

Cyanide: A Strong-Field Ligand for Ferrohemes and Hemoproteins?*

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In memory of Gary Scheidt

Cyanide ion, a versatile diatomic ligand, has been extensively investigated as both a classic inhibitor and as a ligand for exploring properties of hemes and hemoproteins. Unlike CO and O₂, which bind only to iron(II) species, CN⁻ can bind to both iron(II) and iron(III) hemoproteins. Stable low-spin (LS) iron(III) proteins can be straightforwardly prepared.^[1–3] In contrast, (cyano)iron(II) hemoproteins are usually indirectly formed by reduction of (cyano)iron(III) proteins. Cyanide-bound iron(II) forms of myoglobin,^[4] hemoglobin,^[5] horseradish peroxidase,^[6] and a number of cytochrome oxidase derivatives^[7] are known. Many, but not all, of the iron(II) species have lower binding constants than the iron(III) analogues. The equilibrium constant for cyanide binding for iron(III) hemoproteins is often greater than or equal to 10⁵ M⁻¹, compared to not more than 10² M⁻¹ for iron(II) species.^[3]

Since we reported the first isolation of a (cyano)heme species in 1980,^[8] a number of electronic- and geometric-structure issues have been brought forward.^[9] All of the known species are LS iron(III) derivatives, either bis(cyano) [Fe^{III}(Por)(CN)₂]⁻ or mixed-ligand [Fe^{III}(Por)(CN)(L)] complexes (Por = porphyrin).^[9] However, there are no reported (cyano)iron(II) porphyrinate derivatives, presumably because this framework is known to have a lower stability and lower affinity for CN⁻ than iron(III). It might be thought that (cyano)iron(II) species would be preferred, since a filled d⁶ shell should form strong π bonds to the π-accepting cyanide ligand.

We now report the first (cyano)iron(II) porphyrinate species, five-coordinate [K(222)][Fe(tpp)(CN)] (Figure 1, tpp = tetraphenylporphinato, 222 = Kryptofix 222). The average equatorial Fe–N_p bond length (1.986(7) Å) and the axial Fe–C bond length (1.8783(10) Å) are consistent with a

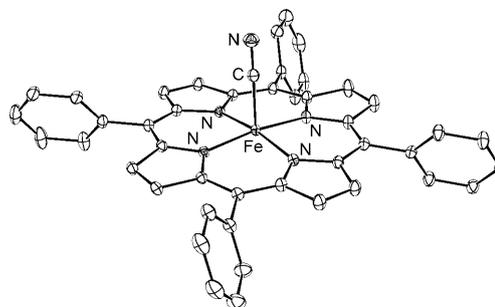


Figure 1. 100 K ORTEP diagram of [Fe(tpp)(CN)]⁻. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms omitted for clarity.

LS state.^[10] However, temperature-dependent Mössbauer spectra reveal a more complicated picture of the iron spin state. A single quadrupole doublet is observed, whose value decreases from 1.827 mm s⁻¹ at 25 K to 0.85 mm s⁻¹ at 300 K; the isomer shift varies between 0.37 to 0.47 mm s⁻¹. The most probable explanation for these data is that a thermally induced spin crossover is occurring, and that interconversion between the two spin states is rapid on the Mössbauer time scale (less than 10⁻⁸ s).^[11a] This interpretation has been confirmed by both DFT calculations and magnetic susceptibility measurements.

The magnetic susceptibility of [K(222)][Fe(tpp)(CN)] was investigated over the temperature range of 2–400 K. Figure 2 shows the product of the molar susceptibility (χ_M; corrected for temperature-independent paramagnetism (TIP)) and temperature (T) in an external magnetic field of 2 T, which provides direct evidence for an S = 0 (LS) ⇌ S = 2 (high-spin,

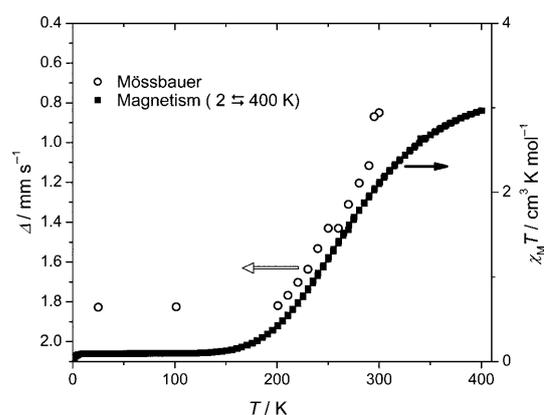


Figure 2. χ_MT versus T for [K(222)][Fe(tpp)(CN)] at 2 T applied field. The Mössbauer quadrupole splitting values are also presented for comparison.

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- [19] We have also synthesized and characterized six-coordinate cyanoferrporphyrinates; all are LS.

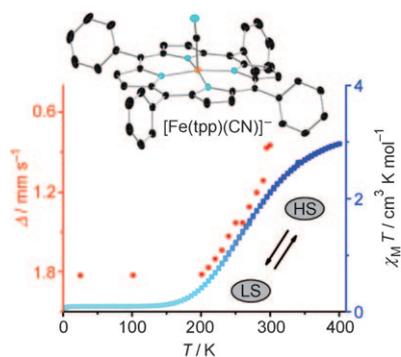
Communications



Spin Crossover

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A CN weakling? The cyanide ligand in the five-coordinate iron(II) porphyrinate complex $[\text{Fe}(\text{tpp})(\text{CN})]^-$ (tpp = tetraphenylporphyrinato) is not a sufficiently strong-field ligand to cause the complex to be in the low-spin state under all conditions. Rather, the complex displays a reversible low-spin to high-spin crossover with no hysteresis.