M[TCNQ]$_y$-Based Magnets (M = Mn, Fe, Co, Ni; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane)

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A family of molecule-based magnets of general formula M[TCNQ]$_y$ (M = Mn, Fe, Co, Ni; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) has been synthesized and characterized. The materials have been synthesized from both $M_a(CO)_b$ and $[M(NCMe)_6][SbF_6]_2$ starting materials, complementing previous studies utilizing $[M(NCMe)_6][BF_4]_2$. Magnetic ordering was observed for all materials with T_c values between 8 K [M = Ni from $Ni(CO)_4$] and 60 K {M = Mn from $[Mn(NCMe)_6][SbF_6]_2$}. The materials from $[M(NCMe)_6][SbF_6]_2$ displayed the highest critical temperatures, followed by those from $M_a(CO)_b$. With the exception of M = Ni, the lowest T_c's are obtained from the $[M(NCMe)_6][BF_4]_2$ route, which was previously reported. The materials from $[M(NCMe)_6][SbF_6]_2$ also exhibit the highest coercivity, followed by those from $[M(NCMe)_6][BF_4]_2$. With the exception of M = Fe, the materials from $M_a(CO)_b$ exhibit the lowest coercive fields. In general, magnets made from $[M(NCMe)_6][SbF_6]_2$ have a reduced $\chi''(T)$ frequency dependence with respect to materials from $[M(NCMe)_6][BF_4]_2$; thus, they exhibit less glassy magnetic behavior. Elemental analysis data indicate that small amounts of counterions and solvent are present in the products of these reactions, but less than better-coordinating $[BF_4]^-$. Thus, the synthetic route has a significant effect on the magnetic properties of the materials, and enhanced T_c's are observed when less-coordinating anions are used. Although the structures of the materials are not known, it is proposed that the $S = 1/2$ $[TCNQ]^{\bullet-}$ sp-hybridized Ns bond to multiple metal ions, thereby facilitating magnetic coupling and ordering.

Introduction

In recent years, the interdisciplinary area of molecule-based magnetic materials has seen significant growth and expansion.[1,2] In 1985, the first organic-containing molecule-based magnet was characterized, $[Fe(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ (TCNE = tetracyanoethylene), and was found to order as a ferromagnet below a critical temperature, T_c, of 4.8 K.[3] Subsequent progress was made with the synthesis of V[TCNE]$_y$•zCH$_2$Cl$_2$, the first room-temperature organic magnet ($T_c \approx$ 400 K), which was initially from the reaction of TCNE and $V^0(C_6H_6)_2$[4] and later from the reaction of TCNE and $V^0(CO)_6$.[5] Further progress was made by utilizing the volatile nature of the precursors, leading to the development of a chemical vapor deposition (CVD) route to solvent-free thin films of the V[TCNE]$_y$ magnet that also exhibited enhanced air stability.[6] V[TCNE]$_y$ is an amorphous, disordered material with a small coercive field at room temperature.[7] Furthermore, it is a magnetic semiconductor with a room-temperature conductivity of $\sim 10^{-4}$ S/cm, and recent magnetotransport studies indicate that electrons in valence and conducting bands are spin-polarized, suggesting spintronic applications.[8] In contrast, the reactions of $Fe(CO)_5$ with TCNE as

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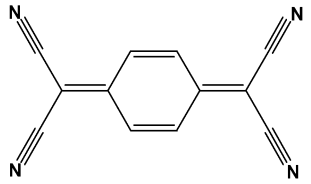
well as TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane, **1**) form $Fe[TCNE]_2$ and $Fe[TCNQ]_2$ that magnetically order



1: 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)

at 100 and 35 K, respectively.[9]

The chemistry of TCNQ has been widely studied,[10] primarily due to its potential application in organic conductors.[10,11] $M[TCNQ]_y$ materials have previously been reported as methanol or water solvates,[10,12] as products of electrochemical synthesis,[11c] and from $Fe(CO)_5$[9] and $[M(NCMe)_6][BF_4]_2$.[13,14] Two routes to $M[TCNQ]_y$-based magnetic materials are explored herein, including via $[M(NCMe)_6][SbF_6]_2$, and several new magnetically ordered materials are reported. Use of $[BF_4]^-$ salts by Dunbar led to glassy magnetically ordered materials that incorporated the anion in the product,[13,14] and, in an attempt to identify a weaker binding anion, $[SbF_6]^-$ [15] was selected to minimize the presence of the anion and enhance T_c.

Experimental Section

Due to the air and water sensitivity of the materials studied, all manipulations and reactions were performed in a Vacuum Atmospheres DriLab glovebox (<1 ppm O_2; <1 ppm H_2O). CH_2Cl_2 and MeCN were dried over two columns of activated alumina.[16] $Ni(CO)_4$ was used as purchased from Strem. *Ni(CO)₄ is extremely hazardous and* ***must*** *be handled with great care.* $Co_2(CO)_8$ (Strem) was sublimed at 40 °C and 50 mTorr. $[M(NCMe)_6][SbF_6]_2$ starting materials were synthesized by a literature method using $Ag[SbF_6]$ (Acros) as the anion source.[17] [*n*-Bu_4N]I (Aldrich) was used as received. TCNQ was a gift from DuPont and was purified by recrystallization from MeCN prior to use.

[*n*-Bu_4N][TCNQ]. [*n*-Bu_4N]I (2.20 g; 5.96 mmol) was dissolved in 8 mL of hot acetonitrile and added dropwise to a stirred solution of TCNQ (0.815 g; 4.00 mmol dissolved in 90 mL) in hot acetonitrile, immediately causing the solution to turn dark green. After heating to reduce the volume to 10 mL, the dark solution was allowed to cool to room temperature and then put in the freezer overnight. The dark blue crystalline product was filtered and dried for 3 h under vacuum (yield: 1.70 g; 95%).

$Ni[TCNQ]_2 \cdot zCH_2Cl_2$ from $Ni(CO)_4$. Special considerations were taken in the preparation of $Ni[TCNQ]_2 \cdot zCH_2Cl_2$ from the reaction of TCNQ and $Ni(CO)_4$ due to the hazardous nature of $Ni(CO)_4$. $Ni(CO)_4$ was condensed into an evacuated Schlenk flask in a liquid N_2 bath; a known volume of CH_2Cl_2 was then added to the flask via vacuum transfer to form a $Ni(CO)_4$ solution of known concentration (12 mM). This solution was immediately taken into the glovebox, where all further manipulations were performed. One equivalent of $Ni(CO)_4$ in solution (11.0 mL; 0.129 mmol) was measured out and added dropwise to a stirred solution of 2 equiv of TCNQ (52.7 mg; 0.258 mmol) in CH_2Cl_2. The mixture was allowed to react overnight, after which it was filtered and dried (yield: 48.6 mg; 80%). The observed elemental analysis (calcd[18]) for $Ni[TCNQ]_2 \cdot zCH_2Cl_2$ from $Ni(CO)_4$ [z = 0.53, $NiC_{24.53}H_{9.06}N_8Cl_{1.06}$: %C = 57.67 (57.54), %H = 1.91 (1.78), %N = 21.66 (21.88)].

$Co[TCNQ]_y \cdot zCH_2Cl_2$ from $Co_2(CO)_8$. One equivalent of $Co_2(CO)_8$ (22.7 mg; 0.0664 mmol) and 4 equiv of TCNQ (53.3 mg; 0.261 mmol) were each dissolved in a minimum amount of CH_2Cl_2. The $Co_2(CO)_8$ solution was then added dropwise to the TCNQ solution, immediately turning it dark. The mixture was allowed to react overnight, after which it was filtered and dried (yield 51.3 mg; ~80%). The observed elemental analysis (calcd[18]) for $Co[TCNQ]_2 \cdot zCH_2Cl_2$ from $Co_2(CO)_8$ [z = 0.58, $CoC_{24.58}H_{9.16}N_8Cl_{1.16}$: %C = 57.00 (57.15), %H = 1.82 (1.79), %N = 21.86 (21.69)].

$M[TCNQ]_y$ from $[M(NCMe)_6][SbF_6]_2$ (M = Mn, Fe, Co). In a typical preparation, 1 equiv of $[M(NCMe)_6][SbF_6]_2$ (110 mg; 0.14 mmol) and a slight excess of [*n*-Bu_4N][TCNQ] (150 mg; 0.34 mmol) were each dissolved in a minimum amount of MeCN, after which the $[TCNQ]^{\bullet -}$ solution was added dropwise to the stirring metal solution. The mixture turned dark immediately with the addition of the first drops of $[TCNQ]^{\bullet -}$ and was allowed to react 20 min at room temperature. The dark, amorphous product was filtered, washed with 2 × 10 mL of MeCN and 3 × 10 mL of ether, and dried (yield: 64 mg; ~80%). Elemental analysis results indicate that small amounts of $[n\text{-}Bu_4N]^+$, MeCN, and a fluorine-containing impurity are present in the samples, although $[SbF_6]^-$ is not readily visible in the IR (~660 cm^{-1}). The observed elemental analysis (calcd[18]): {$Mn[TCNQ]_{1.38}[n\text{-}Bu_4N]_{0.10}[SbF_6]_{0.34} \cdot 1.32MeCN$, $MnC_{20.8}H_{13.08}N_{6.94}Sb_{0.34}F_{2.04}$: %C = 50.50 (50.44), %H = 2.92 (2.66), %N = 19.50 (19.63); $Fe[TCNQ]_{1.98}[n\text{-}Bu_4N]_{0.02}[SbF_6]_{0.04} \cdot 0.31MeCN$, $FeC_{24.70}H_{9.57}N_{8.25}Sb_{0.04}F_{0.24}$: %C = 60.74 (60.90), %H = 2.21 (1.98), %N = 23.56 (23.72); $Co[TCNQ]_2[n\text{-}Bu_4N]_{0.10}[SbF_6]_{0.10}$, $CoC_{25.60}H_{11.60}N_{8.10}Sb_{0.10}F_{0.60}$: %C = 60.14 (59.69), %H = 2.38 (2.27), %N = 21.48 (22.02)}.

$Ni[TCNQ]_y$ from $[Ni(NCMe)_6][SbF_6]_2$. In a typical preparation, 1 equiv of $[Ni(NCMe)_6][SbF_6]_2$ (100 mg; 0.13 mmol) and a slight excess of [*n*-Bu_4N][TCNQ] (140 mg; 0.31 mmol) were each dissolved in a minimum amount of MeCN, after which the $[TCNQ]^{\bullet -}$ solution was added dropwise to the stirring solution. The mixture turned dark immediately with the addition of the first drops of $[TCNQ]^{\bullet -}$ and was allowed to react 4 h at room temperature. (The reaction for $[Ni(NCMe)_6][SbF_6]_2$ to $Ni[TCNQ]_y$ product takes longer than that of the other metals, proceeding through a green kinetic intermediate.[14]) The dark, amorphous

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product was filtered, washed with 2 × 10 mL of MeCN and 3 × 10 mL of ether, and dried (yield: 60.0 mg; ∼50%). Elemental analysis results indicate that small amounts of [*n*-Bu_4N]$^+$, MeCN, and a fluorine-containing impurity are present in the samples, although $[SbF_6]^-$ is not readily visible in the IR (∼660 cm^{-1}). The observed elemental analysis (calcd[18]) for {Ni[TCNQ]$_{1.32}$[*n*-Bu_4N]$_{0.04}$-$[SbF_6]_{0.24}$·0.54MeCN, $NiC_{17.56}H_{8.34}N_{5.86}Sb_{0.24}F_{1.44}$: %C = 50.63 (50.62), %H = 2.21 (2.02), %N = 19.59 (19.70)}.

Powder samples for magnetic measurements were loaded in airtight Delrin holders and packed with oven-dried quartz wool to prevent movement of the sample in the holder. The dc magnetization temperature dependence was obtained by cooling in zero field and then data was collected on warming in an external magnetic field using a Quantum Design MPMS-5XL 5 T SQUID magnetometer equipped with a reciprocating sample measurement system, low field option, and continuous low-temperature control with enhanced thermometry features. The T_c's were obtained from an extrapolation of the low-field $M(T)$ to the temperature at which $M(T) \rightarrow 0$ as used in determining T_c of V[TCNE]$_y$·$z$$CH_2Cl_2$.[4a,7] The ac magnetic susceptibility was measured in $H_{dc} = 0$ and 1 or 3 Oe ac field (zero dc applied field) at 10, 100, and 1000 Hz or 33, 100, and 1000 Hz. Phase-sensitive lock-in detection allowed both the in-phase (χ') and out-of-phase (χ'') linear susceptibilities to be extracted. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 2050 analyzer. Infrared spectra were obtained as KBr pellets using a Bruker Tensor 37 FTIR spectrometer (±1 cm^{-1}). Elemental analyses were performed by Complete Analysis Laboratories Inc. of Parsippany, NJ.

Results and Discussion

Synthesis. Magnetically ordered V[TCNE]$_y$·$z$$CH_2Cl_2$ can by synthesized by the reaction of $V^0(CO)_6$[5] or $V^o(C_6H_6)_2$[4] with TCNE. While mechanistic studies with $V^o(C_6H_6)_2$ reveal that 2 equiv of TCNE are reduced to $[TCNE]^{\bullet -}$ to form V^{II}, $V(CO)_6$ [$E^{-/o} = +0.88$ V vs SCE (CH_2Cl_2)[19]] should not reduce TCNQ [$E^{-/o} = +0.17$ V vs SCE (CH_2Cl_2)[20]] due to the high (albeit irreversible) oxidation potential. Nonetheless, an immediate reaction occurs, forming a dark, amorphous product. Hence, the reaction of TCNQ and $V(CO)_6$ must not initially proceed by electron transfer, but by ligand substitution via nucelophilic attack of the TCNQ and concomitant CO loss, leading to intermediates that reduce the oxidation potential of the V.[21] By analogous reactions, M[TCNQ]$_y$ (M = Fe, Ni, Co) have been synthesized from $M_a(CO)_b$ and TCNQ (eq 1), although their mechanisms are unknown. Formation of Fe[TCNQ]$_2$·$z$$CH_2Cl_2$ from $Fe(CO)_5$ and TCNQ has been previously reported,[9] but the results are included herein for this comparative study.

Redox routes to the targeted materials are avoided via eq 2; however, cations and anions may be occluded or anions may coordinate to M, making the formation of pure products less likely. Since $[BF_4]^-$ is known to coordinate to M, for example, in $Cr(NCMe)_4(BF_4)_2$,[22] it may be a poor anion choice for M[TCNQ]$_y$ syntheses in which the products are often formed quickly and anions, even when coordinated weakly, can become trapped within the structure. Indeed, elemental analysis results reported in Dunbar's work[14] suggest that anions are present in the materials from $[M(NCMe)_6][BF_4]_2$, as experimental and theoretical values reported differed a great deal (2−2.8% in some cases). These deviations could be greatly reduced by the incorporation of counterions and solvent into the suggested formulas. Studies on the coordinating abilities of anions indicate that $[SbF_6]^-$ is a poorer coordinating anion than $[BF_4]^-$;[15] therefore, $[SbF_6]^-$ was chosen for this study.

Table 1. Summary of the IR Properties for M[TCNQ]$_s$-Based (M = Mn, Fe, Co, Ni) Magnetic Materials

M source	δ_{C-H}, cm^{-1}	$\upsilon_{C=C}$, cm^{-1}	$\upsilon_{C\equiv N}$, cm^{-1}
$[Mn(MeCN)_6][SbF_6]_2$	823 m, 805 sh	1504 s	2193 s, 2120s, ∼2060 sh
$[Mn(MeCN)_6][BF_4]_2$[14]	826 m	1505 s	2205 s, 2187 s, 2137 sh
$[Fe(MeCN)_6][SbF_6]_2$	829 m, 807 sh	1503 s	2194 s, 2132 s
$Fe(CO)_5$[9]	826 m	1505 s	2194 s, 2163 s, 2107 s
$[Fe(MeCN)_6][BF_4]_2$[14]	827 m	1505 s	2217 s, 2187 s, 2142 sh
$[Co(MeCN)_6][SbF_6]_2$	829 m, 807 sh	1503 s	2197 s, 2137 s
$Co_2(CO)_8$	825 m, 807 sh	1505 s	2197 s, 2161 m, 2111 s
$[Co(MeCN)_6][BF_4]_2$[14]	827 m	1505 s	2217 s, 2188 s, 2137 sh
$[Ni(MeCN)_6][SbF_6]_2$	826 m, 808 w	1503 s	2208 s, 2194 s, 2141 s, ∼2060 sh
$Ni(CO)_4$	828 m, 808 sh	1503 s	2198 s, 2165 sh, 2046 m
$[Ni(MeCN)_6][BF_4]_2$[14]	829 m	1503 s	2224 s, 2208 s, 2192 s, 2155 sh

All reactions (eqs 1 and 2) were fast, as evidenced by the immediate formation of an insoluble precipitate that was washed thoroughly, except that formation of Ni[TCNQ]$_y$ via eq 2 proceeded slowly for unknown reasons.[23] {The slow formation of Ni[TCNQ]$_y$ from $[Ni(NCMe)_6][SbF_6]_2$ is consistent with that from $[Ni(NCMe)_6][BF_4]_2$.[14]}

$$^1/_aM_a(CO)_b + 2TCNQ \rightarrow M[TCNQ]_y + {}^b/_aCO \quad (1)$$

$$[M(NCMe)_6][SbF_6]_2 + 2[n\text{-}Bu_4N][TCNQ] \rightarrow M[TCNQ]_y + 2[n\text{-}Bu_4N][SbF_6] + 6MeCN \quad (2)$$

$y \approx 2$ M = Mn, Fe, Co, Ni

solvents: CH_2Cl_2 (eq 1), MeCN (eq 2)

IR Spectroscopy. The $\upsilon_{C\equiv N}$ IR spectra for M[TCNQ]$_y$-based materials show multiple absorptions between 2046 and 2208 cm^{-1} (Table 1) with MeCN stretches visible in some of the materials at ∼2314 and 2286 cm^{-1}. These absorptions are lower in energy than that of $TCNQ^0$ at 2222 (s) cm^{-1}, indicating that the products contain reduced TCNQ. The number and broad nature of the $\upsilon_{C\equiv N}$ stretches suggest multiple C≡N environments in the materials. A similar multiple-band $\upsilon_{C\equiv N}$ region is observed for V[TCNE]$_y$·$z$$CH_2Cl_2$, which has a broad absorption at 2090 cm^{-1} and three relatively narrow features at 2214, 2191, and 2152 cm^{-1}.[24] Each of the products from $[M(NCMe)_6][SbF_6]_2$ (M = Mn, Fe, Co) shows two distinct bands at ∼2195 and ∼2135 cm^{-1} . Three $\upsilon_{C\equiv N}$ bands are observed for M = Ni from $[Ni(NCMe)_6][SbF_6]_2$ at 2208, 2194, and 2141 cm^{-1}. The presence of $[TCNQ]^{2-}$ for M = Mn, Ni is suggested by

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the elemental analysis results, which indicate that the products may contain <2 TCNQs per metal. This is supported by the presence of a low-energy shoulder at ~2060 cm^{-1} in the IR, indicative of $[TCNQ]^{2-}$.[25] This shoulder is not present for M = Fe, Co from eq 2, supporting the absence of $[TCNQ]^{2-}$ in these materials suggested by the EA data. MeCN stretches are visible in some of the materials at ~2314 and 2286 cm^{-1}.

The products of eq 1 exhibit three bands in the $\upsilon_{C\equiv N}$ region rather than two. The position of the highest energy $\upsilon_{C\equiv N}$ absorption is consistent between these two reaction routes for M = Fe, Co, but the lower energy peak in the products of eq 2 occurs between the two lower energy peaks in the products of eq 1 and may be a convoluted sum of these two peaks. Surprisingly, the $\upsilon_{C\equiv N}$ stretches appear to be different for the materials from eq 2 than for those reported from $[M(NCMe)_6][BF_4]_2$ starting materials.[12,14] Three peaks were reported for the majority of those materials with an additional peak at higher energy (~2205−2225 cm^{-1}) that is not observed in the products from eq 2. The peak at ~2185−2210 cm^{-1} is the most consistent between the materials from $[M(NCMe)_6][BF_4]_2$ and those from eq 2, although the lowest energy peak is also similar for those materials prepared from $[M(NCMe)_6][BF_4]_2$ in MeCN.[14] Peaks for M = Ni in this region are similar to two observed in a reported $Ni[TCNQ]_2$ prepared from $NiCp_2$ with TCNQ (2205, 2135, and 2060 cm^{-1}).[10c]

Each of the materials shows a single, sharp characteristic $\upsilon_{C=C}$ stretch at ~1503 cm^{-1} that varies only slightly between the materials and is indicative of $[TCNQ]^{\bullet-}$ and $TCNQ^{2-}$ rather than $TCNQ^0$.[25] Another characteristic region in TCNQ materials is the δ_{C-H} region from 800 to 865 cm^{-1}. The materials reported herein show distinct absorptions in this region that are consistent with $[TCNQ]^{\bullet-}$ (826−831 cm^{-1}) rather than $TCNQ^0$ (864 cm^{-1}). In addition, some of the materials exhibit a weak stretch at lower energy (~808 cm^{-1}) that could indicate a small amount of $[TCNQ-TCNQ]^{2-}$ σ-dimer.[12,14] The $\upsilon_{C=C}$ and δ_{C-H} regions show little change between the products of eq 1 and eq 2 for a given metal; additionally, there is little difference between the materials from eq 2 and those from $[M(NCMe)_6][BF_4]_2$ in these regions. Aliphatic υ_{C-H} stretches are also visible in many of the materials below 3000 cm^{-1}, indicative of the presence of CH_2Cl_2 or MeCN solvent.

The TGA data suggests that solvent is present in the materials as supported by the IR and elemental analysis results. For M = Mn, Fe, Co, TGA results show a small mass loss, indicative of coordinated or entrapped solvent between ~100 and 200 °C, followed by a rapid mass loss above ~300 °C, suggestive of decomposition. For M = Ni, TGA data indicates that solvent loss occurs in the same region, but product decomposition may begin at lower temperatures of ~220 °C.

Structure. The rapid reactions that occur in both eq 1 and eq 2 result in the formation of highly amorphous powders. Powder diffraction was attempted on the materials, but unlike the materials reported from $[M(NCMe)_6][BF_4]_2$[14] no diffraction was observed. Enhanced magnetic properties (H_{cr}, T_c) are therefore observed in the more amorphous materials, which is consistent with data observed for similar $M[TCNE]_y$ systems.[26] Although the structures of the materials are not known, it is proposed that the $S = 1/2$ $[TCNQ]^{\bullet-}$ sp-hybridized N's bond to multiple metal ions, thereby facilitating magnetic coupling and ordering.

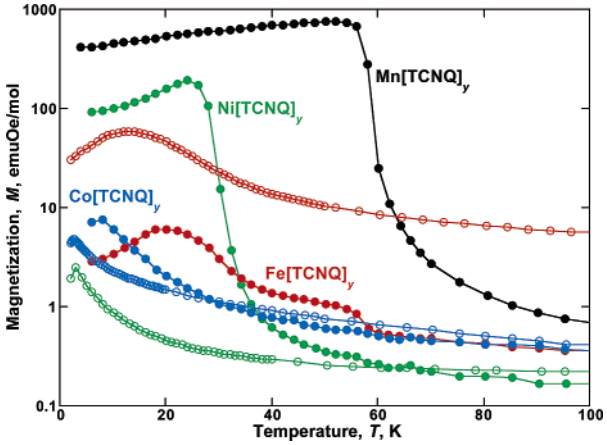

Figure 1. Magnetization versus temperature for $M[TCNQ]_y$ from $M_a(CO)_b$ (○) and $[M(NCMe)_6][SbF_6]_2$ (●). Data were collected in 5 Oe external magnetic field.

Table 2. Summary of the Magnetic Properties for $M[TCNQ]_y$-Based (M = Mn, Fe, Co, Ni) Materials

M source	θ', K	T_c,[a] K	T_b,[b] K	μ_{eff}, μ_B (300 K)	M,[c] emu Oe/mol (2 K)	M_{rem}, emu Oe/mol (2 K)	H_{cr}, Oe (2 K)
$[Mn(MeCN)_6][SbF_6]_2$	65	60	58	7.24	22617	2000	25
$[Mn(MeCN)_6][BF_4]_2$[14]	44[d]	44[e]	~10[f]				20
$[Fe(MeCN)_6][SbF_6]_2$	22	37	56	5.81	8430	1260	3600
$Fe(CO)_5$[9]	30	35	30	6.20	12110[g]	840[g]	1600[g]
$[Fe(MeCN)_6][BF_4]_2$[14]	−10[d]	28[e]	~18[f]				750
$[Co(MeCN)_6][SbF_6]_2$	12	20	16	5.73	3453	680	850
$Co_2(CO)_8$		12	8.5	4.72	6830	9.7	35
$[Co(MeCN)_6][BF_4]_2$[14]	−6[d]	7[e]	~5[f]				190
$[Ni(MeCN)_6][SbF_6]_2$	31	31	30	1.75	8917	770	120
$Ni(CO)_4$	4	8	6	6.73	6055	4.6	11
$[Ni(MeCN)_6][BF_4]_2$[14]	37[d]	24[e]	~17[f]				270

[a] Obtained from an extrapolation of the low-field $M(T)$ to the temperature at which $M(T) \rightarrow 0$. [b] FC/ZFC bifurcation temperature at 5 Oe. [c] M at 5 T, as none of the samples reach saturation. [d] θ values from ref 14. (Obtained from best fitting of $\chi^{-1}(T)$ in 60−300 K range.) [e] T^* values from ref 14. (Obtained from the onset temperature of $\chi''/(T)$ in ac susceptibility measurements.) [f] FC/ZFC bifurcation temperature at 100 Oe. [g] Hysteresis at 4 K.

Magnetic Studies. The 2−300 K magnetic susceptibility, $\chi(T)$, was determined at 500 or 1000 Oe and magnetization, M, was determined at 5 Oe for each material (Figure 1). The data for each material can be fit to the Curie−Weiss expression with θ' values dependent on the identity of M as well as the synthetic route (Table 2). The $\chi^{-1}(T)$ data is generally linear in the region immediately above T_c, but $d[\chi^{-1}(T)]/dT$ decreases above this region, indicative of ferrimagnetic behavior. Values of μ_{eff} [$\equiv(8\chi T)^{1/2}$] at 300 K are in the range 1.75 μ_B {M = Ni from $[Ni(NCMe)_6][SbF_6]_2$} to 7.24 μ_B {M = Mn from $[Mn(NCMe)_6][SbF_6]_2$} and deviate from the theoretical values (6.40, 5.48, 4.58, and 3.74 μ_B for M = Mn, Fe, Co, and Ni, respectively). With the

(25) Khatkale, K. S.; Devlin, J. P. *J. Chem. Phys.* **1979**, *70*, 1851.

(26) Pokhodnya, K. I.; Vickers, E. B.; Bonner, M.; Epstein, A. J.; Miller, J. S. *Chem. Mater.* **2004**, *16*, 3218.

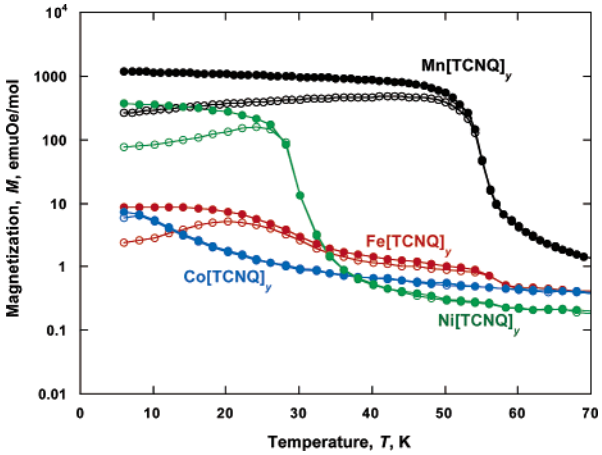

Figure 2. Zero field cooled (ZFC, ○) and field cooled (FC, ●) *M(T)* for M[TCNQ]$_y$ from [M(NCMe)$_6$][SbF$_6$]$_2$. Data were collected in 5 Oe external magnetic field.

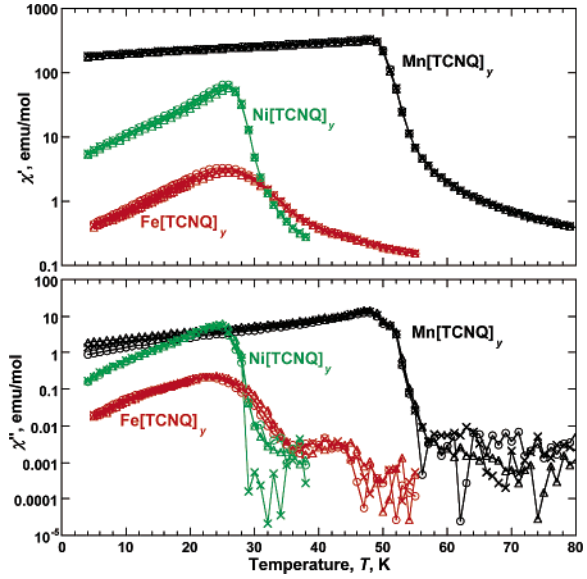

Figure 3. $\chi'(T)$ and $\chi''(T)$ for M[TCNQ]$_y$ from [M(NCMe)$_6$][SbF$_6$]$_2$ in H_{ac} = 1 Oe at 33 (○), 100 (×), and 1000 (△) Hz.

exception of M = Ni prepared from [Ni(NCMe)$_6$][SbF$_6$]$_2$, all μ_{eff} values are lower than the theoretical values. A wide range of ordering temperatures is observed, T_c, ranging from 8 K [M = Ni from Ni(CO)$_4$] to 60 K {M = Mn from [Mn(NCMe)$_6$][SbF$_6$]$_2$}. Bifurcation temperatures, T_b, between 6 K [M = Ni from Ni(CO)$_4$] and 58 K {M = Mn from [Mn(NCMe)$_6$][SbF$_6$]$_2$} are observed in the zero field cooled (ZFC) and field cooled (FC) magnetization curves (Figure 2; Table 2), illustrating that magnetically ordered materials are obtained in the reactions.

The temperature dependencies of the in-phase, $\chi'(T)$, and out-of-phase, $\chi''(T)$, components of ac susceptibility were measured at 10 (or 33), 100, and 1000 Hz (Figure 3). Each material exhibited either one or two peaks in both χ' and χ''. The presence of substantial $\chi''(T)$ signals in these ordered materials supports the proposal that the materials are ferrimagnets. The products of eq 2 exhibited multiple peaks or shoulders in $\chi'(T)$ and $\chi''(T)$, indicating a greater degree of disorder and suggesting multiple phases. The $\chi'(T)$ and $\chi''(T)$ peak positions shift <1 K when the frequency is increased from 10 (or 33) to 1000 Hz, although the broadness

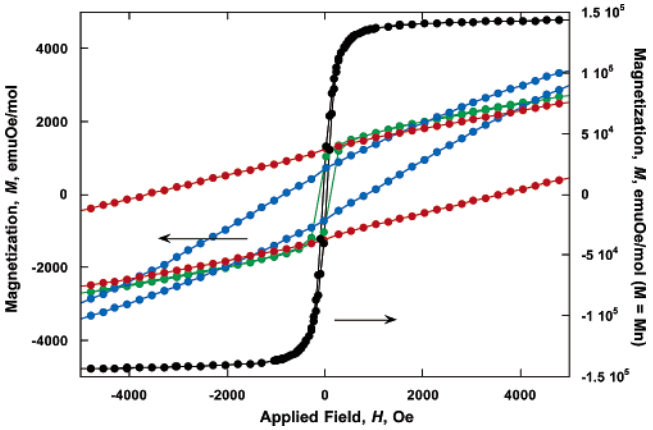

Figure 4. Hysteresis loops at 2 K for M[TCNQ]$_y$ from [M(NCMe)$_6$][SbF$_6$]$_2$. [M = Mn (●), Co (●), Fe (●), Ni(●)].

of the peaks makes the peak position more difficult to determine in some cases. In contrast, the analogous materials from [M(NCMe)$_6$][BF$_4$]$_2$ are reported to be glassy magnets due to their frequency dependence.[14] In these materials, the peak positions increase by up to 2 K when the frequency is increased from 1 to 801 Hz.

Large differences in the TCNQ materials' magnetic properties were also apparent from the field-dependent isothermal magnetization, *M*(*H*), which was determined on each material at 2 or 5 K (Figure 4; Table 2). The curves show a wide variety of shapes ranging from sharp rises at low field that approach saturation at 5 T {M = Mn from [Mn(NCMe)$_6$][SbF$_6$]$_2$} to more linear behavior and more gentle slopes as a function of *H* [M = Co from Co$_2$(CO)$_8$]. The expected M_s values for M^{II} antiferromagnetically coupled to two S = 1/2 [TCNQ]$^{\bullet-}$ are 16755, 11170, 5585, and 560 emu Oe/mol for M = Mn, Fe, Co, and Ni (g = 2.2), respectively. Additionally, the expected M_s values for M^{II} ferromagnetically coupled to two S = 1/2 [TCNQ]$^{\bullet-}$ are 39095, 33510, 27925, and 23460 emu Oe/mol for M = Mn, Fe, Co, and Ni (g = 2.2), respectively. As the *M* values at 5 T for all M[TCNQ]$_y$ materials are closer to the M_s values expected for ferrimagnets (although some show significant deviation from either value), it is proposed that the M[TCNQ]$_y$ materials are ferrimagnets. The systems show coercive fields (H_{cr}) between 11 Oe [M = Ni from Ni(CO)$_4$] and 3600 Oe {M = Fe from [Fe(NCMe)$_6$][SbF$_6$]$_2$} at 2 K. H_{cr} is significantly lower for the products from M$_a$(CO)$_b$ starting materials than those from [M(NCMe)$_6$][SbF$_6$]$_2$. The remanent magnetization (M_{rem}) values fall in the range of 4.6 emu Oe/mol [M = Ni from Ni(CO)$_4$] to 2000 emu Oe/mol {M = Mn from [Mn(NCMe)$_6$][SbF$_6$]$_2$} at 2 K.

In general, the magnetic properties reported herein for the materials from [M(NCMe)$_6$][SbF$_6$]$_2$ are similar to those from [M(NCMe)$_6$][BF$_4$]$_2$ reported by Dunbar and co-workers.[14] Bifurcation temperatures, T_b, obtained from the data are significantly higher than those reported by Dunbar, perhaps due to the different applied fields in which they were obtained (5 and 100 Oe, respectively.) According to the definition used in this work [extrapolation of the low-field *M*(*T*) to the temperature at which $M(T) \rightarrow 0$], T_c's are higher for our materials from [M(NCMe)$_6$][SbF$_6$]$_2$ than for Dunbar's materials from [M(NCMe)$_6$][BF$_4$]$_2$. Again, this may be

partially explained by the different applied fields used in the experiments. A substantial increase in H_{cr} is also observed for our materials for M = Fe, Co as well as a slight increase for M = Mn. Dunbar defines T^* for the materials as the onset temperature of $\chi''(T)$; for M = Mn, Fe, Ni, our materials order at slightly higher temperatures by this parameter as well.

Conclusion

A family of molecule-based magnets of general formula $M[TCNQ]_y$ (M = Mn, Fe, Co, Ni; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) has been synthesized and characterized by IR, TGA, elemental analysis, and magnetic susceptibility measurements (ac and dc). The materials have been synthesized from two routes and metal starting materials, namely, $M_a(CO)_b$ and $[M(NCMe)_6][SbF_6]_2$, complementing previous studies utilizing $[M(NCMe)_6][BF_4]_2$.[14] Although the structures of the materials are not known, it is proposed that the sp-hybridized nitrogens of the CN groups on $S = 1/2$ $[TCNQ]^{\bullet -}$ bond to multiple metal ions, thereby facilitating magnetic ordering. Magnetic ordering was observed for all materials with T_c values between 8 K [M = Ni from $Ni(CO)_4$] and 60 K {M = Mn from $[M(NCMe)_6][SbF_6]_2$}. In general, T_c's are highest for the materials from $[M(NCMe)_6][SbF_6]_2$, followed by those from $M_a(CO)_b$. With the exception of M = Ni, the lowest T_c's are obtained from the previously reported $[M(NCMe)_6][BF_4]_2$ route.[14] The materials from $[M(NCMe)_6][SbF_6]_2$ also exhibit the highest coercivity, followed by those from $[M(NCMe)_6][BF_4]_2$. With the exception of M = Fe, the materials from $M_a(CO)_b$ exhibit the lowest coercivity. Elemental analyses indicate that small but significant amounts of counterions and solvent are present in the products of these reactions, although best fits indicate that fewer counterions are present in the materials from $[M(NCMe)_6][SbF_6]_2$ with respect to those from prepared from $[M(NCMe)_6][BF_4]_2$,[14] as expected due to the larger and more weakly coordinating $[SbF_6]^-$ ion.[15] Hence, the synthetic route has a significant effect on the magnetic properties of the materials for a given metal and that varied amounts of counterions were present in the products.

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