Proton-Mediated Electron Configuration Change in

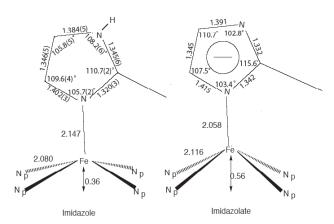
High-Spin Iron(II) Porphyrinates

<u>Chuanjiang Hu¹</u>, Bruce C. Noll¹, Charles E. Schulz², and W. Robert Scheidt¹

¹University of Notre Dame, Department of Chemistry and Biochemistry and ²Knox College, Department of Physics, Knox College

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-MeIm⁻)] and K(222)[Fe(OEP)(2-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 imidazole derivatives have the *d*-electron configuration $(d_{xz})^2(d_{xy})^1(d_{yz})^1(d_{yz})^1(d_{z2})^1$. Supported by NIH GM-38401.