Inorg. Chem. **2000,** *39,* 4674−4675

Structural, Electronic, and Magnetic Properties of $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ (pz = Pyrazolyl): Observation of Unusual Spin-Crossover Behavior

Daniel L. Reger* and Christine A. Little

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Arnold L. Rheingold, Matthew Lam, and Tom Concolino

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

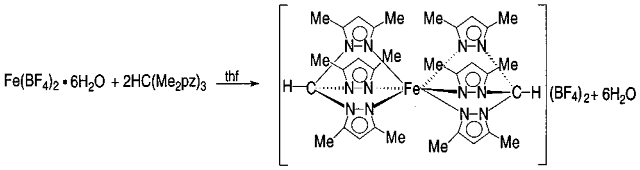
Amitabh Mohan and Gary J. Long*

Department of Chemistry, University of Missouri−Rolla, Rolla, Missouri 65409-0010

Received June 29, 2000

The properties of octahedral iron(II) complexes that undergo thermal spin conversions between the high-spin (HS, $S = 2$) and low-spin (LS, $S = 0$) states have been widely investigated.[1] Tris(pyrazolyl)borate complexes, such as $Fe[HB(pz)_3]_2$ and $Fe[HB(3,5\text{-}Me_2pz)_3]_2$ (pz = pyrazolyl ring), were some of the first to be extensively studied.[2] As part of our investigations[3] into the coordination chemistry of the isoelectronic tris(pyrazolyl)methane ligands, we report here the synthesis, NMR, structural, magnetic, and Mössbauer spectral results on $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ (**1**). In the solid state **1** shows a new type of spin-crossover behavior. Even though only one iron site is observed by X-ray crystallography, the solid changes abruptly from all HS above 206 K to a mixture of HS and LS below 200 K, and the composition of this lower temperature mixture does not change as the temperature is lowered to 5 K.

The reaction of $Fe(BF_4)_2{\cdot}(H_2O)_6$ and $HC(3,5\text{-}Me_2pz)_3$ in a 1:2.5 ratio yields the desired complex.



The complex is white as a powder and single crystals are colorless, indicating that the iron is HS at room temperature.[1,4] The solution-phase ^1H NMR spectrum is broad with chemical shifts ranging from 52 to −42 ppm, a range that is indicative of a paramagnetic HS complex.

The high-spin configuration was verified by a single-crystal X-ray structural analysis carried out at 295 K (Figure S1 in Supporting Information). The complex has a unique iron site, which lies on a center of symmetry, with a N_6 coordination arrangement. The chelate rings restrict the intraligand N−Fe−N angles to an average of 84.3°, making the structure a trigonally distorted octahedron. The average Fe−N bond distance of 2.17 Å clearly demonstrates that the iron is HS; average distances of ca. 1.97 Å are observed in LS octahedral FeN_6 complexes.[5]

Figure 1 shows the solid-state magnetic behavior of **1**. The complex is high-spin from 350 K down to a temperature of 206 K with a μ_{eff} of 4.74 μ_B. Over this temperature range the compound exhibits simple Curie law behavior. Below 206 K the compound undergoes a very abrupt decrease in magnetic moment, but after this abrupt change the susceptibility again follows the Curie law until 90 K, at which time it undergoes a slight change (increase of 0.1 μ_B). After this change the susceptibility again follows Curie law behavior down to 5 K. The magnetic moment of **1** at low temperature is 3.54 μ_B. When the complex is warmed, the susceptibility follows the 85−5 K cooling Curie behavior *all the way up to 200 K*, then shows a very abrupt increase in magnetic moment. After this change the susceptibility again follows Curie behavior with $\mu_{\mathrm{eff}} = 4.89\ \mu_B$. Cooling the sample back down to 5 K results in susceptibility measurements that superimpose on *the first warming curve*, showing only one abrupt change starting at 206 K. The one time small increase in magnetic moment the first time the sample is cooled through 90 K is an irreversible change that results in an increase in the magnetic moment at all temperatures.

An explanation for the major change in magnetic moment as the temperature is varied is that the solid rapidly converts from fully HS above 206 K to a mixture of HS and LS states below 200 K and that mixture *does not continue to change its composition as the temperature is lowered* below 200 K. Visually, the color of the crystals change from colorless above 206 K to purple below, the color expected for LS iron(II).[4] The crystals can be cycled through the critical temperature range without change.

Mössbauer spectroscopy, Figure 2, shows conclusively that the complex is changing over this very small temperature range from a HS state to a mixture of HS and LS. The 280 K spectrum shows a large quadrupole splitting and is similar to that observed in $Fe[HB(3,5\text{-}Me_2pz)_3]_2$ and many other HS octahedral $N_6Fe(II)$ complexes.[1,2] Two similar but distinct doublets are needed to fit this HS iron(II) component in **1**. At low temperatures, the doublets of the HS component are significantly diminished and a new

---

(1) (a) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024 and references therein. (b) Kahn, O.; Krober, L.; Jay, C. *Adv. Mater* **1992**, *4*, 718. (c) Cotton, F. A.; Wilkinson, J.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; pp 785−786.

(2) (a) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3158. (b) Jesson, J. P.; Weiher, J. F.; Trofimenko, S. *J. Chem. Phys.* **1968**, *48*, 2058. (c) Long, G. J.; Hutchinson, B. B. *Inorg. Chem.* **1987**, *26*, 608. (d) Grandjean, F.; Long, G. J.; Hutchinson, B. B.; Ohlhausen, I.; Neill, P.; Holcomb, J. D. *Inorg. Chem.* **1989**, *28*, 4406. (e) Sohrin, Y.; Kokusen, H.; Matsui, M. *Inorg. Chem.* **1995**, *34*, 3928. (f) Buchen, T.; Gütlich, P. *Inorg. Chim. Acta* **1995**, *231*, 221 (g) Hannay, C.; Hubin-Franskin, M.-J.; Grandjean, F.; Briois, V.; Itie, J.-P.; Polian, A.; Trofimenko, S.; Long, G. J. *Inorg. Chem.* **1997**, *36*, 5580.

(3) Reger, D. L. *Comments Inorg. Chem.* **1999**, *21*, 1.

(4) Kahn, O.; Martinez, J. *Science* **1998**, *279*, 44.

(5) (a) König, E. *Struct. Bonding* (Berlin) **1991**, *76*, 51. (b) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527.

10.1021/ic000721z CCC: \$19.00

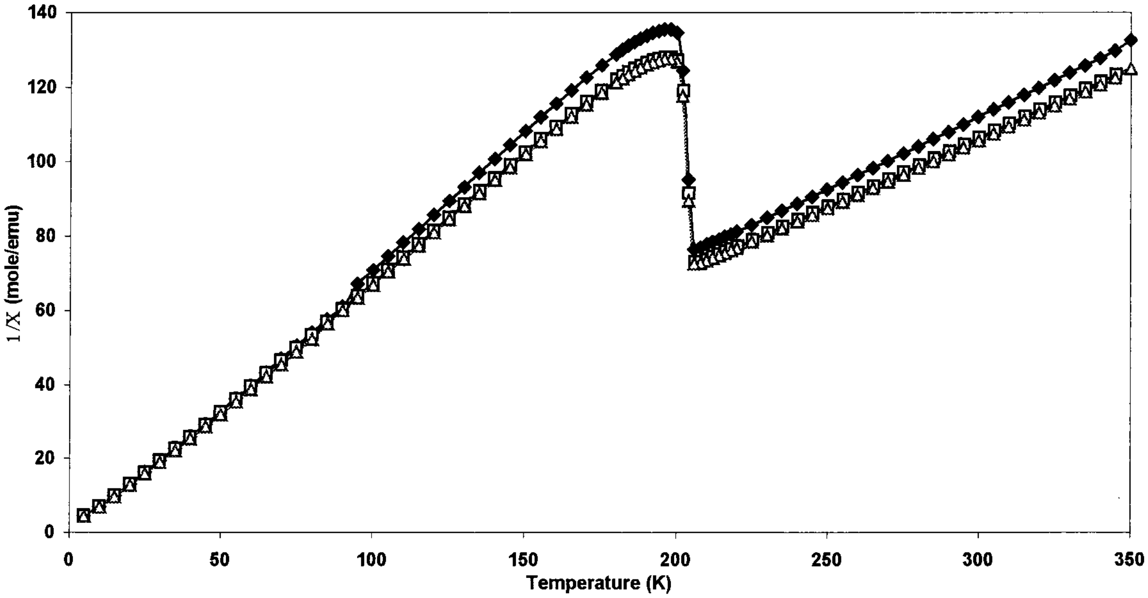


Figure 1. Magnetic data for $\{Fe[HC(3,5-Me_2pz)_3]_2\}(BF_4)_2$. Black diamonds (◆) mark the first cooling curve, squares (□) the first warming curve, and triangles (△) the second cooling curve. The last two curves are superimposed, and all three curves are superimposed below 80 K.

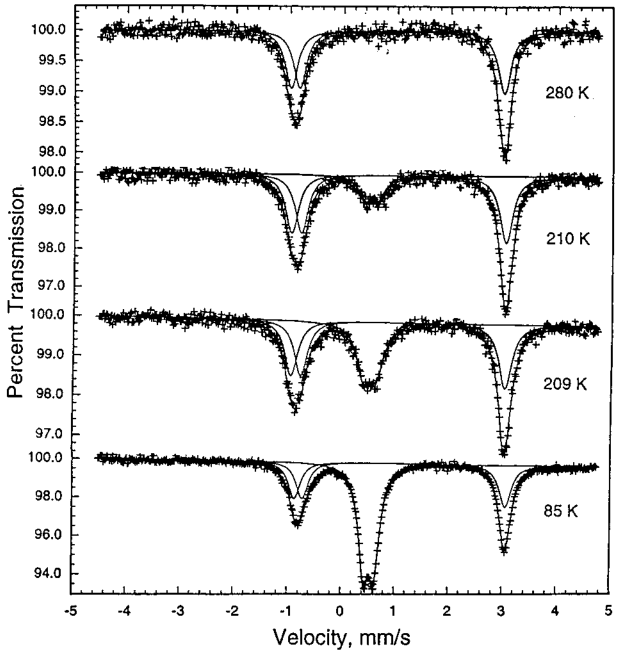


Figure 2. Mössbauer spectra of $\{Fe[HC(3,5-Me_2pz)_3]_2\}(BF_4)_2$ obtained at the indicated temperatures.

doublet, characteristic of LS octahedral N_6Fe(II) complexes,[1,2] is also observed. The spectra obtained at 210 and 209 K show dramatically how the LS component of the low-temperature spectra grows in very rapidly with a small change in temperature. Two doublets are still needed below this change to fit the high-spin iron(II) components of the spectra. The process reverses as the sample is rewarmed. The slight increase in magnetic moment noted in the magnetic studies at 90 K upon cooling the first time is observed by Mössbauer spectroscopy by a slight change in the quadrupole splitting of one of the two doublets of the HS component. We are presently studying this phenomenon in more detail.

The spin-state crossover in $\{Fe[HC(3,5-Me_2pz)_3]_2\}(BF_4)_2$ is superficially similar to that observed for $[Fe(1\text{-methyl-}1H\text{-tetrazole})_6](BF_4)_2$ in which only 50% of the iron(II) is converted to the LS state upon cooling.[6] However, in this complex there are two different iron sites and in Mössbauer spectral studies the disappearance of only one of the HS iron(II) doublets was observed, indicating that one site changes completely from HS to LS and the other remains HS. A number of two-step conversions have been reported in other complexes that contain two distinct iron sites.[1] For **1** the changes are clearly different from these cases; crystallographically there is only one iron site, and the two iron(II) sites observed by Mössbauer spectroscopy are present both above and below the spin-crossover temperature. A number of compounds exist that do not completely convert from high to low spin, but in these cases the percentages of "residual" HS at low temperatures are influenced by how the sample was prepared or handled.[1,7] A ground sample of **1** does undergoe the transition over a much broader temperature range (ca. 50 K), but the ground sample *has the same magnetic properties at high and low temperatures as the crystals.*

Recent review articles and texts list five types of spin-crossover behaviors.[1] The abrupt and reversible spin crossover of **1** below 206 K to yield a mixture of the HS and LS states, a mixture that does *not continue to change its composition as the temperature is lowered* below 200 K, is new for a complex that contains only one crystallographic iron site when it is fully HS and represents the sixth type of spin-crossover behavior.

Acknowledgment is made to the National Science Foundation (CHE-9727325 for D.L.R. and DMR-9521739 for G.J.L.) for support. We thank Professor Hanno zur Loye and Katharine Stitzer for assistance in obtaining the magnetic data.

Supporting Information Available: Synthesis and ORTEP diagram of cation (30% probability) in $\{Fe[HC(3,5-Me_2pz)_3]_2\}(BF_4)_2$ and an X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000721Z

---

(6) Poganiuch, P.; Decurtins, S.; Gütlich, P. *J. Am. Chem. Soc.* **1990**, *112*, 3270.

(7) (a) Müller, E. W.; Spiering, H.; Gütlich, P. *Chem. Phys. Lett.* **1982**, *93*, 567. (b) Müller, E. W.; Spiering, H.; Gütlich, P. *J. Phys. Chem.* **1983**, *79*, 1439. (c) Wei, H. H.; Jean, Y. C. *Chem. Phys. Lett.* **1984**, *106*, 523.