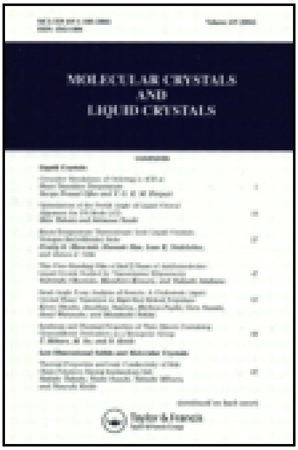

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Linear Chain Ferromagnetic Compounds - Recent Progress

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LINEAR CHAIN FERROMAGNETIC COMPOUNDS - RECENT PROGRESS

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Abstract Since our observation that the kinetically stable 1-D 1:1 phase of $\mathrm{Fe(C_5Me_5)_2^{\dot{+}}(TCNQ)^{\dot{-}}}$ exhibits metamagnetic behavior (T_N = 2.55°K; $H_c \approx 1.5$ KOe) we have pursued the synthesis of compounds with a ferromagnetic ground state. Several new 1-D $\mathrm{Fe(C_5Me_5)_2^{\dot{+}}}$ substances containing radical anions have been prepared. Each compound exhibits different magnetic properties, and some exhibit slow paramagnetic relaxation (in zero field) suggesting spin on the anions.

INTRODUCTION

For the past score of years there has been and continues to be considerable scientific and technological attention paid to linear chain charge transfer crystals, transition metal based chain compounds as well as covalent polymers exhibiting extended unsaturated π backbone as such compounds may exhibit unusually high electrical conductivity. In addition to these areas we have been pursuing the study of charge transfer salts which exhibit cooperative magnetic interactions to identify the key structural features that might ultimately enable us to synthesize an organic ferromagnet.

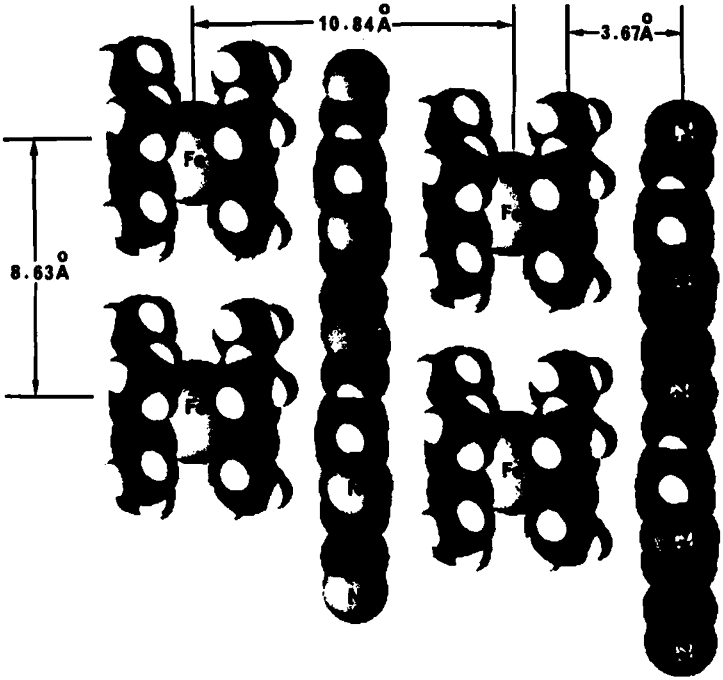


FIGURE 1 Structure of 1-D $Fe(C_5Me_5)_2^{\dot{+}}(TCNQ)^{\dot{-}}$.[2]

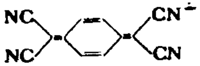
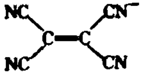
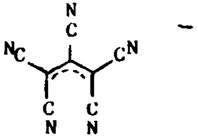
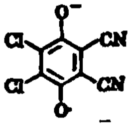
The reaction of decamethylferrocene, $Fe(C_5Me_5)_2$, 1, with acceptors[1] such as TCNQ, TCNE, and DDQ leads to the formation of several poorly conducting one-dimensional complexes of 1:1 composition. Each of these compounds possesses a similar structure composed of alternating S=1/2 $(1)^{\dot{+}}$ and S=1/2 radical anions. Figure 1 illustrates the structure for the case of $(TCNQ)^{\dot{-}}$. Table 1 summarizes the key structural features as well as physical properties for these compounds.

[TCNQ]$^-$ COMPLEX

The reaction of 1 with TCNQ leads to the formation of three phases.[3] The magnetic susceptibility of the 1-D phase has proved to be anomalous. Complexes of $(1)^{\dot{+}}$ containing diamagnetic anions

Table 1

Summary of Structural Data for 1-D $Fe(C_5Me_5)_2$ Salts

Anion	 $(TCNQ)^{\dot{-}}$	 $(TCNE)^{\dot{-}}$	 −	 $(DDQ)^-$
Anion Spin, S	1/2	1/2	0	1/2
Space Group	P2n/n	C2/c	C2/c	Pbna
Crystal System	Monoclinic	Monoclinc	Monoclinc	Orthorhombic
T	RT	−30°C	−100°C	RT
R_F	11.8%	5.89%	3.6%	5.4%
R_w	25%	5.36%	3.9%	
Intrachain Fe-Fe, Å	10.84	10.415	10.305	10.616
C_5Me_5-Anion, Å	3.67	3.51	3.44	3.564
Interchain Fe-Fe, Å	8.628 9.635 10.111 10.382	8.603 8.732 9.651	8.60 9.567 9.939	8.691 9.723 10.033
Mossbauer, 1.4K	12 lines	6 lines	1 line	6 lines
ΔH_{INT}, KOe	404,449	424		451
Magnetism	Metamagnetic	Ferromagnetic	Paramagnetic	Paramagnetic
ESR[a](RT) g	2.0058;	no bulk signal >5°K	--	2.028
H_{pp}	22 Oe			80^b; 525^b Oe

[a] polycrystalline sample; [b] superposition of a narrow and broad signal

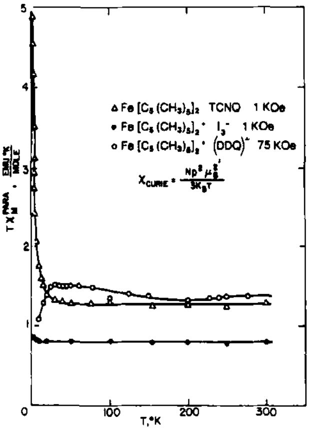


FIGURE 2

Temperature dependence of the magnetic susceptibility of several $Fe(C_5Me_5)_2^+$ salts.

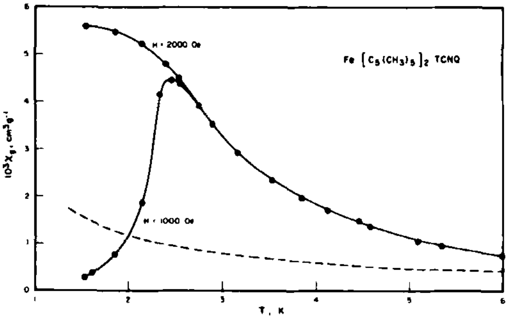


FIGURE 3

The low temperature magnetic susceptibility the 1-D salt of $Fe(C_5Me_5)_2^+$-$(TCNQ)^{\overline{\cdot}}$. The dashed line is the paramagnetism of the high temperature susceptibility extrapolated to lower temperatures.

[e.g., I_3^-, $(TCNQ)_2^{2-}$, and $[(NC)_2C(C_6H_4)C(O)(CN)]^-$ exhibit Curie like behavior while the 1-D salt exhibits Curie-Weiss behavior (θ=3°K). Hence, at low temperatures the susceptibility, χ, of the latter compound, increases dramatically, Fig. 2. For magnetic fields <1.5 KOe the material behaves as an antiferromagnet ($T_N \sim 2.55$°K), Fig. 3 whereas above the 1.5 KOe critical field the substance exhibits ferromagnetism.[4] This metamagnetic behavior[5] is most clearly seen in the magnetic moment, σ, vs. applied magnetic field, H, curves as a function of temperature, Fig. 4. Recently we have noted that $Fe(C_5Me_5)_2(TCNQ)$ exhibits a strong esr signal at room temperature (g=2.006) which rapidly loses intensity below 70°K such that no apparent signal persists below 30°K, Fig. 5. This effect appears to be correlated to the onset of high field ferromagnetism.

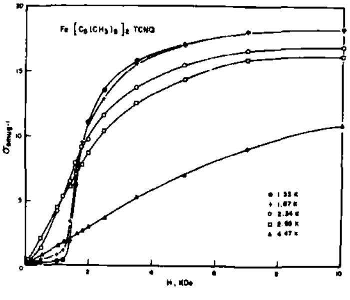


FIGURE 4

Isothermal plots of magnetic moment, σ, as a function of applied magnetic field, H. The sample is composed of small crystals of $Fe(C_5Me_5)_2^{+\cdot}$-$(TCNQ)^{\cdot-}$ as a pressed pellet.

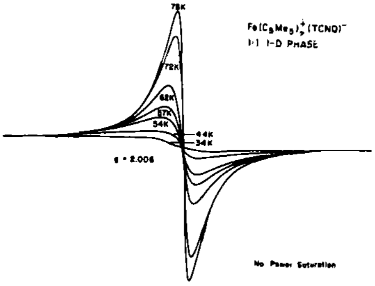


FIGURE 5

Temperature dependence of esr signal from 1-D $Fe(C_5Me_5)_2^{+\cdot}$-$(TCNQ)^{\cdot-}$

Mossbauer spectroscopy (^{57}Fe) clearly shows a singlet characteristic of ferrocenium above 4°K; however, at lower temperatures a pair of six line spectra at the same isomer shift gradually appears, Fig. 6. These six line spectra are due to novel slow paramagnetic relaxation in the spin doublet state of $\underline{1}^{+\cdot}$ in zero external field. These results indicate the importance of the spin density on the radical TCNQ anion.[6] The anion spin leads to an internal dipolar field at the S=1/2 Fe(III) sites, small Zeeman splitting, onset of relaxation broadening and ultimately fully resolved hyperfine splitting.[7] At low temperature (∿1.4°K) the relaxation becomes slow enough so as to see a pair of hyperfine split fields, H_{INT}, of 404 and 449 KOe. The two inequivalent six line patterns suggest inequivalent iron sites in the lattice that were not resolved in the original room temperature structure.[8] The details of the cooperative magnetic interactions have not been completely elucidated at the present time.

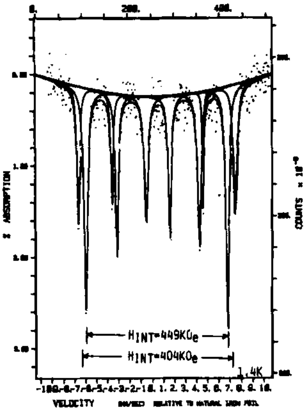


FIGURE 6 Pair of six lines hyperfine split ^{57}Fe Mossbauer resonances. This is the limiting spectra (1.4°K)

$[DDQ]^{\dot{-}}$ COMPLEX

Replacement of $(TCNQ)^{\dot{-}}$ with $(DDQ)^{\dot{-}}$ in the structure nominally does not change the solid state 1-D structure; however, cooperative magnetic interactions are not observed.[9] The reasons for the different $\chi(T)$ behavior are unknown at the present and are under reevaluation. Initially it was thought that the anion was diamagnetic $DDQH^{-}$; however, after noting that complex exhibited a six line hyperfine split ^{57}Fe Mossbauer spectrum (H_{INT}=451 KOe at 1.4°K) in zero field that was similar to that observed for the $(TCNQ)^{\dot{-}}$ salt (vide supra) we proposed that the anion was not S=0 $DDQH^{-}$ but S=1/2 $(DDQ)^{\dot{-}}$.[7] Recently from esr, vibrational and electronic spectra, we have confirmed it to be S=1/2 $(DDQ)^{\dot{-}}$.[10] The esr of the $(DDQ)^{\dot{-}}$ salt is more complex than that of the $(TCNQ)^{\dot{-}}$ salt. A signal which is made up of a broad (ΔH_{pp}=525 Oe) and a narrow line (ΔH_{pp}=80 Oe) at g=2.028 is observed at room temperature at 103°K. Below ∿40°K a half-field absorptive feature starts to grow in at g=4.351 and becomes dominant at 5°K. This feature is probably associated with $(\underline{1})^{\dot{+}}$.[11]

[TCNE]$^{\dot{-}}$ COMPLEX

The (TCNE)$^{\dot{-}}$ salt of Fe(C$_5$Me$_5$)$_2^{\dot{+}}$ also forms a 1-D chain structure. Attempts to grow crystals of Fe(C$_5$Me$_5$)$_2^{\dot{+}}$(TCNE)$^{\dot{-}}$ proved extremely difficult due to the air sensitivity of (TCNE)$^{\dot{-}}$ and the acetonitrile molecule of solvation. Attempts to recrystallize the (TCNE)$^{\dot{-}}$ complex lead to isolation of 1-D Fe(C$_5$Me$_5$)$_2^{\dot{+}}$-[(NC)$_2$C=C(CN)-C(CN)$_2$]$^{\dot{-}}$ which arises from oxidative disproportionation of (TCNE)$^-$.[12] Also, attempts to harvest crystals suitable for single crystal x-ray diffraction continually failed as loss of solvent lead to isolation of apparent single crystals which exhibited diffraction typical of powders. Growing a single crystal in a capillary at low temperature (-30°C) in the diffractometer finally enabled the determination of the structure.[13] This charge transfer salt is esr silent down to 5°K and exhibits a magnetically dipolar split six-line ^{57}Fe Mossbauer spectra at low temperature with H_{INT}=425 KOe. Preliminary magnetic susceptibility measurements characterize this compound as obeying Curie-Weiss relationship with $\theta > 0$. Thus, the material is ferromagnetic.

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