

Invited Contribution from Recipient of ACS Award in the Chemistry of Materials

Organometallic- and Organic-Based Magnets: New Chemistry and New Materials for the New Millennium[†]

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Organometallic- and organic-based materials exhibiting the technologically important property of bulk magnetism have been designed, prepared, and studied. These magnets are prepared via conventional organic chemistry methodologies and unlike conventional inorganic-based magnets do not require metallurgical processing. Furthermore, these magnets are frequently soluble in conventional solvents, and examples have saturation magnetizations exceeding that of iron metal on an Fe or mole basis. Also, magnets with critical temperatures exceeding room temperature, magnets with coercive fields exceeding that of Co₅Sm, and thin-film magnets have been prepared. This article highlights the collective joint research executed in our, as well as Arthur J. Epstein's, laboratories.

Introduction

Magnets have tantalized the imagination for millennia, and for the past century they have been essential for the transformation of our society into the high-technology one of today. The initial curiosity of one type of rock, lodestone, to attract like rocks evolved into a plethora of myths and pseudoscience,¹ as well as into a kingpin in the continuing evolution of science.^{2,3a,4} Man's fascination with magnets has been documented for over two and one-half millennia,⁵ although evidence for earlier discoveries in China exists.⁶ The Western world's naming of the magnet is unclear because two plausible contemporary attributes are recorded: (1) Pliny the Elder's account that the Shepherd Magnes noted that *Magnes Lapis*, now called magnetite or lodestone (Fe₃O₄), adhered to the nails in his shoes and (2) Lucretius' account that *Magnes Lapis* was quarried in

the now Grecian region of Magnesia that was inhabited by Magnes.^{3b} Personally, I suspect that the magic of magnets, i.e., the easily observable, relatively strong force that either attracts or repels like, was first noticed by cave children playing in front of their abode, but as is the case for all discoveries in science, it needed to be recorded for time immemorial, preferably in a peer-reviewed journal, but an unsigned cave drawing would have been more than adequate.

The study of magnets benefited enormously from attracting the attention of the first experimentalist, Petrus Peregrinus de Maricourt.^{3b} Petrus de Maricourt identified that magnets had two poles, labeled by him as north and south, and that opposite poles attracted, as is universally known today. He also noted that breaking a magnet leads to two magnets, not its destruction. It is essential to note that these discoveries were documented in his *Epistola de Magnete* in 1269. Petrus de Maricourt provided a long-lasting service to all society by setting an important example of how the scientific method leads to new knowledge and technology. The study of magnets, and science in general, received an enormous boost when Queen Elizabeth I's physician, William Gilbert, Galileo's choice as the first experimentalist, devoted an enormous effort to scientifically reviewing the growing trove of myths and superstitions. He debunked all except the facts that stood up to the test of scientific scrutiny.² Gilbert also made an unprecedented revelation by deducing that the earth itself was a magnet and prepared the first man-made magnet, iron metal.¹ In so doing, he associated solid-state chemical syntheses as being literally "heat and beat" (Figure 1). Gilbert noted that upon heating iron lost its strong

[†] This paper is largely based on the address for the 2000 ACS Award in Chemistry of Materials presented as INOR 323 at the 219th National Meeting of the American Chemical Society, San Francisco, CA, March 27, 2000.

- (1) Sadly, myths and pseudoscience in the area of magnetism continue to plague society today.
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- (3) (a) Verschuur, G. L. *Hidden Attraction: The History and Mystery of Magnetism*; Oxford University Press: Oxford, UK, 1993. (b) Chapter 1.
- (4) Livingston, J. D. *Driving Force: The Natural Magic of Magnets*; Harvard University Press: Cambridge, MA, 1996.
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- (6) Morrish, A. H. *The Physical Principles of Magnetism*; John Wiley & Sons: New York, 1980; p 1.



Joel S. Miller received his Bachelor of Science in Chemistry from Wayne State University (1967) in his native Detroit, MI doing undergraduate research with Stanley Kirschner, and he received his Ph.D. from UCLA (1971) with Alan L. Balch. After a postdoctoral fellowship at Stanford University with Eugene E. van Tamelen he joined the Xerox Webster Research Center in 1972 and later joined the late Occidental Research Corporation. He was a Visiting Professor of Chemistry at the University of California, Irvine, CA. He joined the Central Research & Development Department at the Du Pont Company in 1983 where he was a Research Supervisor for solid-state science. He has been a Visiting Scientist at the Weizmann Institute (1985) and a Visiting Professor of Chemistry at the University of Pennsylvania (1988). He joined the faculty of the Department of Chemistry at the University of Utah in 1993. He is on the advisory board of *Advanced Materials* and *Journal of Materials Chemistry* and is a member of the Inorganic Synthesis Corporation. His research interests focus on the solid-state magnetic, electrical, and optical properties of molecular (organic, organometallic, and inorganic coordination) compounds and electron-transfer complexes as well as the surface modification of solids. Currently he is actively involved in synthesis and characterization of molecular/organic based ferromagnets. In addition to three patents he has edited 11 monographs and published over 350 papers in these and other areas and was a recipient of the 1996 Pinguin Foundation's Wilhelm Manchot Research Professorship at the Technische Universität Munich, Wayne State University's 1998 Distinguished Alumni Award, and the 2000 American Chemical Society Award for *Chemistry of Materials*.

magnetic behavior, which returned on cooling. Most importantly, Gilbert documented his observations for generations to appreciate and to provide a foundation for the future in his treatise entitled "de Magnete" in 1600.² With the solid base of discarded superstitions as well as being armed with facts, the study of magnetism was poised to lead a scientific assault that led to an explosive growth in man's understanding and exploitation of nature. In 1819, Hans Christian Ørsted discovered that electricity affects magnets,^{7a} and in 1821 Michael Faraday invented the electromagnet.^{7b} Magnets were subsequently essential to the introduction of low-cost ac electricity by Westinghouse in Buffalo, NY in 1886.⁸ The fundamental aspects of magnetism, nonetheless, continued to be elusive until quantum mechanics led to the revelation that the key ingredient of magnetic behavior is the electron spin.⁹



Figure 1. Illustration of an early solid-state chemist honing the "heat and beat" method to prepare magnetized iron. The iron rods are aligned north/south (septentrio/avster). Adapted from ref 2, p 212.

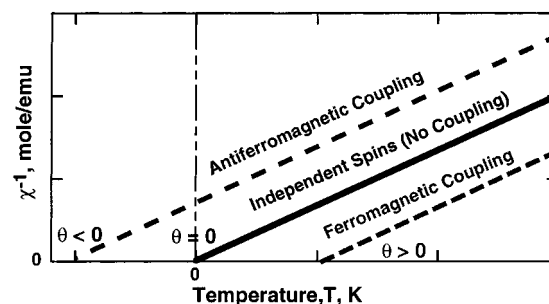


Figure 2. Schematic illustration of the temperature dependence of $\chi^{-1}(T)$ obeying the Curie–Weiss expression at high temperature. The high-temperature linear curve is extrapolated to ~ 0 K, and the intercept θ indicated ferromagnetic coupling ($\theta > 0$) or antiferromagnetic coupling ($\theta < 0$).

The number, proximity, and coupling among electron spins dictate all magnetic behaviors. The magnetic susceptibility (χ) of isolated spins obey the Curie law, $\chi = C/T$, where the Curie constant C is $Ng^2\mu_B^2S(S+1)/(3k_B)$ with N = Avogadro's number, g = Landé g value, μ_B = Bohr magneton, S = spin quantum number ($1/2, 1, \dots$), and k_B = Boltzmann's constant.^{10a} When spins get closer together, most frequently they interact such that the spins oppose each other and lead to a reduced value of the susceptibility with respect to that expected from the sum of the independent spins. This is termed antiferromagnetic coupling. Albeit relatively rare, ferromagnetic coupling, where spin alignment enhances the susceptibility with respect to that expected from the sum of the independent spins, can also occur. Both ferromagnetic and antiferromagnetic coupling can be modeled by the Curie–Weiss law, $\chi = C/(T - \theta)$, where θ is determined from the intercept of the extrapolated slope of the higher temperature $\chi^{-1}(T)$ data with the temperature axis (Figure 2). Positive values of θ indicate ferromagnetic coupling, negative values indicate antiferromagnetic coupling, and $|\theta|$ indicates the magnitude of the coupling.^{10b}

The study and use of magnetically ordered materials has been ongoing for over 2600 years with man-made magnets appearing 400 years ago as noted above. More recently, man-made

(7) (a) Hellemans, A.; Bunch, B. *The Timetables of Science*; Simon and Schuster: New York, 1988; p267. (b) p 281.

(8) Wood, R. *Understanding Magnetism*; TAB Books, Inc.: Blue Ridge Summit, PA, 1988; p 51.

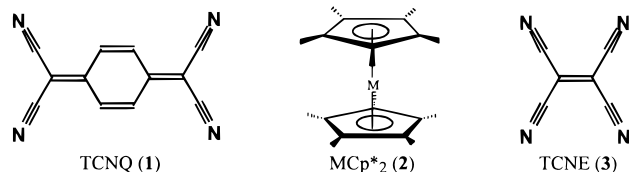
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magnets have evolved from those with electron spins residing on metal sites in d orbitals to those with electron spins residing on metal sites in f orbitals. However, all of these magnets were prepared by high-temperature metallurgical methods, and today improved man-made magnets continue to be an active research area.¹¹

[Metallocene][TCNE]-Based Magnets

The quest to make a magnet with electron spins residing on nonmetal sites in p orbitals evolved from the revelation that metal-like dc electrical conductivity could be achieved in some organic materials possessing segregated chains of reduced TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane, **1**). Stud-



ies of one phase of [Fe^{III}Cp*₂][TCNQ] (Cp* = pentamethylcyclopentadienide) led to the characterization that this material was a metamagnet; i.e., it had an antiferromagnetic ground state, which above a critical field of 1500 Oe had a transition to a high-moment ferromagnetic-like state.¹² [Fe^{III}Cp*₂][TCNQ] was structurally characterized to have parallel linear (1-D) chains comprised of alternating [Fe^{III}Cp*₂]⁺ (2⁺) cations and [TCNQ]⁻ anions, with each ion having an unpaired electron spin.^{12b}

The rare observation of magnetic ordering, albeit to an antiferromagnet state, which had a low-lying ferromagnetic-like state, led to the development of ideas for the stabilization of the ferromagnetic ground state. Noting that magnetic ordering requires spin coupling in the bulk, the use of a smaller radical anion acceptor with respect to [TCNQ]⁻, e.g., [TCNE]⁻; tetracyanoethylene, **3**, with the same amount of spin but delocalized over fewer atoms would have a greater spin density and being smaller should lead to enhanced spin coupling and stabilization of the ferromagnetic with respect to the antiferromagnetic ground state. Hence, [Fe^{III}Cp*₂][TCNE]⁻ was targeted and ultimately prepared.¹³ It should be noted that [FeCp₂][TCNE] (Cp = cyclopentadienide) was known at the time, but TCNE is insufficient to oxidize Fe^{II}Cp₂, and consequently, [FeCp₂][TCNE] is a diamagnetic donor/acceptor complex.¹⁴

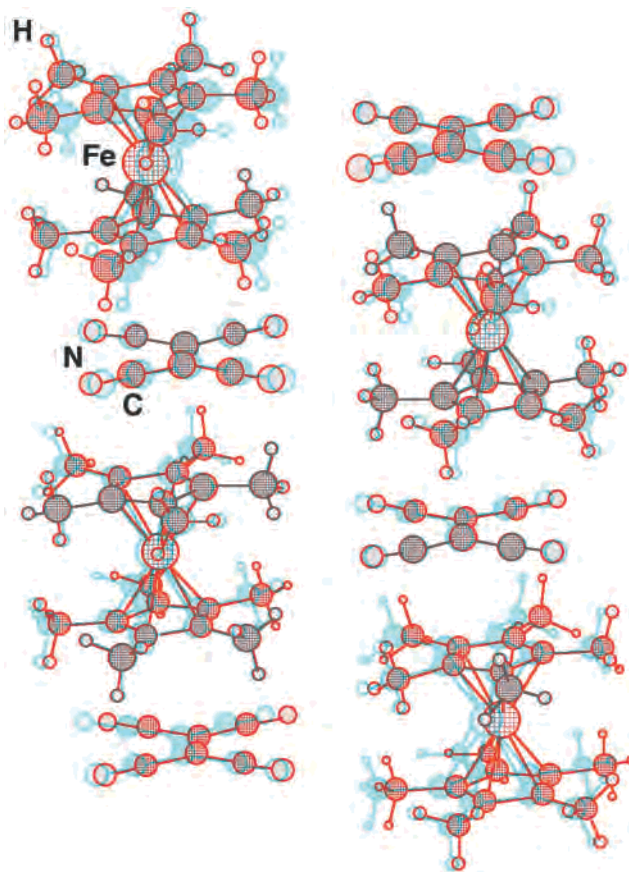


Figure 3. Segment of a single 1-D chain of [Fe^{III}Cp*₂]⁺[TCNE]⁻·MeCN (red = Fe, blue = N, white = H, and gray = C).

The [Fe^{III}Cp*₂]⁺[TCNE]⁻ electron-transfer salt was prepared and structurally characterized as the acetonitrile solvate to have the targeted structure of parallel 1-D chains of alternating [Fe^{III}Cp*₂]⁺ cations and [TCNE]⁻ anions^{13b} (Figure 3). The temperature dependence of the susceptibility, $\chi(T)$, for [Fe^{III}Cp*₂]⁺[TCNE]⁻ above 150 K can be fit to the aforementioned Curie–Weiss expression with a substantial positive θ value of 30 K indicating relatively strong ferromagnetic coupling. Inorganic coordination or organometallic complexes with positive θ values are scarce, and those with double-digit values are exceptionally rare, if they even exist. The necessity for spins to exist on both the cation and anion to stabilize ferromagnetic coupling was confirmed by removing the spin from the cation via the synthesis of isomorphous [Co^{III}Cp*₂]⁺[TCNE]⁻ with diamagnetic [Co^{III}Cp*₂]⁺ and removing the spin from the anion via the synthesis of similarly structured [Fe^{III}Cp*₂]⁺[C₃(CN)₅]⁻ with diamagnetic [C₃(CN)₅]⁻. These compounds have θ values of -1.0 and -1.2 K, respectively, typical of inorganic coordination or organometallic complexes.¹⁵

The magnetic data^{15a} for [Fe^{III}Cp*₂]⁺[TCNE]⁻, however, deviate from Curie–Weiss behavior at low temperature, and the compound undergoes a magnetic phase transition to a

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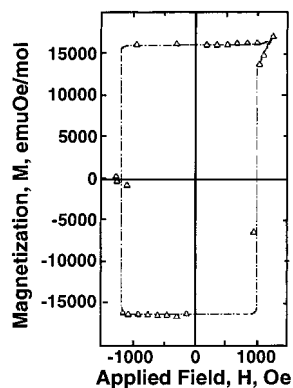


Figure 4. Magnetization M as a function of applied field H for $[\text{Fe}^{\text{III}}\text{Cp}^*_2]^+[\text{TCNE}]^-$ showing a hysteresis loop at 2 K.

magnetically ordered state at 4.8 K (T_c) and exhibits hysteretic behavior (Figure 4) characteristic of magnetic ordering. The 1000 Oe coercive field for $[\text{Fe}^{\text{III}}\text{Cp}^*_2]^+[\text{TCNE}]^-$ at 2 K (Figure 4) exceeds the values for conventional magnets used for magnetic storage, suggesting that these materials might be suitable for magnetic data storage should T_c be raised above room temperature. The highest magnetization attainable for single crystals aligned along the chain axis of $[\text{Fe}^{\text{III}}\text{Cp}^*_2]^+[\text{TCNE}]^-$ in an applied magnetic field is 16 300 emu Oe/mol.^{13c} Assuming g_{\parallel} of 4, the expectation for antiferromagnetic spin alignment, i.e., the spin on Fe(III) opposed the spin on the $[\text{TCNE}]^-$, is 5585 emu Oe/mol, while that expected for ferromagnetic spin alignment, i.e., the spin on Fe(III) is aligned with the spin on the $[\text{TCNE}]^-$, is 16 755 emu Oe/mol. Hence, $[\text{Fe}^{\text{III}}\text{Cp}^*_2]^+[\text{TCNE}]^-$ orders as a ferromagnet, and its magnetization exceeds that of iron metal by 37% on a per mole or per iron basis, but, of course, owing to the high density of iron, not on a volume or gram basis. The ferromagnetic ordering was confirmed by the results from powder neutron diffraction studies.¹⁵ Above T_c the 23 K powder neutron diffraction shows several reflections due to the Bragg structure, whereas below T_c the 1.5 K data show additional intensity in the same reflections that is attributed to it possessing a ferromagnetic magnetic structure.

Single-crystal polarized neutron diffraction studies¹⁸ of $[\text{N}(n\text{-Bu})_4][\text{TCNE}]^-$ show that the spin density of $[\text{TCNE}]^-$ is delocalized over all atoms and that 33% resides on each sp^2 C, 13% on each N, and -5% on each sp C (Figure 5).

Thus, $[\text{FeCp}^*_2]^+[\text{TCNE}]^-$ orders as a bulk 3-D ferromagnet at 4.8 K and is sufficiently strongly magnetic that at low temperature a pellet of it can be attracted to a strong magnet^{15a} (Figure 6). $[\text{FeCp}^*_2]^+[\text{TCNE}]^-$ is (a) the first magnet that relies on a spin residing in a p orbital, albeit delocalized over several p-based orbitals, and (2) the first soluble magnet as it lacks extended network bonding (zero dimensional) (i.e., is comprised of isolated ions) and is more ionic than NaCl and exhibits hysteresis.

Replacement of Fe(III) with Mn(III)¹⁹ and Cr(III)²⁰ in either the $[\text{TCNE}]^-$ or $[\text{TCNQ}]^-$ salt leads to ferromagnets with the

(16) These red/cyan stereoviews require glasses with red/cyan or red/green lens, using the red lens over the left eye. These glasses can be acquired at <http://stereocopy.com/3d-images/glasses.html> or <http://www.stereocopy.com/reel3d/anaglyph-glasses.html> or made, http://www.chem.utah.edu/chemistry/faculty/miller/3d_glasses.pdf.

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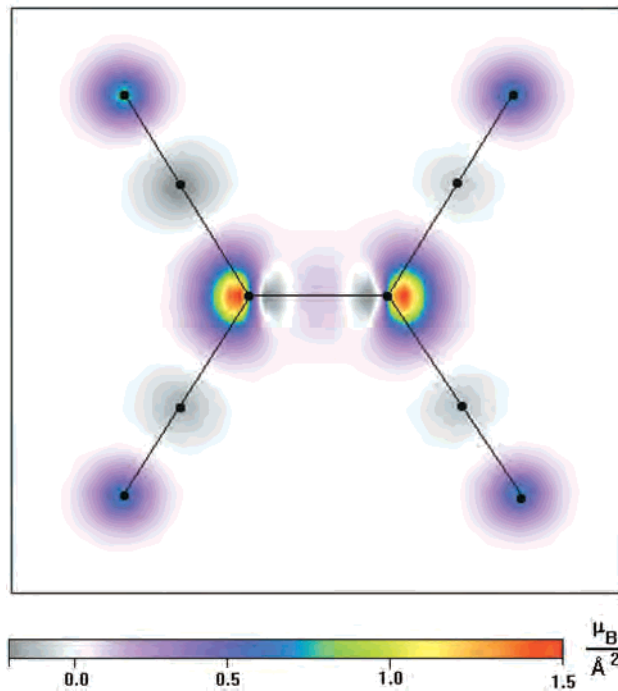


Figure 5. Experimental spin density on $[\text{TCNE}]^-$ in $[\text{N}(n\text{-Bu})_4]^+[\text{TCNE}]^-$.¹⁸

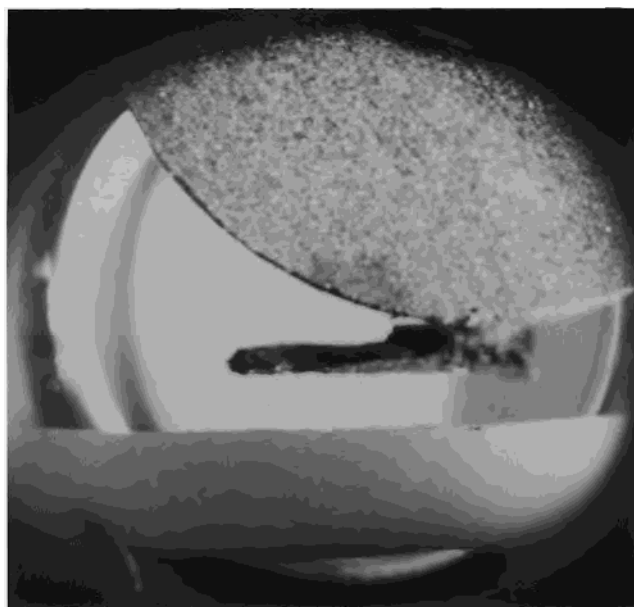


Figure 6. Photograph of a compacted powder sample of $[\text{FeCp}^*_2]^+[\text{TCNE}]^-$ being attracted to a Co_5Sm magnet at low temperature in a liquid helium Dewar. As the Dewar warms, the sample becomes less magnetic and drops away from the Co_5Sm magnet. Upon cooling again, it is again attracted to the Co_5Sm magnet. (Photo due to the efforts of J. V Caspar and R. S. McLean.) Reproduced with permission from ref 15a. Copyright 1994 Wiley-VCH.

T_c 's of the $[\text{TCNE}]^-$ salts exceeding those of the $[\text{TCNQ}]^-$ salts. Additionally, the T_c 's decrease as $\text{Mn} > \text{Fe} > \text{Cr}$ for $[\text{M}^{\text{III}}\text{Cp}^*_2]^+[\text{TCNE}]^-$,^{15,19-21} which deviates from the expectation that $T_c \propto S(S+1)$ (i.e., $\text{Cr} > \text{Mn} > \text{Fe}$). These trends are depicted in Figure 7.

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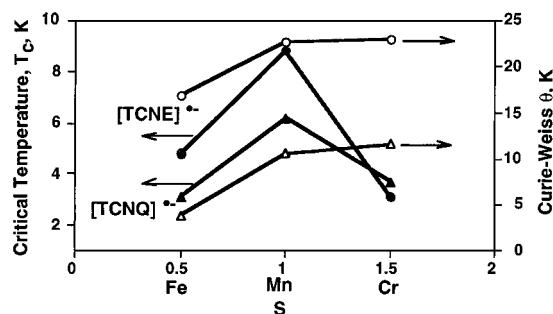
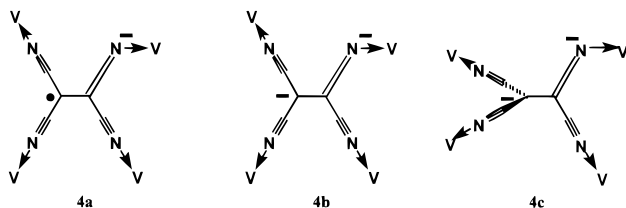


Figure 7. Dependence of T_c (left) and θ (right) as a function of M for both the TCNE and TCNE electron-transfer salts of $[M^{III}Cp^*_2][TCNZ]$ ($Z = E, Q$) composition.

$M[TCNE]_x$ -Based Magnets

The electron-transfer salt with the highest T_c is $[Mn^{III}Cp^*_2]^+ [TCNE]^{2-}$,^{19a} and because $V^0(C_6H_6)_2$ is isoelectronic with $Mn^{II}Cp^*_2$, the reaction of $V^0(C_6H_6)_2$ with TCNE was targeted to lead to the formation of a magnet of $[V^I(C_6H_6)_2]^+ [TCNE]^{2-}$ composition.^{22,23} The reaction of $V^0(C_6H_6)_2$ and TCNE, however, leads to many surprises. First, unlike $[M^{III}Cp^*_2]^+ [TCNZ]^{2-}$ ($M = Cr, Mn, Fe, Co; Z = E, Q$), which forms soluble crystals, a black insoluble amorphous precipitate forms, which is secondly pyrophoric. Third, the ν_{CH} vibration in $V^0(C_6H_6)_2$ disappears in the product. Fourth, the black precipitate can be separated from the solution via a stirring bar (Figure 8) because the precipitate is a strong magnet at room temperature.

$V[TCNE]_x \cdot yS$ ($S =$ solvent) is proposed to be composed of $[TCNE]^{2-}$'s being bound to *up to* four V 's most likely linearly, although some may be bent and each $[TCNE]^{2-}$ is planar (e.g., 4a). Because of the expected hexacoordination of $V(II)$, on



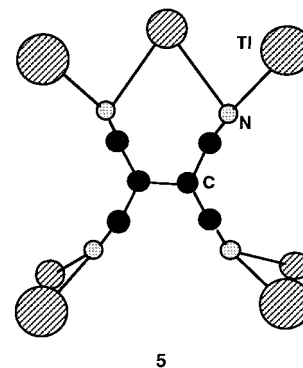
average each $[TCNE]^{2-}$ binds to three $V(II)$'s, although the occupancy of some coordination sites with S will lead to a reduction of this average number, as will the fast precipitation of the magnet leaving some sites vacant. Additionally, because

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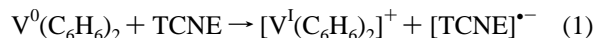
Figure 8. Photograph of a Teflon-coated stir bar magnet separating the room-temperature $V[TCNE]_x \cdot yCH_2Cl_2$ magnet after preparation.

of the presence of some $[TCNE]^{2-}$ (vide infra), which because of free rotation about the central C–C bond, it may be planar (e.g., 4b) or more likely twisted (e.g., 4c) as structurally observed for isolated $[TCNE]^{2-}$ ²⁴ and μ - $[TCNE]^{2-}$.²⁵ The $V \cdots TCNE$ linkages are proposed to be present in differing proportions in the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet. Chelating $[TCNE]^{2-}$, as observed for $Tl^I[TCNE]$ (5), is attributed to the



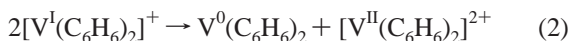
larger cation radius, higher coordination number, and more complex electrostatic bonding and is unexpected.²⁶

The mechanism of formation of the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet from the reaction of $V^0(C_6H_6)_2$ and TCNE was studied.²⁷ Electron transfer,

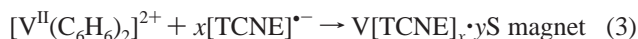


was anticipated to initially occur, forming $[V^I(C_6H_6)_2]^+$ and $[TCNE]^{2-}$. Because the disproportionation of $[V^I(C_6H_6)_2]^+$ in the presence of nucleophiles, such as $[TCNE]^{2-}$, was reported,²⁸ the reaction

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- (25) Yee, G. T.; Calabrese, J. C.; Vazquez, C.; Miller, J. S. *Inorg. Chem.* **1993**, 32, 377.
- (26) Johnson, M. J.; Campana, C.; Foxman, B. M.; Desmarais, W.; Vela, M. J.; Miller, J. S. *Eur. J. Chem.* **2000**, 6, 1805.
- (27) Gordon, D. C.; Deakin, L.; Arif, A. M.; Miller, J. S. *J. Am. Chem. Soc.* **2000**, 122, 290.
- (28) (a) Avilés, T.; Teuben, J. H. *J. Organomet. Chem.* **1983**, 253, 39. (b) Calderazzo, F.; De Benedetto, G. E.; Pampaloni, G.; Mössner, C. M.; Strähle, J.; Wurst, K. *J. Organomet. Chem.* **1993**, 451, 73.



was expected to occur to form $[V^{II}(C_6H_6)_2]^{2+}$ and to generate additional $V^0(C_6H_6)_2$. $[V^{II}(C_6H_6)_2]^{2+}$ could then react with $[TCNE]^{*-}$ to form the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet,



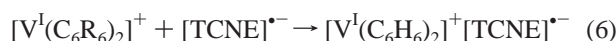
or with the solvent, S, to form solvated V(II),



which could react with $[TCNE]^{*-}$ to form the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet,

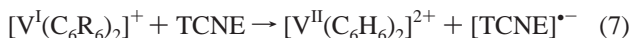


Alkyl substitution of C_6H_6 should facilitate the oxidation of the V^0 complex without significantly affecting the mechanism. However, the reaction of the sterically more encumbering $V^0[1,3,5-C_6H_3(t-Bu)_3]_2$ and TCNE unexpectedly led to the formation of $[V^I 1,3,5-C_6H_3(t-Bu)_3]^+[TCNE]^{*-}$,

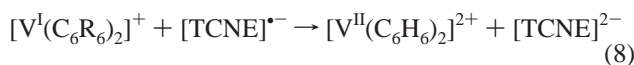


which is not a magnet. $[V^I 1,3,5-C_6H_3(t-Bu)_3]^+[TCNE]^{*-}$ was structurally and magnetically characterized. It can be fit to the Curie–Weiss law above 2 K and hence is not magnetically interesting except to demonstrate that eq 2 is mechanistically unimportant because of the longevity and stability of $[V^I(C_6H_6)_2]^+$.²⁷

Instead of $[V^I(C_6H_3R_3)_2]^+$ disproportionating, it could react with TCNE to form $[V^{II}(C_6H_3R_3)_2]^{2+}$ and an additional $[TCNE]^{*-}$,



or with $[TCNE]^{*-}$ to form $[TCNE]^{2-}$,



Equation 8, however, has to be ruled out on the basis of electrochemical potentials. Hence, the key intermediate $[V^{II}(C_6H_3R_3)_2]^{2+}$ has yet to be isolated but reacts with $[TCNE]^{*-}$ to form the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet (eq 3) or with the solvent S to form solvated V(II) (eq 4), which reacts with $[TCNE]^{*-}$ to form the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet (eq 5). The overall mechanism is described by Scheme 1.

Formation of the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet is easily accomplished; however, the preparation of $V^0(C_6H_6)_2$ is tedious.²² Additionally, the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet is a material; thus, the properties depend on the synthetic route and alternative routes may lead to materials with different and ideally enhanced magnetic properties. Hence, alternative V precursors of the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet were sought and several were tried.²⁹ Among several V precursors that when reacted with TCNE led to magnets, $V^0(CO)_6$ was studied in the greatest detail:



From infrared and Toefler pump studies, the CO content, z, was determined to be zero; hence, the magnet prepared from

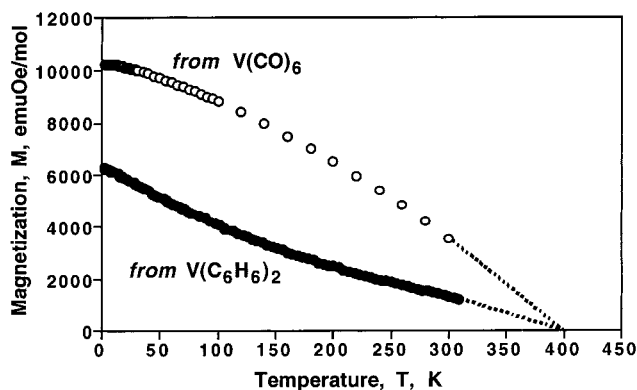
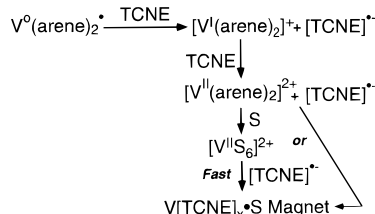


Figure 9. Temperature dependence of the magnetization for the $V[TCNE]_x \cdot yCH_2Cl_2$ magnet prepared from $V^0(CO)_6$ (○) and $V^0(C_6H_6)_2$ (●).

Scheme 1



$V^0(CO)_6$ was nominally the same composition as that prepared from $V^0(C_6H_6)_2$.

Temperature-dependent magnetization, $M(T)$, studies show that the extrapolation of $M(T)$ to $M(T) = 0$ leads to an estimate of $T_c \approx 400$ K, as do magnets prepared from $V^0(C_6H_6)_2$. However, the shape of $M(T)$ differs for magnets prepared from $V(CO)_6$ and $V^0(C_6H_6)_2$ such that M at 4 K and at room temperature are $\sim 133\%$ and $\sim 233\%$ as great for magnets made from $V^0(CO)_6$ with respect to $V^0(C_6H_6)_2$ (Figure 9). Thus, in addition to being easier to prepare, because $V^0(CO)_6$ is easier to make from commercially available precursors than $V^0(C_6H_6)_2$, magnets made from $V^0(CO)_6$ have enhanced magnetic properties with respect to those made from $V^0(C_6H_6)_2$.²⁹

Establishment that $V[TCNE]_x \cdot yCH_2Cl_2$ was one member of a general family of magnets of $M[TCNE]_x \cdot yS$ composition was achieved with the development of new chemistry.³⁰ The reaction of $MI_2 \cdot xMeCN$ ($M = Mn, Fe, Ni, Co$) with TCNE, preferably in dichloromethane, led to $M[TCNE]_2 \cdot yS$ magnets. Each of these materials, like $M = V$ but unlike $M = Cr$ (vide supra), magnetically ordered nominally as a ferrimagnet. The T_c 's ranged from 44 to 100 K. Unfortunately, $M[TCNE]_2 \cdot yS$ represents a family of magnets whose structures are unknown. Replacement of TCNE with TCNQ for $M = Mn$, etc. also leads to magnetically ordered materials,³¹ but as noted for the $[MCP^*]_2[TCNZ]$ ($Z = E, Q$), the family the TCNQ salts^{15a} have reduced T_c 's with respect to the TCNE salts.³¹

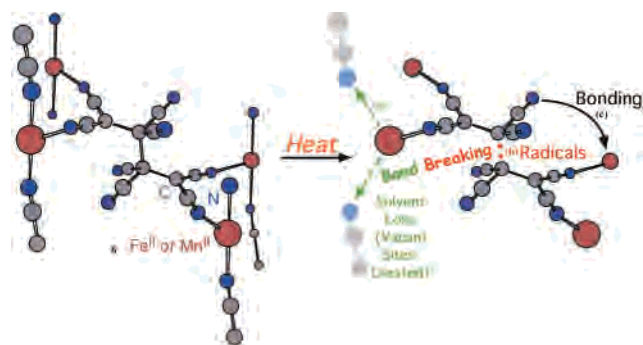
For the study of the family of $M[TCNE]_2 \cdot yS$ magnets, crystals of a nonmagnetically ordered paramagnetic material were isolated for $M = Mn$ and Fe. The single-crystal X-ray structure determination revealed that they possessed the $M[TCNE]_2 \cdot$

(30) Zhang, J.; Ensling, J.; Ksenofontov, V.; Gütllich, P.; Epstein, A. J.; Miller, J. S. *Angew. Chem., Int. Ed.* **1998**, *37*, 657.

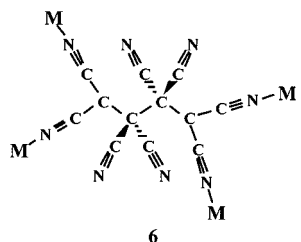
(31) Cowan, J.; Clérac, R.; Heintz, R. A.; O'Kane, S.; Ouyang, X.; Zhao, H.; Dunbar, K. R. *Mol. Cryst. Liq. Cryst.* **1999**, *335*, 113. Zhao, H.; Heintz, R. A.; Ouyang, X.; Grandinetti, G.; Cowan, J.; Dunbar, K. R. In *NATO ARW Supramolecular Engineering of Synthetic Metallic Materials: Conductors and Magnets*; Veciana, J., Rovira, C., Amabilino, D., Eds.; Springer: Berlin, 1998; Vol. C518, p 353.

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Scheme 2



2MeCN·S (M = Mn, Fe) stoichiometry, with each M being hexacoordinate with two *trans* MeCNs and a μ_4 -octacyanobutane diide dianion, $[\text{C}_4(\text{CN})_8]^{2-}$, **6**, bound to four M^{II} s. The



central C–C bond of the ligand is long 1.59(2) Å (M = Mn) and 1.627(14) Å (M = Fe), suggesting that it is a weak bond.^{32,33} Heating $\text{M}[\text{C}_4(\text{CN})_8] \cdot 2\text{MeCN} \cdot \text{S}$ leads to the formation of a magnetically ordered material. As noted in Scheme 2, this is attributed to (a) loss of MeCN solvent opening up two coordination sites per M, (b) breakage of the weak central C–C bond forming two *cis- μ -[TCNE] $^{\bullet-}$* s, and (c) having on average one N per *cis- μ -[TCNE] $^{\bullet-}$* bond to another M. These three steps with expected further rearrangements lead to the formation of the magnet.

Scheme 2 suggests that the elusive $\text{Cr}[\text{TCNE}]_x \cdot y\text{S}$ may be accessible via reaction of $[\text{Cr}^{\text{II}}(\text{C}_6\text{H}_3\text{R}_3)_2]^{2+}$ and TCNE. Previously, the reaction of $\text{Cr}^0(\text{C}_6\text{H}_3\text{R}_3)_2$ and TCNE led only to stable electron-transfer salts of $[\text{Cr}^{\text{I}}(\text{C}_6\text{H}_3\text{R}_3)_2]^+[\text{TCNE}]^-$ composition.³⁴ Since $[\text{Cr}^{\text{I}}(\text{C}_6\text{H}_3\text{R}_3)_2]^+$ is more stable and harder to oxidize than $[\text{V}^{\text{I}}(\text{C}_6\text{H}_3\text{R}_3)_2]^+$, routes to electron-poor analogues with more labile ligands were sought and Cr^0Np_2 (Np = naphthalene) was identified and reacted with TCNE.²⁷ Cr^0Np_2 can be readily oxidized to the dication $[E_{1/2}^{+/0} = -1.19; E_{1/2}^{2+/+} = +0.20 \text{ V (vs Ag/AgNO}_3; \text{THF)}]$,³⁵ and the Np ligand is more labile than benzene-based arene ligands.³⁶ Furthermore, these potentials render the production of either $[\text{TCNE}]^{2-}$ or Cr^{III} unlikely. As expected, black $\text{Cr}[\text{TCNE}]_x \cdot y\text{S}$ immediately formed, and in addition to supporting the proposed mechanism (Scheme

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- (33) Similar results are observed for σ -[TCNQ] $_2^{2-}$ dimers. Hoffman, S. K.; Corvan, P. J.; Singh, P.; Sethukleshmi, C. N.; Metzger, R. M.; Hatfield, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4608. Harms, R. H.; Keller, H. J.; Nöthe, D.; Werner, M.; Grundel, D.; Sixl, H.; Soos, Z. G.; Metzger, R. M. *Mol. Cryst. Liq. Cryst.* **1981**, *65*, 179. Zhao, H.; Heinz, R. A.; Dunbar, K. R.; Rogers, R. D. *J. Am. Chem. Soc.* **1996**, *118*, 12844. Mikami, S.; Sugiura, K.-i.; Miller, J. S.; Y. Sakata, Y. *Chem. Lett.* **1999**, 41.
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- (35) Bush, B. F.; Lagowski, J. J. *J. Organomet. Chem.* **1990**, 386, 37.
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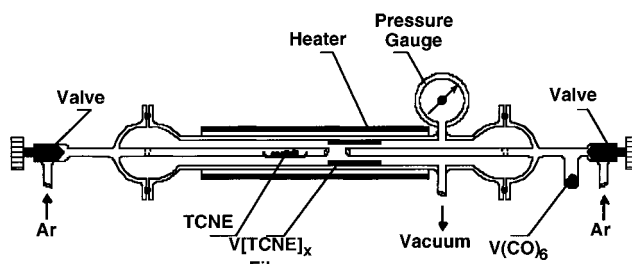


Figure 10. Schematic illustration of the CVD apparatus used to prepare thin films of the $\text{V}[\text{TCNE}]_x$ magnet from the gas-phase reaction of $\text{V}^0(\text{CO})_6$ and TCNE. Reproduced with permission from ref 37. Copyright 2000 Wiley-VCH.

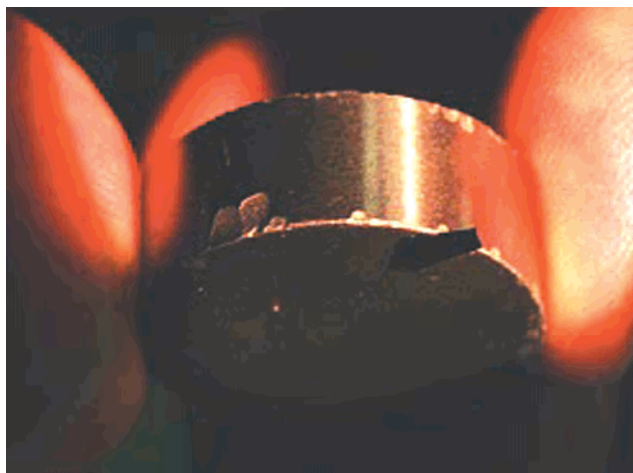


Figure 11. Photograph of ca. 5 μm coating of the $\text{V}[\text{TCNE}]_x$ magnet on a glass cover slide being attracted to a Co_5Sm magnet at room temperature in the air. Reproduced with permission from ref 37. Copyright 2000 Wiley-VCH.

1), $\text{Cr}[\text{TCNE}]_x \cdot y\text{PhMe}$ was available for study. Surprisingly, $\text{Cr}[\text{TCNE}]_x \cdot y\text{PhMe}$ does not magnetically order above 2 K.²⁷

Solvent-free thin films of the $\text{V}[\text{TCNE}]_x$ magnet have been recently prepared via the low-temperature chemical vapor deposition (CVD) of $\text{V}^0(\text{CO})_6$ and TCNE³⁷ in the apparatus depicted in Figure 10. The films are typically 1–5 μm in thickness and can be prepared at 40 °C on a myriad of rigid and/or flexible substrates including glass, quartz, mica, Teflon, NaCl, CsI, gold, silver, aluminum, Si wafers, and amorphous carbon. These films are sufficiently magnetic at room temperature that they are attracted to a magnet (Figures 11 and 12). In contrast to solvent-prepared $\text{V}[\text{TCNE}]_x \cdot y\text{S}$ bulk samples, which decompose at the diffusion rate of oxygen, sometimes pyrophorically, these $\text{V}[\text{TCNE}]_x$ films are relatively air-stable and can be handled in the air (Figure 11). The availability of these thin films enables the determination of the oxidation state of vanadium by X-ray photoelectron spectroscopy (XPS). Peaks characteristic of V(II) are observed at 514.0 and 521.5 eV.³⁷ Hence, the magnet is best formulated as $\text{V}^{\text{II}}\{[\text{TCNE}]^{\bullet-}\}_x \cdot \{[\text{TCNE}]^{2-}\}_{1-x/2}$ or $\text{V}_{1-y}^{\text{II}}\text{V}_y^{\text{III}}\{[\text{TCNE}]^{\bullet-}\}_{x-y}\{[\text{TCNE}]^{2-}\}_{1-x/2+y}$ for $x < 2$, as experimentally observed, and is consistent with the ν_{CN} IR data showing that $[\text{TCNE}]^{\bullet-}$ (**4a,b**) and $[\text{TCNE}]^{2-}$ (**4c**) are present.

As T_c exceeds room temperature, commercial applications for this magnet can be envisioned.³⁸ One application is for magnetic shielding, the attenuation of magnetic fields found in many electronic applications, e.g., high-voltage lines. The

- (37) Pokhodnya, K. I.; Epstein, A. J.; Miller, J. S. *Adv. Mater.* **2000**, *12*, 410.

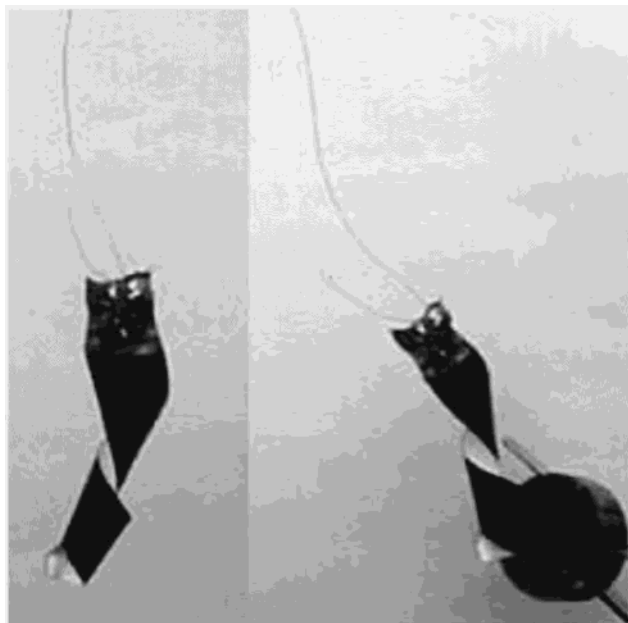
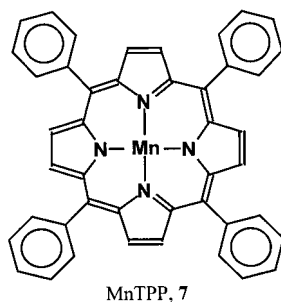


Figure 12. Photograph of a thin coating of the $V[TCNE]_x$ magnet on Teflon tape (a) being attracted to a Co_5Sm magnet at room temperature (b).

feasibility of using $V(TCNE)_x \cdot y(CH_2Cl_2)$ for this applications has been demonstrated³⁹ (Figure 13).⁴⁰

[Mn(porphyrin)][TCNE]-Based Magnets

TCNE forms yet another class of magnets exemplified by $[Mn^{III}TPP]^+[TCNE]^{*-}$ ($H_2TPP = meso$ -tetraphenylporphyrin), which forms a coordination polymer (1-D) that was characterized as a ferrimagnet with a 13 K T_c .^{23,41} Unlike the $[M^{III}Cp^*_2][TCNE]$ and $M[TCNE]_x$ families of magnets, modification of the substituent groups on the cation leads to modulation of the magnetic ordering behavior. Hence, to identify the importance of 1-D with respect to 3-D interactions, to develop structure–function relationships for this class of magnetic materials, and to prepare new molecule-based magnets with enhanced T_c 's, many related materials have been prepared.²³



$[Mn^{III}TPP]^+[TCNE]^{*-}$ forms uniform parallel 1-D chains in the solid state with each $S = 2 Mn^{III}$ bonded to four porphyrin

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N's (ca. 2.00 Å) and axially to two $[TCNE]^{*-}$ N's (ca. 2.30 Å) and each $S = 1/2 [TCNE]^{*-}$ is trans- μ -bonded to two Mn^{III} species^{23,41a} (Figure 14a). The magnetic susceptibility of $[MnTPP]^+[TCNE]^{*-} \cdot 2PhMe$ can be fit by the Curie–Weiss expression above 280 K with $\theta \approx -15$ K and between 115 and 250 K with an effective θ, θ' , of +61 K. A minimum in $\chi(T)$, characteristic of 1-D ferrimagnetic behavior, is observed at ~ 310 K, and field-dependent susceptibility is observed below 50 K. Magnetic ordering occurs below 13 K, and hysteresis with a coercive field of 375 Oe was obtained at 5 K.^{41a} Thus, $[MnTPP][TCNE]$ is a prototype of a new structure type of organic-based magnetic materials and is a model for studying a number of unusual magnetic phenomena, for example, the magnetic behavior of mixed quantum/classical spin systems. It should be noted that antiferromagnetic coupling of parallel chains of alternating organic radicals and metal ions to form ferrimagnets was pioneered by the Gatteschi and Rey groups⁴² and more recently extended to layered systems with T_c 's as high as 46 K.⁴³

In addition to $[MnTPP][TCNE] \cdot 2PhMe$,^{41a} the $[TCNE]^{*-}$ salts of 4-methoxyphenyl,^{44a} 4-chlorophenyl,^{44b} 2-fluorophenyl,^{44a} and *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrinatomanganese(III), $MnTP'P$,^{44c} have been studied by single-crystal X-ray diffraction. Also, the analogous TCNE electron-transfer salt was prepared with the easier-to-oxidize MnOEP ($H_2OEP = octaethylporphyrin$).⁴⁵

$[MnOEP][TCNE]$ has weak ferromagnetic coupling as evidenced by the fit of $\chi(T)$ to the Curie–Weiss expression with a θ' of +7 K.⁴⁵ The differences in the magnetic properties are attributed to structural differences. Both $[MnTPP][TCNE] \cdot 2PhMe$ and $[MnOEP][TCNE]$ form parallel 1-D chains (Figure 14), but a uniform chain is observed for $[MnTPP][TCNE] \cdot 2PhMe$,^{41a} and a nonuniform chain is observed for $[MnOEP][TCNE]$.⁴⁵ Thus, uniform chains appear to be essential to achieve magnetic ordering.⁴⁵

The substituted $[MnTPP][TCNE] \cdot 2PhMe$ electron-transfer salts exhibit different magnetic behavior. To elucidate a correlation between the magnetic behavior and the structure, numerous structural features were correlated with the effective θ, θ' , and the T_c ; hence, the former relates to intrachain 1-D interactions while the latter relates to interchain 3-D interactions (Table 1). Although a correlation between the magnetic behavior and the 3-D interactions remains elusive, a correlation between the dihedral angle, ϕ , between the $[Mn^{III}TPP]^+ MnN_4$ core and $[TCNE]^{*-}$ mean planes with the magnitude of magnetic coupling has been observed for the aforementioned ditoluene solvate (Figure 15).⁴⁶

The smaller the ϕ the stronger the magnetic coupling, i.e., the greater the θ' (Figure 15). Hence, to attain strong intrachain coupling, systems with more acute dihedral angles are sought

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- (45) Miller, J. S.; Vazquez, C.; Jones, N. L.; McLean, R. S.; Epstein, A. J. *J. Mater. Chem.* **1995**, 5, 707.
- (46) (a) Brandon, E. J.; Arif, A. M.; Burkhardt, B. M.; Miller, J. S. *J. Am. Chem. Soc.* **1998**, 120, 1822. (b) Brandon, E. J.; Miller, J. S. *NATO ARW Supramolecular Engineering of Synthetic Metallic Materials: Conductors and Magnets*; Veciana, J.; Rovira, C., Amabilino, D., Eds.; Springer: Berlin, 1998; Vol. C518, p 197.



Figure 13. Illustration of the $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ magnet being an effective magnetic shield at room temperature. Rods (paper clips) of soft-iron (red) are attracted to a Co_5Sm permanent magnet (left) when a 1.7 mm pellet of $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ placed between the Co_5Sm magnet and the rods (red) hang freely (right), demonstrating magnetic shielding.⁴⁰

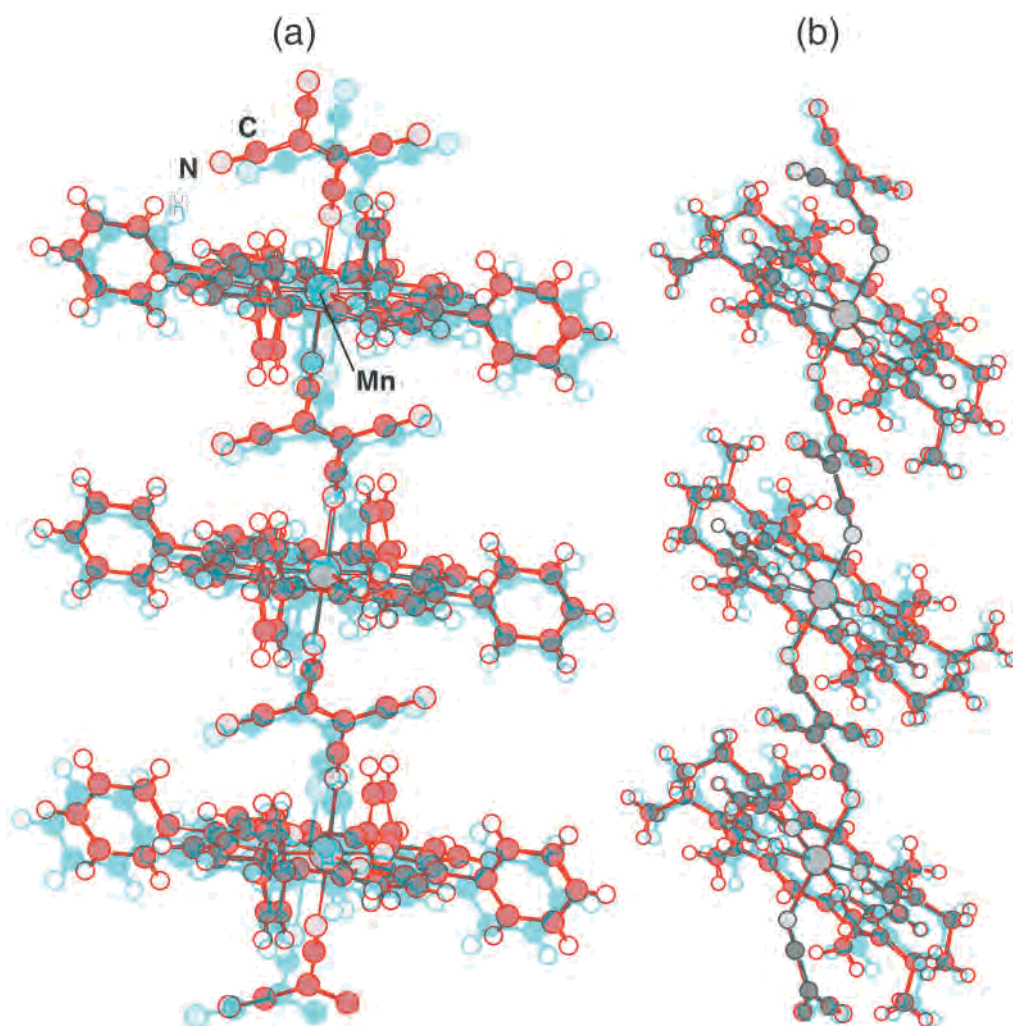


Figure 14. Stereoview of a segment of a uniform chain of the ferrimagnetic $[\text{Mn}^{\text{III}}\text{TPP}][\text{TCNE}] \cdot 2\text{PhMe}^{41a}$ coordination polymer (the solvent is omitted for clarity) (a) and a segment of nonuniform chain as observed for paramagnetic $[\text{Mn}^{\text{III}}\text{OEP}][\text{TCNE}]$ coordination polymer⁴⁵ (b).

and, as empirically observed, 3,5-disubstituted $[\text{MnTPP}]^{+}$ s are preferred over two- or four-substituted $[\text{MnTPP}]^{+}$ s because they have the greatest ϕ values.⁴⁶ To test this postulate, several 3,5-disubstituted systems are being studied. Likewise, pressure also may force such systems to have reduced ϕ angles and may lead to higher T_c values.

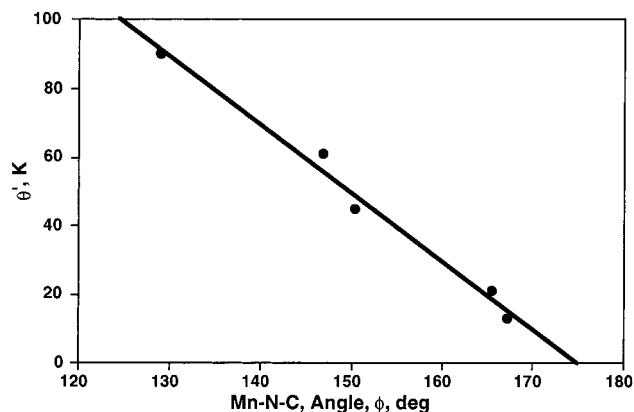
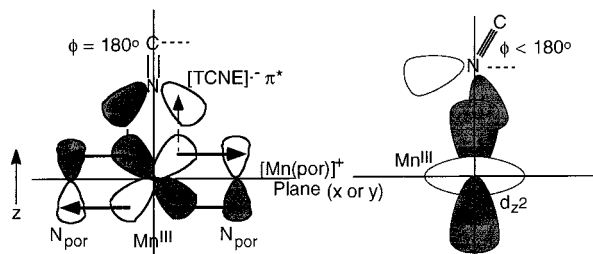
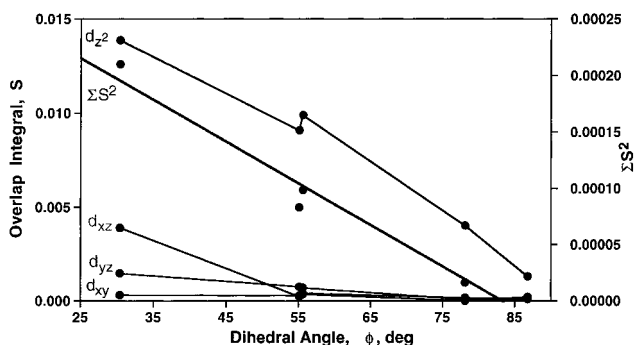
The aforementioned correlation between ϕ and θ' is ascribed to an overlap between the $[\text{TCNE}]^{\ominus}$ N-bound to the Mn^{III} π^* SOMO and the four Mn^{III} SOMO d orbitals [$E(d_{xy})^1$ (b_2) < $E(d_{xz}^1)$, $E(d_{yz}^1)$ (e) < $E(d_z^1)$ (a_1) < $E(d_{x^2-y^2})$ (b_1)⁴⁷]. Chemical intuition based on the well-established back-bonding suggests

that the key overlap is $d_{\pi} - \pi^*$ overlap between the singly occupied π^*_x (and π^*_y) of the $[\text{TCNE}]^{\ominus}$ and the singly occupied d_{xz} (and d_{yz}) on the $\text{Mn}(\text{III})$ (Figure 16a). From semiempirical MO calculations this intuitive $d_{\pi} - \pi^*$ overlap is less significant than the $\sigma - d_z^2\text{Mn}^{\text{III}} - p_z[\text{TCNE}]^{\ominus}$ overlap (Figure 16).^{46a} Furthermore, the smaller the ϕ , the greater the $\sigma - d_z^2\text{Mn}^{\text{III}} - p_z[\text{TCNE}]^{\ominus}$ overlap, which leads to an increased intrachain coupling as reflected in θ' (Figure 17). The decreased importance

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Table 1. Summary of the Structural and Magnetic Parameters for Several [TCNE]^{•-} Magnets^{46a}

| magnet | Mn-N _{TCNE} distance, Å | dihedral angle, ϕ , deg | distance, ^a Å | Mn...Mn θ' , K |
|------------------------|----------------------------------|------------------------------|--------------------------|-----------------------|
| [MnTPP][TCNE]·2PhMe | 2.306 | 55.4 | 10.116 | 61 |
| [MnTCIPP][TCNE]·2PhMe | 2.267 | 86.8 | 10.189 | 13 |
| [MnTOMePP][TCNE]·2PhMe | 2.289 | 78.1 | 10.256 | 21 |
| [MnTFPP][TCNE]·2PhMe | 2.313 | 55.4 | 10.185 | 45 |
| [MnTP'P][TCNE]·2PhMe | 2.299 | 33.6 | 8.587 | 90 |

^a Intrachain.**Figure 15.** Correlation of the dihedral angle, ϕ , between the MnN₄ and [TCNE]^{•-} mean planes with the effective θ value, θ' . Reproduced with permission from ref 46a. Copyright 1998 American Chemical Society.**Figure 16.** Illustration of πd_{π} Mn^{III} and π^* [TCNE]^{•-} overlap (a) and σd_{z^2} Mn^{III} and p_z [TCNE]^{•-} overlap (b).**Figure 17.** Correlation of the dihedral angle, ϕ , between the MnN₄ and [TCNE]^{•-} mean planes with the semiempirical INDO/SCF calculated d_{yz} , d_{xz} , d_{xy} , d_{z^2} -like overlap integrals, S , with the [TCNE]^{•-} π^* SOMO, and the sum of the squares of these overlap integrals, ΣS^2 . Reproduced with permission from ref 46a. Copyright 1998 American Chemical Society.

of the expected d_{π} - π^* overlap is attributed to the significant d_{yz} - π overlap between the d_{xz} and d_{yz} orbitals with the $p_{x,y}$ system of the porphyrin ring.

While the π overlap between the [TCNE]^{•-} p_z and the Mn d_{z^2} orbitals controls the intrachain magnetic exchange, the three-dimensional magnetic ordering temperature, T_c , depends on this

term and the interchain coupling. The latter term is governed by the competition between antiferromagnetic exchange due to orbital overlap between porphyrin moieties of adjacent chains and an effective exchange due to dipolar interactions between chains. The dipolar term can be ferromagnetic or antiferromagnetic depending on the structural order in the compound and the role of single ion anisotropy.⁴⁸

Recently, high coercivity and remanent magnetizations were observed at low temperature for many members of the [MnTPP]-[TCNE] family of magnets. As a prototype, the desolvated phase of [Mn^{III}TBrPP]⁺[TCNE]^{•-}·2CH₂Cl₂ [H₂TBrPP = *meso*-tetrakis(4-bromophenyl)porphyrin] exhibits a temperature-dependent hysteresis (Figure 18), with relatively low coercivity ($H_{cr} < 500$ Oe) for $T \geq 5$ K and dramatically increasing large coercivities below 5 K.⁴⁹ Below 5 K, the initial $M(H)$ curves are characteristic of metamagnets with a critical field needed to induce the phase transition to a new state of higher magnetization.⁵⁰ Unlike typical metamagnetic behavior, reversal of the magnetic field leads to a substantial hysteretic behavior with large-field remanence.

Hysteresis with a 27.0 kOe coercive field and an 11 500 emu Oe/mol remanent magnetization is observed for [Mn^{III}TBrPP]-[TCNE]. Metamagnets do not exhibit hysteresis or remanence.⁵⁰ The 27.0 kOe coercive field is very large and comparable to the metamagnetic critical field. This behavior is observed for virtually all members of the [Mn^{III}(porphyrin)][TCNE] family of organic-based magnets.⁴⁹ The large coercivity for [Mn^{III}TBrPP][TCNE] is comparable to the largest values of commercial magnets at room temperature, namely, 6 kOe for SmCo₅ and 21.3 kOe for Nd₂Fe₁₄B.^{11b} High coercivity is usually associated with significant single-ion anisotropy and is present for many iron- and cobalt-based magnets. In contrast, Mn(III), however, is only weakly anisotropic.⁵¹

The critical field also has an unusual temperature dependence, increasing linearly with decreasing temperature between 2 and ~5 K (Figure 19) and is 28.1 kOe at 2.0 K. The critical temperature, T_c , for the metamagnetic transition of [Mn^{III}TBrPP]-[TCNE], as determined from a plot of $H_c(T)$ where H_c extrapolates to zero, is 5.3 ± 0.1 K (Figure 19).⁴⁹

Organic Magnets

In addition to the magnetically ordered organic and organometallic-based materials discussed above, purely organic systems, i.e., spins that reside solely in a p orbital, have been reported. The earliest report of an organic species magnetically

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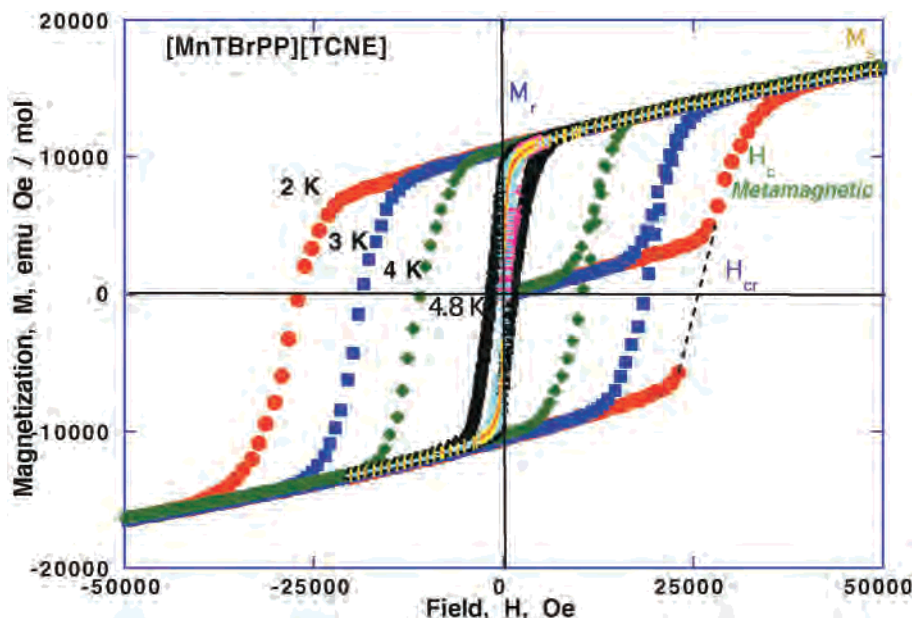


Figure 18. $M(H)$ for $[\text{Mn}^{\text{III}}\text{TBrPP}][\text{TCNE}]$ at 2.0 (●), 3.0 (■), 4.0 (curved diamond), 4.8 (▲), 5.2 (×), 5.5 (—), 6.1 (○), and 6.8 (●) K. Reproduced with permission of ref 49. Copyright 2000 Wiley-VCH.

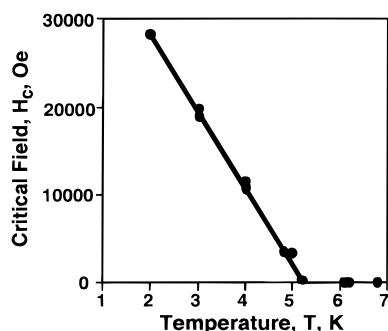


Figure 19. Temperature dependence of the critical field, H_c , for $[\text{Mn}^{\text{III}}\text{TBrPP}][\text{TCNE}]$.⁴⁹

ordering was that of a tanol suberate, which was ultimately characterized to be a metamagnet with a T_c of 0.38 K.⁵² The first and most extensively characterized organic compounds having a ferromagnetic ground state were the β -phase of 4-nitrophenylnitronyl nitroxide ($T_c = 0.6$ K)⁵³ and [tetrakis-(dimethylamino)ethylene][C_{60}] ($T_c = 16.1$ K).⁵⁴ More recently, the β -phase of the 4'-cyanotetrafluorophenyldithiadiazolyl radical was characterized to be a weak ferromagnet with a T_c of 35.5 K.⁵⁵

Mono- and Bimetallic Ion-Based Magnets

Magnets prepared from nonmetallurgical preparative methods have attracted the attention of several groups world-

wide.^{15a,23,40,42,53,56} These magnets rely on electron spin interactions among paramagnetic metal ions linked with organic ligands, of variable degrees of complexity, which do not contribute to the magnetization and only serve to position the spin sites. While in general these materials rely on two different metal ions, the first magnet reported of this type was intermediate spin $S = 3/2$ $\text{Fe}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2\text{Cl}$, which orders as a ferromagnet at 2.46 K but does not exhibit hysteresis.⁵⁷ The next class of magnets prepared via molecular chemistry were ferromagnetically ordered $[\text{Cr}^{\text{III}}(\text{NH}_3)_6]^{3+}[\text{Fe}^{\text{III}}\text{Cl}_6]^{3-}$ ($T_c = 0.66$ K)^{58a} and ferrimagnetically ordered $[\text{Cr}^{\text{III}}(\text{NH}_3)_6]^{3+}[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$ ($T_c = 2.85$ K) ionic bimetallic magnets.^{58b} Subsequently, the deliberate study of network-structured solids with spins residing on adjacent sites being in orthogonal orbitals and thereby leading to ferromagnetic coupling and ferromagnetic ordering evolved.⁵⁹ These fruitful studies led to reports of several classes of ferromagnets, e.g., layered (2-D) structured $\text{Cs}_2[\text{Cr}^{\text{II}}\text{Cl}_4]$ ($T_c = 58$ K),⁶⁰ 3-D Prussian-blue structured $\text{CsNi}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ ($T_c = 90$ K) (Figure 20),⁶¹ and $[\text{N}(n\text{-Bu})_4]\text{Ni}^{\text{II}}[\text{Cr}^{\text{II}}\text{ox}_3]$ (ox = oxalato) ($T_c = 14$ K).⁶² In 1981, chains composed of structurally ordered alternating metal ion sites with a differing number of

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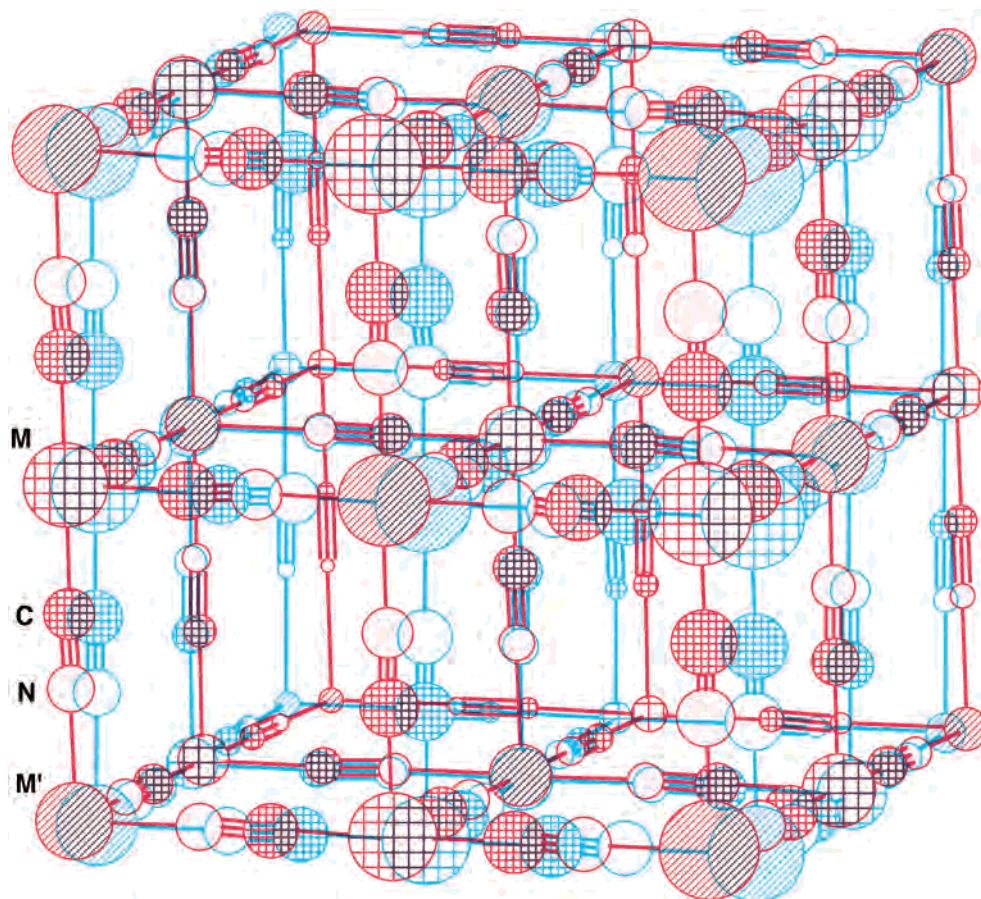


Figure 20. Stereoview of an idealized Prussian blue structure of $M[M(CN)_6]$.

spins per site led to ferrimagnetic coupling.^{63,64} Exploitation of this synthetic approach has led to many ferrimagnetically ordered materials, e.g., $[N(n\text{-Bu}_4)]_2\text{Co}^{\text{II}}_2[\text{Cu}^{\text{II}}(\text{obpo})]_3 \cdot 2\text{H}_2\text{O}$ [obpo = *o*-phenylenebis(oxamato)] ($T_c = 32$ K).⁶⁵ By use of this paradigm, 3-D Prussian blue structured $\text{V}[\text{Cr}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$ was developed and observed to have a T_c above room temperature ($T_c = 315$ K).⁶⁶

Unlike most magnetic materials discussed in this paper, with the notable exception of $M[\text{TCNE}]_x$ magnets, $\text{V}^{\text{II/III}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$ is a complex nonstoichiometric and mixed valent material.⁶⁶ It is a material in the broader sense that, unlike molecule-based magnets (or materials in general), the preparative procedure dictates the properties. Thus, different routes to a material may lead to different properties—chemical and/or physical. Given this nature and our extended group's desire to replicate data in our laboratory, Prof. Michel Verdaguer kindly supplied us with the preparative procedure,⁶⁷ and in our hands even more complex and air-stable (Figures 21 and 22) related materials with T_c 's up to 372 K (99 °C) (Figure 22) were prepared.⁶⁸ Independently and virtually simultaneously, Girolami's group reported additional related materials.⁶⁹

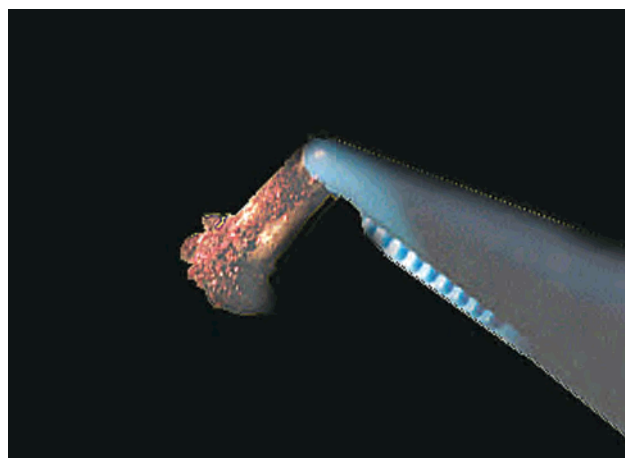


Figure 21. Photograph of a polycrystalline sample of nominal $\text{K}_{0.058}\text{V}^{\text{II/III}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.79} \cdot (\text{SO}_4)_{0.058} \cdot 0.93\text{H}_2\text{O}$ composition being attracted to a Teflon covered magnet in air at room temperature. Reproduced with permission from ref 68. Copyright 1999 Wiley-VCH.

Conclusion

Magnets based on organometallic and organic chemistry have been made. These are the latest materials in the multimillennium quest to prepare, study, exploit, and commercialize magnets. These molecule-based magnets differ from conventional magnets in that they are fabricated by low-temperature organic chemistry methodologies, in contrast to the high-temperature metallurgical methods typical of classical magnets. Additionally, molecule-based magnets have low densities and are, in general, electrical insulators and optically transparent over a significant frequency

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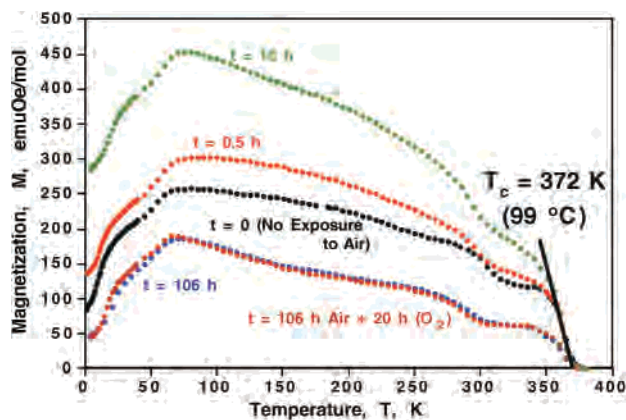


Figure 22. Temperature dependence of the magnetization of nominally $\text{K}_{0.058}\text{V}^{\text{IIIII}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.79} \cdot (\text{SO}_4)_{0.058} \cdot 0.93\text{H}_2\text{O}$ upon exposure to air and pure oxygen, up to 106 h in air and an additional 20 h in O_2 . Note that the 372 K T_c is not altered. Reproduced with permission from ref 68. Copyright 1999 Wiley-VCH.

regime. In addition to work in our laboratory, work worldwide has expanded the list of families as well as properties of organic and molecule-based magnets. So far, T_c 's up to 400 K and that are controllable have been achieved.²² Likewise, high saturation and remanent magnetizations as well as both high and low coercive fields have been reported. Nonetheless, opportunities abound for synthetic chemists with inclinations toward organic, organometallic, inorganic coordination, or polymers chemistry. Much additional work is needed for modeling and computational studies of electron and/or band structures and the magnetization of the materials in the ordered state. Detailed experimental studies on the specific heat, ac susceptibility, optical properties, ferromagnetic resonance, and pressure dependencies, to name a few, are needed. Finally, new theories and twists on existing theories, not to mention new phenomena, are essential for the continued development of the field.

The development of molecule-based magnets, like other areas of chemistry focusing on materials derived from molecular precursors, is a multifaceted interdisciplinary effort and certainly not the result of the efforts from a single group. Because the design, preparation, and study of the chemical and subsequently the magnetic properties require a plethora of skill and expertise, collaborations are essential. This constructive, dynamic, and ongoing necessity for collaborations along with the paramount requirement for electron spins to couple ferromagnetically is depicted in the following illustration:



This illustration was adapted from a 1916 article, which in cartoon fashion depicted the structure of Magnus Green salt, among others.⁷⁰ Clairvoyantly, the author suggested that the strong interactions between the cations and anions within a chain of alternating cations and anions led to the structure and unusual color of Magnus Green salt, $[\text{Pt}^{\text{II}}(\text{NH}_3)_4][\text{Pt}^{\text{II}}\text{Cl}_4]$. I took the liberty of adding the arrows aligned in the same direction to emphasize that electron spins must interact cooperatively to achieve stabilization of magnetic ordering. But more importantly, it is essential for interdisciplinary interactions among synthetic (organic, inorganic, as well as organometallic) chem-

ists, physical chemists, physicists, and materials scientists to propel research in this growing area forward. Among the many collaborations that we have been involved with, the ongoing collaboration with Prof. Arthur J. Epstein and his group at The Ohio State University, in addition to being exemplary, has been essential for the development of my career and progress of the research reported herein. We both joined the Xerox Webster Research Laboratory within a 6-week period in 1972 and soon thereafter joined forces to study the then embryonic area of molecule-based conductors. Our first joint paper appeared in 1976, and we have published papers each year in the past quarter of a century. To date, we have approximately 166 joint papers published, even though both of us have changed careers—he twice and I five times. Our first joint paper on molecule-based magnets appeared in 1985 when we reported that $[\text{FeCp}^*_2]\text{[TCNE]}$ was a ferromagnet.^{13a}

Future

It is clear that magnetism is enjoying a renaissance, since it is being expanded in part by contributions from organometallic and organic chemistry. These include (i) the discovery of bulk ferro- and ferrimagnets based on organic/molecular components^{15a,23,40,42,53,56} with critical temperatures exceeding room temperature, as discussed in this article,^{15a,22,66,68,69} (ii) the discovery that clusters in high, but not necessarily the highest, spin states, due to a large magnetic anisotropy or zero field splitting, have a significant relaxation barrier that traps magnetic flux, enabling a single molecule/ion (cluster) to act as a magnet at low temperature,⁷¹ (iii) the discovery of materials exhibiting large, negative magnetizations,^{41c,72} (iv) the discovery that spin-crossover materials can have large hysteretic effects above room temperature,⁷³ (v) photomagnetic⁷⁴ and (vi) electrochemical⁷⁵ modulation of the magnetic behavior in molecule-based magnets, (vii) the Haldane conjecture⁷⁶ and its experimental realization,⁷⁷ (viii) valence tautomers exhibiting spin crossover,⁷⁸ and (ix) quite-high-spin organic molecules.⁷⁹ Also, (x) giant⁸⁰ and (xi) colossal⁸¹ magnetoresistance effects observed for 3-D network solids have been observed and are being considered for commercial application.

The curiosity of new science as well as the quest for new technology will undoubtedly be the driving force for continued

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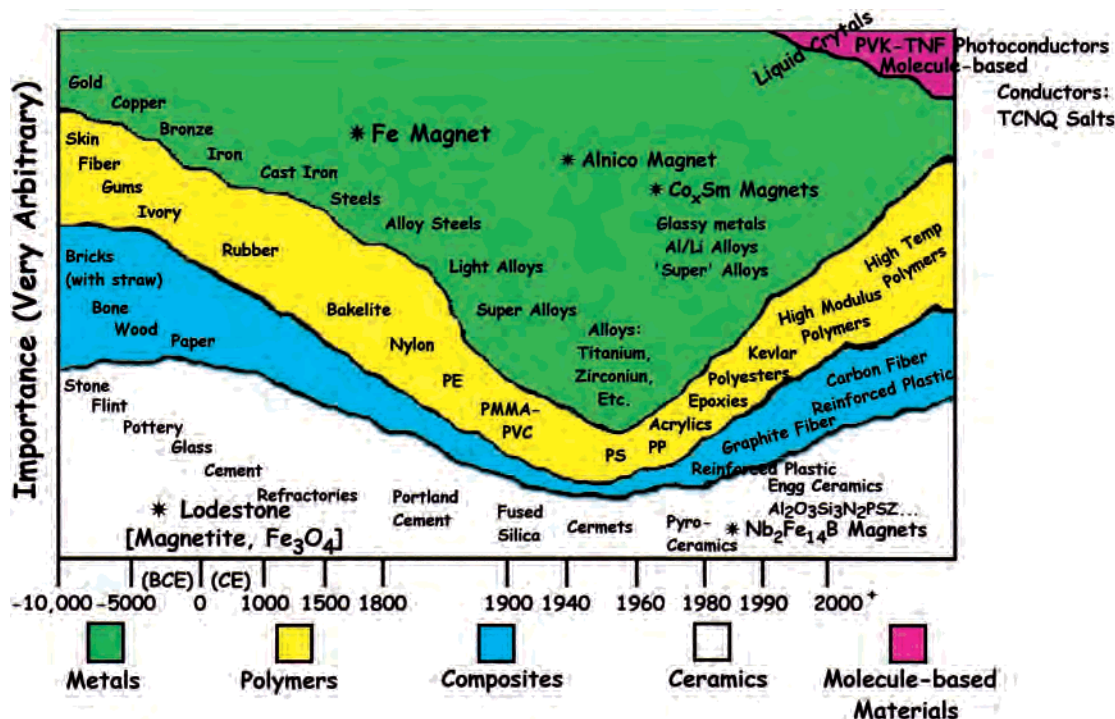


Figure 23. Illustration of the time evolution of practical materials through the millennium as a function of class of material. Neither the abscissa nor the ordinate is linear. Adapted with permission from ref 82a. Copyright 1990 Springer-Verlag GmbH & Co. KB.

developments in the area of magnetism. In short, magnetism has a bright future.

What is around the corner in the next millennium? Such answers are risky propositions. I firmly believe that solid-state chemists are the primary blame for failures in predicting the future, as perfection of the crystal ball has not been achieved. Nonetheless, a condition of acceptance of an American Chemical Society Award is delivering a talk at an ACS meeting. Given that the talk was to be given in the last year of the 20th century, the precipice of the next millennium, it was strongly requested that a prognostication into the next millennium be included. As one of many who has not contributed to perfecting the crystal ball, I prefer not to speculate on what will happen in the 21st century and beyond but simply present a few goals to be conquered. One can be grandiose, but I only list targets related to magnetism and refrain from including others in the larger sector of materials or even science as a whole. My short list of such targets for the next millennium includes the following:

- transparent insulating magnets
- flexible magnets
- photomagnets
- “ultrahard” magnets (very high coercivity)
- high permeability (very “soft”) magnets (very large response to small applied magnetic fields)
- liquid magnets
- detection of the magnetic monopole
- understanding of the reversal of the Earth’s magnetic poles

In addition to the anticipation of progress in the broad area of magnetism, continued growth with the increasing utility of molecule-based materials will be a hallmark of the next millennium. Historically, materials commonly utilized through the millennia for construction, clothing, etc. are metals, ceramics, polymers, and their composites (Figure 23).^{82,83} Initially, naturally occurring materials in these broad classes were used, but as society evolved, man-made materials supplanted natural materials.⁸² This is especially true in the past century, since man-made materials have led to high-tech electronic devices.

Molecule-based materials as a subset of polymers are an embryonic new class of materials because they are now acknowledged to exhibit many properties never previously associated with molecular materials,⁸⁴ e.g., metal-like electrical conductivity, superconductivity, as well as bulk ferromagnetism as discussed in this article. Commercial use of organic materials ranging from liquid crystal displays to conducting solid-state electrolytes⁸⁵ beckon a bright future⁸⁶ for the continued use of molecule-based materials in electronic, optical, and magnetic applications.

Acknowledgment

Success in my research endeavors required unrelenting support from a myriad of people, most importantly and notably from my loving wife, Elaine, who has endured many hours of virtual abandonment while my scientific pursuits marched forward. As we approach our 30th wedding anniversary in September of this year, Elaine has stood by me through many ups and downs and numerous relocations and has been a continuous source of inspiration and support. Our three sons, as the world’s greatest kids, Stephen, Marc, and Alan, deserve special recognition for their sustained encouragement and support. They have all left the nest and are beginning their own careers. In addition to the strong family environment, many mentors have provided crucial guidance and have served as role models. Special gratitude is extended to my undergraduate research advisor, Stanley Kirschner (Wayne State University), graduate research advisor, Alan L. Balch (UCLA), and post-

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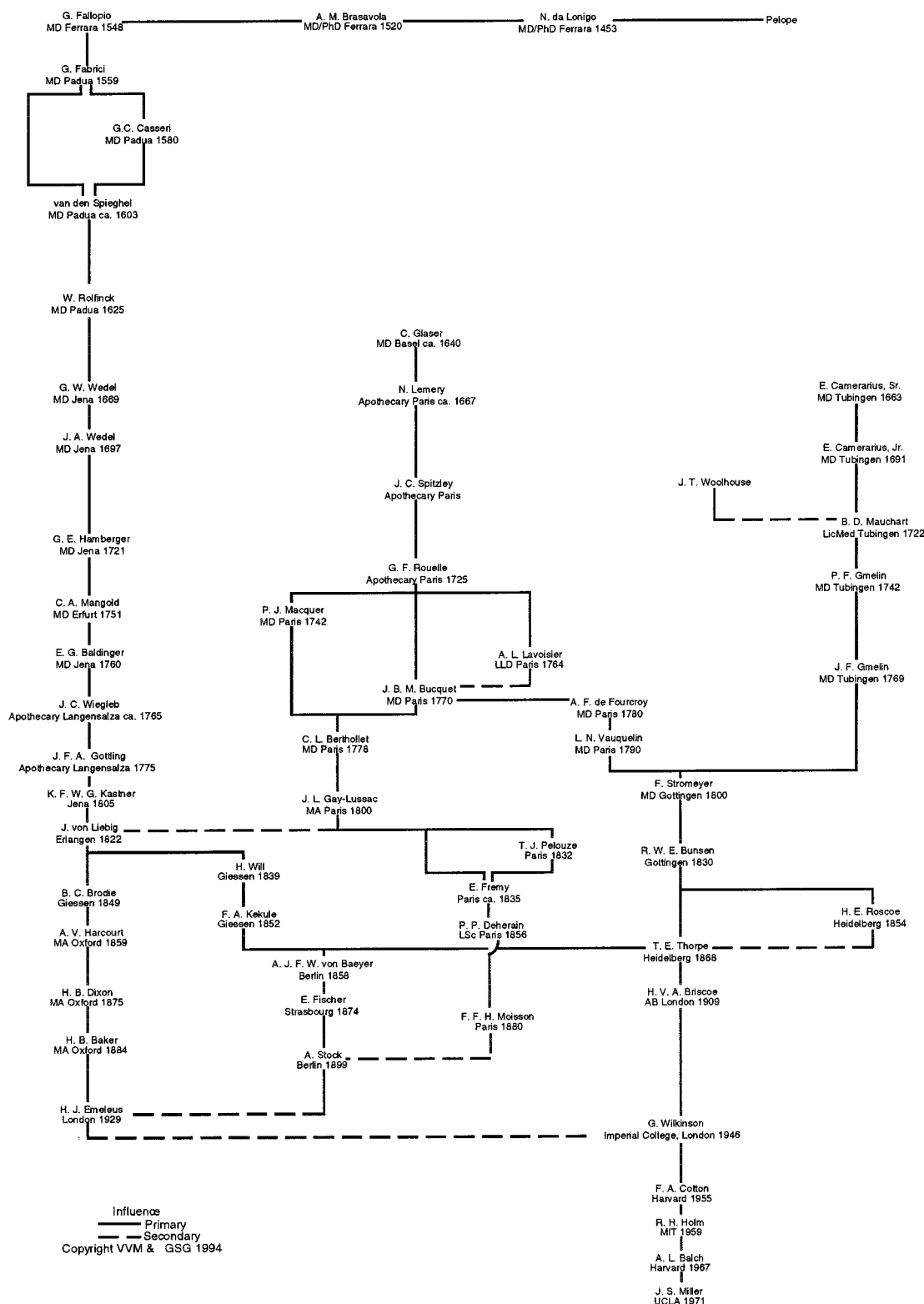


Figure 24. Professional genealogy chart for Joel S. Miller kindly provided and reproduced with permission by Vera V. Mainz and Gregory S. Girolami. Copyright 1994.

doctoral mentor Eugene E. Van Tamelan (Stanford University). Physically, we are what we eat, but intellectually, we are what we learn and they being my primary scientific educators, I am profoundly indebted for the nurturing and training they, among others too numerous to mention without risking errors in memory, instilled into me. The statement that we stand on the shoulders of giants as we move forward and mingle the boundaries of science comes into clear focus when one puts

into perspective my Ph. D. scientific lineage (Figure 24).

Our studies developing and characterizing new classes of magnets have had a circuitous history and evolved from studies of organic metals. Over the past 3 decades among a plethora of supporters for my endeavors, Charles B. Duke, Arthur J. Epstein, Roald Hoffmann, Alan G. MacDiarmid, George W. Parshall, Edel Wasserman, and George M. Whitesides have especially aided my research in noncollaborative roles and are extended

Table 2. Present and Past Co-workers at University of Utah and The Ohio State University^a

| University of Utah | University of Utah and The Ohio State University | The Ohio State University |
|---|--|--|
| <i>Øyvind Hatlevik</i> (G) | <i>Konstantin Pokhodnya</i> (VP) | <i>Stephen Erzkorn</i> (G) |
| <i>Wendy Hibbs</i> (G) | Arno Böhm (PD, BASF) | <i>Carmen Kmety</i> (G) |
| <i>Shireen Marshall</i> (G) | Kai-Ming Chi (PD, Chung-Chen U) | <i>Dusan Pejakovic</i> (G) |
| <i>Rico del Sesto</i> (G) | Dan Glatzhofer (PD, U OK) | <i>Nandyala Raju</i> (PD) |
| <i>Chitoshi Kitamura</i> (PD) | Xiaotai Wang (PD, U CO Denver) | Eric Anderson (G, Kan SU) |
| <i>Jim Raebiger</i> (PD) | Gordon Yee (PD, U CO) | Gang Du (G, Lakeshore) |
| Erik Brandon (G, JPL) | Yuanlin Zhou (PD, Inflazyme) | Keith Cromack (G, Abbott) |
| Doug Gordon (G, deceased) | | Will Brinckerhoff (G, APL Johns Hopkins) |
| Wayne Buschmann (G, PD, LANL) | | Anamish Chackraborty (G, Carnegie Mellon) |
| Mitch Johnson (G, LANL) | | Satish Chittipeddi (G, Lucent) |
| Jamie Manson (G, PD, ANL) | | Mihai Girtu (G, U Constanta) |
| Durrell Rittenberg (G, PD, U Wash) | | Olivier Heres (G, Sorbonne) |
| Laura Deakin (PD, U Alberta) | | Jinsoo Joo (G, Korea U) |
| Jinkwon Kim (PD, Kongju U) | | Steve Long (G, Consulting) |
| Scott Paulson (PD, U Calgary) | | Brian Moran (G, Milliken) |
| Leigh Porter (PD, deceased) | | Sureswaran Narayan (G, Nehru Research Cnt) |
| Ken-ichi Sugiura (PD, Osaka University) | | Patricia Vaca (PD, CNRS, FR) |
| Jie Zhang (PD, Samsung) | | Vasco de Gama (PD, Inst. Nucl. Tech, PT) |
| Lutz Baars-Hibbe (U, Braunschweig) | | Rene Laversanne (PD, CNRS, FR) |
| Sandy Kalm (U, NYU Medical School) | | Chuck Wynn (PD, XonTech) |
| Ben Kalm (U, OSU Medical School) | | Ping Zhou (PD, Rosenthal Securities) |
| Nate Petersen (U) | | Mike Selover (U, Fermi Lab) |
| Michele Yates (U, Graduate School) | | Chris Hahm (U, OSU Grad School) |
| Atta Arif (crystallography) | | Arthur Epstein (P; magnetic studies) |
| Henry White (P; electrochemistry) | | |
| Eugenio Coronado (P; ^b magnetic studies) | | |

^a Current group member in italics. U = undergraduate student; G = graduate student; PD = postdoctoral associate; VP = visiting professor; P = professor. Current affiliation in parentheses. ^b Universidad de Valencia.

Table 3. Non University of Utah and The Ohio State University Collaborators^a

| institution | collaborator |
|---|--|
| DuPont | Joe Calabrese, Dave Dixon, Dick Flippen, Dave Groski, Dick Harlow, Nancy Jones, Paul Krusic, Juan Manriquez, Scott McLean, Dermot O'Hare, Andy Suna, Carlos Vazquez, Mike Ward, Ed Wasserman |
| Osaka University | Ken-ichi Sugiura, Yoshiteru Sakata (syntheses) |
| Johannes-Gutenberg Universität | Jürgen Ensling, Vadim Ksenofontov, Philipp Gütllich (Mössbauer, magnetic studies) |
| Northeastern University | Jian Zhang, Bill Reiff (Mössbauer) |
| NIST | Qing Huang, Ross Erwin, Jeff Lynn (neutron diffraction); George Candela, Lloyd Swartzendruber (magnetic studies) |
| Brookhaven National Laboratory | Goetz Bendele, Silvina Pagola, Peter Stephens (synchrotron X-ray diffraction), Steve Shapiro, Andrei Zheludev (neutron diffraction) |
| Centre d'Etudes Nucléaires (Grenoble, France) | Eric Ressouche, Jacques Schweizer (neutron diffraction) |
| University of Delaware | Ilia Guzei, Chris Incarvito, Do Lee, Louise Liable-Sands, Glenn Yap, Arnie Rheingold (structural studies) |
| University of Alabama | Robin Rogers (structural studies) |
| Brandeis University | William Desmarais, Michael Vela, Jim Fox, Donna Guerrer, Art Reis, Jr., Bruce Foxman (X-ray diffraction) |
| Bruker Instruments | Chuck Campana (X-ray diffraction) |
| Hauptman-Woodward Medical Research Institute | Brian Burkhart (X-ray diffraction) |
| National High Magnetic Field Laboratory | Scott McCall, Jack Crow (specific heat) |
| Quantum Design | Randy Black, Jost Diederichs (specific heat) |
| Technische Universität München | Christian Kollmar (computational studies) |
| National Research Council (Canada) | John Morton, Keith Preston (EPR) |
| University of Houston | Z. J. Huang, F. Cheng, Y. T. Ren, Y. Y. Xue, Paul Chu (magnetic studies under pressure studies) |
| University of Miami | S. Zane, Fulin Zuo (magnetic studies) |
| Columbia University | L. P. Le, A. Keren, G. M. Luke, W. D. Wu, Tomo Uemura (muon spin resonance) |
| Ceram Physics | William Lawless (specific heat) |
| University of Barcelona | Juan Novoa (MO calculations) |

my sincere gratitude. A special thanks is also due to the University of Utah Department of Chemistry and then-chairman Peter J. Stang for inviting me to join them as a colleague and thereby enabling my research to develop and gain a more sustained footing.

The continued diligent work of co-workers and collaborators made the research presented herein a reality. Foremost is the delightful and stimulating close-knit collaboration with Arthur J. Epstein, who, except for my wife and kids, has established the greatest tolerance to me. Through thick and thin Art, with

the support of his wife Paulayne and daughters Melissa and Dana, has been a close friend and an exemplary colleague who has on many occasions gone beyond the call of duty to make our collaboration flourish, and we extend our most sincere gratitude and look forward to the next quarter-century of exciting continued explorations.

The extended research group of Arthur Epstein and myself has been blessed with countless talented and hard-working chemists and physicists as co-workers, and again, at the risk of omitting a name of a key individual, the names of these

associates are listed along with their current affiliation in Table 2. In addition to these scientists, many scientists worldwide have collaborated in special studies, and these individuals, identified in Table 3, are saluted. Among the many identified in Table 2, I make special note of two truly outstanding technicians, namely, R. Scott McLean and Carlos Vazquez,⁸⁷ with whom I had the pleasure of having as co-workers while I was at the DuPont Company. In reality, the individuals listed in Tables 2 and 3 are the heroes that executed the work that will stand the test of time and collectively deserve the full credit, and it is to these individuals that I dedicate this paper. I, however, personally accept the blame for any errors in reporting the collective body of work and in recalling all who contributed to this active research program.

I also extend my deepest appreciation to Arthur Epstein for making this Award Presentation particularly memorable by going out his way to organize an Award Symposium in my honor. He did so, unsuspecting that he would be under an extreme time crunch that materialized because of a variety of pressing personal obligations. Nonetheless, he was in San Francisco for 13 h to preside over the symposium. The call of teaching whisked him away at midnight. The 26 scientists traveling from as far as Europe and Asia solely attending this meeting to participate at this symposium made this meeting a cherished memory. Except for two from southern California, everyone traveled by far much further than I. The participants Jesper Bendix, Arno Böhm, Erik J. Brandon, Wayne E. Buschmann, George Christou, Eugenio Coronado, Peter Day, Kim R. Dunbar, Arthur J. Epstein, Gregory S. Girolami, John A. Gladysz, Kazuhito Hashimoto, David N. Hendrickson, Hiizu Iwamura, Frank H. Köhler, Paul M. Lathi, Juan J. Novoa, Charles J. O'Connor, Dermot M. O'Hare, Fernando Palacio, David A. Shultz, Mark M. Turnbull, Michael D. Ward, Gordon

T. Yee, and Z. John Zhang and session chairs Arthur J. Epstein, Richard D. Kelley, and Edel Wasserman deserve special accolades, as do Lake Shore Cryotronics, Inc. and *Synthetic Metals* (Elsevier Science) for providing financial support for the Award Symposium. Philipp Gülich, however, could not attend because of an illness, and we wish him a speedy recovery. A permanent archive of the proceedings of this symposium will appear by early 2001 as a topical issue of *Synthetic Metals* with Arthur J. Epstein serving as the Guest Editor.

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