

MAGNETIC MOLECULAR CHARGE TRANSFER COMPLEXES

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ABSTRACT

The charge transfer complex $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^-$ \nless unlike either $[\text{Co}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^-$ or $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{C}_3(\text{CN})_5]^-$ exhibits spontaneous magnetization in zero applied field and is a bulk ferromagnet. These three compounds possess the same structural motif, namely, linear chains of alternating cationic donors and anionic acceptors. The high temperature magnetic susceptibility obeys the Curie-Weiss expression with $\theta = +30$, -1.0 , and -1.2 K, respectively, and the latter pair of complexes possess weak antiferromagnetic coupling. The ferromagnet exhibits zero field Zeeman split ^{57}Fe Mossbauer spectra with an internal field of 425.6 kOe at 4.23 K.

INTRODUCTION

We have deliberately sought to prepare a molecular-based ground state bulk ferromagnet since our observation that 1-D 1:1 $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNQ}]^-$ \nless exhibited metamagnetic behavior [1]. Using permethylated metallocenium cations we have prepared a series of charge transfer complexes with a variety of radical anion acceptors in order to elucidate the critical structure-function relationships that might ultimately lead to the preparation of a molecular-based ferromagnet. With the specific goal of increasing the spin density we sought a smaller planar radical anion and selected $S = 1/2$

* Abbreviations: TCNE = tetracyanoethylene, $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane, *p*-($\text{NC})_2\text{CC}_6\text{H}_4\text{C}(\text{CN})_2$.

tetracyanoethyleneide, $[\text{TCNE}]^{\cdot-}$. Herein we summarize the structure, ^{57}Fe Mossbauer, and field-dependent magnetic susceptibility data of the TCNE salt of decamethylferrocene, $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$, which characterizes this charge transfer salt as a 3-D ground state ferromagnet [2].

RESULTS

Structure

The $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$, $[\text{Co}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$, and $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{C}_3(\text{CN})_5]^-$ possess the same structural motif where the cation metallocene donors, **D**, and anion acceptors, **A**, form linear chains of alternating D's and A's, i.e., $\cdots\text{DADADA}\cdots$, Fig. 1. There are no intermolecular interactions less than the sum of the van der Waal radii.

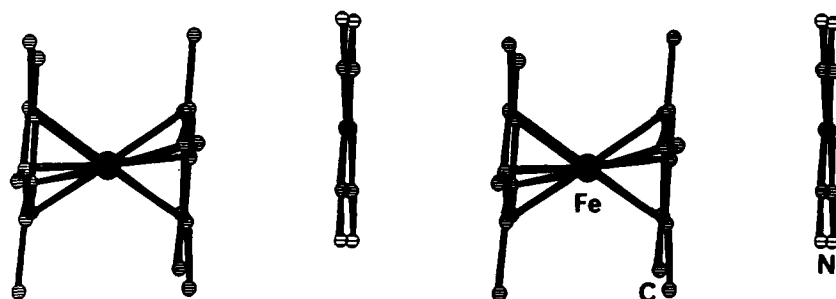


Fig. 1. Alternating donor/acceptor structure of 1-D $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$.

^{57}Fe Mossbauer Spectra

The room temperature ^{57}Fe Mössbauer spectra of 1-D $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$ consist of a narrow ($\Gamma = 0.323$ mm/s) single transition with an isomer shift ($\delta = 0.427$ mm/s) characteristic of low spin Fe(III). Below 12 K the complex exhibits the onset of a Zeeman split spectra in zero applied field which is fully resolved at 10 K. At 4.23 K the internal field is 425.6 kOe which is substantially greater than the expected 110 kOe/spin on the iron atom. In contrast the ^{57}Fe Mössbauer spectra of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{C}_3(\text{CN})_5]^-$ does not exhibit any evidence for zero field Zeeman split spectra above 1.7 K. The $S = 1/2$ $[\text{TCNE}]^{\cdot-}$ radical anion is a dipolar field which induced the Zeeman splitting for the former complex, but not the latter as the anion is $S = 0$.

Magnetic Susceptibility

The magnetic susceptibility of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$, $[\text{Co}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$, and $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{C}_3(\text{CN})_5]^-$ above 1.7 K has been measured by the Faraday technique. The data obeys the Curie-Weiss law, $\chi = C/(T - \theta)$, with $\theta = +30$, -1.0 , and -1.2 K for $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$, $[\text{Co}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$, and $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{C}_3(\text{CN})_5]^-$, respectively, Fig. 2. Thus, $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^{\cdot-}$ has dominant ferromagnetic interactions; whereas the latter pair of complexes comprised of either a $S = 1/2$ donor or

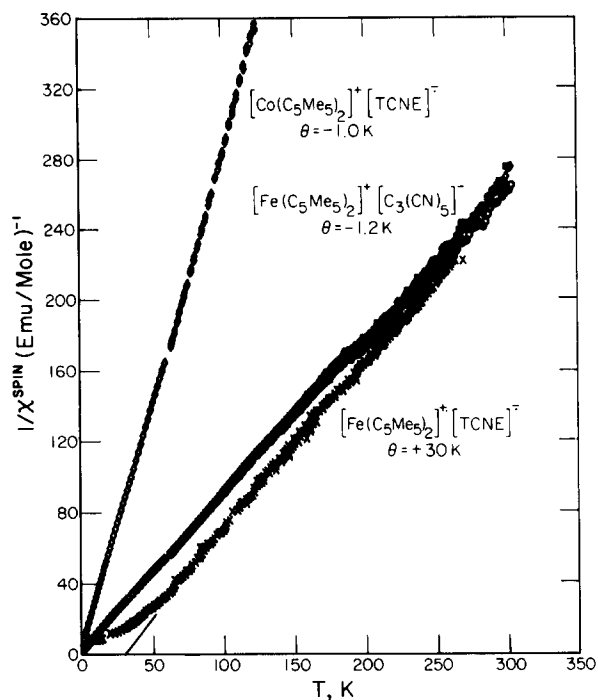


Fig. 2. Fit to the Curie-Weiss expression of χ^{-1} vs. T for $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^-$ (75 kOe), $[\text{Co}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^-$ (20.5 kOe), and $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{C}_3(\text{CN})_5]^-$ (20.5 kOe).

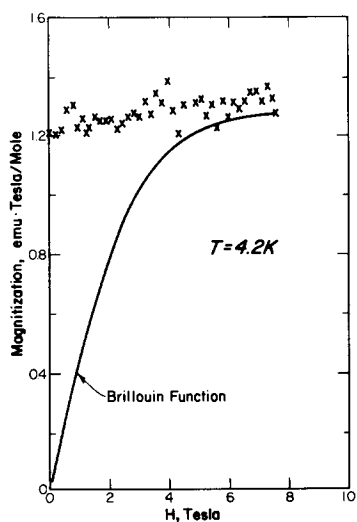


Fig. 3. Saturation magnetization of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^-$ as a function of field for $300 < H < 80,000$ Oe, at 4.2 K.

$S = 1/2$ acceptor, but unlike $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^-$ which possesses both a $S = 1/2$ donor and $S = 1/2$ acceptor, only weak antiferromagnetic behavior is observed above 1.7 K. For $T > 16$ K preliminary calculations suggest that the data can be fit by a 1-D Heisenberg model with ferromagnetic exchange [2]. For polycrystalline samples the magnetization saturates to a value of $1.1 (\pm 0.1) \cdot 10^4$ emu-Oe/mol above 300 Oe, Fig. 3. In zero applied field spontaneous magnetization is observed. Using a modified Faraday technique [3] the $M(H,T)$ was measured for $H \geq 0$. Below 4.5 K the magnetization saturates to $1.1 (\pm 0.1) \cdot 10^4$ emu-Oe/mol at progressively lower applied fields, Fig. 4. In zero applied field a spontaneous magnetization of $\sim 2 \cdot 10^3$ emu-Oe/mol is observed, Fig. 4. The decrease in magnetization may be due to orientational effects in the polycrystalline sample, domain, formation, or ferrimagnetic behavior. The latter is unlikely as the $\chi^{-1}(T)$ data is atypical for a ferrimagnet [4]. The shapes of the $M(H,T)$ curves are qualitatively as expected for a 3-D bulk ferromagnet.

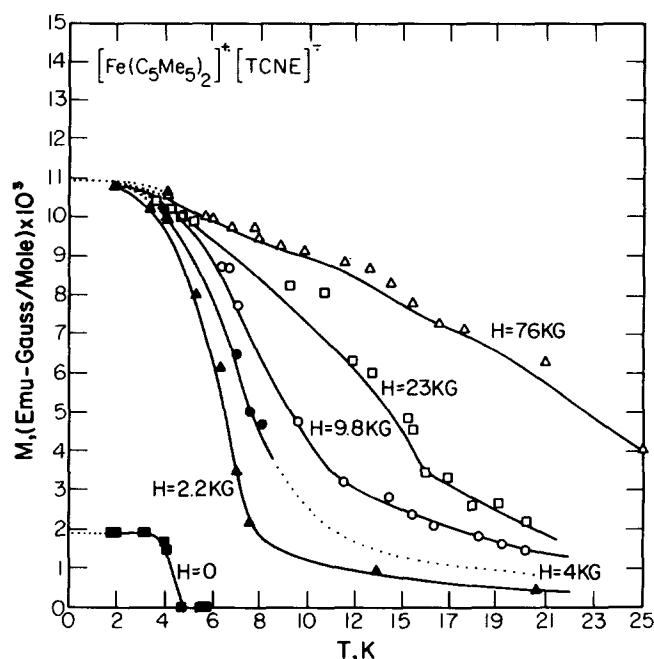


Fig. 4. Temperature dependence of the magnetization as a function of applied field, $M(H,T)$, for polycrystalline samples of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ \cdot [\text{TCNE}]^-$.

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