Molecular Ferromagnets

Joel S. Miller,*† Arthur J. Epstein,‡ and William M. Reiff§

Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station, E328, Wilmington, Delaware 19898, Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

Magnets have captivated mankind since the discovery of iron metal by Hittites ca. 3500 years ago. Millennia later the electrical conducting properties of metals expanded man's horizons, and today both phenomena are crucial to the high-tech age we enjoy. The materials that exhibit these phenomena are inorganic solids with bonding in three dimensions. In 1960 a new class of organic compounds was shown to exhibit metallic-like electrical conductivity,[1] and today examples of organic and polymeric conductors as well as superconductors tantalize one's imagination.[2,3] The possibility of organic-based ferromagnets did not escape attention,[4-8] and recently their existence has been established. Evolution from atom-based inorganic materials to molecule-based organic materials should allow both the modulation of the magnetic properties by conventional organic chemistry and the ease of fabrication often enjoyed by organic materials. These attributes may lead to the use of organic materials in future generations of electronic, magnetic, and/or photonic devices.

In this Account we describe the chemistry and review the physical evidence that an example of a class of molecular-based organic-like compounds is a magnet, i.e., a bulk ferromagnet.[9] To familiarize the reader with this unusual property, we review the most common magnetic behaviors prior to summarizing the structure and magnetic properties of the class of molecular solids that exhibits ferromagnetic behavior. Finally, a model consistent with the observed ferromagnetic behavior for this class of compounds is discussed and used to propose new materials and test theories.

Joel S. Miller obtained his B.S. in Chemistry degree from Wayne State University in 1967 and his 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 late Occidental Research Corp. in 1978. Since 1983 he has been at the Central Research and Development Department at the Du Pont Co., where he is currently a Research Supervisor for solid-state science. 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.

Arthur J. Epstein received his B.S. in Physics from Polytechnic Institute of Brooklyn in 1966 and his Ph.D. in Physics from the University of Pennsylvania in 1971. He joined the Xerox Webster Research Center in 1972 and The Ohio State University in 1985, where he is currently 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 Technion–Israel Institute of Technology and the University of Paris. His research interests include synthetic metals, molecular magnetism, conducting polymers, and ceramic superconductors.

William M. Reiff received 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, an associate scientist at Brookhaven National Laboratory, and 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 is currently a full professor. He is an active visiting professor at the Francis Bitter National Magnet Laboratory, and his current research interests include low-dimensional magnetism of 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.

Magnetic Properties of Materials

Upon application of a magnetic field all substances exhibit a magnetic moment, with the susceptibility, χ, being the proportionality constant. Paramagnetic (open shell) compounds have their induced moment aligned parallel to the field, and in the simplest case χ may be modeled by the Curie expression (i.e., χ is inversely proportional to temperature). Diamagnetic (closed shell) compounds have their induced moment aligned antiparallel to the field and possess a temperature-independent negative susceptibility. In the presence of cooperative magnetic behavior (ferro- or antiferromagnetic) the spins experience an effective parallel (or antiparallel) exchange field due to the neighboring spins which increases (or decreases) the measured χ from the Curie expression value to a value often modeled at higher temperatures by the Curie–Weiss law.

The spins may order at low temperature. If the spins align parallel to each other (ferromagnet), then a macroscopic spontaneous magnetization is present with a characteristic saturation moment. If antiparallel (antiferromagnet) spin alignment occurs, then there is no net moment. Ferrimagnetism occurs when antiferromagnetically aligned spins have different local moments and the incomplete cancellation of the spins results in a reduced, but finite moment. Lodestone (Fe_3O_4) is an example of a ferrimagnet. Highly magnetic (ferro- or ferrimagnetic) materials have the common structural features of a close approach of metal ions and have a covalent- or metallic-bonded 1-D, 2-D, or 3-D network structure.

† E. I. du Pont de Nemours and Co.
‡ The Ohio State University.
§ Northeastern University.

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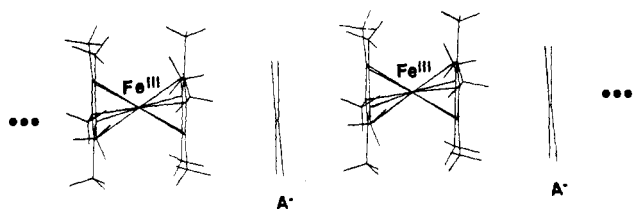
Figure 1. Alternating donor/acceptor, ···D⁺A⁻D⁺A⁻···, linear-chain structure of [Fe^{III}(C₅Me₅)₂]⁺[A]⁻ (A = TCNQ, TCNE, DDQ, C₄(CN)₆), [Fe^{II}(C₅H₅)₂][TCNE] and [Fe^{III}(C₅Me₅)₂]⁺[C₃-(CN)₅]⁻. The structure shown here is for A = TCNE.

Ferromagnetic Interactions in Organic Molecular Solids

Four mechanisms have been postulated for the stabilization of high-spin (ferromagnetic coupling) components of a molecular solid; however, none have been proposed for bulk ferromagnetism. The models are (1) configuration mixing of a virtual triplet excited state with the ground state for a ···D⁺A⁻D⁺A⁻··· chain, where D is a cation (donor) and A is an anion (acceptor),[5,7] (2) very-high-spin multiplicity radicals,[6] (3) Heitler–London spin exchange between positive spin density on one radical and negative spin density on another,[4] and (4) superexchange via a degenerate orbital of a closed-shell ion.[10] These models are discussed in greater detail in ref 9.

Our approach for designing molecular ferromagnets is based on forming ···D⁺A⁻D⁺A⁻··· chains. Thus, the first mechanism is attractive and subsequently it will be discussed in greater detail. The D that we will focus upon is decamethylferrocene, Fe^{II}(C₅Me₅)₂ (1). The A is a planar polycyano hydrocarbon capable of accepting an electron to form a stable radical anion. The specific A's discussed are TCNQ (7,7,8,8-tetracyano-p-quinodimethane) (2) and TCNE (tetracyanoethylene) (3).
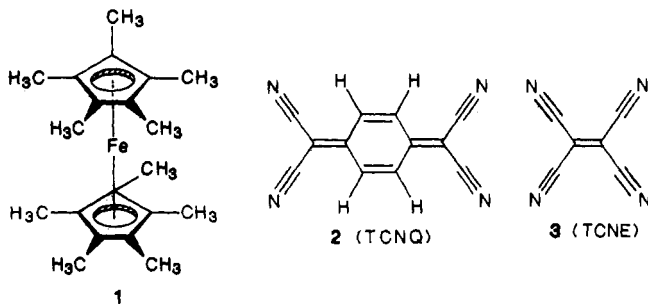
Structure and Magnetic Properties of [Fe(C₅Me₅)₂]⁺[Acceptor]⁻

Rapid crystallization of [Fe^{III}(C₅Me₅)₂]⁺[TCNQ]⁻ enables isolation of a kinetic phase that has a 1-D structural motif based on alternating [Fe^{III}(C₅Me₅)₂]⁺ cation donors, D, and [TCNQ]⁻ anion acceptors, A, i.e., ···D⁺A⁻D⁺A⁻···[11a,b] (Figure 1). The effective moment, μ_{eff}, i.e., 2.83$(\chi T)^{1/2}$, significantly deviates[11c] from the temperature-independent Curie behavior characteristic

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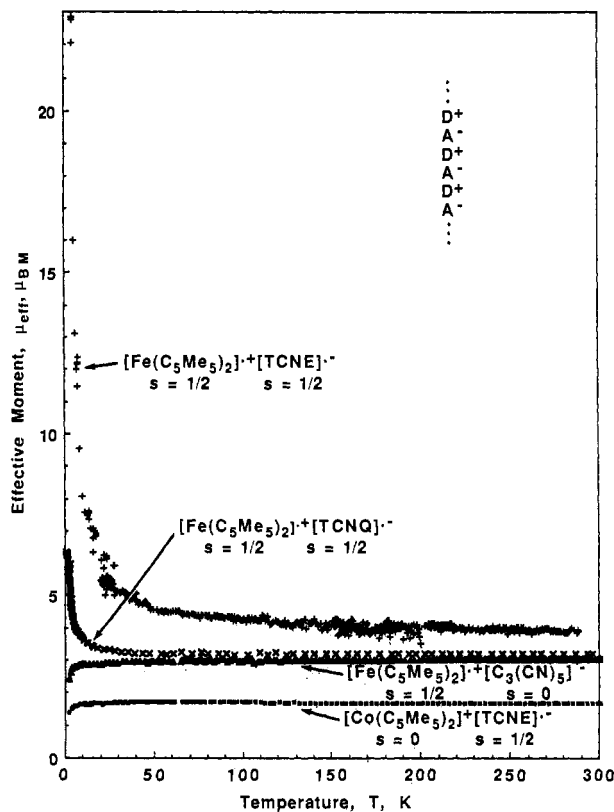
Figure 2. Effective moment as a function of temperature for [Fe^{III}(C₅Me₅)₂][A]⁻ (A = TCNQ, TCNE, [C₃(CN)₅]⁻) and [Co^{III}(C₅Me₅)₂]⁺[TCNE]⁻.
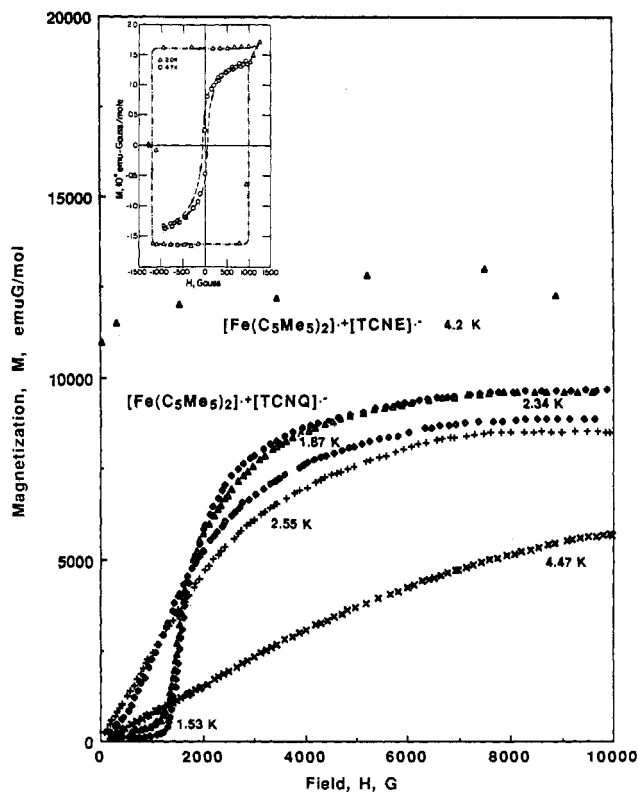
Figure 3. Magnetization, M, as a function of applied field, H, for [Fe^{III}(C₅Me₅)₂]⁺[A]⁻ (A = TCNQ, TCNE). The Neel temperature for [Fe(C₅Me₅)₂]⁺[TCNQ]⁻ is 2.55 K. Insert shows hystersis loops for [Fe^{III}(C₅Me₅)₂]⁺[TCNE]⁻ at 2 K.

of ferrocenium salts[12] (Figure 2). The magnetization reveals metamagnetic behavior; i.e., below an applied

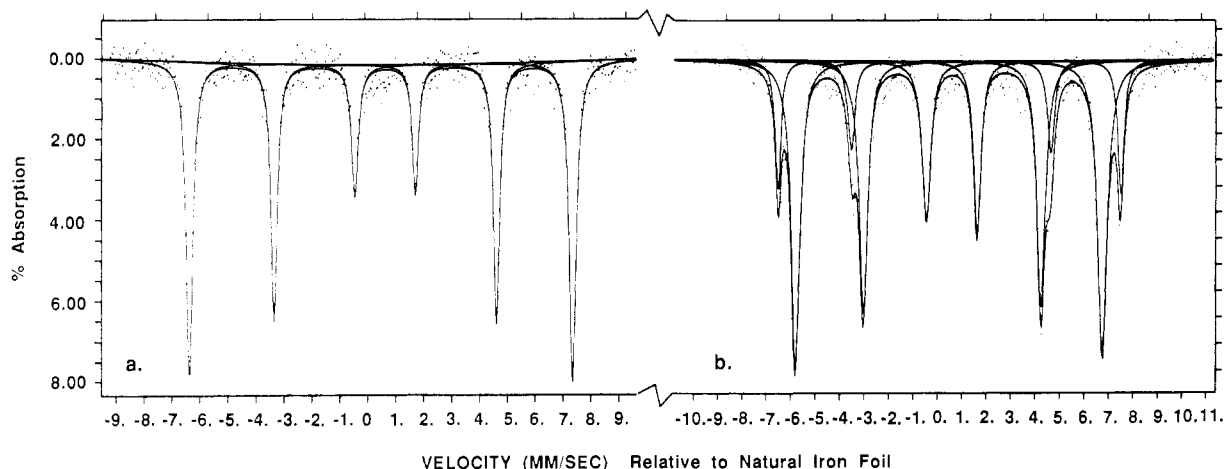**Figure 4.** ^{57}Fe Mössbauer spectra at 1.78 K for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ and 2.00 K for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNQ]^{\cdot-}$.

field of 1600 G the magnetization is characteristic of an antiferromagnet, whereas above 1600 G a sharp rise and approach to magnetization saturation characteristic of a ferromagnet is observed (Figure 3).[9,11c] Several metamagnets, e.g., $FeCl_2$, have been characterized;[13] however, this is the first example where neither a 1-, 2-, nor 3-D covalently bonded network structure is present.[14] Subsequently, we sought to elucidate the structure–function relationship via the systematic modification of A, the C_5Me_5 ring substituent groups, and the metal to understand the steric/electronic features necessary to stabilize ferromagnetism.

On the premise that a smaller radical anion would have a greater spin density which could lead to greater spin interactions, the $[TCNE]^{\cdot-}$ salt of $[Fe^{III}(C_5Me_5)_2]^{\cdot+}$ was prepared and found to possess the $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ motif (Figure 1). The susceptibility of $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ obeys the Curie–Weiss expression with dominant ferromagnetic interactions.[16] With application of only the Earth's magnetic field a spontaneous magnetization is observed. The saturation magnetization for single crystals parallel to the $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ stacking axis is 36% greater than iron on a gram-atom basis and agrees with the calculated saturation moment for ferromagnetic alignment of the donor and the acceptor.[17] The critical (Curie) temperature, T_c, was determined to be 4.8 K. The magnetization versus applied field data exhibits hysteresis loops (Figure 3 insert), with a large coercive field at 2 K.[18]

Fitting the susceptibility data to different models aids in the understanding of the microscopic spin interactions. The data fit a 1-D Heisenberg model with ferromagnetic exchange coupling of 19 cm^{-1} above 16 K.[18] Variation of the low-field magnetic susceptibility with temperature above T_c, magnetization with temperature below T_c, and magnetization with magnetic field at T_c enabled the determination of three critical exponents for the magnetic field parallel to the chain axis. The observed values are consistent with a 3-D behavior. Thus, above 16 K the nearest-neighbor interchain (1-D) spin interactions are sufficient to understand the magnetic coupling, whereas near T_c the 3-D spin interactions are dominant.[18]

Large single crystals necessary for the measurement of the magnetic anisotropy are not readily available. Such crystals of the $[TCNQ]^{\cdot-}$ salt cannot be prepared, as formation of the thermodynamically favored dimer phase, which exhibits independent spin (Curie) magnetic behavior,[11b] occurs. Large crystals of the $[TCNE]^{\cdot-}$ salt can be easily grown from acetonitrile; however, the unit cell contains this solvent, which is lost upon isolation of the crystals, leading to a polycrystalline orthorhombic sample. Small single crystals enabling the determination of the magnetic anisotropy of the orthorhombic phase of the $[TCNE]^{\cdot-}$ salt can be made from tetrahydrofuran; however, due to disorder the anion cannot be refined.[16c] Similarly, anion disorder in the $[C_4(CN)_6]^{\cdot-}$ salt limits the microscopic analysis of the structural features important for understanding of the detailed magnetic properties.[19] Ordered large single crystals are of high priority in order to determine the magnetic anisotropy.

^{57}Fe Mössbauer Spectroscopy

The Mössbauer spectra of ferrocenes have been extensively studied.[20a–d] Typically, the Fe^{II} and oxidized Fe^{III} compounds exhibit temperature-independent quadrupole doublet and singlet spectra, respectively,

(12) Morrison, W. H., Jr.; Krugsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998–2004. Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559–1563.

(13) Stryjewski, E.; Giordano, N. *Adv. Phys.* **1977**, *26*, 487.

(14) A molecular solid is comprised of low molecular weight molecules or ions (organic, organometallic, main group, polymer, and/or inorganic coordination complex) that do not possess extended covalent bonding in the solid state. However, shorter than van der Waals separations may be present in the solid. Dissolution into conventional aqueous or organic solvents leads to solvation of the individual ions or molecules that were used to prepare the molecular solid.[15]

(15) Miller, J. S.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3850.

(16) (a) Miller, J. S.; Krusic, P. J.; Epstein, A. J.; Zhang, J. H.; Reiff, W. M. *Mol. Cryst. Liq. Cryst.* **1985**, *120*, 27. (b) Miller, J. S.; Calabrese, J. C.; Bigelow, R. W.; Epstein, A. J.; Zhang, J. H.; Reiff, W. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1026–1028. (c) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittapeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769–781.

(17) The susceptibility, χ, and saturation magnetization calculated as the sum of the contributions from $[Fe^{III}(C_5H_5)_2]^{\cdot+}$ and $[TCNE]^{\cdot-}$ is 0.00646 emu/mol at 290 K and 16 700 (emu G)/mol, respectively. This is in excellent agreement with the observed values of 0.00667 emu/mol and 16 300 (emu G)/mol for single crystals aligned parallel to the chain axis.[18]

(18) Chittapeddi, S. R.; Cromack, K. R.; Miller, J. S.; Epstein, A. J. *Phys. Rev. Lett.* **1987**, *22*, 2695.

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and six-line Zeeman-split spectra in applied magnetic fields at low temperature. For $[Fe(C_5Me_5)_2]^{\cdot+}[A]^{\cdot-}$, however, the radical 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 unusual observation of Zeeman splitting in zero applied field.[9,11b,16,19,21] For example, a Zeeman-split spectrum with an internal field of 424 kG is observed for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ at 4.2 K[16b,c] (Figure 4a). The metamagnetic $[TCNQ]^{\cdot-}$ salt exhibits a pair of six-line Zeeman-split spectra[11b] in a 2:1 ratio (Figure 4b) with internal fields of 404 and 449 kG below 4.2 K. The latter suggests a magnetostructural transformation perhaps accompanying the ordering process or site inequivalence in the magnetic structure of the ordered phase. These internal fields are substantially greater than the expectation of 110 kG/(spin/Fe).[20e]

Structure–Function Relationship

To identify the structure–function relationship with the goal of a preparing a ferromagnet with a higher critical temperature, the properties of ⋯DADA⋯-structured compounds based on $[M(C_5R_5)_2]^+$ were studied. Three modifiable entities are (1) replacement of the Me groups with H, (2) use of alternate open- and closed-shell anions, and (3) replacement of Fe^{III} with other metal ions.

Alternate C_5 Ring Substituents. Ferrocene is more difficult to oxidize than decamethylferrocene and is not oxidized by TCNE.[22,23] Nonetheless, diamagnetic $[Fe^{II}(C_5Me_5)_2][TCNE]$ forms and belongs to the same structure type[23-25] (Figure 1). Stronger acceptors [e.g., $A = TCNQF_4$,[26] ($TCNQF_4$ = perfluoro-TCNQ), $C_4(CN)_6$[19]] should stabilize complete electron transfer with ferrocene. These complexes were prepared and possess Fe^{III} and $[A]^{\cdot-}$; however, both salts are weakly antiferromagnetic. The $TCNQF_4$ salt does not have the ⋯$D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}$⋯ motif, thus emphasizing the importance of structure type. Since $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[C_4(CN)_6]^{\cdot-}$ exhibits ferromagnetic interactions,[19] the structure of the $[Fe^{III}(C_5H_5)_2]^{\cdot+}[C_4(CN)_6]^{\cdot-}$ should provide important information when it is determined.

Alternate Acceptors. Substitution of TCNQ with either TCNE,[16] $C_4(CN)_6$,[19] $TCNQI_2$,[27] ($TCNQI_2 = 2,5$-diiodo-TCNQ), or DDQ^{21a} (DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone) acceptors leads to ⋯$D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}$⋯-structured complexes with dominant ferromagnetic behavior. However, replacment with diamagnetic $[C_3(CN)_5]^-$ leads to formation of a ⋯$D^{\cdot+}A^-D^{\cdot+}A^-$⋯-structured phase which exhibits essentially Curie susceptibility[16b] (Figure 2). This again

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(26) Miller, J. S.; Zhang, J. H.; Reiff, W. M. *Inorg. Chem.* **1987**, *26*, 600–608.

(27) Chittapeddi, S.; Selover, M. A.; Epstein, A. J.; Miller, J. S.; Zhang, J.; Reiff, W. M., submitted.
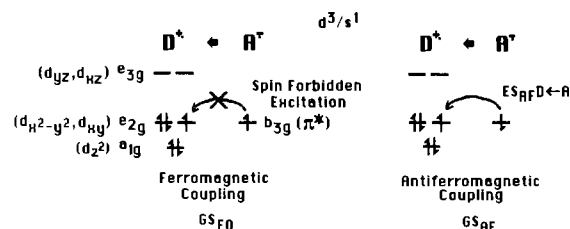
Figure 5. Ferromagnetically (triplet) and antiferromagnetically (singlet) coupled paramagnetic ground states and stabilization of antiferromagnetic coupling via retro charge transfer from an s^1 $[A]^{\cdot-}$ to a d^3 $[D]^{\cdot+}$.

supports the necessity for both radical D's and A's for stabilizing ferromagnetic coupling.

Alternate Metals. The $[Co^{III}(C_5Me_5)_2]^+[TCNE]^{\cdot-}$ complex with a diamagnetic donor has been prepared and exhibits essentially the Curie susceptibility anticipated for $[TCNE]^{\cdot-}$ [16c] (Figure 2). Attempts to prepare $[M^{III}(C_5Me_5)_2]^+$ (M = Ru, Os) salts of $[TCNE]^{\cdot-}$ have yet to lead to compounds suitable for comparison with the highly magnetic Fe^{III} phase.[28] Replacement of Fe^{III} in $[Fe^{III}(C_5Me_5)_2]^+[A]^{\cdot-}$ [A = TCNE, $C_4(CN)_6$] with doublet Ni^{III} or quartet Cr^{III} leads to compounds exhibiting cooperative magnetic properties.[29] The motivation for studying these complexes emanates from our expanded model[15] for the stabilization of ferromagnetic coupling in molecular solids, and their magnetic properties are discussed later.

Consequently, available data emphasize the need for radical D's and radical A's comprising the ⋯$D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}$⋯ structure for stabilizing cooperative magnetic behavior.

Bulk Ferromagnetic Interactions in Molecular Solids

Spin alignment throughout the bulk is required for ferromagnetism. Previously we noted four mechanisms for the pairwise stabilization of ferromagnetic coupling in a molecular solid; however, none have been proposed for bulk ferromagnetism. Since the materials under discussion possess a ⋯$D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}$⋯ chain motif,[5,7] McConnell's configuration mixing is attractive.

Configuration Mixing Stabilization of Ferromagnetic Coupling. $[Fe(C_5Me_5)_2]^{\cdot+}$ with e_{2g}^3 ($d_{x^2-y^2},d_{xy}$) valence orbitals has three electrons in doubly degenerate partially occupied molecular orbitals (POMO)[30] i.e., d^3, while $[TCNE]^{\cdot-}$ has one electron in a nondegenerate π^* POMO, i.e., s^1. In the absence of spin interactions there are two possible ground states for this d^3/s^1 $[D]^{\cdot+}[A]^{\cdot-}$ pair. The ferromagnetically coupled, GS_{FO}, and antiferromagnetically coupled, GS_{AF}, states (Figure 5) exist at equal energy and lead to paramagnetic behavior.[15] Spin interactions between the radical ions can stabilize either ferro- or antiferromagnetic coupling, i.e., lower either GS_{FO} or GS_{AF}.

The GS lowered has the greatest admixing with the lowest energy virtual charge transfer excited state.

(28) O'Hare, D. M.; Green, J. C.; Chadwick, T. P.; Miller, J. S. *Organometallics*, in press.

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$D^{\cdot+} \rightarrow A^{\cdot-}$

GS$_{FO}$

ES$_{FO}$ $^{A \leftarrow D}$

Ferromagnetic
Coupling

$D^{\cdot+} \bullet A^{\cdot-}$ $D^{\cdot+} \bullet A^{\cdot-}$

GS$_{AF}$ GS$_{AF}$

ES$_{AF}$ $^{A \leftarrow D}$ ES$'_{AF}$ $^{A \leftarrow D}$

Antiferromagnetic   Antiferromagnetic
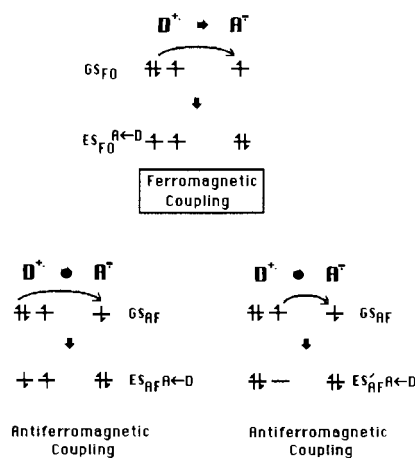Coupling   Coupling

Figure 6. Stabilization of ferromagnetic coupling via forward charge transfer from a d^3 [D]$^{\cdot+}$ to an s^1 [A]$^{\cdot-}$.

Thus, if a triplet excited state, ES, arising from either a triplet D (or A), *but not both*, formed by either virtual retro ($D^0 + A^0 \leftarrow D^{\cdot+} + A^{\cdot-}$), forward ($D^{2+} + A^{2-} \leftarrow D^{\cdot+} + A^{\cdot-}$), or disproportionation (e.g., $D^{2+} + D^0 \leftarrow 2D^{\cdot+}$) configuration admixing with the ground state, GS, then the ferromagnetic coupled ground state, GS$_{FO}$, may be stabilized.[15]

Hund's rule can be used to predict the lowest charge transfer excited state[15] for each direction of virtual charge transfer and thus the cooperative magnetic coupling [i.e., ferro- (FO), ferri- (FI), or antiferromagnetic (AF)]. Consider retro charge transfer for the above case (Figure 5). Since the [Fe(C$_5$Me$_5$)$_2$]$^{\cdot+}$ can only accept a "spin-down" electron via virtual charge transfer from [TCNE]$^{\cdot-}$ and GS$_{AF}$ (not GS$_{FO}$) has a "spin-down" electron, then 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.

For virtual forward charge transfer three excited states (ES$_{FO}$$^{A \leftarrow D}$, ES$_{AF}$$^{A \leftarrow D}$, and ES$'_{AF}$$^{A \leftarrow D}$) are possible (Figure 6). From Hund's rule the most easily excited [D]$^{\cdot+}$ electron is "spin down" and the lowest excited state is ES$_{FO}$$^{A \leftarrow D}$. Thus, forward charge transfer for the d^3/s^1 electron configuration stabilizes the ferromagnetically coupled ground state, GS$_{FO}$ (Figure 6), which may lead to bulk ferromagnetic behavior as observed for [Fe^{III}(C$_5$Me$_5$)$_2$]$^{\cdot+}$[TCNE]$^{\cdot-}$.

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), or higher accidental or intrinsic orbital degeneracies enables the identification of configurations stabilizing ferromagnetic coupling for a specific direction of charge transfer.[15] The results of the evaluation of stabilization are summarized in Table I for homospin and heterospin systems containing singly and doubly degenerate orbitals.[31] For heterospin systems due to incomplete spin cancellation, antiferromagnetic coupling should lead to ferrimagneic behavior,[15] FI, and the FO and FI interactions can be predicted.

Homospin Systems. For an s^1 [A]$^{\cdot-}$ electron configuration ferromagnetic coupling can be stabilized via forward charge transfer from a D with a d^3 electron

(31) The triply degenerate cases can be found in ref 15.

Table I
Magnetic Coupling for Homo- and Heterospin Systems^{a,b} with Singly and Doubly Degenerate HOMO's^{32}

D (or A)	A (or D)	D → A	A → D	example
Homospin Doublet Systems				
s^1	s^1	AF	AF	[TMPD][TCNQ],^{c} [Cr(C$_6$H$_6$)$_2$]I^d [TTF][Pt(S$_2$C$_4$F$_6$)$_2$],^{e,f} V(C$_6$H$_6$)$_2$$^{\cdot g}$
d^1	s^1	AF	FO	[Ni^{III}(C$_5$Me$_5$)$_2$]$^{\cdot+}$[TCNE]$^{\cdot-}$ ^{30}
d^3	s^1	FO	AF	[Fe^{III}(C$_5$Me$_5$)$_2$]$^{\cdot+}$[TCNE]$^{\cdot-}$ ^{16}
d^1	d^1	FO	FO	Co^{II}(C$_5$H$_5$)$_2$$^{\cdot}$,^{31b} NO$^{\cdot h}$
d^3	d^1	AF	AF	
d^3	d^3	FO	FO	
Homospin Triplet Systems				
d^2	d^2	AF	AF	O$_2$,^{i} [Ru(OEP)]$_2$^{j}
Heterospin Doublet/Triplet Systems				
s^1	d^2	FI	FI	
d^1	d^2	FI	FO	
d^3	d^2	FO	FI	

^{a} AF = antiferromagnetic, FO = ferromagnetic, and FI = ferrimagnetic coupling. ^{b} POMO orbital degeneracy (intrinsic or accidental): s = singly (a or b), d = doubly (e). ^{c} TMPD = N,N,N',N'-tetramethyl-p-phenylenediamine. Ohmasa, M.; Kinoshita, M.; Sano, M.; Akamatu, H. *Bull. Chem. Soc. Jpn.* 1968, 41, 1998. ^{d} Karimov, Yu. S.; Chibrikin, V. M.; Shchegolev, I. F. *J. Chem. Phys. Sol.* 1963, 24, 1683. ^{e} TTF = tetrathiafulvalene. ^{f} 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, p 353. ^{g} Fischer, E. O.; Joos, G.; Meer, W. *Z. Naturforsch., B* 1958, 13b, 456–457. ^{h} S = $^1/_2$ NO$^{\cdot}$, d^1, dimerizes at low temperature. Skauup, S.; Skante, P. N.; Boggs, J. E. *J. Am. Chem. Soc.* 1976, 98, 6106. ^{i} Triplet O$_2$ due to dimerization at low temperatures exhibits antiferromagnetic behavior. *Comp. Inorg. Chem.* 1973, 2, 705. ^{j} Collman, J. P.; Barns, C. E.; Sweptson, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* 1984, 106, 3500.

configuration, e.g., [Fe^{III}(C$_5$Me$_5$)$_2$]$^{\cdot+}$[TCNE]$^{\cdot-}$. For retro charge transfer 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 charged transfer and d^3/s^1 for retro charge transfer. The [Ni^{III}(C$_5$Me$_5$)$_2$]$^{\cdot+}$[TCNE]$^{\cdot-}$ complex^{29} possesses the d^1/s^1 electronic configuration and its susceptibility obeys the Curie–Weiss expression with antiferromagnetic interactions[15,29] and thus is consistent with A ← D charge transfer.

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.[15] This mechanism is invoked between [Fe^{III}(C$_5$Me$_5$)$_2$]$^{\cdot+}$'s for stabilizing ferromagnetic coupling between in-registry chains and provides an additional means for establishing bulk ferromagnetic behavior as observed for [Fe^{III}(C$_5$Me$_5$)$_2$]$^{\cdot+}$[TCNE]$^{\cdot-}$.[15,16c]

Heterospin Systems. For the lower symmetry s and d electron configurations two combinations support ferromagnetic coupling; however, illustrative systems have yet to be identified for these electron configurations.[15] Due to an accidental degeneracy of the cation's e$_{2g}$ and a$_{1g}$ orbitals^{30} [Cr^{III}(C$_5$Me$_5$)$_2$]$^{\cdot+}$ possesses a t^3 POMO; thus its [TCNE]$^{\cdot-}$ salt (i.e., half-filled t^3/s^1) is predicted to exhibit ferrimagnetic coupling for either retro or forward charge transfer.[15] Investigation of the magnetic properties of the Cr^{III} system is in progress; however, preliminary magnetization data are consistent with ferrimagnetic behavior.[29]

General Considerations. Assuming the virtural charge transfer involves only the highest energy POMO,^{32} stabilization of ferromagnetic coupling via the
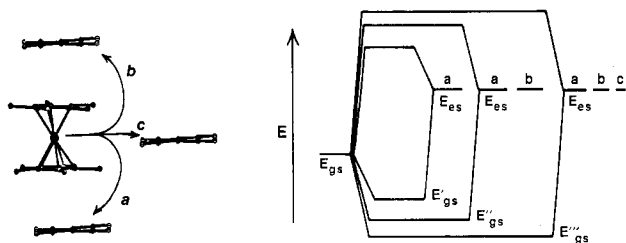
Figure 7. Schematic illustration of (a) mixing of the GS_{FO} with ES_{FO} to lower the energy to GS'_{FO}, (b) mixing of the GS_{FO} with a pair ES_{FO}'s arising from intrachain interactions to lower the energy to GS''_{FO}, and (c) mixing of the GS_{FO} with additional ES_{FO}'s arising from interchain interactions to further lower the energy to GS'''_{FO}, which may lead to the macroscopic spin alignment necessary for bulk ferromagnetic behavior.

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. For radicals with intrinsic POMO degeneracies the relatively high symmetry restricts the choice of radicals to specific point groups. For a d system the molecule or ion must belong to the D_{2d}, C_3, or higher point groups. Furthermore, opposing 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. Additionally, other mechanisms[4,6,10] for molecule-based ferromagnetic behavior may be operative.

In contrast to the McConnell model,[5,7] ions may not be necessary, but stable radicals are required. Homomolecular species (D ≡ A) in principle are sufficient if virtual disproportionation ($D^{2+} + D^0 \leftarrow 2D^{•+}$) dominates and a triplet species if formed. Since the key point is mixing of an excited state with a ground state with spin conservation, a chain structure as proposed by McConnell[5] may not be requisite, but designing materials with strong state mixing is important. Organic- or inorganic-based polymer chain and network structrues[6,34] (albeit not molecular solids[14]) as well as nonchain structures with the proper admixture of excited and ground states should suffice. This type of interchain interaction has been proposed to be present for in-registry chains in $[Fe^{III}(C_5Me_5)_2]^{•+}[TCNE]^{•-}$.[15]

Stabilization of Bulk Ferromagnetism. The model for magnetic coupling by configuration admixing of a virtual triplet excited state with the ground state is limited to the repeat unit, e.g., $[Fe^{III}(C_5Me_5)_2]^{•+}$-$[TCNE]^{•-}$. Inter- *and* intrachain spin alignment are required for bulk ferromagnetism.[9,15,16b] Again mixing of ES_{FO} with GS_{FO} lowers the energy to GS'_{FO} (Figures 6 and 7a). Since the cation is essentially equidistant to a $[TCNE]^{•-}$ above and below it within a chain, virtual transfer of an e_{2g} electron forming the admixable triplet excited state with either $[TCNE]^{•-}$ may occur. Thus,

two excited states can mix with the GS_{FO} to lower further the energy to GS''_{FO}[9] (Figure 7b), leading to intrachain spin alignment. Intrachain spin alignment leads to energy lowering; however, even with complete intrachain spin alignment (i.e., ferromagnetic coupled), if spins on adjacent chains correlate in the opposite sense, then bulk antiferromagnetic coupling may dominate. Macroscopic ferromagnetism will not occur unless interchain spin alignment occurs. If adjacent chains are out-of-registry by one-half the chain axis length, then $[TCNE]^{•-}$'s residing in adjacent chains may be comparably separated from an Fe^{III} site as are the intrachain $[TCNE]^{•-}$'s. Thus, the ES_{FO} on adjacent chains can additionally mix with GS''_{FO}[9] (Figure 7c) to lower further the energy of the system to ES'''_{FO}, leading to the spin alignment throughout the bulk that is necessary for bulk ferromagnetism.

For in-registry chains virtual disproportionation between interchain Fe^{III} sites may provide an additional mechanism to align the spins throughout the bulk and contribute to the stabilization of bulk ferromagnetism. In contrast, in-registry chains with s^1/s^1 interactions (e.g., $[TCNE]^{•-}/[TCNE]^{•-}$) 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. These in-registry and out-of-registry arrangements are present in $[Fe^{III}(C_5Me_5)_2]^{•+}[TCNE]^{•-}$.[16b]

Organic Ferromagnets

The magnetic data on $[Fe(C_5Me_5)_2]^{•+}[TCNE]^{•-}$ demonstrate that ferromagnetism is achievable with organic-based molecular systems. Utilization of a diamagnetic anion instead of a radical anion demonstrates that the organic radical is critical for achieving bulk ferromagnetism. This system contains low-spin Fe^{III}, not high-spin Fe^{II} or Fe^{III} or iron metal. Furthermore, the ferrocenes possess chemical (e.g., reactivity similar to aromatic organic compounds, e.g., benzene) and physical (e.g., solubility in conventional polar organic solvents) properties akin to those of organic compounds and not of network inorganic solids.

Organic-based ferromagnets are of increasing interest,[33] and their study to data has led to small irreproducible effects.[33d,e] Accidental or intrinsic orbital degeneracies are needed for stabilization of ferromagnetic coupling by the McConnell mechanism. Although prevalent for metal coordination compounds, they are rare for organic molecules. Thus, stable D_{2d}, C_3, or higher symmetry radicals with a degenerate POMO[15] are required. Breslow[7,33b] pointed out the necessity of a triplet state[34] and has focused research toward the synthesis of stable C_3 triplets,[7,33b] but neither ferro-

(32) Circumstances where virtual excitation from a lower lying filled (or to a high-lying unfilled) orbital dominates the admixing exciting state are conceivable. For example, $[Cr^I(C_6Me_6)_2]^{•+}[TCNE]^{•-}$ has an s^1/s^1 ground state electronic configuration, and preliminary susceptibility data can be fit by the Curie–Weiss expression with dominant ferromagnetic interactions: Miller, J. S.; O'Hare, D. M.; Chackraborty, A.; Epstein, A. J., submitted.

(33) (a) Iwamura, H.; Sugawara, T.; Itoh, K.; Takai, K. *Mol. Cryst. Liq. Cryst.* **1985**, *25*, 251. Iwamura, H. *Pure Appl. Chem.* **1986**, *58*, 187. (b) Breslow, R. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 261–267. Breslow, R.; Maslak, P.; Thomaides, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 6453. (c) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834–850. (d) Korshak, Yu. V.; Ovchinnikov, A. A.; Shapiro, A. M.; Medvedeva, T. V.; Specktor, V. N. *Pisma Zh. Eksp. Teor. Fiz.* **1986**, *43*, 309–311. Korshak, Yu. V.; Medvedeva, T. V.; Ovchinnikov, A. A.; Specktor, V. N. *Nature (London)* **1987**, *326*, 370–372. (e) Torrance, J. B.; Oostra, S.; Nazzal, A. *Synth. Met.* **1987**, *19*, 708. (f) Miller, J. S.; Calabrese, J. C.; Glatzhofer, D. T.; Epstein, A. J. *J. Chem. Soc., Chem. Commun.*, in press.

(34) This work suggests that a stable triplet may not be necessary for an organic ferromagnet; a stable doublet with a virtually accessible triplet capable of admixing with the ground state, as observed for $[Fe^{III}(C_5Me_5)_2]^{•+}[TCNE]^{•-}$ should suffice.

magnetic coupling nor bulk ferromagnetic behavior has been reported.[37]

Radicals possessing D_{2d} symmetry, albeit rare, in principle may possess a doubly degenerate POMO and should be studied.[15] Oxidation of D_{3v} tris(dicyanomethylene)cyanopropane should lead to a d^3 radical cation.[35] Since it has not been isolated, other derivatives with electron-donating groups, e.g., NR₂, to stabilize the radical cation, e.g., 4, should be studied. Alternatively, with the goal of building a solid where adjacent chains are out-of-register by one-half of a unit cell as noted for the $[Fe(C_5Me_5)_2]^{\bullet+}[A]^{\bullet-}$ system, meta-substituted multilayered cyclophanes,[36] e.g., [2.2.2], 5, are challenging targets for synthesis. These bulky materials may provide the proper solid-state structure enabling bulk ferromagnetic behavior.
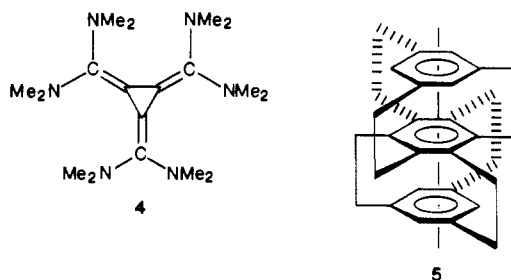
Summary

Quantitative bulk ferromagnetic behavior (spontaneous magnetization) has been established for the organic-like molecular solid $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$. It exhibits a Curie temperature, T_c, of 4.8 K, saturation magnetization of 16 300 (emu G)/mol, and a 2 K coercive field of 1 kG. Above 16 K the dominant magnetic

interactions are along a chain (1-D) and near T_c 3-D bulk effects, as evidenced by the values of the critical exponents, dominate the susceptibility. The extended McConnell model has been developed, and it provides the synthetic chemist guidance for making new molecular materials 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. A microscopic model that accounts for the observations to data has been discussed. These requirements for ferromagnetism are met by $[Fe^{III}(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$. Additionally, this model predicts that the Ni^{III} and Cr^{III} analogues should be respectively antiferromagnetic and ferrimagnetic, as preliminary data suggest.

Extensive chemical syntheses of cleverly designed radicals, as well as physical, experimental, and theoretical insight, are necessary to test and extend these concepts and establish a deeper understanding of cooperative phenomena in molecular solids.

(35) Fukunaga, T. *J. Am. Chem. Soc.* 1976, *98*, 610–611. Fukunaga, T.; Gordon, M. D.; Krusic, P. J. *J. Am. Chem. Soc.* 1976, *98*, 611–613.

(36) Hubert, A. J. *J. Chem. Soc. C* 1967, 13–14.

(37) **Note Added in Proof**: The dication of hexaazaoctadecahydrocoronene has been reported to possess a triplet ground state.[7,33b] Recent structural and magnetic data, however, show that the solid is diamagnetic. Thus, electronic-driven structural distortions are an important consideration in the design of an s/p organic ferromagnet (Miller, J. S.; Dixon, D. A.; Calabrese, J. C.; Krusic, P. J., submitted).

Molecular Hydrogen Complexes: Coordination of a σ Bond to Transition Metals

Gregory J. Kubas

Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545

The activation of hydrogen by metal centers is an important chemical reaction from both commercial and scientific standpoints. The H–H bond is strong (103 kcal/mol) and H₂ addition to unsaturated organic and other compounds must be mediated by metal centers, forming the basis for catalytic hydrogenation. In catalytic mechanisms, hydride complexes formed by cleavage of H₂ have been thought to play a key role.[1,2]

Gregory Kubas was born in Cleveland, OH, in 1945. He obtained his B.S. in chemistry at Case Western Reserve University and Ph.D. from Northwestern University under Duward Shriver. After postdoctoral positions at Princeton with Thomas Spiro and at Los Alamos, he joined the staff at LANL in 1974. He recently was appointed a Laboratory Fellow, and research interests include activation of small, energy-related molecules (SO₂, H₂) by transition-metal complexes.