Glassy Magnets Composed of Metals Coordinated to 7,7,8,8-tetracyanoquinodimethane: $M(TCNQ)_2$ ($M = Mn, Fe, Co, Ni$)[†]

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The homologous series $M(TCNQ)_2$ ($M = Mn(II), Fe(II), Co(II)$, and $Ni(II)$; TCNQ = 7,7,8,8-tetracyanoquinodimethane) prepared from reactions of $[M(CH_3CN)_6][BF_4]_2$ and $[n\text{-}Bu_4N][BF_4]$ in CH_3CN has been carefully analyzed from the perspective of synthetic issues and physical characterization, including complete magnetic analyses by the tools of dc and ac magnetometry. The preparative method was optimized to definitively establish the reproducibility of the chemistry as judged by infrared spectroscopy, thermal gravimetric analysis, powder X-ray crystallography, and elemental analysis. Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) studies results are also in accord with the conclusion that these materials are pure, isostructural phases. The dc magnetic measurements reveal a spontaneous magnetization for the four materials at low temperatures with a weak field coercivity of 20, 750, 190, and 270 G at 2 K for $Mn(TCNQ)_2$, $Fe(TCNQ)_2$, $Co(TCNQ)_2$, and $Ni(TCNQ)_2$, respectively. At low temperatures, ac susceptibility measurements confirm the presence of a magnetic phase at 44, 28, 7, and 24 K for $Mn(TCNQ)_2$, $Fe(TCNQ)_2$, $Co(TCNQ)_2$, and $Ni(TCNQ)_2$, respectively, but do not support the description of this system as a typical magnet. In the absence of the ac magnetic data, the behavior is indicative of ferri- or ferromagnetic ordering (depending on the metal), but in fact a complete investigation of their physical properties revealed their true nature to be a glassy magnet. The glassiness, which is a high magnetic viscosity known to originate from randomness and frustration, is revealed by a frequency dependence of the ac susceptibility data and is further supported by a lack of a lambda peak in the heat capacity data. These results clearly demonstrate that molecule-based materials with a presumed magnetic ordering may not always be exhibiting truly cooperative behavior.

Introduction

The design of new materials from molecular building blocks is rapidly being integrated into the chemical research landscape.[1] Some of the early players in this arena entered the scene in the 1950s when Dupont researchers first synthesized the molecule 7,7,8,8-tetracyanoquinodimethane, commonly referred to as TCNQ. This versatile organic acceptor led to the discovery of the first "organic metal", namely TTF-TCNQ (TTF = tetrathiafulvalene),[2] a finding that led to an explosion of activity regarding the electrical properties of charge-transfer salts of TCNQ.[3,4] Use of the TCNQ radical in

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magnetic materials is much less known, with the exception of studies based on the metallocene family [MCp$^*_2$][TCNQ] (M = Cr,[5] Mn,[6] and Fe [7]). These salts, which exhibit long-range magnetic ordering, are composed of stacks of alternating donors (metallocenes) and acceptors (TCNQ) with no direct bonding between the TCNQ and the transition metal. In addition to this class of TCNQ compounds, there are numerous examples of nonmetallocene compounds of TCNQ in which TCNQ$^{-\bullet}$ acts as an outer-sphere radical anion.[8]

A much less investigated avenue of TCNQ chemistry, and one that is of interest to us, is its use as a nitrile ligand.[9] It has been demonstrated by X-ray crystallographic means that TCNQ coordinates to transition metals in mono-, bi-, tri, and tetradentate binding modes.[9c] These complexes typically contain co-ligands as well as TCNQ ligands.[10,11] Although they are much more rare, one can also find reports of TCNQ compounds that contain only a transition metal along with two or three solvent molecules.[12,13] The first report of such compounds emerged nearly four decades ago when Melby et al. synthesized the series M(TCNQ)$_2$·3(H$_2$O) (M = Mn, Fe, Co, Ni). We recently extended the M(TCNQ)$_2$·(S)$_x$ family to include phases with alcohols, and obtained single crystals of several examples.[14] In addition we performed the first structural characterization of the controversial electronic materials Cu^I(TCNQ) (Phases I and II),[15] and the related phase Ag(TCNQF$_4$),[16] (TCNQF$_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane). Other than Ag(TCNQ), there are no other crystallographically characterized binary phases of TCNQ.[17]

In the aforementioned research on 1:1 M(TCNQ) phases, the interest in these compounds was driven by a desire to obtain interesting conducting rather than the magnetic properties;[12,13] this is not surprising, given that metal ions in these materials are diamagnetic (Cu^I and Ag^I). It occurred to us, however, that 1:2 phases based on divalent paramagnetic metals would be excellent prospects for exhibiting interesting magnetic phenomena. Herein we report a detailed investigation of four isostructural magnets of general formula M(TCNQ)$_2$ (M = Mn, Fe, Co, Ni).[18,19] According to the usual dc magnetic data, these materials appear to be

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ferromagnets or ferrimagnets depending on the identity of the metal, but we have discovered that the magnetism warrants a more precise evaluation. Our findings are not only relevant to the $M(TCNQ)_2$ family of compounds, but are also germane to the general subject of magnetism as it pertains to molecule-based systems. In the course of this work, Miller et al. reported the magnetism of a charge-transfer product of $Fe(CO)_5$ and $TCNQ^0$, namely $[Fe(TCNQ)_2]\cdot 0.70(CH_2Cl_2)$, which exhibits a magnetic ordering at 35 K.[20]

Experimental Section

Starting Materials. Unless otherwise stated, all manipulations were performed at room temperature under anaerobic conditions with the use of standard vacuum and Schlenk techniques. Acetonitrile was dried over 3-Å molecular sieves and distilled prior to use. Diethyl ether was dried and distilled over Na/K amalgam. The precursors $[n\text{-}Bu_4N][TCNQ]$,[16,21] $[Mn(MeCN)_4][BF_4]_2$, $[Fe(MeCN)_6][BF_4]_2$, $[Co(MeCN)_6][BF_4]_2$, and $[Ni(MeCN)_6][BF_4]_2$ were prepared from literature methods.[18,19] TCNQ was purchased from TCI and recrystallized from hot acetonitrile before use. The compound $Mn(TCNQ)_2(MeOH)_2$ was prepared as previously described.[14]

Preparation of $M(TCNQ)_2$ Compounds, where M = Mn (1), Fe (2), and Co(3). A quantity of $[n\text{-}Bu_4N][TCNQ]$ (0.455 g, 1.02 mmol) was dissolved in 20 mL of acetonitrile to give a green solution, which was transferred via cannula into three separate acetonitrile solutions (20 mL each) of $[Mn(MeCN)_4][BF_4]_2$ (0.200 g, 0.51 mmol), $[Fe(MeCN)_6][BF_4]_2$ (0.242 g, 0.51 mmol), and $[Co(MeCN)_6][BF_4]_2$ (0.244 g, 0.51 mmol). A dark purple precipitate formed within minutes in all three cases, with no discernible change during the 20-min reaction period. The samples were collected by filtration under nitrogen, washed with 10 mL of acetonitrile followed by 20 mL of diethyl ether, and dried in vacuo. Yield: (**1**) 0.223 g, 95%; (**2**) 0.224 g, 95%; (**3**) 0.220 g, 93%. Anal. Calcd for $MnC_{24}N_8H_8$: C, 62.20; H, 1.74; N, 24.19. Found: C, 61.71; H, 1.90; N, 21.38. Calcd for $FeC_{24}N_8H_8$: C, 62.10; H, 1.74; N, 24.14. Found: C, 60.78; H, 2.26; N, 22.54. Calcd for $CoC_{24}N_8H_8$: C, 61.68; H, 1.73; N, 23.98. Found: C, 59.87; H, 2.27; N, 21.49. We have noted that the nitrogen analysis is low in the analysis of TCNQ compounds. Characteristic IR data (Nujol mull, KBr plates, cm^{-1}): (**1**) $\nu(C{\equiv}N)$, 2205 s, 2187 s, 2137 sh; $\nu(C{=}C)$, 1505 s; $\delta(C{-}H)$, 826 m. (**2**) $\nu(C{\equiv}N)$, 2217 s, 2187 s, 2142 sh; $\nu(C{=}C)$, 1505 s; $\delta(C{-}H)$, 827 m. (**3**) $\nu(C{\equiv}N)$, 2217 s, 2188 s, 2137 sh; $\nu(C{=}C)$, 1505 s; $\delta(C{-}H)$, 827 m.

Preparation of $Ni(TCNQ)_2$ (4). A quantity of $[n\text{-}Bu_4N][TCNQ]$ (0.455 g, 1.02 mmol) was dissolved in 30 mL of acetonitrile to give a green solution which was slowly added to 30 mL of an acetonitrile solution of $[Ni(MeCN)_6][BF_4]_2$ (0.244 g, 0.51 mmol). The resulting solution was stirred for 3 h in order to bypass a green kinetic intermediate that forms early in the reaction. The final product, which is a dark purple solid, was collected by filtration under nitrogen, washed with acetonitrile (10 mL) followed by diethyl ether (20 mL), and dried in vacuo. Yield: 0.223 g, 94%. Anal. Calcd for $NiC_{24}N_8H_8$: C, 61.72; H, 1.73; N, 23.99. Found: C, 60.02 H, 2.21; N, 23.06. Characteristic IR data (Nujol mull, KBr plates, cm^{-1}): (**4**) $\nu(C{\equiv}N)$, 2224 s, 2208 s, 2192 s, 2155 sh; $\nu(C{=}C)$, 1503 s; $\delta(C{-}H)$, 829 m.

Physical Measurements. X-ray powder diffraction patterns were collected using a Rigaku DMAX/B X-ray powder diffractometer with a Cu rotating anode ($\lambda_{K\alpha} = 1.5418$ Å) and a graphite monochromator. Powder X-ray data were processed using the PowderX software package.[22] Cell refinement and space group assignment were carried out with the program Checkcell in the LMGP package.[23] Infrared spectra were recorded as Nujol mulls on KBr plates in the range 400−4800 cm^{-1} using a Nicolet IR/42 FT-IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Desert Analytics, or in the Chemistry Department at Michigan State University. Static magnetic measurements were obtained on microcrystalline samples with the Quantum Design model MPMS SQUID magnetometers housed in the Physics and Astronomy Department at Michigan State University. The magnetic field was varied from 0 to 1 T on the MPMSR-2 model, and from 0 to 5.5 T with the MPMSR-5 instrument; both sets of experiments were carried out in the temperature range 1.8−350 K. The alternative current (ac) susceptibility measurements were performed with an alternating field of 1 G amplitude in the frequency range 0.1−1000 Hz without any external field applied. The experimental data were corrected for the sample holder and the intrinsic diamagnetic contribution estimated from the Pascal constants.[24] Conductivity measurements were performed by using a Keitley current source (224) and nanovolt-meter (2182) interfaced to the MPMSR-2 magnetometer. Four point contacts were made on pressed pellets of the materials with silver paste and Cu wires. The heat capacity measurements were performed on a Quantum Design PPMS system located at Quantum Design Inc., San Diego, CA. The samples were mounted on the heat capacity addenda (using grease) in an inert-atmosphere glovebox. Field emission scanning electron microscopy measurements (FESEM) were performed on a Hitachi Ltd. model S-4700II with a tungsten filament housed in the W. M. Keck Microfabrication Facility located in the Department of Physics and Astronomy Department at Michigan State University. The four compounds were each imaged at a 10× magnification using 10.0 kV accelerating voltage. TEM images were obtained using a JEOL 120 CX transmission electron microscope located at the Center for Electron Optics at Michigan State University.

Results and Discussion

Synthesis. Reactions of the acetonitrile starting materials $[M(MeCN)_x][BF_4]_2$ (M = Mn, $x = 4$; Fe, Co, Ni, $x = 6$) with $[n\text{-}Bu_4N][TCNQ]$ in acetonitrile lead to rapid formation of dark purple crystalline solids (eq 1). There is no visible decomposition when these materials are exposed to air, moisture, and light.

$$\begin{gathered}[M(CH_3CN)_x][BF_4]_2 + 2[n\text{-}Bu_4N][TCNQ] \xrightarrow{\text{r.t., } CH_3CN} \\ (x = 4 \text{ for Mn and } x = 6 \text{ for Fe, Co, Ni}) \\ M(TCNQ)_2 + 2[n\text{-}Bu_4N][BF_4] + xCH_3CN \quad (1) \\ \text{Yield: } {\sim}90\% \end{gathered}$$

IR spectroscopy, however, indicates that these compounds are hygroscopic when exposed to ambient laboratory atmosphere, and magnetic measurements revealed some changes that can be correlated to air and light exposure over the course of several months (vide infra). When samples are handled anaerobically, analytical data support the empirical formula $M(TCNQ)_2$ in accord with the charge balance of the divalent metal ions. It is noted that the nitrogen analysis is low, which we have observed is a recurrent problem with TCNQ materials. Unlike previously reported materials of this type, e.g., $M(TCNQ)_2(H_2O)_2$ (M = Mn, Fe, Co, and Ni)

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Table 1. Study of Reaction Time on the Composition of the $M(TCNQ)_2$ Phases Using Elemental Analysis

compound/sample no.	reaction time	%C	%H	%N
$Mn(TCNQ)_2$	theoretical %	62.20	1.74	24.19
1	20 min	61.71	1.90	21.38
2	30 min	61.26	1.98	22.41
3	80 min	60.18	2.51	21.68
4	13 h	59.39	2.38	21.87
5	48 h	55.81	2.06	20.82
6	8 days	53.80	2.13	20.06
7	30 days	51.83	1.59	20.03
$Ni(TCNQ)_2$	theoretical %	61.72	1.73	23.99
1	5 min	51.90	2.27	19.64
2	2 h	53.46	2.33	19.72
3	3 h	60.02	2.21	23.06

or $M(TCNQ)(MeOH)_x$ ($x \approx 2$, Mn, Fe; $x \approx 3$, Co; $x \approx 4$, Ni),[14] the present acetonitrile-derived materials retain no coordinated acetonitrile solvent molecules according to TGA analysis and IR data. Once formed, these compounds are completely insoluble in all common solvents except alcohols and water which lead to the formation of new crystalline phases of the type $M(TCNQ)_2(S)_2$ (S = solvent).[14]

Our choice to react the fully solvated acetonitrile cations that contain the "innocent" $[BF_4]^-$ anion with salts of the coordinating $TCNQ^-$ anion is based on the notion that such metathetic reactions will produce solids that are easily separated from the soluble byproducts. Another benefit of preparing $M(TCNQ)_2$ products by this approach is that a pre-selected oxidation state of the metal ion is introduced into the material. Interestingly, we have found that reactions such as direct oxidation of the metal with TCNQ or reduction of TCNQ with iodides do not produce the same results. Indeed, these reactions are known to lead to multiple products when more than one oxidation state is electrochemically accessible for the transition metal.[13c]

In this particular study, which involves sensitive materials and time-consuming measurements, it was imperative that we convince ourselves that $M(TCNQ)_2$ materials could be prepared reproducibly and in high purity. To achieve this, it was necessary to carefully monitor and optimize reaction conditions. It was found that the main factors that affect the overall purity of the products are reaction time and concentration. A time-elapsed study, the results of which are documented in Table 1, indicates that $Mn(TCNQ)_2$ degrades from a crystalline to an amorphous phase with increasing reaction times and prolonged contact with the solvent. Elemental analytical results indicate that the optimal time for the reaction is approximately 20 min. The same analysis was made for $Fe(TCNQ)_2$ and $Co(TCNQ)_2$ materials. Prolonged contact with solution produces materials of average empirical formula $M(TCNQ)_x$ (with $1 < x < 1.5$), which may be a new phase or merely a mixture of decomposed phases. The main conclusion is that increased contact with solution leads to slow degradation of the surfaces of the particles with concomitant loss of TCNQ. Conversely, analyses of various $Ni(TCNQ)_2$ samples over a wide period of time support the conclusion that Ni behaves differently than the other three transition metals: the crystalline, magnetic product does not form until longer reaction times, viz., after approximately 3 h of stirring.

Infrared Spectroscopy. Infrared spectroscopy proved to be very useful for characterizing the $M(TCNQ)_2$ compounds with regards to the oxidation state and metal−TCNQ binding. It also aided in our attempts to address structural changes that accompany decomposition. Even so, analysis of IR data for TCNQ compounds is often difficult because of the extremely versatile nature of the molecule. The three main considerations are that (i) there are three possible oxidation states, namely $TCNQ^0$, $TCNQ^-$, and $TCNQ^{2-}$; (ii) there are various linkage isomers that can form with metal−nitrile interactions; and (iii) there are different types of TCNQ−TCNQ interactions (i.e., π- stacked and σ-dimerized).[25] Several research groups have reported characteristic infrared bands for TCNQ compounds and conveniently correlated these data to the TCNQ oxidation state and the coordination mode of the TCNQ ligand.[4j,11g−h,24] For metal-bound TCNQ ligands, three regions provide important information for assigning charge and understanding the coordination and stacking modes in $TCNQ^{n-}$ salts.[4j,11g−h,26] Values in the $\nu(C{\equiv}N)$ region 2100−2300 cm^{-1} verify the presence of TCNQ and the $\nu(C{=}C)$ region, which often occurs around 1500 cm^{-1} for $TCNQ^-$, is characteristic of π-delocalization within the TCNQ ring. There are difficulties, however, with the interpretation of metal-bound TCNQ compounds in these regions because these stretching modes often shift dramatically upon coordination. A shift to higher frequencies for $\nu(C{\equiv}N)$ occurs if TCNQ acts as a σ-donor, whereas a shift to lower frequencies indicates a significant TCNQ-to-metal π-back-bonding.[24] Unfortunately, multiple stretches in the $\nu(C{\equiv}N)$ region render assignments and correlations to other compounds difficult. To alleviate this problem, the $\delta(C-H)$ bending region has also been used because of its high sensitivity to changes in oxidation state and coordination mode. In this region, oxidation states are more easily distinguished from each other; for example the neutral TCNQ bending mode occurs at 864 cm^{-1}, while $TCNQ^-$ is found between 819 and 830 cm^{-1}. Recently, a rarely observed form of dimerized TCNQ, referred to as the "σ-dimer", $[TCNQ-TCNQ]^{2-}$,[27] has been identified by our research group to exhibit a $\delta(C-H)$ bend at $\approx$802 cm^{-1}.[14] Since this discovery, the bending mode of TCNQ has become an exceedingly useful tool in the study of metal−TCNQ coordination compounds. From crystal structures it was found that both π-stacked and σ-dimerized forms of reduced TCNQ are present in $[Mn(TCNQ)(TCNQ-TCNQ)_{0.5}(MeOH)_2]_\infty$, whereas only a σ-dimer is observed in the closely related polymeric material, $[Mn(TCNQ-TCNQ)_2(MeOH)_4]_\infty$.[14] Armed with these structures, we were able to locate specific IR modes in the crystals and

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Table 2. Infrared Spectroscopic Data in the ν(C≡N), ν(C=C), and δ(C−H) Regions for TCNQ Compounds

compound	ν(C≡N) (cm^{-1})	ν(C=C) (cm^{-1})	δ(C−H) (cm^{-1})
Mn$(TCNQ)_2$ (**1**)	2205 s, 2187 s, 2137 sh	1505 s	826 m
Fe$(TCNQ)_2$ (**2**)	2217 s, 2187 s, 2142 sh	1505 s	827 m
Co$(TCNQ)_2$ (**3**)	2217 s, 2188 s, 2137 sh	1505 s	827 m
Ni$(TCNQ)_2$ (**4**)	2224 s, 2208 s, 2192 s, 2155 sh	1503 s	829 m
TCNQ	2222 s	1541 s	864 s
LiTCNQ	2211 s, 2196 s, 2180 sh, 2154 s	1507 s	826 m
$[Bu_4N]$[TCNQ]	2188 sh, 2180 s, 2162 s, 2157 s	1507 s	824 m

confidently assign to them a particular type of TCNQ ligand (with respect to both oxidation state and binding/stacking mode). In this way, a database of IR modes for TCNQ has been acquired that makes it possible to assign (or at least rule out) the type of TCNQ molecules present in the M$(TCNQ)_2$ materials.

A compilation of infrared data of M$(TCNQ)_2$ **1**−**4** is provided in Table 2. The first notable point is that there are no features that correspond to bound acetonitrile or $[BF_4]^-$ counterions. This is in accord with TCNQ being in its mono-reduced form and acting as the only ligand to the divalent metals. In the ν(C≡N) region of the Mn, Fe, and Co compounds, there are three stretching modes, whereas there are four features in the spectrum of Ni$(TCNQ)_2$. The slight difference may be due, in part, to the presence of an intermediate that is known to form in the Ni$(TCNQ)_2$ reaction or to a solid-state splitting effect not observed in the others. The stretching modes for all four metal compounds are generally lower in energy than the corresponding mode for neutral TCNQ, viz., 2222 cm^{-1}, and are characteristic of $TCNQ^-$. The ν(C=C) stretching region is indicative of the TCNQ phenyl ring. The π-bond delocalization over the ring results in one strong ν(C=C) stretching feature that is typically in the range 1500−1510 cm^{-1} for $TCNQ^-$. Compounds **1**−**3** exhibit modes at 1505 cm^{-1} while the ν(C=C) stretching for **4** is at 1503 cm^{-1}. The δ(C−H) bending region for the four compounds was examined as well. The δ(C−H) modes for $TCNQ^-$, $TCNQ^{2-}$, and mixed-valence stacks of $TCNQ^-$ and TCNQ are well documented in the literature.[28] Compounds **1**−**4** exhibit δ(C−H) frequencies between 826 and 829 cm^{-1} which is well within the expected range for $TCNQ^-$.

An interesting phenomenon that is worth mentioning is that samples of M$(TCNQ)_2$ which have been stirred for long periods of time exhibit the signature low energy δ(C−H) mode that is indicative of the "σ-dimer" form $[TCNQ-TCNQ]^{2-}$. It appears that M$(TCNQ)_2$ is eventually being converted to a new phase that contains both reduced and dimerized forms of TCNQ. Alternatively, it may be that the new phase is composed solely of σ-dimers represented by the formula M[TCNQ−TCNQ]. This phenomenon occurs in all of the M$(TCNQ)_2$ materials.

In summary, infrared spectroscopy has proven to be quite useful for helping to identify the structural components of these M$(TCNQ)_2$ polymers. Although there are slight differences in the IR data in the family, the striking similarities lend support to the conclusion that they contain the same arrangement and oxidation state of TCNQ.

Attempts to Grow Single Crystals of M$(TCNQ)_2$. Numerous methods including slow diffusion of reactants in solutions[29] and in gels[30] were used in attempts to prepare single crystals of M$(TCNQ)_2$ compounds. One must try to prevent rapid precipitation of the products in order to allow time for the growing crystallites to heal their defects and to grow to an appreciable size. Although these phases partially dissolve in water and alcohols, these are not viable media for recrystallizing the compounds because they convert the materials into new phases with coordinated H_2O and ROH.[14] On the other hand, the materials are exceedingly insoluble in CH_3CN. Solvents such as CH_2Cl_2, which are more dense than CH_3CN, were mixed with the metal acetonitrile precursor solutions to further slow the diffusion of the layers. Inevitably only powders or films were obtained in these solvent diffusion experiments. The next level of crystal growth that was attempted was the use of gels prepared from poly-methyl methacrylate (PMMA). A methodical screening of the gel percentage and temperature was performed to find the best conditions for crystallization. This gel method proved to be the most fruitful, as small microcrystals were obtained. Unfortunatly, the crystals diffracted only weakly, thus indexing and data collection could not be carried out. These results, however, suggest that gels will be useful for growing crystals of these neutral phase materials. Additional studies are under investigation in our laboratories to obtain sufficiently large single crystals that can be subjected to CCD X-ray analysis or, at the every least, synchrotron methods.

Electron Microscopies FESEM and TEM. Several important facts have emerged from our analysis of **1**−**4** by electron microscopy techniques. One point is that the compounds are not as crystalline as the copper and silver TCNQ materials.[15a,16] Instead of well-defined crystallites, the bulk products contain spherical shapes that are actually secondary particles that consist of densely packed primary crystallites (Figure 1). The largest spheres are found in samples of Mn$(TCNQ)_2$ (≈0.09 μm), followed by Ni$(TCNQ)_2$ (≈0.05 μm), and finally Fe$(TCNQ)_2$ (≈0.02 μm) and Co$(TCNQ)_2$ (<0.01 μm). The images provide important visual evidence of

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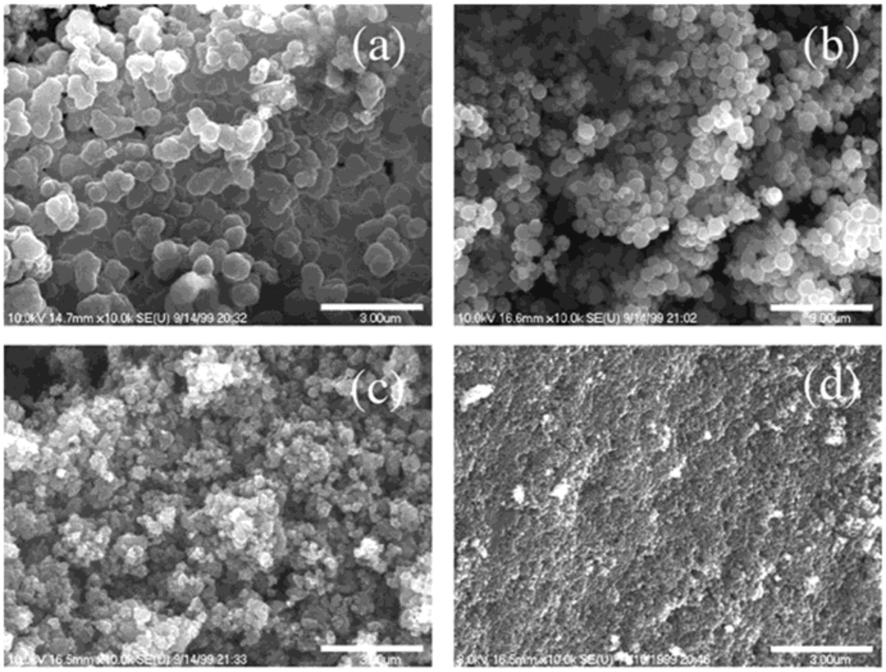

Figure 1. FESEM photographs of (a) $Mn(TCNQ)_2$, (b) $Ni(TCNQ)_2$, (c) $Fe(TCNQ)_2$, and (d) $Co(TCNQ)_2$. The scale is indicated by the white bar at the right bottom corner of each photograph and corresponds to 3 μm.

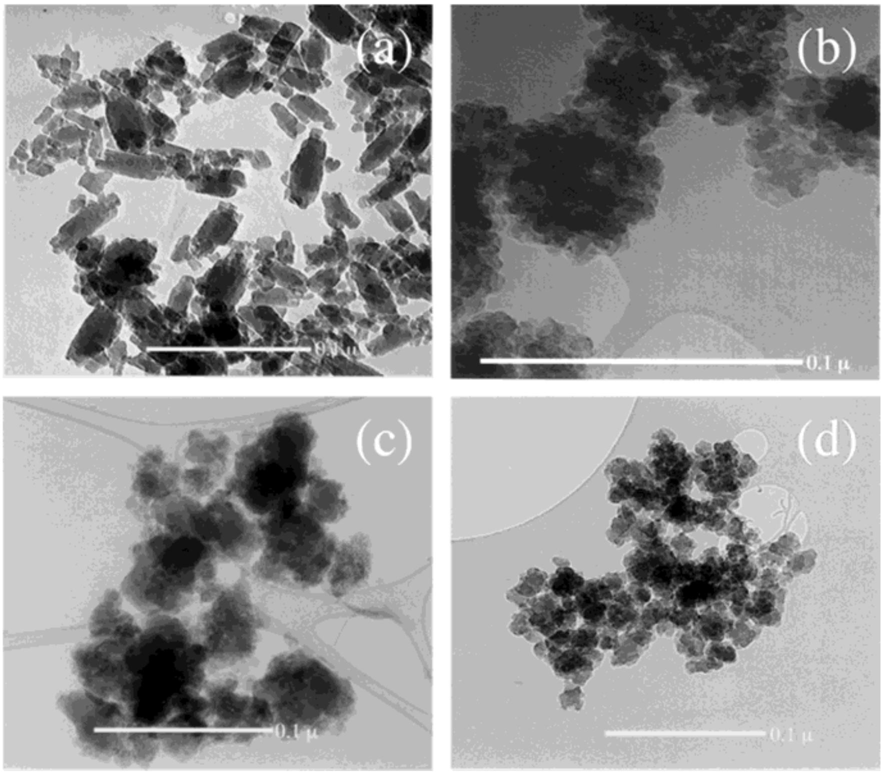

Figure 2. TEM photographs of (a) $Mn(TCNQ)_2$, (b) $Ni(TCNQ)_2$, (c) $Fe(TCNQ)_2$, and (d) $Co(TCNQ)_2$. The scale is indicated by the white bar at the bottom of each photograph and corresponds to 0.1 μm.

the high surface area of these compounds and reveal a homogeneity that is remarkably good. In at least five independent samples of these materials, FESEM studies revealed no evidence for more than one phase. Upon examination at higher magnifications by transmission electron microscopy (TEM) it can be seen that the surface of an individual sphere is rough and uneven (Figure 2). Smaller particles or domains on the surface of each “sphere” are observed. For all samples except $Mn(TCNQ)_2$, there are spherical “clusters” of a homogeneous size distribution throughout the material. The image of the $Mn(TCNQ)_2$ shows that this material forms well-defined crystals (up to $0.05 \times 0.01 \times 0.01$ μm^3).

Powder X-ray Diffraction. Interestingly, and somewhat surprisingly due to their rapid precipitation, the $M(TCNQ)_2$ compounds are crystalline as evidenced by powder X-ray experiments. Most importantly, samples of **1**−**4** exhibit nearly identical powder patterns (Figure 3), which is a clear indication that the four compounds are isostructural. By comparison with the other known

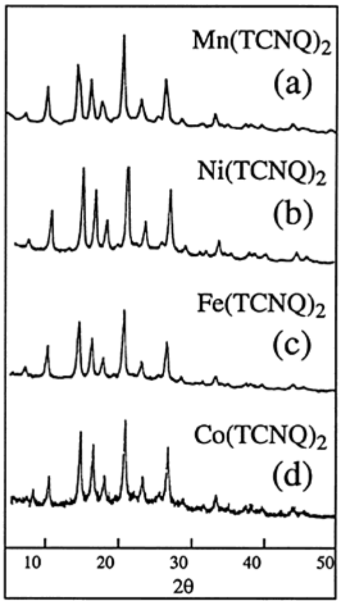

Figure 3. X-ray powder diffraction patterns for (a) Mn(TCNQ)$_2$, (b) Ni(TCNQ)$_2$, (c) Fe(TCNQ)$_2$, and (d) Co(TCNQ)$_2$.

metal−TCNQ materials,[14,15a,e,n,16,17] it is obvious that this structure is unprecedented for M(TCNQ)$_x$ phases. The patterns were indexed and refined which led to a tetragonal cell with parameters $a = 17.280(1)$ Å, $c = 8.687(1)$ Å, and $V = 2593.9$ Å^3 for Mn(TCNQ)$_2$ (**1**) with M(20) = 15 and F(20) = 21 as figures of merit. The indexing is in good agreement with the peak positions as well as their intensities. The indexing of the other three materials gave us similar unit cells as expected for isostructural compounds: $a = 16.90(2)$ Å, $c = 8.785(3)$ Å for **2**; $a = 17.23(2)$ Å, $c = 8.530(2)$ Å for **3;** and $a = 17.029(5)$ Å, $c = 8.508(2)$ Å for **4**. Because of the small particle size of the materials, all the diffraction peaks are broad with a fwhm of 0.4−0.6°. Using the line analysis function of Winfit, the approximate crystallite size for Mn(TCNQ)$_2$ was found to be 0.04 μm. This value is in good agreement with the TEM studies and also with the fact that the samples with larger particle sizes exhibit more intense powder patterns.

Our powder X-ray diffraction investigation allowed us to identify the conversion of the methanol phase [(Mn(TCNQ−TCNQ)$_2$(CH$_3$OH)$_4$]$_\infty$ previously reported into the Mn(TCNQ)$_2$ presented herein. This conversion occurs when the methanol phase loses its solvent molecules by heating at temperatures over 200 °C. As shown in Figure 4, the powder pattern of [(Mn(TCNQ−TCNQ)$_2$(CH$_3$OH)$_4$]$_\infty$ obtained at 225 °C (although less crystalline than the one presented in Figure 3) contains the same features in the X-ray diffraction pattern. The magnetic measurements performed on this material confirms this conversion, i.e., it exhibits the same behavior as the typically prepared Mn(TCNQ)$_2$ (vide infra). This result offers a new possibility for synthesis of M(TCNQ)$_2$ phases from this methanol phase, and also establishes two important points: it confirms the absence of solvent molecules (CH$_3$CN) in the M(TCNQ)$_2$ structure (as already suggested by TGA, IR, and elemental analysis), and it shows that the structure of [(Mn(TCNQ−TCNQ)$_2$(CH$_3$OH)$_4$]$_\infty$ is probably closely related to the structure of the Mn(TCNQ)$_2$ material. We are currently studying this conversion as a possible pathway to grow single crystals of the M(TCNQ)$_2$ materials.

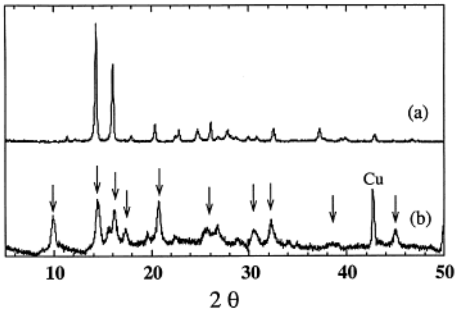

Figure 4. X-ray powder diffraction patterns for [Mn(TCNQ−TCNQ)$_2$(CH$_3$OH)$_4$]$_\infty$ (a) at room temperature and (b) at 225 °C. The arrows are pointing onset of the diffraction peaks of the Mn(TCNQ) phase.

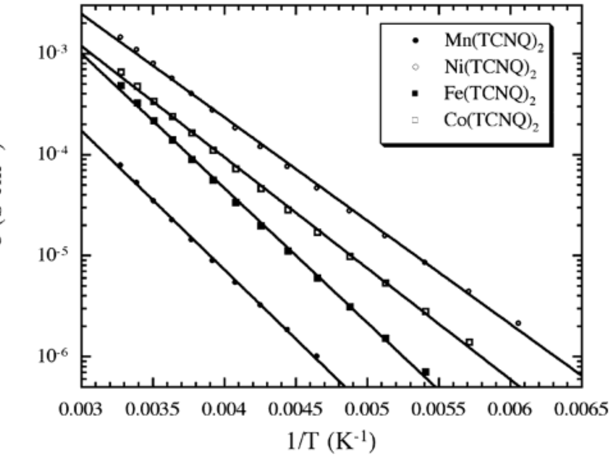

Figure 5. Semilogarithm plots of the conductivity σ (S cm^{-1}) versus $^1/_T$ for samples **1**−**4**.

Conductivity Measurements. The four isostructural materials M(TCNQ)$_2$ were subjected to pressed-pellet conductivity measurements. These compounds exhibit very similar charge-transport properties, as illustrated in Figure 5. With decreasing temperature, the conductivity decreases exponentially ($\sigma \propto \exp(-E_{\mathrm{gap}}/T)$) which is typical for a semiconductor. At room temperature, the conductivities (displayed in Table 3), vary from 1.4 10^{-3} S cm^{-1} for **4** to a nearly insulating value of 7.7 10^{-5} S cm^{-1} for **1** with band gaps from 0.204 to 0.274 eV for **4** and **1**, respectively. It is interesting to note that these values are intermediate between the ones obtained previously for the two phases of Cu(TCNQ). Given that Cu(TCNQ), which is a very poor conductor, undergoes electrical switching with an applied potential,[15,16] it may be that films of these materials will also display unusual electrically induced behavior.

Magnetic and Thermodynamic Studies. The magnetic behavior of the four M(TCNQ)$_2$ materials (M: Mn$^{\mathrm{II}}$ $S = {}^5/_2$; Fe$^{\mathrm{II}}$ $S = 2$; Co$^{\mathrm{II}}$ $S = {}^3/_2$; Ni$^{\mathrm{II}}$ $S = 1$) have been investigated by dc and ac measurements. The compounds were measured on polycrystalline samples obtained by optimized bulk syntheses as previously described.

dc Measurements. The plots of $^1/_\chi$ versus T for the four M(TCNQ)$_2$ presented in Figure 6 reveal that in the high-temperature regime ($T > 60$ K), the data exhibit a Curie−Weiss behavior with $C = 2.9$ emu K mol^{-1}, $\theta =$

Table 3. Summary of Transport and Magnetic Data

compound	σ_{rt} (S cm^{-1})	E_{gap} (eV)	C (emu K mol^{-1})	C_{theo} ($g = 2$) (emu K mol^{-1})	θ (K)	T^* (K)	T_f (K)	H_c (G)	γ
$Mn(TCNQ)_2$ (**1**)	7.7×10^{-5}	0.274	2.9	5.125	44	44	21.7	20	0.009
$Fe(TCNQ)_2$ (**2**)	4.8×10^{-4}	0.265	3.0	3.75	−10	28	21.8	750	0.029
$Co(TCNQ)_2$ (**3**)	6.5×10^{-4}	0.219	2.5	2.625	−6	7	5.2	190	0.057
$Ni(TCNQ)_2$ (**4**)	1.4×10^{-3}	0.204	1.3	1.75	37	24	20.8	270	0.010

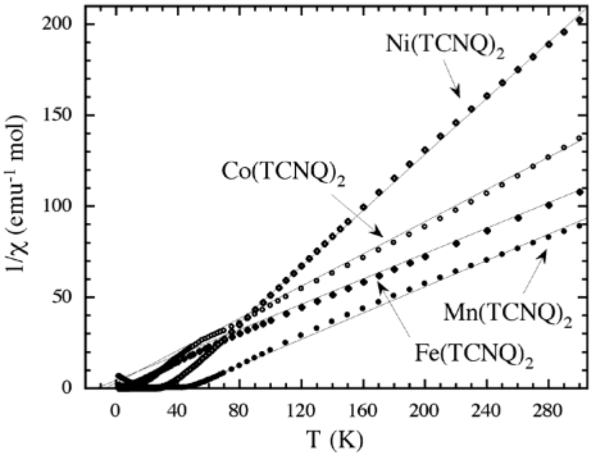

Figure 6. Temperature dependence of $^1/\chi$ for **1**−**4**. The solid black line is the best Curie−Weiss fitting obtained in the range 60−300 K.

44 K for $Mn(TCNQ)_2$; $C = 3.0$ emu K mol^{-1}, $\theta = -10$ K for $Fe(TCNQ)_2$; $C = 2.8$ emu K mol^{-1}, $\theta = -6$ K for $Co(TCNQ)_2$; and $C = 1.3$ emu K mol^{-1}, $\theta = 37$ K for $Ni(TCNQ)_2$. In all cases, the value of the experimental Curie constant is low compared to the value expected for isolated spins (Table 3). This conclusion is based on the assumption of $g = 2$, which is typical for $TCNQ^-$, and also $g = 2$ for the different metals (Mn S = $^5/_2$, Fe S = 2, Co S = $^3/_2$, and Ni S = 1). Preliminary EPR experiments on powder samples exhibit broad resonances (ΔH = 100, 600, 800, and 600 G for **1**, **2**, **3**, and **4** respectively) near $g = 2$. The breadth of the signals indicates that the resonance is not only solely due to an organic radical which should have a narrow line width, but that it is the result of the interactions between the two types of spin centers.[31] It is important to note that there is a good reproducibility of the Curie constants between independent samples. The reason for the low Curie constants in this family of TCNQ materials is not completely clear, but it may be due to various intrinsic factors such as antiferromagnetic correlation of the spins, dimerization of TCNQ units, and structural defects, or to extrinsic factors such as the presence of diamagnetic impurities. As shown in Figure 7, at lower temperatures, the compounds exhibit a marked increase in susceptibility. This increase is most prominent for the Mn and Ni derivatives, which exhibit dominant ferromagnetic interactions as indicated by the positive Weiss constants. In the case of the Fe and Co compounds, the increase of the susceptibility is less pronounced, nevertheless, there is a difference in the zero field cooled (ZFC) and field cooled (FC) susceptibilities at 100 G (insets in Figure 7). This behavior is typically associated with the onset of spontaneous magnetization and coercivity. The field dependence of the magnetization at 2 K for the four compounds is of two types, depending on the nature of the dominant of interactions (Figure 8). For $Mn(TCNQ)_2$ and $Ni(TCNQ)_2$ a rapid increase of the moment at low field (between 0 and 500 G) is observed but no saturation occurs up to 5 *T*. For the $Co(TCNQ)_2$ and $Fe(TCNQ)_2$, the moment increases gradually and does not reach any saturation up to 5 *T*. The field dependence of the magnetic moment reveals hysteresis loops with coercive fields of 20, 750, 190, and 270 G for **1**, **2**, **3**, and **4**, respectively. This characteristic behavior and the increase in moment observed for **1**−**4** indicate that these compounds behave like real magnets.

ac Measurements. To more precisely determine the magnetic properties of this series of materials, ac susceptibility measurements were performed. Plots of the temperature dependence of the in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities are depicted in Figure 9. Measurements were made after the sample was cooled in zero field, and the response was recorded with increasing the temperature in the absence of a dc applied field. For all four analogous TCNQ compounds, χ'' is nonzero at low temperatures which is in accord with the dc measurements. These data allow for a precise determination of the temperature at which spontaneous magnetization occurs, namely T^* at 44, 28, 7, and 24 K for **1**, **2**, **3**, and **4**, respectively.

Plots of the thermal variation of the ac susceptibilities for **1** at different frequencies are presented in Figure 10. The data (which are similar for the other member of this family of materials) reveal a slight frequency dependence of both the maximum and breadth of the transition. The positions of the χ' and the χ'' peaks increase by ∼0.5 and 2 K, respectively, when the frequency is increased from 1 to 801 Hz. This behavior is not expected to occur for true three-dimensional ordered magnets. Indeed, a shift of the peak maximum in χ' with frequency is usually indicative of a glassy magnetic phase or a superparamagnetic phase.[32,33] It

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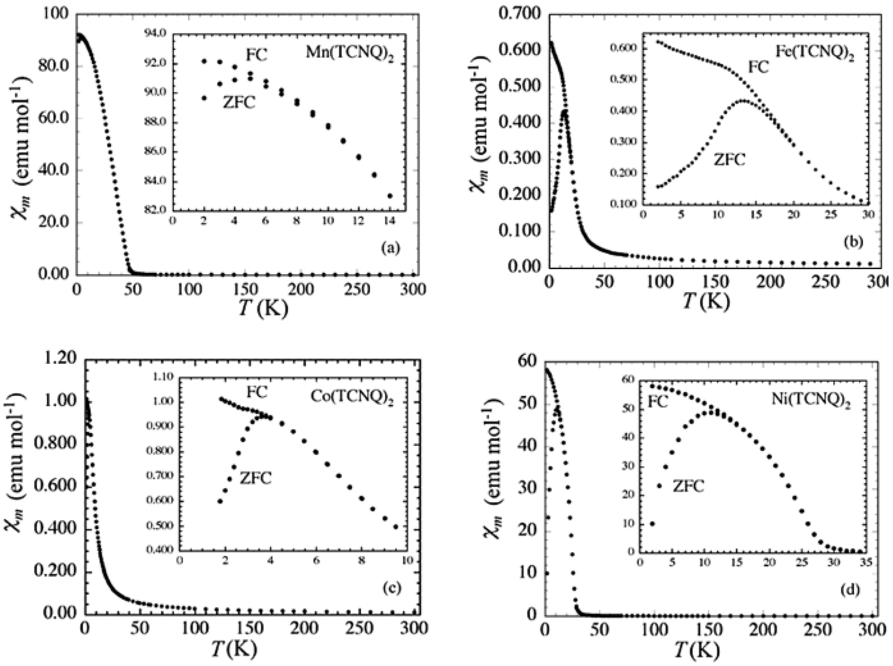

Figure 7. Temperature dependence of χ at 100 G for **1**−**4** (a−d, respectively). Inset: low-temperature region emphasizing the difference between the field cooled (FC) and the zero field cooled (ZFC) experiments.

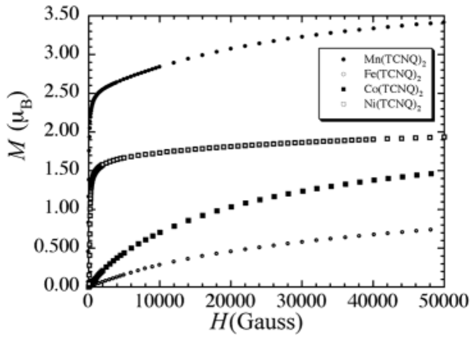

Figure 8. First magnetization of the magnetic moment at 2 K for **1**−**4**.

is worth pointing out that we are avoiding the use of the term *spin-glass* because this term was coined for magnetically dilute systems prepared by random doping of a few atom percent of a magnetic compound into a nonmagnetic, conducting host. A more appropriate term for magnetically concentrated molecule-based magnets is a *glassy magnet.*

Heat Capacity Measurements. To confirm the glassy nature of the magnetic state observed at low temperatures, heat capacity measurements were performed. At T_f or even at T^*, there is no evidence in the heat capacity measurements of a peak or singularity as clearly illustrated in Figure 12. These results are expected for glassy magnets as described by Mydosh.[32a] In fact, the explanation proposed for glassy spin systems is that the absence of a significant peak at T_f in the heat capacity measurements is simply due to the fact that almost all the entropy is already locked into short range order above T_f. So the entropy left is simply not sufficient to produce an obvious, sharp peak at T_f. It is important to note that a very broad peak could exist. This point notwithstanding, it is always difficult to separate out the nonmagnetic contributions (phonons) from the actual magnetic peak, and typically no peak is observed by specific heat measurements for glassy magnets.

Discussion of Magnetic Glassiness. Mydosh established that the frequency dependence of the peak maximum in χ' can be used to distinguish between different types of magnetic behavior.[32a] To quantify the glassiness, the concept of the frequency shift γ was introduced which is defined by the slope normalized at $T_f(0)$ of T_f vs $\log(\nu)$ curve where T_f is the "freezing" temperature located at the peak maximum in χ' at each frequency, $T_f(0)$ is the "freezing" temperature defined as the peak maximum in χ' extrapolated at $\log(\nu) = 0$, and $\log(\nu)$ is the logarithm of the ac frequency. The plots of T_f vs $\log(\nu)$ for the compounds **1**−**4** are displayed in Figure 11. Clearly the T_f is linear in $\log(\nu)$ as expected. According to Mydosh, the values of the frequency shift γ reported in Table 3 are consistent with glassy magnetic behavior and not with superparamagnetism; in the latter case, much larger γ values (> 0.1) are usually observed.[32a,33b,d]

To convince ourselves of the relevance of referring to the M(TCNQ)$_2$ compounds as glassy magnets, we attempted to fit the frequency dependent data to the Arrhenius law ($\nu = \nu_0 \exp(E_a/k_BT_f)$). Knowing that a glassy "transition" is much more complicated than a simple energy-barrier blocking and thermal activation, one can expect that the Arrhenius law fitting will lead to completly unphysical values for the activation energy and the zero frequency constant. Indeed, in the compounds **1**−**4**, the fitting produced these results (for example in the case of the Fe(TCNQ)$_2$ the values are $E_a = 1927$ K and $\nu_0 = 1.7 \times 10^{38}$ Hz).

The ac susceptibility measurements were used to probe the nature of a magnetic phase of Mn(TCNQ)$_2$ materials in a detailed manner, such that it is possible to unambiguously conclude that these compounds are glassy magnets at low temperature. A glassy magnetic phase is a metastable state of frozen spins that does not undergo a true three-dimensional order. Nevertheless, these materials undergo a spontaneous magnetization and exhibit coercivity which classify them as a type

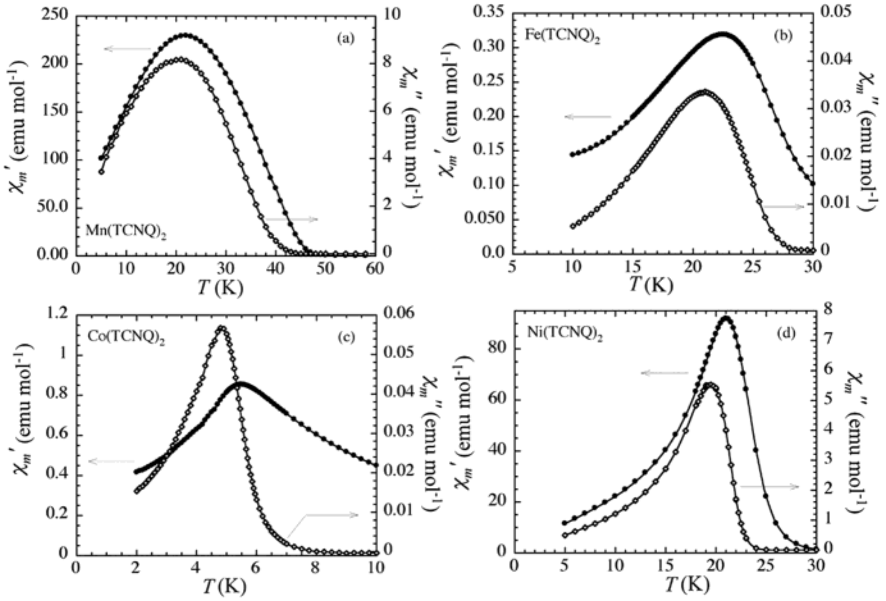

Figure 9. Temperature dependence of the ac susceptibilities for **1**−**4** (a−d, respectively) without a dc field, at 1 Hz and 1 G of ac field amplitude.

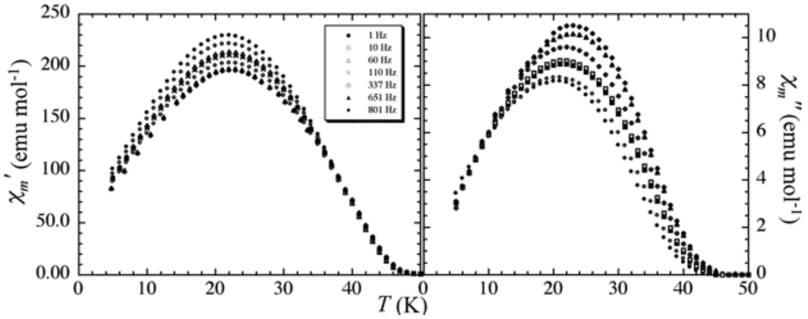

Figure 10. Temperature dependence of the ac susceptibilities χ' and χ'' (a and b, respectively) for **1** without a dc field, at 1 G of ac field amplitude and variable frequencies.

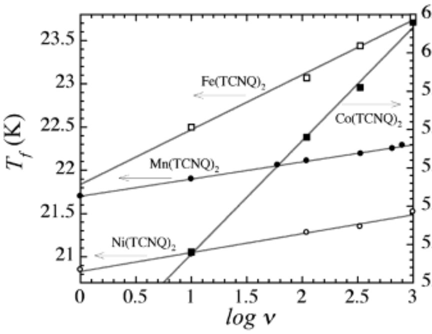

Figure 11. Maximum in temperature of the in-phase ac susceptibility ($T_{\max}$) vs log(ν) where ν is the frequency of the ac field for **1**−**4**.

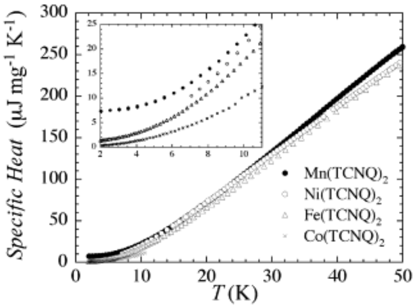

Figure 12. Temperature dependence of the specific heat for samples **1**−**4** below 50 K.

of magnet. Glassiness[32,34] can result from two main origins: (i) randomness (i.e., atom or bond disorder or defect in the crystal structure), and (ii) competing interactions (i.e., between ferro- and antiferromagnetic interactions). Either phenomenon alone can lead to glassy behavior, but in most cases, both are operative. In the present compounds, the presence of well-defined X-ray powder patterns indicates that these materials are crystalline and not amorphous phases. However, the observation of small particles by FESEM and TEM suggests that defect and disorder from the high area surface could be one of the reasons for the glassy behavior. We are not in strong favor of this explanation, however, because various batches of these materials prepared by different methods (e.g., bulk reactions versus layering) were found to lead to reproducible

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magnetic behavior independent of the particle size. A more likely explanation for this glassy behavior is the spin topology which is tied to the solid-state structure. The types of structures (interpenetration, π-stacking, etc.) found in the other binary phases of metal/TCNQ materials, and the presence of two types of spin centers (the metal and the TCNQ radical) is expected to lead to a complicated network of magnetic interactions. Depending on the symmetry, this network contains at least three types of interactions (metal−TCNQ; metal−metal, and TCNQ−TCNQ) which, if they are of a similar magnitude, would result in competition between magnetic interactions and therefore lead to some degree of frustration and hence glassiness.

Conclusion

A new family of molecule-based magnets has been prepared by using the TCNQ radical and first row transition metals. These crystalline compounds have been thoroughly characterized by numerous physical techniques. Although our quest for a single crystal has not been successful, the structural results obtained by SEM, TEM, and powder X-ray diffraction support the purity and crystallinity of these materials. Synchrotron studies are currently underway on powder samples to gain more insight into the solid-state structure of $M(TCNQ)_2$ phases. Even without a definitive structural picture, the challenge of fully delineating the magnetic properties of these molecule-based systems was undertaken. Originally, dc magnetic studies indicated that these materials are ordinary three-dimensionally ordered magnets. This conclusion has been proven to be incorrect by the more sensitive and revealing techniques of ac susceptibility and heat capacity measurements. For the reasons outlined in the paper, it is now clear that these compounds are best classified as glassy magnets. The results of this study point to the need for using alternating current susceptibility methods and thermodynamic data (such as heat capacity measurements) in the study of molecule-based materials. Indeed, these methods have become increasingly routine in recent years due to the advent of new instrumentation, and, consequently, we are achieving a much deeper understanding of the magnetic properties of complex molecule-based materials.

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