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Magnetic Ordering ($T_c = 90$ K) Observed for Layered $[Fe^{II}(TCNE^{\bullet-})(NCMe)_2]^+[Fe^{III}Cl_4]^-$ (TCNE = Tetracyanoethylene)

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Magnets with the controllable modulation and combination of magnetic with other technologically important properties (e.g., optical and electrical) are anticipated via the broad range of synthetic methods pervasive to organic chemistry.[1−5] $V[TCNE]_x{\cdot}zCH_2Cl_2$ (TCNE = tetracyanoethylene; $x \sim 2$; $z \sim 0.5$) is a room temperature ($T_c \sim 125$ °C) organic-based magnet formed from the reaction of TCNE and $V(C_6H_6)_2$[6,7] or $V(CO)_6$.[8] Thin, solvent-free films of $V[TCNE]_x$ have also been prepared via CVD.[9,10] Magnetotransport studies indicate that electrons in valence and conduction bands of $V[TCNE]_x{\cdot}zCH_2Cl_2$ are spin polarized,[11] suggestive of multifunctional "spintronic" applications.[12] Likewise, $Fe[TCNE]_x{\cdot}zCH_2Cl_2$ magnetically orders at ~100 K.[13] However, the understanding and application of these materials is thwarted by their amorphous nature and paucity of structural information beyond the V−N distance.[14]

The reaction of TCNE and $FeCl_2(NCMe)_2$ forms a magnet of $Fe_2(TCNE)Cl_4{\cdot}zMeCN$ ($z \leq 2$) composition.[15] This differs from previously reported organic-based magnets due to (a) the presence of halide and (b) a 1:2, not ~2:1, TCNE:Fe ratio. The 2222 and 2178 cm^{-1} $\nu_{C\equiv N}$ IR absorptions indicate the presence of $[TCNE]^{\bullet-}$, not $[TCNE]^{2-}$, bound to several iron ions,[16] while the 2321, 2310, 2294, and 2283 cm^{-1} absorptions (Figure S1) indicate coordinated MeCN in two crystallographically different environments. Hence, from charge considerations, this material possesses Fe in two valence states: $Fe^{II/III}{}_2(TCNE^{\bullet-})Cl_4{\cdot}zMeCN$.

While single crystals of the brown precipitate did not form, powder X-ray diffraction was observed, and high-resolution patterns were collected at the National Synchrotron Light Source at ambient temperature (Figure 1).[17,18] Rietveld refinement of the synchrotron powder diffraction data reveals that the structure consists of undulating layers of μ_4-$[TCNE]^{\bullet-}$ bound to four Fe ions [average $Fe{-}N_{TCNE} = 2.152(10)$ Å], which additionally have two axial MeCNs [average $Fe{-}N_{MeCN} = 2.102(16)$ Å]. The $[FeCl_4]^-$ anion occupies sites between the $[Fe^{II}(TCNE^{\bullet-})(NCMe)_2]^+$ layers (Figure 2), and there are no covalent bonds between the layers. The planar μ_4-$[TCNE]^{\bullet-}$ is structurally reported for the first time and has a central C−C bond distance of 1.29(4) Å and an average C−CN distance of 1.52(3) Å.

In order to form an extended layer structure based upon the octahedrally preferred 90° N−Fe−N angles (observed: 88.2−92.9°) and 120° (observed: 117.9−121.4°) for the TCNE sp^2 carbons, strain must be accommodated in the bridging sp CN groups. This occurs through buckling of the layer with C−C−N and C−N−Fe angles ranging from 163.2 to 175.4°.

The 5 to 300 K temperature-dependent magnetic susceptibility, χ, of $[Fe(TCNE)(NCMe)_2][FeCl_4]$ is reported as $\chi T(T)$ and $\chi^{-1}(T)$ [$\propto (T - \theta)$] (Figure 3). χT at 300 K has a value of 10.90 emuK/mol that significantly exceeds 7.75 emuK/mol expected for the sum of the spin-only values for $[TCNE]^{\bullet-}$ and high-spin Fe(II) and Fe(III) indicative of strong spin coupling. In accord with the strong coupling, $\chi T(T)$ increases gradually with decreasing temperature and rises significantly at ~110 K and reaches 530 emuK/mol at 75 K, prior to decreasing toward 0 at low temperature. $\chi^{-1}(T)$ is linear between 110 and 190 K with $\theta \sim 100$ K, indicative of significant short-range ferromagnetic coupling. Above 200 K, the slope, $d\chi^{-1}(T)/dT$, decreases, characteristic of a ferrimagnet.

The zero field cooled (ZFC) and field cooled (FC) magnetic susceptibilities, $\chi(T)_{ZFC}$ and $\chi(T)_{FC}$, at 5 Oe rise sharply below 95

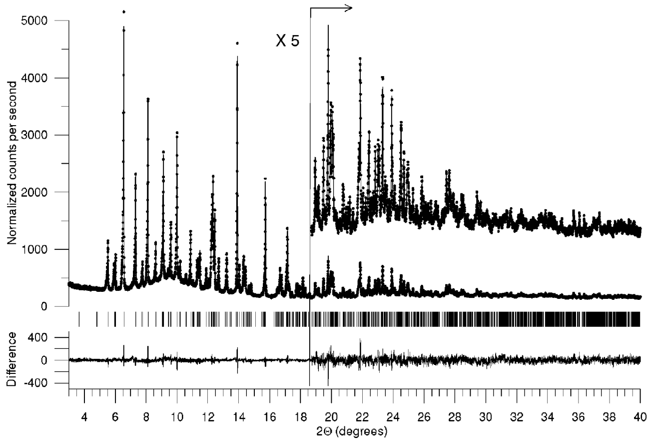

Figure 1. High-resolution synchrotron powder diffraction data and Rietveld fit for the refined structure of $Fe_2(TCNE)Cl_4{\cdot}2MeCN$ (line). The lower trace is the difference, measured − calculated, on the same scale.

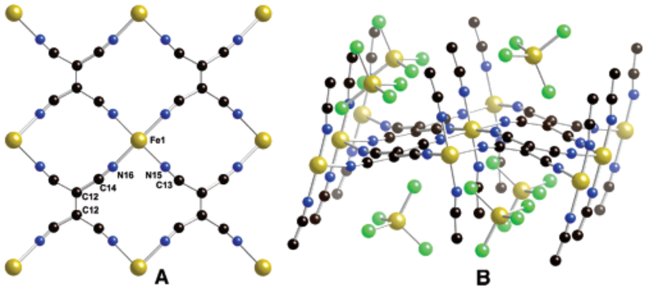

Figure 2. Top view of the structure of $[Fe^{II}(TCNE^{\bullet-})(NCMe)_2]^+[Fe^{III}Cl_4]^-$ showing μ_4-$[TCNE]^{\bullet-}$ bound to four Fe(II)s (the MeCN is omitted for clarity) (A), and side view showing the $[Fe^{III}Cl_4]^-$ and MeCN (B).

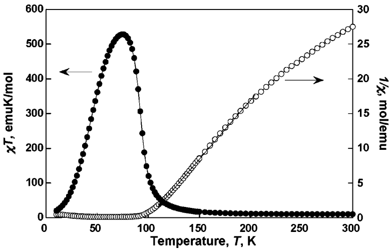

Figure 3. $\chi T(T)$ and $\chi^{-1}(T)$ of $[Fe(TCNE^{\bullet-})(NCMe)_2][FeCl_4]$ (at 1 kOe).

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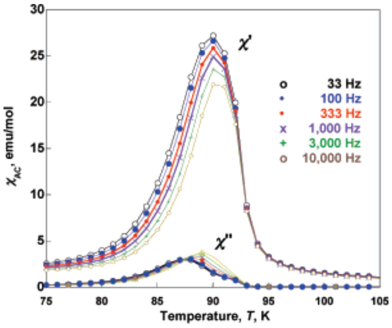

Figure 4. $\chi_{ac}(T)$ [$\chi'(T)$ and $\chi''(T)$] of [Fe(TCNE$^{\bullet-}$)(NCMe)$_2$][FeCl$_4$]).

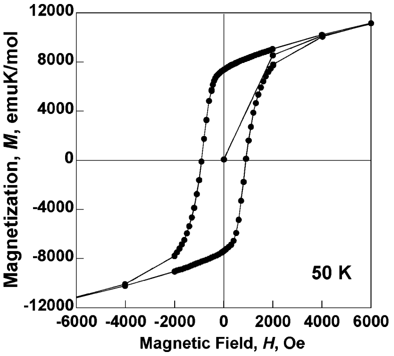

Figure 5. $M(H)$ of [Fe(TCNE$^{\bullet-}$)(NCMe)$_2$][FeCl$_4$] showing hysteresis with H_{cr} = 1730 Oe and M_r = 7500 emuK/mol at 50 K.

K (Figure S2), indicative of a magnetic transition. $\chi(T)_{ZFC}$ reaches maximum at 88 K followed by a rapid decrease, suggesting an antiferromagnetic ground state attributed to antiferromagnetic coupling between ferrimagnetically ordered [Fe[TCNE](NC−Me)$_2$]$^+$ layers. In contrast, $\chi(T)_{FC}$ rises upon further cooling (bifurcation temperature $T_b \sim 90$ K), suggesting a strong irreversibility and indicating the presence of a remanant magnetization below T_b, which increases upon cooling. Both the real, in-phase, $\chi'(T)$, and complex, out-of-phase, $\chi''(T)$, AC susceptibilities exhibit a sharp peak at ~90 K (Figure 4) in accord with an ordering temperature, T_c, of 89.7 ± 0.3 K.

The field-dependent magnetization, $M(H)$, is characteristic of magnetic ordering and exhibits hysteretic behavior with a coercive field, H_{cr}, of 1730 Oe and remanant magnetization, M_r, of 7500 emuK/mol at 50 K (Figure 5).

[Fe(TCNE)(NCMe)$_2$][FeCl$_4$] orders as an antiferromagnet below 90 K. This state is metastable due to a strong structural magnetic anisotropy, and application of a small field irreversibly transforms it into a more stable ferrimagnetic (canted) state. It is the first metal−TCNE magnet with direct bonding between metal ion and [TCNE]$^{\bullet-}$ whose structure has been determined, and it possesses a novel planar μ_4-[TCNE]$^{\bullet-}$ spin coupling unit. Furthermore, it is a prototype for a new class of magnets in which substitution of the solvent with bridging ligands, particularly spin-bearing ligands, in addition to altering the anion, should enable modulation and control of the magnetic properties as well as the development materials with coexisting properties. These results suggest that the intrinsically amorphous room temperature V[TCNE]$_x$-based magnets have a similar pattern of vanadium ions bridged by μ_4-[TCNE]$^{\bullet-}$, but somehow are unable to form a periodic crystal. The new material described herein may aid in the discovery and exploitation of other materials sharing the remarkable room temperature magnetism of V[TCNE]$_x$.

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Supporting Information Available: Crystallographic CIF file for [Fe^{II}(TCNE)(NCMe)$_2$]$^+$[Fe^{III}Cl$_4$]$^-$, IR and ZFC/FC susceptibility of [Fe(TCNE$^{\bullet-}$)(NCMe)$_2$][FeCl$_4$], CCDC 622048. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Reaction of TCNE (34.0 mg, 266 mmol) dissolved in a minimum amount of CH$_2$Cl$_2$ was added to a stirred slurry of FeCl$_2$(NCMe)$_2$ (107.7 mg, 515 mmol) in 10 mL of CH$_2$Cl$_2$. All manipulations were performed in a dry box (<1 ppm O$_2$). After stirring for 21 h, the brown precipitate was filtered, washed with CH$_2$Cl$_2$, and dried in vacuo (yield 114 mg, 95%). Anal. Calcd for Fe$_2$Cl$_4$(TCNE)(MeCN)$_{1.55}$: C, 24.55; H, 1.05; N, 17.46. Found: C, 24.84; H, 1.02; N, 17.10. IR (KBr, cm^{-1}): ν(C≡N) 2321 (m), 2310 (m), 2294 (m), 2283 (m), 2222 (s), 2178 (s).
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(17) A Si(111) double-crystal monochromator selected a highly collimated incident beam of 0.6908(2) Å on the X16C beamline at Brookhaven National Laboratory. The diffracted X-rays were analyzed by a Ge(111) single-reflection crystal and detected using NaI scintillation counter. The capillary was oscillated by 2° during data collection for better averaging of the powder pattern data. EXPO was used to solve the structure by direct method, and subsequent Rietveld refinement was done by TOPAS-Academic [EXPO: SIR program package. Altomare, A. Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Rizzi, R. *J. Appl. Crystallogr.* **1999**, *32*, 339. Bruker AXS (2005): *TOPAS V3: General Profile and Structure Analysis Software for Powder Diffraction Data* (User's Manual); Bruker AXS: Karlsruhe, Germany. TOPAS-Academic is available at http://pws.prserv.net/Alan.Coelho. Anisotropic peak broadening model: Stephens, P. W. *J. Appl. Crystallogr.* **1999**, *32*, 281.
(18) Chemical formula = H$_6$C$_{10}$N$_6$Cl$_4$Fe$_2$, space group = *Pnam* (No. 62); a = 14.3327(1) Å, b = 16.4820(2) Å, c = 7.2800(1) Å, V = 1719.75(3) Å^3, $T \sim 25$ °C, Z = 4, ρ_{calc} = 1.791 g/cm^3, R_p = 0.0326, R_{wp} = 0.0411, χ^2 = 1.277.

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