

A High Pressure *K*-edge X-ray Absorption Spectral Study of the Electronic Properties of  $\{M[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  with  $M = \text{Co}, \text{Ni},$  and  $\text{Cu}$

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It is well known that many pseudo-octahedral iron(II) and cobalt(II) compounds undergo a spin-state crossover from the high-spin to the low-spin electronic state either upon cooling<sup>1-9</sup> or upon the application of pressure.<sup>10-12</sup> Indeed, both low-temperature<sup>6</sup> and high-pressure<sup>10,11</sup> Mössbauer and X-ray absorption near edge structure spectral studies have shown that the iron(II) in  $\text{Fe}[\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2$ , 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 shown<sup>9</sup> that  $\{\text{Fe}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}\text{I}_2$ , **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  $\{\text{Fe}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$ , **2**, are converted from the high-spin to the low-spin state upon cooling; there is virtually no hysteresis.<sup>7,8</sup> Further, it has been shown<sup>13-15</sup> that the partial spin-state crossover in  $\{\text{Fe}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  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  $\{M[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$ , where  $M$  is Co, Ni, and Cu, is believed<sup>14</sup> to be the driving force for the partial spin state crossover in  $\{\text{Fe}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$ .

The goal of this project was to study by XANES the electronic properties of  $\{M[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$ , where  $M$  is Co, Ni, and Cu, and to determine whether high pressure would induce a spin-state crossover from the high-spin state to the low-spin state in  $\{\text{Co}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$ . Single crystal x-ray diffraction has shown<sup>14</sup> that  $\{\text{Co}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  does exhibit the same phase transition at low temperature that drives<sup>13</sup> the partial spin-state crossover in  $\{\text{Fe}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$ . In contrast, the magnetic properties of  $\{\text{Co}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  reveal no spin-state crossover upon cooling to 4.2 K.<sup>14</sup> Our earlier work<sup>10,11</sup> has shown that, in both iron(II) and cobalt(II), this spin-state crossover is more sensitive to applied pressure than to cooling.  $\{\text{Ni}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  was studied by XANES for comparison at high-pressure because it is known<sup>14</sup> to show the same crystallographic phase transition whereas the  $t_{2g}^6 e_g^2$  electronic configuration of nickel(II) prevents any electronic spin-state crossover.  $\{\text{Cu}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  was studied by XANES at high-pressure both because it is known<sup>14</sup> to show the same crystallographic phase transition and because the  $t_{2g}^6 e_g^3$  electronic configuration of copper(II) could easily show additional Jahn-Teller based distortions of the coordination environment at high-pressure.

The goal of this project has been substantially met<sup>16</sup> but the results have also shown the importance of parallel high-pressure x-ray diffraction studies. The XANES spectra of  $\{\text{Co}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  shows a shift to higher energy between 7 and 30 kbar - a shift that is almost surely associated with the same crystallographic phase transition that is observed upon cooling.<sup>14</sup> High-pressure x-ray diffraction studies will be required to confirm this conjecture, but it seems to be the most plausible explanation for the results. Upon applying pressures from 30 to 260 kbar there is virtually no further change in the XANES spectra and we thus conclude that  $\{\text{Co}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  does *not* show any pressure induced spin-state crossover from the high-spin to the low-spin state at least up to 260 kbar.

The XANES spectra of  $\{\text{Ni}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  indicate that its behaviour is very similar to that of  $\{\text{Co}[\text{HC}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  in that they show a shift to higher energy between 1 and 45 kbar, a shift that is associated with the phase transition, and virtually no change between 45 and

275 kbar. Thus, as expected,  $\{\text{Ni}[\text{HC}(\text{3,5}-(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  does show the crystallographic phase transition at low applied pressure and *no* spin-state change with applied pressure. The XANES spectral results for  $\{\text{Cu}[\text{HC}(\text{3,5}-(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$  are different in that in addition to the phase transition associated change between 11 and 50 kbar, there are gradual changes in the shape of the absorption between 50 and 228 kbar, changes that may correspond to a structural distortion of the copper(II) coordination environment.

We are currently in the process of using FEFF 8 and the single crystal x-ray structural results obtained<sup>13,14</sup> above and below the phase transition for  $\{M[\text{HC}(\text{3,5}-(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$ , where *M* is Fe, Co, Ni, and Cu, to model the changes expected in the multiple scattering at the phase transition. A manuscript reporting the experimental results and the multiple scattering calculations is currently in preparation for *Inorganic Chemistry* and should be submitted within a few weeks to months.<sup>16</sup> Further, we will soon request additional ESRF beam time to investigate the x-ray diffraction of  $\{M[\text{HC}(\text{3,5}-(\text{CH}_3)_2\text{pz})_3]_2\}(\text{BF}_4)_2$ , where *M* is Fe, Co, Ni, and Cu, at high pressure in order to confirm the presence of the pressure induced phase transition.

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