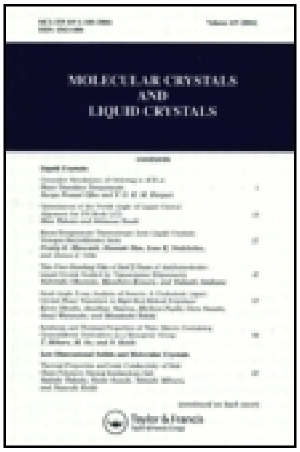

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Magnetic Ground State and its Control in Porphyrin-Based Magnets

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MAGNETIC GROUND STATE AND ITS CONTROL IN PORPHYRIN-BASED MAGNETS

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Abstract Alternating metalloporphyrin-acceptor systems provide a 'laboratory' for study of quasi-one-dimensional magnetic phenomena. For example, the [octaethylporphyrinatomanganate(III)][hexacyanobutadiene], [MnOEP][HCBD], compound is a model alternating classical (spin 2) and quantum (spin 1/2) spin system. While the high temperature susceptibility is well fit to Seiden's model for alternating S = 2 and S = 1/2 chains with antiferromagnetic exchange J/k_B = 172 K, and g for [MnOEP] = 1.92, the low temperature data reveal a transition to a two-dimensional antiferromagnet, followed by a transition to a three-dimensional canted antiferromagnet. The similarly structured [tetraphenylporphyrinatomanganate(III)][tetracyanoethenide], [MnTPP][TCNE], also has ferrimagnetic behavior within the chains, though it has ferromagnetic interactions between the chains. We associate the change in sign of interchain exchange (from antiferromagnetic to ferromagnetic) with an increase in interchain separation and a change in the interchain exchange pathways. Subtle disorder, the magnitude of which depends upon the solvent incorporated within the structure, causes cluster glass-like behavior at low temperatures. The roles of the various constituents of these compounds in determining the ferromagnetic or antiferromagnetic nature of the ground state are discussed.

INTRODUCTION

The design of molecule-based magnets has been an area of increasing interest and remarkable results.[1,2] In many of the approaches used to obtain molecule-based magnets a common trend has been to use chains[1] or layers[3,4] of radicals (spins) with strong magnetic coupling as first steps in building three-dimensional magnets. The challenge is then to order the resulting spins ferromagnetically by controlling the structural packing of the low-dimensional constituents.

We review here results of some of our physical studies regarding the magnetic ground states in a family of quasi-one-dimensional electron transfer salts, consisting of parallel chains comprised of alternating metalloporphyrin electron donors and cyanocarbon electron acceptors. This offers a wide range of controlling factors, including choices of cyanocarbon acceptors that bridge the adjacent porphyrins within a chain at the metal ion, substituent groups at the periphery of the porphyrin that control the interchain interactions, and various solvents that intercalate between the chains. Changing one or more of these chemical features result in a family of related crystal structures and also introduce different degrees of disorder.

Recent studies have uncovered a wide range of magnetic phenomena in these materials, including spin- and lattice-dimensionality crossovers[5,6,7] and cluster-glass formation.[8,9] Progress[10] has been made in understanding the role of the different building blocks forming these materials. We show that the different cyanocarbon bridges used as acceptors, (TCNE, tetracyanoethylene, and HCBD, hexacyanobutadiene) led to similar antiferromagnetic coupling within the chains, causing high temperature one-dimensional ferrimagnetic behavior. The organic constituents attached to the porphyrin have an essential role in determining the three-dimensional ordering by keeping the chains further apart and/or providing exchange pathways. In the case of [MnOEP][HCBD] (OEP = octaethylporphyrinato), there is evidence for antiferromagnetic coupling between adjacent chains in a plane while in the MnTPP (TPP = *meso*-tetraphenylporhyrinato) based compounds, [MnTPP][TCNE]·x(solvent) (where $x \leq 3$), weak ferromagnetic, behavior is observed. Finally, while glassy behavior is not observed in the system without solvent, [MnOEP][HCBD], cluster glass-like behavior is apparent in [MnTPP][TCNE]·x(solvent) using solvents such as PhMe (= toluene), *o*-Xy (= *o*-xylene), and *o*-DCB (= *o*-dichlorobenzene). Thus the presence of nonstoichiometric solvent quantities in the structure may correlate with varying degrees of disorder. These chemical features are linked to the variations in the intra- and inter-chain magnetic coupling, single-ion anisotropy, and disorder.

THE METALLOPORPHYRIN FAMILY

The first member of the manganeseporphyrin family intensively studied was [MnTPP][TCNE]·x(PhMe).[11] Since then a large variety of related compounds have been synthesized.[12,13,14] All these systems are electron transfer salts consisting of parallel chains of electron donors (D = [MnOEP], [MnTPP], etc.) *trans*-μ_2-*N*-σ-bound by cyanocarbon acceptors (A = [TCNE] or [HCBD]), $\cdots D^+A^-D^+A^-\cdots$. The adjacent spins along these chain alternate, $S = 2$ on the donor and $s = 1/2$ on the acceptor.

The chain structures of two such systems are presented in Fig. 1. For [MnOEP][HCBD], Fig. 1a, the intrachain Mn···Mn separation is[12] 10.844 Å while the key interchain Mn···Mn distances are 8.023, 12.332 and 12.550 Å. The Mn···Mn separations in [MnTPP][TCNE]·3(*o*-DCB), Fig. 1b, are[13] 9.489 Å, intrachain, and 12.865, 12.890, 13.800, 13.711 Å, interchain, while in [MnTPP][TCNE]·(*o*-Xy) they are[13] 10.218 Å intrachain and 9.261, 11.111, 13.294 Å, interchain.

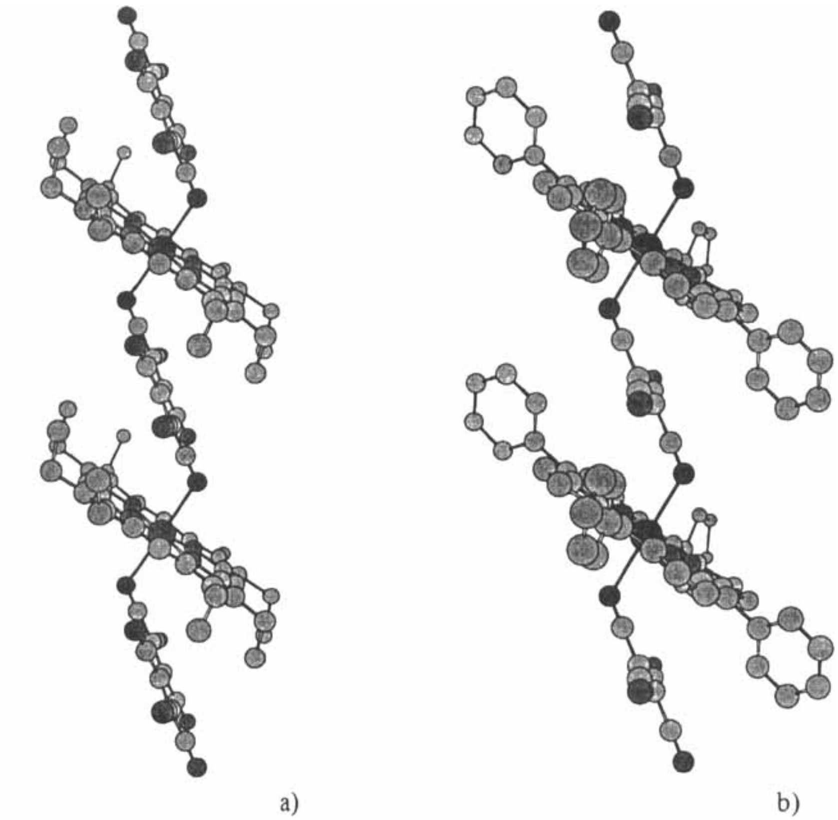

FIGURE 1: Side view of isolated chains of a) [MnOEP][HCBD][12] and b) [MnTPP][TCNE]·x(*o*-DCB)[13].

EXPERIMENTAL

The dc magnetic data was recorded using a MPMS-5 Quantum Design SQUID magnetometer and the dc susceptibility was calculated as the ratio of the magnetization, M, and field, H, $\chi_{dc} = M/H$ (assuming a linear response of M on H). The ac magnetic susceptibility was measured with a Lake Shore 7225 AC susceptometer - DC magnetometer at various ac driving frequencies and amplitudes. A lock-in amplifier allowed phase sensitive detection such that both the in-phase (χ') and out-of-phase (χ'') susceptibilities were recorded. Polycrystalline samples were handled and weighed in an argon environment to avoid exposure to air, and sealed in quartz sample holders, after being evacuated to 10^{-5} mbar. (It is noted that (partial) disolvation may occur during evacuation.) The diamagnetism of the sample holders was measured separately. All susceptibilities reported here have been corrected for both core diamagnetism and sample holder diamagnetism.

RESULTS AND DISCUSSION

Here we review, analyze and contrast the experimental data for [MnOEP][HCBD] and various [MnTPP][TCNE]·x(solvent) compounds.

1. [MnOEP][HCBD]

The high temperature magnetic susceptibility of [MnOEP][HCBD] shows one-dimensional ferrimagnetic behavior, evidenced by the good fit to Seiden's model[15] for chains of alternating classical (S = 2, in this case) and quantum (s = 1/2) spin. Based on the Hamiltonian[16]:

$$H = -2\sum_i J_{intra}(S_i+S_{i+1})\cdot s_i \qquad (1)$$

Seiden derived an expression for the product of the magnetic susceptibility and

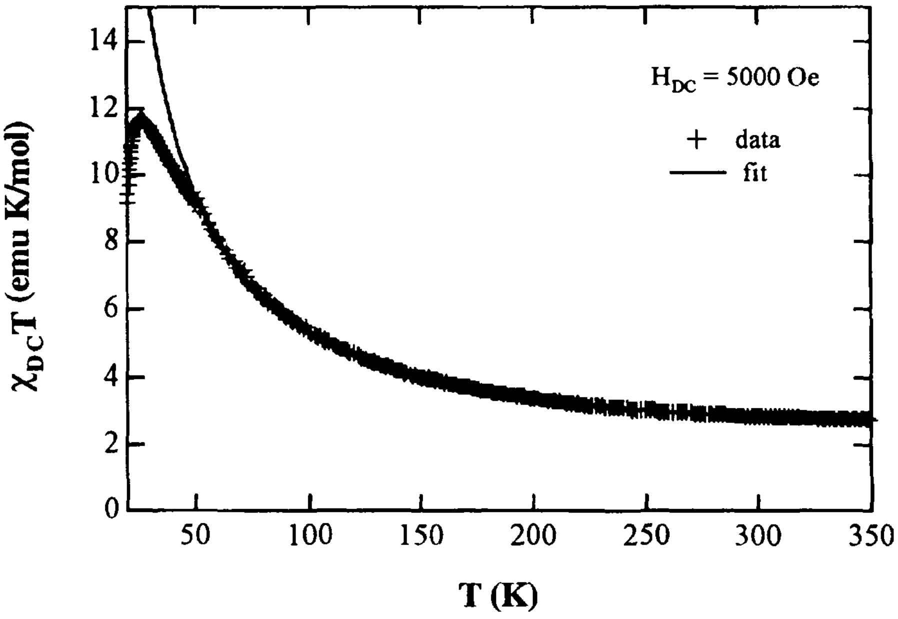

FIGURE 2: $\chi_{DC}T$ vs. T of data, +, and fit to Seiden's model, solid line (from ref. 10).

temperature, χT, as a function of temperature. Given the fixed values of the two types of spins (S = 2 and s = 1/2), Seiden's prediction allows three free parameters: the intrachain exchange, J_{intra} and the Landé g factors of both spins, g_S and g_s. Here we fix g_s = 2.00 in accord with expectations for cyanocarbon radicals.

Figure 2 displays the product $\chi_{DC}T$ for [MnOEP][HCBD] as a function of temperature and the fit to Seiden's model. The conclusion drawn is that the alternating spins strongly interact antiferromagnetically, the values of the exchange constant and the Landé factor on the Mn^{III} site being: $J/k_B = -172$ K, and $g_S = 1.92$. The deviation from Seiden's model that occurs at temperatures below ~ 50 K, is toward smaller values than the one-dimensional predictions, indicating antiferromagnetic correlation between the chains.

The low temperature ac susceptibility data, Fig. 3, has a peak at 22 K in the in-phase susceptibility, χ', with no noticeable out-of-phase component, χ'', indicative of an antiferromagnetic transition associated with it.[17] The antiferromagnetic nature of the transition agrees with the suppression of the experimental $\chi_{DC}T$ from that of an ideal one-dimensional ferrimagnet for temperatures less than 50 K, Fig. 2.

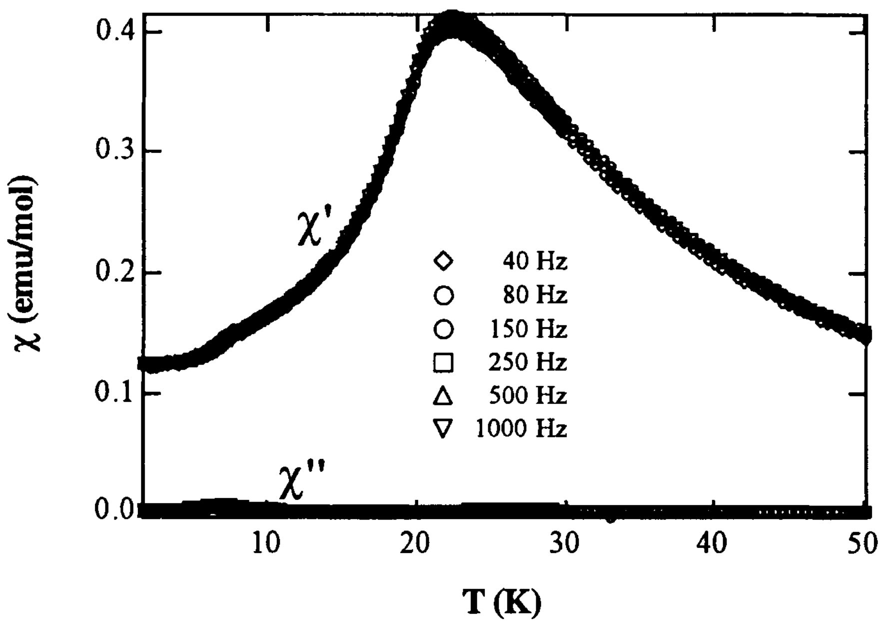

FIGURE 3: In-phase (χ') and out-of-phase (χ'') magnetic ac susceptibility of [MnOEP][HCBD] at frequencies between 40 and 1000 Hz, H_{ac} = 1 Oe (from Ref. 5).

The peak at 22 K in the ac susceptibility is associated[5] with a 19.6 K (based on the maximum in $d(\chi T)/dT$[18]) transition from a one-dimensional ferrimagnetic behavior to a two-dimensional antiferromagnet. We suggest that this transition consists of both lattice- and spin-dimensionality crossovers.[5] At high temperature both the classical and the quantum spins can be considered Heisenberg (isotropic) spins. At low temperatures the small single ion anisotropy (a few Kelvin energy) of the classical spin becomes important leading to a spin-dimensionality crossover to an Ising (anisotropic) spin. The large difference between the Mn···Mn interchain separations, together with the small intrachain Mn-HCBD separation, leads to large differences in both the two interchain magnetic couplings and between them and the intrachain magnetic coupling. As the temperature is lowered the largest interchain interaction becomes important causing a lattice-dimensionality crossover, from a one-dimensional system to a two-dimensional one. This argument is supported by the agreement[5] between the experimental value of the critical temperature and the theoretical estimation based on Onsager's relation[19] for the critical temperature of the two-dimensional Ising model (as a function of the intra- and inter-chain exchange constants), together with the numerical results of Jou and Chen[20] regarding the role of spin anisotropy.

The absence of a frequency dependence in the ac susceptibility associated with the 19.6 K transition is in agreement with the lack of disorder[21] in this compound. However, at 8.8 K there is a shoulder in χ' and a small peak in χ'', suggesting the onset of canting in the two-dimensional ordered plane of spins.

In addition, the irreversibilities present in the field-cooled/zero-field-cooled magnetization data,[6] Fig. 4, below 5 K point to another transition, attributed to a transition from a two-dimensionalcanted antiferromagnet to a three-dimensional canted antiferromagnet. This transition is suggested to occur when the smallest interchain magnetically correlates the antiferromagnetic layers that result from the 19.6 K transition.

The magnetic field independence of the bifurcation point between the field-cooled and zero-field-cooled magnetization data is in agreement with the lack of disorder[21] in this compound suggested by the ac susceptibility data, and demonstrates this bifurcation is not a transition to a glassy state. The argument for this to be a transition to a three-dimensional canted antiferromagnet below 5K is strengthened by the critical analysis near the critical temperature, T_c, of the remanant magnetization, M:

$$M \sim [(T-T_c)/T_c]^{\beta} \qquad (2)$$

which gives[6] a critical exponent of $\beta = 0.31$, as expected for a three-dimensional Ising system. Supporting the canting hypothesis, for [MnOEP][HCBD] as well as [MnTPP][TCNE] and other members of the family, is the low temperature (1.7 to 4.2 K) ac susceptibility data of these compounds[7] which approach a constant value.[1b]

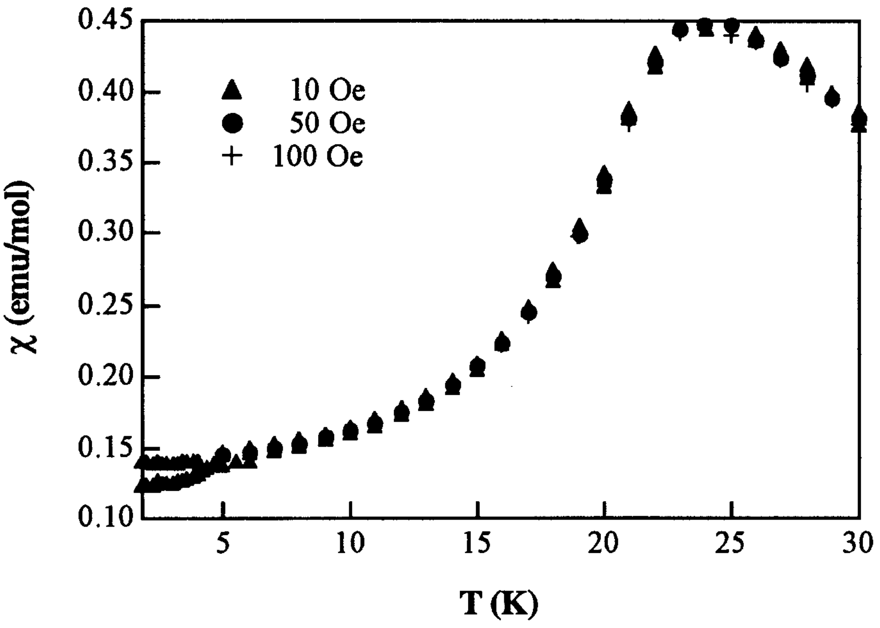

FIGURE 4: Field-cooled (upper points below 5 K) and zero-field cooled (lower points below 5 K) magnetization data measured at 10, 50, and 100 Oe applied fields for [MnOEP][HCBD] (from Ref. 6).

2. [MnTPP][TCNE][solvent]

The [MnTPP][TCNE] compound has been synthesized using a variety of solvents.[11,13,22] Here we concentrate our attention on two of them, [MnTPP][TCNE]·x(*o*-Xy) and [MnTPP][TCNE]·x(*o*-DCB). (Early magnetic studies on the [MnTPP][TCNE]·x(PhMe) compound[11] were reported separately.[23]) Both compounds show one-dimensional ferrimagnetic behavior at high temperatures, with fits to Seiden's model for alternating $S = 2$ and $s = 1/2$ spin chains giving[10] $J/k_B = -84$ K, and $g_S = 2.00$ (for [MnTPP][TCNE]·x(*o*-Xy) and $J/k_B = -140$ K, and $g_S = 2.00$ (for [MnTPP][TCNE]·2(*o*-DCB) for the intrachain exchange, J_{intra} and the Landé g factor of the classical spin. Figure 5 displays the product $\chi_{DC}T$ as a function of temperature and the fit to the theoretical model for [MnTPP][TCNE]·x(*o*-Xy). The $\chi_{DC}T$ product deviates above the one-dimensional behavior predicted by Seiden's model, below ~ 50 K, indicating ferromagnetic correlations between the chains.

The low temperature plots of the effective magnetic moment ($\mu_{eff} = (8\chi_{AC}T)^{1/2}$) of the two compounds, Fig. 6, show that, even though the change in solvents does not affect the overall weak ferromagnetic behavior, it determines, through structural changes, different magnetic moments and different onset of the three-dimensional correlations.

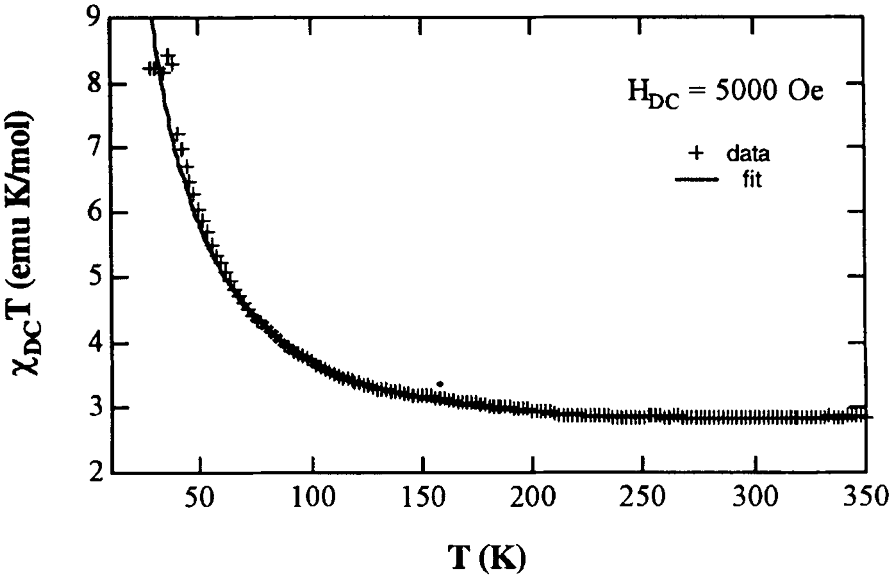

FIGURE 5: $\chi_{DC}T$ vs. T of [MnTPP][TCNE]·x(*o*-Xy) data, +, and fit to Seiden's model, solid line.

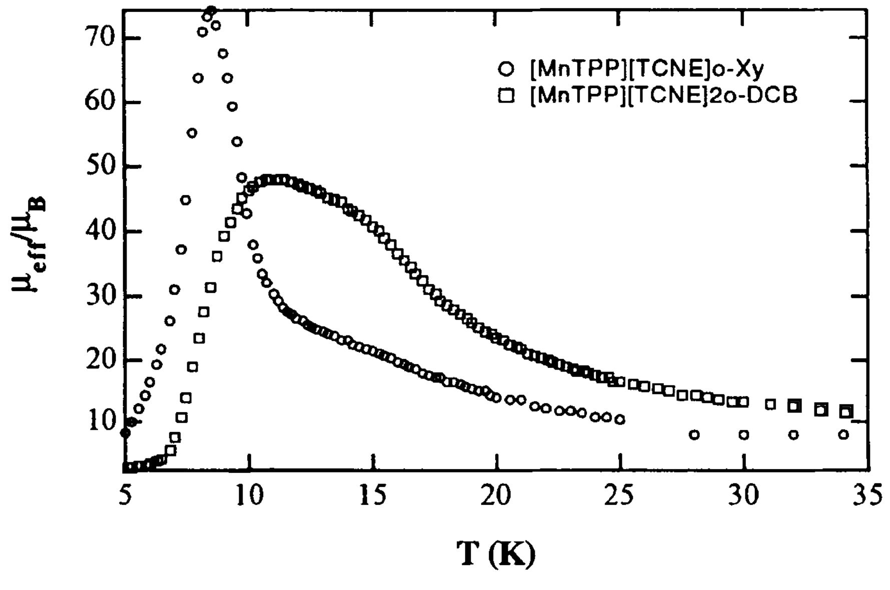

FIGURE 6: μ_{eff} [= $(8\chi_{AC}T)^{1/2}$] vs. T for [MnTPP][TCNE]·x(*o*-Xy) and [MnTPP][TCNE]·x(*o*-DCB) (see Ref. 10).

The critical temperatures of 10 K for [MnTPP][TCNE]·x(*o*-DCB), and 8.5 K for [MnTPP][TCNE]·x(*o*-Xy) were determined[13] based on the value of the peak temperature of the in-phase low temperature ac susceptibility. Figure 7 displays the frequency dependence of the low temperature ac susceptibility data for [MnTPP][TCNE]·x(*o*-DCB). Striking in this figure is the frequency dependence of the

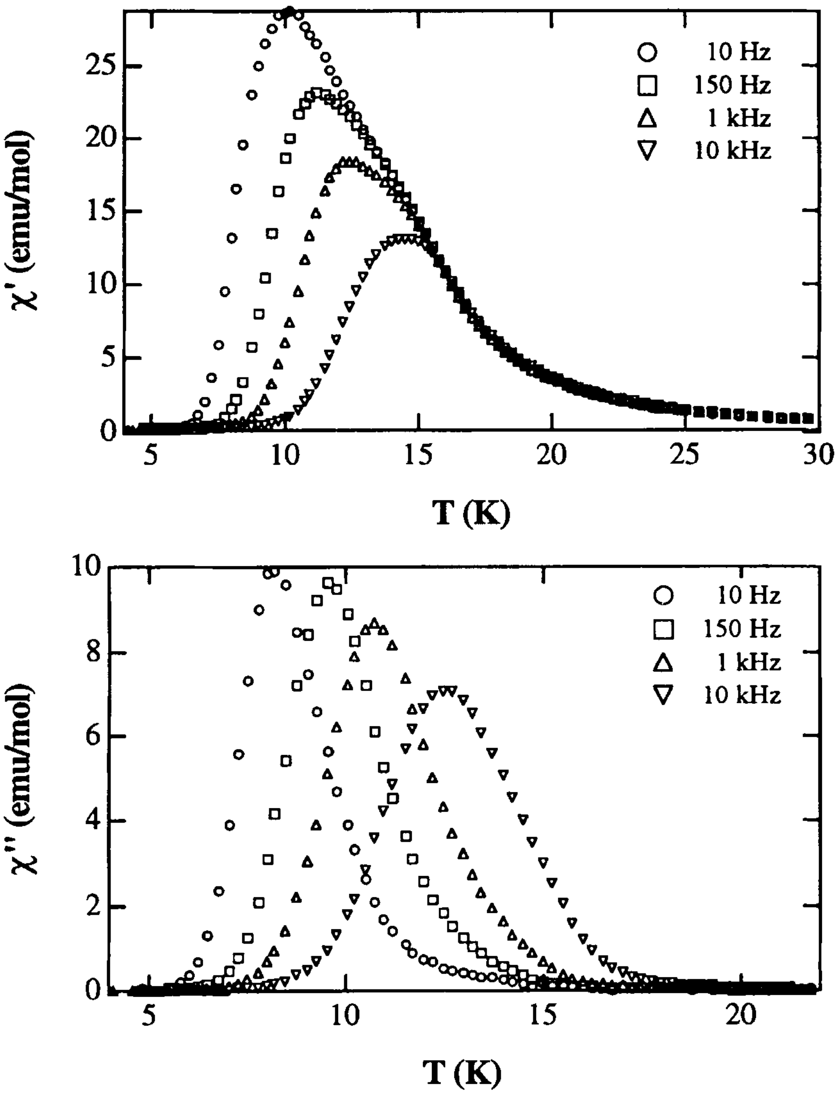

FIGURE 7: In-phase and out-of-phase ac susceptibility for [MnTPP][TCNE]2*o*-DCB, at selected frequencies between 10 and 10,000 Hz (see Refs. 8 and 9).

temperature of the peak in the in-phase susceptibility, suggesting the presence of disorder. The values of the relative variation of the peak temperature per decade of frequency,[8] $(\Delta T_p/T_p)/\Delta(\ln f)$ = 0.147 and 0.038, for the [MnTPP][TCNE]·x(*o*-DCB) and [MnTPP][TCNE]·x(*o*-Xy) samples shown, respectively, place these compounds somewhere between canonical spin glasses (which have typical values[21] of $(\Delta T_p/T_p)/\Delta(\ln f)$ = 0.005-0.02) and superparamagnets (which have typical values[21] of $(\Delta T_p/T_p)/\Delta(\ln f)$ = 0.28), suggesting cluster glass like behavior.

The field-cooled / zero-field-cooled magnetization data for [MnTPP][TCNE]·x(*o*-Xy) reveals a field dependent bifurcation point, Fig. 8, which indicates the presence of disorder[21] in this compound. The small irreversibilities and "oscillations", seen at temperatures above and below the bifurcation point, in the field-cooled / zero-field cooled data may be caused by the presence of multiple metastable minima in the free energy of the system

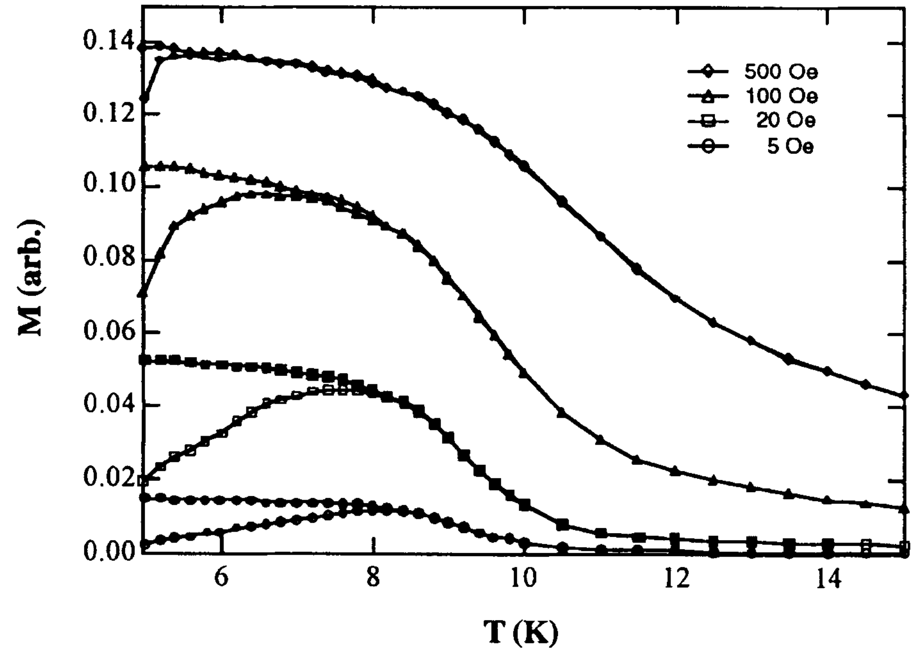

FIGURE 8: Field-cooled (open symbols) and zero-field cooled (filled symbols) data for [MnTPP][TCNE]·x(*o*-Xy) for fields between 5 and 1000 Oe (see Ref. 8).

The nature of the low temperature ground state in the [MnTPP][TCNE] compounds is particularly interesting due to the mixture of weak ferromagnetic and cluster glass like properties. These properties are consistent with the picture of one-dimensional clusters with strong intra-cluster exchange and weak inter-cluster interactions. Indeed, the structural disorder that may be induced by nonstoichiometric solvent concentrations and enhanced by the possibility of the bridging TCNE molecule to rotate[24] may limit the length of the regions of correlated spins along the chain, leading to the formation of clusters. The interchain dipolar interaction, given its dependence on the orientations of the spins, may cant the spins and lead to weak ferromagnetism. Moreover, if disorder is present, the interchain dipolar interaction could cause frustration and the glassy behavior.

Summarizing, the experimental results for the three members of the manganoporphyrin family described herein show that utilizing both $[TCNE]^{\cdot-}$ and $[HCBD]^{\cdot-}$ cyanocarbon bridges as acceptors, lead to antiferromagnetic coupling within the chains and overall one-dimensional ferrimagnetic behavior, as evidenced by the excellent fit to Seiden's model at higher temperatures. The low temperature deviations of the ac susceptibility data from Seiden's one-dimensional model prediction revealed antiferromagnetic coupling between the $[MnOEP]^{+\cdot}$ chains, while the weak ferromagnetic interchain interaction in the $[MnTPP]^{+\cdot}$ salts determined its weak ferromagnetic behavior. Finally the presence of nonstoichiometric amounts of various solvents in the materials may be responsible for their glassy behavior (with different degrees of disorder) as indicated by the frequency dependence in the peak temperatures in the ac susceptibility and the field dependence of the bifurcation point in the field-cooled / zero-field cooled magnetization data.

CONCLUSIONS

The metalloporphyrin family presents a wide variety of magnetic phenomena, ranging from the lattice- and spin-dimensionality crossovers to the various types of glassy behavior and multiple types of transitions. Systematic study of these systems is expected to lead to insight into the control of magnetism in molecule-based magnets.

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