

Ferromagnetic Properties of One-dimensional Decamethylferrocenium Tetracyanoethylenide (1 : 1): $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2]^+\text{[TCNE]}^-$

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$[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+\text{[TCNE]}^-$ has been characterized by magnetic susceptibility to possess dominant ferromagnetic interactions; its structure has been determined by X-ray crystallography.

Since our observation of metamagnetism in the one-dimensional phase of 1:1 decamethylferrocenium 7,7,8,8-tetracyano-*p*-quinodimethanide¹ we have investigated the role of different acceptors with $\text{Fe}(\text{C}_5\text{Me}_5)_2$ (**1**), with the deliberate goal of identifying the critical structural and electronic structure-function relationships that might ulti-

mately lead to the preparation of ferromagnetic organometallic and/or organic compounds. Herein we report the synthesis, and preliminary Mössbauer and magnetic susceptibility data of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+\text{[TCNE]}^-$ (TCNE = tetracyanoethylene) which characterizes this charge-transfer complex as a ferromagnet.

The complex (**1**)⁺[TCNE]⁻ was prepared from equimolar amounts of (**1**) and TCNE in acetonitrile and was crystallized at low temperature (*ca.* -30 °C) as dark green needles. Crystals obtained in this manner were used for physical

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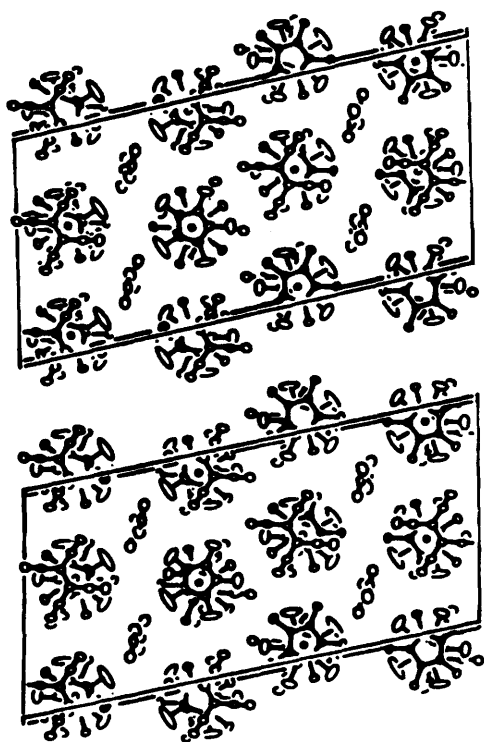


Figure 1. Stereoview of the structure of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+[\text{TCNE}]^- \cdot \text{MeCN}$, down the b -axis (chain axis).

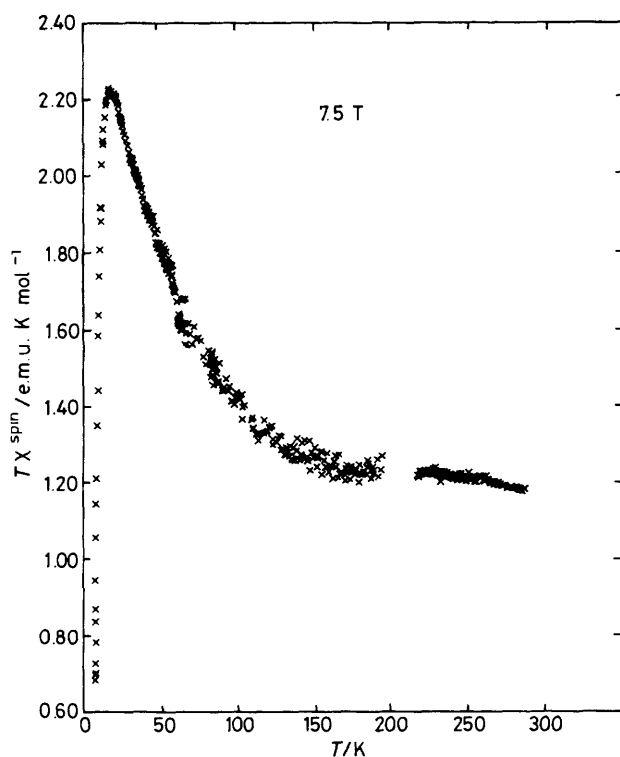


Figure 2. χT vs. T at 75 kG for $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+[\text{TCNE}]^-$. The decrease in χT below 16 K results from the saturation of magnetization [and hence $\chi (\equiv M/H)$] together with the decrease in T .

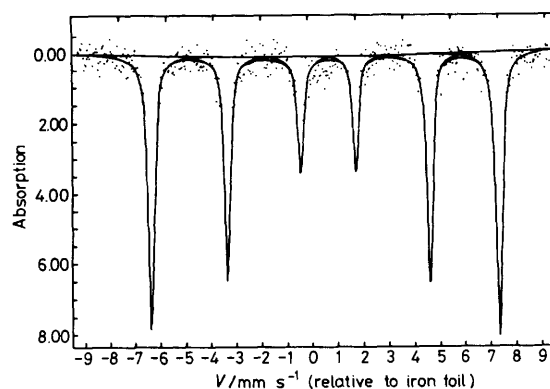


Figure 3. Low temperature (4.23 K) ^{57}Fe Mössbauer spectra of $\text{Fe}(\text{C}_5\text{Me}_5)_2^+[\text{TCNE}]^-$. The observed data are represented by dots. The narrow linewidths ($\langle \Gamma \rangle$ 0.28 mm/s) indicate a small quadrupole perturbation of the Zeeman spectrum (not resolved in the rapidly relaxing paramagnetic (temperature regime spectra), *i.e.*, the shift $\Delta_{1-2} - \Delta_{5-6} = 0.28$ mm/s, $H_n = 424$ kG).

studies; however, such crystals did not diffract well and were judged to be polycrystalline. Crystals suitable for single crystal X -ray analysis were grown in a capillary in the diffractometer at -30°C .[‡] The structure contained a molecule of acetonitrile of solvation which was easily lost upon conventional filtering techniques.[§] The structure consists of linear chains of alternating $(1)^+$ donors (D) and $[\text{TCNE}]^-$ acceptors (A) in a $\cdots\text{DADADA}\cdots$ arrangement (Figure 1). This linear chain arrangement was observed for the $[\text{DDQ}]^-$ ($\text{DDQ} = 2,3$ -dichloro-5,6-dicyanoquinodimethane),² $[\text{TCNQ}]^-$,¹ and $[\text{C}_3(\text{CN})_5]^-$ charge transfer salts of $(1)^+$. The key structural findings are the intrachain $\text{Fe}^{\text{III}}-\text{Fe}^{\text{III}}$ distance of 10.415 Å and the interchain $\text{Fe}^{\text{III}}-\text{Fe}^{\text{III}}$ distances of 8.732, 8.603, and 9.651 Å. The $[\text{TCNE}]^-$ is planar and tilted 2.8° with respect to the C_5Me_5 ring.

The magnetic susceptibility of $(1)^+[\text{TCNE}]^-$ was measured by the Faraday technique between 1.7 and 300 K and fields between 300 and 80 000 G. Above 60 K the complex obeys the Curie-Weiss expression, *i.e.*, $\chi = C/(T - \theta)$, $\theta = 30$ K, thereby characterizing this complex as having dominant, ferromagnetic interactions. The enhanced susceptibility,

[‡] *Crystal data*: Monoclinic, space group $C2/c$; $a = 16.250(3)$, $b = 10.415(2)$, $c = 32.851(9)$ Å, $\beta = 101.76(2)^\circ$; $U = 5443$ Å³, $Z = 8$, $R = 5.9\%$, $R_w = 5.4\%$. Room temperature film data taken on the desolvated sample show that upon loss of MeCN the unit cell becomes orthorhombic with unit cell axes of 10.59, 4.46, and 16.02 Å. This corresponds to either the a or b -axis remaining the same while the c -axis is halving and shrinking due to solvent loss; or alternatively the b -axis remaining the same while the a -axis shrinks, and the c -axis halves. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[§] Attempts to recrystallize $(1)^+[\text{TCNE}]^-$ under ambient conditions lead to the conversion of $S = 1/2$ $[\text{TCNE}]^-$ into $S = 0$ $[\text{C}_3(\text{CN})_5]^-$ isolated as the $(1)^+$ salt. This $[\text{C}_3(\text{CN})_5]^-$ salt was subsequently characterized by single-crystal X -ray diffraction and exhibits similar structural features to the $[\text{TCNE}]^-$ salt. The conversion of $[\text{TCNE}]^-$ into $[\text{C}_3(\text{CN})_5]^-$ and $[\text{C}_2(\text{CN})_3\text{O}]^-$ has been previously established (O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, 1962, **84**, 3678); however, crystals containing $[\text{C}_2(\text{CN})_3\text{O}]^-$ were not observed. A ferrocenium salt of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]_1[\text{C}_2(\text{CN})_3\text{O}]_1$ composition has been reported (B. W. Sullivan and B. M. Foxman, *Organometallics*, 1983, **2**, 187).

measured at 75 kG, is seen in the plot of $T\chi$ vs. T (Figure 2). For temperatures down to 16 K (the maximum in Figure 2) preliminary calculations suggest that the data can be fitted by a one-dimensional Heisenberg model with ferromagnetic exchange.^{3¶} For the polycrystalline samples the magnetization at 4.23 K saturates to a value of $1.1 \pm 0.1 \times 10^4$ e.m.u. G/mol even at the lowest fields measured (*i.e.*, 300 G). Unlike $(1)^{+\cdot}$ [TCNQ] $^{\cdot-}$, we do not have any evidence for metamagnetism, *i.e.* $(1)^{+\cdot}$ [TCNE] $^{\cdot-}$ has a ferromagnetic ground state at 300 G as opposed to the antiferromagnetic ground state observed for $(1)^{+\cdot}$ [TCNQ] $^{\cdot-}$.¹ No e.s.r. signal ascribable to the bulk could be observed above 5 K.

At ambient temperature the ^{57}Fe Mössbauer spectrum exhibits a single transition characterized by a relatively narrow linewidth ($\Gamma \sim 0.323$ mm/s), *i.e.*, no resolved quadrupole interaction, and an isomer shift relative to natural iron of 0.427 mm/s. These values are typical of ground state spin-doublet ferrocenium ions.⁴ In general, below 20 K $(1)^{+\cdot}$ [anion] $^{\cdot-}$ systems² exhibit resolved magnetic hyperfine splittings suggesting various combinations of slow paramagnetic relaxation broadening and co-operative three-dimensional ordering processes depending on the radical anion. For $(1)^{+\cdot}$ [TCNE] $^{\cdot-}$ the 4.23 K spectrum in zero applied magnetic field corresponds to a single internal hyperfine field, H_n , of 424 kG (Figure 3). The latter value of H_n is anomalously large in view of the usual expectation of 110 kG/spin on the iron atom from the Fermi contact (H_f) contribution and suggests a dominant orbital contribution (H_L) to H_n . High-field Mössbauer spec-

troscopic experiments bearing on the nature of H_n for these materials are in progress. The hyperfine splitting process for $(1)^{+\cdot}$ [TCNE] $^{\cdot-}$ initiates at ~ 12 K and is nearly fully resolved at 10 K. This process is essentially coincident with the inflection point in the low magnetic field susceptibility data and is fully consistent with co-operative three-dimensional ferromagnetic ordering for which the Curie temperature, T_c , is estimated to be 16 K from consideration of both the susceptibility ($H > 300$ G) and zero-field Mössbauer spectroscopy data. A more precise value for T_c awaits heat capacity measurements. In addition, careful Mössbauer lineshape analysis for the spectra taken around T_c should enable us to establish whether the linewidth broadening is due to single ion relaxation or to a co-operative effect involving solitons in a one-dimensional magnet.⁵

W. M. R. and J. H. Z. gratefully acknowledge support from a N.S.F. D.M.R. Solid State Chemistry Program grant. J. S. M. gratefully acknowledges stimulating discussions with Dr. Owen Webster (Du Pont C.R. & D.D.) and the low temperature e.s.r. data taken by P. J. Krusic and D. Jones (Du Pont C.R. & D.D.).

Received, 30th December 1985; Com. 1818

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¶ Ferromagnetic coupling of the free radical spins has been suggested for charge-transfer compounds of this type where the donor has an $S = 1/2$ e^3 ground state such that electron transfer would form an $S = 0$ acceptor and an $S = 1$ donor (H. McConnell, as quoted and discussed in R. Breslow, *Pure Appl. Chem.*, 1982, **54**, 927; R. Breslow, B. Jaun, R. Q. Kluttz, and C-Z. Xia, *Tetrahedron*, 1982, **38**, 863). Thus, this model predicts a contribution from $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{2+}[\text{TCNE}]^{2-}$. Although evidence in the literature exists for the dianion, none exists for the dication. The consequences of this model for our compound are under investigation.