Canted Ferromagnetism and Other Magnetic Phenomena in Square-Planar, Neutral Manganese(II) and Iron(II) Octaethyltetraazaporphyrins

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Abstract: Iron(II) octaethyltetraazaporphyrin has been discovered to exist as two polymorphs at room temperature, α- and β-Fe(OETAP). This has been established by X-ray powder diffraction and scanning electron microscopy. Both ac and dc SQUID magnetometry show that the α phase is a soft molecular ferromagnet with $T_{\mathrm{Curie}} = 2.8$ K. The β phase possesses the same number of unpaired spins and a similar g value, but it does not order above ~1 K. Zero-field splitting is likely competing with ferromagnetic coupling in this compound. ^{57}Fe Mössbauer spectroscopy has been used to support the local structural similarity between the two phases and to study the ferromagnetic transition. The isomorphous manganese analogue of α-Fe(OETAP), α-Mn(OETAP), expected to be a ferromagnet with a higher T_{Curie}, exhibits many characteristics of ferromagnetism, notably hysteresis at 1.8 K with $H_{\mathrm{coer}} = 2.5$ kG and $M_{\mathrm{rem}} = 4$ kemu-G/mol. However, in contrast to ferromagnetic α-Fe(OETAP), α-Mn(OETAP) shows strongly frequency-dependent ac susceptibility in the range from 1 to 1000 Hz, indicating that it exists in a spin-glass-like state. This result underscores the need for frequency-dependent ac magnetometry to fully characterize ferromagnetic molecular materials.

Introduction

The first molecular ferromagnetic compound was reported by Wickman et al. in 1967.[1] This five-coordinate, square-pyramidal complex, chlorobis(diethyldithiocarbamato)iron(III), orders ferromagnetically at 2.46 K and is rather unusual because it represents a true molecular solid. By definition, a true molecular solid consists of neutral species bonded intermolecularly only by van der Waals interactions and/or hydrogen bonds.[2] Other examples of true molecular ferromagnets that have been described include the purely organic ferromagnets such as β-(*p*-nitrophenyl)nitronylnitroxide, which has a Curie temperature of 0.6 K,[3] and Rassat's dinitroxide,[4] which has the highest reported ordering temperature for a purely organic compound with $T_{\mathrm{Curie}} = 1.48$ K. In contrast, most of the recently reported ferromagnetic molecular solids are more accurately described as "molecule-based". Examples include the metallocene charge-transfer salts which consist of organic and organometallic anions and cations bound by Coulomb interactions[5] and Prussian Blue analog magnets which are three-dimensional coordination polymers bridged by cyanide anions.[6]

One of the highest Curie temperatures observed among all molecular solids occurs in β-phase manganese(II) phthalocyanine, β-MnPc. The phthalocyanine ligand (Figure 1a) is a planar, tetrapyrrolic dianion which creates a rigid four-coordinate environment. From X-ray crystallography, it is known that, in the β phase, the molecules stack in a herringbone arrangement in which there is a weak axial interaction between the central metal and *meso*-nitrogen atoms in the molecules above and below (Figure 2a).[7] β-MnPc exists in an intermediate spin state possessing three unpaired electrons and obeys the Curie−Weiss Law above 100 K with $\theta = 18.4$ K and $g = 2.2$. Upon cooling below 8.6 K, this compound undergoes a phase transition to a canted ferromagnetic state as has been shown by low-field dc susceptibility measurements.[8] The magnetic moment associated with each molecule is essentially perpendicular to the macrocyclic plane, hence canted with respect to the stacking axis in this crystal structure. As a result, partial cancellation of the

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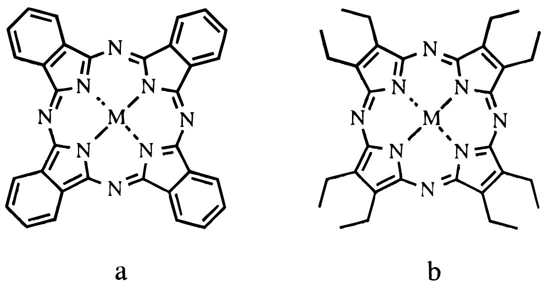

Figure 1. Tetrapyrrolic macrocycles: (a) phthalocyanine and (b) octaethyltetraazaporphyrin.

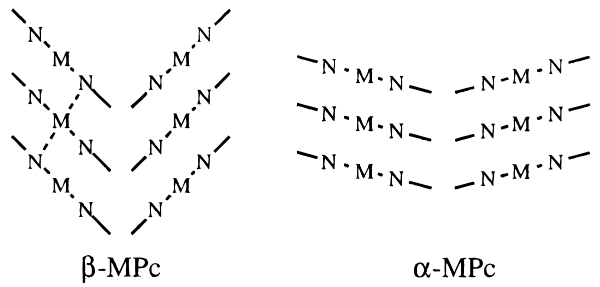

Figure 2. Schematic of the herringbone structure of β-MPc and the proposed structure of α-MPc. (from ref 26).

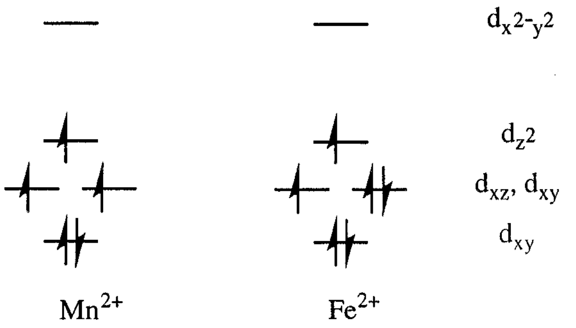

Figure 3. Possible ground-state electron configurations which give rise to intermediate spin states for Mn^{2+} and Fe^{2+}.

moments occurs, giving rise to lower than expected saturation magnetization in the ordered state.

We recently reported only the second example of ferromagnetism in a tetrapyrrolic complex. Iron(II) octaethyltetraazaporphyrin, α-Fe(OETAP) (Figure 1b), undergoes a phase transition at $T_{\mathrm{Curie}} = 5.6$ K to a canted ferromagnetic state as determined by low-field dc magnetometry.[9] The χT product at room temperature is most consistent with intermediate spin $S = 1$, with a significant orbital contribution such that $g = 2.7$ (Figure 4). This result is surprising because all other square-planar, intermediate spin iron(II) porphyrins[10,28b] and phthalocyanines[11] also possess two unpaired electrons and unusually large g values, but their $S = 1$ spin states are zero-field split to yield nonmagnetic ground states ($m_s = 0$) which do not display evidence of cooperative phenomena.

In this contribution, we report on our efforts to more fully understand the structural and magnetic properties of α-Fe(OETAP) utilizing ac and dc SQUID magnetometry, Mössbauer spectroscopy, scanning electron microscopy, and X-ray powder diffraction. In the course of these studies, we have discovered a second polymorph, β-Fe(OETAP), which is paramagnetic with the same number of unpaired electrons and a similar g value, but which does not order above ~1 K.

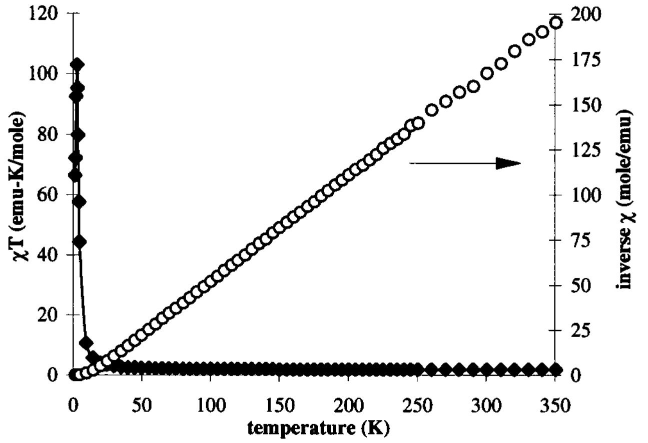

Figure 4. χT vs T and χ^{-1} vs T for α-Fe(OETAP) measured in a 100-G applied field.

We have also synthesized and characterized the isomorphous $S = {}^3/_2$ manganese(II) octaethyltetraazaporphyrin complex, α-Mn(OETAP), expecting to discover a new canted ferromagnet with a higher Curie temperature than its iron analogue. This expectation was based on a rudimentary mean field model which predicts that the Curie temperature will scale roughly with the square of the moment of the spin-containing building block in isomorphous solids.[12] Although dc magnetometry on α-Mn(OETAP) seems to support this view, ac magnetometry indicates that it possesses spin-glass-like properties and is not a true ferromagnet.

Experimental Section

General Considerations. Preparations of air-sensitive compounds were carried out in a nitrogen-filled Braun glovebox maintained at less than 5 ppm of O_2. All solvents were degassed with glovebox N_2 prior to use. All reagents were purchased from Aldrich. Reagents were used as purchased unless noted below. Toluene, tetrahydrofuran, and benzene were distilled under N_2 from sodium benzophenone ketyl. Dimethylformamide was distilled from CaH_2. Benzene-d_6 was vacuum transferred from Na/K benzophenone ketyl. Column chromatography was performed using 150-mesh acidic or neutral alumina which was dried at 100 °C and 10^{-5} Torr overnight and stored in the glovebox. Visible spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker AM 400-MHz spectrometer. Chemical shifts are reported relative to benzene ($\delta = 7.15$ ppm). ^{57}Fe Mössbauer spectroscopy measurements were made with a conventional constant acceleration spectrometer in zero applied field. The samples consisted of 50 mg of material packed into cylindrical 12 mm diameter nylon holders, sealed in 5-min epoxy. Elemental analyses were performed by NuMega Resonance Labs (San Diego, CA). Free-base octaethyltetraazaporphyrin H_2(OETAP) was prepared as described.[13] X-ray powder diffraction measurements were performed on a Scintag diffractometer using Cu Kα radiation. Samples were loaded into shallow wells machined into polycarbonate holders. The samples were covered with adhesive tape to retard reaction with O_2 during the measurement. The broad background in the plots is due to the holder or the tape.

Magnetic Measurements. All of the magnetic measurements were performed on a 5- or 7-T Quantum Design MPMS SQUID magnetometer. Measurements of magnetization as a function of temperature were performed from 1.8 to 350 K and in 100-G (α phase) or 1000-G

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(β phase) fields. To handle air-sensitive compounds, a sample holder was constructed from segments of a 5 mm diameter Wilmad 507 NMR tube.[14] The sample (~25 mg) was placed into the tube in the glovebox and packed tightly with a small piece of glass wool (~10 mg). The tube was attached to a Teflon stopcock by means of an Ultratorr vacuum connector, evacuated by mechanical pump, brought out of the glovebox, and flame-sealed under high vacuum. The diamagnetic correction for each complex was estimated from the measured diamagnetic susceptibility of Ni(OETAP) corrected for the diamagnetic contribution of the metal core electrons using Pascal's constants. The diamagnetic susceptibility of the glass wool was calculated from its measured average gram susceptibility as determined from several independent samples. The diamagnetic susceptibility of the sample holder was taken to be the average value of measurements on several sample holders. The amplitude of the oscillating magnetic field used for ac susceptometry measurements was 5 G. A phase correction was applied to the ac data if χ'' was observed to become negative when plotted vs temperature.[15]

Chloromanganese(III) Octaethyltetraazaporphyrin, Mn(OETAP)Cl. H_2(OETAP) (400 mg, 0.744 mmol) was dissolved in 50 mL of DMF heated at reflux. After complete dissolution of the macrocycle, the solution was allowed to cool and 200 mg (1.58 mmol) of anhydrous $MnCl_2$ was added. The solution was brought back to reflux for an additional 18 h. The blue-green solution was then removed from the glovebox and poured into 300 mL of ice water saturated with NaCl. The green precipitate was filtered on a Celite pad, washed with water, and placed in the vacuum oven overnight and heated at 70 °C. The pad was then eluted with 10:1 chloroform:ethanol, resulting in a deep green solution. The solvent was evaporated and the residue chromatographed on neutral alumina with gradient from pure CH_2Cl_2 to 10:1 CH_2Cl_2:EtOH. The initial purple fraction was unmetalated H_2(OETAP). All green fractions were collected and washed sequentially with 10% HCl, distilled water, and saturated NaCl and finally dried with $MgSO_4$. The solution was then reduced on a rotary evaporator until crystals appeared. The crystals were collected by filtration and washed with hexanes (yield: 200 mg, 43%). Anal. Calcd for $C_{32}H_{40}N_8MnCl\cdot{}^1/_2C_6H_6$: C, 63.10; H, 6.51; N, 16.82. Found: C, 62.97; H, 6.47; N, 16.73. UV−vis (CH_2Cl_2): λ_{max} (nm) = 352 (sh), 366, 425 (sh), 565 (sh), 622.

α-Manganese(II) Octaethyltetraazaporphyrin, Mn(OETAP). Mn(OETAP)Cl (100 mg, 0.16 mmol) was dissolved in 50 mL of 1:1 THF:toluene. Zinc dust (100 mg, 1.5 mmol) was added to the green solution which was allowed to stir at room temperature. Within 2 h, no Mn(OETAP)Cl remained as demonstrated by UV−visible spectroscopy. The deep red solution was then chromatographed on neutral alumina using the same solvent mixture. All red fractions were collected and reduced in volume until microcrystalline purple needles of Mn(OETAP) formed. The needles were collected by vacuum filtration on a medium frit, washed with hexanes, and dried under vacuum. These air-sensitive crystals were denoted the α phase of Mn(OETAP) (15 mg, 16%). Anal. Calcd for $C_{32}H_{40}N_8Mn$: C, 64.96; H, 6.81; N, 18.94. Found: C, 65.19; H, 6.91; N, 18.20. UV−vis (C_6H_6): λ_{max} (nm) = 344, 388, 434, 468, 556, 588 (sh). α-Mn(OETAP) may also be prepared from β phase by vacuum sublimation. Anal. Found: C, 65.66; H, 6.87; N, 17.52.

***β*-Manganese(II) Octaethyltetraazaporphyrin, Mn(OETAP).** α-Mn(OETAP) (100 mg, 0.16 mmol) was placed in a 100-mL round-bottom flask and dissolved in a minimum of hot toluene. The flask was then set aside to cool slowly. The crystals were collected on a medium frit, washed with hexanes, and dried under vacuum. This phase, termed the β phase, appears as irregularly faceted rods and is also air-sensitive. It has solution UV−visible and ^{1}H NMR spectra identical to those of the α phase of Mn(OETAP). Yield = 90 mg (90%). Anal. Calcd for $C_{32}H_{40}N_8Mn$: C, 64.96; H, 6.81; N, 18.94 Found: C, 62.64; H, 6.41; N, 16.89. β-Mn(OETAP) may also be prepared by taking the solution after chromatography to dryness and recrystallizing the solid from toluene.

α-Iron(II) Octaethyltetraazaporphyrin, *β*-Fe(OETAP). This procedure is a slight modification of one described previously.[16] H_2(OETAP) (100 mg, 0.180 mmol) was dissolved in 50 mL of freshly degassed 1:1 THF:toluene with 20 drops of 2,6-lutidine. The solution was heated to reflux to dissolve the macrocycle and then cooled. FeI_2 (100 mg, 1.80 mmol) was added and the mixture returned to reflux for an additional 2−4 days, monitoring the progress of the reaction by UV−vis spectroscopy. Upon completion, the reaction was cooled and chromatographed on neutral alumina with 1:1 THF:toluene. The deep blue solution was reduced in volume until blue-black needles form. The crystals were collected on a medium frit, washed with cool toluene, then hexanes, and dried under vacuum. These air-sensitive needles are denoted the α phase of Fe(OETAP). Yield = 100 mg (98%). Anal. Calcd for $C_{32}H_{40}N_8Fe$: C, 64.86; H, 6.80; N, 18.91. Found: C, 64.65, H, 6.74; N, 18.68.

***β*-Iron(II) Octaethyltetraazaporphyrin, *β*-Fe(OETAP).** This phase was prepared as for α-Fe(OETAP) with the following exception: The deep blue solution is chromatographed on acidic alumina instead of neutral alumina with 1:1 THF:toluene. Upon reduction of the solvent mixture, irregularly faceted, air-sensitive rods crystallize out of solution. These were collected on a medium frit, washed with hexanes, and dried under vacuum. β-Fe(OETAP) has solution UV−visible and ^{1}H NMR spectra identical to those of the α phase. Yield = 100 mg (98%). Subsequent chromatography of the β phase on neutral alumina gives α-Fe(OETAP), but this transformation is irreversible. Anal. Calcd for $C_{32}H_{40}N_8Fe$: C, 64.86; H, 6.80; N, 18.91. Found: C, 65.58, H, 6.58; N, 17.53.

Results and Discussion

The magnetic properties of tetrapyrrolic metal complexes (Figure 1) have been widely studied, beginning with measurements on metallophthalocyanines made by Klemm and Klemm in 1935.[17] Among neutral insulating complexes, the square-planar geometry is perhaps the most magnetically interesting. In this case, the metal $d_{x^2-y^2}$ orbital, which by convention points at the four pyrrolic nitrogens, is predicted to be quite high in energy. Distribution of the metal d electrons into the remaining four orbitals (which are predicted to be energetically similar) results in intermediate spin ground states for d^5 (Mn(II), $S = {}^3/_2$) and d^6 (Fe(II), $S = 1$) electron configurations (Figure 3). The exact relative ordering of the one-electron orbitals is unclear, and one single configuration is generally found to be insufficient to fully describe the ground electronic state. A further consequence of this geometry is incomplete quenching of orbital contributions to the magnetic moment for these metals (and d^7 cobalt(II),[18] as well) in the ground state or low-lying excited states.[19] This gives rise to g values which are typically greater than the free-electron value.

For several reasons, tetrapyrrolic macrocycles would seem to be ideal ligands for synthesizing magnetic molecular solids displaying cooperative phenomena. They feature a highly symmetric D_{4h} coordination environment and a large planar π electron system. The former gives rise to d-orbital degeneracy or near-degeneracy and the possibility of high spin multiplicity. The latter encourages stacking and provides a pathway by which complexes may communicate magnetic information intermolecularly via spin polarization exchange.[20] Additionally, in β-MnPc, the *meso*-nitrogen atoms are thought to provide a superexchange pathway within the stacks for coupling of spin.[8a]

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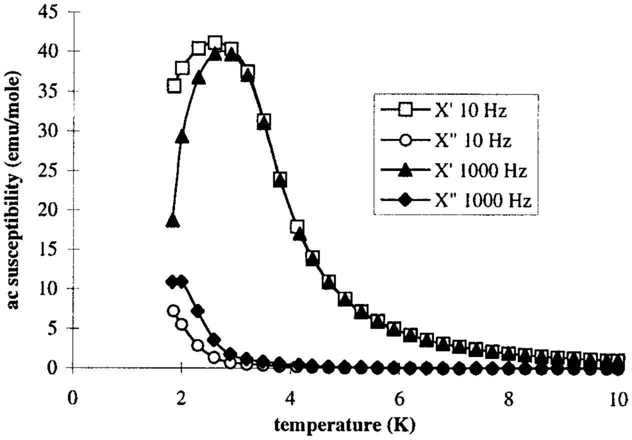

Figure 5. ac Susceptibility for α-Fe(OETAP) at 10 and 1000 Hz.

It is disappointing that of the many square planar paramagnetic complexes known, only a few examples display significant cooperative effects[21] and, until recently, only *β*-MnPc was observed to order ($T_{\text{Curie}} = 8.6$ K) with a nonzero magnetic moment indicating ferromagnetism. We have measured the ac susceptibility of this compound and have confirmed the transition to a ferromagnetic state with $T_{\text{Curie}} = 6.5$ K by this method. The difference between the Curie temperatures using ac and dc techniques is not unusual and has been ascribed to smearing out of the ferromagnetic transition in a finite dc field.[22]

Iron Octaethyltetraazaporphyrin, Fe(OETAP). We recently communicated a second example of ferromagnetism in a tetrapyrrolic complex.[9] Iron octaethyltetraazaporphyrin α-Fe(OETAP) orders as a canted soft ferromagnet below 5.6 K as determined by dc susceptibility measurements. We now report additional dc measurements and frequency-dependent ac susceptibility measurements which confirm the ferromagnetic phase transition.

The dramatic increase in the χT product from approximately 1.8 emu-K/mol to over 100 emu-K/mol (Figure 4) and the linear χ^{-1} vs T plot indicate the presence of ferromagnetic coupling in α-Fe(OETAP). These data may be fitted to a Curie–Weiss Law, giving $g = 2.7$ and $\theta = 8$ K. The peak in the in-phase component (χ' or χ_{real}) of the ac susceptibility at 2.8 K (Figure 5) indicates a magnetic phase transition to an ordered state.[23] The nonzero out-of-phase component (χ'' or $\chi_{\text{imaginary}}$) and, importantly, its near frequency-independence supports that the transition is ferromagnetic in nature. At the present time, we cannot explain the very weak frequency dependence affecting mostly the magnitude of the peak and not its position. The ac susceptibility of ferromagnetic *β*-MnPc shows a similar, very weak dependence on the frequency of the applied field.[24] It is possible that α-Fe(OETAP) is a spin-glass as well, although the differences between it and α-Mn(OETAP) are quite dramatic (*vide infra*).

The M vs H plot at the lowest temperature attainable on the SQUID, 1.8 K, and at 5.0 K (Figure 6) show that the transition is to a soft ferromagnetic state. Canting of the moments is inferred from the low value of the saturation magnetization below T_{Curie} (8000 emu-G/mol (experimental) vs ~15 000 (theoretical based on $g = 2.7$)). Given the evidence for canting in α-Fe(OETAP) and its similar molecular structure, it seems reasonable to assume that the stacking and mechanism for intrastack magnetic coupling (superexchange mediated by the meso nitrogen atoms) are similar to that in *β*-MnPc.[8a]

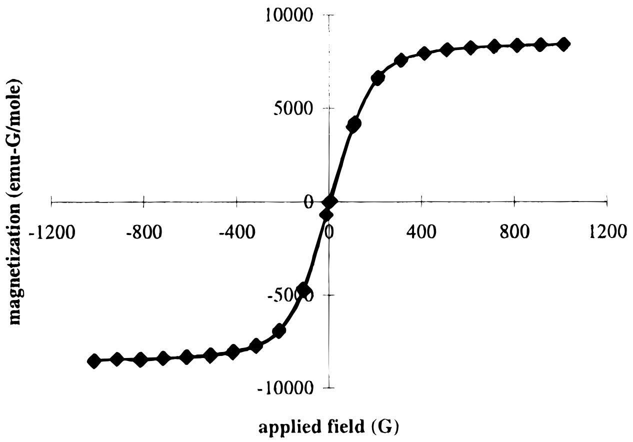

Figure 6. M vs H data at 1.8 K for α-Fe(OETAP) showing it to be a soft ferromagnet.

All efforts to prepare crystals of α-Fe(OETAP) large enough for single-crystal X-ray structural determination were unsuccessful. As may be seen from a scanning electron micrograph (Figure 7a), the ferromagnetic phase consists of bundles of nearly noncrystalline fibers. Individual fibers may be longer than 1 mm. Powder diffraction also indicates the essential noncrystallinity by the presence of peaks only at low angles (Figure 8a). Macroscopically, this phase resembles shiny cotton candy and is isomorphous with air-stable Ni(OETAP) and Cu(OETAP) as indicated by X-ray powder diffraction.

Interestingly, in our efforts to grow larger crystals of α-Fe(OETAP), we have discovered a second, more crystalline polymorph of this compound, *β*-Fe(OETAP) (Figures 7b and 8b) which has a similar room temperature χT value (1.9 emu-K/mol) but which does not order (Figure 9) and likely has its triplet ground-state zero-field split (ZFS) with a positive D, the zero-field splitting parameter. This is inferred from (a) the downturn in the χT product, (b) the Mössbauer spectrum of this phase at low temperature (discussed below), and (c) expectations based on other square planar Fe(II) complexes which possess zero-field split ground states.[10,28d]

The *β* phase was obtained by chromatography of crude Fe(OETAP) on acidic alumina (instead of the usual neutral alumina) in the glovebox, eluting with toluene/THF. Crystallization from hot toluene gives rise to irregularly faceted rods. Chromatography of the nonordering phase on neutral alumina restores the ferromagnetic phase transition but not vice-versa. This would seem to suggest that a trace contaminant not removed by chromatography on acidic alumina catalyzes the crystallization of a different structure. So far, we have been unable to identify the impurity. Elemental analysis of this phase is never entirely satisfactory, also supporting this view.

It is important to note that polymorphism is not unexpected in this family of tetraazaporphyrin molecules. Manganese(II),

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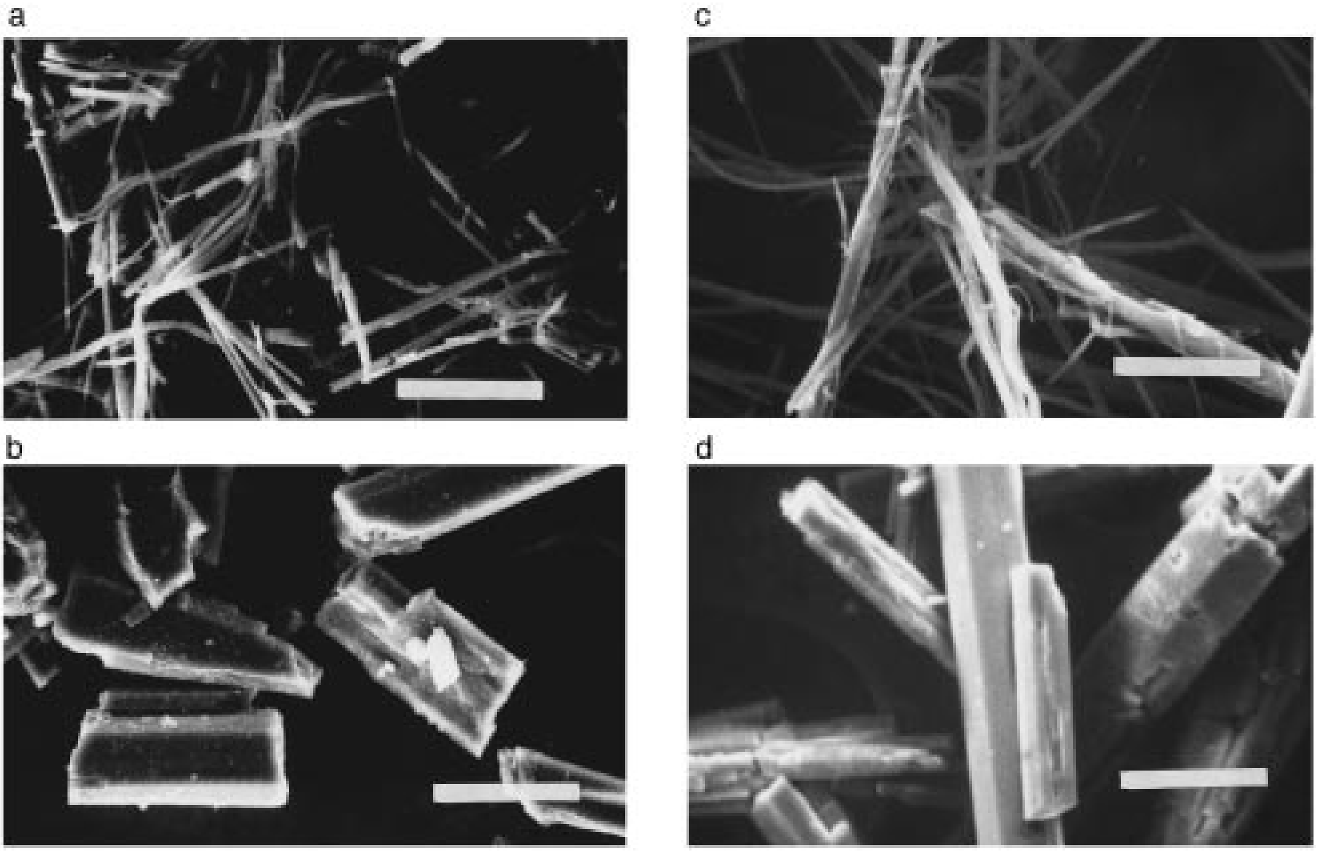

Figure 7. Scanning electron micrographs of (a) α- and (b) β-Fe(OETAP) and (c) α- and (d) β-Mn(OETAP) (white bar = 100 μm).

iron(II), and cobalt (II) phthalocyanine similarly exist in at least two polymorphs (α and β) at room temperature (Figure 2).[25] Whereas the structure of the β polymorph has been solved by single-crystal X-ray diffraction,[7b] Ercolani et al. have modeled the powder diffraction data on α-FePc by holding the interplanar spacing constant while changing the angle of the macrocyclic plane with respect to the stacking axis to decrease the interactions with the axial nitrogen atoms on the adjacent molecules and increase the metal–metal interactions (Figure 2b).[26]

There is also precedence for different magnetic properties observed for polymorphs. The room-temperature magnetic moment for α-CoPc has been reported to be 15% lower than for β-CoPc.[27] Differences in the g values as determined from ESR are also observed. For α, $g_{\|} = 2.007$ and $g_{\perp} = 2.422$, whereas for β, $g_{\|} = 1.91$ $g_x = 2.92$, and $g_y = 2.89$. These differences are ascribed to changes in the admixture of excited-state wave functions in the ground state, an explanation which may pertain to the Fe(OETAP) system (*vide infra*).

Spectroscopic and magnetic measurements on α- and β-Fe(OETAP) have been used to support the assertion of polymorphism. The UV–visible spectra (in toluene) and ^{1}H NMR spectra (in benzene-d_6) derived from α and β phases are identical. The room-temperature g value for β-Fe(OETAP) is not significantly different from that of α-Fe(OETAP) (2.8 vs 2.7, respectively). If the solvent of crystallization or another impurity is incorporated into the β phase, it is not coordinated to the metal; coordination of the central metal by a donor ligand should result in either a high-spin $S = 2$ (weak field ligand) or low-spin $S = 0$ (strong field ligand) complex.[19]

However, the strongest evidence of polymorphism comes from the ^{57}Fe Mössbauer spectroscopy on the α and β phases. The isomer shifts relative to natural iron and quadrupolar splittings (ΔE_Q) for the two polymorphs are provided in Table 1, and sample spectra are shown at 77 K in Figures 10 and 11. It is seen that these spectra are very similar to each other. The isomer shifts and large, essentially temperature-independent, quadrupolar splittings are fairly typical of square-planar intermediate-spin, $S = 1$, Fe(II) complexes.[28]

A closer examination of the data at 77 K shows subtle but important differences that clearly distinguish the α and β polymorphs. First, ΔE_Q for the β phase is greater than that of the α by ≥ 0.2 mm/s at all temperatures investigated. Second, and more obviously, there is spectral asymmetry that has the opposite sense for the two isomers at all temperatures, i.e., $I_-/I_+ < 1$ for α and > 1 for β. We ascribe the origins of this asymmetry to sample texture. No attempts were made to randomize the (neat) samples by grinding them to a finely divided polycrystalline state. Such treatment would have enhanced their already great oxidative instability. The obvious difference in textures from powder diffraction (nearly noncrystalline fibers vs faceted rods) is apparently reflected in the Mössbauer spectra.

As expected for a ferromagnet, we observe a large hyperfine splitting of the Mössbauer spectrum as α-Fe (OETAP) is cooled to below T_{Curie} (2.8 K) in zero applied field. The spectrum becomes that of a classical six-line iron ferromagnet with a surprisingly large internal hyperfine field estimated to be ~62.4 T. In contrast, we observe no change in the Mössbauer spectrum of the β phase over the same temperature range. This indicates that the β phase is a rapidly relaxing paramagnet and is consistent with a ground state that is zero-field split with a positive value of D.[29] A manuscript elaborating on these findings is in preparation.

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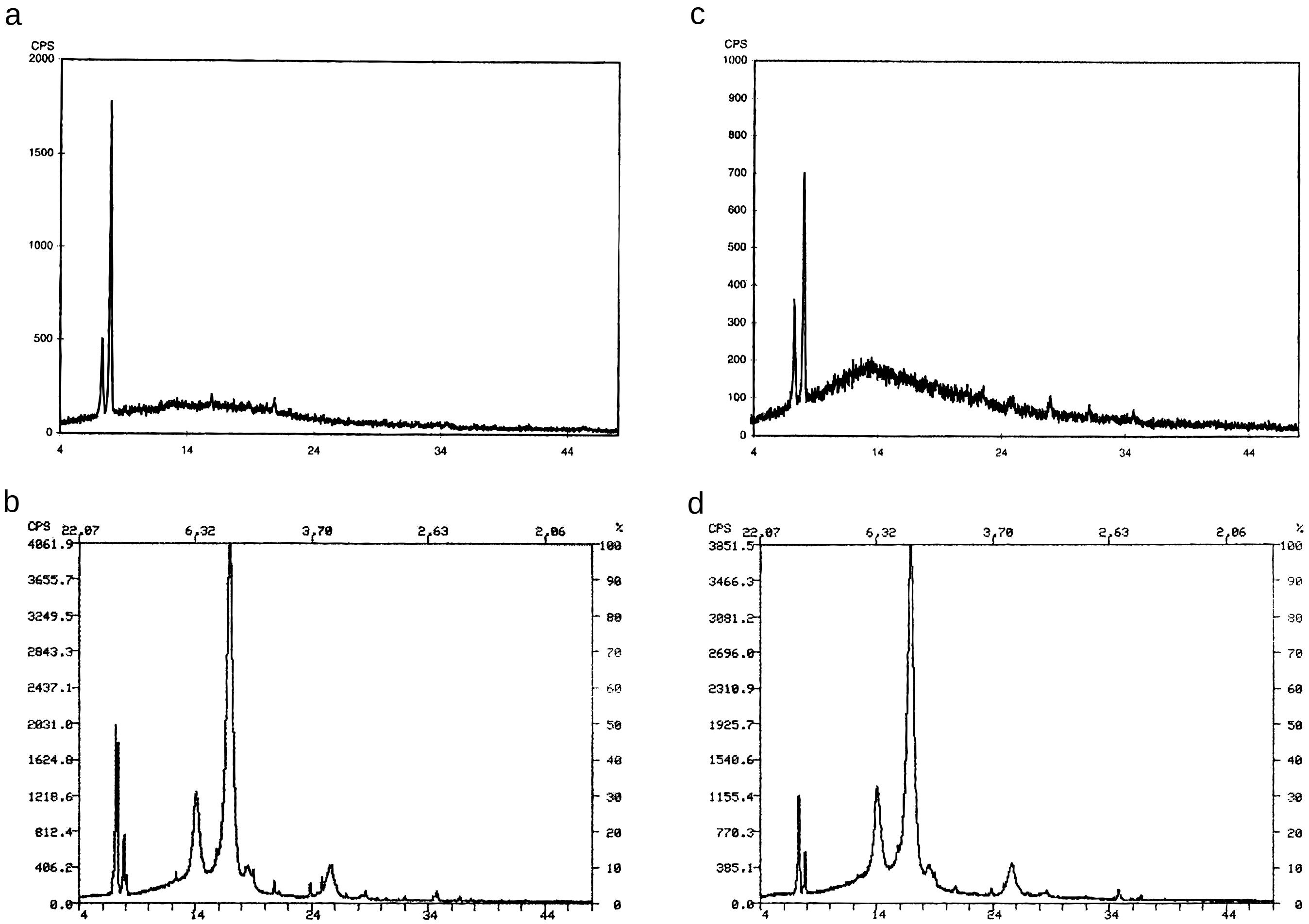

Figure 8. X-ray powder diffraction patterns for (a) α- and (b) *β*-Fe(OETAP), and (c) α- and (d) *β*-Mn(OETAP). The *x* axis represents 2*θ*.

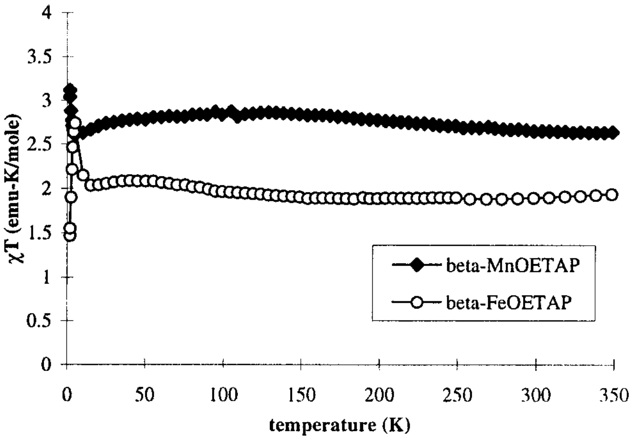

Figure 9. χT vs *T* plots for *β*-Fe(OETAP) and *β*-Mn(OETAP) measured in a 1000-G applied field.

Table 1. Mössbauer Spectroscopy Data for α- and *β*-Fe(OETAP)

	isomer shift (mm/s)[a]	quadrupolar splitting (mm/s)
α-Fe(OETAP) (293 K)	0.29	2.86
α-Fe(OETAP) (77 K)	0.37	3.05
α-Fe(OETAP) (4.6 K)	0.38	3.12
β-Fe(OETAP) (293 K)	0.29	3.06
β-Fe(OETAP) (77 K)	0.38	3.25
β-Fe(OETAP) (4.6 K)	0.37	3.28

[a] Relative to natural iron.

Interpretation. A possible explanation for the observed results for the two polymorphs may be proposed which presumes the existence of differences in crystal packing analogous to those found in metallophthalocyanines. It has previously been shown from spectroscopic measurements and calculations on various square-planar Fe(II) complexes that three states, $^3A_{2g}$, $^3B_{2g}$, and ^3E_g, may all lie close in energy and that the true ground state is quite sensitive to the identity of the tetradentate ligand and environment around the molecule in the solid state.[30-32] Using ab initio UHFS DV-Xα calculations, in 1990, Reynolds and Figgis deduced that, for *β*-FePc, spin−orbit coupled $^3B_{2g}$ and ^3E_g are lowest and very nearly equal in energy but that they differ greatly in their covalency and spin and charge delocalization onto Pc.[30] These authors have predicted that slight modification of the state of axial ligation (e.g., to the nitrogen atom of the adjacent macrocycle) or deviation from ideal D_{4h} symmetry would cause drastic changes in spin density on the macrocycle.

Perhaps the profound contrast in the magnetic properties observed in α-Fe(OETAP) and *β*-Fe(OETAP) are the result of just such a modification. A change in structure could affect the ferromagnetic properties in two ways: without changing the spin density on a particular molecule, it could alter the overlap of the spin density on adjacent molecules or the structural perturbation could give rise to a change in spin density on each molecule via a change in ground state, which, in turn happens to result in decreased intermolecular coupling.

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(30) Coppens, P.; Li, L. *J. Chem. Phys.* **1984**, *81*, 1983−1993 and references therein.

(31) Reynolds, P. A.; Figgis, B. N. *Inorg. Chem.* **1991**, *30*, 2294−2300.

(32) Clack, D. W.; Monshi, M. *Inorg. Chim. Acta* **1977**, *22*, 261−264 and references therein.

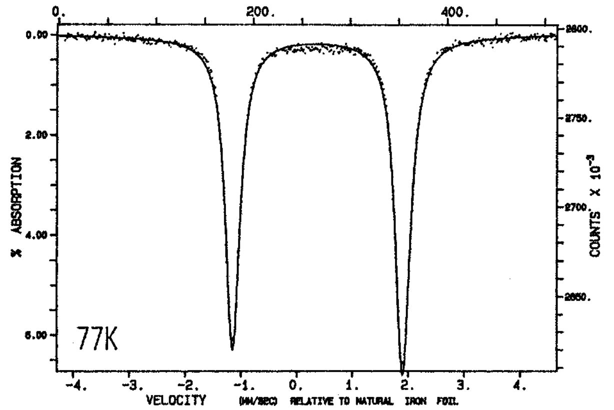

Figure 10. Mössbauer spectrum of α-Fe(OETAP) at 77 K.

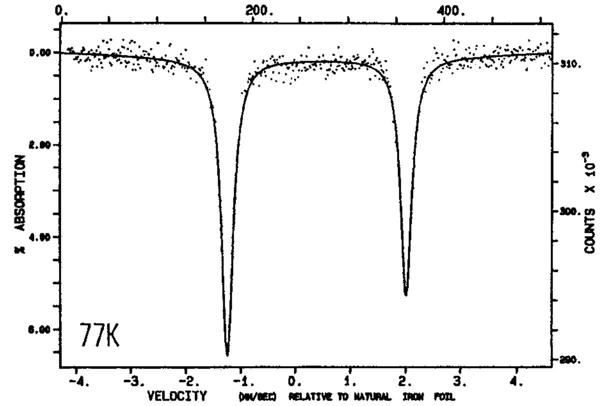

Figure 11. Mössbauer spectrum of β-Fe(OETAP) at 77 K.

Furthermore, it is reasonable to presume that these square-planar complexes would be zero-field split in the absence of other interactions. We propose a model for the observed magnetic properties in Fe(OETAP) which involves a competition between zero-field splitting (D) and an interaction favoring ferromagnetic alignment of the unpaired spins (J). In the α phase, this coupling presumably overwhelms the intrinsic tendency for square planar iron(II) to be zero-field split to give a ferromagnetic ground state, whereas in the β phase, zero-field splitting with a positive value of D dominates, to give a nonmagnetic ground state.

Moriya has previously developed a model for NiF_2 based on this idea and established a theoretical relationship between D and J which predicts that D must be less than $2zJ$ for ordering to occur. Here, z is the number of nearest neighbors.[37] In the Moriya model, the transition is to an antiferromagnetically ordered state; however, the methods used (mean field and crystal field theory) are sufficiently general that a similar relationship probably exists for ferromagnets.

It is difficult to experimentally establish the value of D from the β phase because it is usually slightly contaminated by the α phase, which strongly affects the low-temperature data. However, in one particularly clean sample of β, we determined $D \sim 11$ K, a value comparable to that we observed for iron(II) octaethylporphyrin ($D \sim 22$ K). Thus, even if we take $z = 2$, J needs only be a few Kelvins to satisfy the Moriya criterion, a physically realistic possibility.

There is precedence for a competition between D and J in an ionic solid in which D dominates. Zero-field splitting in $Ni(NO_3)_2{\cdot}6H_2O$ is so large that it prevents the onset of long-range antiferromagnetic order.[33] In this case, the contributions from ZFS and the intermolecular magnetic exchange interaction were determined separately by studying both the magnetic susceptibility and the heat capacity.

Manganese Octaethyltetraazaporphyrin. Our results with α-Fe(OETAP) and the observed canted ferromagnetism in β-manganese(II) phthalocyanine prompted us to investigate the analogous spin-$^3/_2$ complex, manganese(II) octaethyltetraazaporphyrin. On the basis of a simple mean field theory picture, the greater spin at manganese was expected to yield a new ferromagnet with a higher T_{Curie}.[12] An example of a related manganese(II) tetraazaporphyrin complex was recently reported, manganese(II) (octaethylsulfanyl)-5,10,15,20-tetraazaporphyrinate. This compound is found to be high-spin ($S = {}^5/_2$) and weakly antiferromagnetically coupled.[38]

Manganese(II) octaethyltetraazaporphyrin, Mn(OETAP), may be synthesized from free-base octaethyltetraazaporphyrin by metalation with anhydrous $MnCl_2$ in toluene/THF mixtures in the glovebox. The product of this reaction is then brought out of the glovebox and air-oxidized to Mn(OETAP)Cl in the presence of aqueous sodium chloride. Mn(OETAP)Cl is chromatographed on alumina and returned to the glovebox. Reduction with zinc and subsequent chromatography gives Mn(OETAP). This compound also exists as two polymorphs which are isomorphous with their respective iron analogues and are labeled α phase and β phase (Figures 7c,d and 8c,d). The α phase may be obtained in low yield by crystallization from the toluene/THF mother liquor. The β phase may be obtained by reducing the volume of the mother liquor to dryness and recrystallizing the solid from toluene. The α phase may also be obtained from vacuum sublimation of the β phase as evidenced by its chemical analysis, physical appearance, and similar magnetic properties. Like β-Fe(OETAP), β-Mn(OETAP) is paramagnetic with the similar room-temperature properties to α-Mn(OETAP), but the cooperative interactions are quenched (Figure 9). The room-temperature χT product (2.6 emu-K/mol) suggests three unpaired spins with $g = 2.3$ (Figure 9).

The temperature dependence of the χT product and χ^{-1} for the ferromagnetically coupled phase, α-Mn(OETAP), is shown in Figure 12. Again, a dramatic rise in χT (up to a maximum of 55 emu-K/mol) is evident. The room-temperature value corresponds to intermediate-spin $S = {}^3/_2$ with a g value of 2.2. However, the plot of χ^{-1} vs T is not linear over any meaningful temperature range and possesses an inflection point at ~200 K. The low-field data (Figure 13) appear to indicate a ferromagnetic transition with a Curie temperature of ~14 K (based on extrapolation of the field-cooled magnetization data). A hysteresis plot at 1.8 K (Figure 14) indicates substantial remanence (4 kemu-G/mol) and coercive field (2.5 kG) and evolution to a soft ferromagnetic state as the temperature is raised to 5.0 K. The low value of the saturation magnetization is again indicative of canting of the magnetic moments in the ordered phase.

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[33] (a) Herweijer, A.; Friedberg, S. A. *Phys. Rev. B*, **1971**, *4*, 4009–4013. (b) Carlin, R. L. In *Magneto- Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series, Series E, Applied Sciences, Vol. 140; D. Reidel: Dordrecht, The Netherlands, 1983; pp 127–155.

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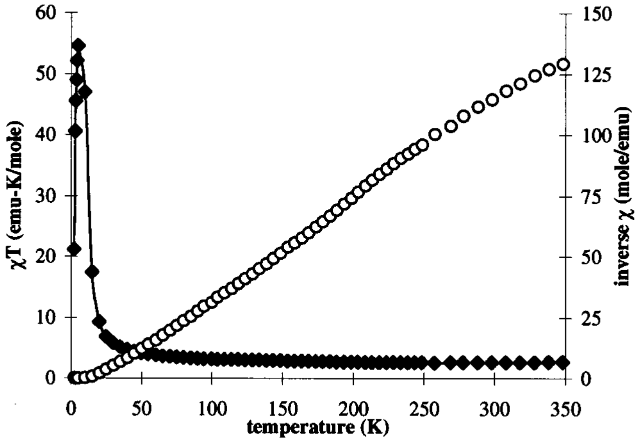

Figure 12. χT vs T and χ^{-1} vs T for α-Mn(OETAP) measured in a 100-G applied field.

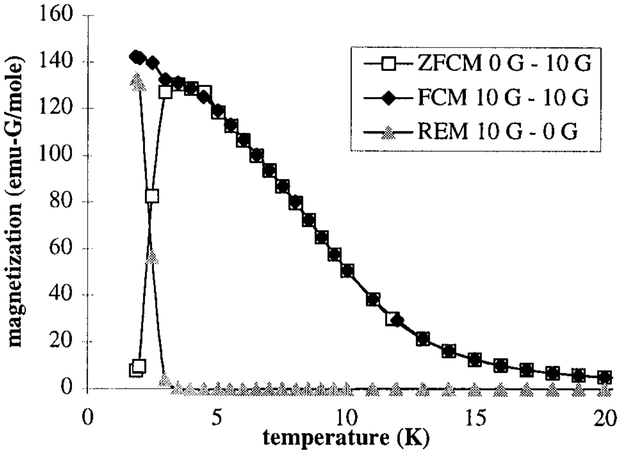

Figure 13. Low-field measurements on α-Mn(OETAP).

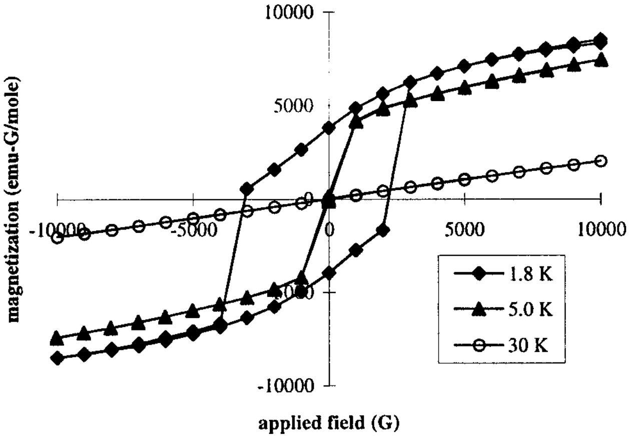

Figure 14. Hysteresis measurements at 1.8, 5.0, and 30 K for α-Mn(OETAP).

All of the above dc susceptibility data seem to indicate a transition to a canted ferromagnetic state with a higher transition temperature than, and superior hysteretic properties to, the corresponding iron compound, supporting the mean field model. However, a more careful examination of the data reveals several unusual observations. First, the remanent magnetization does not go to zero at the same temperature that the field-cooled magnetization does. Second, although not shown completely, the transition is strongly smeared out over a large temperature range. The field-cooled magnetization and zero-field-cooled magnetization only reach near zero above 30 K in 10-G applied field. Third, the hysteresis loop previously described is displaced to the left along the applied field axis. This behavior is rather unusual and has been observed previously in spin-glasses such as 0.5 atom % *Cu*Mn.[34]

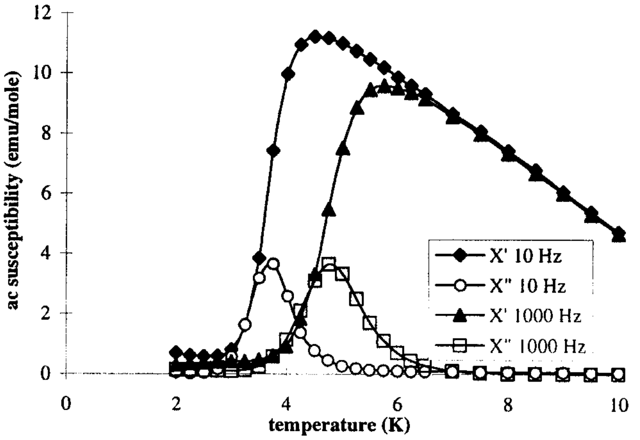

Figure 15. ac Susceptibility data for α-Mn(OETAP) at 10 and 1000 Hz.

Finally, the ac magnetic susceptibility measurements on this compound (Figure 15) reveal a situation which contrasts sharply with its iron analogue. Although the in-phase component of the susceptibility, χ', does peak (5.8 K at 1 kHz) and the out-of-phase component, χ'', becomes nonzero (6.5 K at 1 kHz), the data show a pronounced dependence on the frequency of the applied field and the transition is considerably broader and less sharply peaked than for α-Fe(OETAP). These features are not expected of a true ferromagnet and are evidence for a spin-glass-like state or some other phenomenon.

A spin-glass is a metastable state of frozen spins which does not possess true long-range order but may possess net magnetization in the absence of an applied magnetic field.[34] It is characterized by a ferromagnetic or antiferromagnetic local interactions modified by elements of randomness and disorder which prevent onset of a true phase transition. In this case, the peak in χ' is no longer referred to as the Curie temperature. Instead, one identifies it with a freezing temperature (T_f, if it is a spin-glass) or blocking temperature (T_b, if it is a superparamagnet) which are functions of the applied frequency, ω. The quantity, $\Delta T_f/T_f(0)\Delta(\log \omega)$ (where ΔT_f is the shift in the peak in χ', $\log \omega$ is the logarithm of the applied frequency, and $T_f(0)$ is the position of the peak at zero frequency), is a measure of the sensitivity of the peak in χ' to each change in frequency.[34] For α-Mn(OETAP), plotting T_f vs $\log \omega$ over the range from 1 to 1000 Hz gives a reasonable straight line in which the slope ($\Delta T_f/\Delta(\log \omega)$) is calculated to be ~0.60. $T_f(0)$ is taken to be ~3.0 K from the point at which the dc FCM and ZFCM become equal (Figure 13). These data translate to a value $\Delta T_f/T_f(0)\Delta(\log \omega) = 0.20$, which according to Mydosh indicates behavior between that of a superparamagnet and a spin-glass, a so-called "spin-glass-like" state.[34] The compounds described by Mydosh are all atomic solids, so the validity of this comparison is unclear. Nevertheless, these results underscore the importance of ac susceptometry as a technique for discerning the true magnetic state of a solid.

Interpretation. One possible explanation for the observed ac susceptibility properties of α-Mn(OETAP) is that the sample consists of an ensemble of ferromagnetically coupled particles, most or all of which are below the critical domain size for this compound, giving rise to superparamagnetic properties.[35] This is consistent with the observed morphology (fine, nearly noncrystalline fibers) which would presumably most impact the size of the domain perpendicular to the crystal axis. However, the width of the peaks in powder diffraction plots and scanning electron microscope images of α-Mn(OETAP) and α-Fe(OETAP) indicate that the former are not significantly smaller than the latter. Thus, for this explanation to be correct, α-Mn(OETAP) must possess a larger critical domain than α-Fe(OETAP). One way to test this suggestion is to prepare α-Fe(OETAP) as smaller crystals by, for instance, rapid cooling and to try to "turn on" superparamagnetism. This experiment is currently underway.

In support of the superparamagnetism model, the ac data from α-Mn(OETAP) may be fit to an Arrhenius expression (where ω and T_f are as defined before):

$$\omega = \omega_0 \exp[E_a/k_B T_f]$$

which gives $\omega_0 = 5 \times 10^{10}$ and $E_a/k_B = 100$ K. In this expression, E_a represents the barrier to realignment of the spins along one of two equivalent easy axes.[33] These are physically realistic values which support the assignment of superparamagnetism because true spin-glasses typically do not give realistic values.[34] Perhaps not surprisingly, attempts to fit the magnetization data at different temperatures and applied fields to the Langevin expression for dilute superparamagnets were unsuccessful.

A second possible explanation for the unexpected properties of α-Mn(OETAP) is that the material is not superparamagnetic but is in a spin-glass-like state due to the presence of frustration from opposing ferromagnetic and antiferromagnetic interactions. This is consistent with the lack of a linear regime in the χ^{-1} vs T plot; a superparamagnet would follow the Curie law with very large numbers of spins. The source of frustration is suggested in a theoretical paper by Epstein et al. which addresses the interstack magnetic coupling in tetracyanoethylene-bridged manganese macrocyclic coordination polymers such as MnTPP-[μ_2-TCNE], where TPP = tetraphenylporphyrin.[36] In this family of compounds, the magnetic coupling within a chain, mediated by the bridging tetracyanoethylene radical anion, is relatively strong and ferrimagnetic. A transition to a three-dimensionally ordered state, though, also requires coupling between the chains.

In the Epstein model, a competition exists between a strong, but relatively short-ranged (through-bond, decreasing exponentially) antiferromagnetic exchange interaction and a weak, but relatively long range (through-space, decreasing as r^{-3}) ferromagnetic dipolar interaction. Whichever of these two interactions between chains dominates determines the relative alignment of adjacent chains and the observed magnetic ground state of the bulk.

As applied to our compounds, perhaps the balance between these two coupling mechanisms is more nearly equal in α-Mn(OETAP) than in α-Fe(OETAP), leading to frustration in the former, a crucial element of spin-glass behavior. A source of disorder in this compound, another crucial element of a spin-glass (which is also present in the iron analogue), is the near noncrystallinity. Further work including low-temperature heat capacity measurements may allow us to understand this compound more fully.

Conclusions

The α phase of iron(II) octaethyltetraporphyrin has been confirmed to be a canted molecular ferromagnet by ac and dc magnetometry. A second polymorph, β-Fe(OETAP), has been identified and shown to possess comparable room-temperature magnetic properties. In sharp contrast to the properties of the α phase, the cooperative interactions in the β phase are almost completely quenched and no ordering is observed. A plausible explanation for these results is that a competition exists between ferromagnetic coupling of the unpaired spins and the intrinsic tendency for the spin state of square-planar Fe(II) to be zero-field split. In the α phase, ferromagnetism prevails, and in the β phase, ZFS dominates. The magnitude of D is expected to be similar in both phases because it is principally a molecular property. The strength of the ferromagnetic coupling is attenuated by the structural change from α to β.

The manganese complex isomorphous with α-Fe(OETAP) has been synthesized and characterized. Consistent with the prediction from mean field theory that it should be a ferromagnet with higher T_{Curie}, it displays significant hysteresis at 1.8 K, a temperature at which α-Fe(OETAP) is a soft ferromagnet. However, frequency-dependent ac magnetometry suggests that this compound is in a spin-glass-like state below its freezing temperature, T_f, and is not a true ferromagnet. This behavior may arise from frustration induced by competing ferro- and antiferromagnetic coupling between stacks of molecules together with the intrinsic disorder of this nearly noncrystalline phase.

These results show that tetrapyrrolic complexes may be a fertile area for finding interesting new examples of molecular ferromagnetism. The data presented here also underscore the importance of frequency-dependent ac susceptibility measurements for discerning the true magnetic state of a sample. Compounds identified as ferromagnets only on the basis of dc susceptibility measurements or ac susceptibility measurements at one frequency must be viewed with a skeptical eye.

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