2076 *Inorg. Chem.* **2000,** *39,* 2076−2079

Observation of a Very Large Internal Hyperfine Field (62.4 T) in the Ferromagnetically Ordered State of the $S = 1$ α-Iron(II) Octaethyltetraazaporphyrin

W. M. Reiff,[*,†] C. M. Frommen,[†] G. T. Yee,[*,‡] and S. P. Sellers[‡]

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Received July 30, 1999

The origins of the extraordinarily large internal hyperfine field (62.4 T) for the three-dimensional (weak) ferromagnetically ordered ground state of α-Fe(OETAP) are discussed semiquantitatively in terms of existing physical theory. In particular, the classical Fermi-contact contribution to the internal field is found to be highly enhanced by a very large orbital contribution and a significant dipolar term of the same sign. A rationale for the unexpected ordering of this $S = 1$ non-Kramers system is also presented.

Introduction

In a recent paper[1] we reported on the magnetic properties of the square planar, neutral $S = {}^{3}/_{2}$, α- and β-manganese(II) and $S = 1$, α- and β-iron(II) octaethyltetraazaporphyrins (hereafter abbreviated OETAP). Both compounds show polymorphism, as was demonstrated by scanning electron microscopy and X-ray powder diffraction experiments. The α phase consists of nearly noncrystalline fibers, whereas the β phase exists as faceted rods. We have theorized that the α phase adopts the well-known herringbone structure of β-metallophthalocyanines and that the β phase consists of a "metal-over-metal" structure, which is a common phthalocyanine polymorph,[2] Figure 1.

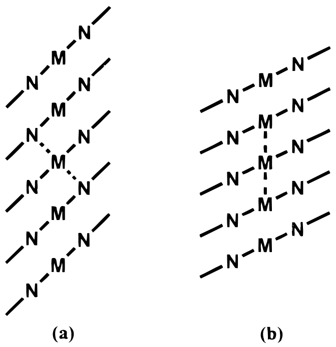

Figure 1. Possible stacking schematics for the α and β polymorphs of Fe(OETAP).

α-Fe(OETAP) is remarkable because it represents a rare example of a *true molecular solid that orders ferromagnetically*. By definition, a true molecular solid consists of neutral species bonded intermolecularly only by van der Waals interactions and/or hydrogen bonds. In contrast, most of the recently reported so-called ferromagnetic "molecular solids" such as the metallocene charge-transfer salts are more accurately described as "molecule-based" or, in the case of Prussian-blue type solids, extended macromolecular structures.

We have now performed additional, detailed ^{57}Fe Mössbauer spectroscopy and susceptibility experiments on α-Fe(OETAP) to provide a better understanding of the magnetic properties of this unique compound. Below T_{Curie}, we observe an internal hyperfine field of 62.4 T, which, to our knowledge, is one of the largest ever reported for iron, regardless of spin and temperature. *This is an especially startling observation in that the title system has only two unpaired electrons*.

Experimental Section

α-Fe(OETAP) was synthesized as previously described.[1] The samples consisted of approximately 50 mg of material packed into a cylindrical 12 mm diameter nylon holders, sealed in 5 min epoxy. The ^{57}Fe Mössbauer spectra in the temperature range 1.08−77 K were obtained in transmission geometry using a standard constant acceleration spectrometer and a conventional exchange gas cryostat. The source material was ^{57}Co/Rh with an activity of 150 mCi. The spectrometer was calibrated at 293 K using a standard thin natural iron absorber. All isomer shifts (δ) reported below are relative to natural iron at 293 K. Magnetic measurements were performed as previously described.

^{57}Fe Mössbauer Spectroscopy

The ^{57}Fe Mössbauer spectroscopy isomer shift (~0.3 mm/s) and quadrupole splitting data (~3.1 mm/s) for the ferromagnetic (α) and paramagnetic (β) forms of Fe(OETAP) are fairly typical of triplet iron(II) and merit no further comment.[3−6]

However, below the ordering temperature of the α phase, there is a vast difference in the behavior between the two polymorphs. The former shows the expected sharp magnetic hyperfine splitting of the Mössbauer spectrum essentially coincident with the previously established Curie temperature, $T_{\mathrm{Curie}} = 2.8$ K. In contrast, the β form exhibits the spectrum shown in the synopsis to as low as ~1 K, i.e., that of an unbroadened, rapidly relaxing paramagnet. The latter result indicates that the zero-field-splitting parameter, D, suggested by the low-temperature moment behavior (decrease of μ below ~20 K) of the β form is, in fact, positive. With $D > 0$, one then has (nominally) a nonmagnetic $m_S = 0$ ground state that

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[*] To whom correspondence should be addressed.

[†] Northeastern University.

[‡] University of Colorado.

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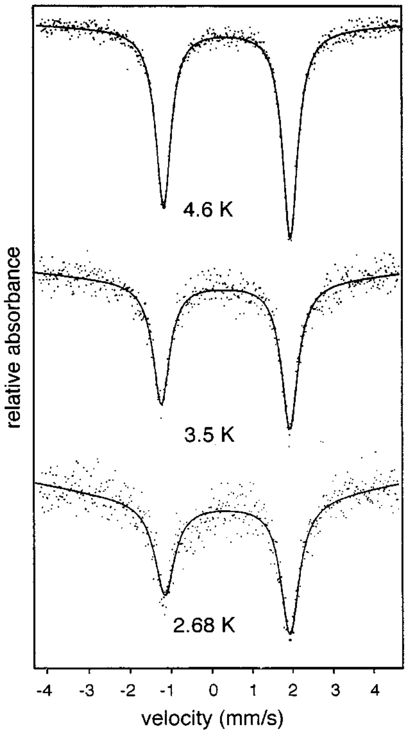

Figure 2. Mössbauer spectra of α-Fe(OETAP) between 2.6 and 4.6 K.

cannot exhibit magnetic hyperfine splitting, at least that owing to slow (single-ion) paramagnetic relaxation. D is also likely positive and of similar magnitude for the ordered α form, since zero-field splitting is primarily a local "single ion" effect.

As stated above, the spectra for α-Fe(OETAP) show a transition to a 3D magnetically ordered state below 2.8 K that manifests as a six-line pattern in the Mössbauer spectrum. We have included a series of spectra in the temperature region $1.08 < T < 4.6$ K in Figures 2 and 3, where ∼4% β impurity is labeled as a stick diagram on the spectrum at 1.98 K. Taking into account the quadrupolar perturbation of the hyperfine spectrum, the measured internal field is indeed extraordinary, 62.4 T. This, to our knowledge, is one of the highest values for H_{int} ever reported for Fe, regardless of its spin state and temperature. The result is all the more remarkable because we are dealing with an $S = 1$ system, whereas other examples of large hyperfine fields are found for high-spin iron(III) ($S = {}^5/_2$) species such as FeF_3 (61.8 T).[7,8] We will use the following section to demonstrate that this surprisingly high value for H_{int} can be rationalized in terms of a favorable addition of major components of the Fermi-contact, orbital, and dipolar contributions to H_{int} along the easy axis of magnetization in the ordered state. Estimates for each term are given subsequently, and we will discuss our findings with reference to the results reported by Dale et al.[6,9] and Barraclough et al.[10] for $S = 1$ ferrous phthalocyanine (FePc), which is assumed to be structurally similar to α-Fe(OETAP) in many respects. We point out that the former molecular solid is not magnetically ordered down to at least 1.57 K (vide infra) and that it was studied using applied field Mössbauer spectroscopy.[6,10]

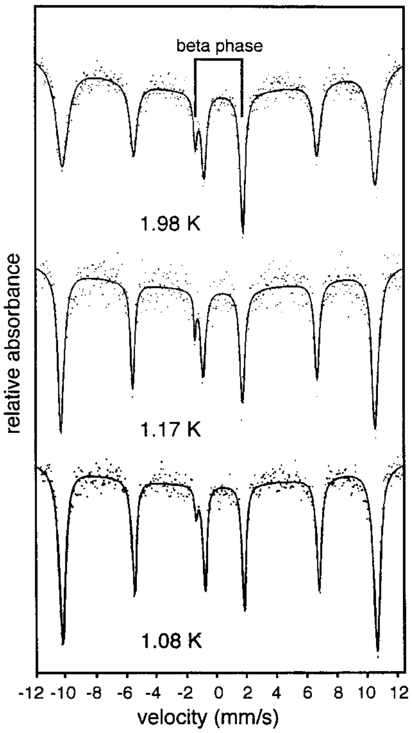

Figure 3. Mössbauer spectra of α-Fe(OETAP) between 1.08 and 1.98 K.

Contributions to H_{int}. In the absence of an externally applied magnetic field, the total field exerted at the iron nucleus, arising entirely from the orbital and spin moments of its "own" electrons, can be written in the form

$$H_{\text{int}} = H_{\text{F}} + H_{\text{L}} + H_{\text{D}} \tag{1}$$

where the individual terms represent the Fermi-contact (H_{F}), orbital (H_{L}), and dipolar (H_{D}) contributions, respectively.[11] We have neglected the demagnetizing field and the Lorentz field because they are relatively small compared to the terms in eq 1. The important contributions to H_{int} are the following:

$$\textit{Fermi contact}:\quad (8/3)\pi\gamma_{\text{e}}\hbar|\Psi(0)|^2\hat{S} \tag{2}$$

$$\textit{orbital}:\quad -\gamma_{\text{e}}\hbar r^{-3}\hat{L} \tag{3}$$

$$\textit{dipolar}:\quad \gamma_{\text{e}}\hbar[r^2 s - 3(rs)r]r^{-5} \tag{4}$$

where γ_{e} is the electronic gyromagnetic ratio, $|\psi(0)|^2$ is the spin density at the nucleus, and $\hat{\text{S}}$ and $\hat{\text{L}}$ are the electronic spin and orbital angular momentum operators, respectively.[12] Alternatively, the individual terms take the following form:[11]

$$\textit{Fermi contact}:\quad (16\pi/3)\mu_{\text{B}}\left\langle \sum_i S_i^{\,z}\delta(r_i)\right\rangle \tag{5}$$

$$\begin{aligned} \textit{orbital}:&\quad -2\mu_{\text{B}}\langle r^{-3}\rangle\langle L\rangle \\ \text{or}&\quad -2\mu_{\text{B}}\langle r^{-3}\rangle(g-2)\langle S\rangle \end{aligned} \tag{6}$$

$$\textit{dipolar}:\quad -2\mu_{\text{B}}\langle 3r(sr)r^{-5} - sr^{-3}\rangle$$

$$\textit{for axial symmetry}\quad -2\mu_{\text{B}}\langle S\rangle\langle r^{-3}\rangle\langle 3\cos^2\theta - 1\rangle \tag{7}$$

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[7] Hyperfine fields reported in other units by other authors have been converted to tesla for the sake of comparison (1 T = 10 kOe).

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where $\langle\hat{S}\rangle$ is the expectation value of the spin angular momentum, $\langle r^{-3}\rangle$ is the radial part of the appropriate 3d wave functions, and θ is the angle between the spin axis and the principal axis of the electric field gradient tensor. Since $e^2qQ = 2e^2Q\langle r^{-3}\rangle\langle 3\cos^2\theta - 1\rangle|\langle S\rangle|$, it follows that $|H_D| = \mu_B q$.

For highly ionic compounds of iron, the Fermi-contact contribution roughly follows the −12.7 T/spin "rule".[11] However, this value can be reduced by as much as 45% owing to covalency delocalization effects[13] as in the case of the $S = 1$ Fe(VI) system K_2FeO_4, which has an internal field of only ∼−14.0 T vs the expected −25.4 T.[14,15] For this example, the origin of H_{int} lies solely in the Fermi-contact contribution. The values of H_D and H_L for this ferrate system are expected to be zero, in view of its nonquadrupole split ^{3}A electronic ground state.

For an approach to estimating the orbital contribution to H_{int} for α-Fe(OETAP), we refer to the work of Dale et al. on FePc.[6,9] In the case of FePc, the major components of the **g**-tensor are $g_{||} = 1.93$ and $g_\perp = 2.86$, yielding an average value of $g = 2.56$, which is consistent with the observed moment of 3.71 μ_B at 25 °C,[10] i.e., a substantial orbital contribution to the moment, μ, over and above the expected value of ∼2.83 μ_B for a ground spin-triplet. From this, these investigators calculated a value of +38.0 T for H_L, taking a $g_\perp$ factor of 2.86 and $\langle r^{-3}\rangle_{3d}$ of 3.6 au into account. In addition, they assumed that the internal field lies in the *xy*-plane perpendicular to the 4-fold symmetry axis of the molecule and therefore chose $g_\perp$ to be the relevant parameter.

We found a magnetic moment of 4.44 μ_B at 25 °C for α-Fe(OETAP), which indicates an even stronger spin−orbit coupling effect and orbital contribution to μ, consistent with a higher value for H_L. On the basis of their assumed structural similarities, we suppose that the **g**-tensor components in α-Fe(OETAP) and FePc have the same character. In the absence of ESR data, we calculate from the average g factor of 3.13(1), obtained from our magnetic moment at room temperature, the components $g_\perp$ and $g_{||}$ to be 3.75(1) and 1.9(1), respectively. The magnitude of the orbital contribution H_L is +78.7(5) T, based on calculations from eq 6, assuming $g = g_\perp = 3.75$.

The dipolar term (H_D) calculated for FePc by Dale et al.[6] is +10.0 T and is equal to $\mu_\perp q$; that is, it scales with the magnitude of the magnetic moment and with the size of the electric field gradient.[11] Since $\Delta E^Q = {}^1/_2 e^2qQ$, H_D is proportional to the magnitude of the quadrupole splitting. Now, ΔE^Q for FePc was reported to be 2.70 mm/s at 4.2 K, whereas for α-Fe(OETAP) it is 3.12 mm/s. Also, recall that the moment in α-Fe(OETAP) at 25 °C is about 4.44 μ_B and that for FePc is 3.71 μ_B. Thus, the dipolar contribution for α-Fe(OETAP) rescales as follows:

$$H_D(\alpha\text{-Fe(OETAP)}) = \frac{\mu(\alpha\text{-Fe(OETAP)})}{\mu(\text{FePc})}\,\frac{\Delta E^Q(\alpha\text{-Fe(OETAP)})}{\Delta E^Q(\text{FePc})}\,H_D(\text{FePc}) \quad (8)$$

Carrying out the above calculation, we obtain a value of +13.8(5) T for H_D in α-Fe(OETAP).

Noncollinearity of V_{zz} and H_{int}. The contribution to the total internal magnetic field by the dipolar field H_D will of course be maximized if the principal component V_{zz} is along the easy axis of magnetization. However, the following calculation shows that V_{zz} and H_{int} are in fact not collinear.

It is apparent from Figure 2 that the separations between the lines 1 ↔ 2 and 5 ↔ 6 are not identical. This indicates the presence of a quadrupolar shift, ϵ (a consequence of a combined magnetic and quadrupolar interaction), that causes a shift in energy of the corresponding resonances. If the electric field gradient tensor is axially symmetric, and if the magnitude of the quadrupole interaction is small compared to the magnetic interaction ($eV_{zz}Q \ll \mu H$), then the quadrupole interaction can be treated as a first-order perturbation to the magnetic interaction. In this case, a relatively simple solution for the energy eigenvalues for this combined interaction exists[11] such that the quadrupole shift ϵ can be shown to be $(eV_{zz}Q/4)(3\cos^2\theta - {}^1/_2)$. From the known difference in line separations of 0.845 mm/s between lines 1 ↔ 2 and 5 ↔ 6 and the magnitude of the quadrupole splitting of 3.090 mm/s (determined above the ordering temperature), and assuming that V_{zz} is positive, we calculate the angle, θ, between V_{zz} and H_{int} to be 60.5°.

This noncollinearity between V_{zz} and H_{int} has an immediate effect on the magnitude of the dipolar contribution to the internal field, since this term corresponds to the "effective" magnitude of the principal component, V_{zz}, of the electric field gradient, that is, its projection onto the easy axis of magnetization.

We can account for this by calculating an *"angular corrected"* (a.c.) dipolar field term H_D(a.c.) simply by multiplying the value that we obtained from the above section ($H_D = 13.8$ T) by the cosine of 60.5°. In doing so, we obtain a value of 6.8 T for H_D(a.c.), again assuming that V_{zz} is positive. We note that FePc is probably structurally similar to the title compound and that its applied field Mössbauer spectra show that V_{zz} is positive. By analogy, we have assumed likewise in the present work. However, whether V_{zz} is positive or negative has little effect on the overall thrust of this study since the related dipolar contribution to the (*enormous*) internal hyperfine field is clearly the smallest (∼10%) of all of the contributions. The orbital effect is clearly dominant.

We are now in a position to check our assumptions and to calculate a value for the Fermi-contact contribution H_F. If we choose a positive sign for the internal field H_{int} in α-Fe(OETAP), the total equation for the internal hyperfine field (in tesla) reads as follows:

$$H_{int} = H_L + H_D(\text{a.c.}) + H_F$$

$$+62.4 = +78.7(5) + 6.8(5) - 23.1(5)$$

The value, −23.1(5) T, obtained for the Fermi contact contribution H_F corresponds to a 9% reduction (owing to covalency effects) of the expected value (−25.4 T) for $S = 1$, based on the −12.7 T/spin "rule".[11] The magnitude of the reduction is quite reasonable for an FeN_4 chromophore in the context of the existing literature[11,13] data on covalency effects and the magnitude of H_{int}. Incidentally, choosing a negative sign for H_{int} and a positive sign for H_L leads to a set of values for H_F that are physically unrealistic. We point out, however, that the definitive determination of the sign of the internal field (and V_{zz} for that matter) α-Fe(OETAP) awaits applied-field Mössbauer spectroscopy experiments.

Further Aspects of the Magnetic Ordering. It is perhaps surprising that the α polymorph orders at all especially when one considers that as a non-Kramers ion, planar $S = 1$ iron(II)

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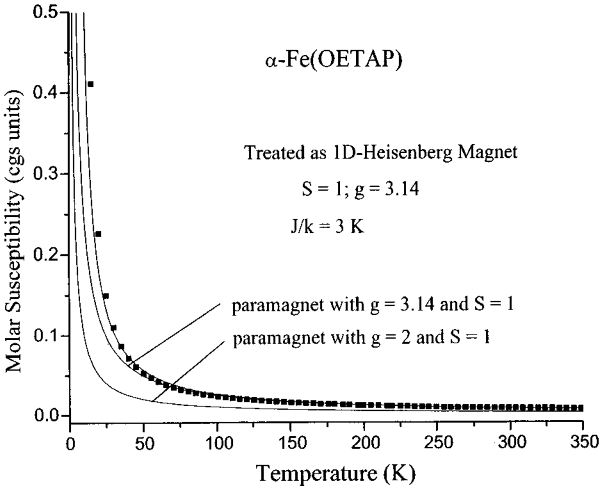

Figure 4. Susceptibility vs temperature for α-Fe(OETAP) measured in an applied field of 10 mT and fit to a 1-D Heisenberg model for $T > T_{Curie}$.

typically exhibits large (positive) zero-field splitting. This generally leads to an isolated nonmagnetic $m_S = 0$ single-ion ground state that cannot support long-range magnetic order. To our knowledge, no other examples of magnetically ordered stacked ferrous porphyrins or phthalocyanines exist. Nevertheless, Moriya[16] has shown that one can expect magnetic ordering (assuming appropriate structural criteria are met) for non-Kramers species such as Ni(II) or Fe(II) when the zero-field-splitting parameter, D, is less than or equal to $2zJ$, where z is the number of nearest magnetic neighbors, assumed to be two for the present chain systems, and where J is the intermolecular exchange coupling. For a magnetically pure sample of the β form, i.e., uncontaminated by the highly magnetic α polymorph, we have determined D to be ∼11 K. At the same time, the molar susceptibility of the α polymorph (Figure 4) can be quite adequately fit to an intrachain exchange $J = +3$ K. It seems clear that these results are consistent with Moriya's criterion and the observed critical temperature of 2.8 K. Significantly larger D values, e.g. 64 cm^{-1} (∼93 K) as found for ferrous phthalocyanine,[10] preclude magnetic order except perhaps possibly for the special case of susceptibility determinations in extremely large applied fields, i.e., field-induced ordering.[17−20] Thus the magnetic ordering of α-Fe(OETAP) is fortuitous and likely due to a favorably small value of D combined with the appropriate chain stacking as to lead to a propitiously large value of J. In this context, it is evident from Figure 1 that the strength as well as nature (direct M- - -M- - -M vs the superexchange pathway M- - -N- - -M) of the exchange interactions are sensitive to specific geometric details (distances between and stacking angles of) of the molecular units.

Summary

We have demonstrated in the preceding sections that the extremely large internal field of 62.4 T in α-Fe(OETAP) can be rationalized semiquantitatively in terms of the addition of a very large orbital and dipolar contribution to the magnetic hyperfine field and a Fermi-contact term reduced some 9%, due to covalency effects. In this context, we bring the following points (among others) to the reader's attention: (a) The values $\langle r^{-3}\rangle_{3d}$ for the radial part of the wave functions (where the brackets denote summation over the whole atom) assume "hydrogenic" 3d orbitals. These values are not accurately known for atomic orbitals and especially not for iron Fe(II) in this unusual $S = 1$ spin-state. (b) A complete expression for the field gradient q has to include an additional factor which accounts for the fact that the nucleus is shielded from the influence of the outer electrons by the core electrons ("Sternheimer effect").[11] These observations have ramifications for the ultimate values of H_L and H_D, respectively, that one calculates. Despite the number of assumptions that have been made and the lack of a truly suitable physical/theoretical model for this complex system, it is gratifying that our estimates reasonably describe the origins of the extraordinary internal field in α-Fe(OETAP).

While not precluded, such a large additive enhancement of H_{int} is certainly exceptional. The only other well-documented examples of this effect with which we are familiar are found among certain charge-transfer ferrocenium ($S = {}^{1}/_{2}$) molecule-based magnets[21] whose limiting internal fields are ∼40 T (vs ∼10−12 T expected from H_F) and arise solely from significant orbital contributions over and above H_F. It is much more common to observe an overall diminution of H_{int} through opposing orbital contributions of similar magnitude. The ultimate example of this phenomenon is anhydrous ferrous chloride ($FeCl_2$), which exhibits no (resolved) hyperfine splitting in its ordered state ($T_N \sim 24$ K), i.e., H_{int} ∼0.4 T.[22,23] These effects appear to be largely a function of the sign and magnitude of the local g-factor anisotropy and to a somewhat lesser extent the dipolar term.

Finally, we note that the basic magnetic properties of FePc and the related ferrous porphyrins have been somewhat problematic ever since their initial investigation.[24] Their ambient temperature magnetic moments are typically ∼4 μ_B, a value almost exactly midway between that of *spin-only* triplet ferrous ($\sqrt{8}\ \mu_\beta$) and the spin-only value ($\sqrt{24}\ \mu_B$) of the much more common quintet ground state. This observation has been explained as due to a large orbital contribution to μ.[25] In this context, the present work serves as clear, initial spectroscopic evidence of classical orbital effects as a dominant feature of the (3D) magnetically ordered ground state.

Acknowledgment. We acknowledge the National Science Foundation (Grant CHE-9727485) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and useful input from Dr. Charles Johnson (Argonne National Laboratory).

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