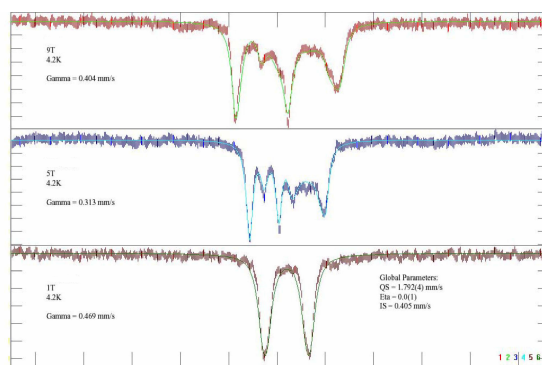
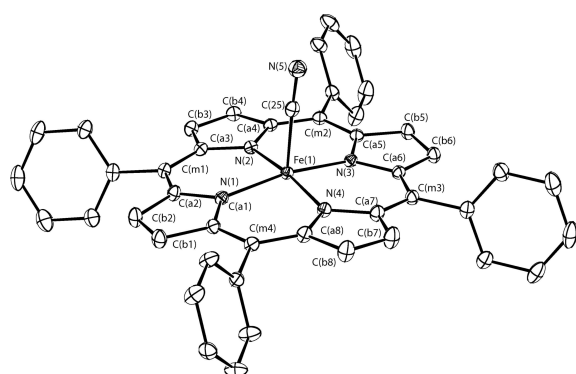


First Five- and Six-Coordinate Cyanoiron(II) Porphyrinates

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The synthesis and structural characterization of the five- and six-coordinate low-spin cyanoiron(II) tetraphenylporphyrinates [K(222)][Fe(II)(TPP)(CN)] and [K(222)][Fe(II)(TPP)(CN)(1-Melm)] are reported. The 100 K structure of [K(222)][Fe(II)(TPP)(CN)] is that expected for a low-spin (porphinato)iron(II) species with an average Fe–N_p bond distance of 1.985 (7) Å, an axial distance of Fe–C = 1.8779 (12) Å and iron displacement $\Delta_{\text{Fe}} = 0.23$ Å. This structure is compared with the previously reported structure of low-spin [Fe(II)(OEP)(CS)]. The structure of [K(222)][Fe(II)(TPP)(CN)(1-Melm)] shows Fe–N_p bond distance of 1.989 (4) Å, axial distances of Fe–C = 1.929 (3) Å and Fe–N_L = 2.050(2) Å, and iron displacement, $\Delta_{\text{Fe}} = 0.04$ Å. These results make for interesting comparisons with the six-coordinate analogues [Fe(II)(OEP)(CS)(1-Melm)], [Fe(II)(TPP)(CO)(1-Melm)] and [Fe(III)(TPP)(CN)(1-Melm)]. Mössbauer data for [K(222)][Fe(II)(TPP)(CN)] were obtained at 4.2 K in a magnetic field (1, 5, and 9 Tesla) indicating a diamagnetic ground state of the central iron. Support by NIH GM-38401.



ORTEP diagram of [K(222)][Fe(II)(TPP)(CN)], cation is omitted for clarity and Mössbauer spectra of [K(222)][Fe(II)(TPP)(CN)] at 4.2 K and applied magnetic field of 1, 5, and 9 Tesla.