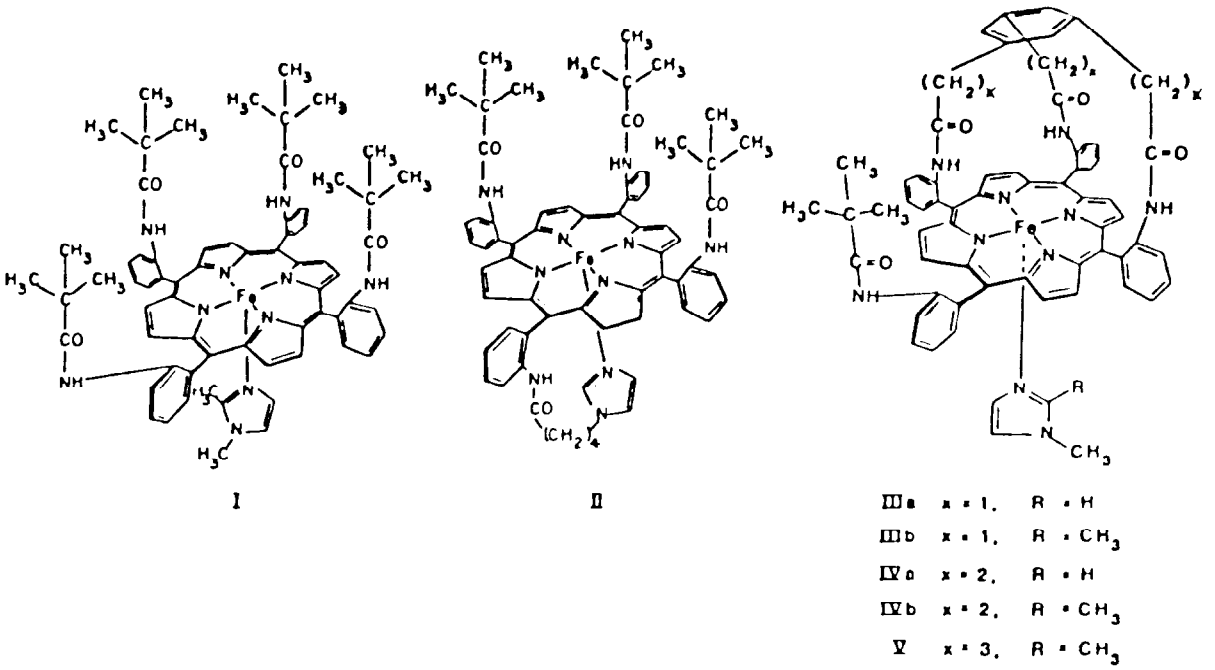

Fig. 1. Five-coordinate iron(II) porphyrins: FeTpivP(1,2-Me_2Im), *I*; $FePiv_3$5ClIm, *II*; FePocPiv(1-MeIm), *IIIa*; FePocPiv(1,2-Me_2Im), *IIIb*; FeMedPoc(1-MeIm), *IVa*; FeMedPoc(1,2-Me_2Im), *IVb*; FeTalPoc(1,2-Me_2Im), *V*.

TABLE I. O_2 and CO Binding to Iron Porphyrins and Hemoproteins[a,b].

	k_B^{CO} (M^{-1} s^{-1})	$P_{1/2}^{CO}$ (torr)	$k_B^{O_2}$ (M^{-1} s^{-1})	$P_{1/2}^{O_2}$ (torr)
Mb[c] [0.1 *M* KPi]	$3-5 \times 10^5$	0.014–0.025	$1-2 \times 10^7$	0.37–1
HbA, R state[c] [0.05–0.1 *M* KPi]	4.6×10^6	0.0014	3.3×10^7	0.22[d], 0.36[e]
HbA, T state[c] [0.1 *M* KPi]	2.2×10^5	0.30	2.9×10^6 [d] 1.2×10^7 [e]	40[d], 140[e]
$FePiv_3$5ClIm (*II*)[f]	3.6×10^7	2.2×10^{-5}	4.3×10^8	0.58
FeMedPoc(1-MeIm) (*IVa*)[f]	1.5×10^6	6.5×10^{-4}	1.7×10^7	0.36[g]
FePocPiv(1-MeIm) (*IIIa*)[f]	5.8×10^5	1.5×10^{-3}	2.2×10^6	0.36
FeTpivP(1,2-Me_2Im) (*I*)[f]	1.4×10^6	8.9×10^{-3}	1.1×10^8	38
FeTalPoc(1,2-Me_2Im) (*V*)[f]		1.1×10^{-3}	7.4×10^8	4
FeMedPoc(1,2-Me_2Im) (*IVb*)[f]	2.1×10^5	0.026	5.2×10^6	12.4
FePocPiv(1,2-Me_2Im) (*IIIb*)[f]	9.8×10^4	0.067	1.9×10^6	12.6

[a]Errors $\leq$ 15%, unless otherwise indicated. [b]For original literature citations see references 1a and 1c. [c]Aqueous, pH 7.0–7.4, 20 °C. [d]Value for α chain. [e]Value for β chain. [f]Toluene, 25 °C. [g]±20% error.

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Redox Potentials of 1Fe- and 4Fe-Ferredoxin Model Complexes of Cysteine-Containing Peptides in Micelle

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Active centers of iron–sulfur proteins and rubredoxin are surrounded with cysteine thiolates and peptide bonds in a hydrophobic environment, where specific interactions, such as NH···S hydrogen

bonds, exist between Fe–S cores and peptide bonds. The active site of rubredoxin consists of one iron and two specific sequences, Cys–X–Y–Cys, as shown in Fig. 1. Thus, Z–Cys–Thr–Val–Cys–OMe and

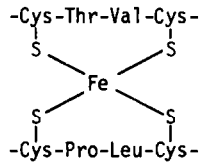

Fig. 1. Active site of rubredoxin.

Z–Cys–Pro–Leu–Cys–OMe were synthesized. Z–Cys–Ala–Ala–Cys–OMe was also examined as a chelating ligand for reference. A dipeptide, Z–Ala–Cys–OMe, was examined as non-chelating peptide. 1Fe and Fe_4S_4 complexes of t-Boc-(Gly–Cys–Gly)$_4NH_2$ were reported by Rydon [1] and Holm [2], respectively. However, the -Gly–Gly- sequence between the two Cys residues is not preferable for turn conformation which is essential for chelation and for formation of the NH···S hydrogen bonds. We reported that Fe(III)/Z–Cys–Ala–Ala–Cys–OMe is a good spectral model of rubredoxin in Me_2SO [3].

The electrochemical properties of 1Fe and Fe_4S_4 complexes are important in aqueous solutions. The redox potentials of ferredoxins are influenced by the core as well as the surrounding environments. In native proteins, the core is non-polar and surrounded by polar aqueous environments. Therefore, we examined these model complexes spectrally and electrochemically in micelle by using 2–10% solutions of Triton X-100. The redox potential values obtainable by cyclic voltammogram in micelle are compared with the values of native rubredoxin or iron–sulfur proteins in aqueous solution.

Fe(II)/Z–Cys–Pro–Leu–Cys–OMe (1:2) complex in aqueous micelle exhibited CD extrema at 309 nm ($\Delta\epsilon$: −24.2) and 332 nm ($\Delta\epsilon$: 10.9), similar to those of reduced rubredoxin [4]. A redox couple of Fe(II)/Fe(III) was observed for Fe(II)/Z–Cys–Pro–Leu–Cys–OMe (1:2) at −0.37 V(SCE) in aqueous micelle, which is very close to −0.30 V(SCE) reported for rubredoxin. Such a positive shift was observed for the first time in synthetic model complexes of rubredoxin. No redox couple was found for Fe(II)/Z–Cys–Thr–Val–OMe (1:2) or Fe(II)/Z–Cys–Ala–Ala–Cys–OMe (1:2) in aqueous micelle, whereas Fe(II)/Z–Ala–Cys–OMe (1:4) decomposed gradually in micelle. Observation of the redox couple of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ [5] at −0.64 V(SCE) in aqueous micelle reveals that the redox potentials of the Fe(II) complexes having two specific peptide ligands (Cys–X–Y–Cys) shift extraordinarily to the positive side.

CD and visible spectra of Fe_4S_4-type complexes of Cys-containing peptides, Z–Cys–Gly–OMe, Z–Cys–Gly–Ala–OMe, and Z–Cys–Gly–Ala–Cys–OMe, in aqueous micelle were found to be very similar to native 4Fe4S proteins. These complexes provided redox couples (2 − /3 −) except for the Fe_4S_4 complex of Z–Cys–Gly–OMe.

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Resonance Raman Studies of Models for the Reduced States of Cytochrome P_{450}

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The catalytic cycle of cytochrome P_{450} includes four stable states: a low spin ferric resting state A, a substrate bound high spin ferric state B, a high spin ferrous state C and a low spin ferrous oxy state D. When the system in state C is exposed to carbon monoxide instead of oxygen a low spin ferrous carboxy state D′ is generated. Several models have been proposed for states B, C, D′ and recently state D [1]. A large variety of spectroscopic techniques have been used to probe the similarities between the model compounds and the actual enzymatic states.

Resonance Raman spectroscopy (RR) is a very sensitive technique to investigate specifically the active site of hemoproteins. RR spectra have been obtained for Cyt P_{450} from various origins [2–4]: when compared to those of other hemoproteins, the frequencies of the so-called 'oxidation state' marker band [5] are unusually low in states C and D′; 'spin marker bands' frequencies [5] have been used to monitor the coordination of the iron atom in the ferric states A and B. Recently the Fe–S stretching mode has been detected at 351 cm^{-1} in oxidized Cyt $P_{450\ CAM}$ [6].

We report here the results of a RR study of $[Fe^{II}(T_{piv}PP)(X^-)(L)]$18C6Na$^+$* complexes, as models

*Abbreviations used: $T_{piv}PP$ = dianion of tetra kis (O-pivaloylamido)phenylporphyrin; TPP = dianion of tetraphenyl porphyrin; 2-MeIm = 2 methyl imidazole; py = pyridine.