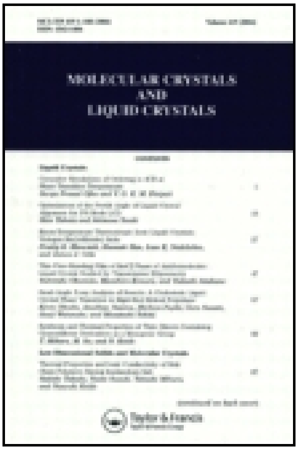

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The Use of Organic Acceptors as Ligands for Paramagnetic Metal Centers: a New Spin on Charge-Transfer Solids

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The Use of Organic Acceptors as Ligands for Paramagnetic Metal Centers: a New Spin on Charge-Transfer Solids

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Low temperature solution routes are being used to prepare solids with organic acceptors directly coordinated to paramagnetic transition metals. This research is currently focused on the elaboration of "hybrid" solids that contain TCNQ radicals. Magnetic and conductivity data regarding the nature of Cu(TCNQ) and several $M(TCNQ)_2$ compounds will be summarized and discussed.

Keywords: binary TCNQ materials; magnetic ordering; bistable switching; spin glass; ac susceptibility; frequency dependence; heat capacity

INTRODUCTION

An important area of current research is materials design at the molecular level.[1-3] This approach involves controlled assembly of molecular building blocks in infinite arrays to form single-phase crystalline solids. The choice of precursors and the manner in which they are assembled ultimately dictates the physical and chemical characteristics of the materials. Along these lines, organic and inorganic building blocks are being incorporated into hybrid materials in an effort to combine the favorable characteristics of both components.[3] These hybrid materials benefit from the versatility of the organic moieties as well as the unique physical properties associated with the inorganic constituents. Some common organic molecules used in these studies are depicted in Figure 1.

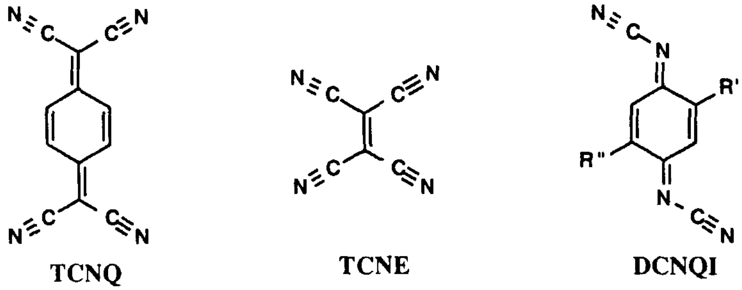

FIGURE 1 Organonitrile acceptors.

In our laboratories, we are endeavoring to prepare materials at the interface of organic conductors and inorganic magnets by incorporating bridging TCNQ and TTF ligands into arrays with paramagnetic transition metals.[4] As demonstrated for the mixed-valence $Cu(DCNQI)_2$[5] and the $M(TCNE)_x$[1a,6] classes of compounds, such metalloorganic materials are capable of exhibiting unusual electronic and magnetic properties. Analogous metal chemistry of TCNQ, while less investigated, has unearthed fascinating compounds such as the electrically bistable material Cu(TCNQ).[7]

The premise of our research with TCNQ ligands is that the majority of the known coordination complexes of this molecule contain co-ligands that restrict the number of open sites available for binding. This, in turn, limits the dimensionality and therefore long-range properties of the materials.[8,9] The crystal structures of a number of these complexes have been determined, and although many of them are paramagnetic, no long range cooperative interactions have been observed.

In this paper we summarize findings regarding the conducting and magnetic properties of materials that contain only transition metals and TCNQ. Similar materials were first reported by researchers at Dupont in the early 1960's, yet very little about their structures or properties is known.[10, 11]

EXPERIMENTAL SECTION

General Considerations

The reactions were carried out under an argon atmosphere unless otherwise indicated. The acetonitrile was dried over 3 Å molecular sieves and distilled prior to use. The precursors $[Bu_4N][TCNQ]$, $[Mn(MeCN)_4][BF_4]_2$, $[Fe(MeCN)_6][BF_4]_2$, $[Co(MeCN)_6][BF_4]_2$, and $[Ni(MeCN)_6][BF_4]_2$ were prepared from literature methods.[10, 12] TCNQ was purchased from TCI and recrystallized before use.

Physical Measurements

X-ray powder diffraction patterns were collected using a Rigaku Rotating Anode X-ray Diffractometer. Infrared spectra were taken on Nujol mulls using a Nicolet FT-IR spectrophotometer. Static magnetic measurements were obtained on microcrystalline samples (~ 30 mg) with the use of Quantum Design, Model MPMS SQUID magnetometers. 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 AC susceptibility measurements were performed with an alternating field in the frequency range 0.1-1000 Hz.

Preparation of Cu(TCNQ)

Two different phases of Cu(TCNQ) can be prepared from the route:

$[Cu(CH_3CN)_4][BF_4] + [Bu_4N][TCNQ] \rightarrow Cu(TCNQ) + [Bu_4N][BF_4]$

Phase I

A quantity of $[Bu_4N][TCNQ]$ (0.500 g,1.12 mmols) is dissolved in 50 mL of acetonitrile. This green solution is then added to a solution of 0.352 g of $[Cu(MeCN)_4][BF_4]$ (1.12 mmols) dissolved in 20 mL of acetonitrile. Immediately upon mixing, dark blue microcrystals are observed to form. The solid is collected by suction filtration on a glass frit and washed with acetonitrile. The product is then dried under vacuum to give 0.265 g (88% yield).

Phase II

Acetonitrile (50 mL) is added to 0.300 g of Phase I, and the resulting suspension and light green solution is stirred at room temperature for 4 days. The acetonitrile is removed under vacuum and the resulting dark blue solid is dried under vacuum. This leads to virtually quantitative conversion of Phase I to Phase II by powder X-ray diffraction.

Preparation of $M(TCNQ)_2$ Compounds.

An example of the experimental procedures used in the synthesis of the series $M(TCNQ)_2$, (M = Mn, Fe, Co, Ni) is provided only for the nickel derivative, but the same procedure applies to the other binary metal/TCNQ materials. A 100 mL Schlenk flask is charged with 0.328 g (0.685 mmol) of $[Ni(MeCN)_6][BF_4]_2$ and 40 mL of acetonitrile to give a light blue solution. A second 100 mL Schlenk flask is charged with 0.610 g (1.366 mmol) of $[Bu_4N][TCNQ]$ in 40 mL of acetonitrile to yield a dark green solution. The $[Ni(MeCN)_6][BF_4]_2$ solution is stirred vigorously and the $[Bu_4N][TCNQ]$ acetonitrile solution is added via cannula. A green precipitate forms immediately upon mixing, and the suspension is stirred for 1 hour at room temperature during which time the precipitate turns from green to blue. The suspension is filtered using a medium Schlenk frit and a 250 mL Schlenk flask. Initially a small amount of the precipitate passed through the frit, but after the solid started collecting on the frit, no additional solid passed through. The blue precipitate is then washed with 4 x 20 mL portions of acetonitrile and dried under vacuum for ~6 hours. A typical yield is 0.220 g (69 %) based on Ni(TCNQ)$_2$. Calc'd for $NiC_{24}N_8H_8$: %C, 61.70; %H, 1.73; %N, 23.99. Found: %C, 60.09; %H, 2.12; %N, 22.93.

The main difference in the preparation of the Ni compound versus the analogous Mn, Fe, and Co derivatives is that the initial precipitates are blue for these metals, with no further changes being observed. Also, the filtration of Ni(TCNQ)$_2$ is slow and can take up to 4-5 hours to complete whereas the filtration of the other materials is much faster.

RESULTS AND DISCUSSION

General Synthetic Considerations

A special sub-class of transition metal/TCNQ coordination complexes is one in which there is only a transition metal and TCNQ. Such binary materials have been much less studied than those that include additional ligands, with the only structurally characterized example being Ag(TCNQ).[11] Cu(TCNQ) has attracted considerable attention due to the electronic and optical switching phenomena associated with thin film devices of this material, but until recent work in our laboratories revealed the existence of two different Cu(TCNQ) materials, these data were puzzling due to lack of reproducibility.[13] Further study of other metal/TCNQ binary phases has been hampered by a lack of convenient synthetic routes to these materials. We have discovered that solvated acetonitrile cations of the transition elements are convenient precursors in this chemistry, and, indeed, we have crystallized several interesting Mn(TCNQ)$_2$(S)$_x$ polymeric materials with H_2O and MeOH co-ligands (S).[14]

A new, non-aqueous synthetic approach in our laboratories has led to the discovery of several new binary materials of TCNQ with paramagnetic transition metals and no solvent ligands. TCNQ binds to the metals through its four nitrile positions which are groups that stabilize high-spin complexes; in contrast cyanide ligands stabilize low-spin compounds. These materials are all isostructural as indicated by the powder patterns displayed in Figure 2. The transition metals used in these materials (Mn, Fe, Co, Ni) are the same as those employed by Melby *et al.*, back in 1962,[10] but the exclusion of H_2O in our synthetic procedure has led to the isolation of completely different phases.

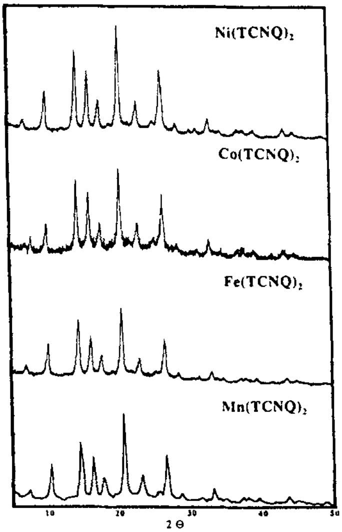

FIGURE 2 Powder XRD of the compounds in the $M(TCNQ)_2$ series.

Solid-State Structures of Cu(TCNQ)

There has been considerable interest in Cu(TCNQ) since the discovery that thin films sandwiched between a copper and aluminum electrode exhibit a bistable switching phenomena.[7a] When an electric field applied to a device consisting of a thin film of Cu(TCNQ) between a copper and aluminum electrode, the device switches from a high resistance state (several megaohms) to a low resistance state (several hundred ohms) at a critical field value. The majority of research on the Cu(TCNQ) material has focused on the elucidation of the mechanism responsible for this switching phenomena. One of the proposed mechanisms involves the formation of neutral TCNQ and Cu^0 to produce a film that contains a mixture of valence states. This could explain the lower resistance because the impeding Coulombic repulsive forces are reduced by allowing electrons to occupy the empty molecular orbitals of neutral TCNQ.

Despite the intensive study of the switching phenomena of the Cu(TCNQ) thin films, no structural studies have been reported. Several crystal structures containing copper and other ligands in addition to TCNQ have been reported but no data on the binary phase of copper and TCNQ have appeared.[8c,g,i,j] Microscopy has been used to observe morphology changes but no comprehensive study on the structural changes by either powder or single crystal X-ray diffraction has been reported.[7g]

The chemical composition and electronic characteristics of the two phases of Cu(TCNQ) are identical but the structures are quite different (Figure 3).

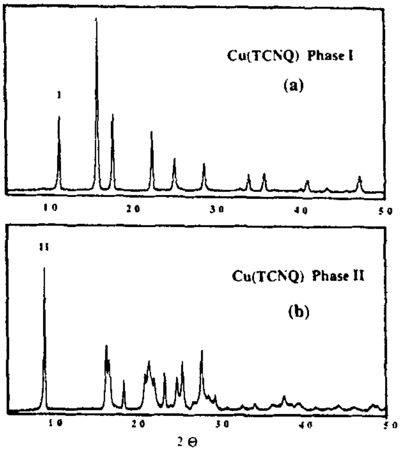

FIGURE 3 Powder X-ray patterns of the two phases of Cu(TCNQ).

Powder XRD studies revealed that both phases are typically present in thin films of Cu(TCNQ) grown on copper substrates, the exact ratio of the two being dependent on reaction conditions. This is undoubtedly the cause of the reported inconsistencies in the properties of Cu(TCNQ) devices. Single crystal X-ray studies have been performed on a needle of Phase I and a platelet of Phase II. The Cu atoms in Phase I are coordinated to four nitrogen atoms in a highly distorted tetrahedral environment. The quinoid rings of the TCNQ units are engaged in interplanar stacking at a distance of 3.24 Å which is smaller than the van der waals distance of 3.4 Å for carbon atoms. Adjacent TCNQ stacks are rotated by 90° with respect to each other which is a standard feature in most binary metal/TCNQ salts. Representations of the structure are depicted in Figure 4 below.

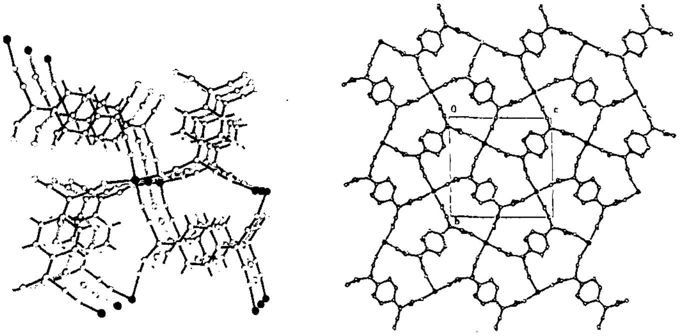

FIGURE 4 Phase I structural features.

In Phase II, the metal geometry is close to tetrahedral and adjacent TCNQ ligands are parallel to each another with the shortest face-to-face contact between nearest neighbors in the same network being 6.8 Å. This arrangement of $TCNQ^{-1}$ ions is unprecedented; typically they are situated around a metal ion as four TCNQ units related by a pseudo-four fold rotational axis such as that found in Ag(TCNQ) and alkali metal TCNQ salts.

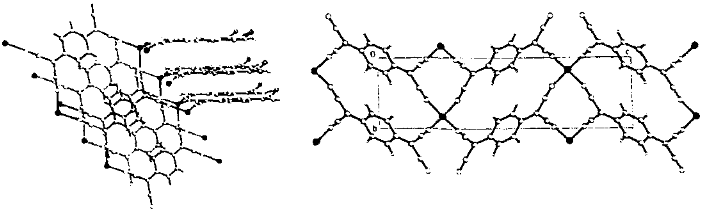

FIGURE 5 X-ray features of Cu(TCNQ) phase II.

Magnetic and Conducting Properties of Cu(TCNQ)

The variable temperature magnetic susceptibilities of the Cu(TCNQ) samples were measured by the SQUID technique. Plots of χ versus T and μ_{eff} versus T are given in Figure 6.

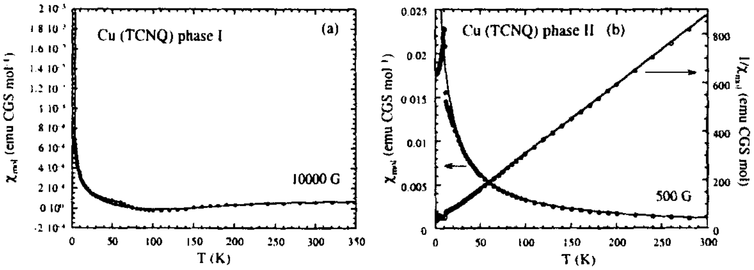

FIGURE 6 Magnetic data for Cu(TCNQ) phases.

The very low susceptibility of Phase I indicates strong magnetic coupling of the unpaired electrons which renders the sample essentially diamagnetic. This is consistent with earlier studies on the magnetism of chemically prepared Cu(TCNQ). Phase II, however behaves as if the $TCNQ^{-1}$ radicals are isolated paramagnets in the high temperature regime (μ_{eff} = 1.58 B.M. at 320 K). At lower temperatures, the moment for Phase II slowly decreases, indicating the onset of antiferromagnetic interactions between the unpaired spins. At 10 K, however, a ferromagnetic ordering occurs (Figure 7).

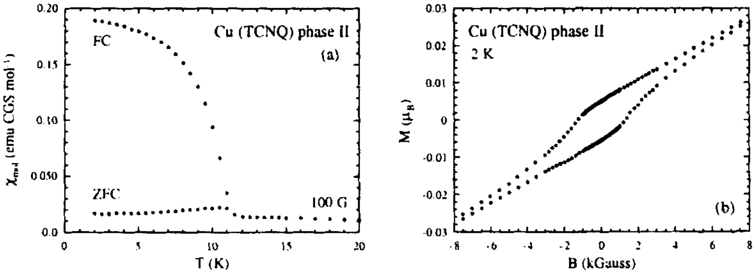

FIGURE 7 (a) ZFC and FC data and (b) hysteresis for Phase II.

A comparison of the zero-field cooled and field-cooled experiments and the hysteresis loop observed at 2 K with a coercive field of 500 G both support the existence of an ordered state below 10K.

The conductivity properties of the Cu(TCNQ) phases were measured by the pressed pellet conductivity method, and it was found that the materials exhibit quite different charge-transport (Figure 8).

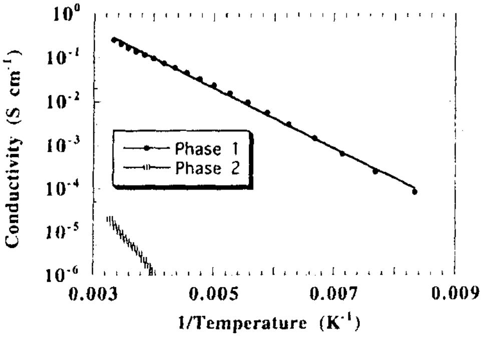

FIGURE 8 Plots of the temperature dependence of the resistivity for Cu(TCNQ) phases.

Both samples are semiconductors, but Phase I exhibits a room temperature conductivity of 0.25 Scm^{-1} whereas Phase II is nearly insulating with a room temperature conductivity of 1.3 x 10^{-5} Scm^{-1}. The band gaps are 0.137 eV and 0.332 eV for Phase I and II respectively. It is interesting to note that these values are very close to the corresponding electrical properties of the "unswitched" and "switched" forms of Cu(TCNQ) in the devices. If the electronic switching of Cu(TCNQ) thin film devices is an intrinsic property of the Phase II material, and not merely a consequence of the contact of the aluminum electrode with the rough Cu(TCNQ) surface, it may involve a phase transition from a three-dimensional structure that does not allow for TCNQ^{-1} stacking to a phase that brings parallel TCNQ radicals into close proximity. The fact that the resting state of the film, Phase II, is a centrosymmetric structure and that Phase I appears to be a non-centrosymmetric structure bodes well for a piezoelectrically driven transition, if, in fact, a phase change is occurring. This possibility is under current investigation in our laboratories.

Magnetic Properties of Binary Metal TCNQ Compounds

The magnetic behavior of two representative compounds from the $M(TCNQ)_2$ family (M= Mn^{II} S=5/2; Fe^{II} S=2; Co^{II} S=3/2; Ni^{II} S=1) have been investigated. $Mn(TCNQ)_2$ and $Ni(TCNQ)_2$ exhibit globally similar magnetic behavior, thus attention will be focused on the Mn sample with a brief mention of the Ni analog. DC measurements as a function of temperature and field revealed a sharp increase in susceptibility at low temperature and a reproducible, small Curie constant. AC measurements, in particular the field dependence of the susceptibility, indicate that the samples are not ordinary ferromagnets.

DC measurements

(a) As a function of temperature.

The temperature dependence of the DC susceptibilities for the $Mn(TCNQ)_2$ and the $Ni(TCNQ)_2$ compounds are presented in Figure 9 a and b respectively.

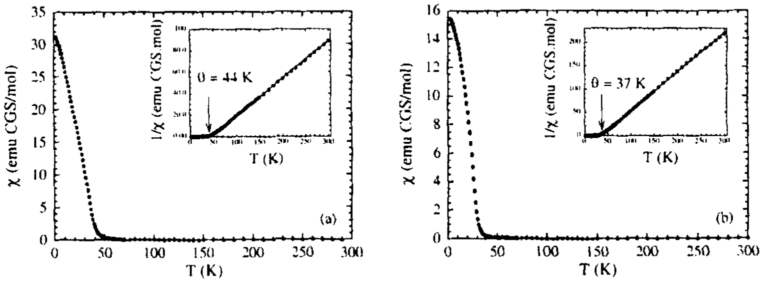

FIGURE 9 Temperature dependence of the static susceptibility (M/B) at 500 G for (a) $Mn(TCNQ)_2$ and (b) $Ni(TCNQ)_2$ samples. Inset: 1/χ versus fit to the Curie-Weiss law between 50-300 K

In the high temperature regime (T >50 K), the susceptibility obeys the Curie-Weiss law with C=2.7 emu CGS/mol, θ=44 K for $Mn(TCNQ)_2$ and C=1.3 emu CGS/mol, θ=37 K for $Ni(TCNQ)_2$. In both cases, the value of the Curie constant is low compared to the value expected for isolated spins; this conclusion is based on the assumption of g=2 which is typical for $TCNQ^{-1}$ and Mn^{II} and g=2.2 for the Ni^{II} as detailed below:

$$Mn(TCNQ)_2 : C_{\text{Theoretical}} = C_{S=\frac{5}{2}} + 2 \times C_{S=\frac{1}{2}} = 5.125 \text{ emu CGS/mol}$$

$$Ni(TCNQ)_2 : C_{\text{Theoretical}} = C_{S=1} + 2 \times C_{S=\frac{1}{2}} = 1.96 \text{ emu CGS/mol}$$

The origin of these low moments at high temperatures is not possible to identify at this point, but it may be related to spin correlation or the presence of diamagnetic impurities.

At lower temperatures (40 K for $Mn(TCNQ)_2$ and 30 K for $Ni(TCNQ)_2$), the compounds exhibit a dramatic increase in the susceptibility that is typically associated with ferromagnetic ordering. This low temperature region will be discussed in more detail in the ac susceptibility section. At 500 G, there is no observed difference between the zero-field cooled and field-cooled curves.

(b) As a function of field.

Figure 10 presents the field dependent magnetization at 2 K for $Mn(TCNQ)_2$.

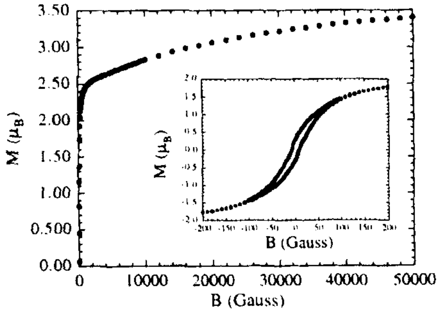

FIGURE 10 Field dependence at 2 K up to 5 T of the first magnetization and hysteresis loop of the magnetization at 2 K for $Mn(TCNQ)_2$ (inset).

A rapid increase of the moment at low field (between 0 and 500 G) is observed, with no saturation occurring up to 5T. This mutual behavior for both materials has been observed for weak or canted ferromagnets. [15,16] Moreover, a narrow hysteresis loop is observed (inset in Figure 10) with approximate coercive fields of 20 G and 270 G for $Mn(TCNQ)_2$ and the $Ni(TCNQ)_2$ respectively.

AC measurements

(a) Field dependence

Plots of the temperature dependence of the in-phase (χ') and out-of-phase (χ") magnetic susceptibilities are depicted in Figures 11 and 12 for $Mn(TCNQ)_2$. In the absence of a field, χ' shows a rapid increase at ~38 K which continues to a maximum at 20 K, after which time a linear decrease with temperature is observed. In the presence of a field, the χ' signal exhibits a significant field dependence, but it is difficult to ascertain the critical temperature for each field.

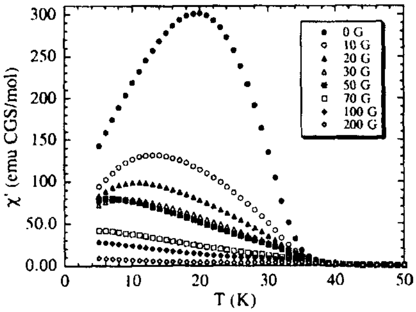

FIGURE 11 Thermal dependence of the in-phase component of the AC susceptibility (1Hz, 1G modulation) at various static fields (0-200 G) for $Mn(TCNQ)_2$.

This temperature is usually defined as the inflection point in the increasing part of the curve, but it is more convenient to examine the imaginary part of the ac susceptibility and to determine where χ" becomes non-zero (Figure 12 a,b). The thermal variation of χ" is also strongly dependent on the applied static field. In the absence of a field, χ'' becomes non-zero at 33 K (Figure 12b) and reaches a maximum at ~17 K before decreasing again at lower temperatures. The changes in the critical temperature in the absence of a field were followed, and plots of the field as a function of critical temperature were used to determine the magnetic phase diagram (T,B) for both materials (Figure 13). The shape of the transition line that separates the paramagnetic phase (χ''=0) from the magnetic phase (χ''>0) is similar in both cases, behavior that underscores the similarity of the physical behavior of these compounds.

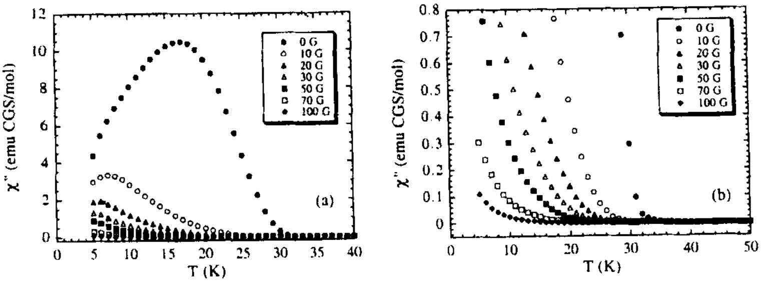

FIGURE 12 (a) Thermal dependence of the out-of-phase component of the AC susceptibility (1Hz, 1G modulation) at various static fields (0-100 G) for $Mn(TCNQ)_2$. (b) Enlargement of the plot for small values of χ''.

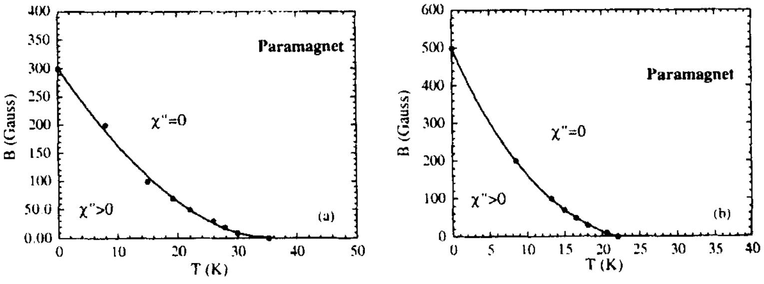

FIGURE 13 Magnetic phase diagrams (T,B) for (a) $Mn(TCNQ)_2$ and (b) $Ni(TCNQ)_2$. The solid lines are only intended to be a guide.

(b) Frequency dependence

Plots of the thermal variation of the AC susceptibilities for different frequencies are presented in Figure 14. The data reveal a pronounced dependence of both the maximum and breadth of the transition with frequency. The position of the χ' and the χ'' peaks increase by ~2 K and 3 K respectively when the frequency is increased from 1 to 997 Hz, which is not expected to occur for a *bona fide* ferromagnetic material. Indeed, this behavior is usually indicative of the spin-glass or superparamagnetic state.

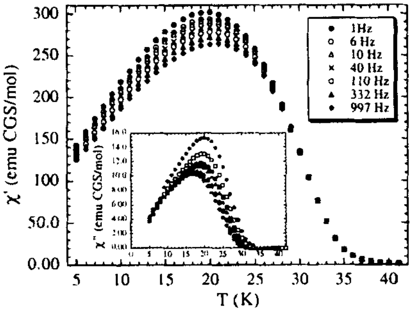

FIGURE 14 Temperature dependence of the in-phase and the out-of-phase components of the AC susceptibility (zero field, 1G modulation) at frequencies between 1-997 Hz.

Discussion of the Magnetic Properties of $Mn(TCNQ)_2$

A spin-glass is a metastable state of frozen spins that does not undergo a true long-range order, but may exhibit spontaneous magnetization in the absence of a static magnetic field.[17] Spin glasses are characterized by ferromagnetic or antiferromagnetic interactions modified by some degree of frustration, randomness or disorder which prevents a phase transition from occurring. The "critical temperature" of a spin glass is actually a freezing temperature T_f that is a function of the applied frequency ν. The important parameter to estimate is the frequency shift γ estimated by the position of the maximum of χ' plot and by the following relation:

$$\gamma = \frac{\Delta T_f}{T_f(0)\,\Delta(\log\nu)}$$

In this equation, ΔT_f is the shift in the peak in χ', $\log\nu$ is the logarithm of the AC field frequency and $T_f\,(0)$ is the temperature of the peak at zero frequency. The plot of T_f vs $\log\nu$ between 1Hz and 1000 Hz is a reasonably good straight line with a slope $(\Delta T_f/\Delta(\log\nu))$ of -0.17. If we take $T_f\,(0)$ to be 19 K (which is the temperature where the ZFC and the FC in the DC measurements are equal in a field of 10 G), the calculated γ value is 0.009. According to Mydosh,[17] this γ value is indicative of spin-glass behavior and not superparamagnetism; in the latter case, much larger γ values (> 0.1) are observed. Further support for the conclusion that these materials are not superparamagnetic is the fact that an attempted fit of $Mn(TCNQ)_2$ data to the Arrhenius law $(\nu = \nu_0 exp(E_a/k_B T_f)$ gives the physically meaningless values of E_a=2272 K and ν_0=4.10^{50} Hz. A real superparamagnet exhibits Arrhenius behavior.

To further assess whether these compounds can be described as spin glasses at low temperatures, we consider the simple mean field theory of spin glasses developed by Sherrington and Kirkpatrick (SK).[18] In the presence of a static field, this theory maintains that the instability line takes the functional form for $T_f \approx T_i$ and an Ising spin glass:

$$B \propto (T_f(0) - T_i(B))^{\frac{3}{2}}$$

In this equation, T_i is the instability temperature at the B field. An experimental consequence of this theory is that below the instability line, one should observe irreversibility in the magnetic properties; this is a signature of the frozen spin-glass state. If we consider that the temperature at which χ'' becomes non-zero is the onset of irreversibility, we should be able to fit the magnetic phase diagram near T_f. Indeed, this rough approximation fits the experimental data as shown in Figure 15. Thus, it appears that the low temperature magnetic phase is best described as spin-glass in nature.

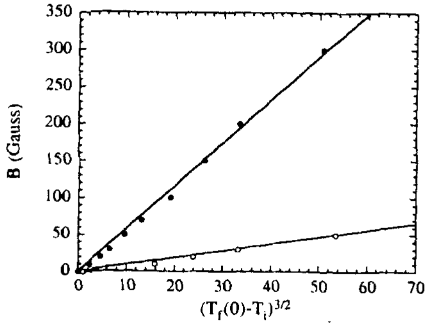

FIGURE 15 Static magnetic field vs $(T_f(0)-T_i)^{3/2}$ for $Mn(TCNQ)_2$ (open circles) and for $Ni(TCNQ)_2$ (black circles). The line is the fit by a linear function.

Conclusions

The results of the Cu(TCNQ) study establish the existence of two different polymorphs of this compound. The key to this discovery was the recognition that the kinetic product (Phase I) dissolves in to yield a more thermodynamically stable material (Phase II). The latter is the dominant phase in films that undergo switching. Spectroscopic data collected on the bulk *kinetic* phase, therefore, are not meaningful for understanding the switching mechanism of the films. While the X-ray structures of Cu(TCNQ) do not, by themselves, explain the apparent switching, they provide convincing evidence that the structural motif dictates the magnetic and electrical properties of the material.

Magnetic studies of $Mn(TCNQ)_2$ and the $Ni(TCNQ)_2$ revealed unexpected and intriguing behavior. The majority of the results point to spin-glass behavior, but the dramatic increase of the susceptibility at a fixed temperature (40 K for the $Mn(TCNQ)_2$ and 30 K for the $Ni(TCNQ)_2$) is not typical of classical spin-glass materials. Nevertheless, heat capacity measurements (Figure 16) in this temperature range do not exhibit a peak indicative of ferromagnetic ordering. The real nature of this magnetic phase seems to be between that of a spin-glass and a ferromagnet. In an effort to provide additional insight into the Mn and Ni phases, detailed magnetic studies of the other two members of this family, namely Fe(TCNQ)$_2$ and Co(TCNQ)$_2$ are in progress.

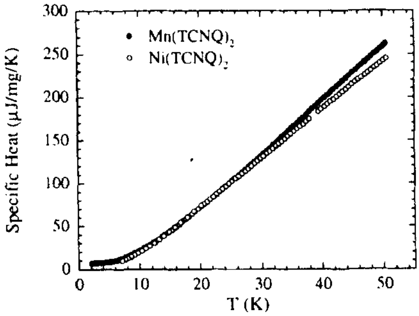

FIGURE 16. Heat capacity measurements on Mn(TCNQ)$_2$ and Ni(TCNQ)$_2$.

Another priority of our on-going work in this area is to improve the crystallinity of the samples (already shown by X-ray powder diffraction). The probability of growing single crystals (by gels, electrocrystallization and different synthetic methods), while not high, is certainly possible, but the most promising method for solving the X-ray structure of a M(TCNQ)$_2$ compound is by powder methods. These studies are in progress. Armed with structural information, we will be in a much better position for understanding these fascinating magnetic results at the microscopic level.

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