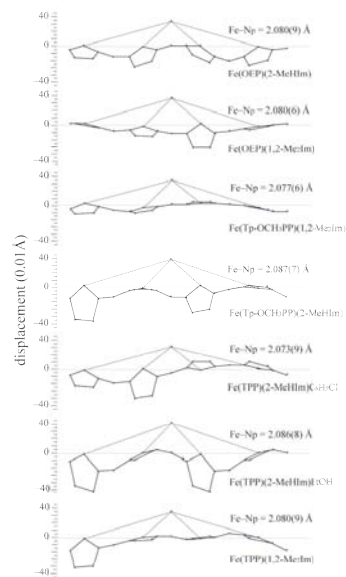


Study of High-Spin Hindered Imidazole Iron(II) Porphyrinate Complexes. W. Robert Scheidt,^a Chuanjiang Hu,^a Arne Roth,^a Mary K. Ellison,^a Jin An,^a Charles E. Schulz,^b ^aUniv. of Notre Dame, Dept. of Chemistry & Biochemistry, Notre Dame, IN, 46556, scheidt.1@nd.edu, hu@nd.edu, ^b Knox College, Dept. of Physics, Knox College, Galesburg, IL 61401.

Five new deoxymyoglobin models have been synthesized with three different porphyrin ligands (H₂OEP, octaethylporphyrin; H₂TPP, tetraphenylporphyrin; H₂Tp-OCH₃PP, tetra-*p*-methoxy-phenylporphyrin) and two different sterically hindered imidazole ligands. They are all characterized by x-ray crystallography, Mössbauer spectra and NRVS vibrational studies. All of these iron(II) complexes are high spin. The average Fe-N_p bond lengths are ~2.08 Å for each compound, Fe-N_{im} bond distances are between 2.12 and 2.16 Å. All the iron atom displacements out of the porphyrin plane are ~0.4 Å which are compatible with those in deoxyhemoglobin. However, the observed core conformations for seven known five-coordinated high-spin Fe(II) complexes show wide variation that in the displacements of the 24 atoms out of the four pyrrole nitrogen atom plane. The dihedral angle between the imidazole plane and Fe-N_p vector is 45° for [Fe(Tp-OCH₃PP)(2-MeH-Im)], 10° for [Fe(OEP)(1,2-Me₂Im)], and about 20° for other three complexes. Quadrupole splitting (ΔE_Q) values range between 1.97 and 2.43 mm/s; Isomer shifts (δ_{Fe}) are between 0.92 and 0.95 mm/s at 4.2 K. Mössbauer data are able to definitively assign the ground state electronic configuration for these high spin species. Nuclear Resonance Vibrational Spectroscopy (NRVS) studies include both powders and oriented single-crystal measurements and provide detailed, highly selective vibrational dynamics for iron.



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