

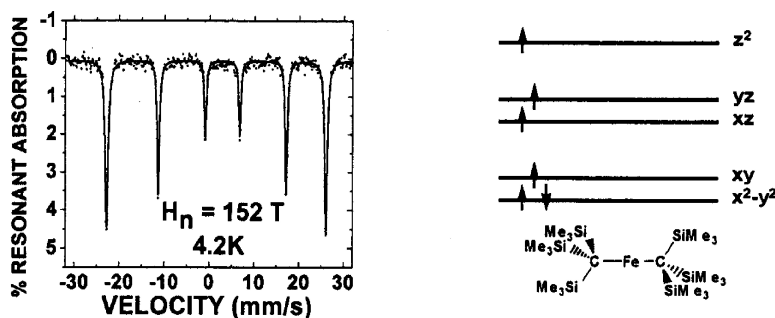
Communication

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## Virtual Free Ion Magnetism and the Absence of Jahn–Teller Distortion in a Linear Two-Coordinate Complex of High-Spin Iron(II)

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Recently there has been interest in the synthesis and detailed study of coordinatively unsaturated compounds of Fe(II). Thus, we<sup>1</sup> have investigated a square planar octaethylporphyrin of Fe(II) whose spin triplet ground state exhibits a substantial additional orbital component that leads to a very large magnetic hyperfine field ( $H_n \approx 62.4$  T) for the long-range magnetically ordered state below 2.8 K. Subsequently, Andres et al.<sup>2</sup> reported a series of three-coordinate spin quintet Fe(II) complexes (local  $C_{2v}$   $FeN_2X$  chromophores) with remarkably large orbital contributions to their ground-state magnetic behavior. These are reflected in  $H_n$  ranging to 82 T. It is reasonable to assume that complexes having near minimal, regular ligation, as is the case for rigorously linear two coordination, afford the possibility of even larger unquenched, orbitally dominated, highly anisotropic magnetic behavior. We now present initial Mössbauer spectroscopy and magnetization results supporting this view for the linear, two-coordinate Fe(II) complex,  $Fe[C(SiMe_3)_3]_2$  (**1**) (Figure 1).

X-ray structures of **1** have been reported by LaPointe<sup>3</sup> and Viefhaus et al.<sup>4</sup> Both studies establish a rigorously linear C–Fe(II)–C chromophore with equal Fe–C distances of 2.05 Å corresponding to local  $D_{\infty h}$  and overall  $D_{3d}$  symmetry. Assuming local  $sp^3$  C– $\sigma$ -bonding anionic ligands, crystal field theory<sup>5</sup> leads to an energy level diagram (Figure 2), for which the orbital doublets must be degenerate since the molecule is linear and cannot Jahn–Teller<sup>6</sup> distort. Hence, the ground state is (neglecting spin–orbit splitting)  $^5\Delta_g$  in local  $D_{\infty h}$ . The consequences for the low-temperature Mössbauer spectrum and magnetism of **1** are now discussed.

At ambient temperature, the Mössbauer spectrum of **1** is a quadrupole doublet undergoing relaxation broadening<sup>7</sup> to the extreme that the low velocity component of the doublet has all but vanished. The isomer shift<sup>8,9</sup> ( $\delta$ ) and quadrupole splitting values ( $\Delta E$ ) are  $\sim 0.4$  and 1.3 mm/s, respectively. The former is quite reasonable for two-coordinate high-spin iron (II) and fits well into the established systematics for isomer shifts as a function of coordination number. Specifically,  $\delta$  decreases with decreasing coordination number for a fixed spin and oxidation state, presumably as a result of increasing “s” electron character to the metal–ligand bonding. Andres et al.<sup>2</sup> extended the  $\delta$  database to include three-coordinate iron(II) in their investigation of  $FeN_2X$  complexes with  $\delta(298\text{ K}) = 0.48$  mm/s ( $X = CH_3^-$ ). The magnitude of  $\Delta E$  for **1** is essentially temperature-independent, implying a ground state that is relatively well-isolated from excited orbital states.

The Mössbauer spectrum of **1** undergoes a transformation to fully resolved hyperfine splitting at  $\sim 50$  K but with broad transitions. This process is obvious over the decreasing temperature interval 125 to 50 K, at which temperature the system is approaching the infinitely slow relaxation limit. The behavior clearly corresponds

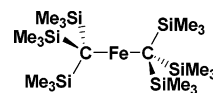


Figure 1. Local structure of **1**.

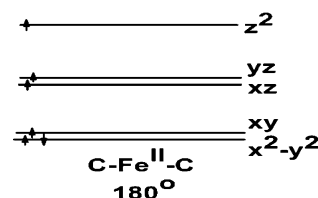


Figure 2. Crystal field splitting for linear two-coordinate  $Fe^{2+}$ .

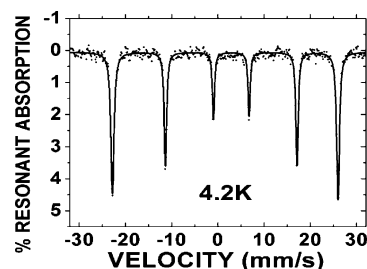


Figure 3. Mössbauer spectrum of **1** at 4.2 K.

to slow paramagnetic relaxation as opposed to long-range magnetic order. Analysis of the spectrum indicates that the internal hyperfine field of **1** is relaxing along the  $C_{\infty}$  axis of the C–Fe–C chromophores parallel to the principal component of the electric field gradient tensor,  $V_{zz}$ ,<sup>7,10</sup> as demanded by the symmetry of **1**. Slow spin–spin relaxation for **1** is consistent with the closest Fe···Fe distances between C–Fe–C units of  $\sim 9$  Å,<sup>3,11</sup> while spin–lattice relaxation times of course lengthen with decreasing T. As expected for infinitely slow relaxation, at 4.2 K (Figure 3), narrow line widths ( $\langle\Gamma_{3\&4}\rangle = 0.53$  mm/s) are observed relative to the overall nuclear Zeeman splitting of 48.8 mm/s for a single hyperfine pattern. The latter indicates an isolated ground spin–orbit doublet resulting from spin–orbit splitting of the 10-fold degenerate ground  $^5\Delta_g$  term of **1**. This hyperfine splitting is extraordinary in the context of all of currently known iron chemistry. The corresponding internal hyperfine field is 151.6 T. Since the spectrum is quadrupole shifted, it is more appropriate to calculate  $H_n$  from the nonquadrupole split  $I = 1/2$  ground-state Zeeman splitting. For **1**, this has a value of 152.4 T, arguably implying its unique nature.

In zero field,  $H_n = H_F + H_D + H_L$ , corresponding to the sum of the Fermi contact, dipolar and orbital contributions, respectively.  $H_F$  is largely determined by the value of  $S$ , i.e.,  $H_F \approx -12.7$  T/spin.<sup>8</sup> Hence, for  $S = 2$ ,  $H_F \approx -51$  T. For **1**, this value should suffer little if any covalence reduction effects<sup>8</sup> via either direct delocalization to empty, low-energy ligand orbitals (there are none for **1**)

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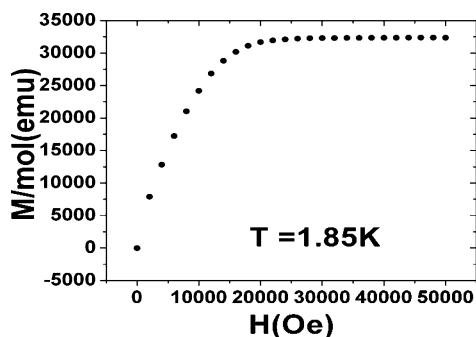


Figure 4. DC magnetization of **1** at 1.85 K, 0–50 000 Oe.

or a cloud expanding (nephalauxetic) effect. There are only two ligands, and these are *nondelocalizing*  $\sigma$ -bonding  $sp^3$ -hybridized carbanions that have no lone pairs for back-bonding. As  $H_D$  scales as the magnitude of the value of  $V_{ZZ}$  of the valence contribution (a maximum of  $\sim +4$  mm/s for either  $d_{xy}$  or  $d_{x^2-y^2}$  occupation),<sup>12</sup> this term is neglected in the context of an overall hyperfine splitting of  $\sim 49$  mm/s. This approximation and the use of the free ion value of  $H_F$  leads to an upper bound on the value of  $H_L$  of  $+203$  T<sup>13</sup> for **1**. Our value is perhaps not that surprising (at least qualitatively) in view of the fact that the analysis of Table 2 in ref 2 yields  $L = 2$  and  $g_{\text{eff}} = 12$  ( $x$ -band) as the maximum values precisely for the (rigorously degenerate) ground pair of **1**, namely ( $d_{xy}$ ,  $d_{x^2-y^2}$ ) in Figure 2, for  $z$ -spin quantization. In any event, detailed analysis clearly shows that current theory<sup>2</sup> does not quantitatively account for the magnitude of  $H_n$  for **1**.

In Figure 4, we present DC Squid magnetization measurements of **1** at 1.85 K for the same crystalline sample used for Mössbauer spectroscopy. The saturation magnetization values ( $M_{\text{sat}}/\text{mol} = g\mu_B N S$ ) for  $J = S$ ,  $L = 0$ , and  $g = 2$  for  $S = 2$  and  $S = 3$  are 22 339 and 33 495 emu/mol, respectively, corresponding to classical spin-only behavior. Figure 4 shows that  $M_{\text{sat}} \approx 32\,500$  emu/mol, i.e.,  $\sim 97\%$   $M_{\text{sat}} S = 3$ . Clearly, **1** has a very large orbital contribution. The maximum orbital contribution for high-spin  $d^6$   $L = 2$ , leads to a moment ( $L + 2S$ ) of 6 Bohr magnetons effectively indistinguishable from spin-only  $S = 3$  ( $6 \times S = 1/2$ ) on the basis of magnitude alone.

The calculated moment of the ground  $^5D_4$  free-ion term  $\{\mu_J = (g_J^2 J(J+1))^{1/2}$ ,  $L = S = 2$ ,  $J = 4$ ,  $g = 3/2\}$  is  $6.71 \mu_B$ , while the spin-only value for  $S = 3$  is  $6.93 \mu_B$ , i.e.,  $\mu$  (free gas-phase ion)  $\approx 97\% \mu(S = 3)$ . Depending on the field magnitude, cooling, and field history, we observe a moment of  $\sim 6.6$  to  $7 \mu_B$  for **1** from susceptibility measurements consistent with the minimal orbital quenching effects indicated by Mössbauer spectroscopy. Whether in the parlance of physicists (magnetization) or the effective moment used by chemists, the orbital contribution for **1** is the maximum and essentially equivalent to adding two full spins relative to spin-only  $S = 2$  behavior. Thus, in the context of the magnitude of the moment of **1**, we have the remarkable situation of virtually free ion magnetic behavior, although large uniaxial anisotropy is expected and observed for **1** in the solid state.

Summarizing, **1** is a simple but highly anisotropic paramagnet for which the overall temperature variation of its effective magnetic moment (via zero field ac susceptibility measurements) is that expected for a molecule having a unique magnetic center with very large first-order orbital momentum,<sup>14</sup> no low symmetry ligand field component, and a Stevens orbital angular momentum reduction factor  $k \approx 1$ , i.e., no reduction.<sup>15</sup> The Renner–Teller effect leading to a reduction in symmetry from local  $D_{\infty h}$  to  $C_{2v}$  via bending<sup>16</sup> will clearly lift the degeneracy in Figure 2 and reduce the orbital contribution. However, such vibrational behavior is expected to be largely precluded at least for the solid state of **1** in view of its bulky ligands.

We have demonstrated for the first time the unprecedented effects of the absence of Jahn–Teller distortion on the magnetism of a linear coordination compound of high-spin iron(II) in the contexts of its low temperature Mössbauer spectrum and dc magnetization. Ac and dc susceptibility study of fully randomized samples and field oriented crystal mosaics, heat capacity, Mössbauer, and ESR spectra investigations of **1** will be published subsequently. Finally, in view of Figure 2, one anticipates likewise unprecedented magnetic behavior for the high-spin  $d^8$  configuration of a Ni(II) analogue of **1** owing to the possibility of a  $^3\pi_g$  ground-state whose degeneracy is maintained in linear (homoleptic) coordination.

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