THE QUEST FOR MOLECULE-BASED MAGNETS

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ABSTRACT

In the past decade a new class of magnets possessing spins on organic species have been discovered and studied. These magnets can be fabricated at room temperature and may enable useful devices and/or processes. Herein we discuss several of the mechanisms that can enable the stabilization of magnetic ordering and also provide examples of molecule-based magnets.

INTRODUCTION

Magnets have been crucial to the development of both society and technology and remain so today. The initial use of magnets was as a compass simplifying the exploration of new lands. Currently they are used in a plethora of applications in everyday life. Applications rely on either the large net magnetic moment of a 'hard' (permanent) magnet to produce an external magnetic field which itself produces a force on another magnet or an electric current, or the high permeability of 'soft' (nonpermanent) magnets which deflects magnetic fields and induces large magnetic moments in response to modest electric currents. Uses for magnets range from magneto-mechanical applications (*e. g.*, frictionless bearings and magnetic separators), acoustic devices (*e. g.*, loudspeakers and headphones), telecommunication/information technology (*e. g.*, switches, sensors, computer memory), motors/generators (*e. g.*, stepping and cranking motors), and magnetic shielding. A typical automobile, for example, has more than twenty magnets.[1] More importantly, magnets in the future are expected to play a key role in the development of 'smart materials.' As a consequence, many research laboratories worldwide are focusing toward the development of new, improved magnetic materials. One approach is the study of magnets prepared via molecular/organic/polymer chemistry. Organic-based magnets should have several features not present in conventional magnets, Table 1, and the past decade has witnessed rapid progress in making magnets comprising organic species as a key component.

Table 1
Representative Desirable Attributes of Organic-based Magnets

Low Density	Processibility at Low Temperature
Flexibility	Low Environmental Contamination
High Strength	High magnetic susceptibilities
Solubility	High magnetizations
Biocompatibility	Low Magnetic Anisotropy
Transparency	Modulation/Tuning of Properties via Organic Chemistry
Semiconducting or Insulating	Compatibility with Other Polymers for Composites

The spins associated with unpaired electrons and the way they interact with each other lead to the magnetic behavior of all magnets. Magnets in use today, *e. g.*, iron, iron oxides, rare earth intermetallics (*e. g.*, $SmCo_5$ and $Nd_2Fe_{14}B$), etc., have spins (unpaired electrons) at metal sites. These spins are close to each other and strongly interact in such a manner that leads to strong magnetic behavior. This need has also been translated into the design of molecule-based magnets. Herein the mechanisms that are invoked to account for the spin coupling needed for molecule-based magnets, summary of the current state-of-the-art, as well as some scientific challenges are described. More comprehensive reviews are available for individuals seeking further details.[2-4]

ACHIEVING MAGNETIC ORDER IN A MOLECULE-BASED MAGNET

A molecule-based magnets, like all magnets, requires alignment of the spins in at least two, but preferably, all three directions. The degree of alignment is described by the exchange interaction J between pairs of spins. For the Hamiltonian $H = -2J\mathbf{S_i}\bullet\mathbf{S_j}$, $J > 0$ signifies ferromagnetic interactions, whereas $J < 0$ signifies antiferromagnetic interactions. Three spin coupling mechanisms[2] are known to stabilize finite values of J, Table 2.

Table 2

Spin coupling mechanisms for the stabilization of antiferromagnetic and ferromagnetic coupling

- Ferromagnetic exchange ($J > 0$) resulting from spins in orthogonal orbitals in the same spatial region (Hund's rule)
- Configuration interaction (CI) admixture of an excited state with ferromagnetic spin coupling to the ground state
- Dipole-dipole, through-space, coupling

Frequently, however, it is unclear which is the primary exchange mechanism for a system and it is likely that more than one mechanism plays a significant role. Furthermore, due to the numerous degrees of complexity of the CI model (middle mechanism), there are several ways to describe this mechanism and properly truncated MO calculations are needed to provide a detailed understanding. Each are discussed below.

Ferromagnetic exchange ($J > 0$) resulting from spins in orthogonal orbitals in the same spatial region (Hund's rule)

High-spin behavior via this approach is achieved by having unpaired electrons (spins) reside in orthogonal orbitals in the same spatial region. The closer the approach of the unpaired electrons in the orthogonal orbitals the greater is J. This occurs for O_2 ($S = 1$) and is the essence of Hund's rule to maximize spin multiplicity. Extension to systems with a large number of spins in nearby orthogonal orbitals can lead to ferromagnetic order. Examples of 2- and 3-D systems with magnetic exchange due to interaction of orthogonal orbitals have been reported.

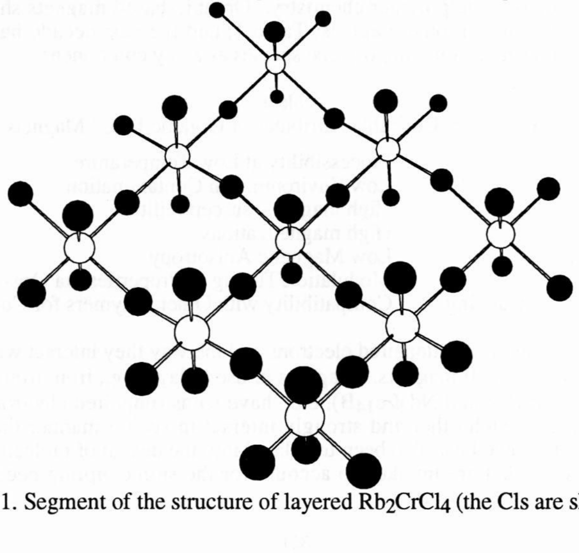


Figure 1. Segment of the structure of layered Rb_2CrCl_4 (the Cls are shaded).

These examples include Rb_2CrCl_4 has an extended 2-D network structures with spins on adjacent Cr^{IV} sites occupying orthogonal orbitals and is a ferromagnet below a T_c of ~55 K, Figure 1. Substitution of Rb^+ with $[RNH_3]^+$ (R = Me, $PhCH_2$ etc.), although increasing the interplanar spacings, does not significantly alter the T_c.[5] These magnets are reasonably transparent. Another layered system is $[Bu_4N][MM'(ox)_3]$ (ox = oxalato; M = Fe, Co, Ni, Mn, Cu) system,[6] Figure 2. For M = Fe the T_c is 12.5 K.[6]

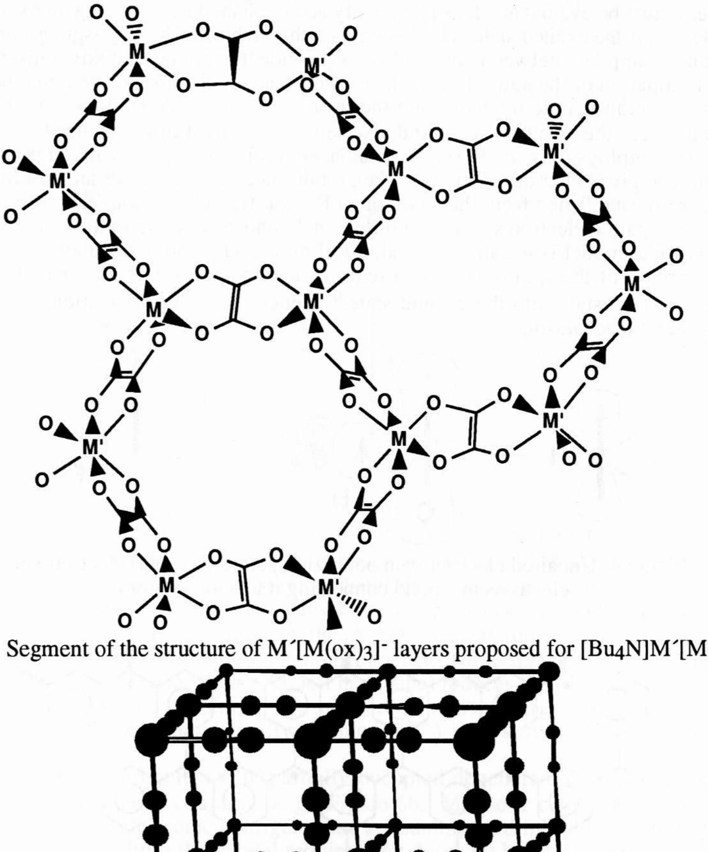


Figure 2. Segment of the structure of $M'[M(ox)_3]^-$ layers proposed for $[Bu_4N]M'[M(ox)_3]$.

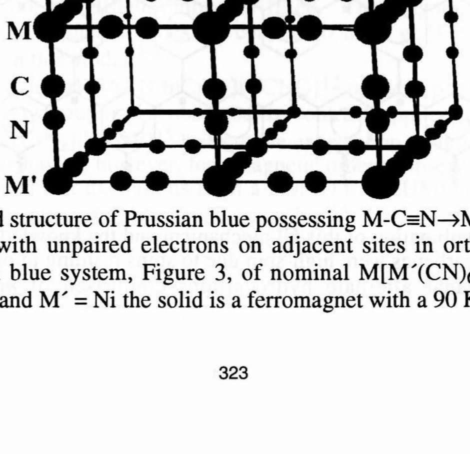


Figure 3. Idealized structure of Prussian blue possessing M-C≡N→M' linkages in 3-D.

A 3-D system with unpaired electrons on adjacent sites in orthogonal orbitals is the ferromagnetic Prussian blue system, Figure 3, of nominal $M[M'(CN)_6]$ composition.[7,8] For example, when M = Cr and M' = Ni the solid is a ferromagnet with a 90 K T_c.[7a] However, when

M = V and M' = Mn or M = Cr and M' = V the materials are ferrimagnets with T_c's of 125 K[7b] and 315 K,[8] respectively.

CI Admixture of an excited state with ferromagnetic spin coupling to the ground state

The previous mechanism is a means to ferromagnetically couple spins reside in the same spatial region. However, to couple spins residing in distant spatial regions the total wavefunction of the system must be evaluated. This is typically accomplished by admixing an excited state into the ground state; if the excited state is high-spin then this stabilizes the high-spin ground state. The CI also can be applied between molecules to provide ferromagnetic (or antiferromagnetic) coupling. Evaluation of the admixture of the excited states to the ground state that best describes the system is complex, time intensive and the results, of course, depend on how the problem is formulated, *i. e.*, the ground state and excited state wavefunctions used. The simplest approximation employs only the POMO's on adjacent molecular-species although more complex formulations can give better descriptions of the ground state. Several cases are described below.

It is well established from the study of EPR hyperfine interactions that a spin in a POMO can polarize the paired electron spins in an orthogonal bond connecting to it, Figure 4. Although a valence bond-like model is usually invoked, a full molecular orbital calculation reveals that the proper description of the spin polarization requires the admixture (CI) of a small amount of an antibonding excited state into the ground state.[9] Hence the spin polarization mechanism is an intramolecular CI mechanism.

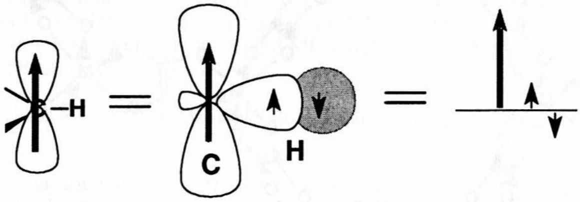
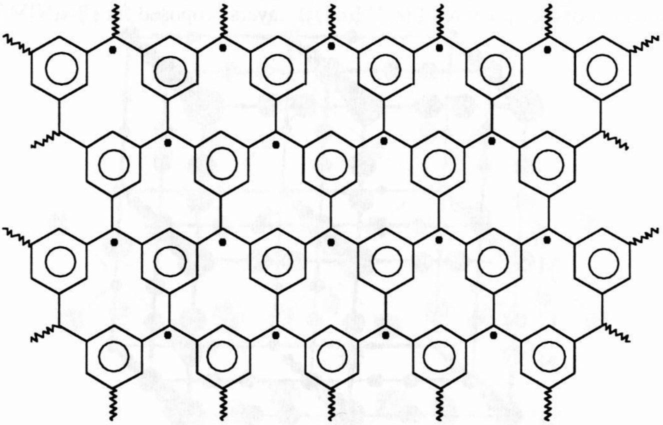


Figure 4. Unpaired electron-spin polarizing paired (bonded) electron-spins electrons in a bond connecting it to another atom.



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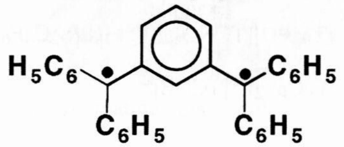
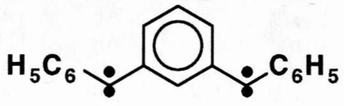
Based on the combination of this CI mechanism and the knowledge that the ground states of dioxygen and some carbenes were high-spin due to spins residing in orthogonal orbitals, larger molecules such as planar alternate hydrocarbons comprised of *meta*-substituted triplet diphenylcarbene moieties were proposed to have a high spin ferromagnetically coupled ground states, Figure 5. Proposed examples of high spin multiplicity polymers[10] include **1**.

Using triplet triarylmethyl, **2**, and quintet diphenylcarbene, **3**, repeat units larger high-spin organic molecules have been prepared.



2, triplet triarylmethyl



3, quintet diphenylcarbene

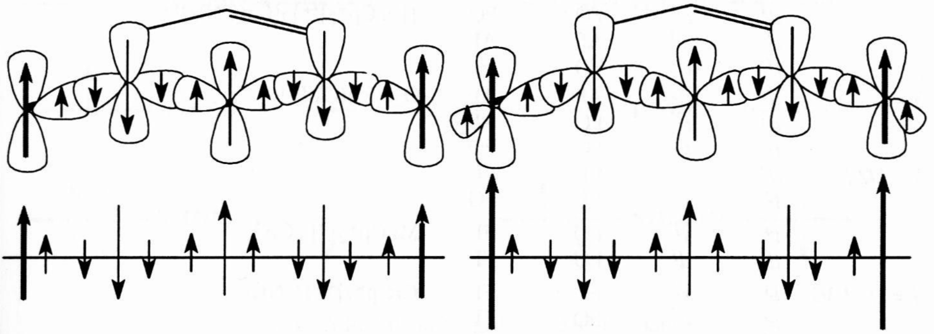


Figure 5. Ferromagnetic coupling through meta-linkages for triarylmethyls and diphenylcarbenes.

The application of CI mixing between molecules of a charge-transfer (CT) excited state with the ground state to stabilize ferromagnetic coupling for a chain of alternating donors (D) and acceptors (A), *i. e.*, $\cdots A^{\cdot-}D^{\cdot+}$ $\cdots$ $\cdots A\cdot^{-}D\cdot^{+}$ was proposed by Harden M. McConnell.[11] Due to the relatively large spatial and energy differences between spins on adjacent sites, only minimal overlapping of the frontier orbitals occurs. However, the spin can couple either ferromagnetically or antiferromagnetically. If the spins of the $A\cdot^{-}D\cdot^{+}$ repeat units reside in half-occupied nondegenerate POMOs the admixture of the higher energy charge-transfer states (Figure 6a, right hand side) with the ground state (Figure 6a, left hand side) reduces the total energy of the system to stabilize antiferromagnetic coupling ('↑↓'). This reduction in energy does not occur when the two electron spins are ferromagnetically coupled ('↑↑') in accord with the Pauli exclusion principle.

Other electronic structures with partially occupied degenerate orbitals may lead to the stabilization of ferromagnetic coupling, *e. g.*, Figure 6b. Magnetic couplings predicted by this model for representative electronic configurations are summarized in Table 3. Achievement of ferromagnetic coupling within this model requires that A (or D) has a degenerate (accidental or intrinsic) orbital that is not half-filled, empty, or filled. The magnetic properties of several electron-transfer salts based on metallocenes and cyanocarbons, *e. g.*, [FeCp*$_2$][TCNE], Figure 7, have been discussed within this model.[2,11]

Application of the model t^4/s^1 [MnCp*$_2$][TCNQ][12] or [MnCp*$_2$][TCNE][13] leads to the expectation of ferromagnetic coupling as observed. In contrast, application of the model to t^3/s^1 [CrCp*$_2$][TCNQ][14] or [CrCp*$_2$][TCNE][15] leads to the expectation of antiferromagnetic coupling leading to ferrimagnetic behavior; however, ferromagnetic order is observed. Extension of the CI model to include intermolecular excitations from a POMO to NLUMO or NHOMO to POMO, Figure 8, leads to the expectation of ferromagnetic coupling.[15]

Table 3

Representative Magnetic Couplings for Homo- and Heterospin Systems with Singly, Doubly, and Triply Degenerate POMO's.[a]

	A (or D)	D (or A)	D <- A	<- D	Example
$S = 1/2$	s^1	s^1	AF	AF	[TMPD][TCNQ], $[TTF]Ni[S_2C_4F_6)_2]_2$
	d^1	s^1	AF	FO	
	d^3	s^1	FO	AF	$[FeCp^*_2]^{\bullet +}[TCNE]^{\bullet -}$
	d^3	d^1	AF	AF	
	t^1	d^1	FO	FO	
	t^5	d^1	AF	AF	
	d^3	d^3	FO	FO	$\{[FeCp^*_2]^{\bullet +}\}_2[C_4(CN)_6]^{2-}$
	t^1	d^3	AF	AF	
	t^1	t^1	FO	FO	
$S = 1$	d^v	d^2	AF	AF	O_2, $[Ru(OEP)]_2$
	d^2	t^2	FO	AF	
	t^2	t^2	FO	FO	
$S = 1/2 / 1$	d^2	s^1	FI	FI	
	t^2	s^1	FI	FO	
	t^4	s^1	FO	FI	$[MnCp^*_2]^{+}[TCNE]^{\bullet -}$
	d^2	d^1	FO	FI	
$S = 1/2 / 3/2$	t^3	s^1	FI	FI	$[CrCp^*_2]^{+}[TCNE]^{\bullet -}$
	t^3	d^1	FO	FI	
	t^3	d^3	FI	FO	

[a] AF => antiferromagnetic coupling; FI => ferrimagnetic coupling; FO => ferromagnetic coupling. Intrinsic or accidental orbital degeneracies: *s* = singly (a or b), *d* = doubly (e), *t* = triply (t).

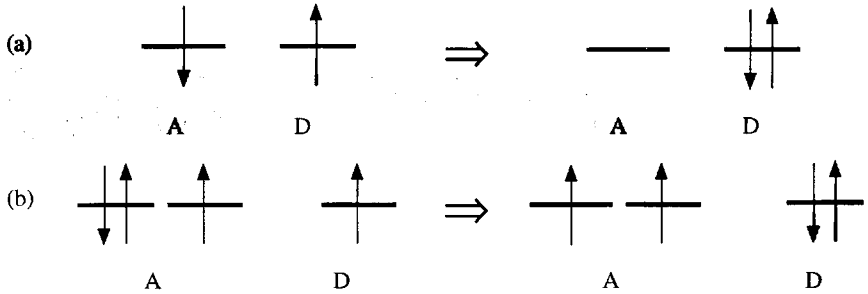


Figure 6. Schematic illustration of the stabilization of ferro- or antiferromagnetic coupling by configurational interaction (CI) only involving POMOs on adjacent sites (A and D). If both A and D have a half-filled nondegenerate POMO (s^1), then the D←A (or A←D) virtual charge transfer excited state stabilizes antiferromagnetic coupling (a). If A (or D) has a nonhalf-filled degenerate POMO (e. g., d^3, assumed here to be A), then either the D←A charge transfer excited state formed (b) will stabilize ferromagnetic coupling (or A←D charge transfer excited states formed via excitation of a 'spin-up' D electron will stabilize antiferromagnetic coupling).

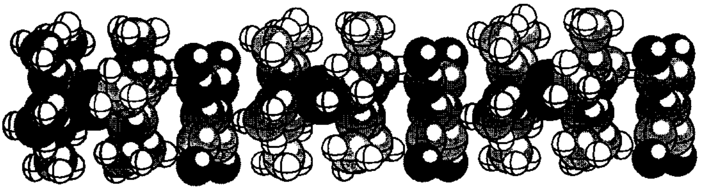
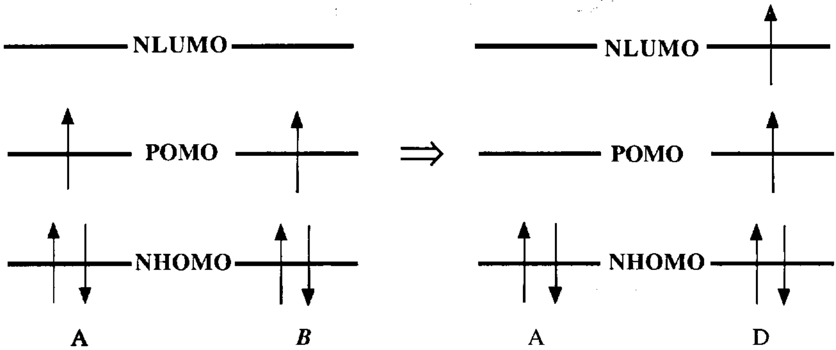
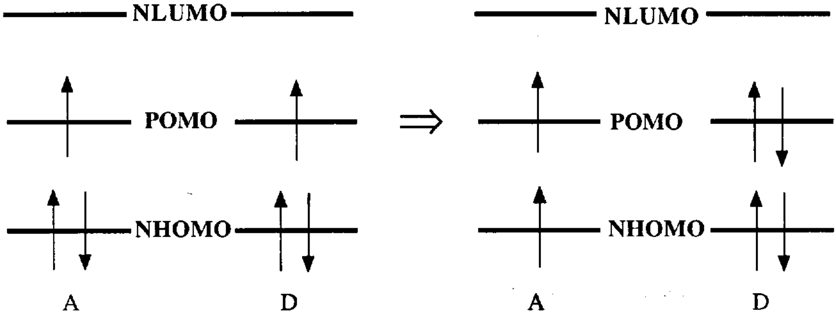


Figure 7. Alternating donor/acceptor linear chain structure of $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$.



(a) D ← A POMO to Virtual NLUMO Excitation



(b) D ← A NHOMO to POMO Excitation

Figure 8. Schematic illustration of stabilization of ferromagnetic coupling by configurational interaction (CI) involving only virtual excitation from a POMO on A to a virtual NLUMO on D (a), or NHOMO on A to a POMO on D (b).

Bulk magnetic ordering requires extension of the model beyond pairwise (AD) interactions in one-dimension. Figure 9 illustrates the lowering of the total energy for the ferromagnetically-coupled system depicted in Figure 6b by the admixture of a CT excited state to the ground state, E_{gs}, with one intrachain, one intrachain plus one interchain, and with a second interchain excited state, E_{es}.[2,11]

Through-space Dipole-dipole Magnetic Coupling

Through-space, dipole-dipole, spin-spin interactions not involving the overlap of electronic orbitals may lead to cooperative magnetic behavior below ~2 K. These weak magnetic interactions are a consequence of the magnetic fields associated with each spin. This mechanism may contribute to the ferromagnetic ordering observed for β-*p*-$NO_2C_6H_4NIT$[16] (NIT = nitronyl nitroxide) (T_c = 0.6 K), **4**, 1,3,5,7-tetramethyl-2,6-diazaadamantane-*N*,*N*'-doxyl[17] (T_c = 1.48 K), **5**, and chlorobis(diethlydithiocarbamate)iron(III),[18] (T_c = 2.46 K), **6**. Interchain dipole-dipole interactions may contribute to the complex behaviors observed for the metallomacrocycle-based magnet family including [MnTPP][TCNE], *vide infra.*

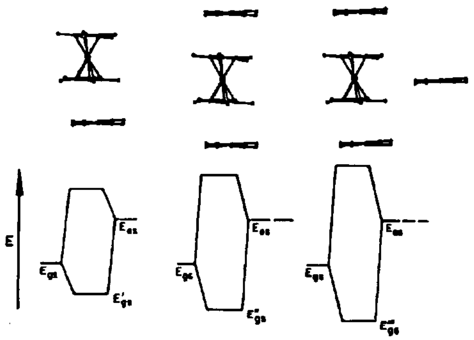
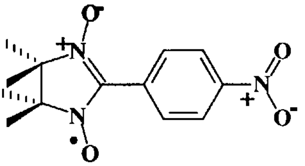


Figure 9. Schematic state diagram depicting the relative energy of the ground, E_{gs}, and excited states, E_{es}, before and after admixing (virtual $D^{\cdot+}A^{\cdot-}$ charge transfer) with a single excited state (a), an intrachain pair of excited states (a) and (b), and with a third interchain excited state arising from admixture with an out-of-registry acceptor to stabilize ferromagnetic coupling (from ref. 1a Copyright 1988 by the American Chemical Society)



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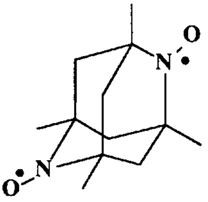

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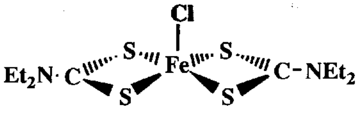

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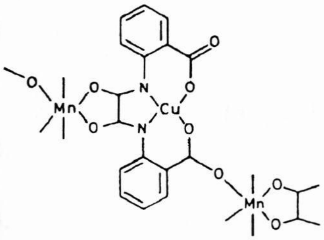
Antiferromagnetic coupling via Alternating Spin Sites

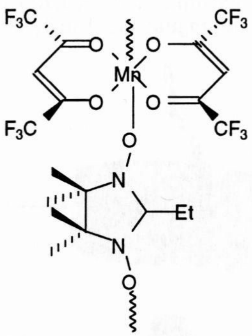
An alternative approach to achieve long range magnetic ordering is to antiferromagnetically couple alternating spin sites with different number of spins per site leading to ferrimagnetic behavior.[2,19] Thus, adjacent spin sites antiferromagnetically ('↑↓') couple leading to ferromagnetically coupled next-adjacent spin ('↑↓↑'). Hence, spin coupling of alternating sites with a larger number of spins (*e. g.*, 5 for $S = 5/2$ Mn^{II}) with sites with fewer spins (*e. g.*, 1 for $S = 1/2$ Cu^{II} or nitroxide ligands) (*i. e.*, '↑↓'), can lead to a ferrimagnetic system. Examples include: $Cu^{II}Mn^{II}(obbz){\cdot}H_2O$,[20] **7**, ($T_c$ = 14 K) and the Mn^{II}/nitroxide system, **8**, which is ferrimagnetic with a 8.1 K T_c.[21]

Other examples of ferrimagnets include electron transfer salts with D = *meso*-tetraphenylporphryinmanganese(II), **9**, and *A* = TCNE which have the alternating $\cdots D^{+}A^{\cdot-}D^{+}A^{\cdot-}D^{+}A^{\cdot-}\cdots$ structure, Figure 10, with a *trans*-geometry about both the $[TCNE]^{\cdot-}$and the Mn^{III}, as the $[TCNE]^{\cdot-}$ binds to two $S = 2$ Mn^{III}'s in an uniform *trans*-μ_2-*N*-σ-bound manner. This salt exhibits magnetic ordering at 14 K.[22]



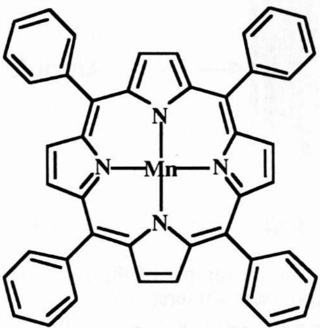
7, $Cu^{II}Mn^{II}(obbz)\cdot H_2O$

obbz = oxamidobis(benzoato)



8, $Mn^{II}(hfac)_2NITEt$

hfac = hexafluoroacetylacetonate; NITEt = ethyl nitronyl nitroxide



Manganese tetraphenylporphine, MnTPP, **9**

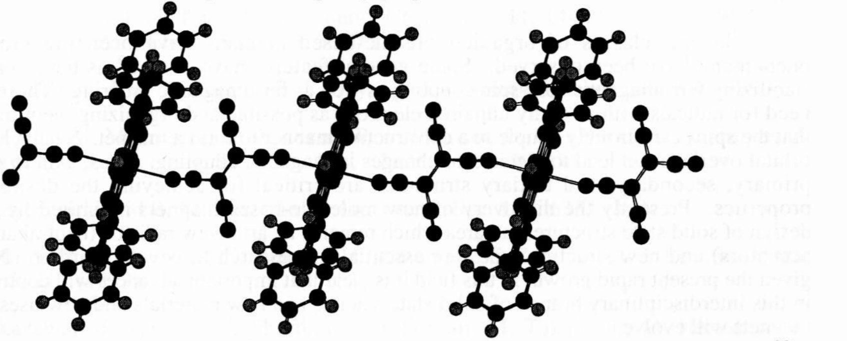


Figure 10. Segment of an uniform 1-D $\cdots D^+A^{\cdot -}D^+A^{\cdot -}D^+A^{\cdot -}\cdots$ chain of [MnTPP][[TCNE].[22]

$[MnTPP]^+[TCNE]^{\cdot -}\cdot 2PhMe$ can fits the Curie-Weiss equation with $\theta = +61$ K. Hysteresis with a coercive field of 375 G was observed at 5 K.[22] The magnetic ordering temperature is 14 K.[23]

Another example of a ferrimagnet with covalently bound alternating D's and A's is the product of the reaction of $V(C_6H_6)_2$ and TCNE in dichloromethane. This product is a black solid of nominal composition of $V(TCNE)_x\cdot yCH_2Cl_2$ ($x \sim 2$; $y \sim 1/2$).[24] It exhibits hysteresis at room temperature and is the first example of molecular/organic based magnet with a critical temperature, exceeding room temperature, Figure 11. The T_c estimated to be ~400 K. Details of its structure remain to be determined.

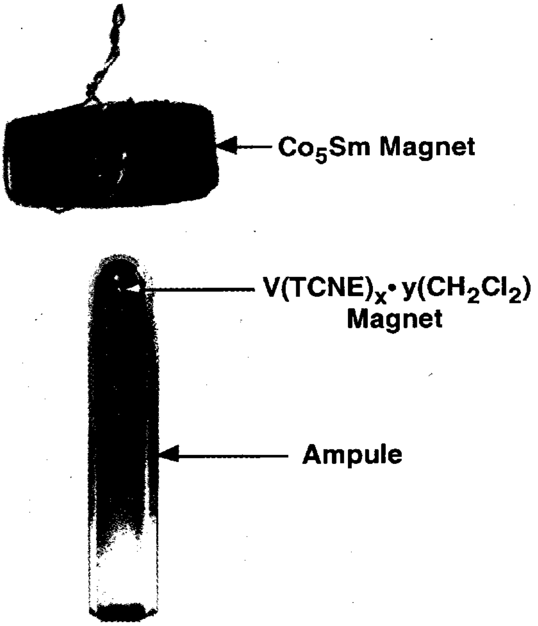


Figure 11. Photograph of a powdered sample of the for $V(TCNE)_x \cdot y(CH_2Cl_2)$ magnet being attracted to a Co_5Sm magnet at room temperature.

CONCLUSION

Several classes of organic/molecule-based magnets have been prepared and new phenomena have been observed. Some general features have evolved as being important for stabilizing ferromagnetic spin-spin coupling as well as ferromagnetic ordering. These include the need for radicals with as many unpaired electrons as possible and organizing them in such a way that the spins can strongly couple in a constructive manner to form a magnet. Small changes in the orbital overlaps can lead to significant changes in magnetic coupling. Thus, akin to proteins, the primary, secondary, and tertiary structures are critical for achieving the desired magnetic properties. Presently the discovery of new molecule-based magnets is limited by the rational design of solid state structures; an area which remains an art. New radicals (neutral and donors or acceptors) and new structure types are essential for research to develop further. Nonetheless, given the present rapid growth in this field it is clear that important advances will continue to occur in this interdisciplinary branch of solid state science and new materials and new uses for age-old magnets will evolve.

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REFERENCES

1. (a) J. S. Miller and A. J. Epstein, Chemtech **21**, 168 (1991); J. S. Miller, Adv. Mater. **6**, 322 (1991). R. M. White, Science **229**, 4807 (1985); A. J. Epstein, and J. S. Miller, Mol. Cryst. Liq. Cryst. **228**, 99 (1993). (b) J. S. Miller, W. M. Reiff, A. J. Epstein, Chem. Rev. **88**, 201 (1988).

2. J. S. Miller and A. J. Epstein, Angew. Chem. **106**, 399 (1994); Angew. Chem. Internat. Edit. **33**, 385 (1994).

3. D. Gatteschi, Adv. Mat. **6**, 635 (1994).

4. O. Kahn, Molecular Magnetism, (VCH Publishers, Inc. 1993).

5. P. Day, Acc. Chem. Res. **14**, 236 (1979); C. Bellito and P. Day, J. Mat. Chem. **2**, 265 (1992).

6. H. Tamaki. Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, H. Okawa, J. Am. Chem. Soc. **114**, 6974 (1992).

7. (a) V. Gadat, T., Mallah, I. Castro, I., M. Verdauger, J. Am. Chem. Soc. **114**, 9213 (1992); (b) W. R. Entley, G. Girolami, Science **268**, 397 (1995).

8. T., Mallah and M. Verdauger, (private communication).

9. A. Carrington, andA. D. McLachlan, Introduction to Magnetic Resonance, (Harper & Row, New York, 1967), p223ff.

10. S. Morimoto, K. Itoh, F. Tanaka, N. Mataga, Preprints of the Symposium on Molecular Structure, Tokyo, 1968, p 6; N. Mataga, Theor. Chim. Acta **10**, 372 (1968).

11. H. M. McConnell, Proc. R. A. Welch Found. Chem. Res. **11**, 144 (1967); J. S. Miller and A. J. Epstein, J. Am. Chem. Soc. **109**, 3850 (1987).

12. W. E. Broderick, J. A. Thompson, E. P. Day, B. M. Hoffman, Science **249**, 410 (1990).

13. G. T. Yee, J. M. Manriquez, D. A. Dixon, R. S. McLean, D. M. Groski, R. B. Flippen, K. S. Narayan, A. J. Epstein, J. S. Miller, Adv. Mater. **3**, 309 (1991).

14. W. E. Broderick and B. M. Hoffman, J. Am. Chem. Soc. **113**, 6334 (1991).

15. J. S. Miller, R. S. Mclean, C. Vazquez, J. C. Calabrese, F. Zuo, and A. J. Epstein, J. Mat. Chem. **3**, 215 (1993).

16. Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita. M. Ishikawa, M., Phys. Rev. B **46**, 8906 (1993); M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi, M. Kinoshita, Chem. Phys. Lett. **186**, 401 (1991).

17. R. Chiartelli, M. A. Novak, A., Rassat , J. Tholence, Nature **363**, 147 (1993).

18. H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull, F. R. Merritt, Phys. Rev. **155**, 563 (1967).

19. O. Kahn, Structure and Bonding **68**, 89 (1987). O. Kahn and Y. Journaux, in Inorganic Materials, edited by D. W. Bruce, D. O'Hare, (J. Wiley & Sons, New York, 1993), p. 59; A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, Acc. Chem. Res. **22**, 392 (1989).

20. F. Nakatani, J. Y. Carriat, Y. Journaux, O. Kahn, F. Lloret, J. P. Renard, Y. Pei, J. Sletten, M. Verdaguer, J. Am. Chem. Soc. **111**, 5739 (1989).

21. A. Caneschi, D. Gatteschi, J. P.Renard, P. Rey, R. Sessoli, Inorg. Chem. **28**, 3314 (1989).

22. J. S. Miller, J. C. Calabrese, R. S. McLean, A. J. Epstein, Adv. Mat. **4,** 498 (1992).

23. A. Böhm, C. Vazquez, R. S. McLean, J. C. Calabrese, S. E. Kalm, J. L. Manson, A. J. Epstein, and J. S. Miller, submitted for publication.

24. (a) A. J. Epstein, J. S. Miller, Proceedings of Nobel Symposium #NS-81 Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure, edited by W. R. Salaneck, I. Lündstrom, B. Rånby, (Oxford University Press, Oxford, UK, 1993), p. 475; J. S. Miller, G. T. Yee, J. M. Manriquez, A. J. Epstein, in the Proceedings of Nobel Symposium #NS-81 Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure, edited by W. R. Salaneck, I. Lündstrom, B. Rånby, (Oxford University Press, Oxford, UK, 1993), p. 461; J. S. Miller, A. J. Epstein, Mol. Cryst., Liq. Cryst. **233**, 133 (1993)