result strongly suggests that mononuclear products can be formed in reactions involving II as the intermediate.

Acknowledgment. We thank Professor Mark Wrighton for sending us preprints of his papers in advance of publication. Helpful discussions with Dr. V. M. Miskowski are acknowledged. This research was supported by the National Science Foundation (CHE75-19086).

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(9) In contrast to the results for R = Ph and O-*i*-Pr, the photoreaction of $P(OMe)_3$ with $Cp_2Fe_2(CO)_4$ in cyclohexane at room temperature ($\lambda \geq 500$ nm) gives exclusively $Cp_2Fe_2(CO)_2[P(OMe)_3]_2$. This reaction does not necessarily involve homolytic cleavage, however, as we have found that III reacts thermally with $P(OMe)_3$ to give $Cp_2Fe_2(CO)_2[P(OMe)_3]_2$. Thus a pathway involving II as the intermediate is a distinct possibility. Details will be presented in a subsequent paper.

(10) It is conceivable that only monosubstituted products could result from homolytic cleavage of the Fe–Fe unit if two substituted fragments, $CpFe(CO)(PR_3)$, were sterically unable to combine to form a dimer. The Stern–Volmer plot rules out this alternative for R = Ph, however. If the fragments generated by homolysis reacted with PPh_3 by an associative pathway, then the Stern–Volmer line extrapolated from the region of high values of $[PPh_3]^{-1}$ would pass through the origin. If the fragments reacted by a dissociative mechanism, then the quantum yield would not depend on $[PPh_3]$ under the conditions used in our experiments.

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Metamagnetic Properties of One-Dimensional Decamethylferrocenium 7,7,8,8-Tetracyano-*p*-quinodimethanide (1:1): $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+}\cdot(TCNQ)^{-}\cdot$

Sir:

In the preceding paper the crystal and molecular structure of the paramagnetic decamethylferrocenium 7,7,8,8-tetracyano-*p*-quinodimethanide dimer $[(DMeFc)^{+}\cdot]_2(TCNQ_2)_2{}^{2-}$ [1a] (**1**) and one-dimensional (1 − D) $(DMeFc)^{+}\cdot(TCNQ)^{-}\cdot$ (**2**)[1b] was reported. At low temperatures **2** exhibits unusual magnetic properties which are consistent with a metamagnetic behavior.[2] A metamagnet exhibits either antiferromagnetic or ferromagnetic behavior depending on the magnitude of the applied external magnetic field. Herein we report the magnetic and Mössbauer properties of **2** and a preliminary model which describes the data.

The magnetic properties of **1**, **2**, and $DMeFc^{+}I_3{}^{-}$ (**3**) have been measured. Complex **2** obeys the Curie–Weiss expression, i.e., $\chi = c/(T - \theta)$ ($\theta = +3$ K), above 3 K, whereas **1** and **3** are similar to the ferrocenium analogue[3] and obey a simple Curie law, i.e., $\theta = 0$ K. Between 3 and 50 K the onset to ferromagnetism is observed for **2** at all magnetic fields. Below 2.5 K and at applied magnetic fields less than 1500 Oe, **2** exhibits antiferromagnetic behavior, and at applied magnetic fields greater than 1500 Oe, a ferromagnetic behavior is observed (Figure 1).

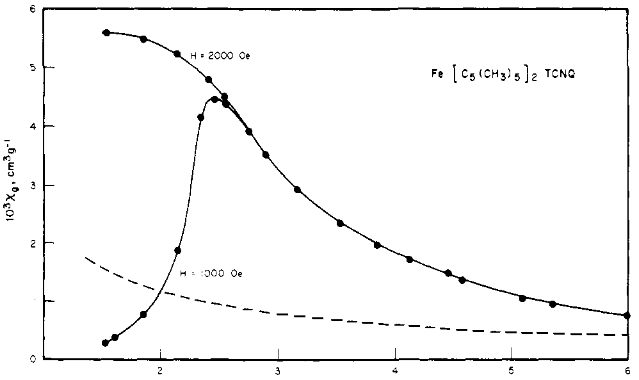

Figure 1. The magnetic susceptibility as a function of temperature between 1.5 and 6 K for **2**. The dashed line is the paramagnetism of the high temperature susceptibility extrapolated to lower temperatures. Complex **2** is antiferromagnetic below 1500 Oe and ferromagnetic above 1500 Oe.

Above 50 K the susceptibility of **2** is greater than that of **1** or **3** by one additional spin per repeat unit. The additional susceptibility arises from paramagnetic $TCNQ^{-}\cdot$ ions. This $Fe^{III}\text{-}TCNQ^{-}\cdot$ formulation results in two unpaired electrons per repeat unit and give a susceptibility in accord with the observed data. At high magnetic fields and low temperatures, the saturation moment is very close to two unpaired spins per repeat unit. This is in excellent agreement with the high temperature susceptibility. ESR data taken at 10 K do not yield any signal presumably owing to relaxation effects.[8]

The ^{57}Fe Mössbauer data taken above 4 K, **2** shows $S = 1/2$ Fe^{III}. The spectra show a single line with a quadrupole splitting of <0.3 mm s^{-1} and an isomer shift with respect to iron metal (298 K) of 0.65 (2), 0.59 (2), and 0.50 (2) mm s^{-1} at 4, 78, and 298 K, respectively. These results correspond closely to the Mössbauer data reported for ferrocenium bromide[5a] and picrate.[6b] These complexes also exhibit near-zero quadrupole splitting and isomer shifts between 0.42 and 0.58 mm s^{-1} at 78 K. In contrast decamethylferrocene, like ferrocene,[5a] exhibits a room temperature quadrupole split (2.45 mm s^{-1}) doublet at 0.42 mm s^{-1} (with respect to iron metal at 298 K).

To further confirm the metamagnetic transition the magnetic moment, σ, was obtained as a function of external magnetic field, H, at various temperatures above and below the Neél temperature, T_N, of 2.55 K (Figure 2). At lower temperatures a sharp transition is observed for **2**. The dependence of the magnetic moment on the applied field is characteristic of a metamagnet;[2,6] however, in contrast to previously reported metamagnets, e.g., $Co^{II}Cl_2$,[2a] $Fe^{II}Cl_2$,[2a] $Co^{II}(pyridine)_2Cl_2$,[2a] and $Co[PhCONHCH_2CO_2]_2\cdot 5H_2O$,[2b] **2** is not derived from an extended covalent bonding network. Long-range magnetic order presumably arises from a one-dimensional donor–acceptor interaction.

The observed metamagnetism may be understood in terms of a simple singlet–triplet model in which the Zeeman splitting γH of the triplet level may exceed the energy separation Δ between the triplet and singlet levels in zero externally applied magnetic field H. Here γ is the intrinsic moment of the triplet state. For N independent singlet–triplet assemblies, the magnetic moment induced by a field H at temperature T will be

$$\sigma = 2N\gamma[\sinh(\gamma H/kT)]/[e^{-\Delta/kT} + 1 + 2\cosh(\gamma H/kT)] \quad (1)$$

where k = Boltzmann's constant. At $T = 0$ K, eq 1 predicts an abrupt transition from a diamagnetic to a ferromagnetic state

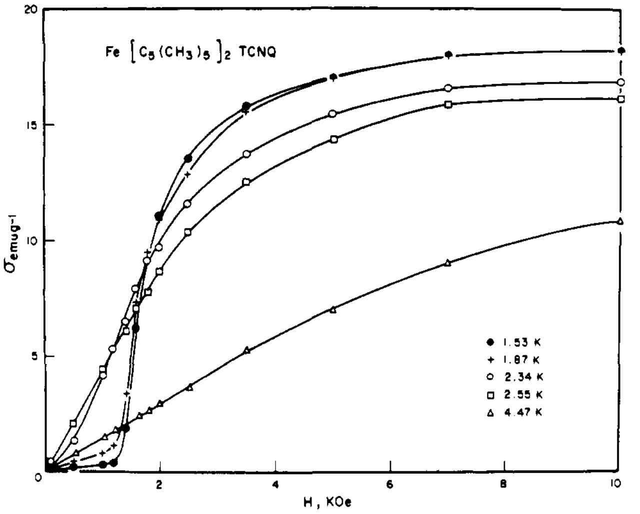

Figure 2. Isothermal plots of magnetic moment, σ, as a function of applied magnetic field, H. The sample is composed of small crystals of **2** as a pressed pellet.

of total moment $\sigma = N\gamma$ to occur at the critical field $H_c = \Delta/\gamma$. At finite T the transition will still be abrupt (although thermally broadened) provided that, at $H = H_c$, $T < \Delta/k \equiv T_N$. For $T > T_N$ the transition is thermally quenched and $\sigma = N\gamma \sinh(\gamma H/kT)/(1 + \cosh(\gamma H/kT))$ becomes a smooth function of H. It may be verified from eq 1 that the low-field slope, $(\partial\sigma/\partial H)_T$ ($T \rightarrow 0$ K), is predicted to increase with temperature for $T < T_N$. These features are in qualitative accord with the data of Figure 1 ($T_N = \Delta/k = 2.55$ K). Further development and consequences of the model will be published elsewhere.

This model, however, does not rule out the more conventional ideas of two magnetic lattices (one anti and the other ferromagnetic) coupled, but the model gives a surprisingly good fit of the data which is not possible within the conventional model.

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Crystal and Molecular Structure of the Paramagnetic 1:1 Decamethylferrocenium 7,7,8,8-Tetracyano-*p*-quinodimethanide Dimer Salt: $\{[Fe(C_5Me_5)_2]^{+}\cdot\}_2(TCNQ)_2{}^{2-}$

Sir:

In the past few years there has been an interest in the chemical and physical properties of the reaction products between inorganic complexes and 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ.[1,2] Such materials exhibit high electrical conductivity, unique structures, and in some cases unusual oxidation states. For example, 1:2 ferrocene complexes of TCNQ were first reported in 1962 to exhibit high electrical conductivity.[2] In order to understand the properties of this class of charge-transfer complexes and in particular to form a volatile complex (which permits the unique physical studies performed on tetrathiofulvalenium TCNQ,[3] (TTF)(TCNQ), to be extended), a series of new TCNQ complexes with decamethylferrocene, DMeFc, namely 1:1 paramagnetic (phase I), metamagnetic (phase II),[4] and a 1:2 salt were prepared. Herein we report the molecular and crystal structure of the paramagnetic 1:1 salt of decamethylferrocene and TCNQ, $(DMeFc^{+}\cdot)_2(TCNQ)_2{}^{2-}$ (**1**).

The dark purple reflecting salt, **1**, which forms flat-plate crystals from 1:1 solutions of DMeFc and TCNQ in acetonitrile[5] upon standing for long periods of time, belongs to the monoclinic $P2_1/c$ (C_{2h}^5, No. 14) space group ($a = 9.7076$ (12), $b = 12.2113$ (17), $c = 23.5849$ (36) Å; $\beta = 95.012$ (2)°; $Z = 4$; and $\rho_{calcd} = 1.265$ g cm^{-3} ($\rho_{obsd} = 1.269$ g cm^{-3} by flotation in cyclohexane and 1,2-dibromoethane)). The structure was determined by a combination of Patterson, direct methods, Fourier, and least-squares refinement techniques to an $R_f = 0.058$ for the 3042 independent observable reflections ($F_{obsd} > \sigma F_{obsd}$) from a total of 3667 reflections collected on a Syntex $P2_1$ automated diffractometer to $2\theta \leqslant 45°$ (Mo K$\bar{\alpha}$).

The crystalline lattice consists of isolated units of $Fe(C_5Me_5)_2/TCNQ/TCNQ/Fe(C_5Me_5)_2$, i.e., dimers of A:B:B:A composition, Figure 1. This result differs from the donor-acceptor complexes reported for ferrocene tetracyanoethylene[6a] and phase I (DMeFc)(TCNQ)[4b] and proposed for ferrocene bis(arene)iron(II).[6b] This is probably due in part to the complete charge transfer in **1** and the tendency of $TCNQ^{-}\cdot$ to dimerize. The A:B:B:A units do not form infinite 1-D chains as previously reported for $Nb_3Cl_6(C_6Me_6)_3(TCNQ)_2$.[1b] Within each dimeric unit the $DMeFc^{+}\cdot$ ion is oriented such that the two C_5 rings are parallel and directly above a $(TCNQ^{-})_2$ ion with the result that the C_{13} of the $TCNQ^{-}\cdot$ lies approximately in the center of the C_5 ring (Figure 1), and the interplanar distance between the C_5 ring and the $TCNQ^{-}\cdot$ ion is 3.554 Å. Like $Fc^{+}\cdot BiCl_4{}^{-}$ [7] the $DMeFc^{+}\cdot$

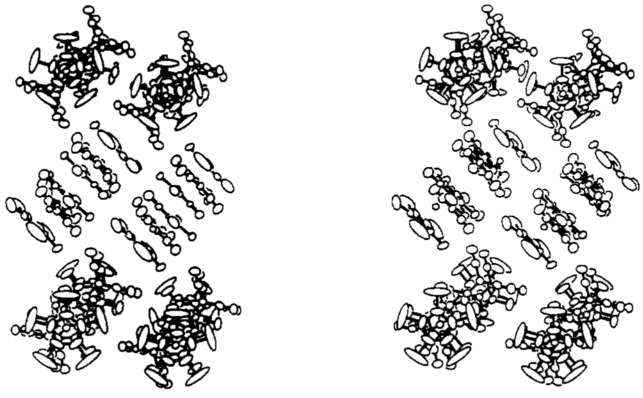

Figure 1. A stereoview of the parallel and perpendicular A:B:B:A (A = $DMeFc^{+}\cdot$; B = $TCNQ^{-}\cdot$) units within the $TCNQ^{-}\cdot$ lattice. Half of the units which lie within the plane of the drawing have been omitted for clarity.

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