J|A|C|S
COMMUNICATIONS

Consequences of a Linear Two-Coordinate Geometry for the Orbital Magnetism and Jahn−Teller Distortion Behavior of the High Spin Iron(II) Complex $Fe[N(t\text{-}Bu)_2]_2$

William M. Reiff,*,† Charles E. Schulz,‡ Myung-Hwan Whangbo,§ Jung In Seo,|| Yoon Sup Lee,|| Gregory R. Potratz,⊥ Charles W. Spicer,⊥ and Gregory S. Girolami*,⊥

Department of Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts 02115, Department of Physics, Knox College, Galesburg, Illinois 61401, Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, Department of Chemistry and School of Molecular Science (BK21), KAIST, Daejeon 305-701, Korea, and School of Chemical Sciences, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

Received August 22, 2008; E-mail: w.reiff@neu.edu; girolami@scs.uiuc.edu

Two-coordinate complexes of open-shell transition metal ions (i.e., those with d^1-d^9 configurations) often exhibit fascinating reaction chemistry and physical properties.[1] A notable representative of this class is the iron(II) tris(trimethylsilyl)methyl complex $Fe[C(SiMe_3)_3]_2$.[2,3] Neglecting spin orbit splitting effects, this high-spin d^6 complex has a degenerate $^5\Delta_g$ ground state in which three electrons occupy the ($d_{x^2-y^2}$, d_{xy}) pair of orbitals. Although such degeneracies normally are lifted by Jahn−Teller distortions,[4] the linearity of the two-coordinate Fe^{II} center leaves the degeneracy intact to first order. A fascinating consequence of this retention of local $D_{\infty h}$ symmetry is that the magnetic moment of 6.8 ± 0.2 μ_B corresponds to the $(g_J{}^2J(J+1))^{1/2} = 6.71\ \mu_B$ value characteristic of the free ion, rather than the $(g^2S(S+1))^{1/2} = 4.90\ \mu_B$ spin-only value.[5] Furthermore, the zero-field Mössbauer spectrum of $Fe[C(SiMe_3)_3]_2$ at 4.2 K exhibits an internal field (H_{int}) of 152 T. This value, which is far larger than that for any other iron complex, corresponds to an orbital field contribution (H_L) of ∼+204 T.

A few other two-coordinate iron(II) compounds have been described,[6−14] but most of these have L−Fe−L angles that deviate significantly from 180° owing to long-range interactions between the iron center and remote substituents on the ligands. These remote interactions increase the effective coordination number.[15]

We have recently prepared a remarkable new example of an iron(II) compound, the di(*tert*-butyl)amide complex $Fe[N(t\text{-}Bu)_2]_2$, **1**.[16] This is the first open-shell transition metal complex of this amide ligand.[17,18] The crystal structure of **1** shows that it is a two-coordinate monomer with Fe−N = 1.880(2) Å (Figure 1). Unlike most other iron amido compounds, the N−Fe−N angle of 179.45(8)° is almost exactly linear and there are no significant Fe···C contacts. The NR_2 planes describe a dihedral angle of 80.5(1)°, and the near-orthogonality may be favored both sterically and electronically: in this geometry, one amide ligand can serve as a π-donor into the d_{xz} orbital and the other into the d_{yz}. The strongly electron-donating *tert*-butyl substituents enhance the π-donation, and as a result the Fe−N distance in **1** is the shortest of all of iron(II) amides, despite the large size of the ligands.[19]

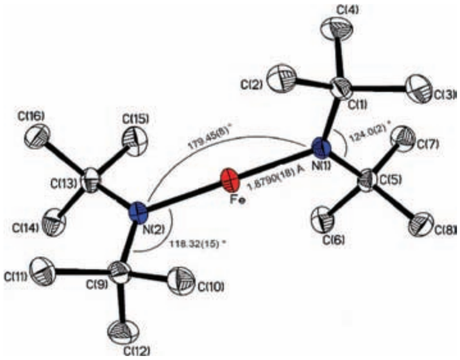

Figure 1. Molecular structure of $Fe[N(t\text{-}Bu)_2]_2$, **1**. The 30% probability density surfaces are shown; hydrogen atoms are omitted.

The zero-field cooled, near-zero-field AC susceptibility data for **1** show that the effective magnetic moment (μ_{eff}) at 25 °C is 5.55 μ_B, which is larger than the spin only value of 4.90 μ_B for a high spin Fe^{II} ($S = 2$) species. Field cooled DC susceptibility measurements indicate that there is significant but probably not complete field induced alignment along g_{max}. The large magnetic moments clearly confirm the presence of significant unquenched (first order) orbital magnetism.[20] At temperatures below 40 K, μ_{eff} decreases owing to depopulation of spin−orbit states.[21] The shape of the susceptibility curve is consistent with a Stevens orbital reduction factor k that is close to 1, as expected for a high-spin ferrous ion with this ligand set.[21,22] Magnetization measurements show that **1** is not saturated even for an H_0 as large as 5 T at 1.8 K (supporting Figures S1 and S2).

The Mössbauer spectrum of **1** in zero field is broad owing to paramagnetic relaxation,[23] and there is no evidence of resolved nuclear Zeeman splitting even at 1.3 K (supporting Figure S3). Most likely, the intermolecular Fe···Fe distances, ∼7.4 Å for **1**, are short enough to promote spin−spin relaxation even at low temperatures.[23] Applying a field H_0 of only 0.075 T slows relaxation sufficiently to reveal the outer components of a hyperfine sextet. Remarkably, the splitting corresponds to an extremely large internal hyperfine field, H_{int} ∼105 T (Figure 2). At a larger applied field of 9 T, all six components of the hyperfine sextet are clearly seen, and $H_{int} + H_0$ increases to ∼113 T, confirming that $H_{int} > 0$. If one neglects the dipolar contribution (H_d) to H_{int}, this value corresponds to an orbital contribution (H_L) of +155 T.

Among all known iron compounds, the remarkably large internal hyperfine field in **1** is ∼20 T larger than those recently found for certain three coordinate high-spin iron(II) systems[24] and is exceeded only by that in the linear iron alkyl $Fe[C(SiMe_3)_3]_2$.[5] The nonzero intensities of the $\Delta M_I = 0$ transitions (components 2 and 5 of the sextet) show that the internal hyperfine field of **1** is not fully polarized parallel to the direction of H_0 and the gamma ray, even

---

† Northeastern University.
‡ Knox College.
§ North Carolina State University.
|| KAIST.
⊥ University of Illinois at Urbana−Champaign.

10.1021/ja806660f CCC: $40.75

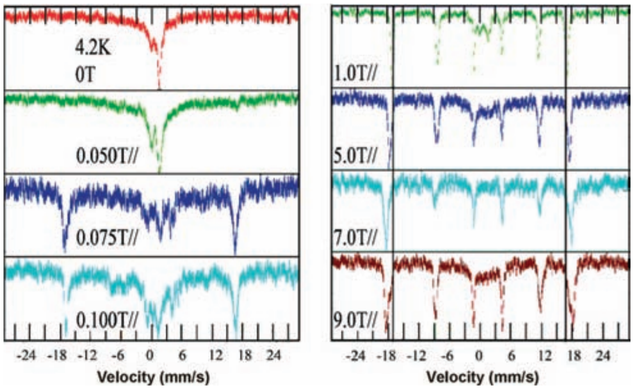

Figure 2. Longitudinal applied field Mössbauer spectra of **1** at 4.2 K with the applied field, H_0, varying from 0.05 to 9 T. The vertical lines at right help show the increase in the hyperfine splitting at higher H_0.

for H_0 as large as 9 T. There is apparently a competition between H_0 and a large local anisotropy that prevents the intensities of the $\Delta M_I = 0$ transitions from approaching zero, even for large applied fields. The presence of shoulders on transitions 1 and 6 at $H_0 = 9$ T suggests that both the up and down electron Zeeman states of the ground spin−orbit level are populated.

The ∼50 T difference in H_{int} between **1** and $Fe[C(SiMe_3)_3]_2$ at H_0 ∼0 is most likely due to a smaller orbital contribution (H_L) to the internal hyperfine field in **1**, consistent with significant spin−orbit state mixing enabled by its lower symmetry. The lower electronic symmetry of **1** relative to that of $Fe[C(SiMe_3)_3]_2$ is also suggested by its X-band EPR spectrum, which is relatively easy to observe, particularly in the parallel detection mode. The resonance at $g_{eff} = 10.34$ (supporting Figure S4) is typical of an integral spin, non-Kramers, ferrous species with a quasi degenerate spin−orbit doublet ground state. A simulation of the EPR spectrum shows that g_z is ∼2.4 and the ground-state splitting Δ is ∼0.1 cm^{-1}.[24] In contrast, for $Fe[C(SiMe_3)_3]_2$, the rigorously degenerate $M_J = \pm 4$ ground state and the absence of significant spin−orbit level mixing in D_{3d} symmetry lead to it being EPR silent[25] and to the ready observation of hyperfine splitting in the Mössbauer spectrum at $H_0 = 0$.

We have carried out first principles electronic structure calculations for **1** as well as the model compounds $Fe[NH_2]_2$ and $Fe[NMe_2]_2$ in their quintet states ($S = 2$). The Fe−N length of 1.90 Å calculated for **1** closely matches the 1.88 Å value found experimentally. The potential energy of **1**, calculated as a function of the dihedral angle θ between the two C−N−C ligand planes, shows a minimum near $\theta = 77°$ (supporting Figure S5), which is likewise reasonably close to the experimental value 80.5°. The potential well is shallow, so that the intermolecular interactions in the crystal, though weak, could influence the exact value of θ.

The local z-axis for the D_{2d} structure of $Fe[NR_2]_2$ (R = H, Me) lies along the N−Fe−N axis. From the one-electron point of view, the lowest energy d-orbitals of $Fe[NR_2]_2$ are the (xy, $x^2{-}y^2$) pair, which are accidentally degenerate because, due to their δ symmetry, they do not interact with the orbitals of the NR_2 fragments. The xz and yz levels, which are rigorously degenerate, are π^* orbitals, whereas z^2 is a σ^* orbital. The Fe $3d_{z^2}$ orbital is strongly hybridized with the Fe^{II} 4s orbital, thereby reducing the antibonding nature of this level; similar behavior is seen for gas phase $FeCl_2$.[26] The orbital orderings of the α and β spin d-orbitals in the ground state of **1** are as follows:

$$(xy,\ x^2-y^2) < z^2 < (xz,\ yz)\ \text{(HOMO) for the alpha spins}$$

$$xy\ \text{(HOMO)} < z^2 < (xz,\ yz) < x^2-y^2\ \text{for the beta spins}$$

Hence, in the rigid orbital (i.e., spin-restricted) approximation, the high-spin Fe^{II} (d^6) ion in D_{2d} $Fe[NR_2]_2$ has the electron configuration $(xy,\ x^2-y^2)^3(z^2)^1(xz,\ yz)^2$. The two lowest-energy quintet states of $Fe[NR_2]_2$, in which the beta-spin HOMO is either the xy or the x^2-y^2 orbital, differ in energy by 0.02, 0.29, and 2.08 kcal mol^{-1} for R = H, Me, and t-Bu, respectively. Thus, these two quintet states are in fact nearly degenerate, consistent with the experimental results above. The nonorthogonal (∼81°) dihedral angle between the ligand planes of **1** lowers the molecular symmetry from D_{2d} to D_2 and further breaks the degeneracy, albeit weakly so. Lowering of the symmetry even further to C_{2v} or C_s via bending, which in principle could occur by action of higher order vibronic terms (Renner−Teller effect),[4] does not lead to an energy lowering as judged from the DFT calculations. The excited states that would mix into the ground state upon bending are high in energy, so that for **1** the driving force for bending is too small to overcome the increased steric strain that would be generated.

In summary, we have described an usual two-coordinate iron(II) amide **1** that retains a linear N−Fe−N framework. The resulting near-degenerate ground state gives rise to a large magnetic moment and a remarkably large internal hyperfine field. Extraordinary orbital magnetic effects can arise in linear transition metal complexes in which orbital degeneracies are not broken by Jahn−Teller or Renner−Teller distortions.

Acknowledgment. G.S.G. thanks the NSF under Grant CHE07-50422 and Mark Nilges for assistance with the EPR spectra. M.-H.W. thanks the U.S. DOE under Grant DE-FG02-86ER45259. The work at KAIST was supported by the Korea Science and Engineering Foundation (R01-2007-000-11015-0, R11-2007-012-03001-0) and the supercomputing center of KISTI.

Supporting Information Available: Crystallographic data and additional spectroscopic and theoretical results for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Power, P. P. *Comments Inorg. Chem.* **1989**, *8*, 177–202.
(2) Viefhaus, T.; Schwarz, W.; Weidlein, J. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2045–2047.
(3) LaPointe, A. M. *Inorg. Chem. Acta* **2003**, *345*, 359–362.
(4) Bersuker, I. B. *Chem. Rev.* **2001**, *101*, 1067–1114.
(5) Reiff, W. M.; LaPointe, A. M.; Witten, E. H. *J. Am. Chem. Soc.* **2004**, *126*, 10206–10207.
(6) Andersen, R. A.; Faegri, K., Jr.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W. P.; Rypdal, K. *Inorg. Chem.* **1988**, *27*, 1782–1786.
(7) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 7563–7564.
(8) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 4338–4345.
(9) Chen, H.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1990**, *112*, 1048–1055.
(10) Bartlett, R. A.; Chen, H.; Power, P. P. *Angew. Chem.* **1989**, *101*, 325–327.
(11) Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1178–1180.
(12) Wehmschulte, R. J.; Power, P. P. *Organometallics* **1995**, *14*, 3264–3267.
(13) Mueller, H.; Seidel, W.; Goerls, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 325–327.
(14) Nguyen, T.; Panda, A.; Olmstead, M. M.; Richards, A. F.; Stender, M.; Brynda, M.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 8545–8552.
(15) Evans, D. J.; Hughes, D. L.; Silver, J. *Inorg. Chem.* **1997**, *36*, 747–748.
(16) Spicer, C. W.; Potratz, G. R.; Girolami, G. S., manuscript in preparation.
(17) Lappert, M. F.; Slade, M. J.; Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1980**, 621–622.
(18) Schumann, H.; Gottfriedsen, J.; Girgsdies, F. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1881–1884.
(19) An Fe−N distance of 1.84 Å has been reported for $Fe[N(SiMe_3)_2]_2$ by gas phase electron diffraction, but there is reason to doubt the accuracy of this measurement.[6] The trends in the Fe−N distances for $Fe[N(SiMePh_2)_2]_2$ and $Fe[N(SiMe_2Ph)_2]_2$ determined by X-ray diffraction[8] suggest that monomeric $Fe[N(SiMe_3)_2]_2$ should have an Fe−N distance of ∼1.89 Å.
(20) Kahn, O. *Molecular Magnetism*; VCH-Wiley: New York, 1993; pp 31−52.
(21) Figgis, B. N.; Lewis, J.; Mabbs, F. E.; Webb, G. A. *J. Chem. Soc. A* **1967**, 442–447.
(22) Gerloch, M.; Miller, J. R. *Prog. Inorg. Chem.* **1968**, *10*, 1–47.
(23) Wignall, J. W. G. *J. Chem. Phys.* **1968**, *44*, 2462–2467.
(24) Andres, H.; Bominaar, E. L.; Smith, J. M.; Eckert, N. A.; Holland, P. L.; Munck, E. *J. Am. Chem. Soc.* **2002**, *124*, 3012–3025.
(25) Reiff, W. M., unpublished results for $Fe(C(SiMe_3)_3]_2$.
(26) Wang, S. G.; Schwarz, W. H. E. *J. Chem. Phys.* **1998**, *109*, 7252–7262.

JA806660F