studies related to donor–acceptor interactions and to the possibility of two simultaneous single-electron transfer events.
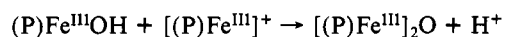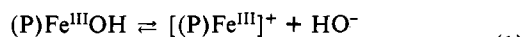
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1H NMR Investigation of Iron(III) 5,10,15,20-Tetrakis(2,6-disubstituted phenyl)porphyrins. Isolation and Characterization of Hydroxy-Ligated (5,10,15,20-Tetrakis(2,6-difluorophenyl)porphinato)iron(III)

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Reaction of iron(III) porphyrins with HO⁻ results in the formation of μ-oxo dimer species. Kinetic studies have shown that hydroxy ligation is a first step in the formation of the μ-oxo dimer. The sequence of reactions of eq 1 have been suggested (where (P)

$$(P)Fe^{III}OH \rightleftharpoons [(P)Fe^{III}]^+ + HO^-$$
$$(P)Fe^{III}OH + [(P)Fe^{III}]^+ \rightarrow [(P)Fe^{III}]_2O + H^+ \tag{1}$$

= porphyrin dianion).[1] Several reports of the characterization of hydroxy-ligated iron(III) porphyrins have recently appeared.[2-5] Success in their preparation is dependent upon the use of porphyrins carrying bulky substituents that prevent face to face approach of the porphyrin rings. This has been accomplished with iron(III) ligated by (i) a "basket-handle" porphyrin,[5] (ii) a "picket fence" porphyrin,[3] and (iii) 5,10,15,20-tetraphenylporphyrins carrying bulky substituents in the 2,6-positions of the phenyl rings.[2]

We now wish to report the preparation and the characterization of hydroxide-ligated (5,10,15,20-tetrakis(2,6-difluorophenyl)-porphinato)iron(III) ((F₈TPP)Fe^III OH) as well as ¹H NMR studies of various HO⁻ and Cl⁻-ligated (5,10,15,20-tetrakis(2,6-disubstituted phenyl)porphinato)iron(III) salts.
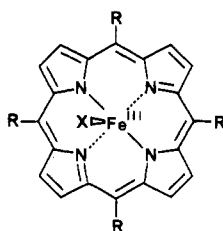
R	structural abbreviation
phenyl	(TPP)Fe^III X
2,6-dimethylphenyl	(Me₈TPP)Fe^III X
2,4,6-trimethylphenyl	(Me₁₂TPP)Fe^III X
2,6-dichlorophenyl	(Cl₈TPP)Fe^III X
2,6-difluorophenyl	(F₈TPP)Fe^III X
pentafluorophenyl	(F₂₀TPP)Fe^III X

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Table I. ¹H NMR Spectral Positions of Iron(III) Porphyrin Complexes (Solvent CD₂Cl₂; Reference Me₄Si at 25 °C)

	δ					
compd	pyrrole	meta	para	ortho	OH^{a,b}	ref
(F₈TPP)Fe^III Cl	81.1 (358 ± 9)^d	13.9 / 12.6	7.5			c
(F₈TPP)Fe^III OH	81.0 (831 ± 6)	10.6 / 11.5	7.6		23.8	c
(Cl₈TPP)Fe^III Cl	80.7 (380 ± 9)	12.8 / 14.1	8.3			c
(Cl₈TPP)Fe^III OH	80.6 (702 ± 6)	10.8 / 11.4	8.1		23.2	c
(Me₈TPP)Fe^III Cl	80.0 (365 ± 8)	15.8 / 14.2	8.2	3.8^b / 6.6^b		c
(Me₈TPP)Fe^III OH	81.1 (809 ± 9)	12.1 / 11.3	8.0	2.8^b	24.9	c
(Me₁₂TPP)Fe^III OH	79.2 (535 ± 25)	11.1 / 12.0	3.3			2

^a Tentatively assigned to OH group. ^b Broad signal. ^c This work. ^d Line width at half-height in hertz.

The (F₈TPP)Fe^III OH salt is of particular interest because of the small steric demands of the fluoro substituent.

Experimental Section

Materials. Pyrrole, 2,4,6-collidine, 2,6-dichlorobenzaldehyde, and 2,6-difluorobenzaldehyde were purchased from Aldrich. Pyrrole and 2,4,6-collidine were purified by vacuum distillation. 2,6-Dimethylbenzaldehyde was purchased from Chemical Services, Inc., Hanover, NJ. Solvents used in all studies were AR grade. Neutral alumina, activity grade 1, type WN-3 was used in all chromatographic studies. 5,10,15,20-Tetrakis(2,6-dimethylphenyl)porphyrin (1), 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (2), and 5,10,15,20-tetrakis(2,6-difluorophenyl)porphyrin (3) were synthesized by the Rothemund method[6] using 2,4,6-collidine instead of pyridine, followed by demetalation of the intermediate zinc(II) complexes in concentrated HCl. The substantial amount of chlorin was converted to the free-base porphyrin by refluxing with 2,3-dichloro-5,6-dicyano-4-benzoquinone in toluene.[7] The purification of the free-base porphyrins was performed by dry chromatography on neutral alumina with CHCl₃ as eluent and recrystallization from CH₂Cl₂/hexane. The UV/visible spectrum of **2** is virtually identical with the literature value.[8] Compounds **1** and **3** were characterized as follows. **1**: ¹H NMR (CDCl₃) δ 8.63 s (8 H, pyrrole H), 7.58–7.63 t (4 H, Ph *p*-H), 7.45–7.48 d (8 H, Ph *m*-H), 1.91 s (24 H, Ph *o*-CH₃), −2.44 s (2 H, NH); UV/visible (CH₂Cl₂) λ_max (ε × 10⁻³) 647 (3.27), 592 (6.54), 547 (5.88), 517 (20.3), 418 (385) nm; mass spectrometry *m/z* 727 (M⁺ + 1). **3**: ¹H NMR (CDCl₃) δ 8.86 s (8 H, pyrrole H), 7.77–7.82 t (4 H, Ph *p*-H), 7.35–7.40 m (8 H, Ph *m*-H), −2.5 s (2 H, NH); UV/visible (CH₂Cl₂) λ_max (ε × 10⁻³) 654 (2.17), 584 (6.3), 508 (19.0), 417 (230) nm; mass spectrometry *m/z* 758 (M⁺).

All porphyrins were converted to the hemin chlorides by the method of Kobayashi.[9] The iron(III) hydroxo complexes (Me₈TPP)Fe^III OH and (Cl₈TPP)Fe^III OH were obtained either by stirring a CHCl₃ solution of hemin chloride with aqueous sodium hydroxide or by chromatography on neutral alumina with CHCl₃ as eluent. The latter procedure was employed to prepare (F₈TPP)Fe^III OH. (F₂₀TPP)Fe^III Cl (Porphyrin Products) was converted to a mixture of μ-oxo and hydroxy species by stirring with aqueous sodium hydroxide as described previously[2] and the composition of the mixture established by ¹H NMR spectroscopy (pyrrole resonances: δ 81.9, 14.1).

Instruments. Proton NMR spectra were recorded on a Nicolet NT-300 spectrometer (300 MHz); chemical shifts are reported with respect to internal Me₄Si, and downfield shifts are given a positive sign. Spectra were run in methylene-*d₂* chloride. Mass spectra for (F₈TPP)-Fe^III OH were performed under the auspices of the Mass Spectral Facility at UCR. UV/visible spectra were recorded on a Perkin-Elmer Model 553 spectrophotometer. Mass spectra for the free-base porphyrins were measured on a VG 70-250 HF mass spectrometer. Infrared spectra were recorded on a Bio-Rad Digilab Division FTS-60. EPR spectra were

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Table II. Ultraviolet/Visible Spectral Data for Iron(III) Porphyrin Complexes (Solvent CH_2Cl_2)

compd	λ_{max}, nm (ϵ, cm⁻¹ mM⁻¹)					
$(F_8TPP)Fe^{III}Cl$	690 (2.7)	660 (2.5)	575 (3.0)	510 (12.0)	419 (100)	375 (50)
$(F_8TPP)Fe^{III}OH$	572 (10.2)	412 (104)	377 (58.6)			
$(Cl_8TPP)Fe^{III}Cl$	645 (3.9)	580 (4.0)	509 (11.6)	417 (100)	365 (46.7)	
$(Cl_8TPP)Fe^{III}OH$	578 (9.4)	415 (100)	342 (34.5)			
$(Me_8TPP)Fe^{III}Cl$	695 (3.2)	660 (3.0)	576 (4.0)	510 (13.8)	418 (105)	377 (58.6)
$(Me_8TPP)Fe^{III}OH$	580 (7.7)	417 (110)	334 (32)			

recorded in the X-band on an IBM Bruker ER-200D spectrometer in frozen methylene chloride at 100 K.

¹H NMR data are provided in Table I. Ultraviolet visible spectral data are provided in Table II.

Results and Discussion

Differentiation of the nature of axial ligands of iron(III) porphyrins is often possible by UV/visible spectra. Thus, as shown in Table II, the spectra are quite different when chloride and hydroxide represent axial ligands. The λ_{max} values of the hydroxyl-ligated species are blue shifted relative to those of the chloro species in the Soret region and exhibit one prominent band in the β-region. It is difficult, however, to distinguish between hydroxyl-ligated iron(III) porphyrins and the corresponding μ-oxo species by UV/visible spectra alone. Balch and co-workers[2] have shown with (5,10,15,20-tetrakis(2,4,6-trisubstituted phenyl)porphinato)iron(III) that both chloro and hydroxy complexes exhibit typical large downfield ¹H NMR spectral shifts (80 ppm) of the pyrrole moieties and a doublet signal associated with the meta protons of the phenyl substituent. Correlations between metalloporphyrin electronic structure and proton NMR contact shift values are now well-defined for the first-row transition series.[10,11] Thus, a large downfield contact shift for the pyrrole proton signals of a TPP complex is associated with unpaired spin in the σ-type $d_{x^2-y^2}$ orbital. On the other hand, depopulation of $d_{x^2-y^2}$ and single population of π-type d_{xz} and/or d_{yz} orbitals have been consistently associated with an upfield pyrrole proton contact shift.[12] Thus, on the basis of the observed shift pattern and a broad pyrrole proton signal all complexes of Table I are formulated as high-spin iron(III) species. Furthermore, splitting of 3,5-phenyl proton signals indicates displacement of the iron atom out of the porphyrin plane toward a single axial ligand.

¹H NMR has been employed in the establishment that a mixture of the μ-oxo and hydroxy species are obtained when $(F_{20}TPP)Fe^{III}Cl$ is stirred with aqueous NaOH.[2] We have isolated $(F_8TPP)Fe^{III}OH$ by chromatography of $(F_8TPP)Fe^{III}Cl$ on neutral alumina. The identity of the complex was established by UV/visible (Table I), ¹H NMR (Table II), high-resolution MS, IR, magnetic susceptibility measurement, and EPR spectroscopy. The low-temperature EPR spectrum of $(F_8TPP)Fe^{III}OH$ indicates a typical high-spin species with $g_\perp = 5.9$ and $g_\parallel = 2.0$. The structure $(F_8TPP)Fe^{III}OH$ is supported by laser desorption Fourier transform mass spectrometry, which yielded a positive molecular ion at m/e 830 ($M^+ + 1$). The Fourier transform infrared spectrum in CH_2Cl_2 solution shows a prominent absorbance at 3688 cm⁻¹ in the region of the OH stretch. Absence of a strong absorbance at 850 cm⁻¹ is indicative of a monomeric structure. The room-temperature solution magnetic moment of $\mu_{eff} = 5.7$ μ_B determined by the method of Evans[13] is further supportive of the $S = {}^5/_2$ spin state determination of iron made by NMR. In addition to the anticipated ¹H NMR characteristics for a species as $(F_8TPP)Fe^{III}OH$ a small broad peak was observed at ∼23 ppm. Addition of D_2O to the solution did not cause the disappearance of the peak. A broad peak at this position is characteristic of hydroxy-ligated iron(III) porphyrin (Table I). This would appear a priori to be due to the hydroxy proton. However, addition of traces of NaOD resulted in the formation of a mixture of μ-oxo dimer and hydroxy species. The complex $(F_8TPP)Fe^{III}OH$ is stable in CD_2Cl_2 for several weeks, not showing any tendency for transformation to the μ-oxo species.

From ¹⁹F NMR studies with $(F_{20}TPP)In^{III}Cl$ it was shown that the o-fluorine signals do not coalesce even at +130 °C on the NMR time scale. With (tetrakis(2-substituted phenyl)porphinato)- and tetra(kis(2,6-disubstituted phenyl)porphinato)metal complexes NMR results indicated that the rate of rotation about the carbon meso to phenyl carbon bond varies in the order CH_3 > OH ≪ H ≫ F, which is consistent with the steric requirement of the substituents at the 2- and 6-positions.[14] The size of the F substituent permits a sufficiently close approach to two porphyrin molecules to allow μ-oxo dimer formation.[2] Nevertheless, fluoro substitution allows isolation of the $(F_8TPP)Fe^{III}OH$ complex.

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