) exist at equal energy and lead to paramagnetic behavior.[19]

As suggested by McConnell the GS lower in energy is the one with the greatest probability of configurational admixing with the lowest energy virtual charge-transfer excited state. Specifically, if an $m_s = 1$ excited state (ES) arising from either an $m_s = 1$ donor (D) or an $m_s = 1$ acceptor (A), but not both, formed by either virtual (1) retro ($D^0 + A^0 \leftarrow [D]^{\bullet+} + [A]^{\bullet-}$), (2) forward ($[D]^{2+} + [A]^{2-} \leftarrow [D]^{\bullet+} + [A]^{\bullet-}$), or (3) disproportionation (e.g., $[D]^{2+} + D^0 \leftarrow 2[D]^{\bullet+}$) charge transfer admixes
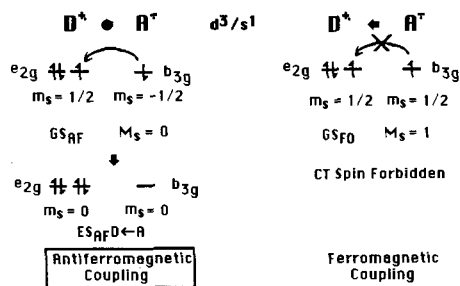
Figure 18. Stabilization of antiferromagnetic coupling via retro charge transfer from an s^1 $[A]^{\bullet-}$ to a d^3 $[D]^{\bullet+}$.
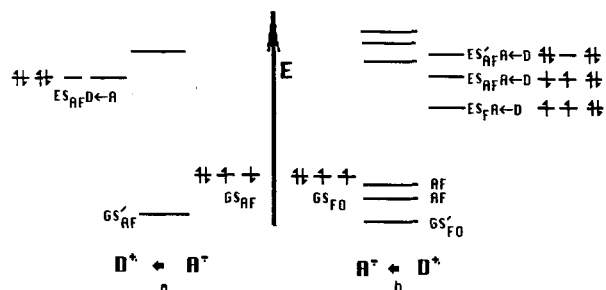
Figure 19. Schematic state diagram depicting the relative energy of the ground and excited states before and after admixing (a) to stabilize antiferromagnetic coupling for virtual $[D]^{\bullet+}[A]^{\bullet-}$ charge transfer and (b) ferromagnetic coupling for virtual $[D]^{\bullet+}[A]^{\bullet-}$ charge transfer via the McConnell mechanism. The energy scale is arbitrary.

with the ground state (GS), then the ferromagnetic coupled ground state (GS_{FO}) will be stabilized.[19] This behavior can be described by using the Hubbard model generalized for the presence of a doubly degenerate level[19,24,76] (vide infra).

For each direction of virtual charge transfer Hund's rule can be used to predict the lowest charge-transfer excited state.[19,77] Thus, cooperative magnetic coupling [ferro- (FO), ferri- (FI), or antiferromagnetic (AF)] can be predicted for a specific direction of charge transfer. An example is retro charge transfer for the above case (Figure 18). Since the $[D]^{\bullet+}$ can only accept an $m_s = -1/2$ electron via virtual charge transfer from $[A]^{\bullet-}$ and GS_{AF}, not GS_{FO}, has an $m_s = -1/2$ electron, admixture of the $ES_{AF}D\leftarrow A$ excited state will lower the energy of GS_{AF} (to GS'_{AF}) with respect to GS_{FO} and stabilize antiferromagnetic coupling (Figure 19).

For virtual forward charge transfer three excited states ($ES_{FO}A\leftarrow D$, $ES_{AF}A\leftarrow D$, and $ES'_{AF}A\leftarrow D$) are possible (Figure 20). From Hund's rule the easiest excited $[D]^{\bullet+}$ electron has $m_s = -1/2$ and the lowest excited state is $ES_{FO}A\leftarrow D$. Thus, forward charge transfer for the d^3/s^1 electron configuration stabilizes the ferromagnetically coupled ground state (GS_{FO}) (Figure 19b), which may lead to bulk ferromagnetic behavior as observed[24] for $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$.

Since $S = 1$ $[Fe^{IV}(C_5Me_5)_2]^{2+}$ is an unknown species and $S = 0$ $[TCNE]^{2-}$ possesses a D_{2d} ground-state geometry,[56] the $A\leftarrow D$ (unlike the $D\leftarrow A$) excitation is counterintuitive to chemists. Several solid-state driving forces, however, should stabilize $[Fe^{IV}(C_5Me_5)_2]^{2+}$-$[TCNE]^{2-}$. They include Madelung stabilization (2+/2– should be greater than 0/0)[78] and Coulombic repulsion (~ 6 eV for d electrons on the same site[79] and ~ 2.3 eV for electrons delocalized on a planar organic accep-

TABLE 4.[a,b] Magnetic Coupling for Homospin Systems[9,11b]

D (or A)	A (or D)	D → A	A → D	example
		Spin $^1/_2$ Systems		
s^1	s^1	AF	AF	[TMPD][TCNQ],[c] [Cr(C$_6$H$_6$)$_2$]I[f] [TTF][Pt(S$_2$C$_4$F$_6$)$_2$],[d,11b,12] V(C$_6$H$_6$)$_2$•[e]
d^1	s^1	AF	FO	[Ni^{III}(C$_5$Me$_5$)$_2$]•⁺[TCNE]•⁻ [45]
d^3	s^1	FO	AF	[Fe^{III}(C$_5$Me$_5$)$_2$]•⁺[TCNE]•⁻ [11] [Fe^{III}(C$_5$Me$_5$)$_2$]•⁺[C$_4$(CN)$_6$]•⁻ [28]
t^1	s^1	AF	FO	
t^5	s^1	FO	AF	
d^1	d^1	FO	FO	Co^{II}(C$_5$H$_5$)$_2$•,[83b] NO•(g)
d^3	d^1	AF	AF	
t^1	d^1	FO	FO	
t^5	d^1	AF	AF	
d^3	d^3	FO	FO	[Fe^{III}(C$_5$Me$_5$)$_2$]•⁺[BF$_4$]⁻
t^1	d^3	AF	AF	
t^5	d^3	FO	FO	
t^1	t^1	FO	FO	
t^5	t^1	AF	AF	
t^5	t^5	FO	FO	
		Spin 1 Systems		
d^2	d^2	AF	AF	O$_2$,[h] [Ru(OEP)]$_2$[82]
d^2	t^2	FO	AF	
d^2	t^4	AF	FO	
t^2	t^2	FO	FO	
t^2	t^4	AF	AF	
t^4	t^4	FO	FO	
		Spin $^3/_2$ Systems		
t^3	t^3	AF	AF	V(C$_5$H$_5$)$_2$• [83b]
		Spin 2 Systems		
q^4	q^4	AF	AF	
		Spin $^5/_2$ Systems		
p^5	p^5	AF	AF	Mn^{II}(C$_5$H$_5$)$_2$[83a]

[a] AF refers to antiferromagnetic coupling and FO to ferromagnetic coupling. [b] POMO degeneracy (intrinsic or accidental): s = singly (a or b), d = doubly (e), t = triply (t), q = quadruply, or p = quintuply. [c] Ohmasa, M.; Kinoshita, M.; Sano, M.; Akamatu, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1998. [d] Bray, J. W.; Interrante, L. V.; Jacobs, I. S.; Bonner, J. C. *Extended linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 3, pp 353–415. [e] Fischer, E. O.; Joos, G.; Meer, W. *Z. Naturforsch. B* **1958**, *13b*, 456–457. [f] Karimov, Yu. S.; Chibrikin, V. M.; Shchegolev, I. F. *J. Chem. Phys. Sol.* **1963**, *24*, 1683–1685.

TABLE 5.[a,b] Magnetic Coupling for Heterospin Systems[9,11b]

D (or A)	A (or D)	D → A	A → D	example
		Spin $^1/_2$–Spin 1 Systems		
s^1	d^2	FI	FI	
s^1	t^2	FO	FI	
s^1	t^4	FI	FO	
d^1	d^2	FI	FO	c
d^1	t^2	FO	FO	
d^1	t^4	FI	FI	
d^3	d^2	FO	FI	
d^3	t^2	FI	FI	
d^3	t^4	FO	FO	
t^1	d^2	FI	FO	
t^1	t^2	FO	FO	
t^1	t^4	FI	FI	
t^5	d^2	FO	FI	
t^5	t^2	FI	FI	
t^5	t^4	FO	FO	
		Spin $^1/_2$–Spin $^3/_2$ Systems		
s^1	t^3	FI	FI	[Cr^{III}(C$_5$Me$_5$)$_2$]•⁺[TCNE]•⁻ [45]
d^1	t^3	FI	FO	
d^3	t^3	FO	FI	
t^1	t^3	FI	FO	
t^5	t^3	FO	FI	
		Spin 1–Spin $^3/_2$ Systems		
d^2	t^3	FI	FI	
t^2	t^3	FI	FO	
t^4	t^3	FO	FI	
		Spin $^1/_2$–Spin 0 Systems		
s^1	d^0	FO		d
s^1	d^4		FO	d
s^1	t^0	FO		d
s^1	t^6		FO	d

[a] Since $S_D \neq S_A$, FI refers to ferrimagnetic coupling and FO to ferromagnetic coupling. [b] POMO degeneracy (intrinsic or accidental): s = singly (a or b), d = doubly (e), t = triply (t), q = quadruply, or p = quintuply. [c] Proposed for segregated chains of ferromagnetic organic metals.[84] [d] Proposed for ferromagnetic superexchange (see text).[49]
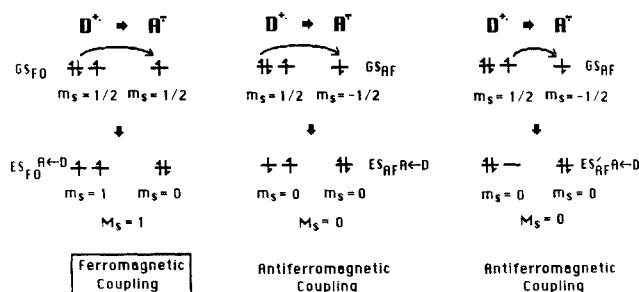
Figure 20. Stabilization of ferromagnetic coupling via forward charge transfer from a d^3 [D]•⁺ to an s^1 [A]•⁻.

tor).[56,80] Electron transfer predicted to be unfavorable by >0.25 eV frequently occurs in the solid.[81]

These d^3/s^1 electron configuration examples lead to contrasting magnetic coupling depending on the direction of virtual charge transfer. Extension of the mechanism to other electron configurations possessing singly (s), doubly (d), triply (t), or higher accidental or intrinsic orbital degeneracies enables the identification of configurations stabilizing ferromagnetic coupling for a specific direction of charge transfer.[19] The results of the evaluation of stabilization are summarized in Table 4 for homospin ($S_D = S_A$) and Table 5 for heterospin ($S_D \neq S_A$) systems containing only singly, doubly, and triply degenerate orbitals. For heterospin systems due to incomplete spin cancellation, antiferromagnetic coupling should lead to ferrimagnetic behavior[19] (FI), and the FO and FI interactions can be predicted.

1. Homospin Systems

For an s^1 [A]•⁻ electron configuration ferromagnetic coupling can be stabilized via forward charge transfer from a D with a d^3 electron configuration (Figure 20). As described above the d^3/s^1 [Fe^{III}(C$_5$Me$_5$)$_2$]•⁺[TCNE]•⁻ complex possesses a ferromagnetic ground state. For retro charge transfer, although antiferromagnetic cou-

pling is predicted[19] for the d^3/s^1 electron configuration, ferromagnetic coupling can result if the D possesses a d^1 electron configuration. Antiferromagnetic coupling is, however, predicted for d^1/s^1 complexes with forward charge transfer. The [Ni^{III}(C$_5$Me$_5$)$_2$]•⁺[TCNE]•⁻ complex[45] possesses the d^1/s^1 electronic configuration and its susceptibility obeys the Curie–Weiss expression with $\Theta = -10$ K, consistent with dominant antiferromagnetic interactions.[19,45]

Virtual disproportionation where an electron on one site is transferred to an adjacent site can stabilize ferromagnetic coupling for a d^1/s^1 or d^3/d^3 electron configuration[19] (Figure 21). For example, for the d^3/d^3 case for ferromagnetically coupled GS$_{FO}$, the electron

TABLE 6. Electron Configuration of Representative Radicals[a]

electron config	S	radical	acronym	symmetry
s[1]	1/2	p-[(CN)$_2$CC$_6$H$_4$C(CN)$_2$][·⁻]	[TCNQ][·⁻]	D_{2h}
		[C$_4$(CN)$_6$][·⁻]		C_{2v}
		p-[Cl$_2$C$_6$(CN)$_2$O$_2$][·⁻]	[DDQ][·⁻]	C_{2h}
		[CC(CN)$_2$]$_3$[·⁻]		D_{3h}
		[H$_2$C$_2$S$_2$C]$_2$[·⁺]	[TTF][·⁺]	D_{2h}
		[F$_2$CCF$_2$][·⁻]		C_{2h}
		[V(C$_6$H$_6$)$_2$][·]		D_6
		p-[Me$_2$NC$_6$H$_4$NMe$_2$][·⁺]	[TMPD][·⁺]	D_{2h}
		[M(S$_2$C$_2$R$_2$)$_2$][·⁻]		D_{2h}
		R$_2$NO[·]		C_{2v}
		[M(phthalocyanine)][·⁺]	[MPc][·⁺]	D_{4h}
		[C(NMe$_2$)$_3$][·]		D_{3h}
		[Tc$_2$Cl$_8$]$^{3-}$		D_{4h}
		[Re$_2$Cl$_4$(PR$_3$)$_4$][·⁺]		D_{4h}
		[(CN)$_2$CC(CN)$_2$][·⁻]	[TCNE][·⁻]	D_{2h}
		[Cr(C$_6$H$_6$)$_2$][⁺]		D_6
d[1]	1/2	NO[·]		$C_{\infty v}$
		Co(C$_5$R$_5$)$_2$[·]		D_5
		[Ni(C$_5$R$_5$)$_2$][·⁺]		D_5
		[Ru(octaethylporphyrin)][·⁺]	[Ru(OEP)]$_2$[·⁺]	D_{4d}
		[O$_2$][·⁺]		$D_{\infty h}$
		[M(octacyanophthalocyanine)][·⁻]		D_{4h}
		[Fe(C$_6$R$_6$)$_2$][·⁺]		D_6
		[Co(S$_2$C$_4$R$_4$)$_2$]$^{2-}$		D_{3h}
d[2]	1	[Ru(octaethylporphyrin)]	[Ru(OEP)]	D_{4h}
		O$_2$		$D_{\infty h}$
		[C$_6$N$_2$(Et)$_2$C$_2$H$_4$]$_3$$^{2+}$		C_{3h}
		[C$_6$(NC$_2$H$_4$)$_6$]$^{2+\,92}$		C_{3h}
		[C$_5$R$_5$][⁺]		D_{5h}
		[Co(C$_6$R$_6$)$_2$][⁺]		D_6
		Ni(C$_5$H$_5$)$_2$	Ni(Cp)$_2$	D_5
		[Co(S$_2$C$_4$R$_4$)$_2$][⁻]		D_{2h}
		[Fe(S$_2$C$_2$(CN)$_2$)$_2$]$^{2-}$		D_{2h}
d[3]	1/2	[Fe(C$_5$R$_5$)$_2$][·⁺]		D_5
		[C$_6$(NEt(CH$_2$))$_6$][·⁺]		C_{3h}
		[C$_6$(NC$_2$H$_4$)$_6$][·⁺]		C_{3h}
		[Ru(octaethylporphyrin)][·⁻]	[Ru(OEP)]$_2$[·⁻]	D_{4h}
		[C(NMe$_2$)$_3$]$^{2+}$		C_{3h}
		[C$_6$H$_2$(OMe)$_2$]$_3$[·⁺]		C_{3h}
		[(Me$_2$N)$_2$CC(NMe$_2$)$_2$][·⁺]		
		[(SR)$_2$CC(SR)$_2$][·⁺]		
t[3]	3/2	[Cr(C$_5$R$_5$)$_2$][⁺]		D_5
		[Ru(O$_2$CO)$_2$]$_2$[⁺]		D_{4h}
		[Ru(O$_2$CMe)$_2$]$_2$[⁺]		D_{4h}
		V(C$_5$H$_5$)$_2$	V(Cp)$_2$	C_5
t[4]	1	[V(C$_6$R$_6$)$_2$][⁺]		D_6
		[Mn(C$_5$H$_5$)$_2$][⁺]		D_5
		Cr(C$_5$H$_5$)$_2$	Cr(Cp)$_2$	C_5
t[5]	1/2	[Ti(C$_6$H$_6$)$_2$][⁺]		C_6
q[5]	5/2	Mn(C$_5$H$_5$)$_2$	Mn(Cp)$_2$	D_5

[a] See ref 19 for references.

Figure 21. Schematic illustration of stabilization of ferromagnetic coupling via disproportionation between d^3 radicals, R[·⁺]. ES$_{FO}$ is stabilized as ES$_{AF}$ is a higher excited state than ES$_{FO}$; i.e., ES$_{FO}$ < ES$_{AF}$.

Assuming the virtual charge transfer involves only the highest energy POMO,[84] all half-filled POMO cases are expected to exhibit antiferromagnetic coupling. For example, the complex [Ru^{II}(OEP)]$_2$ (OEP = octaethylporphyrin) possesses parallel chains of ground-state $S = 1$ (d^2) dimers[82a] in the solid. Preliminary susceptibility data are consistent with the presence of antiferromagnetic behavior.[82b]

2. Heterospin Systems

Heterospin systems, i.e., systems with different spin magnitudes on the donors and acceptors, provide an opportunity to obtain ferrimagnetic as well as ferromagnetic solids. Within this simple nearest-neighbor model antiferromagnetic coupling of adjacent spins of the D and A sublattices could only produce incomplete cancellation of the total spin and thus lead to ferrimagnetic behavior. Ferromagnetic superexchange has been proposed[49] for s^1/d^0 (or s^1/d^4) systems where a virtual triplet is formed via a simultaneous pair of A←D (or D←A) virtual excitations. Attempts to experimentally realize this mechanism with the ···D[·⁺]A[⁻]D[·⁺]A[⁻]··· complex N,N,N',N'-tetramethyl-p-phenylenediamine pentacyanocyclopentadienide, [TMPD][·⁺][C$_5$(CN)$_5$][⁻], have not been successful.[49]

$m_s{}^D = 1/2$; $m_s{}^A = 1$. For the lower symmetry s and d electron configurations two combinations support ferromagnetic coupling, i.e., d^3/d^2 with forward charge transfer and d^1/d^2 with retro charge transfer. Several combinations (d^1/t^2, d^3/t^4, t^1/t^2, and t^5/t^4) are ferromagnetic invariant of direction of electron transfer. Illustrative systems have yet to be identified for these electron configurations.

$m_s{}^D = 1/2$; $m_s{}^A = 3/2$. Several electron configurations, depending on the direction of virtual charge transfer, can stabilize ferromagnetic coupling. The t^3/s^1 configuration expected for [Cr(C$_5$Me$_5$)$_2$]$^+$[TCNE][·⁻] due to an accidental degeneracy of the cation e$_{2g}$ and a$_{1g}$ orbitals[83] is predicted to exhibit ferrimagnetic coupling for either retro or forward charge transfer. Preliminary magnetic susceptibility data show high susceptibility that is characteristic of either ferri- or ferromagnetic, but not paramagnetic, behavior.[45] Detailed analysis is required to distinguish between these two magnetic states.

with $m_s = -1/2$ can be virtually transferred to the adjacent site which can only accept an electron with $m_s = -1/2$. For the antiferromagnetically coupled GS$_{AF}$ the site can only accept an $m_s = +1/2$ electron; however, loss of such an electron from the donor would result in the formation of a higher excited state (Figure 19). Thus, ES$_{FO}$ is lower in energy than ES$_{AF}$ and ferromagnetic coupling is stabilized. This mechanism is invoked between [Fe^{III}(C$_5$Me$_5$)$_2$][·⁺]'s as an additional mechanism for stabilizing ferromagnetic coupling between in-registry chains and provides a means for establishing bulk ferromagnetic behavior as observed for [Fe^{III}-(C$_5$Me$_5$)$_2$][·⁺][TCNE][·⁻].[11b] Cobaltocene and its analogues (d^1) might be a model system to investigate this point as ferromagnetic coupling is predicted for this homomolecular compound. The t^1/d^1 and t^5/d^3 configurations should stabilize ferromagnetic coupling regardless of the direction of virtual charge transfer. Examples of such systems, however, have yet to be identified.
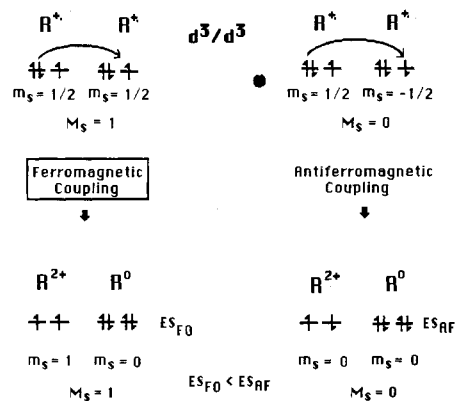
$m_s{}^D = {}^1/_2$; $m_s{}^A = 1$. This electron configuration has been proposed by Dormann, Wudl, and co-workers[84] for the design of a ferromagnetic organic metal. They suggest that segregated chains of mixed-valent donors (i.e., $S = 1$ D•• and $S = {}^1/_2$ D•+) with a diamagnetic A⁻ counterion. Examples of suitable materials to test this situation have not been reported.

D. Generalized Hubbard Model

The importance of the excited state configurational mixing to the lowering of the total ground-state energy in principle can be evaluated by a generalized Hubbard model.[76] This model is useful in examining the competition between delocalization (i.e., as indicated by the nearest-neighbor charge-transfer integral, β) and the energy of transferring an electron between the neighboring sites, ΔE. For $\Delta E \gg \beta$, the energy difference between singlet (antiferromagnetic) and triplet (ferromagnetic) alignments is $\sum J_{ij} \mathbf{A}_i \cdot \mathbf{S}_j$, where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins on adjacent sites i and j, and J_{ij} is an effective exchange interaction. From perturbation analysis the effective exchange interaction, i.e., $J_{ij} \sim \beta^2 / \Delta E$, results from each virtual excitation. The sign of each of the contributions of J_{ij} is determined by the spin of the virtual excited state. That is, J_{ij} is negative (ferromagnetic) if the virtual excited state is a triplet and positive (antiferromagnetic) if it is a singlet. The sum of all of the possible exchange interactions between a pair of neighboring sites is $J_{ij} \sim \sum \beta_n{}^2 / \Delta E_n$, where n refers to each allowed virtual excitation (e.g., as shown in Figures 17 and 18, for d³ D•+ and d¹ A•⁻). Thus, the resulting J_{ij} is the sum of the contributions from each possible excitation weighted by the square of the overlap integral (which varies with excitation and is inversely proportional to the excitation energy) and in principle can be evaluated.

The magnetic coupling of the solid is dependent upon the total sum of pairwise interactions among the spins, $\sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$. Hence, the generalized Hubbard model can be used as a guide to the chemical and physical modifications of the solid to enhance the ferromagnetic coupling. For example, chemical modifications (e.g., design features) of the molecular units to decrease ΔE_n and/or increase β_n should increase the ferromagnetic exchange interaction and lead to the stabilization of ferromagnetic coupling. Thus, application of pressure should increase the overlap and consequently the relative and absolute magnitude of the β_n and should improve the magnetic properties. Application of this generalized Hubbard model to the permethyl-metallocenium radical anion salts is in progress.

E. General Considerations

Assuming the virtual charge transfer involves only the highest energy POMO,[85] stabilization of ferromagnetic coupling via the McConnell mechanism requires that the *stable radicals possess a non-half-filled degenerate POMO*. These radicals must not have structural/electronic distortions that lower the symmetry and break the degeneracies, e.g., the Jahn–Teller effect; however, accidentally degenerate systems (e.g., high-spin transition, lanthanide, and actinide metal coordination complexes) suffice. Furthermore, opposing
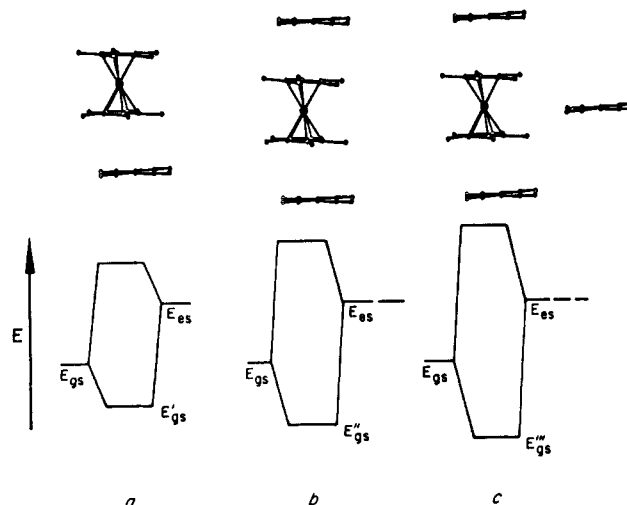

Figure 22. Schematic illustration of (a) mixing of the GS$_{FO}$ with $m_s = 1$ ES$_{FO}$ to lower the energy to GS′$_{FO}$, (b) mixing of the GS$_{FO}$ with a pair of $m_s = 1$ ES$_{FO}$'s arising from intrachain interactions to lower the energy to GS″$_{FO}$, and (c) mixing of the GS$_{FO}$ with additional $m_s = 1$ ES$_{FO}$'s arising from interchain interactions to further lower the energy to GS‴$_{FO}$, which may lead to the macroscopic spin alignment necessary for bulk ferromagnetic behavior.

effects (e.g., retro vs 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, e.g., para-, meta-, or ferrimagnetism.[14] Additionally, other mechanisms[49,50,52,53] for molecular-based ferromagnetic behavior may be operative.

For radicals with intrinsic POMO degeneracies the relatively high symmetry restricts the choice of radicals to specific symmetry point groups. For a d system the molecule or ion must belong to the D_{2d}, C_3, or higher point groups. The orbital symmetry can be accidental. For an intrinsically degenerate t system cubic or icosahedral molecules are necessary.

In contrast to the McConnell model[50,51] ions may not be necessary, but stable radicals are required. Homomolecular species (D ≡ A) in principle are sufficient if virtual disproportionation ([D]²⁺ + D⁰ ← 2 [D]•+) dominates and one of species formed via disproportionation has $S > {}^1/_2$; vide infra. Since the key point is mixing of an excited state with a ground state with spin conservation, a chain structure as proposed by McConnell[50] may not be requisite, but designing materials with strong state mixing is important. Organic or inorganic-based polymer chain and network structures[17] (albeit not molecular solids[18]) as well as nonchain structures with the proper admixture of excited and ground states should suffice.

F. Stabilization of Bulk Ferromagnetism

The admixing of a virtual triplet excited state with the ground state for stabilization of the ferro- or antiferromagnetic coupling model is limited to the repeat unit, i.e., [Fe^{III}(C$_5$Me$_5$)$_2$]•+[TCNE]•⁻. Bulk ferromagnetism requires inter- *and* intrachain spin alignment.[11b,19] Reiterating, mixing of the ES$_{FO}$ with GS$_{FO}$ leads to lowering of the energy to GS′$_{FO}$ (Figures 19b and 22a). Since the cation is essentially equidistant to a [TCNE]•⁻ above and below it within a chain, virtual
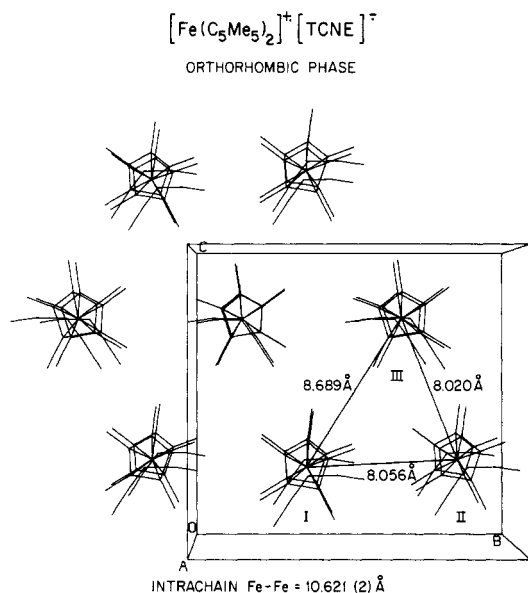
$$[Fe(C_5Me_5)_2]^+[TCNE]^{\cdot-}$$

ORTHORHOMBIC PHASE

INTRACHAIN Fe-Fe = 10.621 (2) Å

Figure 23. Unique chains, I, II, and III, of orthorhombic $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$.

transfer of an e_{2g} electron forming the admixable $M_s = 1$ excited state with either $[TCNE]^{\cdot-}$ may occur. Thus, two excited states can mix with the GS_{FO} to further lower the energy to $GS''_{FO}{}^{11b}$ (Figure 22b), leading to intrachain spin alignment. Intrachain spin alignment leads to energy lowering; however, even with complete intrachain spin alignment (i.e., ferromagnetically coupled), if spins on adjacent chains are aligned in the opposite sense, then bulk antiferromagnetic coupling should dominate. Macroscopic ferromagnetism will not occur unless ferromagnetic interchain spin alignment occurs. If adjacent chains are out-of-registry by one-half the chain axis length, then $[TCNE]^{\cdot-}$'s residing in adjacent chains may be comparably separated from a Fe^{III} site as are the intrachain $[TCNE]^{\cdot-}$'s. Thus, the ES_{FO} on adjacent chains can additionally mix with $GS''_{FO}{}^{11b}$ (Figure 22c) to further lower the energy of the system to ES'''_{FO}, leading to the spin alignment throughout the bulk necessary for bulk ferromagnetism.

For in-registry chains virtual disproportionation between interchain Fe^{III} sites (vide supra) may provide an additional mechanism to align the spins throughout the bulk and contribute to the stabilization of bulk ferromagnetism.[11b] In contrast, in-registry chains with s^1/s^1 interactions (e.g., $[TCNE]^{\cdot-}/[TCNE]^{\cdot-}$) will lead to antiferromagnetic coupling between the chains. The relative magnitude of the resulting interchain ferro- and antiferromagnetic exchange terms will determine if a particular salt will form a 3-D ordered ground state. The unit cell of orthorhombic $[Fe^{III}(C_5Me_5)_2]^{\cdot+}$-$[TCNE]^{\cdot-}$ has three unique adjacent chains, I, II, and III (Figure 23). These in-registry and out-of-registry arrangements (Figure 24) can lead to ferromagnetic and antiferromagnetic as well as unusual magnetic phenomena.

VI. Organic Ferromagnets

The magnetic data on $[Fe(C_5Me_5)_2]^{\cdot+}[A]^{\cdot-}$ demonstrate that ferromagnetism is achievable in organic-based molecular systems. Replacement of $S = ^1/_2$ $[A]^{\cdot-}$

with $S = 0$ $[A]^-$ demonstrates that the organic $[A]^{\cdot-}$ is a critical ingredient for achieving bulk ferromagnetism. In addition to requiring an unpaired electron in a totally organic p-based orbital, this system, of course, contains iron; however, these charge-transfer complexes are more akin to organic compounds than an inorganic network solid. The iron is low-spin Fe^{III}, not high-spin Fe^{II} or Fe^{III} or iron metal. Unlike highly magnetic inorganic materials, these complexes are soluble in conventional polar organic solvents. Furthermore, ferrocenes exhibit a chemical reactivity pattern more similar to that of aromatic organic compounds, e.g., benzene,[86] than that of iron metal or iron oxides.

Nonetheless, the quest for an s or p orbital (organic) based ferromagnet maintains academic interest.[17,46,48,49,73,74,84] Relatively high symmetry or an accidental orbital degeneracy is necessary for the stabilization of ferromagnetic coupling by the McConnell mechanism. These situations are documented for transition-metal-based, coordination-based compounds but are rare for organic compounds. Thus, attention focuses toward stable D_{2d}, C_3, or higher symmetry $S = ^1/_2$ radicals with a degenerate POMO.[87] Breslow[46,51] previously pointed out the necessity of a triplet state[87] and has focused research toward the synthesis of stable organic triplets[46,88] with C_3 or higher symmetry. His group has successfully prepared $S \geq ^1/_2$ organic radicals; however, neither ferromagnetic coupling nor bulk ferromagnetic behavior has been reported.

Radicals possessing D_{2d} symmetry, though rare, in principle may possess a doubly degenerate POMO and should be studied.[19] Hexacyanotrimethylenecyclopropane is predicted to have a d^4 HOMO and oxidation should lead to a d^3 radical cation.[89] Since hexacyanotrimethylenecyclopropane has never been isolated, other derivatives with electron-donating groups, e.g., NMe_2, to stabilize the radical cation, e.g., **13**, would have to be
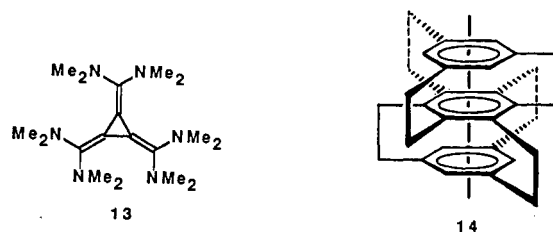
prepared and studied. Alternatively, with the goal of building a solid where adjacent chains are out-of-registry by one-half of a unit cell (as noted for the $[Fe(C_5Me_5)_2]^{\cdot+}[A]^{\cdot-}$ system) permeta-substituted multilayered cyclophanes,[90,91] e.g., [2.2.2] (**14**) or [3.3.3], are challenging targets to prepare. These bulky materials may provide the proper solid-state structure enabling bulk ferromagnetic behavior.

VII. Summary

Quantitative bulk ferromagnetic behavior (spontaneous magnetization) has been established for the organic-like molecular solid $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$. This complex exhibits magnetic behavior characterized by a Curie–Weiss constant (Θ) of +30 K, a Curie temperature (T_c) of 4.8 K, a saturation magnetization of 16 700 (emu G)/mol, and a coercive field of 1 kG at 2 K. Above 16 K the dominant magnetic interactions are
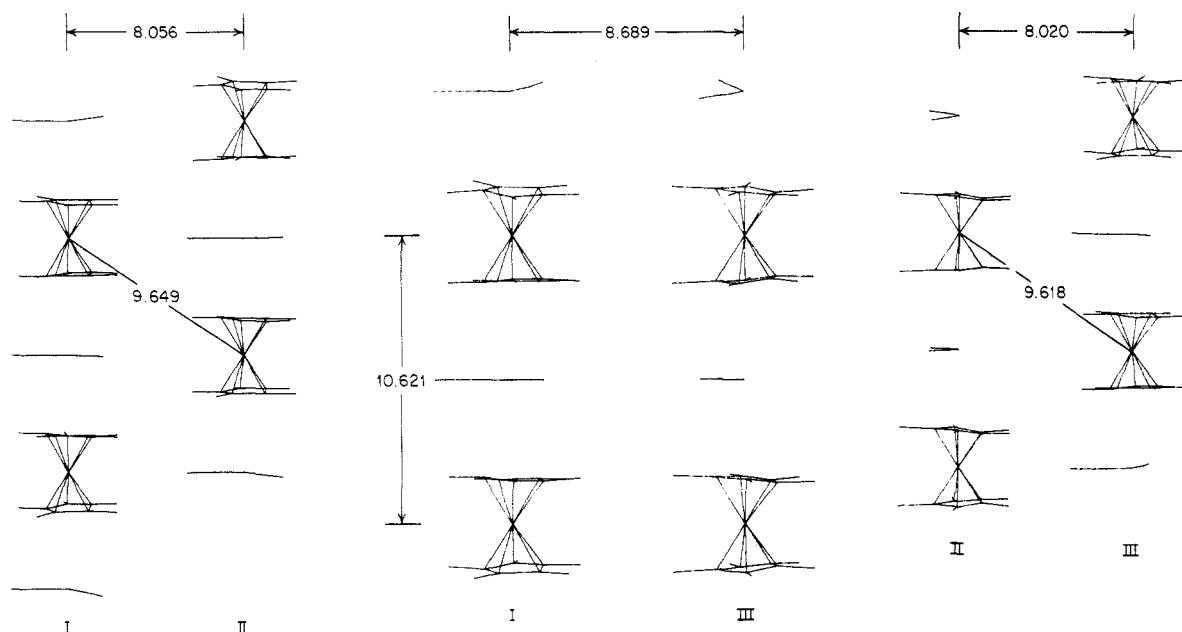
Figure 24. In-registry and out-of-registry chain interactions for orthorhombic $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$.[11b]

along a chain (1-D) and near T_c 3-D bulk effects as evidenced by the value of the critical exponents dominate the susceptibility. Additionally, six-line zero applied magnetic field Zeeman-split ^{57}Fe Mössbauer spectra with large internal fields (>400 kG) are observed.

The structural requirements necessary to prepare molecular ferromagnetic compounds are evolving. The only structure type reported to date possesses parallel $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ linear chains where both the donor (D) and acceptor (A) are radicals. The best studied systems possess decamethylmetallocenium donors; however, replacement of the C_5Me_5 ligand with C_5H_5 does not lead to materials exhibiting ferromagnetic behavior. Preliminary data suggest that C_6 ligands can be utilized to prepare charge-transfer complexes exhibiting ferromagnetic behavior. Substitution of $[TCNE]^{\cdot-}$ with $[DDQ]^{\cdot-}$, $[C_4(CN)_6]^{\cdot-}$, or $[TCNQI_2]^{\cdot-}$ leads to similarly structured complexes exhibiting dominant ferromagnetic behavior. In contrast, the $[TCNQ]^{\cdot-}$ salt exhibits metamagnetic behavior with a Neel temperature of 2.55 K and critical field of ~1.6 kG. The planar $[TCNQF_4]^{\cdot-}$ salts, $[M(S_2C_2(CN)_2)]^-$ salts (M = Ni, Pt), and three polymorphs of the 1:1 $[C_6(CN)_6]^{\cdot-}$ salts as well as the tetrahedral $[FeX_4]^-$ (X = Cl, Br) salts possess different structural motifs and do not exhibit ferromagnetic behavior. Alternate first-row (3d) metallocenes as the $[TCNE]^{\cdot-}$ salt lead to differing magnetic behaviors; i.e., $S = 0$ Co^{III} is paramagnetic, $S = 1/2$ Ni^{III} is antiferromagnetic, and $S = 3/2$ Cr^{III} is ferrimagnetic. Analogous complexes based on second-row (4d) and third-row (5d) Ru^{III} and Os^{III} donors have yet to be prepared.

The extended McConnell model was developed and provides the synthetic chemist with guidance for making new molecular materials (organic, organometallic, main group, polymer, and/or inorganic coordination complex) to study cooperative magnetic coupling in systems. Assuming the electron-transfer excitation arises from the POMO, to achieve ferromagnetic coupling in a molecular solid via the McConnell mechanism

a stable radical (neutral, cations/anions, or ions with small diamagnetic counterions) must possess a degenerate POMO that is not half-filled and the lowest excited state formed via virtual charge transfer (retro or forward) possesses the same spin multiplicity and mixes with the ground state. This requirement limits the structure of a radical to D_{2d}, C_3, or higher symmetry where symmetry-breaking distortions do not occur. Intrinsic doubly and triply degenerate orbitals are not necessary and accidental degeneracies suffice.

To achieve bulk ferromagnetism, ferromagnetic coupling must be established throughout the solid, and a microscopic model based on the intra- and interchain configurational mixing of excited states was discussed. These requirements are met by $[Fe^{III}(C_5Me_5)_2]^{\cdot+}$-$[TCNE]^{\cdot-}$, $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[C_4(CN)_6]^{\cdot-}$, etc. Additionally, this model suggests that the Ni^{III} and Cr^{III} analogues should be respectively antiferromagnetic and ferrimagnetic, as preliminary data suggest. The bulk nature of the magnetic behavior emphasizes the importance of not only the primary and secondary, but the tertiary structure in this class of materials. We are probing these effects via acceptor substitution and studying the structure/property relationship. We are looking toward the development of computational methods to aid in the understanding of the structure/magnetic behavior. Extensive chemical syntheses of cleverly designed radicals as well as physical, experimental, and theoretical insight are necessary to test these concepts and establish a deeper understanding of cooperative phenomena in molecular solids.

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