A High-Pressure Iron *K*-edge X-ray Absorption Spectral Study of the Spin-State Crossover in $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}I_2$ and $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$

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It is well known that many pseudooctahedral iron(II) compounds undergo a spin-state crossover from the high-spin to the low-spin electronic state either upon cooling[1-9] or upon the application of pressure.[10-12] Indeed, both low-temperature[6] and high-pressure[10,11] Mössbauer and X-ray absorption near edge structure spectral studies have shown that the iron(II) in $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$, where pz is the pyrazole ring, is completely converted from the high-spin state above ca. 195 K to the low-spin state below 195 K or upon the application of pressures above ca. 20 kbar.

In a similar fashion we have recently shown[9] that $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}I_2$, **1**, is completely converted from the high-spin to the low-spin state upon cooling, albeit with a rather large hysteresis upon heating and cooling, see Figure 1a. In contrast, only 50 percent of the crystallographically identical iron(II) sites in $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$, **2**, are converted from the high-spin to the low-spin state upon cooling; there is virtually no hysteresis.[7,8] Further, it has been shown[13] that the partial spin-state crossover in $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$ is accompanied by a crystallographic phase transition between 220 and 173 K to a structure with two crystallographically different iron(II) sites, one high-spin and one low-spin. This phase transition, which is also observed in $\{M[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$, where M is Co, Ni, and Cu, is believed[14] to be the driving force for the partial spin state crossover in $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$.

Because of the differences in the spin-state crossover behavior[8,9] shown in Figure 1, we have undertaken an X-ray absorption spectral study at the iron *K*-edge of $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}I_2$ and $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$ at high-pressures using an opposed diamond anvil cell on beam-line ID24. The sample, along with a small ruby chip, was placed in a Chervin-type membrane diamond anvil cell which was equipped with a stainless steel gasket and standard Drukker diamonds; silicone oil was used as a pressure transmitting medium in order to improve hydrostatic conditions on the sample. The pressure was determined from the pressure induced shift in the energy of the ruby fluorescence.

The iron(II) in $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}I_2$, undergoes the expected gradual spin-state crossover from the high-spin to the low-spin state with increasing pressure. In contrast, the iron(II) in $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$ remains high-spin between ambient and 78 kbar and is only transformed to the low-spin state at an applied pressure of between 78 and 94 kbar. No visible change is observed in the pre-edge peak in the spectra of $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}I_2$ upon increasing pressure, whereas the pre-edge peak in the spectra of $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$ changes as expected for a high-spin to low-spin crossover unpon increasing pressure. The difference in the spin-state crossover behavior of these two complexes is likely related to the unusual behavior of $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$ upon cooling.

We conclude that the crystalline arrangement of $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$ resists the change to low-spin, necessitating very high pressure to affect the spin-state crossover. We propose that the application of pressure may not change the spin state of any of the iron(II) in $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$ until the pressure has induced the same[13] or possibly a similar crystallographic phase transition at which point the applied pressure converts all the iron(II) to the low-spin state. Alternatively, it may be possible that only half of the iron(II) sites have been converted to the low-spin state, but this seems less likely because the shape of its spectrum at 94 kbar is virtually identical to that of $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}I_2$ at 88 kbar, a pressure at which all the iron(II) sites have undergone the spin-state crossover.

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References

(1) Gütlich, P. in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*; Long, G. J., Ed.; Plenum: New York, 1984; Vol. 1: p 287.

(2) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem. Int. Ed.* **1994**, *33*, 2024.

(3) Gütlich, P. *Structure and Bonding (Berlin)* **1981**, *44*, 83.

(4) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527; *Structure and Bonding (Berlin)* **1991**, *76*, 51.

(5) Gütlich, P.; Hauser, A. *Coord. Chem. Rev.* **1990**, *97*, 1.

(6) Grandjean, F.; Long, G. J.; Hutchinson, B. B.; Ohlhausen, L.; Neill, P.; Holcomb, J. D. *Inorg. Chem.* **1989**, *28*, 4406.

(7) Reger, D. L.; Little, C. A.; Rheingold, A. L.; Lam, M.; Concolino, T.; Mohan, A.; Long, G. J. *Inorg. Chem*. **2000**, *39*, 4674.

(8) Reger, D. L.; Little, C. A.; Rheingold, A. L.; Lam, M.; Liable-Sands, L. M.; Rhagitan, B.; Concolino, T.; Mohan, A.; Long, G. J.; Briois, V.; Grandjean, F. *Inorg. Chem.* **2001**, *40*, 1508.

(9) Reger, D. L.; Little, C. A.; Smith, M. D.; Rheingold, A. L.; Lam, K.-C.; Concolino, T. L.; Long, G. J.; Hermann, R. P.; Grandjean, F. *Eur. J. Inorg. Chem.* **2002**, 1190.

(10) Long, G. J.; Hutchinson, B. B. *Inorg. Chem.* **1987**, *26*, 608.

(11) Hannay, C.; Hubin-Franskin, M. J.; Grandjean, F.; Briois, V.; Itié, J. P.; Polian, A.; Trofimenko, S.; Long, G. J. *Inorg. Chem.* **1997**, *36*, 5580.

(12) Pebler, J. *Inorg. Chem.* **1983**, *22*, 4125.

(13) Reger, D. L.; Little, C. A.; Young, Jr., V. G.; Park, M. *Inorg. Chem*. **2001**, *40*, 2870.

(14) Reger, D. L.; Little, C. A.; Smith, M. D.; Long, G. J. *Inorg. Chem*. **2002**, *41*, 4453.

(15) C. Piquer, F. Grandjean, O. Mathon, S. Pascarelli, D. L. Reger, C. Little, and G. J. Long, *Inorg. Chem*., in press.