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T. David Harris
Marshall University

Michael Castellani
Marshall University, castella@marshall.edu

Arnold L. Rheingold

William M. Reiff

Gordon T. Yee

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T. David Harris,[†] Michael P. Castellani,[,†] Arnold L. Rheingold[‡], William M. Reiff[&] and Gordon T. Yee*[,#]*

[†] Department of Chemistry, Marshall University, Huntington, WV 25755

[‡] Department of Chemistry and Biochemistry, University of California at San Diego, San Diego, CA 92093

[&]Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115

[#]Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

castella@marshall.edu, arnrhein@chem.ucsd.edu; w.reiff@neu.edu, gyee@vt.edu

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Structure and Properties of [Fe(C$_5$EtMe$_4$)$_2$]$^+$[TCNE]$^-$

1,1´-Diethyl-2,2´,3,3´,4,4´,5,5´-octamethylferrocene has been utilized as a one-electron donor in the synthesis of a tetracyanoethylene charge-transfer salt, [Fe(C$_5$EtMe$_4$)$_2$]$^+$[TCNE]$^-$. Structural

characterization shows that it adopts an arrangement of anions and cations completely different from the usual π stacking seen in analogous decamethylferrocenium compounds. The TCNE radical sits along side of the ferrocene, nearly perpendicular to the planes of the C_5 rings. It crystallizes in the triclinic space group P-1 with unit cell dimensions a = 10.4024(9) Å, b = 10.7491(9) Å, c = 12.9992(11) Å and α = 75.656(2)°, $\square\beta$ = 77.715(2)° and γ = 67.9460(10)° and Z = 2. The nearly square geometry of the TCNE anion creates disorder over two orientations. $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$ is a simple paramagnet exhibiting neither long range magnetic order nor slow paramagnetic relaxation to the lowest measured temperatures (*ca.* 1.8 K) as determined by both ac and dc magnetic susceptibility and Mössbauer spectroscopy (*ca.* 1.3 K).

Introduction

Although dozens of magnetic charge-transfer salts incorporate decamethylmetallocenes as building blocks [1], related metallocene donors with other substituents have lacked this versatility. Whereas decamethylferrocene reacts with tetracyanoethylene to give a ferromagnet with T_c = 4.8 K, unsubstituted ferrocene combines with tetracyanoethylene to yield a diamagnetic non-ionic solid, $[FeCp_2][TCNE]$ because the donor is not sufficiently strong to reduce the acceptor [1]. The analogous salt $[Fe(C_5HMe_4)_2]^+[TCNE]^-$ has been reported to be paramagnetic, with ferromagnetic coupling (θ = 7 K), but does not order [2]. The compound $[Fe(C_5Et_5)_2]^+[TCNE]^-$ behaves similarly (θ = 7.5 K) [3]. $[Fe(C_5HMe_4)_2]^+[TCNE]^-$ has been crystallographically characterized and exhibits the usual donor-acceptor mixed stack arrangement of cations and anions which results in π overlap between the acceptors and the C_5 ring [1]. It is believed that $[Fe(C_5Et_5)_2]^+[TCNE]^-$ adopts a similar structure.

We have now prepared and characterized $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$. Surprisingly, the structural motif is entirely different from the commonly observed mixed stack, consisting instead of TCNE radical anions oriented side-on to the metallocene. Not unexpectedly, because this compound lacks the π stacking seen in magnetically ordering solids, it exhibits no evidence of significant magnetic exchange interactions.

Synthesis and Characterization

General Considerations. Preparation of air-sensitive compounds was carried out in a nitrogen-filled Vacuum Atmospheres glove box maintained at less than 5 ppm O_2 and by utilizing standard Schlenk techniques. Solvents (Fisher) were distilled from the appropriate drying agent under nitrogen: hexane (sodium/benzophenone), tetrahydrofuran (THF, potassium/benzophenone), diethylether (sodium/benzophenone), and dichloromethane (CaH_2). $Fe(C_5EtMe_4)_2$ was prepared by a minor modification of a literature procedures [4]. Tetracyanoethylene (Aldrich) was sublimed prior to use and stored in the glove box. $FeCl_2$ (Strem), 1.6 M n-butyl lithium in hexanes and C_5EtMe_4H (Aldrich) were used as received. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany.

Magnetic measurements. All the magnetic measurements were performed on a 7 Tesla Quantum Design MPMS SQUID magnetometer. Samples were prepared as previously described [5]. Measurements of magnetization as a function of temperature were performed from 2 K to 300 K in 5000 G applied field. Samples were cooled in zero field and measured upon warming. Diamagnetic corrections were applied based on Pascal's constants. The data were corrected for a small temperature independent paramagnetism term (~3 x 10^{-4} emu/mol) adjusted so that the inverse chi vs. temperature plot was linear.

Mössbauer Spectroscopy. Mössbauer spectroscopy measurements were conducted as described previously [6].

X-ray crystallography. Crystallographic data are collected Table 1. No symmetry higher than triclinic was observed. The centrosymmetric alternative was selected based on the absence of correlation effects. In this setting, the TCNE molecules are disordered in two coplanar, orthogonal

positions located on an inversion center in which the CN groups are shared equally. The structure was solved by direct methods and refined with all nonhydrogen atoms anisotropic and hydrogen atoms treated as idealized contributions. All software used the SHELXTL libraries as distributed by Bruker/Nonius, Madison, WI.

[Fe(C₅EtMe₄)₂]⁺[TCNE]⁻. Dichloromethane (10 mL) was added to a solid mixture of $Fe(C_5EtMe_4)_2$ (0.300 g, 0.846 mmol) and TCNE (0.106 g , 0.828 mmol). The dark green solution was filtered via cannula and layered with 10 mL hexanes to yield 0.308 g (0.638 mmol, 77%) of dark green crystals. Visible λ_{max} (CH$_2$Cl$_2$) 402, 408, 418, 428, 440, 446, 460, 650 (sh), 700 (sh), 780 nm. Calcd for $C_{28}H_{34}N_4Fe$: C, 69.71; H, 7.10. Found C, 69.16; H, 7.04.

Results and Discussion

A general mechanism for through-space magnetic exchange in molecule-based systems has not yet been elucidated. To address this problem, we have focused on preparing families of magnetic solids in which only through-space coupling exists. Charge-transfer salts present an attractive framework for these investigations because their synthesis is intrinsically modular and because we have found that the structure is tolerant, at least with decamethylmetallocene donors, to many different organic one-electron acceptor building blocks. By systematic modification of the building blocks to tune their steric or electronic properties, we hope to gain insights into the molecular level understanding of through-space coupling.

For the most part, research in this area has focused on changing the organic acceptor, while holding the donor decamethylmetallocene constant. This is due, at least in part, to the fact that few other donors have been found to support long-range magnetic order [1]. We have recently turned our attention to the possibility of making a minimal modification to decamethylferrocene and identified 1,1´-diethyl-2,2´,3,3´,4,4´,5,5´-octamethylferrocene as presenting one of the smallest changes to the electrochemical and structural properties. An added motivation for examining this set of donors was the observation that

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the crystal structures of $[CrCp*_2]^+[DEtDCF]^- \cdot 2CH_2Cl_2$ where DEtDCF is diethyl dicyanofumarate [7], and $[FeCp*_2]^+[TCNE]^- \cdot CH_3CN$ [8] are solvates and it was hoped that the flexibility of the added methylene groups in the title compound might negate the need for a solvent of crystallization.

The X-ray crystal structure of $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$ is displayed in Figs. 1 and 2. There are two independent half molecules of TCNE, each residing on an inversion center. Additionally, each TCNE ion is rotationally disordered, as shown, with the minor-occupancy positions drawn with dotted outlines. One of the ethyl groups is also disordered over two positions. Bond angles and distances within the $Fe(C_5EtMe_4)_2^+$ cation are similar to those in $Fe(C_5Me_5)_2^+$ [8]. The major difference between these structures arises because the terminal methyl group on the ethyl substituent in $Fe(C_5EtMe_4)_2^+$ lies distal to the metal atom on both faces of the C_5 ring. These out-of-plane methyl groups prevent the $TCNE^-$ anion from lying parallel planar to the C_5 ring as it does in $M(C_5Me_5)_2^+$ (M = Fe [8], Cr [9]) and $Fe(C_5HMe_4)_2^+$ [2]. Surprisingly, the $TCNE^-$ ion actually lies along side of the $Fe(C_5EtMe_4)_2^+$ ion in an orientation almost perpendicular to the plane of the C_5 ring.

The magnetic properties of $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$ are consistent with a paramagnet with no significant interactions between the spins. The plot of χT vs. T (Fig. 3) is essentially linear and only below 10 K does it drop off more sharply. Based on a fit of χ^{-1} vs. T to the Curie-Weiss law, C = 1.32 emu-K/mol and θ = –1.5 K. Assuming g = 2.0 for the organic radical, g = 3.17 is calculated for the decamethylferrocenium ion, consistent with previous reports of significant orbital contribution to the magnetic moment [10]. The downward curve could be the result of weak antiferromagnetic coupling or from the depopulation of low lying spin-orbit levels of the cations as opposed to incipient antiferromagnetic exchange, as has been reported for ferrocenium cations with diamagnetic anions [11]. The lack of ferromagnetic exchange as seen for other TCNE salts is perhaps not surprising given the orientation of the $TCNE^-$ radical relative to the metallocene cation and the presumed necessity of π stacking for strong magnetic exchange interactions.

The ambient temperature Mössbauer spectrum of this compound (Fig. 4) is asymmetrically broadened, consistent with an unresolved quadrupole doublet ($\Delta E \sim 0.2$ mm/s) with an isomer shift of

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~ 0.5 mm/s. These observations are fairly typical for $S = 1/2$ ferrocenium species [12]. At low temperatures, there is no evidence of spectral broadening or magnetic hyperfine splitting. The material appears to be a simple, rapidly relaxing paramagnet as suggested by the SQUID magnetization results (*vide supra*).

Conclusions

The modification made to the donor results in a compound with an unexpected, entirely different crystal packing motif and consequent magnetic properties consistent with very weak, perhaps non-existent magnetic exchange interactions at least at the limit of our low temperature capabilities. This result supports the general notion that π stacking is a prerequisite for strong coupling in this class of compounds. Future work will focus on examining the family of octamethylferrocenophane donors, which should provide the needed π stacked structure while still allowing us to systematically tune other properties.

Acknowledgments

Supporting Information Available

Crystal data in CIF format is available free of charge via the Internet at http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi.

FIGURE CAPTIONS

Fig. 1. The structure and labeling scheme for **1** with 30% thermal ellipsoid probabilities. Crystallographic disorder is discussed in the text.

Fig. 2. Unit cell of $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$.

Fig. 3. χT (squares) vs. T and χ^{-1} (diamonds) for $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$ measured in 5000 G.

Fig. 4. Mössbauer spectra for $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$ at 298 K and 1.5 K.

TABLE TITLE

Table 1. Crystallographic data for $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$

SYNOPSIS TOC

1,1´-Diethyl-2,2´,3,3´,4,4´,5,5´-octamethylferrocene has been utilized as a one-electron donor in the synthesis of a tetracyanoethylene magnetic charge-transfer salt, $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$, a compound that adopts an arrangement of anions and cations completely different from the usual π stacking seen in analogous decamethylferrocenium compounds.

Table 1. Crystallographic data for [Fe(C$_5$EtMe$_4$)$_2$]$^+$[TCNE]$^-$

|	
Empirical formula	C$_{28}$H$_{34}$FeN$_4$
Formula weight	482.44
Temperature	219(2) K
Wavelength	Mo Kα: 0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.4024(9) Å α= 75.656(2)°.
	b = 10.7491(9) Å β= 77.715(2)°.
	c = 12.9992(11) Å γ = 67.9460(10)°.
Volume	1293.52(19) Å^3
Z, Z'	2, 1
Density (calculated)	1.236 Mg/m^3
Absorption coefficient	0.605 mm^{-1}
Crystal size	0.40 x 0.30 x 0.20 mm^3
Theta range for data collection	1.63 to 28.26°.
Data / restraints / parameters	6017 / 0 / 328
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1117
R indices (all data)	R1 = 0.0444, wR2 = 0.1149
Largest diff. peak and hole	0.480 and -0.311 e.Å^{-3}
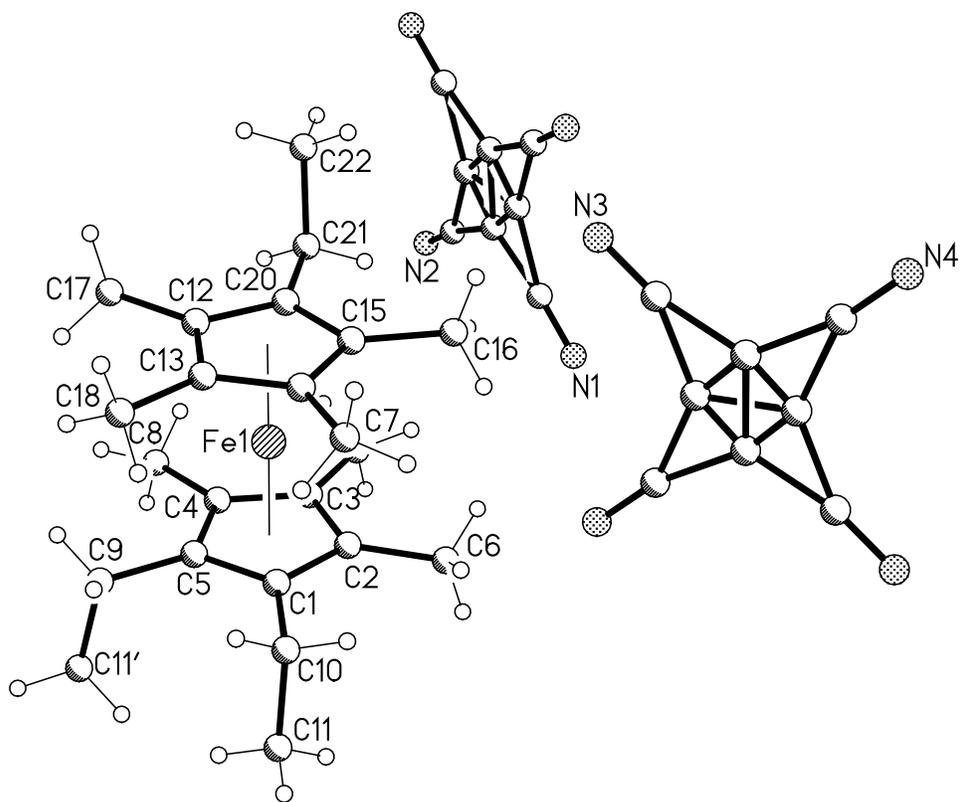
Figure 1. The structure and labeling scheme for **1** with 30% thermal ellipsoid probabilities. Crystallographic
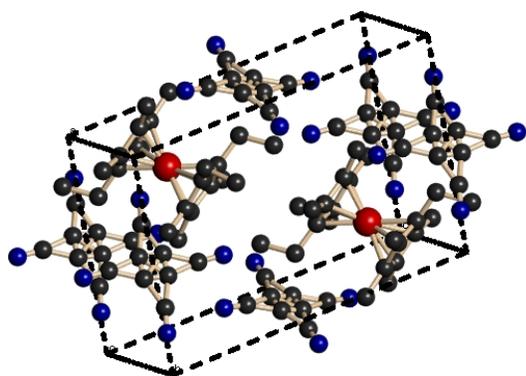
disorder is discussed in the text.

Figure 2. Unit cell of $[Fe(C_5EtMe_4)_2]^+[TCNE]^-$.

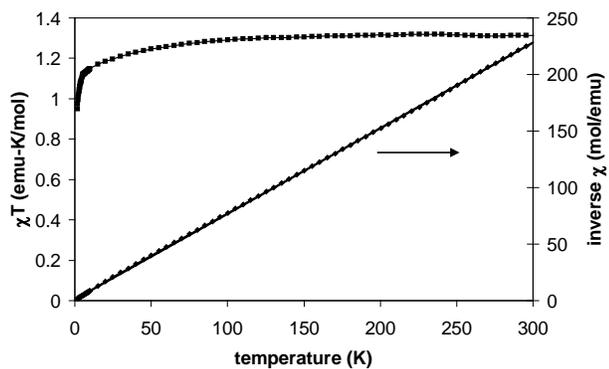**Figure 3.** χT (squares) and inverse χ (diamonds) vs. T for [Fe(C₅EtMe₄)₂]⁺[TCNE]⁻ measured in 5000 G.
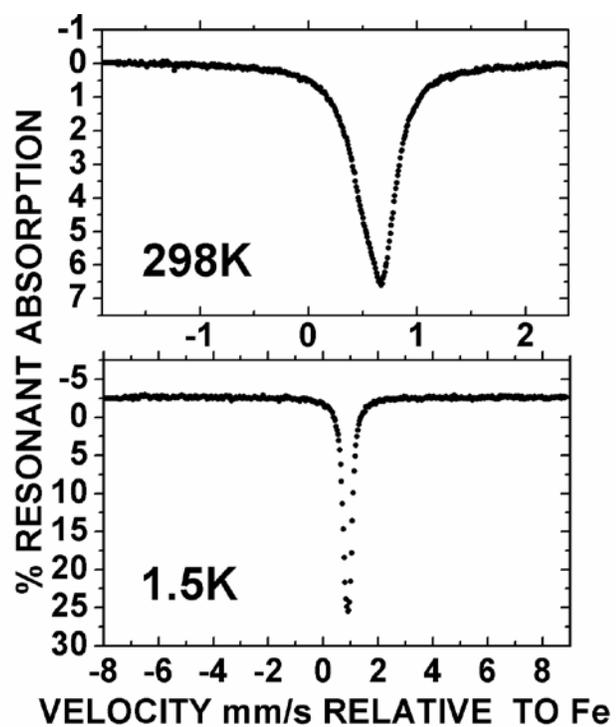
Figure 4. Mössbauer spectra for [Fe(C₅EtMe₄)₂]⁺[TCNE]⁻ at 298 K and 1.5 K

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