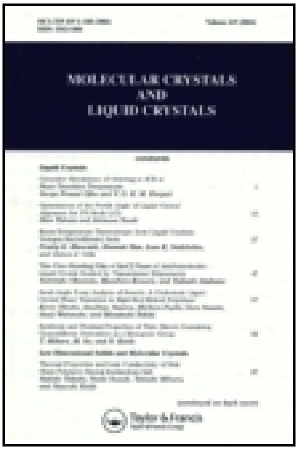

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An Internal Hyperfine Field of 62.4 T in Ferromagnetically Ordered α-Iron(II) Octaethyl-Tetraazaporphyrin

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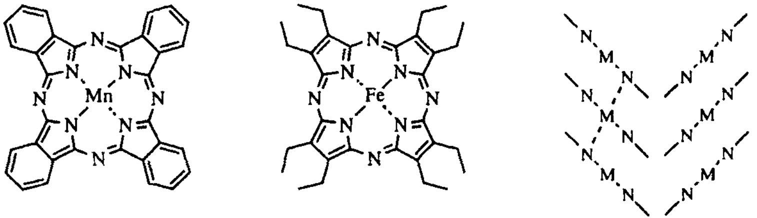
We report on the magnetic properties of the molecular solids derived from square-planar, neutral iron(II) octaethyltetraazaporphyrin, FeOETAP. This compound exists as two polymorphs, α and β. dc SQUID and ac susceptometry measurements (1–1000 Hz) show that the α polymorph orders as a soft molecular ferromagnet below $T_{Curie} = 2.8$ K, whereas the β form, with the same number of unpaired spins and a similar g value, exhibits zero-field splitting to a non-magnetic ground state. ^{57}Fe-Mössbauer spectroscopy indicates that α-FeOETAP exhibits a remarkably large internal hyperfine field, H_{int}, of 62.4 T. This, to our knowledge, is the highest value of H_{int} ever reported for Fe, regardless of its spin state.

Keywords: canted molecular ferromagnetism; Mössbauer spectroscopy

INTRODUCTION

Until recently, manganese(II) phthalocyanine, MnPc, (Figure 1) was the lone example of a neutral, square planar, tetrapyrrolic complex to show three dimensional magnetic order.[1] This compound is a true molecular solid and appears to order as a canted ferromagnet with a Curie temperature of 8.6 K. It possesses three unpaired electrons and is known from crystallography to exist in a herringbone structure in which there is a weak axial interaction between the manganese cation and *meso* nitrogen atoms from the macrocycles above and below. (Figure 1)



MnPc FeOETAP

FIGURE 1 Manganese(II) phthalocyanine, iron(II) octaethyltetraazaporphyrin and the herringbone structure of the ferromagnetic phase.

The electronic structure of this molecule is explained by noting that 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 2) 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 in the ground state or low lying excited states.[2] This gives rise to g values which are typically greater than the free-electron value and g-factor anisotropy, which has a profound effect on properties such as the internal fiel at the spin-triplet ferrous centers for the ordered state.

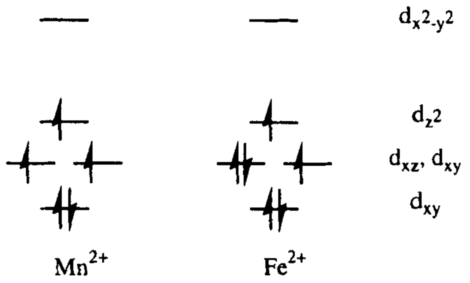


FIGURE 2 Orbital scheme for rationalizing the intermediate spin state.

IRON(II) OCTAETHYLTETRAAZAPORPHYRIN

In this report, we describe the properties of the related, and more soluble, tetrapyrrolic complex, iron(II) octaethyltetraazaporphyrin (FeOETAP, Figure 1) that is found to exist as two polymorphs at room temperature, α and β.[3] This has been established by X-ray powder diffraction and scanning electron microscopy, although their respective structures are not fully known. By dc magnetometry we have determined that α-FeOETAP is a canted, soft molecular ferromagnet with two unpaired electrons and T_{Curie} = 5.6 K.[4] The compound obeys the Curie-Weiss law over the temperature range of 1.8-350 K with $\theta = 8$ K and $g = 2.7$. No hysteresis is observed at the lowest accessible temperature, 1.8 K. (Figure 3)

The low value of the saturation magnetization indicates canting of the moments as previously observed in MnPc. Thus, by analogy to MnPc, we assume the α phase is also in the herringbone structure.

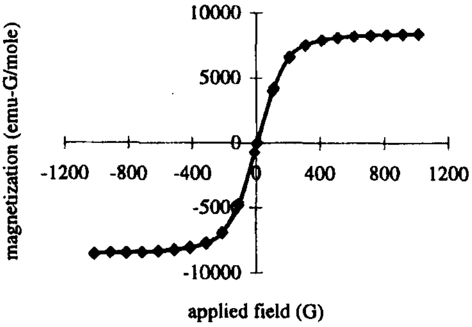


FIGURE 3 M vs. H for α-FeOETAP at 1.8 K.

The other polymorph, β-FeOETAP, possesses the same number of unpaired spins and a similar g value, but it does not magnetically order above ~1 K. (Figure 4) Zero-field splitting is apparently dominating ferromagnetic coupling in this compound. This behavior is more typical of square-planar iron(II) complexes such as iron phthalocyanine, FePc.[5]

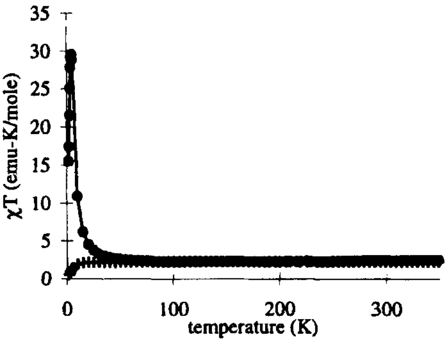


FIGURE 4 χT vs. T for α-FeOETAP (●) and β-FeOETAP (+).

It is unclear why such a profound difference exists between α-FeOETAP and FePc. Presumably, a competition exists between ferromagnetism and zero-field splitting and the latter is much smaller in α-FeOETAP. We rationalize the behavior of β-FeOETAP by postulating that it adopts a structure that precludes strong intermolecular ferromagnetic coupling. This enhances the effect of zero-field splitting.

ac SUSCEPTOMETRY

The ac susceptibility of α-Fe(OETAP) has been measured to confirm the existence of a ferromagnetic phase transition. (Figure 5) This experiment was carried out in zero dc bias field at two frequencies, 10 Hz and 1 kHz with an ac signal amplitude of 5 G.

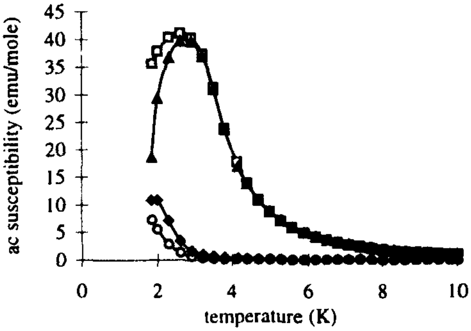


FIGURE 5 ac Susceptibility of α-Fe(OETAP) at 10 Hz χ' (□) χ" (○) and 1 kHz χ' (▲) χ" (◆).

By this technique, the Curie temperature, taken as the peak in χ', is determined to be 2.8 K. Non-zero χ" below this temperature confirms the assignment of a ferromagnetic phase transition. The frequency dependence is relatively small, though not zero.

MÖSSBAUER SPECTROSCOPY

For iron-containing ferromagnets, ^{57}Fe Mössbauer spectroscopy is available to study the phase transition and the magnetically ordered state. In this technique, the first nuclear excited state is populated by the absorption of a γ-ray. As expected for a square planar Fe(II) complexes, at 77 K, the spectra fo both α and β are that of a quadrupolar split doublet. The spectrum for the α phase is shown in Figure 6. The spectrum for β at this temperature is not shown, but looks very similar. The magnitude of the quadrupolar splittings and the chemical shifts for both polymorphs are consistent with other square

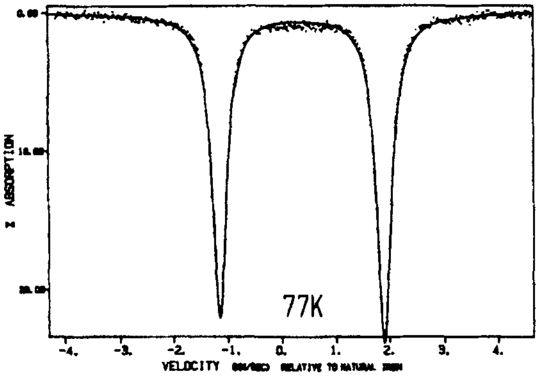


FIGURE 6 Mössbauer spectrum in zero applied magnetic field for α-FeOETAP at 77 K.

planar iron(II) tetrapyrrolic complexes.[6] As a function of temperature, the spectrum of β is essentially unchanged down to 1 K (Figure 7). This corresponds to an unordered, rapidly relaxing paramagnet. Note the opposite sense of the texture-induced intensity asymmetry for the β-form relative to the α-form in Figure 6.

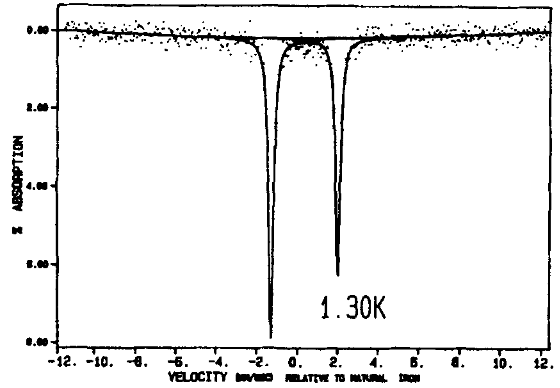


FIGURE 7 Mössbauer spectrum in zero applied magnetic field for β-FeOETAP at 1.3 K.

As the temperature is lowered for α, however, magnetic ordering of the iron centers results in evolution of the spectrum to a six-line hyperfine split spectrum. (Figure 8) The spectrum can be modeled to calculate the magnitude of the internal hyperfine field which gives a value of 62.4 T, the largest ever observed. This result is more remarkable because there are only two unpaired electrons associated with each iron center. Values of the internal field nearly as large have only been seen for antiferromagnetically ordered iron(III) compounds which possess five unpaired electrons.[7] In the case of α-FeOETAP, the incomplete quenching of the orbital angular momentum is playing a role.

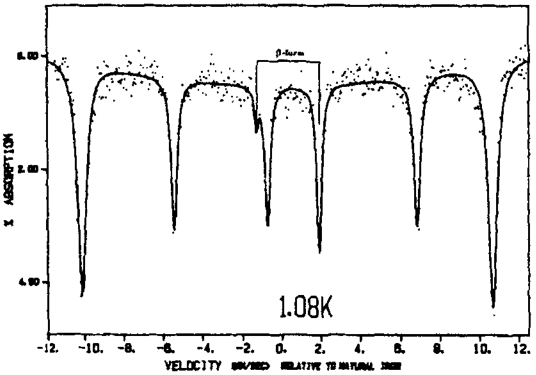


FIGURE 8 Mössbauer spectrum in zero applied magnetic field for α-FeOETAP at 1.08 K showing Zeeman-splitting in the ordered state. The inset corresponds to ≈ 4% unordered, rapidly relaxing, paramagnetic β-form.

For the present, we can give a qualitative explanation of this extraordinary hyperfine field. Specifically, such an unusually large value is explicable in terms of **a)** a large dipolar (H_D) contribution (as implied by the quadrupole splitting effect), and a significant orbital contribution (H_L) to the internal hyperfine field (as implied by the spin-orbit coupling obvious in the high-temperature moment behavior, e.g. μ_{obs} at 293 K is 4.12 μ_B vs. the expected spin-only value of 2.83 μ_B) and **b)** the propitious addition of these contributions to the well-known Fermi-contact term in the ordered state of this material. However, the complete quantitative explanation, particularly in terms of an emphasis on the role of the local g-factor anisotropy, is beyond the scope of this article and will be presented elsewhere.

ACKNOWLEDGMENTS

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