Organic and Molecular Ferromagnets

Unlike common ferromagnets such as iron, nickel, cobalt or even cobalt–samarium and Nb–Fe–B, it is extremely rare for a discrete molecule, especially an organic or polymeric material, to have cooperative magnetic interactions. Since the mid-1980s a few such materials have been prepared which demonstrate that ferromagnetic interactions can be present in a molecular-based system. The reports have stimulated studies as to the origins as well as to the properties of molecular/organic ferromagnets. Three routes have led to highly magnetic molecular/polymeric materials: (a) chains of isolated alternating radical cations and radical anions, (b) covalently bonded chains containing alternating different metal ions, and (c) covalently bonded chains involving metal ions and nitroxide radicals.

Bulk ferromagnetic behavior has been reported for the linear chain electron transfer salt $[Fe(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$ where $[Fe(C_5Me_5)_2]$ is decamethylferrocene (see Fig. 1) and [TCNE] is tetracyanoethylene (see Fig. 2). Crystals of $[Fe(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$ are composed of parallel linear chains of alternating radical $[Fe(C_5Me_5)_2]\cdot^+$ cations D$\cdot^+$ and $[TCNE]\cdot^-$ anions A$\cdot^-$ without any close interior interactions (see Fig. 3). This material spontaneously becomes a ferromagnet below a Curie (transition) temperature T_C of 4.8 K. Its saturation magnetization M_s of 16.3 A m^2 mol^{-1}

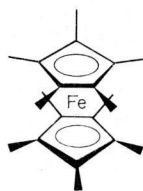$(1.63 \times 10^4$ emu G mol$^{-1})$ (36% greater than that of iron metal (on either a per mole or iron basis)) and its 80 kA m^{-1} coercive field are much greater than that of iron. Consistent with the magnetic order and a transition to ferromagnetic behavior at T_C the measured critical exponents are $\alpha = 0.09$, $\beta \simeq 0.5$, $\gamma = 1.21$ and $\delta = 4.4$. Ferromagnetic ordering was also detected by neutron diffraction. Zero-applied-field Zeeman split ^{57}Fe Mössbauer spectra are observed at low temperatures. The $[TCNE]\cdot^-$ acts as an internal dipolar field inducing the Zeeman splitting with extraordinarily large internal fields (> 30 MA m^{-1}). The Mössbauer data confirms that all iron is low-spin Fe^{III} and that iron metal is not present. Ferromagnetic interactions are lost on replacing either ion radical with similarly structured diamagnetic ions demonstrating the necessity of having radicals at both the donor and acceptor sites.

Replacement of manganese for iron leads to the formation of $[Mn(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$ with a T_C of 8.8 K and an M_s of 20 A m^2 mol^{-1} (2×10^4 emu G mol^{-1}). The 2.0 K coercive field is 100 kA m^{-1} for $[Mn(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$. A mean-field Heisenberg model containing two different spin sites has been developed for $[M(C_5Me_5)_2][TCNE]$ (M = Fe, Mn). This enables the scaling of T_C for these iron and manganese magnets. For a specific set of exchange interactions, T_C for the manganese magnet should exceed that of the iron magnet by 87% in excellent agreement with the observed value of 83%.
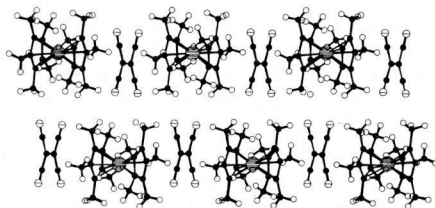

Figure 1
Tetracyanoethylene structure

Figure 3
Alternating ... D$\cdot^+$A$\cdot^-$D$\cdot^+$A$\cdot^-$ ... structure of $[Fe(C_5Me_5)_2]\cdot^+[TCNE]\cdot^-$ D = Fe(C$_5$Me$_5$)$_2$ and A = TCNE); hydrogens have been omitted for clarity
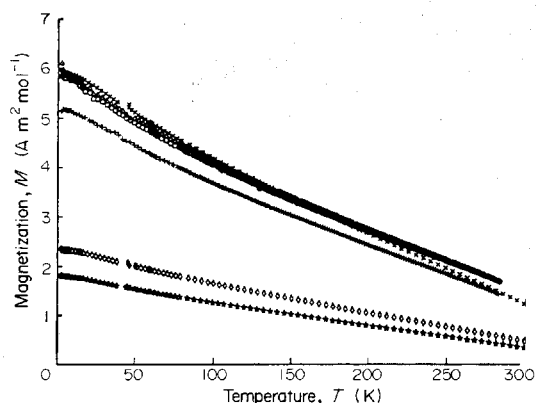
Figure 4
Magnetization M as a function of temperature T at
1.56 MA m^{-1} ($\bigcirc$), 1.28 MA m^{-1} ($\triangle$), 1.42 MA m^{-1} ($+$),
0.16 MA m^{-1} ($\times$), 0.04 MA m^{-1} ($\diamondsuit$) and 0.01 MA m^{-1} ($\star$)
for V(TCNE)$_x$·y(CH$_2$Cl$_2$) (after Manriquez et al. 1991.
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Figure 5
Hysteresis $M(H)$ of V(TCNE)$_x$·y(CH$_2$Cl$_2$) at room
temperature. The data was taken on a vibrating sample
magnetometer (after Manriquez et al. 1991. © AAAS,
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Research aimed towards high-T_C molecular-based
magnets was extended to the reaction of bis(benzene)
vanadium and TCNE. This reaction results in the
formation of a disordered, air-sensitive, thermally
unstable black solid material of nominal V(TCNE)$_x$
·yCH$_2$Cl$_2$ ($x \sim 2$; $y \sim \frac{1}{2}$) composition which exhibits
a field-dependent magnetic susceptibility and magnet-
ization M (see Fig. 4). The unusual nearly linear
increase of M with decreasing T most likely reflects
the contribution of two or more spin sublattices of
this ferrimagnet. Hysteresis with a coercive field of
5 kA m^{-1} is observed at room temperature (see Fig.
5). This is the first example of molecular/organic-
based material with a critical temperature above room
temperature. The critical temperature exceeds 350 K,
the thermal decomposition temperature of the sam-
ple. The linear extrapolation of the temperature at
which the magnetization should vanish leads to an
estimation of a T_C of 400 K. From spin wave theory
and data taken below 20 K a spin wave dispersion
coefficient has been estimated for the vanadium-based
magnet. This also leads to an estimation of T_C to be
400 K. Due to the disordered nature and variable
composition of the magnetic material the disordered
structure has yet to be elucidated. The TCNEs, how-
ever, probably bind up to four different vanadiums
via σ–N bonds enabling the formation of a three-
dimensional network structure. The disorder leads to
random anisotropy which results in a correlated spin-
glass or wandering axis ferrimagnet behavior depend-
ing on the amount and type of solvent present,
temperature and applied magnetic field.

Bulk ferrimagnetic behavior arising from the anti-
ferromagnetic coupling of $S = \frac{5}{2}$ Mn^{II} alternating with
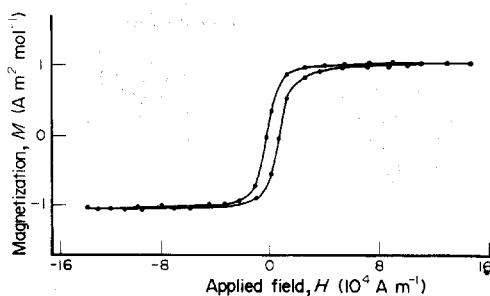either $S = \frac{1}{2}$ Cu^{II} or $S = \frac{1}{2}$ nitronyl nitroxides has been
reported for several systems containing covalently
bonded chains. The solid Cu^{II}Mn^{II}[oxamidobis(ben-
zoato)]·H$_2$O (see Fig. 6) exhibits an ordering tempera-
ture T_C of 14 K, a saturation magnetization of
23.4 A m^2 mol^{-1} (2.34×10^4 emuG mol^{-1}) and a coer-
cive field of 5 kA m^{-1} whereas Mn^{II} (hexafluoroacetyl-
acetonate)$_2$NITEt (NITEt = 2-ethyl-4,4,5,5-tetra-
methyl-4,5-dihydro-1H-imidazole-1-oxyl-3-oxide or
ethyl nitronyl nitroxide) (see Fig. 7) exhibits a T_C of
8.1 K, an M_s of 19.4 A m^2 mol^{-1} (1.94×10^4 emu
G mol^{-1}) and a coercive field of 37.5 kA m^{-1}.

The origins of the magnetic behavior of
[Fe(C$_5$Me$_5$)$_2$]·$^+$[TCNE]·$^-$ are important for the design
of new ferromagnetic materials with higher saturation
magnetization and critical temperatures. Stabilization
of ferromagnetic coupling via the configurational
admixture of a charge transfer excited state with the
ground state is the basis of the present understanding
of the spin exchange in this system. Essentially, if an
alternating chain of radicals, $\cdots$D·$^+$A·$^-$D·$^+$A·$^-\cdots$
(where D = donor = [Fe(C$_5$Me$_5$)$_2$]·$^+$; A = acceptor =
[TCNE]·$^-$), exists, such that on virtual electron
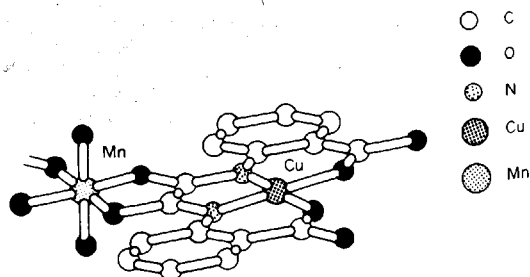transfer from either D or A, but not both, either D or

Figure 6
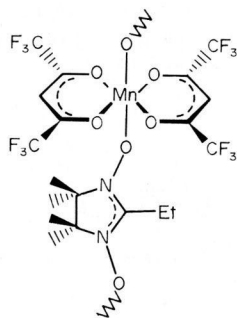Cu^{II}Mn^{II}[oxamidobis(benzoato)]·H$_2$O structure

Figure 7
Mn^{II}(hexafluoroacetylacetonate)$_2$NITEt structure

A becomes a triplet, then ferromagnetic coupling could be stabilized. That is, on removing one electron from either D or A and the remaining electrons having a moment equivalent to two electron moments aligning parallel, the ferromagnetic coupling could be stabilized. Since [Fe(C$_5$Me$_5$)$_2$]$\cdot^+$[TCNE]$\cdot^-$ has the prescribed structure and triplet [Fe(C$_5$Me$_5$)$_2$]$^{2+}$ could form on virtual electron transfer from D$\cdot^+$ to A$\cdot^-$, this model can account for the observed ferromagnetism. Note that if either the donor or acceptor is spinless (diamagnetic) the system has only weak exchange confirming the importance of both radicals. Electron transfer between [Fe(C$_5$Me$_5$)$_2$]$\cdot^+$ on adjacent chains also leads to ferromagnetic alignment while electron transfer between [TCNE]$\cdot^-$ on adjacent chains leads to antiferromagnetic alignment. The competition between ferromagnetic and antiferromagnetic alignment may account for the ferromagnetic ground state in [Fe(C$_5$Me$_5$)$_2$]$\cdot^+$[TCNE]$\cdot^-$ and [Mn(C$_5$Me$_5$)$_2$]$\cdot^+$-[TCNE]$\cdot^-$ (discussed earlier), the metamagnetic ground state in [Fe(C$_5$Me$_5$)$_2$]$\cdot^+$[TCNQ]$\cdot^-$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) and the antiferromagnetic ground state in [Ni(C$_5$Me$_5$)$_2$]$\cdot^+$[TCNE]$\cdot^-$. Likewise, as discussed earlier.

The presence of $\cdots$D$\cdot^+$A$\cdot^-$D$\cdot^+$A$\cdot^-\cdots$ chains within the crystal leads to important anisotropy effects. For example, specific heat measurements of [Fe(C$_5$Me$_5$)$_2$]$\cdot^+$[TCNE]$\cdot^-$ are consistent with only around 4% of the magnetic entropy results from the three-dimensional ordering of the spins at 4.8 K. The majority of the entropy is involved in magnetic correlation that persists along the stacks to temperatures of the order of the intrachain exchange energy ($J_{intra} \simeq$ 25 K) for [Fe(C$_5$Me$_5$)$_2$]$\cdot^+$[TCNE]$\cdot^-$. One consequence of this quasi-one-dimensionality is that the three-dimensional ordering temperature of 4.8 K is dramatically reduced by the introduction of spinless sites. For example, replacement of 2.5% of the $S = \frac{1}{2}$ [Fe(C$_5$Me$_5$)$_2$]$\cdot^+$ sites with spinless $S = 0$ [Co(C$_5$Me$_5$)$_2$]$^+$ leads to a 43% reduction in T_C. For potential polymer ferromagnets, where the anisotropy of the exchange (J_{inter}/J_{intra}) may be larger than that for the metallocenes the suppression of T_C for oligomers may be even more dramatic.

See also: Organic Superconductors: Anisotropic Molecular Metals

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