New Five- and Six-Coordinate Imidazole and Imidazolate Complexes of Ferric Tetraphenylporphyrin

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Abstract: The syntheses of several new imidazole and imidazolate complexes of ferric tetraphenylporphyrin (TPP) are reported. The following complexes have been made with L = imidazole (ImH) or 4-methylimidazole (4MeImH) and L^- = imidazolate (Im^-) or 4-methylimidazolate ($4MeIm^-$): FeTPP(L)(L^-), [FeTPP(L^-)$_2$]$^-$, and [FeTPP(L)](SbF_6). Addition of Im^- to FeTPPCl resulted in the formation first of the imidazolate-bridged complex [(FeTPP)$_2$(Im)]$^+$ and then of [FeTPP(Im)$_2$]$^-$. Similar addition of $4MeIm^-$ to FeTPPCl resulted in the formation first of the high-spin mononuclear complex FeTPP(4MeIm) and then of [FeTPP(4MeIm)$_2$]$^-$. The affinity of [FeTPP(4MeImH)](SbF_6) for a second 4MeImH was found to be very high, with $K \geq 10^7$ M^{-1} in toluene, 25 °C. By contrast, 4MeImH was found preferentially to hydrogen bond to Fe(TPP)(4MeIm), with $K \simeq 5 \times 10^4$ M^{-1} in THF, 25 °C. Coordination of 4MeImH was only observed at high concentrations of ligand ($K \simeq 50 \pm 10$ M^{-1}). The monoimidazole complex [FeTPP(L)](SbF_6) was concluded to be high spin after a comparison of the visible spectral properties of a large number of ferric TPP complexes.

Introduction

Changes in the degree of hydrogen bonding or total deprotonation of histidyl imidazole rings acting as axial ligands to iron in hemoproteins represent mechanisms whereby the properties of the iron center can be affected by changes in the polypeptide environment surrounding the heme.[1-14] Recent studies of ferrous porphyrin complexes have shown that there are marked differences in properties when imidazolate (Im^-) is an axial ligand rather than imidazole (ImH). For example, the visible absorption bands of the imidazolate complex [Fe^{II}P(Im)(CO)]$^-$ (P = porphyrin) have been found to occur at lower energy than those of the corresponding imidazole complex Fe^{II}P(ImH)(CO)[9] and the binding affinity and rate constant for CO binding to the five-coordinate imidazolate complex [Fe^{II}P(Im)]$^-$ have been found to be lower than those of its protonated analogue Fe^{II}P(ImH).[3,9,11]

Similar studies of ferric porphyrin complexes have frequently been frustrated by the tendency of imidazolate to act as a bridging ligand and the consequent formation of binuclear or polynuclear imidazolate complexes.[2,15-17] We have recently discovered that bi- and polynuclear complex formation is inhibited when 4-methylimidazolate rather than imidazolate is reacted with ferric porphyrin complexes. Presumably the 4-methyl group sterically hinders the attachment of a second (Fe^{III}P)$^+$ to the mononuclear complex.

Another problem that has frustrated studies of ferric porphyrin imidazole and imidazolate complexes as analogues for hemoproteins has been the absence of a synthetic route to monoimidazole complexes.[18,19] Five-coordination has been proposed to occur in a number of ferric hemoproteins,[9,20-25] e.g., horseradish peroxidase and cytochrome *c'*. But reaction of imidazole with most ferric porphyrin complexes has led to the observation only of bisimidazole complexes, with no evidence for formation of stable monoimidazole intermediates.[26] Even in the case of the perchlorato complex Fe^{III}(TPP)(ClO_4) (TPP = tetraphenylporphinato), additions of ligands L such as *N*-methylimidazole (NMeIm) and 2-methylimidazole to solutions of the complex result only in formation of complexes of the form [Fe^{III}(TPP)L_2]ClO_4.[20] We have discovered that the reactivity of Fe^{III}(TPP)(SbF_6) with imidazole and imidazole derivatives differs substantially from that of the corresponding perchlorato complex in that the addition is stepwise and hence monoimidazole complexes can be observed and characterized in solution. The properties of these new monoimidazole complexes as well as those of the other new imidazole and imidazolate complexes which we have prepared are the subject of this paper.

Experimental Section

General Procedures. All reactions and distillations were carried out under an inert atmosphere (Ar or He) using Schlenkware or a Vacuum Atmospheres inert-atmosphere chamber. All materials and glassware were made rigorously water-free in order to protect against formation of (FeTPP)$_2$O.

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Table I. Visible and EPR Spectral Data for Various Ferric Porphyrin Complexes

complex	conditions	vis absorption bands, nm	EPR (77 K) solvent	EPR (77 K) *g* values
$[FeTPP(ImH)_2]^+$ (1a)	CH_2Cl_2 or toluene; FeTPPCl; excess ImH	416, 456 (sh), 548, 580 (sh)[a]	CH_2Cl_2	2.92, 2.30, 1.56
$[FeTPP(4MeImH)_2]^+$ (1b)	CH_2Cl_2 or toluene; FeTPPCl; excess 4MeImH	416, 456 (sh), 548, 580 (sh)	CH_2Cl_2	2.87, 2.29, 1.54
$[FeTPP(ImH)_2]^+$ (1a)	toluene; reaction 7	416, 456 (sh), 547, 576 (sh)	CH_2Cl_2	2.93, 2.28, 1.54
$[FeTPP(4MeImH)_2]^+$ (1b)	toluene; reaction 7	416, 456 (sh), 547, 576 (sh)	CH_2Cl_2	2.89, 2.29, 1.54
FeTPP(Im)(ImH) (2a)	CH_2Cl_2; reaction 1a	418, 444 (sh), 552, 585 (sh)	CH_2Cl_2	2.73, 2.28, 1.74
FeTPP(4MeIm)(4MeImH) (2b)	toluene; reaction 1b	418, 444 (sh), 552, 585 (sh)	toluene	2.76, 2.28, 1.77
$[FeTPP(Im)_2]^-$ (3a)	CH_2Cl_2; reaction 1a or 2	425, 444 (sh), 556, 595	CH_2Cl_2	2.73, 2.28, 1.76
$[FeTPP(4MeIm)_2]^-$ (3b)	toluene; reaction 1b or 3	424, 444 (sh), 556, 595	toluene	2.73, 2.28, 1.78
$[K(18C6)][FeTPP(4MeIm)_2]$ (4)	Me_2SO	424, 444 (sh), 557, 596	Me_2SO	2.67, 2.28, 1.82
$[(FeTPP)_2Im]^+$ (5)	CH_2Cl_2 or benzene; reaction 2	403, 561, 595	CH_2Cl_2	none
FeTPP(4MeIm) (6)	toluene; FeTPPCl + $4MeIm^-$; reaction 4	416, 576, 621 (sh)		
	toluene; $FeTPP(SbF_6)$ + $4MeIm^-$; reaction 4	415, 573, 617 (sh)	toluene	5.9, 2.0
	THF; FeTPPCl + $4MeIm^-$; reaction 4	415, 572, 618 (sh)		
	4 in toluene	416, 576, 622 (sh)		
$FeTPP(ImH)(SbF_6)$ (7a)	toluene; reaction 7	413, 511, 572 (sh), 695		
$FeTPP(4MeImH)(SbF_6)$ (7b)	toluene; reaction 7	413, 511, 572 (sh), 695		
FeTPP(4MeIm)···4MeImH (8)	THF	414, 570, 620 (sh)		
FeTPPCl	toluene	369, 418, 506, 572, 648 (sh), 658	CH_2Cl_2	6.0, 2.0
$FeTPP(SbF_6)$	toluene	406, 517, 571 (sh), 666	toluene	5.8, 4.8, 2.0
	CH_2Cl_2	400, 518, 633 (sh), 668		
	THF	399, ~500 (sh), 525, 657		
$FeTPP(OCH_3)$[b]	benzene	415, 578, 630 (sh)	solid	5.30, 2.00
$[FeTPP(NMeIm)_2]^+ + OH^-$	CH_2Cl_2; toluene	415, 573, 625 (sh)		
FeTPPCl + OH^-	toluene	415, 578, 625 (sh)		
FeTPPCl + $tBuO^-$	toluene	416, 575, 620 (sh)		
$(FeTPP)_2O$[c]	benzene	408, 571.5, 612		
FeTPP(4,5-diPh-2MeIm)[d]	toluene	373 (sh), 413, 570, 608		

[a] sh = shoulder. [b] Reference 34; visible absorption bands estimated from a figure. [c] Fleischer, E. B.; Srivastava, T. S. *J. Am. Chem. Soc.* 1969, *91*, 2403–2405. [d] Reference 17.

Materials. Py,[27] NMeIm, DMA, dichloromethane, petroleum ether, Me_2SO and methanol were distilled from CaH_2 or P_2O_5. DME was distilled from CaH_2 and then from Na. Benzene, toluene, and THF were distilled from Na/benzophenone. All of the above solvents were stored over activated 4A molecular sieves following distillation. K(tBuO) (Eastman) was used as obtained. Solutions of $tBuO^-$ were prepared using K(tBuO) and 18C6.[28] Hydroxide solutions were prepared by using tetrabutylammonium hydroxide either in MeOH or in 9:1 benzene/MeOH (Eastman). 18C6 was synthesized and purified by a literature procedure.[29] It was further purified by recrystallization from 2:1 petroleum ether/DME by cooling in dry ice/acetone and filtering while cold.[28] K222 (MCB), $AgSbF_6$ (Ventron), and $(ImH_2)^+(CF_3SO_3)^-$ were dried over P_2O_5 in vacuo before use and *p*-toluenesulfonic acid was dried in vacuo at 55 °C.

FeTPPCl was prepared by literature methods[30] using chlorin-free H_2TPP.[31] It was recrystallized from toluene/petroleum ether and dried at 80 °C in vacuo. $FeTPP(SbF_6)$ was prepared by a modification of a literature procedure.[20] One equivalent of $AgSbF_6$ was added to a 1 mM solution of FeTPPCl in toluene. The mixture was refluxed under Ar for approximately 2 h, at which time the visible absorption bands due to FeTPPCl had disappeared. The mixture was filtered to remove AgCl and the resulting solution was reduced in volume by one-half under reduced pressure. Cooling at 5 °C resulted in precipitation of the product, $FeTPP(SbF_6)$, which was recovered by filtration and dried in vacuo.

ImH was decolorized with activated charcoal and recrystallized from hot toluene or benzene. It was dried in vacuo. 4MeImH (ROC/RIC) was obtained as a yellow-brown hygroscopic solid. It was vacuum distilled to yield an almost colorless, viscous liquid which slowly solidified to an almost white solid. Further purification was accomplished by recrystallization of the oxalate salt followed by regeneration of the free base with aqueous K_2CO_3.[32] 4MeImH was then extracted with anhydrous ether, and the ether was removed first by distillation under Ar and finally under vacuum. The resulting white solid was dried over P_2O_5 in vacuo for 7 days and the P_2O_5 was changed daily. Anal. Calc for $C_4H_6N_2$: C, 58.51; H, 7.37; N, 34.12. Found: C, 58.30; H, 7.29; N, 34.34; H_2O, 0.50.

K(Im) was synthesized by reaction of ImH with K metal.[33] Typically, 13.4 g of ImH was dissolved in 150 mL of benzene and refluxed with 4.13 g of K for 24 h. The solid product was dried for 12 h. in vacuo. Anal. Calcd. for $KC_3H_3N_2$: C, 33.94; H, 2.85; N, 26.39; K, 36.83. Found: C, 33.89; H, 3.16; N, 26.35; K, 36.22.

K(4MeIm) was synthesized by reaction of 4MeImH in toluene with less than 1 equiv of KH. Typically, 2.0 g of 4MeImH (24 mmol) was dissolved in 30 mL of toluene, and 0.7 g of KH (17 mmol) was added over several hours. The resulting mixture was stirred for 7 days and the product was isolated by filtration, washed with toluene, and dried in vacuo.

[K(K222)](4MeIm) was synthesized by addition of 173 mg of K(4MeIm) to 30 mL of a THF solution containing 0.8 g of K222 and 22 mg of 4MeImH. After the solution was stirred for 12 h and filtered, the solution volume was reduced under vacuum to ~5 mL. After addition of 5 mL of toluene and cooling in dry ice/acetone, a white solid precipitated which was isolated by filtration of the cold solution and dried in vacuo. The yield of product was less than 10%. The solid product, [K(K222)](4MeIm), dissolved readily in THF to give 2 mM solutions. Anal. Calcd. for $C_{22}H_{41}N_4O_6K$: C, 53.20; H, 8.32; N, 11.28; K, 7.87. Found: C, 53.09; H, 8.23; N, 11.38; K, 7.78.

Synthesis of [K(18C6)][FeTPP(4MeIm)$_2$]. To a 1 mM solution of FeTPPCl in toluene were added 3.8 equiv of K(4MeIm) and 13.3 equiv of 18C6. The mixture was stirred for 4 h and then filtered. The resulting purple solid was redissolved in DMA. Addition of toluene followed by cooling to −20 °C led to the precipitation of a purple crystalline product which was removed by filtration and dried in vacuo. Anal. Calcd. for $C_{64}H_{62}N_8O_6FeK$: C, 67.78; H, 5.51; N, 9.88; K, 3.45; Cl, 0. Found: C, 66.27; H, 5.58; N, 9.80; K, 2.91; Cl, 0.24.

Methods. Visible absorption spectra were recorded on a Cary 118C, a Cary 17D, or a Beckman 5270. Titrations were typically carried out under Ar with 10^{-4}–10^{-5} M porphyrin solutions in 1.0-cm path length

(27) Abbreviations used in this paper are as follows: TPP, tetraphenylporphyrin; OEP, octaethylporphyrin; PPIX, protoporphyrin IX; PPIXDME, protoporphyrin IX dimethyl ester; DPIXDME, deuteroprotoporphyrin IX dimethyl ester; PPIXDBE, protoporphyrin IX di-*tert*-butyl ester; ImH, imidazole; 4MeImH, 4-methylimidazole; Im^-, imidazolate; $4MeIm^-$, 4-methylimidazolate; NMeIm, *N*-methylimidazole; NPrIm, *N*-propylimidazole; 2MeImH, 2-methylimidazole; 4,5-diPh-2MeIm$^-$, 4,5-diphenyl-2-methylimidazolate; 4PhImH, 4-phenylimidazole; py, pyridine; $tBuO^-$, *tert*-butoxide; 18C6, 18-crown-6, 1,4,7,10,13,16-hexaoxacyclooctadecane; K222, Krytofix 222, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; DMA, dimethylacetamide; DMF, dimethylformamide; DME, dimethoxyethane; THF, tetrahydrofuran; Me_2SO, dimethyl sulfoxide; Mb, myoglobin.

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cuvettes fitted with threeway stopcocks. When higher porphyrin concentrations were used, 0.1- or 1.0-mm path length cuvettes fitted with septum caps were used. Absorbance measurements for equilibrium constant determinations were carried out with a cell holder thermostated at 25.0 ± 0.1 °C. EPR spectra were obtained at 77 K and were recorded on a Varian E-12 calibrated with a Hewlett-Packard frequency counter 5245L and Mn^{2+} in strontium oxide as a standard. IR spectra were recorded on a Beckman 4260.

Results and Discussion

Deprotonation of Bisimidazole Complexes. The complexes $[FeTPP(ImH)_2]^+$ (**1a**) and $[FeTPP(4MeImH)_2]^+$ (**1b**), were prepared in solution by the reaction of FeTPPCl with excess ligands in several different solvents (toluene, Me_2SO, CH_2Cl_2). Titrations with several different bases (OH^-, $tBuO^-$, Im^-, $4MeIm^-$) resulted in virtually identical visible spectral changes. For example, stepwise addition of OH^- to **1a** (see Table I for listing of designations of compounds using arabic numerals) in CH_2Cl_2 resulted in an isosbestic point at 585 nm for **up** to 1 equiv of base. Subsequent additions of OH^- produced yet another species[2] (see Table I). When this reaction was followed by EPR using 10^{-3} M **1a** in CH_2Cl_2, addition of 1 equiv of OH^- resulted in a substantial shift in g values from 2.92, 2.30, and 1.56 for **1a** to 2.73, 2.28, and 1.74. At large excesses of base, only minor changes were observed, resulting in g values of 2.73, 2.28, and 1.76. These observations are consistent with a two-step deprotonation reaction as shown in reactions 1a and 1b. Reaction 1 was reversed by

$$\mathbf{1a} \xrightarrow[\text{excess ImH}]{OH^-} \underset{\mathbf{2a}}{FeTPP(Im)(ImH)} \xrightarrow[\text{excess ImH}]{OH^-} \underset{\mathbf{3a}}{[FeTPP(Im)_2]^-} \quad (1a)$$

$$\mathbf{1b} \xrightarrow[\text{excess 4MeImH}]{OH^-} \underset{\mathbf{2b}}{FeTPP(4MeIm)(4MeImH)} \xrightarrow[\text{excess 4MeImH}]{OH^-} \underset{\mathbf{3b}}{[FeTPP(4MeIm)_2]^-} \quad (1b)$$

the addition of protons; addition of $(ImH_2)(CF_3SO_3)$ to **3a** resulted in a visible spectrum identical with that of **1a**.

To ensure that these observations were not due to coordination of OH^-, $[FeTPP(NMeIm)_2]^+$ was reacted with OH^- under similar conditions. Spectral changes were observed which were complete upon addition of 1 equiv of OH^-. The resulting visible spectrum was very different from those observed for ImH or 4MeImH (see Table I). Similarly, reaction of FeTPPCl with OH^- in toluene or CH_2Cl_2 resulted in a spectrally distinct product.

We attribute the changes in visible and EPR spectral properties accompanying titrations of $[FeTPP(L)_2]^+$, L = ImH or 4MeImH, with B^- = OH^-, $tBuO^-$, Im^-, or $4MeIm^-$ to the sequential deprotonation of coordinated imidazoles. The fact that a variety of bases produces the same spectral changes implies that actual coordination of base is unlikely. By contrast, when no acidic protons are available, as in the case of $[Fe(TPP)(NMeIm)_2]^+$, OH^- and $tBuO^-$ are observed to coordinate. In this latter case, the products have visible spectra very similar to those observed upon reaction of OH^- or $tBuO^-$ with FeTPPCl and also similar to the spectrum of $FeTPP(OCH_3)$.[34] It therefore seems likely in these cases that the products are the high-spin complexes FeTPP(OH) and FeTPP(tBuO).

Further support for deprotonation of coordinated imidazole comes from analysis of the EPR spectra of these low-spin ferric porphyrin complexes using a method developed by Peisach et al.[4,5,35] This method classifies such complexes by their locations on a plot of rhombicity, R, vs. tetragonality, T, both parameters being derived from the EPR spectra of the complexes. R is a number of purely geometric significance while T is a nonlinear function of the electron density on the iron atom. Values of R and T, obtained by the method of Taylor,[36] for various ferric porphyrin complexes and ferric heme proteins have been calculated, tabulated in Table II, and graphed in Figure 5. Peisach et al.[4,5,35] found that complexes which have ligand sets in common are clustered in regions on an R vs. T plot. Examination of Figure 5 reveals three such regions containing either (I) complexes of imidazole, (II) complexes of Im^- or ImH with a strong hydrogen bonder, or (III) complexes of the form FeP(L)(OR), where L = ImH, py, and NMeIm and OR^- = OH^-, alkoxides, and phenoxides. The large separation between regions II and III is particularly striking. This analysis strongly supports our contention that the products formed upon titration of $[FeTPP(L)_2]^+$ (L = ImH or 4MeImH) with OH^- are not FeTPP(L)(OH) or related hydroxo complexes but rather FeTPP(L)(L′) (L′ = Im^-, $4MeIm^-$) or $[FeTPP(L')_2]^-$.

Table II. EPR Data for Various Low-Spin Ferric Porphyrin Complexes

complex	EPR g values	rhombicity	tetragonality	ref
Group I				
$[FeTPP(ImH)_2]Cl$	2.92, 2.30, 1.56	0.612	3.25	*a*
$[FeTPP(4MeIm)_2]Cl$	2.87, 2.29, 1.54	0.649	3.11	*a*
$[FeTPP(ImH)_2](SbF_6)$	2.93, 2.28, 1.54	0.589	3.29	*a*
$[FeTPP(4MeImH)_2](SbF_6)$	2.89, 2.29, 1.54	0.632	3.15	*a*
$[FeTPP(NMeIm)_2]^+$	2.92, 2.30, 1.55	0.617	3.20	4
$[FeOEP(ImH)_2]^+$	2.96, 2.25, 1.53	0.538	3.47	4
$[FeOEP(NMeIm)_2]^+$	2.96, 2.25, 1.53	0.538	3.47	18
$[FePPIX(ImH)_2]^+$	3.02, 2.24, 1.51	0.500	3.54	13
$[FeDPIXDME(ImH)_2]^+$	2.93, 2.27, 1.53	0.581	3.30	*b*
$[FePPIXDME(4MeImH)_2]^+$	2.87, 2.26, 1.59	0.584	3.56	*c*
$[FePPIXDME(4PhImH)_2]^+$	2.90, 2.26, 1.54	0.586	3.35	*c*
$[FePPIXDME(NMeIm)_2]^+$	2.92, 2.28, 1.53	0.601	3.22	*c*
cytochrome b_5	3.03, 2.23, 1.43	0.516	3.23	13
ferric Mb(ImH)	2.91, 2.26, 1.53	0.583	3.32	*d*
Group II				
[FeTPP(Im)(ImH)	2.73, 2.28, 1.74	0.650	4.08	*a*
FeTPP(4MeIm)(4MeImH)	2.76, 2.28, 1.77	0.598	4.44	*a*
$[FeTPP(Im)_2]^-$	2.73, 2.28, 1.76	0.636	4.25	*a*
$[FeTPP(4MeIm)_2]^-$; toluene	2.73, 2.28, 1.78	0.621	4.44	*a*
$[FeTPP(4MeIm)_2]^-$; Me_2SO	2.67, 2.28, 1.82	0.656	4.65	*a*
$[FePPIX(ImH)_2]^+ + OH^-$	2.78, 2.26, 1.72	0.582	4.25	13
$[FeDPIXDME(ImH)_2]^+ + F^-$	2.75, 2.27, 1.72	0.626	4.07	*b*
cytochrome b_5; pH 12	2.76, 2.28, 1.68	0.659	3.71	13
Group III				
FePPIXDME(OEt)(py)	2.44, 2.14, 1.92	0.491	9.24	18
FePPIXDME(OEt)(NMeIm)	2.44, 2.15, 1.92	0.520	8.75	18
$FeOEP(OCH_3)(NMeIm)$	2.43, 2.15, 1.92	0.535	8.67	18
FePPIXDBE(OAr)(NMeIm)[f]	2.56, 2.21, 1.85	0.609	5.75	*e*
FePPIXDBE(OAr)(py)	2.61, 2.19, 1.84	0.518	6.23	*e*
FePPIXDBE(OAc)(py)	2.61, 2.19, 1.84	0.518	6.23	*e*
ferric Mb(OH)	2.55, 2.17, 1.85	0.528	6.61	13

[a] This work. [b] Momenteau, M.; Mispelter, J.; Lexa, D. *Biochim. Biophys. Acta* 1973, *320*, 652–662. [c] Ozaki, T.; Yoshimura, T. *Inorg. Chim. Acta* 1979, *36*, L421–L422. [d] Hiroshi, H. *Biochim. Biophys. Acta* 1971, *251*, 227–235. [e] Ainscough, E. W.; Addison, A. W.; Dolphin, D.; James, B. R. *J. Am. Chem. Soc.* 1978, *100*, 7585–7591. [f] OAr = OC_6H_3-2,6$(OCH_3)_2$.

Reactions Using Imidazolate. The solution species $[FeTPP(Im)_2]^-$ (**3a**) and $[FeTPP(4MeIm)_2]^-$ (**3b**) could also be produced by the reaction of FeTPPCl with excess K(Im) or K(4MeIm) solubilized with excess crown ether (18C6). These two species have virtually identical visible spectra and similar EPR spectra. Attempts to isolate the monomeric complex **3a** failed due to formation of a polymeric material, $[FeTPP(Im)]_n$.[15] However, **3b** could be obtained readily as a purple crystalline solid, [K(18C6)][FeTPP(4MeIm)$_2$] (**4**). An X-ray crystal structural study has confirmed that **4** is a six-coordinate complex as formulated.[37] Hence substitution of a methyl group at the 4-position of imidazolate apparently inhibited the formation of the polynuclear complex which was formed when unsubstituted imidazolate was used.

Dramatic differences between Im^- and $4MeIm^-$ were also evident at low ligand-to-porphyrin ratios. Under such conditions,

(34) Kobayashi, H.; Higuchi, T.; Kaizu, Y.; Osada, H.; Aoki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3137–3141.
(35) Blumberg, W. E.; Peisach, J. *Adv. Chem. Ser.* **1971**, *100*, 271–291.
(36) Taylor, C. P. S. *Biochim. Biophys. Acta* **1977**, *49*, 137–148.
(37) Quinn, R.; Valentine, J. S.; Strouse, C. E., manuscript in preparation.

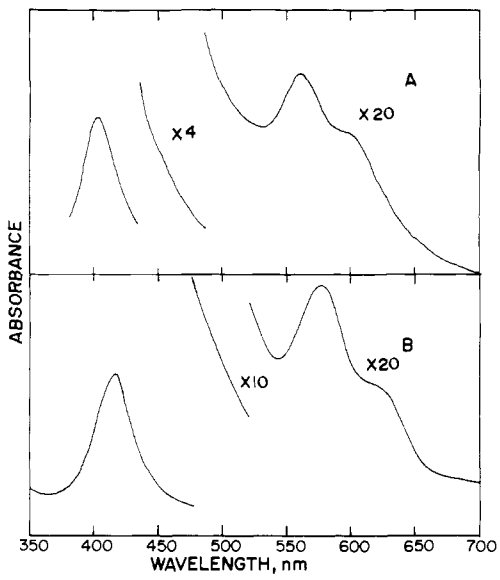


Figure 1. Visible spectra of 1.0×10^{-5} M FeTPPCl in the presence of K(Im) or K(4MeIm) solubilized with 18C6: (A) benzene, 2.0×10^{-5} M K(Im); (B) Toluene, 2.0×10^{-5} M K(4MeIm).

Im^- and $4MeIm^-$ reacted with FeTPPCl gave two species with very different properties. Subsequent additions of ligand, however, resulted in species **3a** and **3b**, respectively, as shown in reactions 2 and 3. Species **5** is EPR silent. In addition, its visible spectrum

$$\text{FeTPPCl} \xrightarrow[Im^-]{\sim 2 \text{ equiv}} \mathbf{5} \xrightarrow[Im^-]{>20 \text{ equiv}} \underset{\mathbf{3a}}{[\text{FeTPP}(\text{Im})_2]^-} \quad (2)$$

$$\text{FeTPPCl} \xrightarrow[4MeIm^-]{\sim 2 \text{ equiv}} \mathbf{6} \xrightarrow[4MeIm^-]{>20 \text{ equiv}} \underset{\mathbf{3b}}{[\text{FeTPP}(4\text{MeIm})_2]^-} \quad (3)$$

shows a marked blue shift of the Soret band relative to that of FeTPPCl (see Figure 1). These observations lead us to speculate that **5** was an imidazolate-bridged dimer.[2] By contrast, **6** has visible and EPR spectra totally unlike those of **5** and, importantly, characteristic of a mononuclear ferric porphyrin complex (see Figure 1).

To determine the spin state of **6**, the reaction of $FeTPP(SbF_6)$ with $4MeIm^-$ was followed by EPR (see Figure 2). $FeTPP(SbF_6)$ is present in toluene as a mixture of high- and intermediate-spin species,[20] resulting in weak, broad signals at $g \sim 5.8$, 4.8, and 2.0 at 77 K. Addition of $4MeIm^-$ to such solutions resulted in the appearance of a moderately intense signal at $g \sim 5.9$ and a weaker signal at $g \sim 2.0$, confirming the presence of a high-spin ferric complex. Further additions of $4MeIm^-$ resulted in the disappearance of the high-spin signals and the appearance of signals at $g \sim 2.7$, 2.3, and 1.8, corresponding to formation of low-spin $[FeTPP(4MeIm)_2]^-$ (**3b**).

The nature of the products **5** and **6** resulting from the reaction of FeTPPCl with 2 equiv of either Im^- or $4MeIm^-$ (reactions 2 and 3) can be deduced from their visible and EPR spectra. Species **5** formed with Im^- is EPR silent, indicting interaction of the paramagnetic iron centers. This observation suggests that Im^- is functioning as a bridging ligand. The insoluble polymeric species $[FeTPP(Im)]_n$ has low-spin $(FeTPP)^+$ centers linked by Im^- bridges.[15] By contrast, **5** is soluble and has a visible spectrum resembling that of $(FeTPP)_2O$ (see Table I). We therefore formulate **5** as a binuclear imidazolate-bridged complex with two high-spin Fe^{III} centers, i.e., $(TPPFe-Im-FeTPP)^+$. This formulation is consistent with the observed blue shift of the Soret band which is frequently observed for porphyrin dimers[38,39] (see Table I). This formulation is also supported by the observation that introduction of a single methyl group in the 4-position of imidazolate results in an entirely different product (see below).

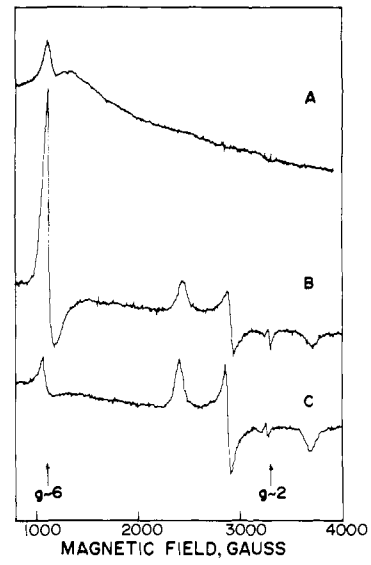


Figure 2. EPR spectra at 77 K of $FeTPP(SbF_6)$ in toluene in the presence of various concentrations of K(4MeIm) solubilized with 18C6: (A) 10^{-3} M $FeTPP(SbF_6)$, no K(4MeIm); (B) 3.3×10^{-4} M $FeTPP(SbF_6)$, 6.6×10^{-4} K(4MeIm) ($g = 2.7$, 2.3, and 1.8 are due to formation of a small amount of $[FeTPP(4MeIm)_2]^-$); (C) 3.3×10^{-4} M $FeTPP(SbF_6)$, $\sim 10^{-3}$ M K(4MeIm). Instrument settings are the same for all spectra: modulation frequency, 100 kHz; modulation amplitude, 2.5 G; receiver gain, 8×10^3; microwave power, 30 mW.

When $4MeIm^-$ rather than Im^- is reacted with FeTPPCl, **6** rather than **5** is observed. We attribute the different reaction pathway to steric inhibition of coordination of a second $(Fe^{III}TPP)^+$ by the 4-methyl group. While **5** is EPR silent, **6** has an EPR spectrum typical of a high-spin Fe^{III} complex. Hence, coupling between iron centers is not occurring and the complex is presumed to be mononuclear. The visible spectrum of **6** is characteristic of a monomeric ferric porphyrin and similar in appearance to that of $FeTPP(OCH_3)$.[34] There is no marked blue shift of the Soret band relative to FeTPPCl. Visible and EPR spectral results therefore support the formulation of **6** as a five-coordinate, high-spin ferric complex complex, as shown in reaction 4.

$$\text{FeTPPX} + 4MeIm^- \rightarrow \underset{\mathbf{6}}{\text{FeTPP}(4\text{MeIm})} + X^- \quad (4)$$

$$X = Cl, SbF_6$$

We also observed the formation of **6** by another route. The bis(4-methylimidazolate) complex **3b** can only be formed in solution in the presence of a large excess of imidazolate. It is therefore not surprising that solid **4** when dissolved in nonpolar solvents such as toluene dissociated to give solutions of **6** (see Table I). Addition of slightly less than 1 equiv of FeTPPCl to a toluene solution of **4** resulted in the formation of more **6**. The reaction sequence is summarized in reaction 5. By contrast, **4** did not

$$\underset{\mathbf{4}\text{ (solid)}}{[K(18C6)][FeTPP(4MeIm)_2]} \xrightarrow{\text{toluene}} \underset{\mathbf{6}}{\text{FeTPP}(4\text{MeIm})} +$$

$$[K(18C6)](4MeIm) \xrightarrow{\text{FeTPPCl}} \underset{\mathbf{6}}{\sim 2\text{FeTPP}(4\text{MeIm})} \quad (5)$$

dissociate appreciably in the polar solvent Me_2SO. In this case, a visible spectrum almost identical with that of **3b** was obtained (see Table I).

The properties of **6** are similar in several respects to those of other ferric porphyrin complexes with anionic axial ligands. Such complexes are usually five-coordinate and high spin. Further support for five- rather than six-coordination comes from the quite similar visible spectra of FeTPP(4MeIm) whether obtained by reaction with FeTPPCl or $FeTPP(SbF_6)$ (see Table I). The

(38) Collman, J. P.; Chong, A. O.; Jameson, G. B.; Oakley, R. T.; Rose, E.; Shmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516–533. Collman, J. P.; Elliott, C. M.; Halbert, T. R.; Tovrog, B. S. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 18–22.

(39) Chang, C. K.; Kuo, M.-S.; Wang, C.-B. *J. Heterocycl. Chem.* **1977**, *14*, 943–945. Chang, C. K. *Ibid.* **1977**, *14*, 1285–1288.

dissociation of solid **4**, [K(18C6)][FeTPP(4MeIm)$_2$], in toluene yielding **6**, FeTPP(4MeIm), also suggests that **6** is five-coordinate. Coordination of the only potential sixth ligand, 4MeIm$^-$, can be excluded since the observed visible spectrum is totally unlike that of [FeTPP(4MeIm)$_2$]$^-$. In fact, reaction of a solution prepared by dissolving **4** (see reaction 5) with FeTPPCl results in the formation of more FeTPP(4MeIm).

Recently, isolation of a five-coordinate ferric porphyrin imidazolate complex, FeTPP(4,5-diPh-2MeIm), was reported and the complex was shown to be high spin.[17] The visible spectrum of this species shows band maxima which are similar but somewhat shifted from those of **6** (see Table I). Whereas use of 4,5-diphenyl-2-methylimidazolate led to successful isolation of the five-coordinate complex, our attempts to isolate FeTPP(4MeIm) failed due to formation of an insoluble porphyrin complex believed to be polymeric. Apparently, the 4-methyl group of MeIm$^-$ inhibits but does not exclude polymer formation. In the case of 4,5-diphenyl-2-methylimidazolate, not only do the phenyl substituents inhibit binding of (FeTPP)$^+$ to N-3, but the 2-methyl substituent inhibits formation of a six-coordinate complex in which the iron atom is in the plane of the porphyrin. By contrast, examination of molecular models demonstrates that 4MeIm$^-$ forms a sterically unhindered bond to the ferric porphyrin.

The success of our isolation of the mononuclear complex [K(18C6)][FeTPP(4MeIm)$_2$], while the analogous reaction using Im$^-$ led to formation of [FeTPP(Im)]$_n$, is also presumably the result of the reduced tendency of 4MeIm$^-$ to act as a bridging ligand between ferric porphyrins.

A comparison of the properties of [FeTPP(4MeImH)$_2$]$^+$ (**1b**), and of [FeTPP(4MeIm)$_2$]$^-$ (**3b**), reveals some significant differences between imidazole and imidazolate as ligands in ferric porphyrin complexes. In particular, comparison of visible spectra in polar solvents shows a substantial red shift of bands due to deprotonation of imidazole (see Table I). Similar red shifts have been observed by Peisach et al.[13] upon deprotonation of ImH in [Fe(PPIX)(ImH)$_2$]$^+$ in Me$_2$SO. Comparison of visible spectra of ZnTPP(ImH) and [ZnTPP(Im)]$^-$ revealed similar effects.[28] Mincey and Traylor[9] have shown that such red shifts are characteristic of ferrous porphyrin imidazolate complexes. Nappa et al.[28] have shown that such red shifts are generally found for zinc porphyrin complexes when anionic ligands are substituted for neutral ligands.

Substantial differences in the EPR g values are also apparent for **1b** and **3b**, indicating a change in the nature of the iron center. Examination of R vs. T plots indicates a larger value for the tetragonality of the imidazolate complex. This observation is in accord with our expectations since Im$^-$ is a better σ donor than ImH and we therefore expect that **3b** will have a higher electron density at the iron center than **1b**.

A comparison of Fe–L stretching frequencies is also instructive. The values of ν_{Fe-N} for **1b** as the SbF_6^- salt and **4** are 368 and 370 cm^{-1}, respectively, suggesting that the Fe–N bonds in both are similar. But this conclusion is complicated by the trans influence of the other ligand. That is to say one is comparing Fe–N(Im$^-$) trans to Im$^-$ with Fe–N(ImH) trans to ImH. Ideally one wishes to compare stretching frequencies for feTPP(4MeIm) and FeTPP(4MeImH)$^+$, neither one of which has been obtained as a solid or in solution at sufficiently high concentrations for IR measurements.

The magnitudes of ν_{Fe-N} for **1b** (SbF_6), 368 cm^{-1}, and **4**, 370 cm^{-1}, can be compared with those of [Fe(PPIX)(ImH)$_2$]Cl, 384 cm^{-1},[40] [Fe(PPIX)(NMeIm)$_2$]Cl, 381 cm^{-1},[40] and [FeOEP(ImH)$_2$](ClO_4), 377 cm^{-1}.[41] Apparently the magnitude of ν_{Fe-N} in ferric porphyrins is not particularly sensitive to changes in the nature of the imidazole ligand.[42]

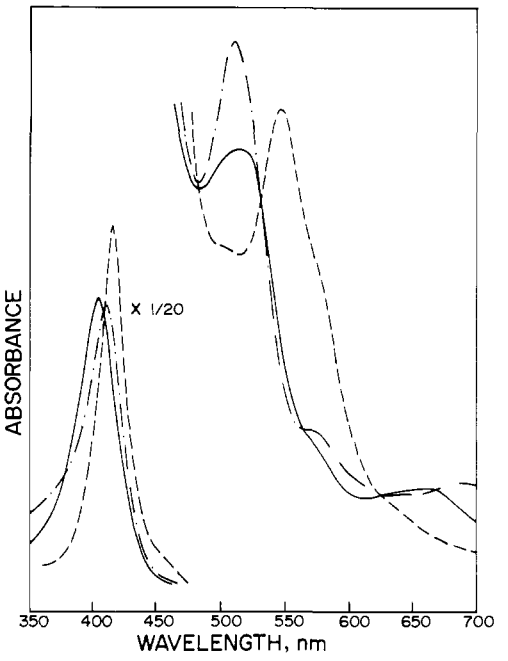


Figure 3. Visible spectra of 1.7×10^{-5} M FeTPP(SbF_6) in toluene in the presence of various concentrations of 4MeImH: (—)no 4MeImH; (-·-) ~1 equiv of 4MeImH; (---) ~2 equiv of 4MeImH.

An analysis of the 4000–3200-cm^{-1} region of the IR spectrum of [K(18C6)][FeTPP(4MeIm)$_2$] (**4**), shows no absorbance in the N–H stretching region, confirming that imidazole is actually deprotonated and present as imidazolate. By contrast, [FeTPP(4MeImH)$_2$](SbF_6) exhibits a broad absorption at 3385 cm^{-1}, which we assign to the hydrogen-bonded N–H···FSbF_5^- stretch of coordinated imidazole. This value should be compared with 3240 cm^{-1} for [FeOEP(ImH)$_2$](ClO_4)[41], where ClO_4^- is hydrogen bonded to ImH,[43] with 3050–2587 cm^{-1} for ν_{N-H} of ImH hydrogen bonded to another ImH,[44] and with 3500 cm^{-1} for ν_{N-H} of free, non-hydrogen-bonded ImH.[45]

Monoimidazole Complexes. As expected from the work of other investigators, reaction of FeTPPCl in toluene with ImH or 4MeImH resulted only in a bisimidazole complex[26] (reaction 6).

$$\underset{}{\text{FeTPPCl}} + 2\text{L} \rightleftharpoons \underset{\mathbf{1}}{[\text{FeTPP(L)}_2]^+} + \text{Cl}^- \qquad (6)$$

L = ImH, 4MeImH

No intermediate species, i.e., monoimidazole complexes, were observed. Reaction of FeTPP(SbF_6), 10^{-5} M in toluene, with ImH or 4MeImH, however, proceeded in a stepwise fashion as shown in reaction 7 (see Figure 3). The visible spectra of **7a** and **7b**

$$\text{FeTPP}(SbF_6) \xrightarrow[1\text{ equiv}]{\text{L}} \underset{\mathbf{7a,b}}{\text{FeTPP(L)}(SbF_6)} \xrightarrow[1\text{ equiv}]{\text{L}} \underset{\mathbf{1a,b}}{[\text{FeTPP(L)}_2]^+} + SbF_6^- \qquad (7)$$

a, L = ImH; **b**, L = 4MeImH

are described in Table I. Addition of more than 2 equiv of L caused no further changes in the visible spectra, indicating that the reaction was complete after a stoichiometric amount of ligand had been added. Assuming that 5% unreacted **7a** or **7b** would be detectable, we estimate a minimum equilibrium constant for reaction 8 to be $K_2 = 10^7$ M^{-1}. Complexes **1a** or **1b** were readily

$$\underset{\mathbf{7}}{\text{FeTPP(L)}(SbF_6)} + \text{L} \overset{K_2}{\rightleftharpoons} \underset{\mathbf{1}}{[\text{FeTPP(L)}_2](SbF_6)} \qquad (8)$$

(40) Yoshimura, T.; Ozaki, T.; Shintani, Y.; Watanabe, H. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1879–1883.
(41) Ogoshi, H.; Watanabe, E.; Yoshida, Z.; Kincaid, J.; Nakamoto,. K. *J. Am. Chem. Soc.* **1973**, *95*, 2845–2849.
(42) By contrast, deprotonation of 2MeImH in the ferrous porphyrin FeOEP (2MeImH) results in a substantial shift of $\nu_{Fe-N(2MeImH)}$ from 212 to 239 cm^{-1}.[10]
(43) Takenaka, A.; Sasada, Y.; Watanabe, E.; Ogoshi, H.; Yoshida, Z. *Chem. Lett.* **1972**, 1235–1238.
(44) Cordes, M.; Walter, J. L. *Spectrochim. Acta, Part A* **1968**, *24*, 237–252.
(45) Zimmermann, H. *Z. Elektrochem.* **1961**, *65*, 821–840.

isolated as their SbF_6^- salts by reaction of 2 equiv of ImH or 4MeImH with 1 mM FeTPP(SbF_6) in toluene. The solid products precipitated from the reaction mixture.

The visible spectrum of **7** suggests that it is high spin. Inspection of the visible spectra of numerous ferric TPP complexes has led us to the conclusion that these spectra fall into three general classes, classes a–c. The visible spectra in class a are characterized by the presence of three or four bands in the α,β region, with the most intense absorption between 470 and 530 nm. Included in class a are the high-spin anionic complexes of the form FeTPPX, with X^- = F^-,[46] Cl^-,[47] I^-,[47] Br^-,[47] OAc^-,[47] SCN^-,[47] NO_3^-,[48] and N_3^-,[49] the intermediate-spin complexes of the same form, with X^- = SbF_6^- or ClO_4^-;[20] and the high-spin six-coordinate complexes of the form $[FeTPP(L)_2]^+$, with L = Me_2SO,[50] DMF,[50] and H_2O.[51] The visible spectra of class b are characterized by the presence of two major absorption bands in the α,β region separated by 1000–1200 cm^{-1}. Included are the low-spin complexes of the form $[FeTPP(L)_2]^+$, L = ImH, 4MeImH, 2MeImH,[26] NMeIm,[26] Im^-, and CN^-,[52,53] and the mixed-ligand complexes FeTPP(ImH)(Im) and FeTPP(py)(N_3).[49] The visible spectra in class c resemble those of class b, but the complexes are high spin. The complexes that give class c spectra are anionic complexes with alkoxide ligands, e.g., FeTPP(OCH_3)[34] and Fe(TPP)(tBuO) (see Table I). The former is known to be high spin.[34] The product of the reaction of FeTPPCl with OH^- has a spectrum similar to that of FeTPP(OCH_3). This has led us to predict that the product is FeTPP(OH). The imidazolate complex **6**, FeTPP(4MeIm), also exhibits this type of spectrum. Since it has been shown to be high spin by EPR (see Figure 2), **6** must also be assigned to class c. The visible spectra of **7a** and **7b** clearly fall in class a; i.e., they are typically high-spin spectra, characterized by four absorptions in the α,β, region, the most intense at 511 nm (see Table I and Figure 3). Unfortunately, high enough concentrations of **7a** or **7b** for reliable EPR analysis could not be obtained. Nevertheless, the visible spectra suggest strongly that **7a** and **7b** are high spin. We are not, however, able to come to a conclusion concerning five- vs. six-coordination. Ogoshi et al.[54] have reported that reaction of FeOEP(ClO_4) with ImH also leads to the formation of a monoimidazole complex. They observed only minor visible spectral changes, however, which suggests that ImH may not, in fact, have been coordinating.

It is interesting to note that the monoimidazole complex has a class a visible spectrum while the monoimidazolate complex **6** has a class c spectrum. Kobayashi et al.[34] have presented theoretical arguments which suggest that the differences between class a and class c spectra can be explained by the degree of mixing of the porphyrin-to-Fe^{III} charge transfer (P-to-Fe CT) excited state with the porphyrin triplet excited states. Class a complexes have P-to-Fe CT energies lower than those of class c, e.g., 800 nm for FeTPPCl, class a, and 571 nm for FeTPP(OCH_3), class c. This shift in the CT energies can be accounted for by the greater electron-donating properties of the axial ligand in class c complexes, which are expected to decrease the electron affinity of the ferric ion to which they are bound and thereby raise the energy of the P-to-Fe CT excited states. Hence for class a spectra, the CT states are of low enough energy to mix effectively with the porphyrin triplet states. Class c spectra have a different appearance because the same CT state is too high in energy for effective mixing. Since we expect Im^- to be a better electron donor than ImH, this explanation could account for the observation that **7** and **6** give class a and class c spectra, respectively.

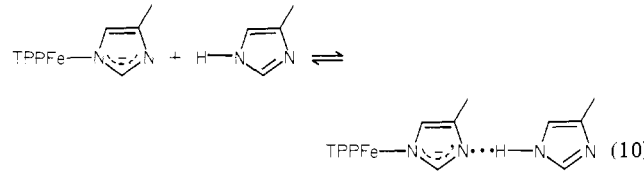
Ligand Binding to Monoimidazole and Monoimidazolate Complexes. By comparing the ligand binding properties of **6** with those of **7b**, we have been able to examine the effect of deprotonation of coordinated imidazole on the affinity of the monoimidazole complex for a sixth ligand. The reaction of **6** with 4MeImH was studied in order to obtain binding constants. We encountered several difficulties with this experiment. Large excesses of 4MeImH were required to observe the product. Under such conditions, precipitation occurred in toluene. The solid is believed to be the less soluble ionic salt $[FeTPP(4MeImH)_2]X$. Chlorinated solvents could not be used because $4MeIm^-$ reacts slowly with them, liberating Cl^-. THF proved to be the most useful solvent in that no precipitation or reaction with the solvent occurred. But, at very high concentrations of 4MeImH, partial reduction of the ferric to the ferrous porphyrin was observed, resulting in the formation of $Fe^{II}TPP(4MeImH)_2$. Reduction may also have occurred to a lesser extent at lower ligand concentrations. Such effects made determination of an equilibrium constant difficult.

In spite of these difficulties, we were able to make some estimates which we believe to be reliable. The behavior observed for the reaction of **6** and 4MeImH in THF and toluene indicated that a stepwise process was occurring. In the initial portion of such a titration (Figure 4), when the ligand concentration was low, relatively small changes occurred in the magnitudes of the absorbance as well as slight shifts in the absorption band maxima, with an isosbestic point appearing at 648 nm. At high concentrations of 4MeImH (see Figure 4), new bands began to appear due to formation of **2b**, FeTPP(4MeIm)(4MeImH), and a different isosbestic point was observed. Hence the optical data support a reaction scheme as in reaction 9.

$$\underset{\mathbf{6}}{\text{FeTPP(4MeIm)}} \overset{\text{4MeImH}}{\underset{K_1}{\rightleftharpoons}} \mathbf{8} \overset{\text{4MeImH}}{\underset{K_2}{\rightleftharpoons}} \underset{\mathbf{2b}}{\text{FeTPP(4MeIm)(4MeImH)}} \quad (9)$$

There are limited possibilities for the nature of the intermediate species, **8**. Actual coordination of 4MeImH is unlikely since the visible spectrum of **8** is similar to that of FeTPP(4MeIm), **6**, and very different from that of **2b**. Two possibilities remain: (1) that 4MeImH is exerting some sort of "solvation" effect or (2) that 4MeImH hydrogen bonds to the imidazolate ligand. The former possibility appears unlikely because spectral changes are observed when very small quantities (<10 equiv) of 4MeImH are added, much less than one would expect for a solvation effect. To investigate the latter possibility, we carried out a study of the effect of addition of other hydrogen-bond donors to **6**. Addition of CH_3OH, a potential hydrogen-bond donor, to solutions of **6** led to spectral changes similar to those observed upon addition of 4MeImH. Similar additions of NMeIm (see Figure 4) or pyridine had no effect on the spectrum of **6**.

The formation of **8** was also observed when solid **4** was dissolved in toluene and reacted with acid. In such a solution, equimolar quantities of **6** and [K(18C6)](4MeIm) are present (see reaction 5). Addition of *p*-toluenesulfonic acid resulted in spectral changes characteristic of those for the conversion of **6** to **8** due to protonation of uncoordinated $4MeIm^-$ and subsequent hydrogen bonding to coordinated $4MeIm^-$. The evidence therefore suggests that **8** is formed by hydrogen bonding of 4MeImH to the $4MeIm^-$ ligand.



(10)

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(51) Scheidt, W. R.; Cohen, I. A.; Kastner, M. E. *Biochemistry* **1979**, *18*, 3546–3552.
(52) The spectrum of $[FeTPP(CN)_2]^-$ has three major bands in the α,β region, two of which are separated by 1000–1200 cm^{-1}. Hence, its spectrum is more like class b than a.
(53) Scheidt, W. R.; Haller, K. J.; Hatano, K. *J. Am. Chem. Soc.* **1980**, *102*, 3017–3021.
(54) Ogoshi, H.; Sugimoto, H.; Yoshida, Z.-I.; Biochim. *Biophys. Acta* **1980**, *621*, 19–28.

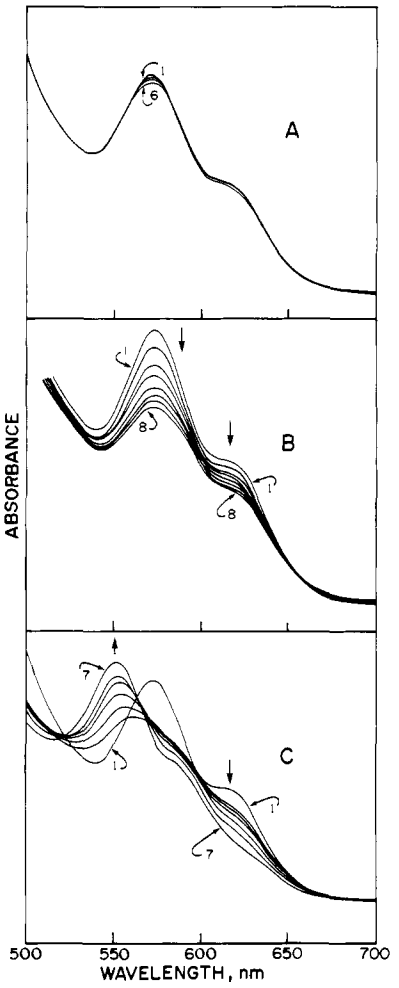


Figure 4. (A) Spectral changes for titration of FeTPP(4MeIm) with NMeIm. The starting solution was prepared by reaction of 2 equiv of K(4MeIm) solubilized with excess 18C6 with 4.0×10^{-5} M FeTPPCl in THF. NMeIm concentrations (M): (1) 0; (2) 4.8×10^{-5}; (3) 9.6×10^{-5}; (4) 1.4×10^{-4}; (5) 2.9×10^{-4}; (6) 5.7×10^{-4}. (B) Spectral changes for titration of FeTPP(4MeIm) with 4MeImH. The starting solution was prepared by reaction of 1.5 equiv of [K(K222)](4MeIm) with 4.0×10^{-5} M FeTPPCl in THF. 4MeImH concentrations (M): (1) 0; (2) 1.2×10^{-5}; (3) 2.4×10^{-5}; (4) 3.9×10^{-5}; (5) 7.7×10^{-5}; (6) 1.1×10^{-4}; (7) 1.5×10^{-4}; (8) 5.2×10^{-4}. (C) Spectral changes from titration of FeTPP(4MeIm) with greater than 100 equiv of 4MeImH. The starting solution was prepared as in B. 4MeImH concentrations (M): (1) 0; (2) 4.6×10^{-3}; (3) 7.0×10^{-3}; (4) 9.3×10^{-3}; (5) 1.2×10^{-2}; (6) 1.4×10^{-2}; (7) 1.8×10^{-2}.

A value of K_1 for the hydrogen bonding of 4MeImH to **6** in THF (reaction 9) was determined by the method of Brown,[55] which permits calculation of large equilibrium constants. Most other methods require that $[L]_{total} >> [L]_{bound}$, which is not the case when K is large. The equilibrium concentration of ligand, $[L]_{eq}$, is given by $[L]_{eq} = [L]_{total} - C_T\Delta A/\Delta A_{max}$, where C_T is the total porphyrin concentration, ΔA in the absolute value of the difference between the observed and initial absorbances, and ΔA_{max} is the absolute value of the difference between final and initial absorbances. Plotting $\Delta A/[L]_{eq}$ vs. ΔA leads to a straight line with a slope of $-1/K_{eq}$ and y intercept of ΔA_{max}. Using data from absorbance changes at 573 nm for a 10^{-5} M porphyrin in THF solution, we obtain a linear plot ($r = 0.9995$) and the result that $K_1 = 5 \times 10^4$ M^{-1}.

At higher concentrations of 4MeImH, **8** was observed to react further with 4MeImH, forming FeTPP(4MeIm)(4MeImH), **2b**. Under similar conditions, titrations of **6** with NMeIm or pyridine resulted only in gradual reduction to $Fe^{II}TPP(L)_2$. Evidence for the intermediate formation of $Fe^{III}TPP(4MeIm)(L)$ was not

(55) Brown, K. L. *Inorg. Chim. Acta* **1979**, *37*, L513–L516.

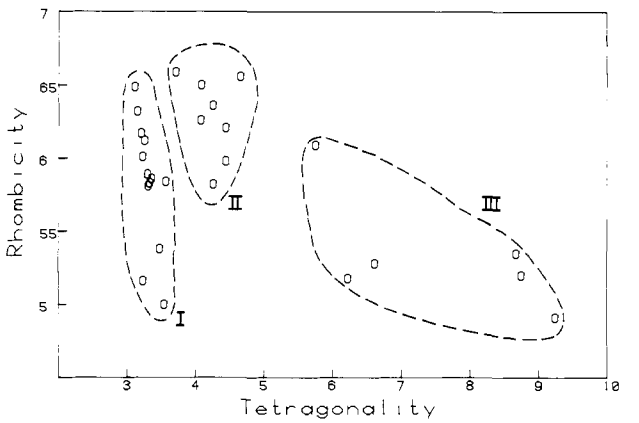


Figure 5. Rhombicity vs. tetragonality plot of low-spin ferric porphyrin complexes listed in Table II: (I) Complexes of imidazoles; (II) complexes of imidazolate or imidazole with a strong hydrogen bonder; (III) complexes of the form FeP(L)(OR), where L = ImH, NMeIm, and py and $OR^- = OH^-$, alkoxides, and phenoxides.

observed. The equilibrium constant K_2 for the binding of 4MeImH to **8** in THF is much smaller than K_1. Therefore the assumption that $[L]_{total} >> [L]_{bound}$ is valid. The absorption spectrum of the fully formed FeTPP(4MeIm)(4MeImH) cannot be accurately determined, however, due to partial reduction at concentrations of 4MeImH sufficiently high to drive the reaction to completion. For this reason, the method of Ketelaar et al.,[56] which requires no knowledge of the absorbance of the product, was used. Absorbance changes for a 4×10^{-5} M solution of FeTPP(4MeIm) in THF were monitored at 552 and 540 nm. Plots of $1/[L]$ vs. $1/\Delta A$ were found to be linear ($r = 0.9987$, 0.9993), with a slope of $1/K\Delta A_{max}$ and a y intercept of $1/\Delta A_{max}$. Values of K_2 were 54 and 43 M^{-1} at 552 and 540 nm, respectively. Hence a value of 50 ± 10 M^{-1} is a reasonable estimate of K_2.

The low value of K_2 is illustrated by two further experimental observations. Reaction of $[FeTPP(4MeImH)_2](SbF_6)$ in toluene with $tBuO^-$ in the absence of excess 4MeImH leads to formation of FeTPP(4MeIm), **6**, rather than of FeTPP(4MeIm)(4MeImH), **2b** (reaction 11). Similarly, reaction of $[FeTPP(ImH)_2]Cl$ in

$$[FeTPP(4MeImH)_2]^+ \xrightarrow[\text{(no excess 4MeImH)}]{tBuO^-} FeTPP(4MeIm) + 4MeImH \quad (11)$$

CH_2Cl_2 with OH^- or $tBuO^-$ in the presence of only enough excess ligand to form the bis complex resulted in formation of **5**, $[(FeTPP)_2Im]^+$, rather than **3a**, FeTPP(Im)(ImH). To observe the mixed complexes **2a** or **2b** in such base titrations, large excesses of ligand are required (reaction 1).

Affinity for Six-Coordination. Comparison of the affinities of the monoimidazole complex **7b** and the monoimidazolate complex **6** for a sixth ligand demonstrates that deprotonation of coordinated imidazole has a marked affect on the reactivity of the ferric center. The affinity of **7b** for a second 4MeImH is very large. The reaction is essentially complete after a stoichiometric amount of ligand has been added. But the affinity of **6** for a sixth ligand is, by contrast, greatly reduced. Our best estimate of the equilibrium constant at 25 °C for reaction 9 is $K_2 = 50 \pm 10$ M^{-1}. As described above, we estimate a *minimum* value of K_2 for **7b** (reaction 8) to be 10^7 M^{-1}, or a minimum of 5 orders of magnitude higher than that for the analogous $4MeIm^-$ complex. Furthermore, it should be recalled that the ligand addition reaction of 4MeImH with **6** actually involves addition of the ligand to the hydrogen-bonded complex, **8**. Hydrogen bonding is expected to make the coordinated imidazolate more "imidazole-like". Hence, one would predict a still lower value of K_2 for **6** in which hydrogen bonding is absent. The presence of $4MeIm^-$ clearly exerts a pronounced trans influence on the binding of a sixth ligand. The effect is not limited to binding of 4MeImH. Both NMeIm and

(56) Foster, R. "Organic Charge-Transfer Complexes", Academic Press: New York, 1969, pp 132–133.

Table III. Equilibrium Constant Values for the Ligand Addition Reaction of FeP(X)

$$FeP(X) + L \underset{}{\overset{K}{\rightleftharpoons}} FeP(L)(X)$$

FeP(X)	L	K, M^{-1}	T, °C	solvent	ref
$FeTPP(N_3)$	py	1.75	23	CH_2Cl_2	49
	ImH	79	23	CH_2Cl_2	49
	NMeIm	145	23	CH_2Cl_2	49
FeTPPCl	NPrIm	9.5	20	acetone	*a*
	NMeIm	9	25	$CHCl_3$	26
	2MeImH	16	25	$CHCl_3$	26
	py	~.2	25	$CHCl_3$	26
FeTPP(4MeIm)	4MeImH	50	25	THF	this work
FePPIXDBE($OC_6H_3$2,6(OCH_3)$_2$)	NMeIm	~100	24	CH_2Cl_2	*b*
FePPIXDMECl	ImH	630	25	$CHCl_3$	*c*
	4MeImH	500	25	$CHCl_3$	*c*
	NMeIm	40	25	$CHCl_3$	*c*
	2MeImH	56	25	$CHCl_3$	*c*

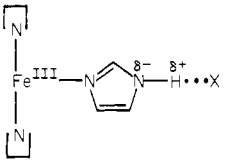
[a] Burdige, D.; Sweigart, D. A. *Inorg. Chim. Acta* 1978, *28*, L131-L133. [b] Ainscough, E. W.; Addison, A. W.; Dolphin, D.; James, B. R. *J. Am. Chem. Soc.* 1978, *100*, 7585-7591. [c] Yoshimura, T.; Ozaki, T. *Bull. Chem. Soc. Jpn.* 1979, *52*, 2268-2275.

pyridine are observed not to bind to FeTPP(4MeIm).

The stabilization of ferric porphyrins by anionic ligands has been noted previously by Reed et al.[20] It has also long been known that most complexes of the type FeTPPX do not readily bind a sixth ligand, forming FeTPP(X)(L). For example, Adams et al.[49] have demonstrated that, although $FeTPP(N_3)$ binds neutral ligands such as py, ImH, or NMeIm to form the low-spin complex $FeTPP(N_3)(L)$, the equilibrium constants for these reactions are quite low (see Table III). The behavior of FeTPP(4MeIm) in coordinating a sixth ligand is thus simialr to that of $FeTPP(N_3)$. Equilibrium constants for ligand addition to other $Fe^{III}PX$ complexes are also found to be low (see Table III).

Simialr effects are also seen for ferrous porphyrins. Mincey and Traylor[9] have demonstrated that deprotonation of 2MeImH in Fe^{II}(PPIXDME)(2MeImH) leads to a reduced affinity for CO. Reduced CO affinity has also been observed for the thiolate complex $[Fe^{II}TPP(SC_2H_5)]^-$.[57] Hence reduced affinities for a sixth ligand may well be a property common to all five-coordinate ferric and ferrous porphyrin complexes of monovalent anions.

Comparisons with Hemoproteins. Several investigators have suggested that imidazolate, rather than imidazole, may act as an axial ligand in a variety of hemoproteins.[4-10,13] Considering that the pK_a of ferric porphyrin bisimidazole complexes is approximately 10,[58] it would at first appear unlikely that imidazole would be deprotonated in the physiologically attainable pH range. But no estimate is available for the pK_a of a five-coordinate ferric porphyrin imidazole complex. The propensity of five-coordinate ferric porphyrins for anionic ligands suggests that the pK_a of imidazole in a five-coordinate complex may be substantially lower than that for six-coordinate complexes. It has also been suggested that ferric horseradish peroxidase and cytochrome *c'* may contain five-coordinate hemes with one axial histidyl ligand[20-25] and further that this histidyl ligand may be deprotonated in horseradish peroxidase.[7] It is interesting to speculate that five-coordination in ferric hemoproteins may be due to the trans effect of an imidazolate ligand or of an imidazole ligand that is strongly hydrogen bonded to another residue within the protein and hence has become "imidazolate-like".



Summary

(1) The following new imidazole and imidazolate complexes have been prepared and characterized: FeTPP(L)(L^-), [FeTPP(L^-)$_2$]$^-$, [FeTPP(L)](SbF_6) (L = ImH, 4MeImH; L^- = Im^-, $4MeIm^-$), [(FeTPP)$_2$(Im)]$^+$, and FeTPP(4MeIm). (2) The monoimidazole complex [FeTPP(L)](SbF_6) binds another L with high affinity. (3) By contrast, the affinity of the monoimidazolate complex FeTPP(4MeIm) for six-coordination is much lower than that of the monoimidazole complex. (4) 4MeImH is observed initially to hydrogen bond to FeTPP(4MeIm) and is only observed to coordinate to iron at high concentrations.

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Registry No. 1a, 52155-41-6; **1b**, 59910-77-9; **2a**, 64408-29-3; **2b**, 80925-69-5; **3a**, 64433-00-7; **3b**, 80925-70-8; **4**, 80925-71-9; **5**, 80925-72-0; **6**, 80925-73-1; **7a**, 80925-75-3; **7b**, 80925-77-5; 4MeImH, 822-36-6; FeTPPCl, 16456-81-8; $FeTPP(SbF_6)$, 79949-97-6; [FeTPP(ImH)$_2$]Cl, 25442-52-8; [FeTPP(4MeIm)$_2$]Cl, 61056-84-6; [FeTPP(ImH)$_2$](SbF_6), 80939-25-9; [FeTPP(4MeImH)$_2$](SbF_6), 80939-26-0; [FeTPP(NMeIm)$_2$]$^+$, 52155-25-6.

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(58) Morishima, I.; Neya, S.; Yonezawa, T. *Biochim. Biophys. Acta* **1980**, *621*, 218-226.