

Linear Chain Ferromagnetic Charge Transfer Compounds

JOEL S. MILLER,^{a*} ARTHUR J. EPSTEIN^{b*} AND WILLIAM M. REIFF^{c*}

^aE.I. du Pont de Nemours and Co., Inc., Experimental Station E328, Wilmington, DE 19898, USA;

^bDepartments of Physics and Chemistry, Ohio State University, Columbus, OH 43210-1106, USA; and ^cDepartment of Chemistry, Northeastern University, Boston, MA 02115, USA

(Received August 1986)

Abstract. Charge transfer complexes possessing a $\cdots\text{DADA}\cdots$ structure with both the donor, D, and acceptor, A, being $S = 1/2$ radicals may exhibit cooperative magnetic phenomena. The complex $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ [\text{TCNQ}]^-$ exhibits metamagnetic behavior. The similarly structured $[\text{TCNE}]^-$ and $[\text{C}_4(\text{CN})_6]^-$ complexes are ferromagnets, whereas the $[\text{DDQ}]^-$ salt is a paramagnet. The high temperature magnetic susceptibility obeys the Curie-Weiss expression with $\theta = +30$, $+30$, and $+3$ for the $[\text{TCNE}]^-$, $[\text{C}_4(\text{CN})_6]^-$, and $[\text{TCNQ}]^-$ salts, respectively. The ferromagnetic $[\text{TCNE}]^-$ salt exhibits zero field Zeeman split ^{57}Fe Mossbauer spectra with an internal field of 425.6 kOe at 4.23 K. After reviewing the current papers discussing ferromagnetism in molecular (organic) compounds, a qualitative model consistent with the necessary bulk spin alignment required for a ferromagnet is presented.

INTRODUCTION

Since the first report that segregated linear chain charge transfer salts based on TCNQ^1 may exhibit high dc electrical conductivity (as well as other interesting solid state properties)² and the conjecture that a high temperature excitonic superconductor based on a linear chain compound could be prepared,³ the past quarter of a century has witnessed substantial multidisciplinary efforts focused toward understanding this fascinating class of materials.⁴⁻⁷ In contrast, linear chain complexes comprised of alternating donors and acceptors (D/A) are in general poor conductors; however, they exhibit a variety of interesting magnetic phenomena, Table 1.

The phenomena include diamagnetism where both the D and A are diamagnetic and paramagnetism for some cases where either D or A is paramagnetic. The magnetic susceptibility of $[\text{TTF}][\text{M}\{\text{S}_2\text{C}_2(\text{CF}_3)_2\}]$ ($\text{M} = \text{Cu}, \text{Au}$)¹ obeys the Curie-Weiss expression at 300 K with antiferromagnetic exchange and undergoes a spin-Peierls transition for $T \leq 12$ K.¹⁹ We have extended the list of magnetic phenomena observed for molecular based materials with our observation of meta- and ferromagnetic behavior in the $[\text{TCNQ}]^-$ ²⁰ and $[\text{TCNE}]^-$ ^{15,16a} salts, respectively, of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$. Herein we review the prevailing concepts and types of molecular materials proposed to exhibit ferromagnetism and summarize our research aimed at preparing, characterizing and understanding molecular based materials which exhibit cooperative magnetic phenomena and describe how our research contributes to evolution of the field.

MOLECULAR FERROMAGNETS

In the mid-1960s McConnell via a pair of short notes provided intuition for achieving ferromagnetic coupling in organic radicals.^{22,23} In 1963 he conjectured²² that radicals, preferably odd-alternate, possessing large positive and negative π -spin densities aligned so that the positive spin densities on atoms of one radical exchange couple with negative spin densities on adjacent radicals, would undergo a ferromagnetic exchange

interaction. However, close proximity could enhance bond formation as well as the spin exchange interaction between atoms possessing positive and negative π -spin densities. Thus, ferromagnetic coupling must dominate over the overlap of half-filled π -orbitals to form a $S = 0$ bond. Hydrocarbon radicals, R \cdot , are well known to dimerize to form R-R. Even stable π -radicals are known to form $S = 0$ σ -bonded or tight π -like dimers. For example, $[\text{TCNQ}]^-$ is known to form tight π -like²⁴ and σ -bonded²⁵ $[\text{TCNQ}]_2^-$ dimers (Figs. 1,2). Likewise, $[\text{TCNE}]^-$ is dimeric in the $[\text{Fe}(\text{C}_5\text{H}_4)_2\text{C}_3\text{H}_6]^+$ ²⁶ (1:1) salt. The $[\text{TCNE}]_2^-$ dimer possesses a short intradimer separation of 3.05 Å and each $[\text{TCNE}]^-$ moiety deviates from planarity by 15° with the deformation conforming to a b_{3u} vibration²⁶ (Fig. 3). Although these dimers form, it is feasible for the positive spin densities^{16b,27} on either the N or dicyanomethylene carbon to overlap the negative spin density located on the cyano carbon on an adjacent radical anion (Fig. 4). Thus, to comply with McConnell's overlapping spin density model materials will have to be designed such that partially occupied molecular orbital enables the spin interaction to occur while inhibiting bonding. This condition may be difficult to achieve as singly occupied molecular orbitals can always dimerize via an eclipsed structure. Radicals with sufficient steric bulk to prohibit direct bonding may also possess sufficient steric interactions to limit the spin interactions necessary for stabilizing ferromagnetic behavior. The synthesis of materials with the desired magnetic properties based on these concepts will require cleverly designed materials.

In 1967 McConnell postulated²³ that in a molecular crystal comprised of alternating $S = 1/2$ cations and $S = 1/2$ anions such that either the cation or the anion (but not both) has a triplet ($S = 1$) neutral form, mixing of the virtual $S = 1$ excited state with the ground state will lower the energy of the system enabling ferromag-

netic coupling. Breslow²⁸ expanded this to include the formation of either triplet dications or dianions and suggested that 1-D, 2-D, and 3-D ferromagnetic domains might exist. Currently his group is studying ways to stabilize triplet organic radicals with the objective of preparing organic ferromagnets. However, to date only

materials exhibiting antiferromagnetic ordering or $S = 1$ paramagnetic behavior have been prepared.^{28,29} Due to the similarity between the electronic structure of our series of metallocene donors and the idealized donor described in this model some insightful analogies can be made (*vide infra*).

Table 1. Representative Magnetic Phenomena Observed for 1-D ...DADA... Structures

Magnetic Phenomena [D][A] Complex ¹	Charge Transferred	S_D^a	S_A^b	Ref.
Diamagnetic				
[Co(C ₅ Me ₅) ₂][C ₃ (CN) ₅]	1	0	0	8
[Fe(C ₆ Me ₆) ₂][C ₆ (CN) ₆]	2	0	0	9
[perylene]{Ni[S ₂ C ₂ (CF ₃) ₂] ₂ }	0	0	0	10
[Pt(NH ₃) ₄][PtCl ₄]	2	0	0	11
Paramagnetic				
[Co(C ₅ Me ₅) ₂][DDQ]	1	0	1/2	14
[Fe(C ₅ Me ₅) ₂][C ₃ (CN) ₅]	1	1/2	0	16a
[Fe(C ₅ Me ₅) ₂][DDQ]	1	1/2	1/2	17
[TTF][Chloranil] ^c ('neutral' phase)	0.3	1/2	1/2	12,13
[TTF][Chloranil] ^c ('ionic' phase)	0.73	1/2	1/2	12,13
[TMPD][TCNQ]	0.7	1/2	1/2	18
Antiferromagnetic				
[TTF]{Cu[S ₂ C ₂ (CF ₃) ₂] ₂ } ^d	1	1/2	0	19
Metamagnetic				
[Fe(C ₅ Me ₅) ₂][TCNQ]	1	1/2	1/2	20
Ferromagnetic				
[Fe(C ₅ Me ₅) ₂][TCNE]	1	1/2	1/2	15, 16a
[Fe(C ₅ Me ₅) ₂][C ₄ (CN) ₆]	1	1/2	1/2	21

^a Donor spin.

^b Acceptor spin.

^c Undergoes a 'neutral' to ionic transition at 84 K.

^d Undergoes a Spin-Peirels transition at 12 K.

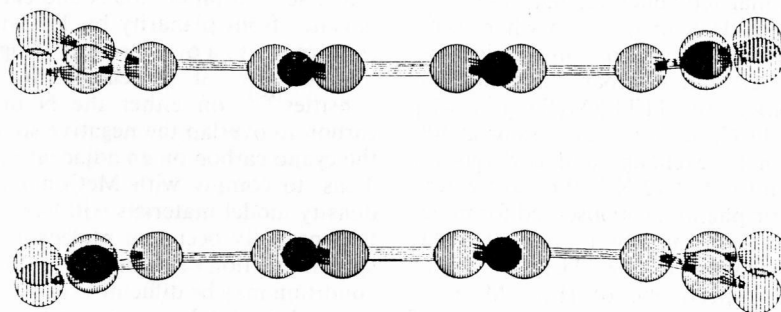


Fig. 1. π -bonded $S = 0$ [TCNQ]₂²⁻ dimer.²⁴

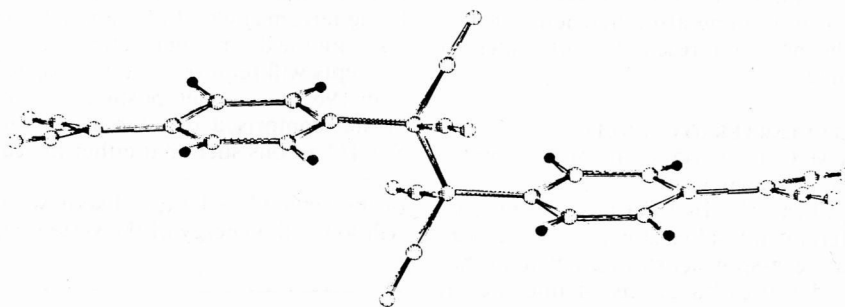


Fig. 2. σ -bonded $S = 0$ [TCNQ]₂²⁻ dimer.²⁵

In 1968 Mataga³⁰ suggested that extended high spin multiplicity organic molecules based on one-half filled nonbonding orbitals occurring for *meta*-substituted aromatic compounds might be ferromagnetic. The simplest member of this series is diphenyl carbene, **1**, whose triplet electronic structure is illustrated in Fig. 5a. Addition of *m*-phenylene groups in principle could lead to a polymeric material with high spin multiplicity (Fig. 5b).

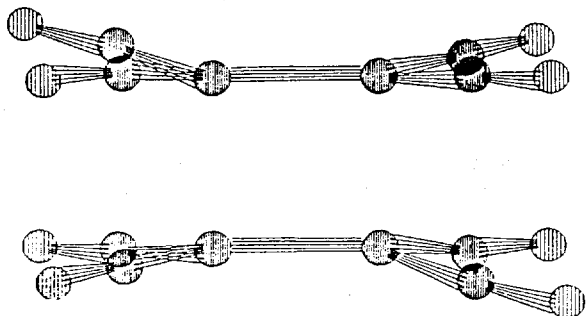


Fig. 3. π -bonded $S = 0$ $[\text{TCNE}]_2^{2-}$ dimer.²⁶

The spin multiplicity would increase with x as $S = x + 1$. This assumes that neither the bonding/nonbonding nor nonbonding/antibonding gaps become comparable to kT or that correlation effects lower the energy of nonmagnetic states to such an extent that the magnetic states do not dominate and thwart the realization of ferromagnetic interactions. Also, distortions or chemical reactions that tend to pair electrons must be avoided. Recently a nonet state tetracarbene generated *in situ* by photolysis of a tetrakis diazo compound was reported to exhibit Curie susceptibility above 65 K, and two regimes of Curie-Weiss behavior for $T < 65$ K. In both regimes the Curie-Weiss constant, θ , was characteristic of antiferromagnetic behavior, i.e., $\theta < 0$. Like dioxygen, O_2 , intramolecular ferromagnetic-like coupling was reported. However, macroscopic intermolecular ferromagnetic coupling was not established for these thermally unstable compounds.³¹

Additionally, in 1978 Ovchinnikov³² identified large odd-alternating conjugated organic molecules as a specific class of materials which if made sufficiently large could exhibit intramolecular ferromagnetic coupling. High spin multiplicity hypothetical compounds were proposed, however, none of them has been character-

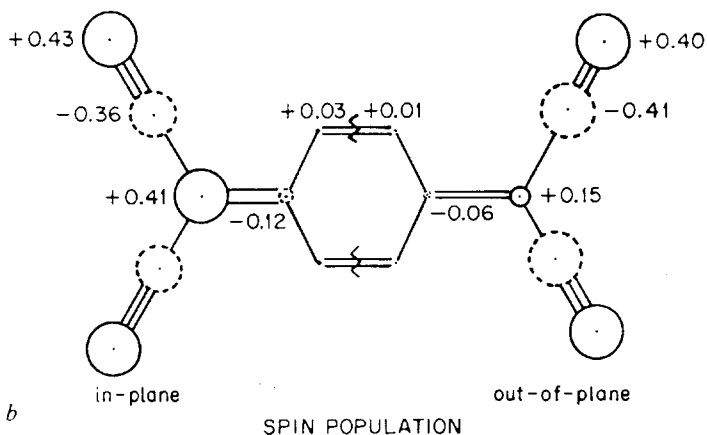
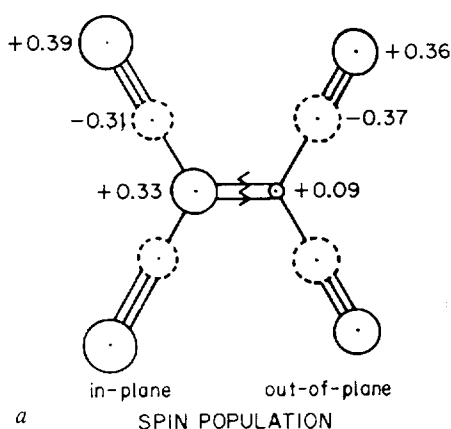


Fig. 4. Calculated spin densities for $[\text{TCNE}]^{\cdot-15}$ and $[\text{TCNQ}]^{\cdot-27}$.

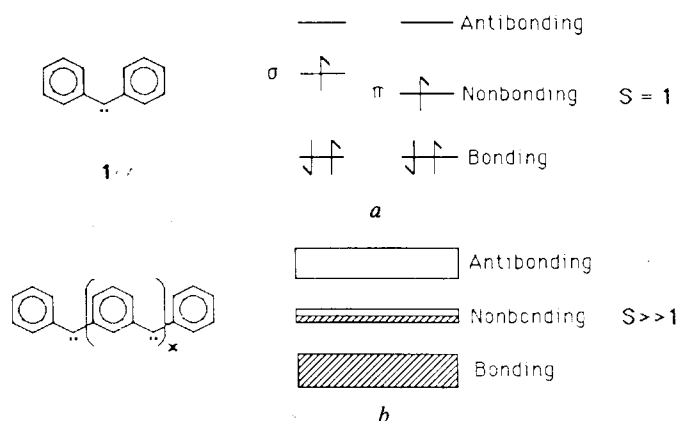


Fig. 5. Schematic electronic structures for diphenylcarbene (a) and higher spin multiplicity related *m*-substituted polymers (b).³⁰

ized to date. Several high spin organic radicals, e.g., $[\text{C}_5\text{Cl}_5]^+$, $[\text{C}_6\text{R}_6]^{2+}$, and $\text{H}_5\text{C}_6\dot{\text{C}}[(\text{C}_6\text{H}_4)\dot{\text{C}}]_3\text{C}_6\text{H}_5$, have been characterized,^{28,31} however, sufficient chemical stability has been lacking. Possibly some of the structures proposed by Ovchinnikov when prepared will possess the requisite chemical stability and exhibit ferromagnetic interactions.

ALTERNATING DONOR/ACCEPTOR SALTS BASED ON DECAMETHYLFERROCENE

The reaction of decamethylferrocene, $\text{Fe}(\text{C}_5\text{Me}_5)_2$, **2**, with acceptors such as TCNQ,^{20,27,33,34} TCNE,^{15,16a} $\text{C}_4(\text{CN})_6$ ²¹ and DDQ^{14,17} leads to the formation of several poorly conducting one-dimensional complexes of 1:1 composition. Each of these compounds possesses a similar structure composed of alternating $S = 1/2$ $[\text{2}]^+$ and $S = 1/2$ radical anions. Fig. 6 illustrates the structure for the 1:1 $[\text{TCNQ}]^-$ salt and Table 2 summarizes the key structural features as well as physical properties for this series of compounds.

$[\text{TCNQ}]^-$ COMPLEX

The reaction of **2** with TCNQ leads to the formation of three phases.³³ The magnetic susceptibility, χ , of the alternating 1-D phase has proved to be anomalous. Complexes of $[\text{2}]^+$ containing diamagnetic anions (e.g., I_3^- , $[\text{TCNQ}]_2^{2-}$, and $[p\text{-}(\text{NC})_2\text{C}(\text{C}_6\text{H}_4)\text{C}(\text{O})(\text{CN})]^-$ ^{20,24,27}) exhibit Curie like behavior while the 1-D 1:1 TCNQ salt exhibits Curie-Weiss, $\chi \propto (T - \theta)^{-1}$,

behavior with $\theta = +3$ K.²⁰ Thus, the product of temperature, T , and the susceptibility of the latter compound, which is temperature independent for $T > 50$ K, increases dramatically at low temperatures (Fig. 7). Interestingly the susceptibility is dependent upon the applied external field. That is, for magnetic fields less than 1.6 kG the complex behaves as an antiferromagnet ($T_N \sim 2.55$ K); however, above the 1.6 kG critical field the substance exhibits ferromagnetism (Fig. 8).²⁰ This metamagnetic behavior³⁵ is most clearly seen in the magnetic moment vs. applied magnetic field curves as a function of temperature.²⁰ Mossbauer spectroscopy (⁵⁷Fe) clearly shows a singlet characteristic of ferrocenium above 4° K; however, at lower temperatures a pair of six line spectra at the same isomer shift gradually appears and is fully resolved at 1.4 K. These six line spectra are due to ordering in the spin doublet state of $[\text{2}]^+$ in zero external field.²⁷ These results indicate the importance of the spin density on the radical $[\text{TCNQ}]^-$ anion.³⁶ The anion spin leads to an internal dipolar field at the $S = 1/2$ Fe(III) sites, small Zeeman splitting, onset of relaxation broadening and ultimately fully resolved hyperfine splitting.²⁷ At low temperature the relaxation becomes slow enough to enable the resolution of a pair of hyperfine split fields, H_{INT} , of 404 and 449 kG. The pair of six line spectra suggests inequivalent iron sites in the lattice that were not present in the -106 C structure determination.³⁴ The details of the cooperative magnetic interactions have not been completely elucidated at the present time.

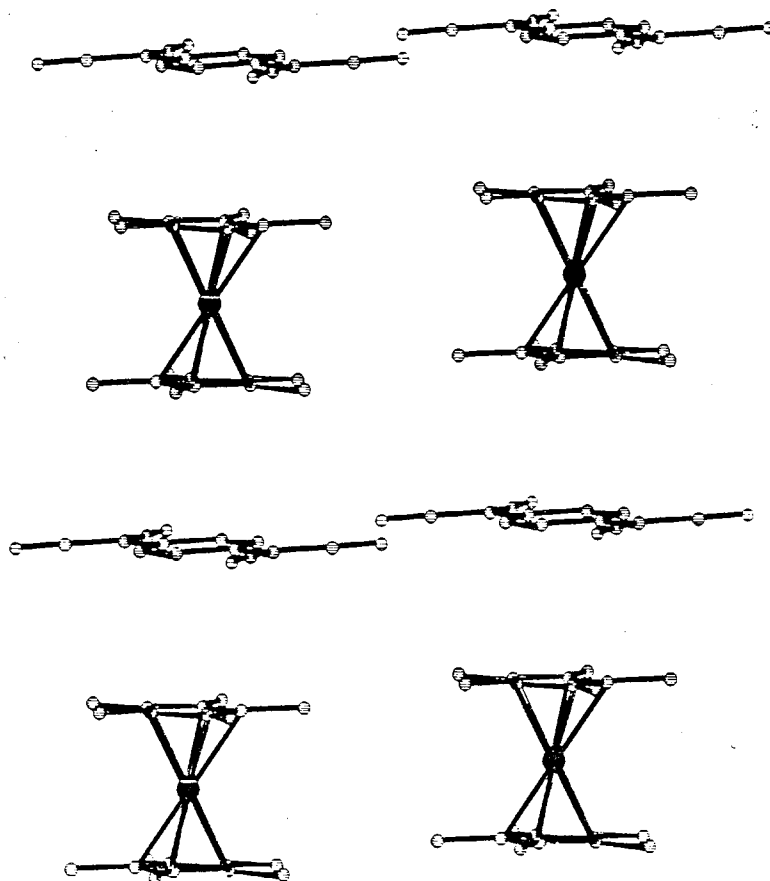


Fig. 6. $\cdots\text{D}^+\text{A}^- \text{D}^+\text{A}^- \cdots$ chain structure of $[\text{Fe}(\text{C}_5\text{Me}_5)_2][\text{TCNQ}]$.²⁷

Table 2. Summary of Structural and Magnetic Properties of Decamethylferrocene Base ...DADA... Complexes

Anion	$C_3(CN)_5^-$	TCNE ^a	TCNE	TCNQ	DDQ	$C_4(CN)_6^-$
Anion Spin, S	0	0	+ 1/2	+ 1/2	+ 1/2	+ 1/2
Anion Charge	1—	0	1—	1—	1—	1—
Space Group	C2/c	P $\bar{1}$	C2/c	P $\bar{1}$	Pbna	P2 ₁ /n
Crystal System	Monoclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
R _f (T), % (C)	3.6(—100)	14(RT)	5.9(—30)	6.0(—106)	5.4(RT)	6.2(—106)
Intrachain Fe-Fe, Å	10.305	9.750 ^d	10.415	10.549	10.616	10.783
C ₅ Me ₅ Anion, Å	3.440	3.280	3.510	3.670	3.564	3.700
C ₅ Me ₅ Anion, deg	0.000	—	2.800	3.900	3.330	26.400
Dihedral angle, deg	8.600	6.78	8.603	8.628	8.691	8.719
Interchain Fe-Fe, Å	9.567	7.700	8.732	9.348	9.723	9.865
	9.939	7.890	9.651	—	10.033	10.030
	—	8.086	—	—	—	—
$\nu(CN)$, nujol. cm ⁻¹	2106s,2207s	2203,2180 ^b	2144s,2183s	2153s,2179s	2206s	2168s,2186s
Mossbauer Lines, 1.4 K	1	2	6	12	6	6
H _{int} , kG (1.4 K)	—	—	424	404; 449	451	449
Curie-Weiss, K	1—	—	30	3	—	30
T _{ordering} , K	—	—	16	2.55;	—	7.5
Magnetism	Paramagnetic	Diamagnetic ^d	Ferromagnetic	Metamagnetic	Paramagnetic	Ferromagnetic
Reference	16	c	15,16	27,34	17	21

^a as the Fe(C₅H₅)₂ complex; ^b KBr; ^c E. Adman, M. Rosenblum, S. Sullivan and T. N. Margulis, *J. Am. Chem. Soc.* **89**, 4540 (1967); ^d J. S. Miller, J. H. Zhang, and W. H. Reiff, unpublished; B. W. Sullivan, B. M. Foxman, M. D. Ward, M. Rosenblum, R. W. Fish and C. Bennet, *J. Am. Chem. Soc.*, **86**, 5166 (1964).

[DDQ]⁻ COMPLEX

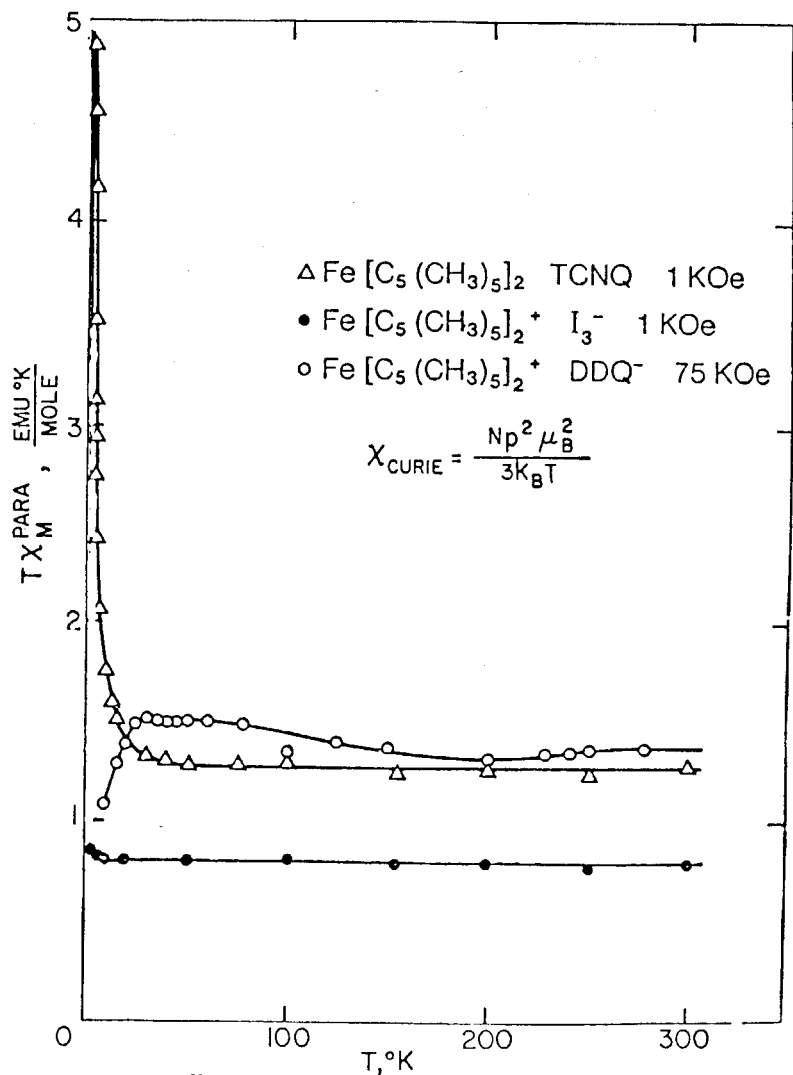
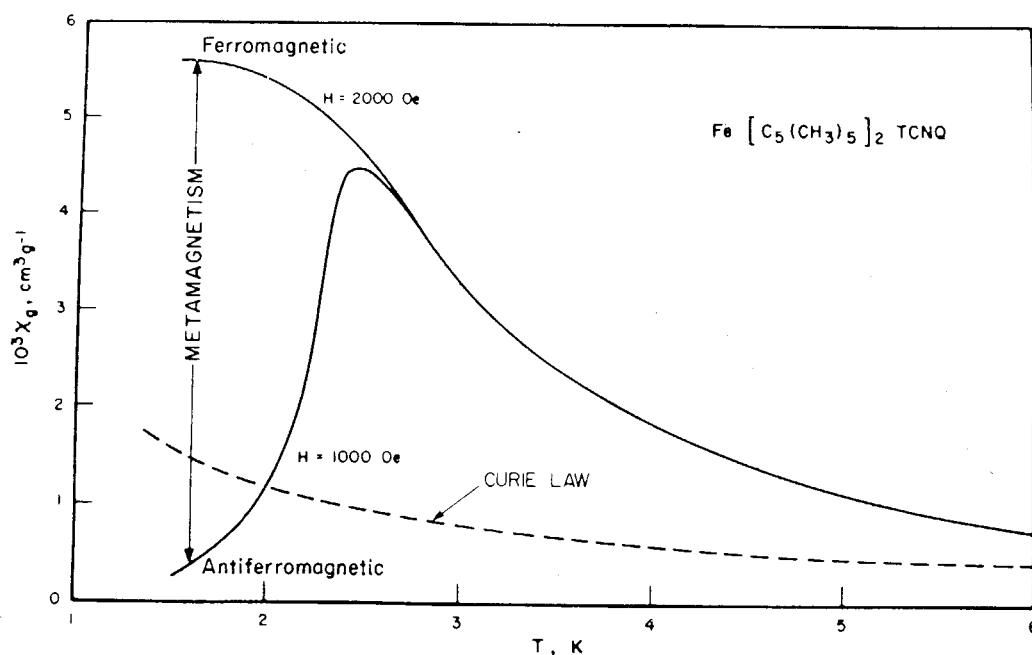
Replacement of [TCNQ]⁻ with [DDQ]⁻ in the structure nominally does not change the solid state 1-D structure; however, cooperative magnetic interactions are not observed.¹⁷ The reasons for the different $\chi(T)$ behavior are unknown. Initially it was thought that the anion was diamagnetic [DDQH]⁻. However, after noting that the complex exhibited a six line hyperfine split ⁵⁷Fe Mossbauer spectrum [H_{INT} (1.4 K) = 451 kG] arising from slow paramagnetic relaxation that was qualitatively similar to that observed for the [TCNQ]⁻ salt (*vide supra*) we reformulated the anion as S = 1/2 [DDQ]⁻. Recently from interpretation of vibrational and electronic spectra and esr of solutions, we have confirmed the S = 1/2 [DDQ]⁻.¹⁴ The lower symmetry of this acceptor and its consequential interchain cation/anion interactions might be important in understanding why this complex does not exhibit cooperative magnetic interactions.

[TCNE]⁻ COMPLEX

The [TCNE]⁻ salt of [Fe(C₅Me₅)₂]⁺ also forms a fully charge transferred alternating 1-D ...DADA... structure. Attempts to grow crystals of [Fe(C₅Me₅)₂]⁺[TCNE]⁻ proved extremely difficult due to the air sensitivity of [TCNE]⁻^{15,16a,37} and an easily lost acetonitrile molecule of solvation. Attempts to recrystallize the [TCNE]⁻ complex under ambient conditions leads to the isolation of 1-D [Fe(C₅Me₅)₂]⁺[(NC)₂C=C(CN)C(CN)₂]⁻^{10a} which arises from oxidative disproportionation of [TCNE]⁻.^{37,38} Also, attempts to collect crystals suitable for single crystal X-ray diffraction continually failed as loss of solvent led to isolation of apparent single crystals which diffracted like powders. A single crystal was ultimately grown in a capillary within a diffractometer at -30°C and ena-

bled the determination of the structure.^{15,16a} This charge transfer salt has no detectible esr signal attributable to the bulk above 5 K.³⁹ At room temperature the ⁵⁷Fe Mossbauer spectrum exhibits a single transition ($\delta = 0.427$ mm/sec, $\Gamma = 0.323$ mm/sec) typical of ferrocenium ions. Below 15 K this system exhibits the onset of magnetic hyperfine splittings suggesting combinations of slow paramagnetic relaxation broadening and cooperative three-dimensional ordering processes. The hyperfine splitting process for [2]⁺[TCNE]⁻ initiates at ~12 K and is nearly fully resolved at 10 K (Fig. 9). The 4.23 K spectrum in zero applied magnetic field corresponds to a single internal hyperfine field of 424 kG. This process is essentially coincident with the inflection point in the low field magnetic susceptibility data and is consistent with cooperative three-dimensional ferromagnetic ordering for which the Curie temperature is estimated to be ≤ 16 K in consideration of both the susceptibility and zero field Mossbauer spectroscopy data.^{16a}

The magnetic susceptibility of [2]⁺[TCNE]⁻ was measured by the Faraday and SQUID techniques for 1.7 < T < 300 K and 0.3 < H < 80 kG. Above 60 K the complex obeys the Curie-Weiss expression, i.e. $\chi = C/(T - \theta)$, $\theta = +30$ K, thereby characterizing this complex as having dominant ferromagnetic interactions. The enhanced susceptibility is seen in the plot to $T\chi$ vs. T, Fig. 10. Above 16 K (the maximum in Fig. 10) preliminary calculations suggest that the data can be fit by a 1-D Heisenberg model with ferromagnetic exchange.^{15,16a} For the polycrystalline samples the magnetization at 4.23 K saturates to a value of $1.1 \pm 0.1 \cdot 10^4$ emuG/mol.^{15,16a} This is comparable to $1.20 \cdot 10^4$ emuG/mol value for iron metal.⁴⁰ Initial measurements demonstrate that a sizable moment persists in zero applied magnetic field at the lowest temperatures measured (i.e., 2 K).^{16a}

Fig. 7. χT vs. T for [Fe(C₅Me₅)₂][TCNQ].²⁰Fig. 8. Low temperature $\chi(T,H)$ for [Fe(C₅Me₅)₂][TCNQ].²⁰

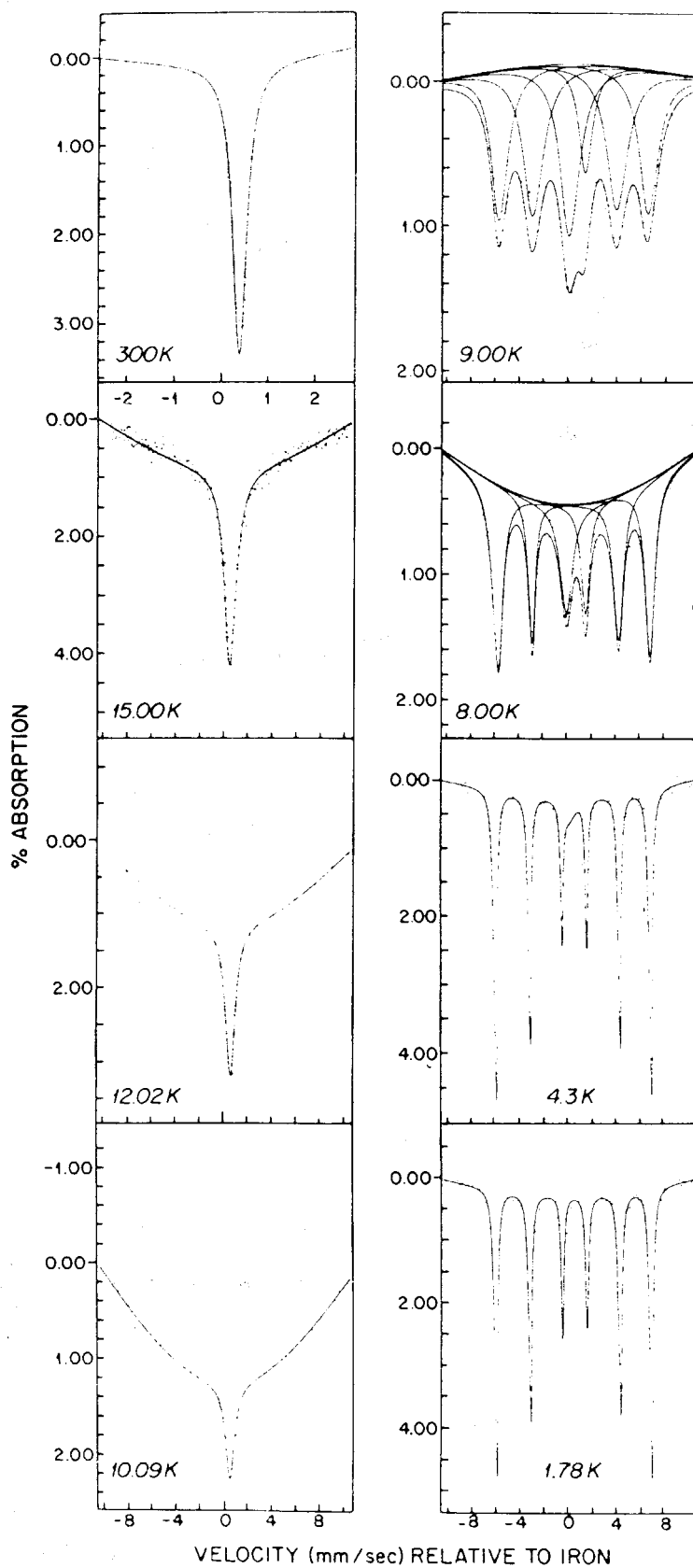
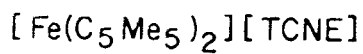


Fig. 9. Temperature dependence of the ^{57}Fe Mossbauer spectra for $[\text{Fe}(\text{C}_5\text{Me}_5)_2][\text{TCNE}]$.^{16a}

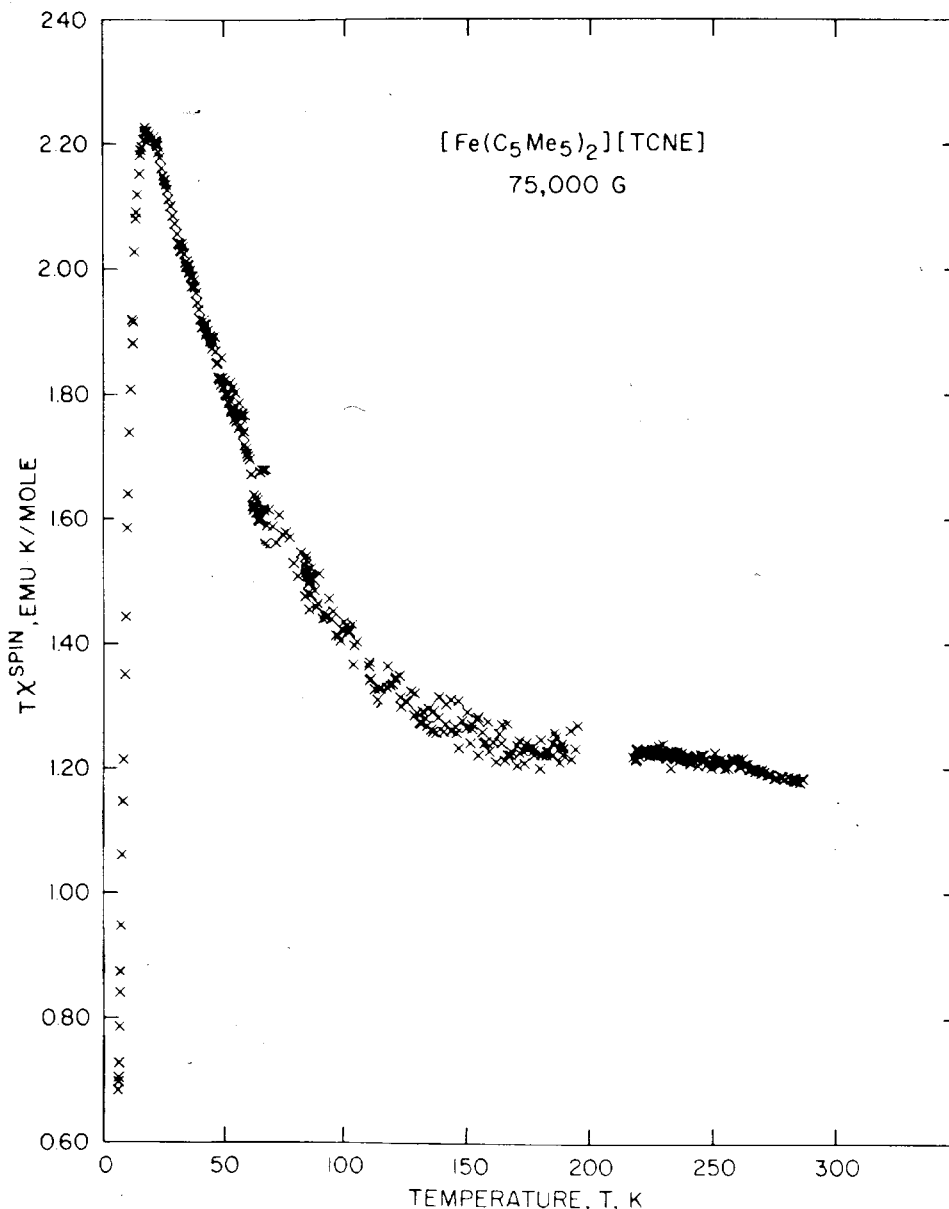


Fig. 10. χT as a function of T for $[\text{Fe}(\text{C}_5\text{Me}_5)_2][\text{TCNE}]$.¹⁵

$[\text{C}_4(\text{CN})_6]^-$ COMPLEX

The $[\text{C}_4(\text{CN})_6]^-$ salt also forms a 1:1 1-D completely charge transferred salt. Unlike the previous three salts discussed the $[\text{C}_4(\text{CN})_6]^-$ is disordered in the solid.²¹ Above 10 K ^{57}Fe Mossbauer spectra exhibit a narrow singlet typical of ferrocenium cations; however, below ~ 9 K spectral broadening and hyperfine splitting are evident with near full resolution and internal field saturation achieved ~ 7.5 K. The overall Mossbauer behavior is qualitatively similar to that observed for the $[\text{TCNE}]^-$ salt. High temperature ($T > 50$ K) susceptibility measurements show that $[\text{Fe}(\text{C}_5\text{Me}_5)_2][\text{C}_4(\text{CN})_6]$ obeys the Curie-Weiss law, $\chi_M \propto (T - \theta)^{-1}$, with $\theta = +30$ K. Thus, this material also possesses dominant ferromagnetic interactions. Ferromagnetic magnetic behavior dominate to the lowest fields measured, i.e., 30 G. Furthermore, the susceptibility becomes mar-

kedly field dependent between 6 and 7 K. This is nearly coincident with the onset of magnetic hyperfine splitting of the Mossbauer spectra and with the Mossbauer spectral data suggests an ordering temperature of 7.5 K.²¹

DISCUSSION

We have demonstrated that both $[\text{Fe}(\text{C}_5\text{Me}_5)_2][\text{TCNE}]$ and $[\text{Fe}(\text{C}_5\text{Me}_5)_2][\text{C}_4(\text{CN})_6]$ exhibit dominant ferromagnetic interactions at the lowest fields accessible to us at the present time. McConnell's 1967 model suggests a conceptual framework that enables us to begin to understand the microscopic origins of ferromagnetic behavior for this class of compounds. Recalling from the introduction, McConnell states that if a $S = 1$ state is available to mix with the ground state upon virtual charge transfer, the spin alignment or ferromagnetic

interactions may be stabilized.²³ The $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$ cation has a $S = 1/2$ $a_{1g}^2 e_{2g}^3$ ground state (Fig. 11a) and upon virtual transfer of an e_{2g} electron to the $b_{3g} \pi^*$ orbital of $[\text{TCNE}]^-$ forming $S = 0$ $[\text{TCNE}]^{2-}$ a $S = 1$ $2+$ cation possessing the $a_{1g}^2 e_{2g}^2$ electronic configuration results (Fig. 11b). Mixing of the ground state, ϕ_{gs} , with the excited state, ϕ_{es} , forms a new ground state ϕ'_{gs} of lower energy, E'_{gs} (Fig. 12a). Thus, spin alignment lowers the energy of the system. Since the cation is essentially equidistant to a $[\text{TCNE}]^-$ above and below it within a chain, a virtual transfer of its e_{2g} electron

forming the excited $S = 1$ state to either $[\text{TCNE}]^-$ may occur. Thus, two excited state configurations would mix with the ground state further lowering the energy to E''_{gs} (Fig. 12b). This 'spin delocalization' can propagate along a chain leading to stabilization of the system via spin alignment. In the limit that the spins in one $\cdots \text{DADA} \cdots$ chain are aligned, i.e., ferromagnetically coupled, macroscopic ferromagnetism will not occur unless the spins on each chain are aligned. If the spins on adjacent chains are in the opposite sense, then depending on whether the spins completely cancel or

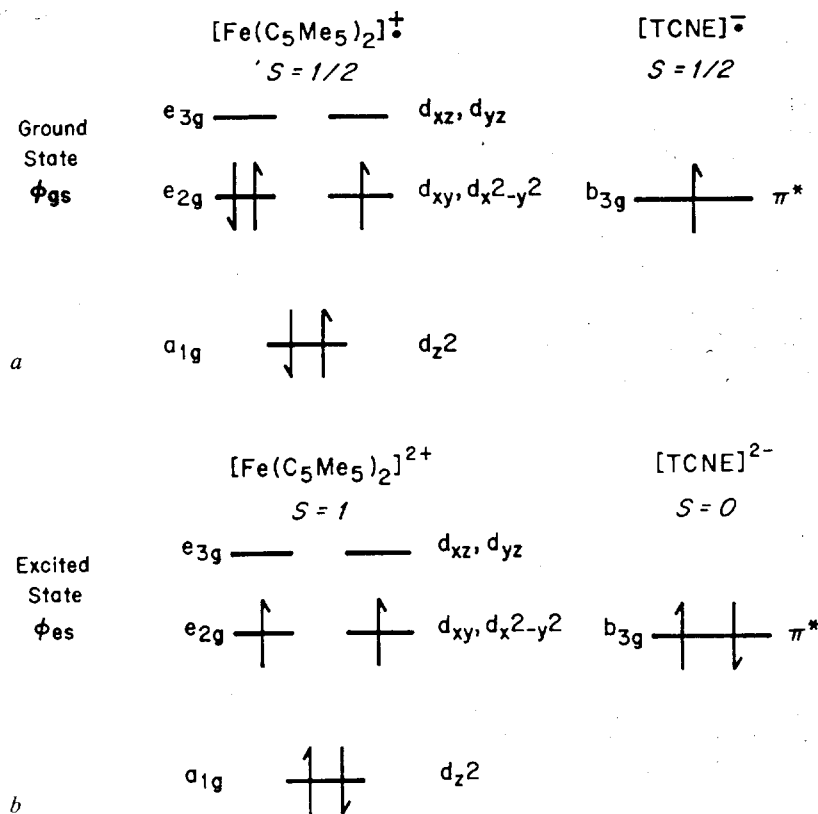


Fig. 11. Schematic ground state electronic structure for $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ [\text{TCNE}]^-$ (a) and allowed excited state electronic structure for $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{2+} [\text{TCNE}]^{2-}$ (b).

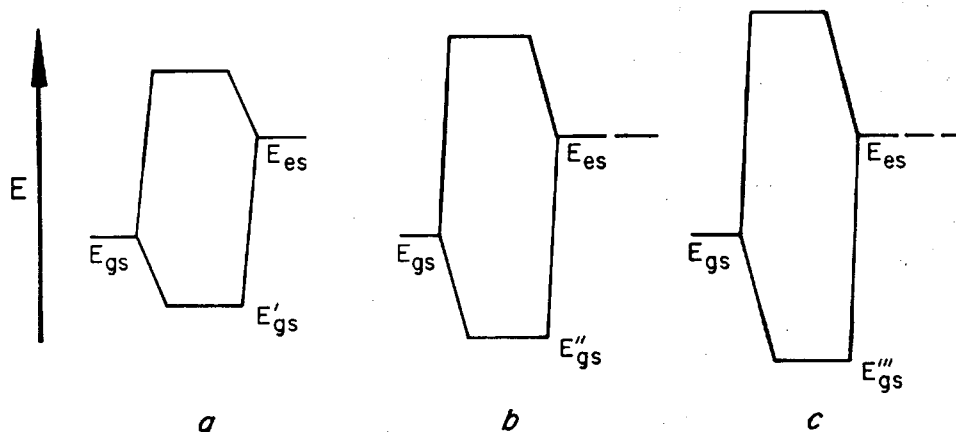


Fig. 12. Stabilization of the ground state via mixing with the excited states. (a) Mixing of ground state and $S = 1$ excited state; (b) mixing of ground state and pair of localized excited states; and (c) mixing of ground state and pair of intrachain and interchain localized excited states.

not, antiferromagnetic or ferrimagnetic behavior should dominate.

Spin alignment between chains can occur if the [TCNE]⁻ residing in an adjacent chain is proximal to the Fe^{III}. If the inter- and intrachain [TCNE]⁻'s are comparably separated from a Fe^{III} site, then an e_{2g} electron can be transferred to a b_{3g} [TCNE]⁻ orbital on an adjacent chain to further stabilize the system (Fig. 12c) and align spins on adjacent chains. This could lead to macroscopic ferromagnetic interactions. This proximity of [TCNE]⁻ to Fe^{III} between some parallel chains is comparable to the intrachain separations suggesting that virtual electron transfer between chains is viable.^{16a}

An additional, but presumably less important, mechanism for spin alignment between chains is electron transfer mediated 'self-spin' exchange between like cations and independently between like anions. For example, to a virtual S = 1 [Fe(C₅Me₅)₂]²⁺ on site I an electron could be transferred from a S = 1/2 [Fe(C₅Me₅)₂]⁺ on site II (located on an adjacent chain), such that the S = 1/2 + cation was subsequently on site I and the S = 1/2 + cation on site II. Likewise, electron transfer (spin exchange) could occur for S = 0 [TCNE]²⁻ and S = 1/2 [TCNE]⁻ on adjacent chains. The structure^{16a} of [Fe(C₅Me₅)₂][TCNE] possesses both parallel chains in- and out-of-registry. The in-registry chains have cations in close proximity with cations (as well as anions in close proximity to anions) to support cation²⁺/cation⁺ and anion²⁻/anion⁻ electron transfer mediated spin exchange to further stabilize the system and align spins on adjacent chains. The intra- and interchain alignment of spins are necessary for macroscopic ferromagnetism.

SUMMARY

The area of molecular based ferromagnetic compounds is in its infancy.^{28,41} Our data demonstrate that ferromagnetic behavior is achievable and we hope that it will also be observed for totally organic systems. Our system, of course, possesses iron; nonetheless, these charge transfer complexes are more akin to an organic compound than an inorganic solid. The iron in our system is low spin Fe^{III} not high spin Fe^{II}, or Fe^{III} or iron metal that one typically associates with ferro^{42a} or ferrimagnetic^{42b} iron compounds. The anion is, of course, completely organic. Unlike highly magnetic inorganic substances, the [Fe(C₅Me₅)₂][anion] complexes are soluble and recrystallizable from conventional polar organic solvents and are insoluble or decompose in aqueous solvents. Furthermore, from a chemical reactivity viewpoint ferrocenes are considered to be similar to aromatic compounds like benzene.⁴³

Verification and extension of McConnell's model in our systems as well as work on preparing and characterizing new highly magnetic compounds are in progress.

Acknowledgment WMR gratefully acknowledges the financial support of U.S. National Science Foundation, Division of Materials Research, Solid State Chemistry Program Grants 8016441 and 8313710.

REFERENCES AND NOTES

1. TCNQ = 7,7,8,8-Tetracyanoquinodimethane; TCNE = tetracyanoethylene; TTF = tetrathiafulvalene; DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone; TMPD = N,N,N',N'-tetramethyl-p-phenylenediamine.
2. D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R.

- Melby, R. E. Benson and W. E. Mochel; *J. Amer. Chem. Soc.*, **82**, 6408 (1960); R. G. Kepler, P. E. Bierstedt, and R. E. Merrifield, *Phys. Rev. Lett.*, **5**, 503 (1960).
3. W. A. Little, *Phys. Rev.*, **134**, 1416 (1964); *Sci. Amer.* **212**(2), 21 (1965).
4. See for example J. S. Miller, ed., *Extended Linear Chain Compounds*, Vols. 1-3, Plenum Publishing Corporation, N.Y.
5. For detailed overview, see the proceedings of the recent series of international conferences: (a) *Mol. Cryst. Liq. Cryst.* **117-121** (1985) (C. Pecile, G. Zerbi, R. Bozio, and A. Girlando, eds.); (b) *J. Phys. (Paris) Colloque*, **44-C3** (1983) (R. Comes, P. Bernier, J. J. Andre, and J. Rouxel, eds.); (c) *Mol. Cryst. Liq. Cryst.*, **77**, **79,82**, **83**, **85** and **86** (1981) (A. J. Epstein, and E. M. Conwell, eds.); (d) *Chemica Scripta*, **17** (1981) (K. Carneiro, ed.); (e) *Lecture Notes in Physics* **95** and **96** (1979) (S. Bartsic, A. Bjelis, J. R. Cooper, and B. A. Leontic, eds.); and (f) *Ann. N.Y. Acad. Sci.*, **313** (1978) (J. S. Miller and A. J. Epstein, eds.).
6. J. Simon and J. J. Andre, *Molecular Semiconductors*, Springer Verlag, NY (1985).
7. A. J. Epstein and J.S. Miller, *Sci. Amer.* **241** (4), 52(1979); K. Bechgaard and D. Jerome, *Sci. Amer.*, **247**(2), 52 (1982).
8. M. D. Ward, unpublished results.
9. J. S. Miller, unpublished results.
10. R. D. Schmitt, R. M. Wing and A. H. Maki, *J. Am. Chem. Soc.*, **91**, 4394 (1969).
11. G. M. Summa and B. A. Scott, *Inorg. Chem.*, **19**, 1079 (1980); F. Mehran and B. A. Scott, *Phys. Rev. Lett.*, **31**, 99 (1973).
12. P. Batail, S. J. LaPlaca, J. J. Mayerle and J. B. Torrance, *J. Am. Chem. Soc.*, **103**, 951 (1981); J. J. Mayerle, J. B. Torrance, and J. T. Crowley, *Acta Cryst.* **B35**, 2988 (1979); Y. Kanai, M. Tani, S. Kagoshima, Y. Tokura, and Y. Koda, *Syn. Met.*, **10**, 157 (1984/5); R. M. Metzger and J. B. Torrance, *J. Am. Chem. Soc.* **107**, 117 (1985).
13. J. B. Torrance, private communication.
14. J. S. Miller, P. J. Krusic, D. A. Dixon, W. M. Reiff, J. H. Zhang, E. Anderson and A. J. Epstein, *J. Am. Chem. Soc.*, **108**, 4459 (1986).
15. J. S. Miller, J. C. Calabrese, A. J. Epstein, R. W. Bigelow, J. H. Zhang and W. M. Reiff, *J. Chem. Soc. Chem. Commun.*, 1026 (1986).
16. (a) J. S. Miller, J. C. Calabrese, S. R. Chittapeddi, A. J. Epstein, R. W. Zhang, W. M. Reiff and A. J. Epstein, *J. Am. Chem. Soc.*, **109**, 769 (1987). (b) D. A. Dixon and J. S. Miller, *J. Am. Chem. Soc.*, in press.
17. E. Gebert, A. H. Reis, Jr., J. S. Miller, H. Rommelmann, and A. J. Epstein, *J. Amer. Chem. Soc.* **104**, 4403 (1982).
18. M. Kinoshita, and H. Akamatu, *Nature*, **207**, 291 (1965); M. Ohmasa, M. Kinoshita, M. Sano and H. Akamatu, *Bull. Chem. Soc. Jap.*, **41**, 1998 (1968).
19. J. W. Bray, L. V. Interrante, J. S. Jacobs and J. C. Bonner, in J. S. Miller, ed., *Extended Linear Chain Compounds*, Vol. 3, Plenum Pub. Corp., New York, N.Y. 1983, p. 353.
20. G. A. Candela, L. Swartzendruber, J. S. Miller and M. J. Rice, *J. Amer. Chem. Soc.*, **101**, 2755 (1979).
21. J. S. Miller, W. M. Reiff and J. H. Zhang, *J. Am. Chem. Soc.*, in press.
22. H. M. McConnell, *J. Phys. Chem.*, **39**, 1910 (1963).
23. H. M. McConnell, *Proc. R.A. Welch Found. Chem. Res.*, **11**, 144 (1967).
24. e.g., A. H. Reis, Jr., L. D. Preston, J. M. Williams, S. W. Peterson, G. A. Candela, L. J. Swartzendruber and J. S. Miller, *J. Am. Chem. Soc.*, **101**, 2756 (1979).
25. S. K. Hoffmann, P. J. Corvan, P. Singh, C. N. Sethulekshine, R. M. Metzger and W. E. Hatfield, *J. Am. Chem. Soc.*, **105**, 4608 (1983); R. H. Harms, H. J. Keller, D. Nothe and M. Werner, *Mol. Cryst. Liq. Cryst.*, **65**, 179 (1981).
26. D. A. Lemerovshii, R. A. Stukan, B. N. Tarasevich, Ya. L. Slovokhotov, M. Ya Antipin, A. E. Kalinia and Yu. T. Struchov, *Koord. Khim.*, **7**, 240 (1981).

27. J. S. Miller, W. M. Reiff, J. H. Zhang, L. D. Preston, A. H. Reis, Jr., E. Gebert, M. Extine, J. Troup, D. A. Dixon and A. J. Epstein, M. D. Ward, *J. Phys. Chem.*, in press.
28. R. Breslow, *Pure Appl. Chem.*, **54**, 927 (1982); R. Breslow, B. Jaun, R. Q. Klutz and C.-Z. Xia, *Tetrahedron*, **38**, 863 (1982).
29. R. Breslow, P. Maslak and J. S. Thumäides, *J. Amer. Chem. Soc.*, **106**, 6453 (1984); R. Breslow, *Mol. Cryst. Liq. Cryst.*, **125**, 261 (1985).
30. N. Mataga, *Theor. Chim. Acta*, **10**, 372 (1968); H. Iwamura, T. Sugawara, K. Itoh and K. Takai, *Mol. Cryst. Liq. Cryst.*, **125**, 251 (1985); T. Sugawara, S. Bandow, K. Kimura, H. Iwamura and K. Itoh, *J. Am. Chem. Soc.*, **108**, 368 (1986); H. Iwamura, *Pure Appl. Chem.*, **58**, 187 (1986).
31. T. Sugawara, S. Bandow, K. Kimura and H. Iwamura, *J. Amer. Chem. Soc.*, **106**, 6449 (1984).
32. A. A. Ovchinnikov, *Dok. Nauk Akad. USSR*, **236**, 928 (1977); *Theor. Chim. Acta*, **47**, 297 (1978).
33. J. S. Miller, A. H. Reis, Jr. and G. A. Candela, *Lect. Notes Phys.*, **96**, 313 (1978).
34. J. S. Miller, A. H. Reis Jr., E. Gebert, J. J. Ritsko, W. R. Salaneck, L. Kovnat, T. W. Cape and R. P. Van Duyne, *J. Amer. Chem. Soc.*, **101**, 7111 (1979).
35. E. Stryjewski and N. Giordano, *Adv. Phys.*, **26**, 487 (1977).
36. Similar phenomena although over different temperature ranges are also observed for the [TCNE]⁻, [DDQ]⁻, and [C₄(CN)₆]⁻ salts of [2]⁺.
37. W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **80**, 2795 (1958).
38. B. Bertolasi and G. Gilli, *Acta Cryst.*, **C39**, 1242 (1983); G. A. Sim, D. I. Woodhouse and G. R. Knox, *J. Chem. Soc., Dalton*, 629 (1979); W. P. Jensen and R. A. Jacobson, *Inorg. Chim. Acta*, **50**, 189 (1981); B. W. Sullivan and B. M. Forman, *Organometallics*, **2**, 187 (1983).
39. J. S. Miller, P. J. Krusic, A. J. Epstein, W. M. Reiff and J. H. Zhang, *Mol. Cryst. Liq. Cryst.*, **120**, 27 (1985).
40. C. Kittel, *Introduction to Solid State Physics*, 5th ed., J. Wiley & Sons, NY, NY, 1976, p. 465; R. C. Weist, *Handbook of Chemistry and Physics*, Chem. Rubber Pub. Co., 64th ed., 1984, p. E107.
41. O. Khan, *Angew. Chem., Internat. Edit.*, **24**, 834 (1985).
42. (a) e.g., Fe²⁺, (b) e.g., Fe₃O₄.
43. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., J. Wiley & Sons, 1980, p. 1166.