Inorg. Chem. **2003**, *42*, 982–985

Inorganic Chemistry

Article

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 $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$

Cristina Piquer and Fernande Grandjean

Institut de Physique, B5, Université de Liège, B-4000 Sart-Tilman, Belgium

Olivier Mathon and Sakura Pascarelli

European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France

Daniel L. Reger and Christine A. Little

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

Gary J. Long*

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

Received July 15, 2002

The room temperature iron K-edge X-ray absorption near edge structure spectra of $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}I_2$ and $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}(BF_4)_2$ have been measured between ambient and 88 and 94 kbar, respectively, in an opposed diamond anvil cell. 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 state 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 preedge peak in the spectra of $\{Fe[HC(3,5\text{-}(CH_3)_2pz)_3]_2\}I_2$ with increasing pressure, whereas the preedge 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 with 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.

Introduction

It is well-known that many pseudooctahedral iron(II) compounds undergo a spin-state crossover from the high-spin electronic state 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

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* Author to whom correspondence should be addressed. E-mail: glong@umr.edu.

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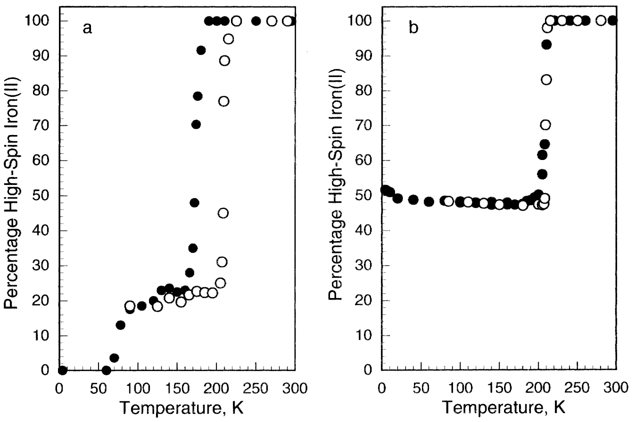

Figure 1. Temperature dependence of the percentage of high-spin iron(II) observed in **1** left, and **2**, right. The closed symbols correspond to values obtained upon cooling, and the open symbols correspond to values obtained upon subsequent heating. The left panel is adapted from ref 9, and the right panel is adapted from ref 8.

studies have shown that the iron(II) in $Fe[HB(3,5\text{-}(CH_3)_2\text{-}pz)_3]_2$, 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 state to the low-spin state upon cooling, albeit with a rather large hysteresis upon heating and cooling; see Figure 1a. In contrast, only 50% 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 state 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.

Experimental Section

The samples of **1** and **2** used in this study are the same samples as have been used in previous studies.[7−9]

The high-pressure X-ray absorption studies were carried out in an opposed diamond anvil cell on beam-line ID24[15] at the European Synchrotron Radiation Facility in Grenoble, France. This beam line uses parallel detection of the entire X-ray absorption spectrum through the use of energy dispersive highly focusing X-ray optics. The spectrometer is coupled to two low K undulators in a high β section of the synchrotron ring through a Kirkpatrick Baez optical system which permits operation between 5 and 27 keV. The optical system produces a stable X-ray beam of ca. 900 μm^2 area at the diamond anvil cell.[16,17] The spectrometer was calibrated with α-iron foil for which the maximum in the slope of the rising edge was taken as 7112 eV. All spectra reported herein are given relative to 7112 eV, and the energy resolution is 0.25 eV. The spectra were normalized at the maximum in the slope of the rising edge of the oscillation found at about 60−70 eV, i.e., at ca. 55 eV.

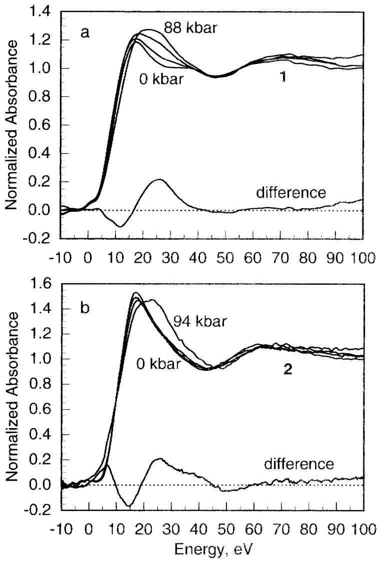

Figure 2. Normalized iron K-edge XANES spectra of **1**(a) obtained at 0, 40, 60, and 88 kbar and **2** (b) obtained at 0, 35, 78, and 94 kbar. The difference is a plot of the highest pressure absorption minus the ambient pressure absorption.

The sample, along with a small ruby chip, was placed in a Chervin-type membrane diamond anvil cell[18] which was equipped with a stainless steel gasket and standard Drukker diamonds; silicone oil was used as a pressure-transmitting medium to improve the hydrostatic conditions on the sample. The pressure was determined from the pressure-induced shift in the energy of the ruby fluorescence[19,20] and is accurate to ±4 kbar. All studies were carried out at room temperature.

Results and Discussion

The normalized iron K-edge X-ray absorption near edge structure spectra, the XANES spectra, of **1** and **2** are shown in Figure 2 as a function of increasing pressure.

A visual microscopic observation of **1** in the diamond anvil cell indicated that it was, as expected, white at ambient pressure and was gradually transformed to red at higher pressures. In contrast, the color of **2** remained essentially white from 0 to 78 kbar but was red at 94 kbar. In both compounds the color change was completely reversible upon the release of the pressure.

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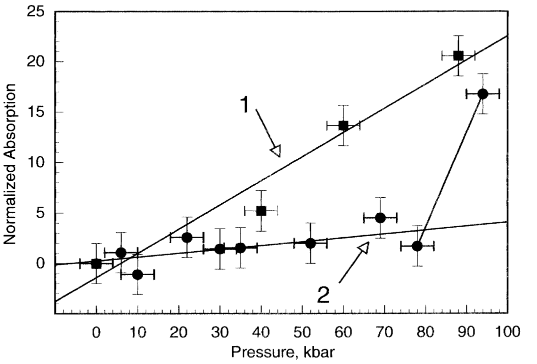

Figure 3. Percentage variation, relative to ambient pressure, of the normalized iron K-edge XANES absorption observed at 25 eV for **1** (■) and **2** (●) as a function of applied pressure.

The difference in the pressure dependence of the two compounds is clearly revealed in Figure 2. The changes observed in the shape of the XANES spectrum of **1** are rather typical of those observed[11] for other iron(II) compounds which gradually convert from the high-spin state to the low-spin state with increasing pressure. This change typically manifests itself as both a small gradual shift in the rising edge and in peak position to higher energies and an increase in the absorption at ca. 25 eV. The changes in the normalized absorption at 25 eV with increasing pressure are shown in Figure 3, a plot that clearly reveals the differences in the spin crossover for the two compounds.

From the changes shown in Figures 2 and 3, it is apparent that **1** is gradually and completely transformed from the high-spin state at ambient pressure to the low-spin state at 88 kbar. In contrast, the behavior of **2** is quite different in that little if any change in the XANES absorption is observed between ambient pressure and 78 kbar. But there is a dramatic change in the spectrum of **2** between 78 and 94 kbar, a change which presumably corresponds to a complete transformation of the iron(II) in **2** to the low-spin state at the higher pressure. This difference is most easily apparent in Figure 4, which shows the difference between **1** at 88 kbar and **2** at 78 kbar, Figure 4a, and 94 kbar, Figure 4b. In Figure 4a the difference between the low-spin **1** and the high-spin complex **2** is indicated by the shift of the XANES spectra of **1** at 88 kbar to higher energies, a difference which is typical of the different iron(II) spin states.[21] In Figure 4b, the major difference in the spectra of the two compounds, both of which are low-spin at these pressures, is the difference in absorbance, a difference which results either from a difference in sample thickness and/or a difference in scattering by the iodide anions as compared to the BF_4 anions.

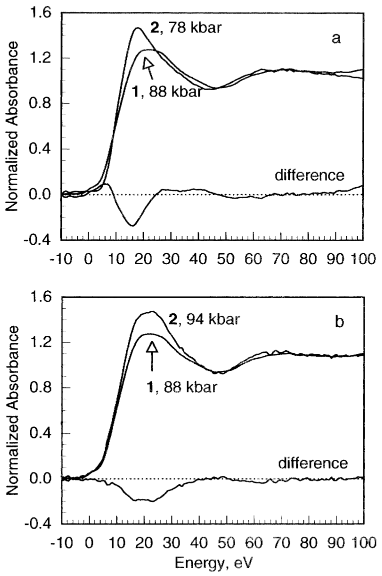

Figure 4. A comparison of the normalized iron K-edge XANES spectra of **1** and **2** at 88 and 78 kbar, respectively (a), and 88 and 94 kbar, respectively (b). In each case, the difference is a plot of the spectrum of **1** minus the spectrum of **2**.

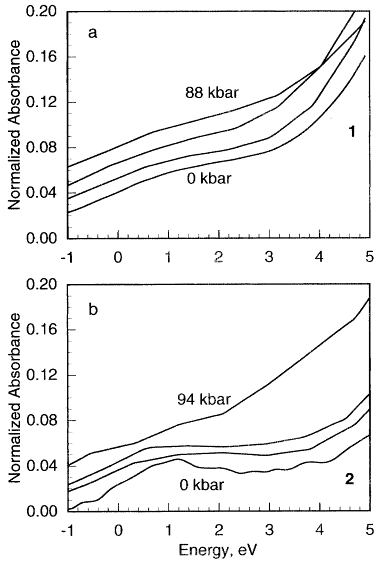

Figure 5. Preedge region of the iron K-edge XANES spectra of **1** (a) obtained at 0, 40, 60, and 88 kbar and **2** (b) obtained at 0, 35, 78, and 94 kbar.

In addition to the obvious increase in the absorption at ca. 20−30 eV with increasing pressure, a characteristic of the transformation of iron(II) from the high-spin state to the low-spin state, see Figures 2 and 4, there are other changes with increasing pressure that should be noted. All the spectra exhibit the so-called "preedge" peak between 0 and 3 eV, a peak that is assigned[22−24] to symmetry-forbidden electronic transitions from the 1*s* state to the 3*d* state. The changes occurring in the preedge region of **1** and **2** with increasing pressure are shown in parts a and b, respectively, of Figure 5. In **1**, there is no visible change with pressure, except perhaps a decrease in intensity in the preedge peak. In **2**, for pressures of less than 80 kbar, the preedge peak has a shape which is very similar to that observed[22] for the high-spin iron(II) complexes, particularly those observed[23] for [Fe(imidazole)$_6$]Cl_2 and [Fe(H_2O)$_6$][SiF_6]. Unfortunately, the energy resolution of 0.25 eV makes very difficult a

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comparable[22−24] and realistic decomposition of the preedge peak into three peaks covering an energy range of at most 4 eV. Further, the signal-to-noise ratio of the data achieved in the high-pressure cell is not as good as that obtained at 10 K in ref 23, and makes difficult, if not impossible, a more detailed analysis of the preedge peak. However, a change in the shape of the preedge peak is observed, see Figure 5, at 94 kbar, a change which is expected[23] to accompany a high-spin to low-spin transition. **2** shows two weak features at ca. 1.0 and 3.5 eV, features which are similar to those observed[23] in Fe[HB(pz)$_3$]$_2$. Further, in the 94 kbar spectrum of **2**, there is a clear shoulder that appears on the rising edge at ca. 8 eV. This shoulder is also found[11] in the XANES spectra of Fe[HB(3,5-(CH$_3$)$_2$pz)$_3$]$_2$ at higher pressures and in Fe[HB(pz)$_3$]$_2$ at 10 K.[23] Photoelectron multiple scattering calculations[21] have shown that this shoulder is related to the scattering by the first carbon near neighbors of the iron atom at a distance of 3.06 Å. For some unknown reason, a similar shoulder is not observed in the XANES spectra of **1** at higher pressures.

The differences in spin-state behavior with increasing pressure of **1**and **2** may be understood on the basis of their structural and electronic behavior upon cooling. As is apparent in Figure 1, **1** behaves like most iron(II) complexes with an N$_6$ coordination sphere and undergoes a complete spin-state crossover at ca. 180 K upon cooling,[9] although its spin-state crossover does show a substantial thermal hysteresis. In contrast, **2** exhibits[8] a partial but sharp spin-state crossover at ca. 210 K, a crossover that is accompanied by a reversible phase transition[13] in which the single high-spin iron(II) crystallographic site observed above 220 K is transformed into two iron(II) sites, one high-spin and one low-spin, at 173 K and below.

We conclude that the crystalline arrangement of **2** resists the change to the low-spin state, 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 **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) in **2** to the low-spin state. Alternatively, it may be possible that only half of the iron(II) sites in **2** 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 **1** at 88 kbar, a pressure at which all the iron(II) sites have undergone the spin-state crossover.

Acknowledgment. Beam time for this experiment was granted through ESRF peer review as experiment HE1294. We thank the technical and engineering staff of ID24 for valuable assistance in conducting the experimental work.

IC0204530