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Synthesis and Magnetic Properties of a [Ni^{II}(TCNE)$(NCMe)_{2-\delta}$][BF_4] Magnet ($T_c = 40$ K)

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The reaction of (NBu_4)(TCNE) (TCNE = tetracyanoethylene) and [$Ni(NCMe)_6$][BF_4]$_2$ in CH_2Cl_2 forms layered [Ni(TCNE)$(MeCN)_{2-\delta}$][BF_4], a magnet ($T_c = 40$ K) with a ferromagnetic interaction within Ni-μ_4-[TCNE]$^{\bullet-}$ layers, and a new general route to the preparation of [M(TCNE)$(NCMe)_2$][anion] magnets has been identified.

M^{II}[TCNE]$_2$ (M = Fe, Mn, Co, Ni; TCNE = tetracyanoethylene) magnets have be prepared from the reaction of an anhydrous metal(II) iodide (such as the MeCN solvate) with TCNE in CH_2Cl_2.[1] The alternative route of reacting metal carbonyls (Fe,[2] Co,[3] and Ni[4]) with TCNE in CH_2Cl_2 was also exploited; however, magnetically ordering materials were only obtained for iron and nickel. The Fe[TCNE]$_2$ magnets prepared by both routes have very similar powder X-ray diffraction patterns, suggesting a close similarity of their structures. Recently, the structure of the carbonyl-made Fe[TCNE]$_2\cdot z CH_2Cl_2$ was revealed from the Rietveld refinement of high-resolution synchrotron powder diffraction data[5] and consists of Fe^{II}-μ_4-[TCNE]$^{\bullet-}$ layers coupled via the diamagnetic μ_4-[$C_4(CN)_8$]$^{2-}$ anion. Thus, it is formulated as Fe^{II}[TCNE][$C_4(CN)_8$]$_{1/2}\cdot z CH_2Cl_2$.

Recently, another reaction mechanism and composition were discovered for the Fe[TCNE] system. The reaction of TCNE and $FeCl_2(NCMe)_2$ in CH_2Cl_2 forms the aforementioned positively charged Fe^{II}-μ_4-[TCNE]$^{\bullet-}$ layers with two axial MeCN ligands bonded to the Fe^{II} ion, and [$Fe^{III}Cl_4$]$^-$, which forms when TCNE is reduced, is located between layers.[6,7] Formation of the magnetic layers was hypothesized to occur from the reaction between [$Fe^{II}(NCMe)_6$]$^{2+}$ and [TCNE]$^{\bullet-}$. In this reaction, half of the Fe^{II} ion is oxidized to [$Fe^{III}Cl_4$]$^-$. Extension to M^{II}'s that is more difficult to oxidize, e.g., Ni^{II}, Mn^{II}, and Co^{II}, however, requires a different approach. To eliminate the redox step, we hypothesized that the reaction of [TCNE]$^{\bullet-}$ and [$M^{II}(NCMe)_6$]$^{2+}$ in CH_2Cl_2 should form the M^{II}-μ_4-[TCNE]$^{\bullet-}$ layer-type structure pattern essential for magnetic ordering. Additionally, we hypothesized that the use of Ni^{II}, due to its electron spins residing in e_g orbitals that are orthogonal to π^* of [TCNE]$^{\bullet-}$, should lead to ferromagnetic interactions within the layer, in contrast to antiferromagnetic interactions reported for Fe, V, and Mn analogues.

Hence, to demonstrate the feasibility of these hypotheses, the reaction between [$Ni(NCMe)_6$][BF_4]$_2$ and NBu_4(TCNE) in CH_2Cl_2 (eq 1) was studied, and this led to a new magnet of Ni(TCNE)$BF_4(MeCN)_{2-\delta}$ ($\delta = 0.15$) composition (**1**).[8] Its powder diffraction pattern, although poor because of a partial loss of MeCN, does not show evidence for [$Ni(NCMe)_6$][BF_4]$_2$.

$$[\mathrm{Ni(NCMe)_6}][\mathrm{BF_4}]_2 + \mathrm{NBu_4(TCNE)} \rightarrow [\mathrm{Ni(TCNE)(NCMe)_2}][\mathrm{BF_4}](s) + \mathrm{NBu_4}[\mathrm{BF_4}] + 4\mathrm{MeCN} \quad (1)$$

The IR spectrum of **1** has ν_{CN} absorptions at 2329, 2300, 2250, and 2208 cm^{-1}, suggesting two types of nitrile coordination, and an intense broad band at 1060 cm^{-1} characteristic of BF_4^-.[9] The frequencies of the first two peaks are similar to those observed for [$Ni(NCMe)_6$][TFPB]$_2$ (TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; 2326

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(8) A total of 1 equiv of (NBu_4)(TCNE) dissolved in a minimum amount of CH_2 Cl_2 was added to a stirred slurry of 1 equiv of [$Ni(NCMe)_6$][BF_4]$_6$[13] in CH_2 Cl_2 in a drybox. After stirring for 1 day, the precipitate was filtered, washed with CH_2 Cl_2, and dried in vacuo for 2 h (95%). IR (KBr): ν_{CN} 2329(8) (m), 2300(8) (m), 2250(8) (s), 2208(8) (s), ν_{BF} ~1060(8) (s) cm^{-1}. Anal. Calcd for Ni (TCNE)$BF_4(MeCN)_{2-\delta}$ ($\delta = 0.15$), $C_{9.7}H_{5.55}BF_4N_{5.85}Ni$: C, 33.33; H, 1.60; N, 23.44. Found: C, 33.49; H, 1.39; N, 23.40.

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10.1021/ic702336j CCC: $40.75

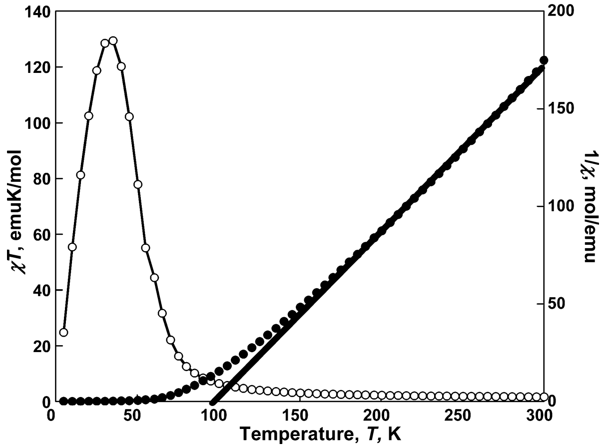

Figure 1. $\chi T(T)$ (○) and $\chi^{-1}(T)$ (●) of **1** at 1 kOe.

and 2299 cm^{-1}) and are assigned to MeCN ν_{CN} vibrations. The two lower frequency bands are assigned to ν_{CN} in μ-[TCNE]$^{\bullet-}$. These frequencies are substantially higher (~30 cm^{-1}) than those for [Fe(TCNE)(NCMe)$_2$][FeCl$_4$].[6] In general, M←:N≡C bonding causes a blue shift of ν_{CN} stretching modes with respect to those in isolated [TCNE]$^{\bullet-}$ due to σ-type electron donation.[10] However, for the early 3d metal ions, this shift can be partially compensated for by π back-bonding. In electron-rich **1**, the π back-bonding is substantially suppressed, causing an increase of the metal–ligand bond strength, in contrast to the less electron-rich Fe compound. Moreover, in electron-poor V^{II}[TCNE]$_x$ (ν_{CN} = 2158 cm^{-1})[11] back-bonding almost totally compensates for the σ donation. Besides, there is structural evidence for this effect; namely, the average C≡N bond length in [Ni(NCMe)$_6$][NiI$_4$] is 2% shorter than that in the similar [Fe(NCMe)$_6$][FeI$_4$].[12] Despite the ~40 cm^{-1} blue shift in the ν_{CN} absorptions for [M(NCMe)$_6$]$^{2+}$ (vs uncoordinated MeCN) that is primarily due to σ donation, a modest 6 cm^{-1} red shift was observed as M was varied from Ni to V.[8] Therefore, suppressed back-bonding in electron-rich Ni[TCNE] compounds results in a larger blue shift with respect to that in Fe[TCNE] compounds, as observed.

The 5−300 K temperature-dependent magnetic susceptibility, χ, of the powder sample of **1** is reported as $\chi T(T)$ and $\chi^{-1}(T)$ [$\propto(T - \theta)$; Figure 1]. χT at 300 K is 1.65 emu·K/mol in accordance with the sum from the contributions for a high-spin octahedral Ni^{II} (1.20 emu·K/mol)[13] and that expected for [TCNE]$^{\bullet-}$ (0.375 emu·K/mol). It provides additional evidence for the proposed composition of compound **1**. $\chi^{-1}(T)$ is linear between 175 and 300 K with θ of 97.3 K indicative of considerable short-range ferromagnetic coupling and also is responsible for a slightly higher than expected χT value at 300 K. $\chi T(T)$ gradually increases with decreasing temperature for **1** and rises significantly at ~110 K, reaching the maximum of 128 emu·K/mol at 32 K, prior to decreasing toward zero.

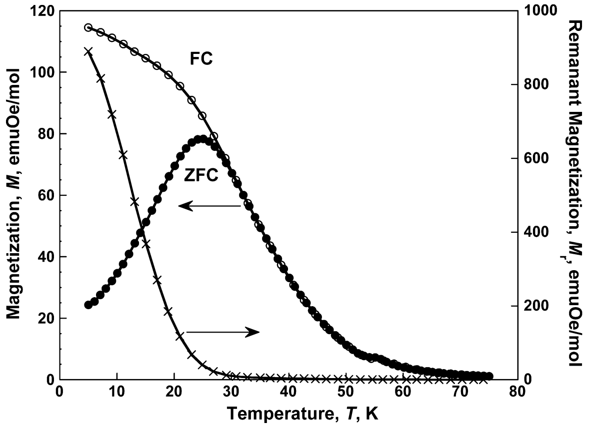

Figure 2. Temperature dependence of ZFC (●), $M(T)_{ZFC}$, and FC (○), $M(T)_{ZFC}$, magnetization of **1** in a 5 Oe external field. Temperature dependence of the remanant magnetization (×), $M_r(T)$, measured on warming at zero field after cooling at 100 Oe to 5 K.

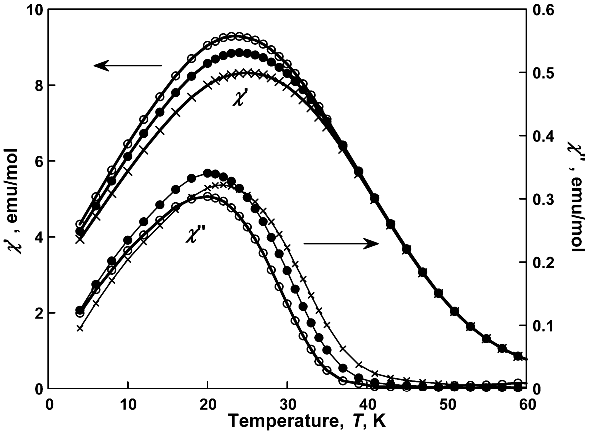

Figure 3. ac susceptibility, $\chi_{ac}(T)$ [$\chi'(T)$ and $\chi''(T)$], of [Ni(TCNE)-(NCMe)$_{1.85}$][BF$_4$] at 10 (○), 100 (●), and 1000 (×) Hz.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations, $M(T)_{ZFC}$ and $M(T)_{FC}$, respectively, rise sharply below 70 K (Figure 2), indicative of an onset of magnetic transition. $M(T)_{ZFC}$ reaches a maximum at 25 K, followed by a gradual decrease presumably due to a domain wall freezing. In contrast, $\chi(T)_{FC}$ rises upon further cooling and has a bifurcation temperature T_b ~ 30 K, suggesting a strong irreversibility. This suggests the presence of a remanant magnetization below T_b, which increases upon cooling, and a sharp increase of a remanant magnetization (Figure 2) is observed below 30 K.

The temperature dependencies of the in-phase, $\chi'(T)$, and out-of-phase, $\chi''(T)$, components of the complex alternating current (ac) susceptibility for **1** have a broad peak at T_f ~ 22 K (similar to that in direct current measurements; Figure 3). The rapid increase of $\chi''(T)$ below 40 K is indicative of the presence of remanant magnetization, suggesting an onset of the magnetic transition at 40 K (T_c). The temperature of the maximum in both $\chi'(T)$ (T_f) and $\chi''(T)$ gradually increases with increasing frequency, indicating the presence of time-dependent relaxation processes. The normalized frequency

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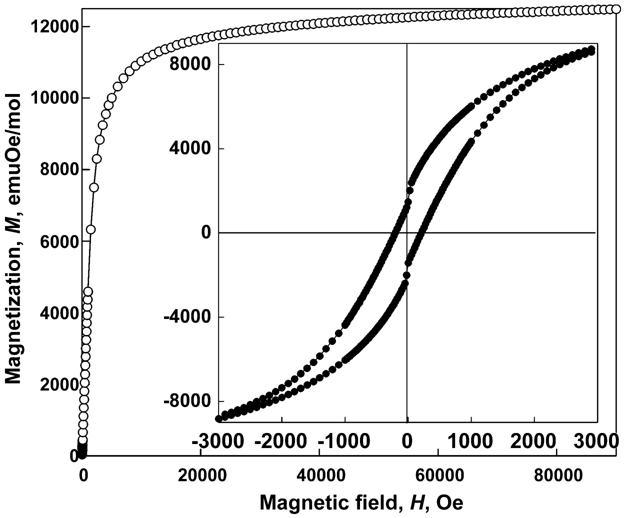

Figure 4. 2 K $M(H)$ of **1** (the inset is the hysteresis loop in the low-field region).

shift of T_f per a frequency (ω) decade, $\phi = \Delta T_f/[T_f\Delta(\log \omega)]$, is 0.033, which is characteristic of spin-glass-like materials.[14] This is attributed to structural disorder arising from the partial loss of the MeCN ligand, because ideally two MeCN units per formula unit should be present, as occurs for $[Fe(TCNE)(NCMe)_2][FeCl_4]$, for which there is less structural disorder and commitment order-of-magnitude decrease in ϕ to 0.003.[6]

The low-temperature isothermal magnetization $M(H)$ was obtained by zero-field cooling of the sample down to 2 K and subsequent measurement of the magnetization in the field up to 90 kOe. $M(H)$ of **1** increases rapidly with the field that is characteristic of magnetic ordering and approaches saturation above ~5 kOe (Figure 4). It also exhibits hysteretic behavior with a coercive field, H_{cr}, of 205 Oe and a remanant magnetization, M_r, of 1450 emu·K/mol at 2 K (inset in Figure 4).

Note that for both $Fe[TCNE]_2$ $\{= Fe^{II}[TCNE][C_4(CN)_8]_{1/2}\}$[5] and $[Fe(TCNE)(NC\text{-}Me)_2][FeCl_4]$[6] the interaction between high-spin Fe^{II} ($S = 2$) and $[TCNE]^{\bullet-}$ ($S = {}^1/_2$) is antiferromagnetic, resulting in a ferrimagnetic ordering within the layer, with the effective magnetic moment corresponding to three unpaired spins. Assuming a similar interaction for **1** and $g \sim 2.3$, high-spin Ni^{II}, a saturated magnetization of 7260 emu·Oe/mol is expected. However, at 90 kOe $M(H)$ is 12 500 emu·Oe/mol, which is substantially higher (72%) than anticipated, suggesting that the $Ni^{II}[TCNE]^{\bullet-}$ interaction is ferromagnetic in origin, as sought. For octahedral Ni^{II}, the two unpaired spins occupy antibonding e_g-derived orbitals. They are orthogonal to the partially occupied $[TCNE]^{\bullet-}$ π^* orbital, resulting in ferromagnetic coupling between these spins in accordance with the lack of back-bonding effecting **1**. $M(H)$ should saturate to 18 430 emu·Oe/mol for ferromagnetic ordering. This, however, is substantially higher than the observed value of 12 500 emu·Oe/mol, and this difference is attributed to the noncollinearity of Ni^{II} magnetic sublattice spins with respect to the $[TCNE]^{\bullet-}$ sublattice, which resulted in a lower than expected saturated magnetization at low temperatures.

In summary, a ferromagnetic interaction within M-μ_4-$[TCNE]^{\bullet-}$ layers has been characterized for the first time, and a new, more general route to the preparation of the $[M(TCNE)(NCMe)_2]$[anion] composition has been identified.

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