Proton-Mediated Electron Configuration Change in High-Spin Iron(II) Porphyrinates

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We report that deprotonating a coordinated imidazole to form the five-coordinate high-spin imidazolate-ligated Fe(II) porphyrinate leads to a change in the coordination geometry and a change in the electron configuration of iron. Two new five-coordinate, imidazolate-ligated Fe(II) porphyrinates, $K(222)[Fe(TPP)(2\text{-}MeIm^{-})]$ and $K(222)[Fe(OEP)(2\text{-}MeIm^{-})]$, have been synthesized with a sterically hindered imidazolate ligand. They have been characterized by X-ray crystallography and Mössbauer spec-troscopy.As shown in the figure, the bond distances in the five-membered rings show changes consistent with imidazolate versus imidazole. Imidazolate is a better σ donor, and forms a stronger axial Fe-N bond; the $Fe–N_{im}$ bond distances are ~0.09 Å shorter than those in imidazole-ligated complexes. At the same time, the average equatorial $Fe–N_p$ bond lengths and the iron atom displacements in imidazolate- ligated complexes are both larger than those in imidazole-ligated complexes by 0.036 and 0.20 Å, respectively. Mössbauer spectra in applied magnetic field show that the imidazolate derivatives have quadrupole splittings that are large and positive (greater than +3.5 mm/s) whereas the imidazoles have quadrupole splitting that are negative and smaller (about 2.0-2.4 mm/s). These data are consistent with the imidazolate derivatives having the *d*-electron configuration $(d_{xz})^1(d_{yz})^1(d_{xy})^2(d_{x2-y2})^1(d_{z2})^1$, whereas the imidazaole derivatives have the *d*-electron configuration $(d_{xz})^2(d_{xy})^1(d_{yz})^1 (d_{x2-y2})^1(d_{z2})^1$. Supported by NIH GM-38401.