PF-Fe^{II}PhCN, 104423-75-8; [a-PF-Fe^I]⁻, 90857-60-6; [a-PF-Fe^0]$^{2-}$, 90838-25-8; e-(C12)₂-AC-Fe^{III}Cl, 104486-31-9; e-(C12)₂-AC-Fe^{II}, 104486-36-4; e-(C12)₂-AC-Fe^{II}DMF, 104486-27-3; e-(C12)₂-AC-Fe^{II}N-MA, 104423-65-6; e-(C12)₂-AC-Fe^{II}PhCN, 104423-72-5; e-(C12)₂-AC-Fe^{II}PrCN, 104423-79-2; [e-(C12)₂-AC-Fe^I]⁻, 90838-01-0; [e-(C12)₂-AC-Fe^0]$^{2-}$, 104486-30-8; e-(C12)₂-AT-Fe^{III}Cl, 104486-32-0; e-(C12)₂-AT-Fe^{II}DMF, 90898-40-1; e-(C12)₂-AT-Fe^{II}NMA, 104486-33-1; e-(C12)₂-AT-Fe^{II}PhCN, 104486-35-3; e-(C12)₂-AT-Fe^{II}PrCN, 104423-80-5; [e-(C12)₂-AT-Fe^I]⁻, 104486-29-5; [e-(C12)₂-AT-Fe^0]$^{2-}$, 90898-39-8; e-(C12)₂-CT-Fe^{III}Cl, 79198-03-1; e-(C12)₂-CT-Fe^{II}, 70196-65-5; e-(C12)₂-CT-Fe^{II}DMF, 90838-10-1; e-(C12)₂-CT-Fe^{II}NMA, 104423-66-7; e-(C12)₂-CT-Fe^{II}PhCN, 104438-55-3; e-(C12)₂-CT-Fe^{II}PrCN, 104423-81-6; [e-(C12)₂-CT-Fe^I]⁻, 79209-91-9; [e-(C12)₂-CT-Fe^0]$^{2-}$, 90838-06-5; e-(diC₄Ph)₂-CT-Fe^{III}Cl, 83460-51-9; e-(diC₄Ph)₂-CT-Fe^{III}OH, 104423-88-3; e-(diC₄Ph)₂-CT-Fe^{II}DMF, 90838-11-2; e-(diC₄Ph)₂-CT-Fe^{II}NMA, 104423-67-8; e-(diC₄Ph)₂-CT-Fe^{II}PhCN, 104423-73-6; e-(diC₄Ph)₂-CT-Fe^{II}PrCN, 104423-82-7; [e-(diC₄Ph)₂-CT-Fe^I]⁻, 90838-03-2; [e-(diC₄Ph)₂-CT-Fe^0]$^{2-}$, 90838-07-6; a-(C12)₂-AC-Fe^{III}Cl, 104486-26-2; a-(C12)₂-AC-Fe^{II}, 104423-86-1; a-(C12)₂-AC-Fe^{II}DMF, 90898-43-4; a-(C12)₂-AC-Fe^{II}NMA, 104423-70-3; a-(C12)₂-AC-Fe^{II}PhCN, 104423-76-9; a-(C12)₂-AC-Fe^{II}PrCN, 104527-26-6; [a-(C12)₂-AC-Fe^I]⁻, 90898-44-5; [a-(C12)₂-AC-Fe^0]$^{2-}$, 90898-45-6; a-(C12)₂-AT-Fe^{III}Cl, 90838-13-4; a-(C12)₂-AT-Fe^{II}DMF, 90838-18-9; a-(C12)₂-AT-Fe^{II}NMA, 104486-34-2; a-(C12)₂-AT-Fe^{II}PhCN, 104423-77-0; a-(C12)₂-AT-Fe^{II}PrCN, 104423-84-9; [a-(C12)₂-AT-Fe^I]⁻, 104423-57-6; [a-(C12)₂-AT-Fe^0]$^{2-}$, 90838-24-7; a-(C12)₂-CT-Fe^{III}Cl, 90838-12-3; a-(C12)₂-CT-Fe^{II}, 93646-94-7; a-(C12)₂-CT-Fe^{II}DMF, 90838-17-8; a-(C12)₂-CT-Fe^{II}NMA, 104438-54-2; a-(C12)₂-CT-Fe^{II}PhCN, 104438-56-4; a-(C12)₂-CT-Fe^{II}PrCN, 104438-57-5; [a-(C12)₂-CT-Fe^I]⁻, 90838-20-3; [a-(C12)₂-CT-Fe^0]$^{2-}$, 90838-23-6; a-(diC₄Ph)₂-CT-Fe^{II}Cl, 104423-60-1; a-(diC₄Ph)₂-CT-Fe^{III}OH, 104423-87-2; a-(diC₄Ph)₂-CT-Fe^{II}DMF, 104423-56-5; a-(diC₄Ph)₂-CT-Fe^{II}N-MA, 104423-71-4; a-(diC₄Ph)₂-CT-Fe^{II}PhCN, 104423-78-1; a-(diC₄Ph)₂-CT-Fe^{II}PrCN, 104423-85-0; [a-(diC₄Ph)₂-CT-Fe^I]⁻, 104423-58-7; [a-(diC₄Ph)₂-CT-Fe^0]$^{2-}$, 104423-59-8; Cl⁻, 1112-67-0; NBu₄ClO₄, 1923-70-2; LiClO₄, 7791-03-9.

Notes

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Iron–Sulfur Bond Lengths in Ferrous–CO Heme Complexes as a Function of Sulfur Donor Type

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The structural characterization of iron coordination is of considerable importance in understanding the mechanism of action of heme iron enzymes. To that end, metalloporphyrin complexes have been used extensively as both structural and functional models for heme proteins since their ligand composition can be more easily varied than that of the proteins they are intended to mimic.

The role of sulfur donor ligation in the function of heme proteins is incompletely understood at present. For example, both cytochrome P-450 (P-450)[2,3] and secondary amine monooxygenase[4] catalyze reduced pyridine nucleotide- and O₂-dependent N-dealkylation reactions but have different axial heme ligands (cysteinate and histidine, respectively). In contrast, the spectroscopic similarities between P-450 and chloroperoxidase have suggested an identical heme coordination structure for the two enzymes (pentacoordinate, cysteinate ligated),[5] despite their functional differences (monooxygenase and peroxidase, respectively).

To date, only a very small number of sulfur-donor-ligated ferrous porphyrins have been structurally defined. Weiss and co-workers[6,7] have used X-ray crystallography to investigate penta- and hexacoordinate ferrous porphyrin thiolate complexes, with CO and O₂ trans to thiolate in the latter case. For ferrous porphyrin complexes containing neutral sulfur donors, only the hexacoordinate bis(thioether),[8] thioether/imidazole,[8] and thioether/O₂[9] adducts have been structurally characterized. No such investigations of ferrous porphyrin complexes containing a dialkyl disulfide axial ligand have appeared; neither have the previously reported hexacoordinate thiol/CO[10,11] and thioether/CO[11] complexes been structurally defined. The present report substantially increases this database of Fe(II)–S bond distances to include ferrous porphyrin adducts having thiol, thioether, and disulfide ligands trans to CO. All three of these sulfur donor types represent potential axial ligands in biological systems. The Fe(II)–S bond length has been found to vary systematically as a function of the sulfur donor type.

The method we have employed for this structural analysis of sulfur-ligated heme complexes is extended X-ray absorption fine structure (EXAFS) spectroscopy, a technique that has been previously shown to accurately probe the iron coordination environment of heme proteins and metalloporphyrins.[12] The EXAFS spectra contain local structural information about the type, number, and distance of atoms surrounding the absorbing Fe atom. These spectra can be collected on solutions in a short time and provide accurate metrical details. In contrast, protein crystallographic studies require good single crystals and the diffraction data analysis and refinement are lengthy processes. A limitation of the EXAFS technique is its inability to discriminate between atoms adjacent in the periodic table (e.g. C, N, O) due to their similar backscattering properties; however, this is not a problem in sulfur-ligated heme complexes since the contributions of the axial sulfur (S$_{ax}$) and porphyrin pyrrole and axial ligand nitrogens

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(3) Abbreviations: DMA, *N,N*-dimethylacetamide; EtS⁻, ethanethiolate; EXAFS, extended X-ray absorption fine structure; L$_{ax}$, axial ligand; MeSSMe, dimethyl disulfide; *N*, the number of ligand atoms; N$_{ax}$, axial nitrogen donor; N$_p$, porphyrin pyrrole nitrogen; OEP, octaethylporphyrinato; P-450, cytochrome P-450; PrS⁻, propanethiolate; PrSH, propanethiol; S$_{ax}$, axial sulfur donor; THT, tetrahydrothiophene; TpivPP, *meso*-tetrakis(α,α,α,α-*o*-pivalamidophenyl)porphyrinato; TPP, *meso*-tetraphenylporphyrinato; TPP(C5Im), imidazole-tailed TPP; TTP, *meso*-tetra-*p*-tolylporphyrinato.

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Table I. Structural Comparisons of Various Sulfur-Donor-Ligated Ferrous Porphyrin Complexes and Heme Proteins

complex[a]	Fe–N$_p$		Fe–S$_{ax}$		ref
	R,[b] Å	N[c]	R, Å	N	
Five-Coordinate: Thiolate					
FeOEP(SPr)$^{-d}$	2.05	3.8	2.33	0.4[e]	this work
FeTPP(SEt)$^{-f}$	2.096	4	2.360	1	6
Fe^{2+}P-450-CAM^d	2.08	3.0	2.34[g]	0.6	13
Six-Coordinate: Thiolate/π-Acceptor					
FeOEP(SPr)(CO)$^{-d}$	2.00	4.4	2.33	0.2[e]	this work
FeTTP(SEt)(CO)$^{-f}$	1.993	4	2.352, 2.388	1	6, 7
Fe^{2+}P-450-CAM + CO^d	1.98	3.3	2.32	1.0	13
FeTpivPP(SC$_6$HF$_4$)(O$_2$)$^{-f}$	1.990	4	2.369	1	7
Six-Coordinate: Non-Thiolate/π-Acceptor					
FeOEP(PrSH)(CO)^d	2.01	5.1	2.41	0.8	this work
FeOEP(THT)(CO)^d	2.00	5.2	2.41	0.4[e]	this work
FeTpivPP(THT)(O$_2$)^h	1.99–2.00	4	2.49	1	9
FeOEP(MeSSMe)(CO)^d	2.03	5.9[i]	2.40	0.7	this work
Six-Coordinate: Non-Thiolate/Non-π-Acceptor					
FeTPP(THT)$_2^f$	1.996	4	2.336	2	8
FeTPP(C5Im)(THT)^f	1.99	4	2.31	1	8

^{a} Abbreviations are explained in text footnote 3. ^{b} Bond length (in angstroms). ^{c} Number of atoms at the distance indicated. ^{d} On the basis of EXAFS measurements; bond distance uncertainties are 0.02 Å. ^{e} All samples measured in this work were examined in solution. Analysis of solution data using paremeters derived from the solid-state EXAFS of structurally defined model complexes may result in low values for $N(S_{ax})$ due to Debye–Waller effects. ^{f} On the basis of crystal structure; bond distance uncertainties range from 0.003 to 0.010 Å. ^{g} Best fit to filtered EXAFS data. Fe–S$_{ax}$ = 2.38 Å when unfiltered EXAFS data were analyzed. ^{h} "Semiquantitative" structural analysis of X-ray crystal data. ^{i} The unexpectedly large value of $N(N_{ax})$ may be the result of significant contributions from the carbon of the bound CO to the pyrrole nitrogen EXAFS.

(N_p, N_{ax}) to the observed EXAFS are readily distinguishable.[5d,13,14]

Experimental Section

Solvents and ligands (Aldrich) were purified before use according to literature methods.[15] The potassium salt of propanethiolate was prepared as previously described.[16] Dibenzo-18-crown-6 cyclic polyether (Aldrich) and (octaethylporphyrinato)iron(III) chloride [Fe^{3+}OEP(Cl)] (Aldrich) were used without further purification.

FeOEP(CO)(X),[17] where X = PrSH or THT,[3] was prepared by the reduction of Fe^{3+}OEP(Cl) dissolved in neat ligand with aqueous dithionite[18] in the presence of CO gas.[10] FeOEP(CO) was prepared in a similar manner using toluene or 20% DMA in toluene as the solvent. FeOEP(MeSSMe)(CO) was prepared by the addition of neat MeSSMe to a toluene solution of FeOEP(CO) until no further spectral changes were noted. These complexes were distinct from either FeOEP(CO), FeOEP(X), FeOEP(X)$_2$, or Fe^{3+}OEP(Cl), as judged by their electronic absorption spectra.[16,19] FeOEP(SPr)$^-$ was obtained by using a modification[19] of the method described by Chang and Dolphin.[16] FeOEP-(SPr)(CO)$^-$ was prepared by bubbling a solution of FeOEP(SPr)$^-$ with CO gas.[16] All samples were 2–8 mM in FeOEP.

Due to their extreme O$_2$ sensitivity, the preparation and handling of all complexes were done in an inert-atmosphere box (Vacuum Atmospheres), in a glovebag, or with glassware that was grease-sealed and glass-stoppered to exclude O$_2$. Electronic absorption spectral measurements were obtained on a Cary 210 or Cary 219 spectrophotometer (Varian). Samples were prepared in South Carolina and shipped to California in flame-sealed glass tubes stored on dry ice. All X-ray absorption data were collected at the Stanford Synchrotron Radiation Laboratory as fluorescence excitation spectra[20,21] on beam lines II-2 or VII-3 using a Si[220] double-crystal monochromator. The storage ring was operated at 3.0 GeV and 35–60 mA. Analysis of the data was performed as previously reported.[12,22]

Results and Discussion

The curve-fitting results for Fourier-filtered first-shell data fits of various sulfur donor-ligated ferrous porphyrin model complexes are given in Table I. This EXAFS data analysis will give an accuracy of approximately ±0.02 Å in distance determination and 25–35% in coordination number determination.[12,22] Although some values of N, the number of ligand atoms in a given shell, for S$_{ax}$ are small (Table I), the contribution of S$_{ax}$ is significant for the following reason: In the process of curve-fitting analysis, the function value F (which is χ^2 and measures the goodness of fit compared to the experimental data) decreases significantly after including the Fe–S$_{ax}$ shell into the fits. The improvement is between 60 and 80% for all the cases reported.

EXAFS analysis of the pentacoordinate FeOEP(SPr)$^-$ and hexacoordinate FeOEP(SPr)(CO)$^-$ complexes in solution (Table I) showed that the Fe–S$_{ax}$ distance (2.33 Å) remained constant, whereas the Fe–N$_p$ distance decreased from 2.05 to 2.00 Å upon CO ligation, as expected for the change in coordination number.[23] This result is in good agreement with previous X-ray crystallographic results of analogous TPP-type adducts.[6] A similar trend was seen by Collman and co-workers[24] in the case of FeTpivPP-(2-methylimidazole), where the Fe–N$_{ax}$ bond length did not differ appreciably in the presence and absence of ligated O$_2$ (2.107 and 2.095 Å, respectively).

In contrast, changing the axial ligand from thiolate to thiol in the hexacoordinate CO-bound ferrous porphyrin complexes caused a distinct increase in the Fe–S$_{ax}$ distance from 2.33 to 2.41 Å (Table I) but did not affect the Fe–N$_p$ bond length. Such a large increase in the Fe–S$_{ax}$ bond length (0.08 Å) upon protonation of bound thiolate indicates that the orbital interaction between heme iron and thiolate sulfur atoms is more extensive. Iterative extended Hückel calculations have demonstrated that the d$_\pi$ orbitals of CO-bound heme iron are perturbed to a greater extent by thiolate than by thiol trans to CO.[25] It is the interaction of

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the p† orbitals of thiolate sulfur with the a$_{2u}(\pi)$ orbital of the ferrous porphyrin that is believed to cause the unique spectral characteristics of the CO-ligated adduct.[25] The shortening of the Fe–S$_{ax}$ bond upon deprotonation of the ligated thiol can also be explained by electrostatic considerations.

The other hexacoordinate complexes, FeOEP(THT)(CO) and FeOEP(MeSSMe)(CO), serve as models for methionine and cystine axial ligation in heme proteins and are structurally characterized for the first time herein. The structural properties of both complexes are similar to those of FeOEP(PrSH)(CO) and distinct from those of FeOEP(SPr)(CO)$^-$. Also, only one of the structurally equivalent sulfur atoms in the disulfide-containing complex was found to be bound to the iron. These observations are not altogether unexpected since the sulfur atoms in PrSH, THT, and MeSSMe are all uncharged, are presumably sp^3-hybridized, and are poor π-donors; thus, their bonding to FeOEP-(CO) should be similar. The Fe–S$_{ax}$ distance in the THT-ligated ferrous porphyrin with CO as the trans ligand is somewhat longer than those of the analogous complexes in which imidazole (2.31 Å)[8] and THT (2.336 Å)[8] are trans. This can be explained by the greater interaction of the d$_\pi$ orbitals of the iron with CO (π-acceptor) than with either imidazole or THT (σ-donors), thus reducing the electron density in the iron-to-trans ligand bond. A similar lengthening of the Fe–L$_{ax}$ bond trans to a π-acceptor has been noted upon replacement of 1-methylimidazole[26] with O$_2$[24] in Fe(porphyrin)(1-methylimidazole)(L) and piperidine[27] for NO[28] in Fe(porphyrin)(piperidine)(L) complexes.[29]

These results suggest the existence of two distinct structural categories for sulfur-donor-ligated, hexacoordinate Fe(porphyrin)(RSY)(CO) complexes (R is an alkyl moiety). When the Y group is H, R, or SR (thiol-like), the ligated sulfur is present as an uncharged σ-donor ligand, resulting in a Fe–S$_{ax}$ distance of 2.40 Å or greater. When the Y group is absent (thiolate), the ligated sulfur is present as an anionic π-donor ligand that is able to more extensively interact with the molecular orbitals of the iron, causing a Fe–S$_{ax}$ bond length contraction to ~2.33 Å. These results are of particular importance in the structural analysis of sulfur-donor-ligated heme proteins. In the past, it was not possible to use EXAFS to distinguish the kind of sulfur ligand bound to ferrous iron, only its distance and number. With the present findings, assignment of the nature of the axial ligand trans to CO as being either thiolate or thiol-like can be made with greater certainty. In the case of the CO adduct of P-450, axial ligation by a sulfur donor other than cysteinate can be completely ruled out on the basis of its Fe–S$_{ax}$ distance, thus confirming the previous conclusion from spectral data.[11] Identification of the sulfur donor in heme proteins such as cytochrome c$_1$[31] and hemoprotein H-450,[32] which have been proposed to contain sulfur donor axial ligands, should now be possible on the basis of EXAFS measurements of their ferrous–CO adducts.[33] Inspection of the data

for ferrous–O$_2$ complexes[7,9] (Table I) reveals a similar difference of ~0.1 Å in the Fe–S$_{ax}$ bond distance for thiolate and non-thiolate (thioether) sulfur donors.[34]

In summary, the length of the Fe–S$_{ax}$ bond trans to CO in hexacoordinate Fe^{2+}OEP(CO)(sulfur donor) complexes has been found to fall into two distinct groups (2.33 and 2.40–2.41 Å) depending on the nature of the sulfur donor (thiolate and non-thiolate, respectively). The Fe(II)–S$_{ax}$ distances in the thiol-, thioether-, and disulfide-ligated ferrous–CO complexes (models for cysteine, methionine, and cystine ligation, respectively) are significantly longer (up to 0.10 Å) than those in other sulfur-donor-containing ferrous porphyrin complexes, with the exception of a thioether/O$_2$ ferrous porphyrin;[9] the Fe(II)–S bond length depends on either the protonation state (thiolate vs. thiol-like) of the sulfur donor or the trans axial ligand (CO or O$_2$ vs. imidazole and thioether). These results substantially expand the database of Fe(II)–S$_{ax}$ bond lengths in ferrous porphyrin complexes. Identification of sulfur donor ligands as either thiolate or non-thiolate in ferrous-CO heme protein complexes using Fe(II)–S$_{ax}$ distances determined from EXAFS analysis can now be accomplished with greater certainty.

(34) Note added in proof: The ferrous–dioxygen adducts of cytochrome P-450-CAM and of chloroperoxidase have been structurally characterized for the first time by using EXAFS spectroscopy (Dawson, J. H.; Kau, L.-S.; Penner-Hahn, J. E.; Sono, M.; Eble, K. S.; Bruce, G. B.; Hager, L. P.; Hodgson, K. O. *J. Am. Chem. Soc.*, in press). Both contain an axial sulfur atom trans to dioxygen with an Fe–S bond length of 2.37 Å and have Fe–N$_p$ bond distances of 2.00 Å; these values are extremely similar to those reported by Weiss and co-workers for a thiolate/O$_2$-ligated ferrous heme model complex (Table I).

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(33) The complexes studied herein are structurally unconstrained. Assuming that the strain on axial bond lengths in heme proteins is less than 0.04 Å (see ref 24b), the proposed distinction of sulfur donor types based on EXAFS measurements should be feasible.

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1,12-Bis(hydroxymethyl)decahydrododecaborate(2−) and B$_{12}$H$_{10}$(CH$_2$X)$_2$$^{2-}$ and B$_{12}$H$_{10}$(CH$_2$L)$_2$ Derivatives

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Carbonyl-substituted *closo* polyhedral boranes with B$_{10}$ and B$_{12}$ cages are important classes of derivatives capable of transformation to cyanide, amide, keto, ester, amine, etc. functions.[1] Only the perchloro B$_{10}$ dicarbonyl, however, has been reduced to the hy-

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