$$^3\overline{AQH\cdot\cdot S} \rightarrow {}^1\overline{AQH\cdot\cdot S} \rightarrow AQH\text{-}S \quad (3)$$

$$^3\overline{AQH\cdot\cdot S} \rightarrow AQH\cdot + \cdot S \quad (4)$$

$$^3\overline{AQH\cdot\cdot S} + O_2 \rightarrow AQ + \cdot S + HO_2\cdot \quad (5)$$

$$AQH\cdot + O_2 \rightarrow AQ + HO_2\cdot \quad (6)$$

$$DPBF + HO_2\cdot \rightarrow \rightarrow DBB \quad (7)$$

Upon photoirradiation of AQ in a micelle, the excited triplet state of AQ ($^3$AQ) abstracts a hydrogen atom from a dodecyl sulfate anion (HS) to give the triplet pair ($^3\overline{AQH\cdot\cdot S}$) of AQH· and dodecyl sulfate radical (·S). The intersystem crossing (isc) to the singlet pair ($^1\overline{AQH\cdot\cdot S}$) and dissociation of the triplet pair to free radicals occur competitively. The singlet pair may react to give covalent product (AQH-S).[8] The AQH· radical in the triplet pair and the AQH· free radical in water may react with oxygen to form the $HO_2$· radical. The $HO_2$· radicals generated in the micelle may escape into the water phase. Finally, these $HO_2$· radicals may attack DPBF solubilized in another micelle,[9] resulting in the formation of DBB as a stable photoproduct.[10,11] The MF effect shown in Figure 2 is mostly interpreted in terms of the radical pair model of CIDNP,[12,13] where the AQH· radical (an initiator of oxidation) concentration is affected by the magnetic field. At zero field, all triplet sublevels ($T_+$, $T_0$, and $T_-$) in the triplet radical pair undergo electron–nuclear hyperfine-induced isc to the singlet state (S). In a weak magnetic field, the isc of only $T_0$–S and $T_-$–S may occur because of the Zeeman splitting of triplet sublevels as described in the previous paper.[8a] This change of the isc rate results in the enhancement of the AQH· radical yield and the reduction of $\phi$ of AQ. Actually, the MF-induced increase of the triplet radical pair lifetime and of the AQH· free radical concentration was already reported in laser flash photolysis.[8a] The decrease of the $Q$ value of AQ is in parallel with the previous observation.[8b]

The triplet excited state of AQ does not seem to be involved in the present oxidation because of its short lifetime (≲30–40 ns). Although the excited triplet state of pyrene sensitizes the oxidation of DPBF in SDS micellar solution,[5] no MF effect was observed. The addition of a singlet oxygen scavenger, $NaN_3$ ($9 \times 10^{-3}$ M) into the AQ–DPBF micellar solution does not cause a reduction of $\phi$ of DPBF but actually a slight increase. No heavy water effect on $\phi$ was observed, though the lifetime of the singlet oxygen was reported to be very sensitive to heavy water substitution.[14] No superoxide generation was detected in the photolysis of the aerated SDS micellar solution of AQ ($1 \times 10^{-4}$ M) containing nitro blue tetrazolium ($3 \times 10^{-5}$ M).[15] These facts suggest that neither the singlet oxygen nor the superoxide enters the present oxidation mechanism. Furthermore, benzophenone was also used as the initiator of the DPBF oxidation, since the photochemistry and its MF dependence are similar to those of AQ:[16,17] Benzophenone-photosensitized oxidation of DPBF in SDS micellar solution does show a MF effect as expected (the $Q$ value of DPBF is 60% at 2.6 kG). This fact also supports the present mechanism. Since the oxidation of DPBF by radical initiators was already reported,[10,11] the present observation is attributable to a remarkable magnetic field effect on the radical initiation reaction.

An exceptionally large MF-induced change was reported on the dibenzyl ketone photosensitized emulsion polymerization of styrene:[18] The average polymer molecular weight increases about 400% at magnetic field of 1–10 kG due to the MF-induced concentration change of benzyl radical, a polymerization initiator. The present MF effect is comparable with that of the styrene polymerization. The present result clearly demonstrates the importance of the magnetic field for controlling photochemical processes.

**Acknowledgment.** We are grateful to Professor T. Tsuchiya and Dr. J. Kurita, Hokuriku University, for their suggestion on the product analysis and to S. Shima for experimental assistance.

**Registry No.** DPBF, 5471-63-6; AQ, 84-65-1; SDS, 151-21-3.

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## Low-Spin Five-Coordinate Ferric Porphyrin Complex: [5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrinato](hydrosulfido)iron(III)

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*Received June 18, 1984*

Recent studies have indicated that the heme center in cytochrome P-450 has an axial thiolate ligand in the resting state,[1] and this ligand appears to remain coordinated during at least part of the reaction cycle.[2] Correspondence of various spectroscopic properties of chloroperoxidase (CPO) with those of cytochrome P-450 has led to the proposal that the heme environment in these enzymes is similar.[1,3] These proposals have been strengthened by the finding that only model systems that contain thiolate axial ligation are able to mimic[3,4] the unique spectral properties of cytochrome P-450 and CPO. To date, synthetic ferric porphyrins with a single axial thiolate ligand are all high spin;[5-7] addition of a Lewis base is necessary to convert the iron atom to the

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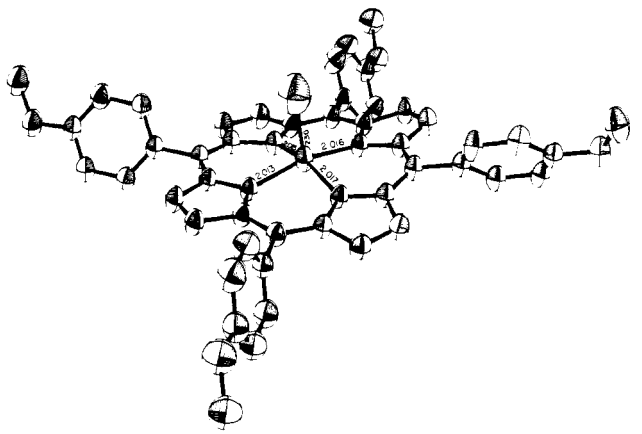


**Figure 1.** Computer-produced model in perspective (50% ellipsoids) of the Fe(TAP)SH molecule. The individual S–Fe–N(1–4) angles are, respectively, are 100.8 (1)°, 99.5 (1)°, 100.4 (1)°, and 97.3 (1)°.

low-spin state.[5-7] We wish to report the isolation and characterization of a ferric porphyrin complex with a hydrosulfido ($SH^-$) axial ligand. This compound contains an iron(III) ion that is low spin while being only five-coordinate, and it therefore represents a new class of iron porphyrin complexes.

A solution containing primarily $Li_2S$ was prepared from 1 equiv of sulfur and 2 equiv of $LiB(C_2H_5)_3H$ in THF.[8,9] Addition of an excess of this solution to Fe(TAP)Cl in dry 1,1,2-trichloroethane under nitrogen results in the formation of a new species, Fe(TAP)SH.[10,11] The optical spectrum of Fe(TAP)SH in $CH_2Cl_2$ has maxima at 412, 523, and 612 nm with extinction coefficients of $1.2 \times 10^5$; $1.3 \times 10^4$, and $2 \times 10^3$ $M^{-1}$ $cm^{-1}$, respecitvely. It is extremely oxygen sensitive in solution; exposure to dry $O_2$ results in immediate formation of $(Fe(TAP))_2O$. Addition of a Lewis base, B (e.g., 1-methylimidazole), to Fe(TAP)SH causes immediate conversion to $Fe(TAP)(B)_2$. Fe(TAP)SH slowly decomposes over a period of days to four-coordinate FeTAP in solvents such as benzene and toluene. It is stable in air for days as a dry solid.

Fe(TAP)SH in the solid state has a magnetic moment corresponding to a $S = {}^1/_2$ system.[12] A toluene glass of Fe(TAP)SH is EPR silent at 77 K, but a spectrum with a sharp feature centered at $g = 3.9$ and a broad feature at $g = 1.74$ is seen at 4 K. This spectrum is similar to those seen for "atypical low-spin ferriheme complexes".[13] The Mossbauer spectrum of Fe(TAP)SH at 141 K consists of a single doublet with an isomer shift of 0.30 mm/s and a quadrupole splitting of 2.05 mm/s. The room-temperature $^1H$ NMR spectrum[14] shows the pyrrole resonance at −18.7 ppm vs. $Me_4Si$. These data are consistent with a monomeric low-spin ferric center.[15]

The $^1H$ NMR resonance of the sulfur-bound proton occurs at 6.75 ppm. This peak is not seen when the compound is synthesized with $LiB(Et)_3D$. Splitting of the ortho and meta resonances[14] is consistent with five-coordination in the complex. The infrared spectrum, taken as a CsI pellet or a Nujol mull, of Fe(TAP)SH is virtually identical with that of Fe(TAP)Cl except for the lack of the Fe–Cl stretch at 350 $cm^{-1}$; no bands due to Fe–S or S–H vibrations are seen.[16]

The stereochemistry of Fe(TAP)SH has been confirmed by a single-crystal X-ray analysis.[17,18] The structure is shown in Figure 1. The average $Fe-N_{por}$ distance of 2.015 (2) Å is consistent with low-spin iron(III) (the typical $Fe-N_{por}$ distance for high-spin ferric porphyins is 2.06 (1) Å).[19] The Fe–S distance of 2.298 (3) Å and the Fe out-of-plane distance of 0.33 Å are slightly shorter than those of high-spin ferric thiolate porphyrin complexes.[5b,6a]

The Mossbauer spectrum of Fe(TAP)SH splits into a six-line pattern in the presence of external magnetic fields of 10 and 60 kG, at 10 K. Simulation of this pattern reveals that the effective magnetic field felt at the iron nucleus is about 500 kG. This is a large effective field for a low-spin ferric system and suggests a substantial orbital contribution to the paramagnetism of the system. This is confirmed by a magnetic moment,[12] which is significantly above the spin-only value at all temperatures and by the EPR spectrum, which has highly anisotropic $g$ values.

As mentioned previously, chloroperoxidase exhibits properties that suggest thiolate ligation in the resting state. Chemical studies have indicated that the two cysteine residues in chloroperoxidase are bonded together as a disulfide,[20a] although this result has been questioned.[3] Fe(TAP)SH presents a plausible alternative to cysteinate ligation in which exogenous sulfur plays a role in the axial ligation of the heme site, a possibility that has been speculated upon before.[20b] Further spectroscopic studies of Fe(TAP)SH and other derivatives are in progress to investigate their relation to sulfur-ligated heme proteins.

**Acknowledgment.** We thank Michelle Cohn for helpful discussions regarding simulation of Mossbauer spectra. This research was supported by the National Institutes of Health (Grants PHS-2R01-HL13652 to D.N.H., PHS-2R01-HL25934 to K.S.S., and PHS-2R01-HL15627 to W.R.S.).

**Supplementary Material Available:** Table I, atomic coordinates, Table II, anisotropic temperature factors, Table III, bond distance and angles for Fe(TAP)SH, and Figure 1, stereodiagram of the unit cell (7 pages). Ordering information is given on any current masthead page.

(8) Abbreviations used: THF, tetrahydrofuran; TAP, 5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrinato(2−); $Me_4Si$, tetramethylsilane; EPR, electron paramagnetic resonance.

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(11) The reaction sequence leading to the formation of Fe(TAP)SH is not fully understood at present. When a solution prepared from 1 equiv of sulfur and 2 equiv of $LiB(C_2H_5)_3H$ is added to 2 equiv of Fe(TAP)Cl in dry 1,1,2-trichloroethane under nitrogen, it results in quantitative reduction of the iron porphyrin to the ferrous complex. In the presence of excess of this reagent, the reduction is not observed, and only Fe(TAP)SH is formed. Fe(TAP)SD is produced (confirmed by NMR) when the "$Li_2S$" solution is prepared from $LiB(C_2H_5)_3D$. Thus, the source of the sulfur-bound hydrogen is the reducing agent. LiSH or trace adventitous water may be playing a role in determining the ultimate product. It was initially expected that this synthetic route would yield the putative $\mu$-S(FeTAP)$_2$; we have not, however, observed this species.

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