Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Structure-Magnetic Coupling Relationships for Metallocene-Acceptor Based Charge Transfer Complexes

Joel S. Miller [a] & Arthur J. Epstein [b]

[a] Central Research and Development, E. I. du Pont de Nemours and Co., Inc., Experimental Station-E328, Wilmington, DE, 19880-0328

[b] Department of Physics and Department of Chemistry, The Ohio State University, Columbus, OH, 43210-1106, U. S. A.

Version of record first published: 22 Sep 2006.

To cite this article: Joel S. Miller & Arthur J. Epstein (1989): Structure-Magnetic Coupling Relationships for Metallocene-Acceptor Based Charge Transfer Complexes, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 176:1, 347-357

To link to this article: http://dx.doi.org/10.1080/00268948908037493

Mol. Cryst. Liq. Cryst., Vol. 176, pp. 347–358
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

STRUCTURE-MAGNETIC COUPLING RELATIONSHIPS FOR METALLOCENE-ACCEPTOR BASED CHARGE TRANSFER COMPLEXES

JOEL S. MILLER[a] AND ARTHUR J. EPSTEIN[b]
[a]Central Research and Development, E. I. du Pont de Nemours and Co., Inc., Experimental Station-E328, Wilmington, DE 19880-0328
[b]Department of Physics and Department of Chemistry, The Ohio State University, Columbus, OH 43210-1106 U. S. A.

Abstract The electron transfer complex $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (TCNE = tetracyanoethylene) is a bulk ferromagnet below the Curie temperature of 4.8 K. The deliberate synthesis of additional bulk ferromagnets via the selective *i*) replacement of the metal ion, *ii*) replacement of Me substitutent groups with H, *iii*) use of C_6-ring ligands instead of C_5-ring ligands, and *iv*) replacement of TCNE with alternate acceptors has been carried out. Although several systems exhibit ferromagnetic coupling, a second bulk ferromagnet has not been identified. Replacement of Fe^{III} with Cr^{III}, Ni^{III}, and Fe^{II} leads to complexes with antiferromagnetic coupling, ferrimagnetic behavior, and almost no magnetic interaction, respectively. These results are consistent with a model of configuration mixing of the lowest charge transfer excited state with the ground state developed earlier to understand the magnetic coupling in such systems. The model predicts the magnetic coupling as a function of electron configuration and direction of charge transfer and is a useful guide to design new organic and/or organometallic complexes with cooperative magnetic coupling.

INTRODUCTION

Recently the molecular based ferromagnet $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (TCNE = tetracyanoethylene) has been synthesized and characterized.[1-3] This discovery parallels the discovery of organic based superconductors and extends the studies of cooperative phenomena in molecular/organic materials. This broad range of phenomena in the molecular/organic solid state combined with the anticipated modification of the physical properties via conventional synthetic organic chemistry as well as the ease of fabrication

enjoyed by soluble materials may ultimately lead to utility in future generations of electronic and/or photonic devices.

In previous papers we have reviewed the common idealized magnetic behaviors expected in materials[3] and summarized the configuration mixing of a virtual triplet excited state with the ground state for an alternating donor-acceptor, D/A, 1-D chain model for the stabilization of ferromagnetic coupling for $[Fe^{III}(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$.[1-4] A more comprehensive discussion on the several models for ferromagnetic coupling in molecular/polymeric materials can also be found in recent reviews.[1-4] Herein we focus on the effect of substitution of the key chemical features of $[Fe^{III}(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$ with the goal of preparing additional bulk ferromagnets ideally with higher Curie temperatures.

The ferromagnet $[Fe^{III}(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$ in principle can be modified in several ways; i. e., *i*) substitute of Fe^{III} with other first, second, and third row metal ions, *ii*) substitute Me with alternate organic substitutent groups, *iii*) substitute the five membered ring with a six membered ring, or *iv*) substitute TCNE with other acceptors. The results of representative examples of these substitutions are described below.

ALTERNATE METAL IONS

Decamethylmetallocenes which could be utilized to replace $Fe(C_5Me_5)_2$ in $[Fe^{III}(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$ are listed in Table I. The Co^{III} analog, $[Co^{III}(C_5Me_5)_2]^+[TCNE]\cdot^-$, has been prepared and exhibits essentially the Curie susceptibility anticipated for S = 1/2 $[TCNE]\cdot^-$.[1-3] Since the cation is diamagnetic the electron transfer complex has only one spin per formula unit. Thus, it appears that the $\cdots D\cdot^+A\cdot^-D\cdot^+A\cdot^-\cdots$ 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. Attempts to prepare $[M^{III}(C_5Me_5)_2]\cdot^+$ (M = Ru, Os) salts of $[TCNE]\cdot^-$ have yet to lead to suitable compounds for comparison with the highly magnetic Fe^{III} phase.[5] Formation of $[Ru^{III}(C_5Me_5)_2]\cdot^+$ is complicated by disproportionation to $Ru^{II}(C_5Me_5)_2$ and $[Ru^{IV}(C_5Me_5)_2)(C_5Me_4CH_2)]^+$.[6] The Os^{III} analog has lead to the preparation of a 1:2 salt with TCNE; however, low susceptibilities and crystals unsuitable for single crystal X-ray studies[5] have hampered progress in this area. Replacement of Fe^{III} in $[Fe^{III}(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$ with Ni^{III} (S = 1/2) or Cr^{III} (S = 3/2) leads to compounds exhibiting cooperative magnetic properties.[7]

The motivation for studying these metal ion substituted complexes emanated from the extended McConnell model for the stabilization of ferromagnetic coupling in molecular solids.[4,8] Antiferromagnetic coupling is predicted for d^1/s^1 complexes [s^1 = one electron in a nondegenerate orbital on, for example, the donor; d^1 = one electron in a doubly degenerate (or accidentally degenerate) orbital on, for example, the acceptor] $s^1 \leftarrow d^1$ charge transfer and ferromagnetic coupling for $d^1 \leftarrow s^1$ charge transfer.[2,3] The $[Ni^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ complex possesses this electronic configuration and its susceptibility obeys the Curie-Weiss expression with θ = -10 K. This is consistent with dominant antiferromagnetic interactions and $s^1 \leftarrow d^1$ charge transfer.[1-2,7] A consequence of the model is that if each site possesses a half-filled POMO cases then antiferromagnetic coupling is expected.

TABLE I Decamethylmetallocenes

Metallocene	Electronic Configuration of Cation	Electronic Configuration of $[M^{III}(C_5Me_5)_2]$-[TCNE] Salt	Predicted Magnetic Behavior	Observed Magnetic Behavior
Cr^{III}	$3d^3$ (hs)[a]	t^3/s^1	Ferrimagnetic	Ferrimagnetic[2,7]
Mn^{III}	$3d^4$ (hs)[a]	t^4/s^1	Unstable - Salt Cannot Be Isolated	
Fe^{III}	$3d^5$ (ls)[a]	d^3/s^1	Ferromagnetic	Ferromagnetic[1]
Co^{III}	$3d^6$ (ls)[a]	t^2/s^1	Paramagnetic	Paramagnetic[1]
Ni^{III}	$3d^7$ (ls)[a]	d^1/s^1	Antiferromagnetic	Antiferromagnetic[7]
Ru^{III}	$4d^5$ (ls)[a]	d^3/s^1	Unstable - Salt Cannot Be Isolated[5]	
Os^{III}	$5d^5$ (ls)[a]	s^1/s^1	1:1 Salt Cannot Be Isolated[5]	

[a] hs = high spin; ls = low spin.

The heterospin $[Cr^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ system (S = 3/2 cation; S = 1/2 anion) is predicted to exhibit antiferromagnetic behavior leading to ferrimagnetic coupling (as the spin states cannot cancel) for either $A^{\cdot-} \leftarrow D^{\cdot+}$ or $D^{\cdot+} \leftarrow A^{\cdot-}$ charge transfer.[1-4] Investigation of the magnetic properties of the

Cr^{III} system is in progress; however, the preliminary magnetization data is consistent with ferrimagnetic behavior.[7]

ALTERNATE ORGANIC SUBSTITUTENT GROUPS

Stable radicals are crucial to form ferromagnetically coupled chains; thus, electron transfer must occur for closed shell donors and acceptors to be candidates for magnetic materials. Ideally to conform with the necessity (within the McConnell mechanism) of having a non-half-filled partially occupied molecular orbital intrinsic symmetry of C_n (n > 2) or D_{2d} is required. Thus, metallocene donors with low ionization potential and high molecular symmetry meet these minimal requirements. The one-electron solution reversible reduction potential, E^o, provides a means to estimate whether or not electron transfer might occur for a solid.

Maintainence of five-fold symmetry

To modulate the ionization potential without sacrificing the molecular symmetry, alternative ferrocenes with five-fold symmetry were selected for study. The most obvious species ferrocene is unsuitable as it is more difficult to oxidize (by 0.5 V) than decamethylferrocene and does not reduce TCNE.[9-11] Nevertheless, the diamagnetic ferrocene analog of $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$, *i. e.*, $[Fe^{II}(C_5H_5)_2][TCNE]$, forms[10-12] the identical structural motif.[12]

The 1,2,3,4,5-pentamethylferrocene donor is an alternative with 5-fold symmetry. It was studied as the $[TCNE]^{\cdot-}$ salt.[13] Unfortunately, unlike the $[TCNE]^{\cdot-}$ salts of $[Fe(C_5Me_5)_2]^{\cdot+}$ and $[Fe(C_5H_5)_2]^{\cdot+}$ the simple 1:1 $[Fe(C_5H_5)(C_5Me_5)]^{\cdot+}$ salt could not be isolated and the isolated complex 2:3 salt does not possess the desired ···DADADA··· 1-D chain structure. As this structural motif is the only one observed to support cooperative magnetic interactions (e. g., ferro- and metamagnetic), we were unsuccessful in preparing a new material to extend our understanding of cooperative magnetic behavior in molecular materials. The formation of $[Fe(C_5H_5)(C_5Me_5)]_2[TCNE]_3 \cdot THF$ emphasizes the inability to predict solid state compositions let alone structure types.

Reduction of the five-fold symmetry

To ascertain the effect of lowering the molecular symmetry in addition to modulating the ionization potential several substituted ferrocenes were selected for study as the TCNE charge transfer salt, Table II. This in effect probes the necessity of a ^2E ground state.

TABLE II Ferrocenes

Ferrocene	Molecular Symmetry of Cation	+/o Reduction Potential, E^o, V vs. SCE	$[TCNE]^{\cdot-}$ Salt
$Fe(C_5H_5)_2$	C_5	+0.40	1:1 No e^- transfer, ···DADA··· Chains, Diamagnetic
$Fe(C_5H_5)(C_5H_4Me)$	C_s	+0.33	No e^- transfer
$Fe(C_5H_4Me)(C_5H_4Me)$	C_{2h}	+0.29	e^- transfer; $[TCNE]^{\cdot-}$as $[TCNE]_2^{2-}$
$Fe(C_5H_4)_2(C_3H_6)$	C_{2h}	+0.34	e^- transfer; $[TCNE]^{\cdot-}$ $[TCNE]^{\cdot-}$as $[TCNE]_2^{2-}$
$Fe(C_5H_5)(C_5Me_5)$	C_5	+0.12	e^- transfer; 2:3 salt $[TCNE]^{\cdot-}$ as $[TCNE]_2^{2-}$
$Fe(C_5Me_4H)_2$	C_{2h}	+0.07	e^- transfer; 1:1 salt ···D·+A·-D·+A·-··· Chains
$Fe(C_5Me_5)_2$	C_5	-0.12	e^- transfer; 1:1 salt· ···D·+A·-D·+A·-··· Chains Bulk Ferromagnet

Methylferrocene does have sufficient reducing power to reduce TCNE and like ferrocene does not form an electron transfer salt. The disubstituted 1,1'-dimethylferrocene[14] and 1,1'-trimethyleneferrocene[15] form 1:1 electron transfer salts with TCNE; however, the TCNE is not a radical as it forms diamagnetic $[TCNE]_2^{2-}$ not $[TCNE]^{\cdot-}$ in the solid.[16] Thus, it does not contribute spins necessary for ferromagnetic coupling. In contrast the D_{2d} $Fe(C_5Me_4H)_2$ donor forms 1:1 electron transfer salts with ···D·+A·-D·+A·-··· chains.[17] The magnetic susceptibility can be fit by the Curie-Weiss expression between 2.2 and 320 K and the moment is consistent with two independent spins. The absence of three-dimensional ferromagnetic or antiferromagnetic ordering

above 2.2 K in $[Fe(C_5Me_4H)_2]^{\cdot+}[TCNE]^{\cdot-}$ contrasts with the behavior of $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$. In accord with the ^{57}Fe Mossbauer data which only shows nuclear quadrupole splitting for the $[Fe(C_5Me_4H)_2]^{\cdot+}$ salts and not zero-field Zeeman splitting. The lack of magnetic ordering may arise from poorer intra- and intermolecular overlap within and between the chains leading to substantially weaker magnetic coupling for $[Fe(C_5Me_4H)_2]^{\cdot+}[TCNE]^{\cdot-}$. This would suppress any spin ordering temperature. Alternatively, due to the C_{2h} symmetry, the $[Fe(C_5Me_4H)_2]^{2+}$ charge transfer excited state may be a singlet, not a triplet as expected for $[Fe(C_5Me_5)_2]^{2+}$.[17] The admixture of a singlet, not a triplet charge transfer excited state should lead to antiferromagnetic not ferromagnetic coupling.[1-3]

C_6-rings

The study of the effect of using six-membered rings instead the five-membered cyclopentadiene rings of the metallocenes led to the preparation of bis(arene)chromium electron transfer salts of TCNE.[16,18] Two phases of 1:1 salt of $[Cr^I(arene)_2][TCNE]$ have been isolated. The structurally characterized phase possesses S = 1/2 cations and S = 0 $[TCNE]_2^{2-}$ and like the 1,1'-disubstituted ferrocenes are paramagnetic without evidence of ferromagnetic coupling. A second phase which has yet to be structurally characterized has infrared evidence for the presence of S = 1/2 $[TCNE]^{\cdot-}$ an not S = 0 $[TCNE]_2^{2\cdot-}$. The magnetic susceptibility of the $[Cr^I(C_6Me_xH_{6-x})_2]^{\cdot+}[TCNE]^{\cdot-}$ (x = 3, 6) salts are consistent with two unpaired electrons per formula unit. These salts exhibit dominant ferromagnetic coupling as evidenced from a fit of the high temperature susceptibility to the Curie-Weiss expression with θ = +11.4 K.[16] Crystals suitable for single crystal X-ray analysis, however, have not been prepared; thus, the structures of these salts are unknown. With the observation of ferromagnetic coupling in other charge transfer salts with $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ linear chains[1-3] and the infrared evidence for isolated $[TCNE]^{\cdot-}$ and not $[TCNE]_2^{2-}$, we conjecture that these ferromagnetically coupled complexes also possess this structural arrangement. Specific details of the intra- and interchain interactions arising from the canting and interchain registry of the chains as well as the interatomic separations must await the structural determinations.

A motivation for this study was to probe the effect of the electronic structure on the magnetic behavior. As was discussed earlier, the present understanding of the mechanism for stabilization of ferromagnetic coupling in

molecular based donor/acceptor complexes is configurational admixing of a charge transfer excited state with the ground state. The model predicts that for excitation from the HOMO of a donor to a LUMO acceptor both with a half-filled nondegenerate POMO, as is the case for these $[TCNE]^{\cdot -}$ salts, only antiferromagnetic coupling is stabilized. Since the $[Cr(arene)_2]^{\cdot +}$ cation has an $e_g^4a_{1g}^1$ electronic structure and an $^2A_{1g}$ ground state,[19] antiferromagnetic behavior is predicted. The observed ferromagnetic coupling, thus, suggests that the model is inadequate. The model, however, is consistent with the observed data if we consider that the $A^{\cdot -} \leftarrow D^{\cdot +}$ charge transfer excitation results from the next highest occupied molecular orbital, not the POMO of the cation, to the radical anion POMO. Thus, ferromagnetic coupling which may ultimately lead to bulk ferromagnetic behavior is achievable for systems where both the donor and acceptor have ^2A_g ground states.

Alternate Acceptors

The effect of using alternate acceptors instead of TCNE led to the preparation of several decamethylferrocenium salts, Table III. Several trends can be observed. Ferromagnetically coupled systems are limited to those salts possessing both radical cations, $D^{\cdot +}$, and radical anions, $A^{\cdot -}$, and parallel 1-D $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ chains. Salts with diamagnetic anions, e. g., $[C(CN)_3]^-$,[20] $[C_5(CN)_4Cl]^-$,[14] $[C_5(CN)_5]^-$,[14] $[TCNQF_4]_2^{2-}$,[21] and $\{Ni[S_2C_2(CN)_2]_2\}_2^{2-}$, are paramagnetic with the spin contributed solely by the $[Fe^{III}(C_5Me_5)_2]^{\cdot +}$ radical cation.

For the electron transfer salts with parallel 1-D $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ chains, i. e., the $[TCNE]^{\cdot -}$,[1] $[C_4(CN)_6]^{\cdot -}$,[23] $[C_6(CN)_6]^{\cdot -}$,[24] $[DDQ]^{\cdot -}$,[25] $[TCNQ]^{\cdot -}$,[26] $[TCNQI_2]^{\cdot -}$,[27] and $\{Ni[S_2C_2(CF_3)_2]_2\}^{\cdot -}$,[22] differing magnetic behavior is observed. The intrachain $D^{\cdot +}/A^{\cdot -}$ (d^3/s^1) coupling is ferromagnetic, however, a competition between ferromagnetic interchain $D^{\cdot +}/D^{\cdot +}$ (d^3/d^3) and $D^{\cdot +}/A^{\cdot -}$ (d^3/s^1) and antiferromagnetic interchain $A^{\cdot -}/A^{\cdot -}$ (d^3/d^3) interactions exists and presumably subtle changes in the intrachain and interchain overlaps lead to changes in the net interchain magnetic coupling.

The importance of the ferromagnetic parallel 1-D $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ $D^{\cdot +}/A^{\cdot -}$ (d^3/s^1) coupling is illustrated by study of a series of four $[Fe^{III}(C_5Me_5)_2][M(S_2C_2R_2)_2]$[22] complexes, Table IV. The $[Fe(C_5Me_5)_2]$-$\{Ni[S_2C_2(CN)_2]_2\}$ comprises isolated, centrosymmetric $D^{\cdot +}A_2^{2-}D^{\cdot +}$ dimers with

TABLE III Decamethylferrocene Salts with Representative Acceptors

Acceptor	Structure Motif	Magnetic Coupling
$[C(CN)_3]^-$	Not ···D·+A⁻D·+A⁻··· Chains	Paramagnet
$[C_2(CN)_4]\cdot^-$, $[TCNE]\cdot^-$	Parallel ···D·+A·⁻D·+A·⁻··· Chains	Bulk Ferromagnet $T_C = 4.8$ K
$[C_3(CN)_5]^-$	Parallel ···D·+A⁻D·+A⁻··· Chains	Paramagnet
$[C_4(CN)_6]\cdot^-$	Parallel ···D·+A⁻D·+A⁻··· Chains	Ferromagnetic
$[C_5(CN)_4Cl]^-$	Parallel ···D·+A⁻D·+A⁻··· Chains	Paramagnet
$[C_5(CN)_5]^-$	Not ···D·+A⁻D·+A⁻··· Chains	Paramagnet
$[C_6(CN)_6]\cdot^-$	Parallel ···D·+A⁻D·+A⁻··· Chains	Ferromagnetic
$[DDQ]\cdot^-$	Parallel ···D·+A·⁻D·+A·⁻··· Chains	Ferromagnetic
$[TCNQ]\cdot^-$	Parallel ···D·+A·⁻D·+A·⁻··· Chains	Metamagnet $T_N = 2.55$ K
$[TCNQI_2]\cdot^-$	Parallel ···D·+A·⁻D·+A·⁻··· Chains	Ferromagnetic
$[TCNQF_4]\cdot^-$	Isolated D·+$[A]_2^{2-}$D·+ Dimers	Paramagnet
$[Ni(S_2C_2(CF_3)_2]\cdot^-$	Parallel ···D·+A·⁻D·+A·⁻··· Chains	Ferromagnetic
$\{Ni[S_2C_2(CN)_2]_2\}\cdot^-$	Isolated D·+$[A]_2^{2-}$D·+ Dimers	Paramagnet
$[FeCl_4]^-$ (S = 5/2)	Not ···D·+A·⁻D·+A·⁻··· Chains	Paramagnet[28]
$[FeBr_4]^-$ (S = 5/2)	Not ···D·+A·⁻D·+A·⁻··· Chains	Paramagnet[28]

with spins only on the cations. As evidenced from the Curie-Weiss θ of 0 K the spins are independent of each other. The α- and β- polymorphs of $\{Pt[S_2C_2(CN)_2]_2\}^-$ have ···D·+A·⁻D·+··· planes and ···D·+A·⁻D·+A·⁻··· chains in addition to arrangements with diamagnetic $[A]_2^{2-}$ units. The higher effective moment is consistent with more spins per repeat unit and the Curie-Weiss θ of ~6 - 10 K suggests ferromagnetic coupling. The $[Ni(S_2C_2(CF_3)_2]\cdot^-$ electron transfer salt possesses only 1-D ···D·+A·⁻D·+A·⁻··· chains with two spins per

repeat unit. This complex has the greatest effective moment and largest θ suggesting the greatest ferromagnetic coupling.[22]

TABLE IV Ferromagnetic Coupling in $[Fe(C_5Me_5)_2][M(S_2C_2R_2)_2]$ Salts[22]

$[M(S_2C_2R_2)_2]$	Structure Motif	Spins / Magnetic Parameters
$\{Ni[S_2C_2(CN)_2]_2\}^-$	$D^{\cdot+}[A]_2^{2-}D^{\cdot+}$ Isolated Dimers	$D^{\cdot+}$ / repeat unit $\theta = 0$ K; $\mu_B = 2.83\ \mu_B$
α-$\{Pt[S_2C_2(CN)_2]_2\}^-$	$\cdots D^{\cdot+}[A]_2^{2-}\cdots$ Chains and $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}\cdots$ Planes	$D^{\cdot+}$ + 1/3 $A^{\cdot-}$ / repeat unit $\theta = +6.6$ K; $\mu_B = 3.05\ \mu_B$
β-$\{Pt[S_2C_2(CN)_2]_2\}^-$	$\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ Chains and Isolated $D^{\cdot+}[A]_2^{2-}D^{\cdot+}$ Dimers	$D^{\cdot+}$ + 1/3 $A^{\cdot-}$ / repeat unit $\theta = +9.8$ K; $\mu_B = 3.10\ \mu_B$
$[Ni(S_2C_2(CF_3)_2]^{\cdot-}$	$\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ Chains	$D^{\cdot+}$ + $A^{\cdot-}$ / repeat unit $\theta = +15$ K; $\mu_B = 3.73\ \mu_B$

CONCLUSION

The quest for s/p orbital based ferromagnets remain the focus of intense interest worldwide. The magnetic data on $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ demonstrates that ferromagnetism is achievable in organic based molecular systems. Simple substitution of the metal ion, Me substitutent group, C_5-ring, or radical anion acceptor has lead to the preparation of several new molecular complexes with ferromagnetic coupling; however, identification of a second bulk ferromagnet has to date proved elusive. The competition between ferromagnetic interchain $D^{\cdot+}/D^{\cdot+}$ (d^3/d^3) and $D^{\cdot+}/A^{\cdot-}$ (d^3/s^1) and antiferromagnetic interchain $A^{\cdot-}/A^{\cdot-}$ (s^1/s^1) interactions and ferromagnetic intrachain $D^{\cdot+}/A^{\cdot-}$ (d^3/s^1) coupling exists. The design of better systems requires a deeper understanding of these interactions as subtle changes in the intrachain and interchain overlaps lead to changes in the magnetic coupling.

It must be emphasized that the rational design of solid state structures remains an art that limits our ability to prepare the secondary and tertiary structures needed to test many concepts in solid state chemistry. Frequently, as illustrated with $[Fe(C_5Me_5)(C_5H_5)]_2[TCNE]_3\cdot THF$ complex, solvated

compositions with undesired or new structure types form instead of the desired phase. In addition several polymorphs may form in lieu of the desired structure type. This is particularly crucial for the formation of a bulk ferromagnet as ferromagnetism is a 3-D (bulk) not 1-D property.

ACKNOWLEDGMENT

The authors gratefully acknowledge partial support by the Department of Energy Division of Materials Science (Grant No. DE-FG02-86ER45271.A000). We deeply thank our co-workers (R. W. Bigelow, J. C. Calabrese, S. Chittipeddi, A. Chakraborty, K. Ming-Chi, K. R. Cromack, D. A. Dixon, P. J. Krusic, D. M. O'Hare, W. M. Reiff, H. Rommelmann, C. Vazquez, M. D. Ward, D. Wipf, and J. H. Zhang) for the important contributions they have made enabling the success of the work reported herein.

REFERENCES

1. J. S. Miller, J. C. Calabrese, R. W. Bigelow, A. J. Epstein, J. H. Zhang, S. Chittipeddi, and W. M. Reiff, *Chem. Commun* **1986**, 1026-1028. J. S. Miller, J. C. Calabrese, H. Rommelmann, S. Chittipeddi, J. H. Zhang, W. M. Reiff, and A. J. Epstein, *J. Am. Chem. Soc.* **109**, 769 (1987). S. Chittipeddi, K. R. Cromack, J. S. Miller, and A. J. Epstein, *Phys. Rev. Lett.* **58**, 2695 (1987).
2. J. S. Miller and A. J. Epstein, *NATO Adv. Study Ser.* **1987**, *168B*, 159. J. S. Miller, A. J. Epstein, and W. M. Reiff, *Acc. Chem. Res.* **1988**, *23*, 114. J. S. Miller, A. J. Epstein, and W. M. Reiff, *Science* **1987**, 240, 40. J. S. Miller and A. J. Epstein, *Adv. Org. Chem.* **XX**, 000 (1989).
3. J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.* **1988**, *88*, 201.
4. H. M. McConnell, *Proc. R. A. Welch Found. Chem. Res.* **11**, 144 (1967).
5. D. M. O'Hare and J. S. Miller, Organomet. **1988**,
6. U. Kolle and J. Grub, *J. Organomet. Chem.*, **1985**, *289*, 133-139.
7. J. S. Miller and A. J. Epstein, in preparation.
8. J. S. Miller and A. J. Epstein, *J. Amer. Chem. Soc.*, **1987**,*109*, 3850.
9. J. L. Robbins, N. Edelstein, B. Spencer, and J. C. Smart, *J. Am. Chem. Soc.* **104**, 1882 (1982).
10. O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.* **1962**, *84*, 3678-3684. M. Rosenblum, R. W. Fish, and C. Bennett, *J. Am. Chem. Soc.* **1964**, *86*, 5166-5170. R. L. Brandon, J. H. Osipcki, and A. Ottenberg, *J. Org. Chem.* **1966**, *31*, 1214-1217.
11. Miller, J. S.; Zhang, J. H.; Reiff, W. M. in preparation.
12. Adman, E.; Rosenblum, M.; Sullivan, S.; Margulis, T. N. *J. Am. Chem. Soc.*, **1967**, *89*, 4540-4542. Foxman, B. private communication; Sullivan, B. W.; Foxman, B. *Organometallics* **1983**, *2*, 187-189.

13. Miller, J. S.; Glatzhofer, D. T. submitted.
14. Miller, J. S. unpublished results.
15. Lemervoskii, D. A.; Stukan, R. A.; Tarasevich, B. N.; Slovokhotov, Yu. L.; Antipin, M. Yu.; Kalinin, A. E.; Struchov, Yu. T.*Struct. Khim.* **1981**, *7*, 240.
16. Miller, J. S.; O'Hare, D. M.; Chackraborty, A.; Epstein, A. J. submitted.
17. Miller, J. S.; Glatzhofer, D. T.; O'Hare, D. M.; Reiff, W. M.; Chakraborty, A.; Epstein, A. J. submitted.
18. O'Hare, D. M.; Miller, J. S. *Mol. Cryst. Liq. Cryst.*, **1989**, XXX, 0000.
19. Anderson, S. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 4244.
20. Dixon, D. A.; Calabrese, J. C.; Miller, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 2582-2588.
21. D. A. Dixon, J. C. Calabrese, and J. S. Miller, *J. Phys. Chem.* **1989**, 93, 2284.
22. J. S. Miller, J. C. Calabrese, and A. J. Epstein, submitted
23. Miller, J. S.; Zhang, J. H.; Reiff, W. M. *J. Am. Chem. Soc.*, **1987**, *109*, 5484.
24. Miller, J. S.; Zhang, J. H.; Reiff, W. M., and M. D. Ward, in preparation
25. Gebert, E.; Reis, A. H., Jr.; Miller, J. S., Rommelmann, H.; Epstein, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4403-4410; Miller, J. S.; Krusic, P. J.; Dixon, D. A.; Reiff, W. M.; Zhang, J. H.; Anderson, E. C.; Epstein, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 4459-4466.
26. Candela, G. A.; Swarzendruber, L.; Miller, J. S.; Rice, M. J. *J. Amer. Chem. Soc.*, **1979**, *101*, 2755-2756. Miller, J. S.; Reiff, W. M.; Zhang, J. H.; Preston, L. D.; Reis, A. H., Jr.; Gebert, E.; Extine, M.; Troup, J.; Dixon, D. A.; Epstein, A. J., Ward, M. D. *J. Phys. Chem.*, **1987**, *91*, 4344-4360.
27. Miller, J. S., J. C. Calabrese, J. H. Zhang, W. M. Reiff, S. Chittipeddi, M. A. Selover, and Epstein, A. J., in preparation.
28. Miller, J. S.; Zhang, J. H.; Reiff, W. M. in preparation.