MCD spectra of ferrous CPO and P-450-CAM adducts with isocyanides are presented in Fig. 2. While very similar overall, some spectral differences are observed, especially in the more intense visible region MCD features of the CPO adduct. The MCD spectra of the ferrous NO and ferric KCN derivatives of CPO and P-450-CAM are displayed in Fig. 3. As has been observed for native ferric, ferrous and ferrous-CO CPO and P-450-CAM [4], the MCD spectral features of the NO or KCN adducts of both enzymes are similar except for some minor intensity and line shape differences.

In contrast to the above spectral similarities observed between analogous CPO and P-450-CAM derivatives, we have observed significant differences between the two enzymes in the spin state distribution of certain ferric ligand adducts. Although most anionic ligands listed in Table I and some neutral ligands (pyridine, isocyanide, imidazole and NO) form exclusively low spin complexes with ferric CPO, the adducts with other ligands such as neutral sulfur donors are instead a mixture of high and low spin. In addition, formate (low spin) and acetate (mixed spin) behave differently even though both are carboxylate anions at pH 6. Finally, among the heme ligands studied, only fluoride forms a high spin complex with ferric CPO. These diverse spin state properties of the ferric CPO·ligand complexes stand in contrast to the uniformly low spin nature of all ferric P-450-CAM ligand complexes [10].

In conclusion, the hyperporphyrin spectra that are observed for the complex obtained through ligation of a strongly acidic thiol to ferric CPO provide compelling evidence for the presence of an endogenous thiolate ligand to the heme iron of the *ferric* enzyme. The additional spectral similarities observed between analogous ligand complexes of CPO and P-450-CAM add further support to this conclusion for both the ferric and ferrous CPO cases. However, since ligand complexes of P-450-CAM and thiolate-ligated heme models are exclusively low spin, the spin state distribution distinctions seen between some weak field ligand complexes of ferric CPO and P-450 suggests that the heme-iron: thiolate-sulfur interaction in chloroperoxidase is somewhat different from that in P-450 and model complexes. Additional work is in progress to try to identify the cause of these differences.

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Q20

Electron Transfer at Crystallographically Known Long Distances (25 Å) in [Zn^{II}, Fe^{III}] Hybrid Hemoglobin

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In [Zn, Fe] hybrid hemoglobins, a zinc protoporphyrin (ZnP) and heme are held rigidly at known orientation, with Zn–Fe distance of 25 Å in the functional α_1-β_2 electron transfer entity. Room temperature electron transfer from flash photolytically generated ^{3}ZnP to the partner aquoferriheme occurs with rate, $k_t = 60 \pm 25\ s^{-1}$. Oxidation of ferroheme by the partner $(ZnP)^+$ π-cation radical occurs with rate $k_e = 3.3(\pm 0.7) \times 10^3\ s^{-1}$.

Q21

Gold-induced Spin-state Changes in Haem Proteins

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During the course of our work on anti-arthritic gold drugs, we discovered that Et_3PAuCl converted