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Magnetic Materials

Cross-Linked Layered Structure of Magnetically Ordered $[Fe(TCNE)_2]\cdot z\,CH_2Cl_2$ Determined by Rietveld Refinement of Synchrotron Powder Diffraction Data**

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In memory of Robert W. Parry

Since the report of the first organic-based magnet $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (TCNE = tetracyanoethylene),[1] organic-based materials have been synthesized with enhanced and controllable magnetic properties.[2] $[V(TCNE)_x]\cdot z\,CH_2Cl_2$ ($x \approx 2$; $z \approx 0.5$) prepared by the reaction of TCNE and $[V(C_6H_6)_2]$[3a] or $[V(CO)_6]$[3b] is an amorphous organic magnet with a ferrimagnetic ordering temperature (T_c) of approximately 400 K. Solvent-free thin films of $[V(TCNE)_x]$ have been prepared by chemical vapor deposition and show similar magnetic behavior.[4] Magnetotransport studies indicate that electrons in valence and conduction bands of $[V(TCNE)_x]$ are spin polarized, which suggests that it could be suitable for "spintronic" applications.[5]

With the goal of identifying new organic-based magnets, $[Fe(TCNE)_2]\cdot z\,CH_2Cl_2$ ($T_c \approx 100$ K)[6a,b] was prepared through the reaction of TCNE and FeI_2[6c] or $[Fe(CO)_5]$,[6b] and $[Mn(TCNE)_2]\cdot z\,CH_2Cl_2$ ($T_c \approx 75$ K)[6d] was formed from the reaction of TCNE and MnI_2.[6c] Albeit important, the structures of $[M(TCNE)_2]\cdot z\,CH_2Cl_2$ (M = V, Mn, Fe) have been elusive because of the unavailability of single crystals. Herein, we report the structure of $[Fe(TCNE)_2]\cdot z\,CH_2Cl_2$ determined from synchrotron powder diffraction data and the implications it provides with respect to the structure of the $[V(TCNE)_x]$ room temperature magnet.

Although single crystals of the brown compounds $[M(TCNE)_2]\cdot z\,CH_2Cl_2$ (M = Mn, Fe) did not form, X-ray powder diffraction (XRPD) was observed and indicated that they are isomorphous.[6c] Thus, a high-resolution XRPD pattern for M = Fe was collected at the National Synchrotron Light Source at ambient temperature (Figure 1).[7]

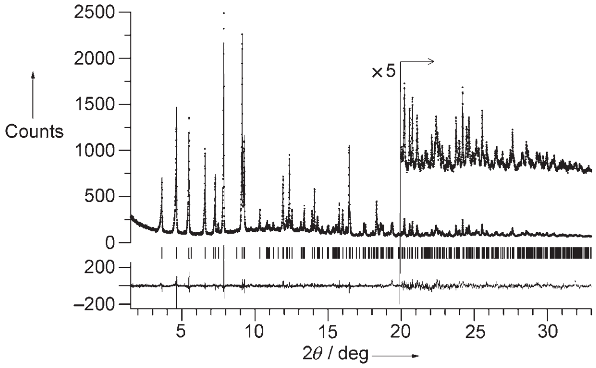

Figure 1. High-resolution synchrotron powder diffraction data (dots) and Rietveld fit of the data for $[Fe(TCNE)_2]\cdot zCH_2Cl_2$ (line). The lower trace is the difference (measured−calculated) plotted against the same vertical scale.

The XRPD pattern was indexed as a *C*-centered orthorhombic lattice by using the computer program ITO,[8a] and the lack of further systematic absences requires the space group to be *Cmmm*, or, unlikely, one of its acentric subgroups. Real-space simulated annealing, assuming that only Fe atoms and TCNE exist in the unit cell, failed to find a solution. The solution was found by using independent atoms (i.e. no molecular shape constraint) in simulated annealing with dynamic occupancy correction in FOX,[8b] which revealed the unexpected bonding of $[TCNE]^{\cdot-}$ as $[C_4(CN)_8]^{2-}$ as well as the presence of highly disordered solvent molecules. The structure was refined by using TOPAS-Academic.[8c] The $[C_4(CN)_8]^{2-}$ moieties are disordered in sites of *mmm* symmetry,[9a] and there is a significant number of disordered solvent molecules in channels running along the *c* axis, which could not be characterized in detail.

Rietveld refinement of these data revealed a structure consisting of six N atoms octahedrally coordinated to Fe^{II}, with adjacent octahedra canted by 15° (Figure 2). Each Fe^{II} ion bonds to four μ_4-$[TCNE]^{\cdot-}$ anions in layers that undulate about the *ac* plane as a result of the canting of the octahedra. The Fe−N bond length is 2.18(2) Å, and the Fe-N-C angle is 173(1)° for the four μ_4-$[TCNE]^{\cdot-}$ anions, each bound to four Fe^{II} ions. The average C−C and C−CN bond lengths are 1.35(2) and 1.42(2) Å, respectively, and the average NC-C-

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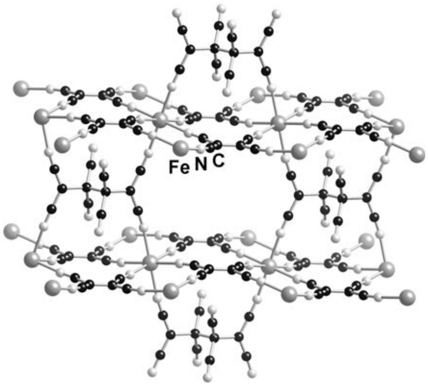

Figure 2. Structure of [Fe(TCNE)$_2$]·zCH$_2$Cl$_2$ (that is, [Fe(TCNE){C$_4$(CN)$_8$}$_{1/2}$]·zCH$_2$Cl$_2$, $z\approx0.32$)[9b] possessing undulating layers of μ$_4$-[TCNE]$^{•-}$ bound to four Fe^{II} ions, which are connected by μ$_4$-[C$_4$(CN)$_8$]$^{2-}$. The CH$_2$Cl$_2$ solvent molecules are disordered in the channels and not shown for clarity.

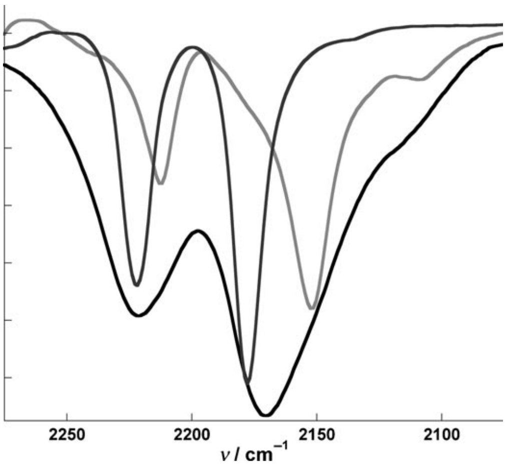

Figure 3. ν_{CN} region of the IR spectra of [Fe(TCNE)$_2$]·zCH$_2$Cl$_2$ ($z\approx0.32$) (black), μ$_4$-[C$_4$(CN)$_8$]$^{2-}$ observed for [Fe{C$_4$(CN)$_8$}(MeCN)$_2$] (light gray),[10] and μ$_4$-[TCNE]$^{•-}$ present in [Fe(TCNE)(NCMe)$_2$][FeCl$_4$] (dark gray).[13]

CN, C-C≡N, and C-C-CN angles are 121(1), 170(1), and 119(1)°, respectively.

From geometrical considerations, to form an extended layer structure based upon the octahedrally preferred 90° N-Fe-N angles (observed values range from 89.4° to 90.6°), the preferred 180° bonding angle of the sp-hybridized NC group to the Fe center would have to be decreased to 165°. The observed canting of the octahedra leads to undulation of the extended {Fe^{II}(TCNE)$^{•-}$} plane, which decreases this deviation of the Fe-N-C angle to the observed compromise value of 173°. Hence, [M(TCNE)$_2$]·zCH$_2$Cl$_2$ (M = Fe, Mn) is best formulated as [M(TCNE){C$_4$(CN)$_8$}$_{1/2}$]·zCH$_2$Cl$_2$.

These {Fe^{II}(TCNE)$^{•-}$} layers are interconnected by μ$_4$-[C$_4$(CN)$_8$]$^{2-}$ ligands with an Fe–N bond length of 2.16(1) Å, Fe-N-C angle of 174(1)°, and C-C-CN angles of 116(1) and 122(1)°. The backbone CCC–C and CC–CC bond lengths and C-C-C angle are 1.52(1) Å, 1.59(2) Å, and 114(1)°, respectively (Figure 2). The geometry of the μ$_4$-[C$_4$(CN)$_8$]$^{2-}$ ligand is comparable to that reported for [M{C$_4$(CN)$_8$}(NCMe)$_2$] (M = Mn, Fe).[10] The juxtaposition of the Fe^{II} ion and the μ$_4$-[C$_4$(CN)$_8$]$^{2-}$ N atoms, which prefer bonding angles of 90 and 180°, respectively, presumably contributes to the canting of the FeN$_6$ octahedra. This interconnecting motif has linear channels along the c axis (Figure 2), where the highly disordered CH$_2$Cl$_2$ solvent molecules reside.[11]

This complex motif possesses two different forms of reduced TCNE and is the second structural characterization of μ$_4$-[TCNE]$^{•-}$,[12,13] but occurs for the related μ$_4$-[TCNQ]$^{•-}$ (TCNQ = 7,7,8,8-tetracyano-p-quinodimethane) as observed for tetracoordinate [M^{I}(TCNQ)] (M = Ag,[14a] Cu[14b]), and [Ag(TCNQF$_4$)].[14c] The layer-interconnecting μ$_4$-[C$_4$(CN)$_8$]$^{2-}$ motif is rare,[10,12] but the TCNQ analogue has been reported.[15]

The presence of two different forms of reduced TCNE in the [Fe(TCNE)$_2$]·zCH$_2$Cl$_2$ structure is also evident in its IR spectrum, which has ν_{CN} absorptions at 2221 and 2172 cm^{-1} (Figure 3). Absorptions at 2213 and 2153 cm^{-1} are characteristic for single crystals of materials possessing of μ$_4$-[C$_4$(CN)$_8$]$^{2-}$, but the shape and positions of these peaks are very sensitive to structural disorder.[10,12] The absorptions at 2222 and 2178 cm^{-1} are assigned to μ$_4$-[TCNE]$^{•-}$ in accord with that observed for μ$_4$-[TCNE]$^{•-}$ present in [Fe(TCNE)(NCMe)$_2$][FeCl$_4$],[13] and the inhomogeneous broadening of both peaks from the low-energy side is attributed to the presence of μ$_4$-[C$_4$(CN)$_8$]$^{2-}$.

Within the layers a strong spin coupling is provided by direct exchange between the $S = 2$ Fe^{II} and the $S = 1/2$ μ$_4$-[TCNE]$^{•-}$ ions, and the layers are coupled by superexchange through the diamagnetic μ$_4$-[C$_4$(CN)$_8$]$^{2-}$ ligand. The latter coupling is much weaker; hence, the dominant spin exchange contributing to the magnetic ordering as a ferrimagnet at 100 K resides within the layers.

It has been noted that heating paramagnetic [M{C$_4$(CN)$_8$}(NCMe)$_2$]·zCH$_2$Cl$_2$ (M = Mn, Fe) yields materials with magnetic properties comparable to those of the present [Fe(TCNE)$_2$]·zCH$_2$Cl$_2$ compound and its Mn analogue.[10] This is attributed to breaking of the long central C–C bonds of μ$_4$-[C$_4$(CN)$_8$]$^{2-}$ to re-form $S = 1/2$ [TCNE]$^{•-}$, which, owing to its ability to form direct spin exchange, can significantly enhance the spin coupling.

The present structure has implications for the interpretation of the reported saturation magnetization of [Fe(TCNE)$_2$]·zCH$_2$Cl$_2$ (i.e. [Fe(TCNE){C$_4$(CN)$_8$}$_{1/2}$]·zCH$_2$Cl$_2$).[6] Albeit still slowly increasing, its $M(H)$ value at 2 K and 9 T is 16400 emu Oe mol^{-1} (Figure 4). This value is substantially higher than that expected for a spin-only $S = 2$ Fe^{II} center antiferromagnetically coupled to two $S = 1/2$ [TCNE]$^{•-}$ ions ($M_s = 11200$ emu Oe mol^{-1}). In contrast, the presence of [C$_4$(CN)$_8$]$^{2-}$ decreases the number of antiferromagnetically coupled [TCNE]$^{•-}$ species, and the expected M_s is 16800 emu Oe mol^{-1}, in good agreement with the observed data.

The magnitude of the pairwise spin coupling J in units of K can be calculated from the mean field expression for two different spin sites i and j [Eq. (1)] as 0.177 T_c with $z_{TCNE} =$

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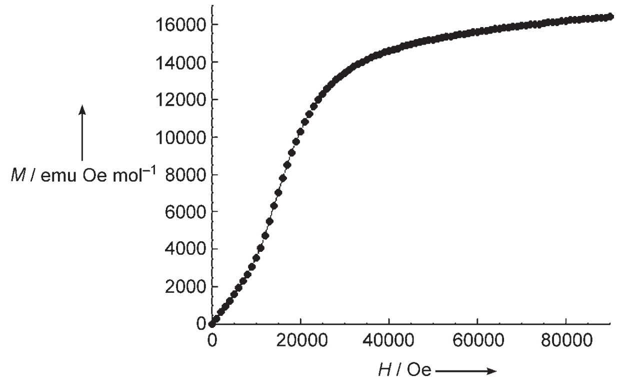

Figure 4. $M(H)$ for $[Fe(TCNE)\{C_4(CN)_8\}_{1/2}]\cdot CH_2Cl_2$ at 2 K. The line is a guide.

$z_{Fe} = 4$, $S_{TCNE} = 1/2$, and $S_{Fe} = 2$. As $T_c = 100$ K, $J/k_B = 17.7$ K (12.3 cm^{-1}).

$$T_c = \frac{2|J|\sqrt{z_i z_j}\sqrt{S_i(S_i+1)\,S_j(S_j+1)}}{3\,k_B} \tag{1}$$

The structure of $[Fe^{II}(TCNE)_2]\cdot z\,CH_2Cl_2$ implies that the room-temperature $[V(TCNE)_x]$-based magnets most probably have V^{II} ions bridged by μ_4-$[TCNE]^{\bullet-}$ ligands within a layer and are also connected by μ_4-$[TCNE]^{\bullet-}$ ligands between layers and not μ_4-$[C_4(CN)_8]^{2-}$ as observed herein for $[Fe^{II}(TCNE)_2]\cdot z\,CH_2Cl_2$. The antiferromagnetic coupling of $S = 3/2$ V^{II} to a larger number of μ_4-$[TCNE]^{\bullet-}$ spins leads to the observed lower saturation moment with respect to $[Fe^{II}(TCNE)_2]\cdot z\,CH_2Cl_2$. Alternatively, $\{V(\mu_4\text{-}[TCNE])^{\bullet-}\}$ layers may be interconnected by *trans*-$\{\mu\text{-}[TCNE]\}^{\bullet-}$ linkages. Both of the bridging moieties have one unpaired spin that can provide a strong interlayer coupling leading to the observed above-room-temperature ordering temperature.

The *trans*-$\{\mu\text{-}[TCNE]\}^{\bullet-}$ spin-coupling linkage has been established for the $[Mn^{III}(porphyrin)]^+[TCNE]^{\bullet-}$ family of linear chain ferrimagnets, and depending on the dihedral angle between the $\{MN_4\}$ and $[TCNE]^{\bullet-}$ planes can stabilize strong antiferromagnetic coupling $[\,|J|/k_B > 250$ K (175 cm^{-1}); $H = 2J\mathbf{S}_a\mathbf{S}_b]$.[16] Thus, although these two descriptions for the structure of $[V(TCNE)_x]$ cannot be differentiated at present, both provide insight into key aspects of the structure that has been elusive. It should be noted that $[V(TCNE)_x]$ is amorphous; the proposed local structural order is therefore prone to defects including the presence of $[TCNE]^{2-}$ (evident from the low-energy ν_{CN} absorption[3]), which requires a vacant $[TCNE]^{\bullet-}$ site for charge balance.

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[9] a) Space group *Cmmm*; $a = 14.317(1)$, $b = 17.402(1)$, $c = 7.3334(5)$ Å, $V = 1827.1(4)$ Å^3, $\rho_{calcd} = 1.32(1)$ g cm^{-3}, ambient temperature, $R_{wp} = 4.88$, $\chi^2 = 1.957$. CCDC-623463 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A refinement without disorder in the $[C_4(CN)_8]^{2-}$ moieties in space group *C2/m* yields an essentially equivalent fit with $\beta = 90.000 \pm 0.003°$ ($R_{wp} = 4.87$, $\chi^2 = 1.954$); the data do not distinguish between the two cases. b) $z = 0.32$ was determined from a fit to the elemental analysis.

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