Molecular/Organic Ferromagnets

JOEL S. MILLER, ARTHUR J. EPSTEIN, WILLIAM M. REIFF

Some molecular/organic solids comprised of linear chains of alternating metallocenium donors (D) and cyanocarbon acceptors (A) with spin state $S = 1/2$ ($\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$) exhibit cooperative magnetic phenomena, that is, ferro-, antiferro-, ferri-, and metamagnetism. For $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{-\cdot}$ (Me = methyl; TCNE = tetracyanoethylene), bulk ferromagnetic behavior is observed below the Curie temperature of 4.8 K. A model of configuration mixing of the lowest charge-transfer excited state with the ground state was developed to understand the magnetic coupling as a function of electron configuration and direction of charge transfer. This model predicts that ferromagnetic coupling requires stable radicals with a non–half-filled degenerate valence orbital and a charge-transfer excited state with the same spin multiplicity that mixes with the ground state. Ferromagnetic coupling must dominate in all directions to achieve a bulk ferromagnet. Thus, the primary, secondary, and tertiary structures are crucial considerations for the design of molecular/organic ferromagnets.

MAGNETS HAVE FASCINATED MAN SINCE THE OBSERVATION that iron is attracted to lodestone. Early in history the Chinese took advantage of this observation and invented the compass. Today highly magnetic ferro- (for example, Fe and CrO_2) and ferrimagnetic (for example, Fe_3O_4) materials are used in technological applications ranging from household magnets to complex digital recording media. A goal of contemporary materials research is to improve their properties (*1*). These highly magnetic materials share the common structural features of (i) being atomic-based, (ii) having *d* or *f* orbital metal-based spin sites, and (iii) having one-dimensional (1-D), 2-D, or 3-D network bonding. Molecular/organic–based compounds (*2, 3*) with *p* or even *d* orbitals contributing to the cooperative magnetic properties have captivated the imagination of scientists for the past quarter of a century (*4*), but until recently such magnets were unknown. Their discovery parallels the advent of molecularly based superconductors and the exploration of cooperative phenomena in molecular/organic materials (*5*). This broad range of phenomena in the molecular/organic solid state combined with the anticipated modification of the physical properties through conventional synthetic organic chemistry as well as the ease of fabrication enjoyed by organic materials may lead to their use in future generations of electronic or photonic devices.

In this review we first summarize the common idealized magnetic behaviors and the models postulated for stabilizing ferromagnetic coupling in molecular/organic compounds and describe the structure and magnetic properties of the unusual class of charge-transfer molecular solids that exhibits bulk ferromagnetic behavior. We then discuss models for the stabilization of ferromagnetic coupling and bulk ferromagnetic behavior for this class of charge-transfer compounds that are used to propose new organic and polymeric materials that test these theories.

Idealized Magnetic Behavior in Molecular/Organic Solids

Above a spin-ordering temperature, all substances exhibit a magnetic moment M upon application of a magnetic field H with the susceptibility χ being the proportionality constant ($M = \chi H$). Paramagnetic (open-shell) compounds have their induced moment aligned parallel to the field. For noninteracting localized spins, χ may be modeled by the Curie expression ($\chi \propto T^{-1}$). Diamagnetic (closed-shell) compounds have their induced moment aligned antiparallel to the field and have a negative temperature-independent susceptibility.

In the presence of cooperative magnetic behavior (ferro- or antiferromagnetism), the spins are subject to an effective parallel (or antiparallel) exchange field due to the neighboring spins, which either increases or decreases the measured χ from the Curie expression. At higher temperatures χ may be modeled by the Curie-Weiss expression, $\chi \propto (T - \theta)^{-1}$. For ferro- and antiferromagnetic interactions, θ is respectively greater or less than zero (Fig. 1A). Chemists frequently report the effective moment, μ_{eff} [$=(8\chi T)^{1/2}$],

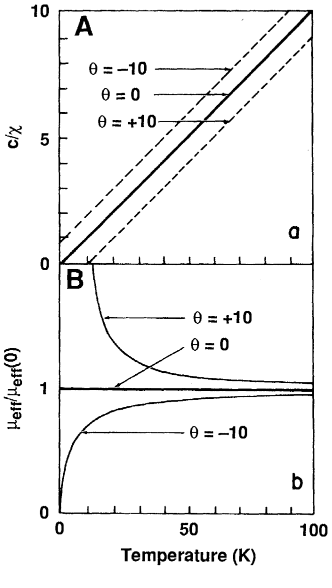


Fig. 1. The reciprocal susceptibility, χ^{-1}, extrapolated from the high-temperature data (**A**) and the effective moment, μ_{eff} (**B**), as a function of temperature for $g = 2$, $S = 1/2$ independent ($\theta = 0$ K) spins, as well as ferromagnetically coupled ($\theta = +10$ K) and antiferromagnetically coupled ($\theta = -10$ K) spins.

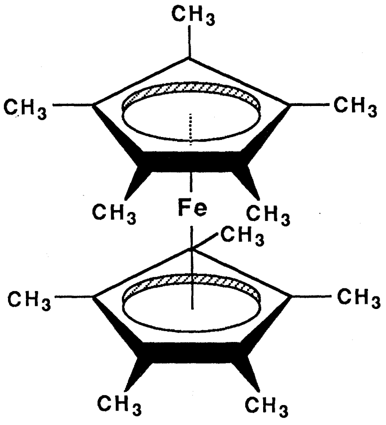
J. S. Miller is at the Central Research and Development, E. I. du Pont de Nemours and Co., Inc., Experimental Station-E328, Wilmington, DE 19898. A. J. Epstein is in the Department of Physics and Department of Chemistry, Ohio State University, Columbus, OH 43210. W. M. Reiff is in the Department of Chemistry, Northeastern University, Boston, MA 02115.

in units of Bohr magnetons (μ_B) (Fig. 1B), which has characteristic temperature dependencies for independent, ferro-, and antiferromagnetic interactions.

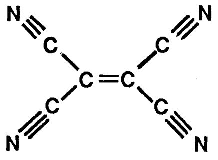
Ordering of the spins may occur at low temperatures. If spins align parallel (ferromagnetic) to each other, then a macroscopic spontaneous magnetization at zero applied field is present, as well as a characteristic saturation moment, M_s (for example, 1.2×10^4 emuG/g-atom for iron) (*6*). No spontaneous macroscopic moment occurs when the spins are antiparallel (antiferromagnetic) (*7*). Ferrimagnetism occurs when antiferromagnetically aligned spins have different local moments and the incomplete cancellation of the spins results in a reduced but finite spontaneous moment. For ordered spin-spin systems, the $M(H)$ behavior is hysteretic and is dependent on the orientation of the applied field with respect to the direction of spin alignment.

Postulated Mechanisms for Stabilizing Ferromagnetic Coupling in Molecular/Organic Solids

Spin alignment throughout the bulk is essential for ferromagnetism. Four mechanisms have been postulated for the pairwise stabilization of ferromagnetic coupling of spins. These mechanisms are insufficient for explaining bulk (3-D) ferromagnetic behavior and a model to account for this is discussed. The models are (i) configuration mixing (Hubbard) of a virtual triplet excited state with the ground state for a $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ chain (*8–10*), (ii) very high spin multiplicity radicals (*11*), (iii) Heitler-London spin exchange between positive spin density on one radical and negative spin density on another (*12*), and (iv) superexchange through a degenerate orbital of a closed-shell molecule or ion (*13*). Insufficient space is available to adequately discuss these models, although reviews of these mechanisms are available (*4*). Since experimental evidence for ferromagnetic behavior in a molecular compound has been limited to the charge-transfer salt of decamethylferrocene, $Fe^{II}(C_5Me_5)_2$ (Me, methyl group), **1**, with tetracyanoethylene, TCNE, **2** (*14, 15*), and because this compound has both the crystal and electronic structures prescribed by the first mechanism, this mechanism will be discussed in greater detail.



1



2

There is great interest in molecular/organic ferromagnets. Crystals comprised of a solid solution of galvanoxyl-hydroxygalvanoxyl have been reported to exhibit ferromagnetic coupling. Hysteresis curves characteristic of a bulk ferromagnet, however, were not observed (*16*). Attempts to prepare a ferromagnetic polymer via the iodine oxidation of 1,3,5-triaminobenzene (*17*) and topochemical polymerization of a dinitroxyldiacetylene (*18*) have been reported, although neither reproducible chemical nor physical characterization have been achieved. The reported magnetization corresponded to only ~0.1 to 2% of the maximum theoretical magnetization. The poor chemical characterization, low value of the magnetization, and marked variation between samples suggest that the ferromagnetic behavior in these polymers may not be intrinsic.

Structure and Magnetic Properties of $[Fe(C_5Me_5)_2]^{\cdot +}[Acceptor]^{\cdot -}$

Charge-transfer salts comprised of linear chains of alternating donors (D) and acceptors (A), that is, ···DADADA···, are poor conductors (*19*), in contrast with segregated chain salts. Coopera-

Table 1. Summary of the properties of $[Fe(C_5R_5)_2]$[anion] complexes possessing a ···DADA··· 1-D structure; s, strong.

Property	Anion*				
	$[C_3(CN)_5]^-$	TCNE	$[TCNE]^{\cdot -}$	$[TCNE]^{\cdot -}$†	$[TCNQ]^{\cdot -}$
Anion spin	0	0	1/2	1/2	1/2
Space group	*C2/c*	$P\bar{1}$	*C2/c*	$Cmc2_1$	$P\bar{1}$
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
$R_f(T)$	3.6 (−100°C)	14 (25°C)	5.9 (−30°C)		6.0 (−106°C)
Intrachain Fe–Fe distance (Å)	10.305		9.750	10.621	10.549
C_5Me_5-anion distance (Å)	3.44	3.28	3.51		3.67
C_5Me_5-anion dihedral angle (degrees)	0		2.8		3.9
In-registry Fe–Fe distances (Å)	8.600 9.567 9.939	6.78 7.70 7.89	8.603 8.732 9.651	8.649 9.618 9.649	8.628 9.348 10.033
ν(CN) mineral oil (cm^{-1})	2106s, 2207s	2203, 2180	2144s, 2183s	2144s, 2183s	2153s, 2179s
Mössbauer transitions, 1.4 K	1	2		6	12
H_{int}, 1.4 K (kG)				424	404, 449
Curie-Weiss, θ (K)	−1			30	3
Critical temperature (K)				4.8‡	2.55§
Magnetism	Paramagnetic	Diamagnetic		Ferromagnetic	Metamagnetic
Reference	(*14*)	(*29*)	(*14*)	(*14*)	(*21*)

*Cations are $[Fe(C_5Me_5)_2]^{\cdot +}$ except for the neutral TCNE complex, for which the donor is $[Fe(C_5H_5)_2]$. †Loss of MeCN solvent leads to formation of the orthorhombic phase; anion is disordered and has not been refined. ‡Curie temperature. §Neel temperature.

Table 2. Magnetic coupling for homo- and heterospin systems with singly and doubly degenerate HOMOs (*3*). Abbreviations and symbols: POMO orbital degeneracies are either single, *s* (*a* or *b* symmetry), double, *d* (*e* symmetry), or triple, *t*; AF, antiferromagnetic; FO, ferromagnetic; FI, ferrimagnetic; TMPD, *N′*,*N′*,*N′*,*N′*, tetramethyl-*p*-phenylenediamine; TTF, tetrathiafulvalene; and OEP, octaethylporphyrin.

D (or A)*	A (or D)*	D→A	A→D	Example systems
		Homospin ½ systems		
s^1	s^1	AF	AF	[TMPD][TCNQ] (*34*) $[TTF][Pt(S_2C_4F_6)_2]$, $V(C_6H_6)_2\cdot$
d^1	s^1	AF	FO	$[Ni^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$ (*33*)
d^3	s^1	FO	AF	$[Fe^{III}(C_5Me_5)_2]^{\cdot -}[TCNE]^{\cdot -}$ (*14, 15*)
d^1	d^1	FO	FO	$Co^{II}(C_5H_5)_2\cdot$, NO·
d^3	d^1	AF	AF	
d^3	d^3	FO	FO	
		Homospin 1 systems		
d^2	d^2	AF	AF	O_2, $[Ru(OEP)]_2$
		Representative heterospin systems		
s^1	d^0	FO		$[TMPD]^{\cdot +}[C_5(CN)_5]^-$ (*13*)
s^1	d^4		FO	$[Co^{III}(C_5Me_5)_2]^+[TCNE]^{\cdot -}$ (*14*)
s^1	d^2	FI	FI	
d^1	d^2	FI	FO	
d^3	d^2	FO	FI	
t^3	s^1	FI	FI	$[Cr^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$ (*33*)

*D and A can be interchanged.

tive magnetic phenomena, including bulk meta- (*4, 20*) and ferromagnetism (*4, 14, 15*) as well as spin-Peierls transition (*21*), have been reported for these alternate chain materials.

Our approach for designing molecular ferromagnets evolved from the study of the magnetic properties of $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[TCNQ]^{\cdot -}$ (*4, 20, 22*) (TCNQ = 7,7,8,8,-tetracyano-*p*-quinodimethane). Rapid crystallization led to the isolation of the kinetic phase, which has a 1-D structural motif based on alternating $[Fe^{III}(C_5Me_5)_2]^{\cdot +}$ cation donors and $[TCNQ]^{\cdot -}$ anion acceptors, $(\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots)$ both with spin $S = 1/2$ (*22*) (Fig. 2). The value of μ_{eff} significantly deviates (*4*) from the temperature-independent Curie behavior characteristic of ferrocenium salts (*4, 23*) (Fig. 3). The magnetization reveals metamagnetic behavior; for $H < 1.6$ kG the magnetization is characteristic of an antiferromagnet, whereas for $H > 1.6$ kG a sharp rise and approach to magnetization saturation characteristic of a ferromagnet is observed (Fig. 4) (*4*). Several metamagnets such as $FeCl_2$ are known (*24*), but this is the first example where neither a 1-D, 2-D, nor 3-D covalent network structure is present—only a conventional, organic-solvent–soluble molecular solid (*2*).

With the discovery of the molecular metamagnet, we sought to elucidate the structure-function relation through systematic modification of A, the cyclopentadiene ring substituent groups, and the metal to understand the steric and electronic features necessary to prepare a molecular ferromagnet. On the premise that a smaller radical anion would have a different spin distribution that could lead to greater spin interactions, the $[TCNE]^{\cdot -}$ salt ($S = 1/2$) of $[Fe^{III}(C_5Me_5)_2]^{\cdot +}$ salt was synthesized. The unit cell obtained for acetonitrile grown crystals contained a molecule of solvent that was completely lost with transformation from a monoclinic to an orthorhombic cell (*14*). Both phases have the $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ motif (Fig. 2), although the anion is disordered and unrefinable in the latter phase (*14*). The magnetic and Mössbauer data were obtained on the orthorhombic phase.

The high-temperature susceptibility of $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$ fits the Curie-Weiss expression with $\theta = +30$ K (Fig. 5), indicating dominant ferromagnetic interactions (*14*). A spontaneous magnetization is observed for polycrystalline samples below 4.8 K in the earth's magnetic field (*14*). For single crystals aligned with an external field parallel to the stacking axis, the saturation magnetization is 1.6×10^4 emuG/mol (*15*). This is 36% greater than for iron metal on a per iron atom basis and agrees with the calculated saturation moment for ferromagnetic alignment of the donor ($S = 1/2$; $g_{\parallel} = 4$) (g = Landè factor) and the acceptor ($S = 1/2$; $g = 2$) (*25*). The critical (Curie) temperature, T_c, is 4.8 K, and hysteresis loops characteristic of ferromagnetic materials are observed (Fig. 6). A large coercive field of 1 kG is recorded at 2 K (*15*).

The single-crystal susceptibility can be compared with the results from different physical models to understand the microscopic spin interactions. For samples oriented parallel to the field, the susceptibility above 16 K fits a 1-D Heisenberg model with ferromagnetic exchange of $J = 19\ \mathrm{cm}^{-1}$ (*15*). Variation of the low-field magnetic susceptibility for an unusually broad temperature range above $T_c[\chi \propto (T - T_c)^{-\gamma}]$, magnetization with temperature below $T_c[M \propto (T_c - T)^{-\beta}]$, and the magnetization with magnetic field at $T_c(M \propto H^{1/\delta})$ enabled the determination of the critical exponents β, γ, and δ. The values of 1.2, ~0.5, and 4.4, respectively, were determined for the magnetic field parallel to the chain axis. These values are consistent with a mean-field–like 3-D behavior. Thus 1-D nearest-neighbor spin interactions are sufficient to understand the magnetic coupling above 16 K, but 3-D spin interactions are dominant near T_c. The key physical properties for $[Fe(C_5Me_5)_2]^{\cdot +}[A]^{\cdot -}$ are summarized in Table 1.

The large single crystals that are necessary for measurement of magnetic anisotropy are not readily grown. Such crystals of the 1-D $[TCNQ]^{\cdot -}$ salt cannot be prepared, as the thermodynamically favored dimer phase, which exhibits independent spin (Curie) magnetic behavior (*4, 22*), forms. Large crystals of the $[TCNE]^{\cdot -}$ salt can be easily grown from acetonitrile; however, they contain acetronitrile that is lost upon isolation of the crystals to form a polycrystalline sample (*14*). Small single crystals enabling the determination of the magnetic anisotropy of the TCNE salt can be made from tetrahydrofuran; however, the refinement of the anion cannot be made because of disorder (*14*).

The ^{57}Fe Mössbauer spectra of the TCNE and TCNQ salts of $Fe(C_5Me_5)_2$ are informative. Atypical six-line Zeeman-split spectra are observed in zero applied magnetic field at low temperature as the radical anions provide an internal dipolar field. For example, a Zeeman-split spectrum with an internal field of 424 kG (4.2 K) is observed for the $[TCNE]^{\cdot -}$ salt (*14*), whereas the metamagnetic $[TCNQ]^{\cdot -}$ salt exhibits a pair of six-line Zeeman-split spectra (*22*), implying a pair of inequivalent Fe^{III} sites below 4.2 K. The internal fields are substantially greater than the expectation of 110 kG per spin per iron atom (*26*).

Effect of Chemical Modification

The properties of ···DADA··· structured compounds based on $[M(C_5R_5)_2]^+$ were studied to deduce the effect of changes in the chemical composition. Three modifications were: (i) the use of ferrocenium $[Fe^{II}(C_5H_5)_2]^{\cdot +}$ as the cation, (ii) use of alternate open- and closed-shell anions, and (iii) replacement of Fe^{III} with other metal ions.

Ferrocene is 0.5 V more difficult to oxidize than decamethylferrocene and is not oxidized by TCNE (*27, 28*). Nonetheless, diamagnetic $[Fe^{II}(C_5Me_5)_2][TCNE]$ forms and has the same structure type (*29, 30*) (Fig. 2). Stronger acceptors should stabilize complete electron transfer with ferrocene. The electron transfer complex $[Fe^{III}(C_5H_5)_2]^{\cdot +}[C_4(CN)_6]^{\cdot -}$ (*31*) was prepared and possessed Fe^{III} and $[A]^{\cdot -}$; however, it is essentially paramagnetic. Since $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[C_4(CN)_6]^{\cdot -}$ exhibits ferromagnetic interactions (*31*), the structure of the $[Fe^{III}(C_5H_5)_2]^{\cdot +}[C_4(CN)_6]^{\cdot -}$ should provide important information when suitable crystals can be grown to enable its determination.

Replacement of TCNQ with TCNE (*14*), $C_4(CN)_6$ (*31*), or similar acceptors led to $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ complexes with dominant ferromagnetic behavior ($\theta \geq 10$ K). In contrast, replacement with diamagnetic $[C_3(CN)_5]^-$ (*14*) led to the formation of a $\cdots D^{\cdot +}A^{-}D^{\cdot +}A^{-}\cdots$ structured phase, which exhibited essentially Curie susceptibility ($\theta = -1.2$ K) (Figs. 3 and 5). The marked change in the ground state magnetic behavior upon substitution of the radical anion suggests that the interchain anion-anion interactions are important.

The $[Co^{III}(C_5Me_5)_2]^+[TCNE]^{\cdot -}$ complex with an $S = 0$ donor has been prepared. It exhibits the Curie susceptibility anticipated for $S = 1/2$ $[TCNE]^{\cdot -}$ ($\theta = -1.0$ K) (Figs. 3 and 5) (*14*). 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 (*32*). In contrast, replacement of Fe^{III} in $[Fe^{III}(C_5Me_5)_2]^+[A]^{\cdot -}$ [A = TCNE, $C_4(CN)_6$] with Ni^{III} ($S = 1/2$) or Cr^{III} ($S = 3/2$) led to compounds exhibiting cooperative magnetic properties (*33*). The motivation for studying these complexes emanates from our expanded model (*3*) for the stabilization of ferromagnetic coupling in molecular solids; their magnetic properties are discussed below.

The available data support the conclusion that the $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ structure type with both $S \geq 1/2$ donors and $S \geq 1/2$ acceptors is necessary but insufficient for stabilizing cooperative highly magnetic behavior.

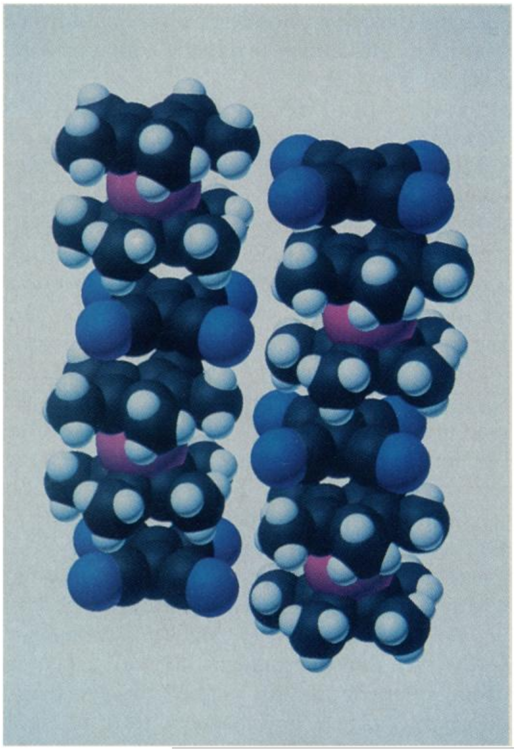


Fig. 2. Alternating donor-acceptor, linear-chain structure $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ of $[Fe^{III}(C_5Me_5)_2]^{\cdot +}$ [A = TCNQ, TCNE, DDQ, $C_4(CN)_6$], $[Fe^{II}(C_5H_5)_2][TCNE]$, and $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[C_3(CN)_5]^{\cdot -}$. The structure shows adjacent out-of-registry chains for A = TCNE.

Bulk Ferromagnetic Interactions in Molecular Solids

Ferromagnetism requires spin alignment throughout the solid. The model of configuration mixing of a virtual-triplet excited state with the ground state for a $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ chain, originally introduced by McConnell (*8*), is an appropriate starting point, since $[Fe(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$ has the prescribed crystal and electronic structures. After applying this model to this system we extended to other systems. This model only describes the magnetic coupling within the repeat unit, $[Fe(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$. A mechanism extending the magnetic couplings throughout the bulk is described herein.

The large separations and energy differences between ions on adjacent sites leads to small overlaps of the frontier orbitals and prevents the formation of metallic energy bands for mixed-stack charge-transfer salts. Instead, a $D^{\cdot +}A^{\cdot -}$ pair with a half-occupied nondegenerate highest occupied molecular orbitals (HOMOs), for example, $[TMPD]^{\cdot +}[TCNQ]^{\cdot -}$ (TMPD = *N,N,N′,N′*-tetramethy-*p*-phenylenediamine), exhibits antiferromagnetic coupling among the spins (Ia in Fig. 7) (*34*). The antiferromagnetic coupling lowers the total electronic energy by admixing the higher energy charge-transfer states with the ground state (IIb and IIc in Fig. 7) where an electron is delocalized onto an adjacent site. This delocalization and energy reduction do not occur when the two electron spins are parallel (ferromagnetically aligned in accord with the Pauli exclusion principle). In this manner, antiferromagnetic coupling can be achieved along and between chains.

The effective antiferromagnetic exchange interaction J can be accounted for within a nearest neighbor Hubbard model with transfer integral t between the $D^{\cdot +}$ and $A^{\cdot -}$ and energy cost ΔE for double occupancy of the nondegenerate orbital (*35, 36*). For $\Delta E >> t$ and $\Delta E >> k_B T$ (k_B is the Boltzmann constant), the exchange interaction J is approximately $t^2/\Delta E$. Since the $D^{\cdot +}$ and $A^{\cdot -}$ sites are not identical, ΔE depends upon the direction of charge

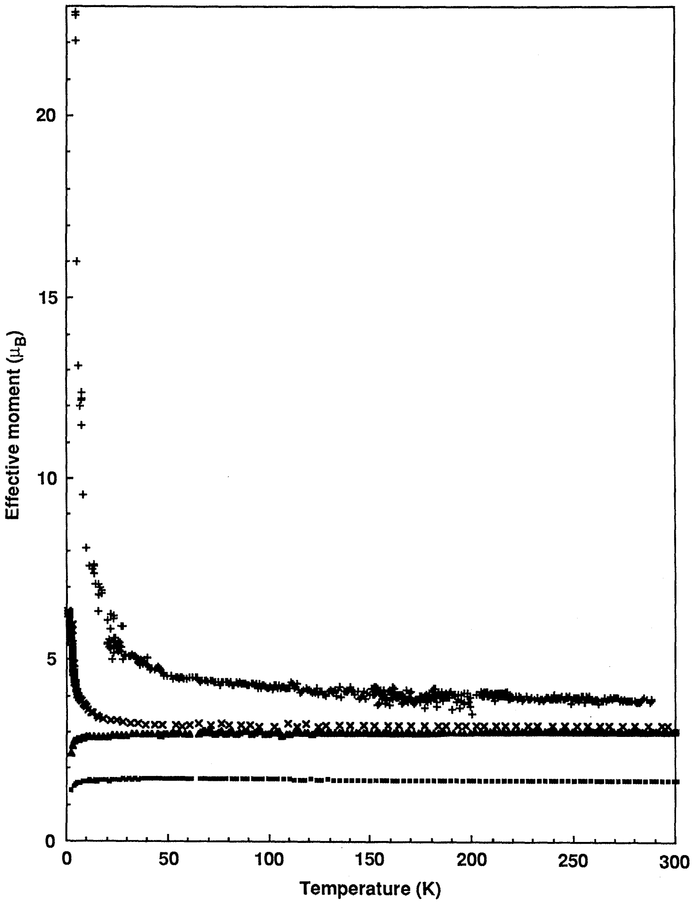


Fig. 3. The effective moment as a function of temperature for $[Fe^{III}(C_5Me_5)_2][A]^{\cdot -}$ [A = TCNQ (x), TCNE (+), $[C_3(CN)_5]^{\cdot -}$ (▲)] and $[Co^{III}(C_5Me_5)_2{}^+[TCNE]^{\cdot -}$ (■).

transfer. For singly occupied nondegenerate orbitals on each site, (s^1/s^1), J is positive, and antiferromagnetic coupling dominates, as the excited state is a singlet.

The situation differs for $[Fe(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$, as the cation has three electrons in a degenerate partially occupied molecular orbital (POMO), d^3 (IIa in Fig. 7). Thus several states may be admixed to lower the energy. The possibilities indicated in II of Fig. 7 include: (b) $D^{\cdot +} \leftarrow A^{\cdot -}$ charge transfer, as well as (c) and (d), $A^{\cdot -} \leftarrow D^{\cdot +}$ charge transfer. Admixing of any of these three excited states leads to antiferromagnetic coupling. In contrast, excitation of the minority spin ("spin down") electron from the $D^{\cdot +}$ to $A^{\cdot -}$ leads to ferromagnetic coupling (IIe in Fig. 7). The net exchange interaction between adjacent degenerate (for example, $[Fe(C_5Me_5)_2]^{\cdot +}$) and nondegenerate (for example, $[TCNE]^{\cdot -}$) sites depends upon the competition between forward and reverse charge transfer. For forward charge transfer, Hund's rule suggests that ferromagnetic alignment (IIe in Fig. 7) dominates. For a bulk ferromagnet, the important interchain ferromagnetic interaction can also be stabilized by this mechanism.

A third type of interaction germane for the pairwise interaction between doubly degenerate sites, each with three electrons (d^3/d^3, for example, $[Fe(C_5Me_5)_2]^{\cdot +}$–$[Fe(C_5Me_5)_2]^{\cdot +}$) is illustrated in IIIa of Fig. 7. By the above arguments, the exchange interaction resulting from admixing of this higher energy charge transfer (disproportionation) state is ferromagnetic (IIIb in Fig. 7). These interactions are important for stabilization of the intrachain (d^3/s^1) and interchain (d^3/s^1, d^3/d^3, and s^1/s^1) interactions relevant for $[Fe(C_5Me_5)_2]^{\cdot +}$ $[TCNE]^{\cdot -}$.

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 (*3*). The results of the evaluation of stabilization are summarized in Table 2 of homospin ($S_D = S_A$) and heterospin ($S_D \neq S_A$) systems containing only singly and doubly degenerate orbitals (*37*). For heterospin systems with incomplete spin cancellation, antiferromagnetic coupling should lead to ferrimagnetic behavior (*3*), and the ferro- and ferrimagnetic interactions can be predicted. Heterospin systems with a closed shell species, such as s^1/d^0 (or s^1/d^4), comply with superexchange through a degenerate orbital of a closed shell species model (*13*). Mixed-valent open shell species, such as d^1/d^2, are the basis of a ferromagnetic organic metals model (*10*). Realization of materials with properties consistent with the latter two models have yet to be achieved.

Several examples corresponding to those listed in Table 2 have been realized. As described above, the d^3/s^1 $[Fe^{III}(C_5Me_5)_2]^{\cdot +}$-$[TCNE]^{\cdot -}$ complex possesses a ferromagnetic ground state. Antiferromagnetic coupling is, however, predicted for d^1/s^1 complexes with forward charge transfer. The $[Ni^{III}(C_5Me_5)_2{}^{\cdot +}[TCNE]^{\cdot -}$ complex has this electronic configuration and its susceptibility obeys the Curie-Weiss expression with $\theta = -10$ K (Fig. 5). This is consistent with dominant antiferromagnetic interactions (*3, 32*). A outcome of the model is that all half-filled POMO cases are expected to exhibit antiferromagnetic coupling.

For heterospin systems [the lower symmetry s and d electron configurations (*36*)], two combinations support ferromagnetic cou-

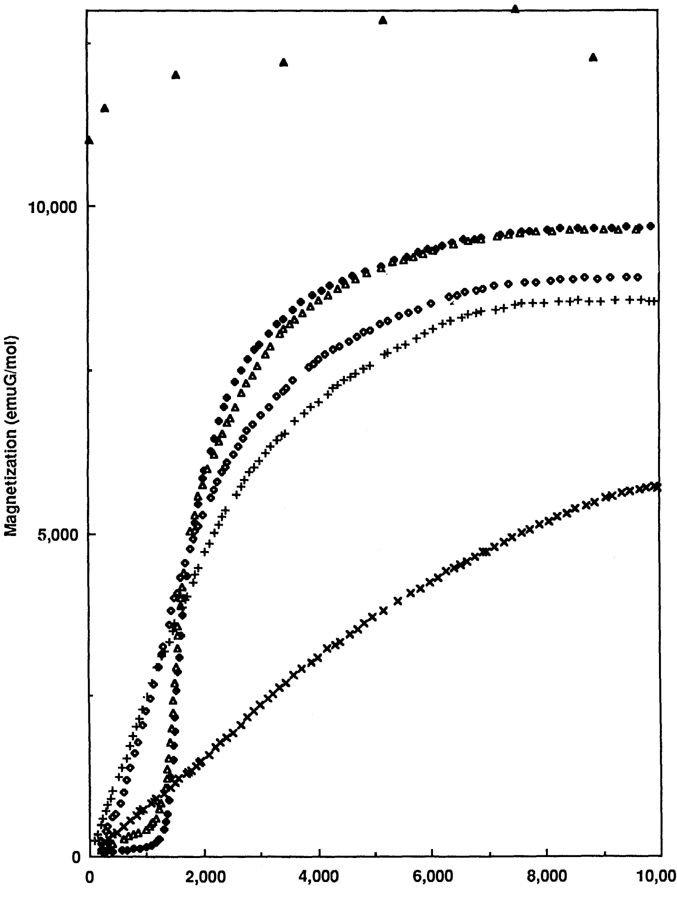


Fig. 4. The magnetization M as a function of applied field H for $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[A]^{\cdot -}$ [A = TCNQ, (◆, 1.53 K; △, 1.87 K; ◇, 2.34 K; +, 2.55 K; x, 4.47 K), and TCNE (▲, 4.2 K)]. The antiferromagnetic critical temperature (Neel temperature) for $[Fe(C_5Me_5)_2]^{\cdot +}[TCNQ]^{\cdot -}$ is 2.55 K.

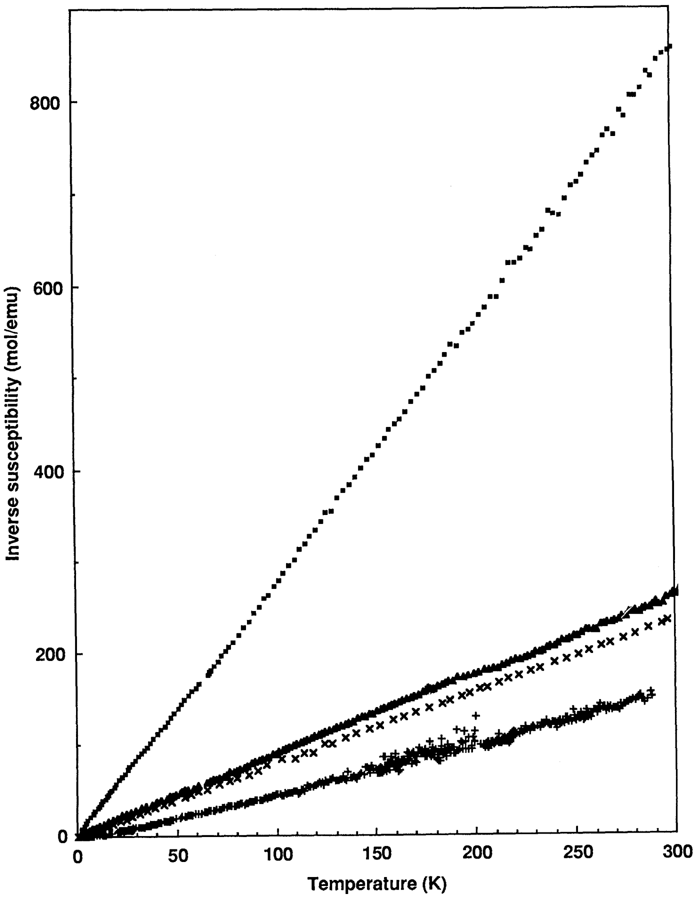


Fig. 5. The reciprocal magnetic susceptibility χ^{-1} as a function of temperature for $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[A]^{\cdot -}$ [A = TCNQ (x, $\theta = 3$ K), TCNE (+, $\theta = 30$ K), $[C_3(CN)_5]^-$ (▲, $\theta = -1.2$ K)] and $[Co^{III}(C_5Me_5)_2]^+[TCNE]^{\cdot -}$ (■, $\theta = 1$ K).

pling; however, illustrative systems have yet to be identified for these electron configurations (*3*). Due to an accidental degeneracy of the e_{2g} and a_{1g} orbitals of the cation (*27*), $[Cr^{III}(C_5Me_5)_2]^{\cdot+}$ has a t^3 POMO; thus its $[TCNE]^{\cdot-}$ salt (that is, half-filled t^3/s^1) is predicted to exhibit ferrimagnetic coupling for either reverse or forward charge transfer (*3*). Preliminary magnetization data are consistent with ferrimagnetic behavior (*33*).

Guidance for the Design of Molecular/Organic Ferromagnets

The McConnell mechanism leads to several important criteria for the design of a molecular/organic ferromagnet. Foremost is the requirement that the stable radicals possess a non–half-filled degenerate POMO (*38*). These radicals must not have structural or electronic distortions that lower the symmetry and significantly break the degeneracies (such as the Jahn-Teller effect). Accidentally degenerate systems (for example, high-spin transition, lanthanide, and actinide metal coordination complexes), however, suffice. Furthermore, opposing effects (such as retro versus forward virtual charge transfer) or the magnitude of the stabilization (for example, inversely proportional to distance and energy difference between the mixing states) may obscure the effect and lead to other phenomena. Additionally, other mechanisms (*8–13*) for molecular-based ferromagnetic behavior may be present.

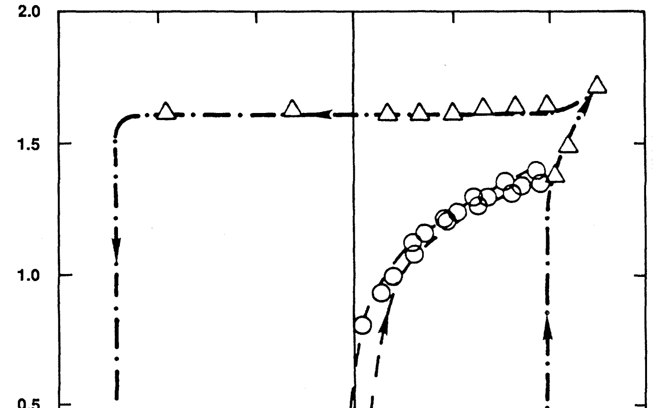


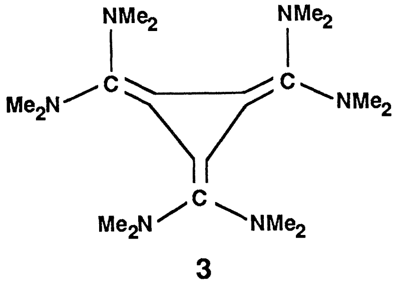
Fig. 6. The magnetization M as a function of applied field H for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (○, 4.7 K) shows hysteresis loops for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ at 2 K (△).

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} or $C_{\geq 3}$ point groups. Low symmetries suffice if accidental degeneracies occur. Ions may not be necessary, but stable radicals are required. Homomolecular species (D ≡ A) in principle are sufficient if the third type of interaction described above dominates and one of the excited state species formed has $S \geq 1/2$. Since the essence of the mechanism is mixing of an excited state with a ground state with spin conservation, a chain structure may not be requisite, but designing materials with strong state mixing is important. Organic- or inorganic-based polymer chain and network structures (*39*) [albeit not molecular solids (*2*)], as well as nonchain structures with the proper admixture of excited and ground states, should suffice.

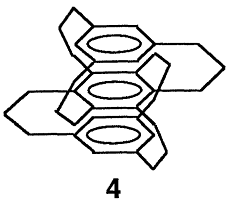
In addition to the criteria applicable to the individual radicals, the inter- and intrachain interactions are important for bulk ferromagnetic, as subtle changes in the anion can substantially alter the magnetic behavior. This structure-function relation is the subject of current study.

Organic Ferromagnets

The quest for ferromagnets based on *s* or *p* orbitals is of intense interest (*7, 13, 16–19, 36, 40, 41*). The magnetic data on $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ demonstrates that ferromagnetism can occur in molecular/organic systems. Replacement of the doublet organic acceptor with a diamagnetic acceptor demonstrates that the organic species is crucial for achieving bulk ferromagnetism. This system contains low-spin Fe^{III}, not high-spin Fe^{II} or Fe^{III} or iron metal. The ferrocenes possess chemical reactivity (similar to aromatic organic compounds such as benzene) and physical properties (such as solubility in conventional polar organic solvents) akin to organic compounds and not to inorganic network solids.



3



4

Accidental or intrinsic orbital degeneracies, albeit rate for organic molecules, are needed for stabilization of ferromagnetic coupling by the McConnell mechanism. Thus stable D_{2d} or $C_{\geq 3}$ symmetry radicals with $S = 1/2$ and a degenerate POMO (*4*) are required. Breslow (*9*) reemphasized the necessity of a triplet state (*42*) and has focused research toward the synthesis of stable C_3 triplets, but neither ferromagnetic coupling nor bulk ferromagnetic behavior has been reported (*9, 41, 42*). Radicals with D_{2d} symmetry, albeit rare, in principle may possess a doubly degenerate POMO and should be studied (*3*). Oxidation of D_{3h} hexacyanotrimethylenecyclopropane should lead to a d^3 radical cation (*43*). As this species has not been isolated, other derivatives with electron-donating groups, such as NR_2, to stabilize the radical cation, for example, **3**, should be studied. Alternatively, with the goal of building a structure similar to that observed for the $[Fe(C_5Me_5)_2]^{\cdot +}[A]^{\cdot -}$ system (*4, 14*), meta-substituted multilayer cyclophanes (*44*), for example, [3.3.3], **4**, are challenging targets for synthesis. These bulky materials may provide the proper solid-state structure for bulk ferromagnetic behavior.

Summary

Quantitative bulk ferromagnetic behavior has been established for the molecular/organic solid $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$. Above 16 K the dominant magnetic interactions are along a 1-D chain and, near T_c, 3-D bulk effects as evidenced by the value of the critical exponents dominate the susceptibility. The extended McConnell model was developed and provides the synthetic chemist with guidance for making new molecular materials to study cooperative magnetic coupling in systems. Assuming the electron-transfer excitation arises from the POMO, ferromagnetic coupling by the McConnell mechanism requires stable radicals (neutral, cations/anions, or ions with small diamagnetic counterions) with a non–half-filled POMO. The lowest excited state formed via virtual charge transfer (retro or forward) must also have the same spin multiplicity and mix with the ground state. These requirements limit the structure of a radical to D_{2d} or $C_{\geq 3}$ symmetry where symmetry breaking distortions do not occur. Intrinsic doubly and triply degenerate orbitals are not necessary and accidental degeneracies suffice. To achieve bulk ferromagnetism, ferromagnetic coupling must be established throughout the solid and a microscopic model has been discussed. These requirements are met by $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$. Additionally this model suggests that the Ni^{III} and Cr^{III} analogs should be antiferromagnetic and ferrimagnetic, respectively, as preliminary data suggest. Additional studies are necessary to test and further develop the consequences of these concepts.

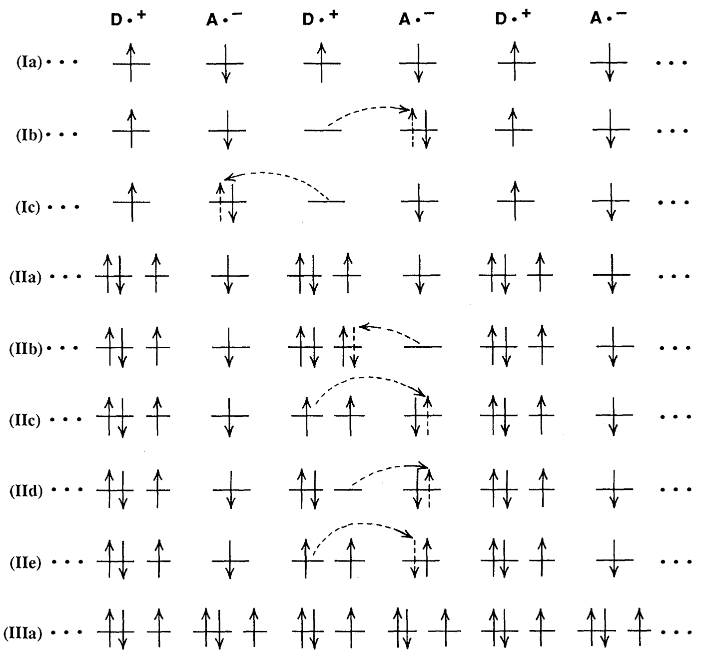


Fig. 7. Schematic illustration of stabilization of antiferromagnetic or ferromagnetic coupling. If both the D and A have a half-filled nondegenerate POMO (s^1) (Ia), then the A ← D (or D ← A) charge-transfer excited state (Ib, or equivalently Ic) stabilize antiferromagnetic coupling. If either the D or A have a non–half-filled degenerate POMO (for example, d^3, assumed here to be the D) (IIa), then the D ← A charge-transfer excited state formed (IIb) or A ← D charge-transfer excited states formed through excitation of a "spin-up" D electron (IIc or IId) will stabilize antiferromagnetic coupling. In contrast, the excited state formed through the D ← A charge transfer (IIe) stabilizes ferromagnetic coupling. Hund's rule predicts this to be the dominent excited state that admixes with the ground state. If the D (or A) has a half-filled degenerate POMO (for example, d^3) (IIIa) then the A ← D (or D ← A) charge transfer (disproportionation) excited state (IIIb) stabilizes ferromagnetic coupling.

REFERENCES AND NOTES

1. R. M. White, *Science* **229**, 11 (1985).
2. Molecular/organic solids are comprised of low molecular weight molecules or ions (including organic, organometallic, main group, polymer, or inorganic coordination complex) that do not possess extended covalent bonding in the solid state. However, separations shorter than van der Waals distances may be present in the solid. Dissolution into conventional aqueous or organic solvents should solvate the individual ions or molecules that were used to prepare the molecular solid (*3*).
3. J. S. Miller and A. J. Epstein, *J. Am. Chem. Soc.* **109**, 3850 (1987).
4. ———, *NATO Adv. Study Ser.*, in press; ———, W. M. Reiff, *Chem. Rev.*, in press; *Acc. Chem. Res.*, in press.
5. J. M. Williams *et al.*, *Acc. Chem. Res.* **18**, 261 (1985); D. Jerome and K. Bechgaard, *Contemp. Phys.* **23**, 583 (1982).
6. *Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, ed. 58, 1977), p. E120.
7. However, either an external field perpendicular or a large parallel field to the spin ordering direction will produce a moment in the antiferromagnet.
8. H. M. McConnell, *Proc. R. A. Welch Found. Chem. Res.* **11**, 144 (1967).
9. R. Breslow, *Pure Appl. Chem.* **54**, 927 (1982); ———, B. Jaun, R. Q. Klutz, C.-Z. Xia, *Tetrahedron* **38**, 863 (1982).
10. E. Dormann, M. J. Nowak, K. A. Williams, R. O. Angus, Jr., F. Wudl. *J. Am. Chem. Soc.* **109**, 2594 (1987).
11. N. Mataga, *Theor. Chim. Acta* **10**, 372 (1968); A. A. Ovchinnikov, *ibid.* **47**, 297 (1978).
12. H. M. McConnell, *J. Chem. Phys.* **39**, 1910 (1963).
13. T. P. Radhakrishnan, Z. Soos, H. Endres, L. J. Azevedo, *ibid.* **85**, 1126 (1986).
14. J. S. Miller *et al.*, *J. Am. Chem. Soc.* **109**, 769 (1987).
15. S. Chittapeddi, K. R. Cromack, J. S. Miller, A. J. Epstein, *Phys. Rev. Lett.* **58**, 2695 (1987).
16. K. Awaga, T. Sugano, M. Kinoshita, *J. Chem. Phys.* **84**, 2211 (1986); *Chem. Phys. Lett.* **141**, 540 (1987).
17. J. B. Torrance, S. Oostra, A. Nazzal, *Syn. Met.* **19**, 708 (1987).
18. Yu. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, V. N. Specktor, *Nature (London)* **326**, 370 (1987); J. S. Miller, D. T. Glatzhofer, J. C. Calabrese, A. J. Epstein, *Chem. Commun.*, in press.
19. Z. G. Zoos, *Annu. Rev. Phys. Chem.* **25**, 1 (1974).
20. G. A. Candela, L. Swartzendruber, J. S. Miller, M. J. Rice, *J. Am. Chem. Soc.* **101**, 2755 (1979).
21. J. W. Bray, L. V. Interrante, I. S. Jacobs, J. C. Bonner, *Extended Linear Chain Compounds*, J. S. Miller, Ed. (Plenum, New York, 1983), vol. 3, p. 353.
22. J. S. Miller *et al.*, *J. Phys. Chem.* **91**, 4344 (1987).
23. W. H. Morrison, Jr., S. Krugsrud, D. N. Hendrickson, *Inorg. Chem.* **12**, 1998 (1973); D. N. Hendrickson, Y. S. Sohn, H. B. Gray, *ibid.* **10**, 1559 (1971).
24. E. Stryjewski and N. Giordano, *Adv. Phys.* **26**, 487 (1977).
25. The susceptibility χ and saturation magnetization M_s 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 emuG/mol, respectively. This is in excellent agreement with the observed values of 0.00667 emu/mol and 16,300 emuG/mol for single crystals aligned parallel to the chain axis (*15*).
26. N. N. Greenwood and T. C. Gibbs, *Mössbauer Spectroscopy* (Chapman & Hall, London, 1971), p. 103.
27. J. L. Robbins, N. Edelstein, B. Spencer, J. C. Smart, *J. Am. Chem. Soc.* **104**, 1882 (1982).
28. O. W. Webster, W. Mahler, R. E. Benson, *ibid.* **84**, 3678 (1962); M. Rosenblum, R. W. Fish, C. Bennett, *ibid.* **86**, 5166 (1964); R. L. Brandon, J. H. Osipcki, A. Ottenberg, *J. Org. Chem.* **31**, 1214 (1966).
29. J. S. Miller, J. H. Zhang, W. M. Reiff, unpublished results.
30. E. Adman, M. Rosenblum, S. Sullivan, T. N. Margulis, *J. Am. Chem. Soc.* **89**, 4540 (1967); B. Foxman, private communication; B.W. Sullivan and B. Foxman, *Organometallics* **2**, 187 (1983).
31. J. S. Miller, J. H. Zhang, W. M. Reiff, *J. Am. Chem. Soc.* **109**, 4584 (1987).
32. D. M. O'Hare, J. C. Green, T. P. Chadwick, J. S. Miller, *Organometallics*, in press.
33. J. S. Miller and A. J. Epstein, unpublished results.
34. M. Ohmasa, M. Kinoshita, M. Sano, H. Akamatu, *Bull. Chem. Soc. Jpn.* **41**, 1998 (1968).
35. C. Lyon-Caen and M. Cyrot, *J. Phys. C* **8**, 2091 (1975); J. Hubbard, *Proc. R. Soc. London Ser. A* **276**, 338 (1963); *ibid.* **281**, 401 (1964).
36. K. Nasu, *Phys. Rev. B.* **33**, 330 (1986).
37. The triple degenerate cases can be found in (*3*).
38. This assumes that the virtual charge transfer involves only the highest energy POMO. Circumstances where virtual excitation from a lower lying filled (or to a high-lying filled) orbital dominate the admixing exciting state are conceivable and the orbital degeneracy and symmetry restrictions are relaxed. For example, $[Cr^{I}(C_6Me_6)_2]^{\cdot +}[TCNE]^{\cdot -}$ has an s^1/s^1 ground-state electronic configuration, and preliminary susceptibility data can be fit by the Curie-Weiss expression with

$\theta = +12$ K, suggesting dominant ferromagnetic interactions (J. S. Miller, D. M. O'Hare, A. Chackraborty, A. J. Epstein, unpublished results).
39. O. Kahn, *Angew. Chem. Int. Ed.* **24**, 834 (1985).
40. D. Gattesche, *NATO Adv. Study Ser.* in press; A. Caneschi, D. Gattesche, J. Laugier, P. Rey, *J. Am. Chem. Soc.* **109**, 2191 (1987); H. Iwamura, T. Sugawara, K. Itoh, K. Takai, *Mol. Cryst. Liq. Cryst.* **125**, 251 (1985). H. Iwarmura, *Pure Appl. Chem.* **58**, 187 (1986).
41. R. Breslow, *Mol. Cryst. Liq. Cryst.* **125**, 261 (1985); R. Breslow, P. Maslak, J. S. Thomaides, *J. Am. Chem. Soc.* **106**, 6453 (1984); T. J. LePage and R. Breslow *ibid.* **109**, 6412 (1987).
42. 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 ground state, as observed for $[\mathrm{Fe}^{\mathrm{III}}(\mathrm{C_5Me_5})_2]^{\cdot +}[\mathrm{TCNE}]^{\cdot -}$, should suffice.
43. T. Fukunaga, *J. Am. Chem. Soc.* **98**, 610 (1976); ———, M. D. Gordon, P. J. Krusic, *ibid.*, p. 611.
44. A. J. Hubert, *J. Chem. Soc. C* **1967**, 13 (1967).
45. A.J.E. and J.S.M. gratefully acknowledge partial support by the Department of Energy Division of Materials Science (grant DE-FG02-86ER45271.A000). W.M.R. gratefully acknowledges support by the NSF DMR Solid State Chemistry Program grant 8313710. We thank our co-workers (R. W. Bigelow, J. C. Calabrese, G. A. Candela, S. Chittipeddi, A. Chackraborty, K. R. Cromack, D. A. Dixon, P. J. Krusic, D. M. O'Hare, W. M. Reiff, M. J. Rice, H. Rommelmann, L. Swartzendruber, C. Vazquez, M. D. Ward, D. Wipf, and J. H. Zhang) for the important contributions they have made to this work.

Computers in Molecular Biology: Current Applications and Emerging Trends

CHARLES DELISI

The rate of generation of molecular sequence data is forcing the use of computers as a central tool in molecular biology. Current use of computers is limited largely to data management and sequence comparisons, but rapid growth in the volume of data is generating pressure for the development of high-speed analytical methods for deciphering the codes connecting nucleotide sequence with protein structure and function.

ALMOST 20 MILLION DNA NUCLEOTIDES FROM HUNDREDS of organisms have now been sequenced, and the number continues to rise nearly exponentially, with a doubling time in the range of 2 to 3 years (Fig. 1). For some of the simpler organisms such as *Escherichia coli*, the complete genome will very likely be worked out within the next few years; for humans, the sequence could be available by the turn of the century (*1*). The key to rapid progress would then change from the generation of data to its analysis, from finding the text to reading it.

The development of methods for generating this information has, however, far outstripped the development of methods that would aid in its management and speed its assimilation. As a result, we are witnessing enormous growth in data of the most fundamental and important kind in biology, while at the same time we lack the ability to assimilate these data at a rate commensurate with the potential impact they could have on science and society. Projections based on near-term trends indicate that the problem could rapidly grow worse: during the next 5 to 8 years, projects to map and sequence the human genome (*2, 3*) are expected to increase data flow to about 10^6 bases per day—nearly two orders of magnitude more than the current rate.

The management problem (collecting, organizing, standardizing, disseminating, and so forth) has been widely discussed during the past year, and it will likely be solved during the next several years, largely by scientific cooperation (*4*). The problem of analysis requires linking nucleic acid sequences to the expression, structure, and function of proteins far more rapidly than is currently possible, and will require understanding the series of codes that connect sequence with function far better than we now do. The crucial messages are embedded in the local geometry of the DNA regions that regulate the magnitude and timing of gene expression and in the linear amino acid sequence of the protein itself, which, in a given environment, determines higher order structure and therefore function.

The Computer as Catalyst

As a simple example of converging lines of research in mathematical and molecular biology, consider the implications of data generation for understanding genetic disease. Genes associated with several hundred human diseases have now been assigned to chromosomes (*5*) and often to particular regions, but precise localization has been difficult. Almost 2 years have passed since the cystic fibrosis gene—carried by approximately 1 in 20 Americans of European ancestry—was localized to within a megabase on chromosome 7, but the gene itself still has not been identified. The precise map of such regions is essential for understanding the molecular basis of disease, determining, for example, whether the defect is in the gene itself or in its regulation.

The efficiency of locating genes can be increased by developing a cohesive set of biological, engineering, and mathematical tools. These would consist of an ordered set of DNA clones to provide material for sequencing and mapping, rapid sequencing methods to provide the data for analysis, and new computational methods for the analysis itself (*3*).

The role of computation can be understood by considering the prospect of sequencing a megabase in a day—several hundredfold

---

This article was written while the author was at the Office of Health and Environmental Research, U.S. Department of Energy, Washington, DC 20545. His present address is Department of Biomathematical Sciences, Mount Sinai School of Medicine, New York, NY 10029.