Inorg. Chem. **2002**, *41*, 1996–1997

Inorganic Chemistry
Communication

Iron Pentacarbonyl as a Precursor for Molecule-Based Magnets: Formation of $Fe[TCNE]_2$ ($T_c = 100$ K) and $Fe[TCNQ]_2$ ($T_c = 35$ K) Magnets

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Received December 18, 2001

The reaction of tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) with $Fe(CO)_5$ leads to formation of magnetically ordered materials of $Fe[TCNE]_2$ ($T_c = 100$ K) and $Fe[TCNQ]_2$ ($T_c = 35$ K) composition, respectively. In contrast, the reaction with 1,2-dichloro-5,6-dicyanobenzoquinone (DDQ) leads to a paramagnetic material.

Magnetic ordering is crucial for several commercial applications, and magnets derived from molecule-based precursors are a contemporary research focus.[2,3] Magnets of $M[TCNE]_x \cdot xS$ (M = V, Mn, Fe, Co, Ni; TCNE = tetracyanoethylene; S = CH_2Cl_2) composition have been reported with magnetic ordering temperatures (T_c) as high as 125 °C.[3] The room temperature $V[TCNE]_x$ magnet was initially prepared via the reaction of $V(C_6H_6)_2$ and TCNE in CH_2Cl_2; however, greater reproducibility was achieved via the reaction of $V(CO)_6$ and TCNE in CH_2Cl_2.[3] The chemical vapor deposition (CVD) of $V[TCNE]_x$ has led to the development of a solvent-free thin film magnet with improved magnetic properties.[4] In contrast, $M'[TCNE]_x \cdot xS$ (M′ = Mn, Fe, Co, Ni) magnets are prepared from the reaction of MI_2 and TCNE[3,5] and thin films have yet to be prepared. In order to develop thin film $M'[TCNE]_x$ magnets, volatile precursors need to be identified. Metal carbonyls, as demonstrated with $V(CO)_6$, in principle are suitable and were studied.

The reaction of TCNE with $Cr(CO)_6$[6] and $Mn_2(CO)_{10}$,[7a] albeit slow, leads to CO-containing products. In contrast, the reaction of $Co_2(CO)_8$ in CH_2Cl_2 leads to an immediate black CO-free paramagnetic product that does not magnetically order above 2 K.[7b] Nonetheless, magnetically ordered $Co[TCNE]_2 \cdot xS$ ($T_c = 44$ K), has been made from CoI_2.[5] The reaction of TCNE with $Fe(CO)_5$ in CH_2Cl_2, albeit slow, leads the formation of a brown-green solid of $Fe[TCNE]_2 \cdot 0.32(CH_2Cl_2)$, **1**, composition after drying in vacuo for 3 days at 70 °C.[8] The IR spectrum of **1** has ν_{CN} absorptions at 2222, 2178, and 2172 cm^{-1} in accord with $Fe[TCNE]_2 \cdot 0.75(CH_2Cl_2)$ prepared from FeI_2 (i.e., 2221, 2177, and 2174 cm^{-1})[5] and indicates that the σ-dimer of $[TCNE]^{\bullet -}$, $[C_4(CN)_8]_2{}^{2-}$, is not present.[9]

The 6.11 emu K/mol value for the room temperature χT product for **1** indicates strong magnetic coupling as it significantly exceeds the expected spin-only value ($S = 2 + {}^1/_2 + {}^1/_2$) of 3.75 emu K/mol, and the 5.10 emu K/mol value that takes into account a full contribution of orbital angular momentum for Fe(II) ($\chi T = 4.35$ emu K/mol for $[Fe^{II}(NCMe)_6]^{2+}$ [10]). The zero field cooled (ZFC) and FC temperature dependence of the susceptibility, $\chi(T)$, of **1** reveals a bifurcation ($\chi_{ZFC} \neq \chi_{FC}$) at 120 K and two magnetic transitions at 12 and 100 K (Figure 1) that are comparable to 24 and 97 K transitions reported for $Fe[TCNE]_2$ prepared from FeI_2.[11a] Ac susceptibility studies show that the low-temperature peak position is frequency dependent, while the

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(8) In a typical preparation neat $Fe(CO)_5$ (24 μL; 0.18 mmol) was dropwise added to a stirred solution of TCNE (46 mg; 0.36 mmol) in 15 mL of CH_2Cl_2. The mixture was stirred for 5 days with venting, and, as color changes from yellow to dark brown, a precipitate forms. ***CAUTION:*** *$Fe(CO)_5$ is very toxic and needs to be handled carefully in a well-vented hood.* The product was filtered, washed with CH_2Cl_2, and dried (yield: 43 mg (85%). The TCNQ and DDQ materials were prepared by the same methods using TCNQ and DDQ, respectively. Elemental anal. Obsd (calcd) for $Fe[TCNE]_2 \cdot 0.32(CH_2Cl_2)$: C, 43.50 (43.77); H, 0.00 (0.18); N, 33.24 (33.20). For $Fe[TCNQ]_2 \cdot 0.70(CH_2Cl_2)$: C, 56.91 (56.65); H, 1.81 (1.81); N, 21.40 (21.29). For $Fe[DDQ]_2 \cdot 1.02(CH_2Cl_2)$: C, 34.28 (34.03); H, 0.34 (0.43); N, 9.39 (9.67).

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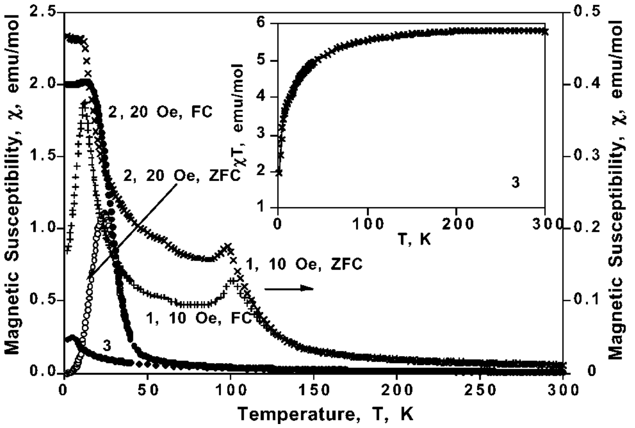

Figure 1. ZFC and FC susceptibility, $\chi(T)$, of **1** (×, +) and **2** (●, ○), as well as $\chi(T)$ at 1000 Oe of **3** (◆). Inset is $\chi T(T)$ for **3**, and the line is a fit to the data as described in the text.

high-temperature peak is not. We speculate that at 100 K the magnetization component parallel to the applied magnetic field orders ferrimagnetically while the perpendicular component remains disordered[12a] and freezes at 12 K, and additional studies are in progress.

M[TCNQ]$_2$·yS (M = Mn, Fe, Co, Ni; S = MeOH, H_2O; TCNQ = 7,7,8,8-tetracyano-p-quinodimethane) exhibits Curie−Weiss behavior characteristic of isolated metal ions due to formation of $S = 0$ σ-dimerized [TCNQ]$_2^{2-}$ units.[13] However, upon annealing at 160 °C or X-ray irradiation, magnetic ordering occurs for M = Mn, in which the S = 0 μ_4-[TCNQ]$_2^{2-}$ dimers break to form two $S = {}^1/_2$ [TCNQ]$^{\bullet-}$. The $S = {}^1/_2$ [TCNQ]$^{\bullet-}$ spin couples with Mn^{II}, leading to ferrimagnetic ordering at ~50 K based on a deviation of $\chi^{-1}(T)$ from the Curie−Weiss law.[13] Similar σ-[TCNE]$_2^{2-}$ dimers were observed for M[TCNE]$_2$ (M= Mn, Fe),[9] which also magnetically order upon thermal treatment.[9] Thermolysis breaks the long, central σ-dimer bond (ca. 1.6 Å)[9,13] and subsequently forms two $S = {}^1/_2$ radicals. In addition, the M−solvent bond breaks and solvent loss occurs to open up sites for either $S = {}^1/_2$ [TCNQ]$^{\bullet-}$ or [TCNE]$^{\bullet-}$ to bind to the M stabilizing sufficiently strong magnetic coupling and ferrimagnetic ordering.[9]

The reaction of Fe(CO)$_5$ with TCNQ and subsequent annealing in vacuo at 70 °C forms a new magnetically ordered material of Fe[TCNQ]$_2$·0.70(CH_2Cl_2), **2**, composition[8] (ν_{CN}, 2194, 2163, and 2107 cm^{-1}; δ(C−H), 826 cm^{-1}). χT (300 K) for **2** is 4.81 emu K/mol, close to the theoretically predicted 5.10 emu K/mol for the $S = 2$ Fe^{2+} (possessing an orbital contribution to the moment) and two $S = {}^1/_2$ spin-only [TCNE]$^{\bullet-}$ species. The ZFC and FC $\chi(T)$ of **2** indicate that the system orders ferrimagnetically below ~55 K (Figure 1) on the basis of a deviation of $\chi(T)$ from the Curie−Weiss law. The bifurcation starts at ~30 K and becomes much more pronounced below 24 K, suggesting a correlated spin-glass ground state. The temperature dependencies of the in-phase (χ') and out-of-phase (χ'') components of the complex ac susceptibility measured at different frequencies (10−1000 Hz) for the compound **2** are shown in Figure 2. Both $\chi'(T)$ and $\chi''(T)$ display maxima at 20−24 K, which demonstrate a gradual shift toward higher temperatures as the frequency increases, which is characteristic for spin-glasses.[12] The ordering temperature, T_c, is ~35 K, based on the onset of $\chi''(T)$.

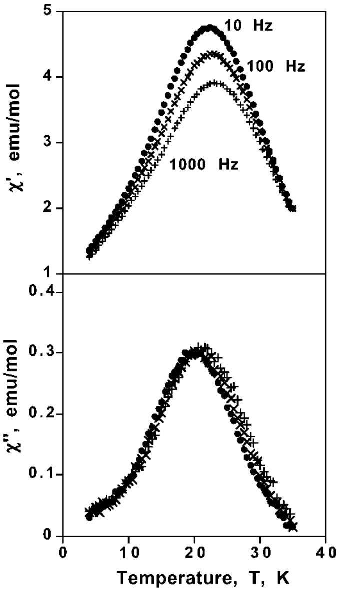

Figure 2. The temperature dependencies of the in-phase (χ') and out-of-phase (χ'') components of the complex ac susceptibility of **2** at 10 (●), 100 (×), and 1000 (+) Hz.

In contrast to formation of magnetically ordered materials with either TCNE or TCNQ, the reaction of Fe(CO)$_5$ with DDQ (DDQ = 1,2-dichloro-5,6-dicyanobenzoquinone) led to Fe[DDQ]$_2$·1.02(CH_2Cl_2), **3**[8] (ν_{CN}: 2234 cm^{-1}). **3** exhibits Curie−Weiss behavior characteristic of isolated metal ions and $S = {}^1/_2$ [DDQ]$^{\bullet-}$ above 2 K, with a room temperature moment of 4.81 emu K/mol that is close to the theoretically predicted one for the $S = 2$ Fe^{II} and two [TCNE]$^{\bullet-}$. $\chi(T)$ can be fit to a model including zero field splitting (D) for Fe^{II} [14] with $D = -6$ K, $g_{Fe} = 2.25$, and $\theta = -23.5$ K as expected for a paramagnetic system with Fe(II) and two $S = {}^1/_2$ [TCNE]$^{\bullet-}$ species with $g = 2.00$.

Hence, Fe(CO)$_5$ is a useful precursor for the preparation of molecule-based magnets. The TCNQ analogue of an M[TCNE]$_x$ magnet, as observed for M = Fe, has a substantially reduced T_c. This reduction in T_c is also observed for the [M(C_5Me_5)$_2$][TCNX] (M = Cr, Mn, Fe; X = E, Q) family of ferromagnets.[2b]

Acknowledgment. We gratefully acknowledge the support from the U.S. Department of Energy (Grants DE FG 03-93ER45504 and DE FG 02-86BR45271).

IC011288B

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