the potential to attain a formal oxidation state similar to d^8 by electron transfer) and not a vacant coordination position appears to be the requirement for the ring-bonded peroxo mode of dioxygen binding. This conclusion supports the electron-transfer step proposed by Halpern et al.[2] to account for the reported product isolated from the reaction of $Co(PMe_2Ph)_3(CN)_2$ with O_2.

Upon cooling solutions of the trigonal-bipyramidal chloride and bromide complexes (CoP_3Br_2) in the presence of dioxygen, no color change is observed, and the O_2 adduct signal is not detected in the EPR. On the other hand, the trigonal-bipyramidal complex, $Co(PMe_2Ph)_3F_2$, undergoes the characteristic color change for oxygenation upon cooling as does the square-pyramidal thiocyanate complex.

The experiments described above provide a substantial variation in the factors that could potentially influence dioxygen binding stability. Binding ability does not correlate with the initial geometrical configuration for both trigonal-bipyramidal and tetragonal-pyramidal complexes from adducts. The ligand field strength does not appear to be a determining factor inasmuch as the thiocyanate ion (N bonded) and chloride ion have comparable coordination tendencies. Based upon electronic arguments both the bromide and chloride systems should form dioxygen adducts if the fluoride and thiocyanate complexes do. These results suggest that steric factors could be contributing to the instability of the chloride and bromide adducts of dioxygen. The S-bonded thiocyanate system apparently contradicts this conclusion, but it is possible that this ion could be nitrogen bound in the O_2 adduct, even though it is sulfur bound in the five-coordinate complex. Though these studies do provide insight into the requirements for ring-bonded O_2 coordination, more quantitative work is needed to gain a better appreciation of the factors influencing the strength of binding of dioxygen to transition metals.

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References and Notes

(1) J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973), and references cited therein.
(2) J. Halpern, B. L. Goodall, G. P. Khare, H. S. Liu, and J. J. Pluth, *J. Am. Chem. Soc.*, **97**, 2301 (1975).
(3) B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1976).
(4) R. S. Drago, T. Beugelsdijk, J. A. Breese, and J. P. Cannady, *J. Am. Chem. Soc.*, **100**, 5374 (1978).
(5) J. Solodar, *Synth. Inorg. Met.-Org. Chem.*, **1**, 141 (1971).
(6) P. Rigo, M. Bressan, and A. Turco, *Inorg. Chem.*, **7**, 1460 (1968).
(7) This program was provided by Professor R. L. Belford and is designed in Mark Nilges, Ph.D. Thesis, University of Illinois, 1977.
(8) R. S. Drago, "Physical Methods in Chemistry", W. B. Saunders, Philadelphia, 1977, p 472.
(9) O. Stelzer, W. S. Sheldrich, and J. Subramanian, *J. Chem. Soc., Dalton Trans.*, 966 (1977).
(10) The room temperature spectra of $Co(PMe_2Ph)_3(CN)_2$ and $Co(PMePh_2)_3(CN)_2$ could not be fit using one g value and phosphorus hyperfine because the peak at low field is broader than the peak at high field. Two g values (for $Co(PMe_2Ph)_3(CN)_2$ $g_\parallel = 2.10$, $g_\perp = 2.13$, and for $Co(PMePh_2)_3(CN)_2$ $g_\parallel = 2.09$ and $g_\perp = 2.15$) were required. $\langle g \rangle = \frac{1}{3} g_\parallel + \frac{2}{3} g_\perp$.
(11) J. A. Ibers and J. Stalich, *Inorg. Chem.*, **8**, 1090 (1969).
(12) L. Vaska, *Science*, **140**, 809 (1963).
(13) R. S. Drago and J. H. Elias, *J. Am. Chem. Soc.*, **99**, 6570 (1977).
(14) We would hasten to point out, in the event anyone is interested, that both cobalt and iridium have an oxidation state of three in these O_2 adducts.
(15) A referee has suggested that oxidation of the phosphine to phosphine oxide might have depleted the O_2 so no resonance for the O_2 adduct is observed. This is inconsistent with our observation of an O_2 adduct spectrum at low phosphine to cobalt ratios. More than enough phosphine was present to scavenge all the O_2 in those systems. It is also inconsistent with the stability of the phosphine on long standing in experiments by Halpern et al.[2]

Axial Ligation Constants of Iron(II) and Cobalt(II) "Capped" Porphyrins

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Abstract: Equilibrium constants for the addition of ligands to cobalt(II) and iron(II) complexes of the "capped" and "homologous capped" porphyrins are reported. For the equilibrium $Fe^{II}(Cap) + B \rightleftharpoons Fe^{II}(Cap)(B)$ (K^B), a plot of log K^B vs. the pK_a of the conjugate acid of the ligand shows a linear relationship among structurally similar base ligands. π-Bonding ligands form more stable complexes than predicted by their pK_a values. Sulfur base binding to $Co^{II}(Cap)$ shows a relative binding order for S-donor ligands of thiolates $\gg$ thioethers $>$ mercaptans. Unlike the Fe(Cap), which can bind only one axial base ligand, Fe(HmCap) can bind two small ligands axially in the usual manner. Intermediate-size ligands, such as 1-methylimidazole, however, weakly coordinate a second base leading to an unusual six-coordinate complex with an intermediate electronic spin of $S = 1$.

Introduction

Investigations on the variations in the biological role of the naturally occurring hemoproteins which are associated with changes in axial ligation of the heme moiety are necessary and desirable. This can best be done by means of metalloporphyrin model complexes owing to the versatility and relative simplicity of the binding of axial ligands to these complexes.

Although several research groups have reported on the axial ligation of cobalt(II) porphyrins[1-5]

$$Co^{II}(Por) + B \overset{K^B}{\rightleftharpoons} Co^{II}(Por)(B)^6 \quad (1)$$

there is much less information on similar axial ligation to iron(II) porphyrins. This is largely because of the difficulty in obtaining direct experimental values for K^B and $K_B{}^B$, since the high-to-low electronic spin change of the iron(II) complexes causes the anomaly of $K_B{}^B > K^B$:

$$Fe(Por) + B \overset{K^B}{\rightleftharpoons} Fe(Por)(B) \quad (2)$$

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$$\mathrm{Fe(Por)(B)} + \mathrm{B} \overset{K_B^B}{\rightleftharpoons} \mathrm{Fe(Por)(B)_2} \qquad (3)$$

The monobase adducts of iron(II) porphyrins which have been investigated to give K^B necessitate the use of hindered bases,[7,8] weak-field ligands,[9,10] or error-prone mathematical separations of K_B^B from K^B.[7,9-12] The Fe(Cap), however, does not form bis base complexes with axial ligands owing to steric encumbrance of the attached cap.[13] This means that for measurements of base addition constants (K^B), which correspond to the five-coordinate iron(II) in the natural hemoproteins, Fe(Cap) has a distinct advantage over other ferrous porphyrins. In this system K^B can be directly determined instead of having to be estimated. We now report the syntheses, characterization, magnetic properties, and axial ligation of the Fe(II) and Co(II) "cap" and "homologous cap" complexes.

Experimental Section

Reagents. Toluene was reagent grade and was distilled under N_2 from benzophenone ketyl immediately prior to use. Pyridine was distilled over BaO under N_2 immediately prior to use. All liquid organic bases were dried and purified by standard methods and distilled prior to use. Solid organic bases were recrystallized from benzene two times prior to their use. The N_2 was Matheson prepurified grade and was passed through Ridox and molecular sieve columns to remove residual O_2 and water.

Analyses. Elemental analysis of C, H, and N were performed by H. Beck of this department.

Syntheses. Fe(Cap)Cl, Fe(Cap), and Cap H_2 were prepared by the method of Baldwin and co-workers.[13,14]

Co(Cap)[15] was prepared by refluxing a solution of $CapH_2$ (0.35 g) in a $CHCl_3$ (50 mL)–acetic acid (50 mL) mixture, to which was added $Co(C_2H_3O_2)_2{\cdot}4H_2O$ (0.30 g). The mixture was refluxed for 3 h, and then the reaction mixture was tested for $CapH_2$ by the long-wavelength UV light technique.[16] When no more porphyrin free base was noted, water (100 mL) was added and the solution was slowly cooled to 0 °C. Crystallization of the product did not occur, so the $CHCl_3$ layer was extracted twice with H_2O (150 mL) to remove any acetic acid and the $CHCl_3$ removed with a rotary evaporator. The residue was extracted with $CHCl_3$ (75 mL) and chromatographed on dry alumina, eluting with $CHCl_3$. The solvent was removed and the residue recrystallized from CH_2Cl_2/heptane and dried at 100 °C under vacuum to yield 220 mg of pure Co(Cap): λ_{max} (CH_2Cl_2) 413, 529, 565 sh nm.

Anal. Calcd for $CoC_{62}H_{42}N_4O_{12}$: C, 68.07; H, 3.87; N, 5.12. Found: C, 67.99; H, 3.92; N, 5.16.

***o*-(2-Hydroxypropoxy)benzaldehyde ("Monoaldehyde").** Whenever possible the synthetic techniques of Baldwin and co-workers[13] were followed in the following syntheses leading to the synthesis of $HmCapH_2$. These compounds were prepared without precaution to exclude air and water. Salicylaldehyde (405 g) was added dropwise over 1.5 h to a vigorously stirred solution of NaOH (133 g in 2500 mL of H_2O). The color of the solution changed from yellow to dark brown during the addition. 2-Chloropropanol (300 g) was then added dropwise with stirring over 1.5 h, and the solution was subsequently heated on a steam bath for 14 h. After slow cooling to room temperature, the solution was further cooled to about −20 °C with a dry ice/acetone bath. While keeping the temperature below 10 °C, NaOH was slowly added until the solution was strongly basic (pH 10). The solution was slowly warmed to room temperature and extracted with 5 × 750 mL of CH_2Cl_2. The extracts were bulked and washed with 4 × 400 mL of saturated aqueous NaCl. The resulting solution was dried over $MgSO_4$ and evaporated to a brown oil. The oil was dissolved in a 3:2 by volume mixture of $CH_3CO_2C_2H_5/CH_2Cl_2$ and chromatographed on silica gel to give a light yellow oil. Although impure, the NMR spectrum showed the oil to be essentially the desired monoaldehyde, yield of crude monoaldehyde 70 g.

Pyromellitoyl Chloride. This procedure is a modification of the method of Baldwin and co-workers.[13] Pyromellitic dianhydride (352 g) and PCl_5 (704 g) were mixed thoroughly and heated to 190 °C. After reflux began, the temperature was lowered to 150 °C and heating was continued for 3 h. The $POCl_3$ was removed by vacuum distillation and the pyromellitoyl chloride purified by further vacuum distillation: yield of pyromellitoyl chloride 435 g; mp 64–65 °C; NMR ($CDCl_3$) δ 7.40 (s).

Tetra-2-(2-formylphenoxy)propyl Pyromellitoate ("Tetraaldehyde"). The pyromellitoyl chloride (31.9 g) dissolved in 100 mL of dry THF was added dropwise over a period of 2 h to a stirred solution of the monoaldehyde (70 g) and triethylamine (39.3 g) in dry THF (800 mL) with the temperature maintained at −20 ± 5 °C. After complete addition, the solution was allowed to warm to ambient temperature overnight. The white $(C_2H_5)_3NH^+Cl^-$ precipitate was collected on a filter, and the solvent was removed by vacuum to give a golden-brown oil. The oil was dissolved in $CHCl_3$, and again most of the solvent was evaporated to remove any residual THF. The oil was again dissolved in $CHCl_3$ and washed with aqueous NaCl. The organic layer was dried over $MgSO_4$ and the solvent was evaporated to give a residual oil. This oil was dissolved in CH_3CN, and H_2O was added dropwise at an extremely slow rate (1 mL/10 min), while the solution was stirred to induce crystallization. The white precipitate was recrystallized from hot ethanol: yield 36 g; NMR ($CDCl_3$) δ 2.3 (8 H, m), 4.2 (8 H, m), 4.5 (8 H, m), 7.05 (8 H, m), 8.05 (2 H, s), 10.48 (4 H, s).

Homologous Capped Porphyrin ($HmCapH_2$).[17] A 12-L, three-necked flask fitted with a mechanical stirrer, dropping funnel, condenser, and gas inlet tube was charged with 9400 mL of propionic acid and heated to reflux. A stream of air was blown through the stirring acid, and pyrrole (13.5 g) was added to the solution. A solution of the tetraaldehyde (21.7 g) in warm propionic acid (625 mL) was added dropwise over a 10-min period and, when approximately half of the tetraaldehyde solution was added, an additional portion of pyrrole (13.5 g) was added to the solution. The mixture was refluxed for 1.5 h and filtered while still hot. The solvent was removed from the filtrate to give a black solid. The solid was dissolved in hot $CHCl_3$ and treated with a saturated aqueous solution of $NaHCO_3$. The $CHCl_3$ was removed by a rotary evaporator, the aqueous phase filtered, and the precipitate washed with copious amounts of H_2O (3 L). The solid was then dissolved in benzene (1 L), and any remaining H_2O was removed by azeotropic distillation. The benzene solution was then evaporated to dryness and the black solid was dissolved in $CHCl_3$ (2500 mL). The $CHCl_3$ solution was refluxed with 150 g of activated carbon for 1 h. After three treatments with activated carbon the filtered $CHCl_3$ solution was evaporated to dryness on a rotary evaporator to produce 7.5 g of crude $HmCapH_2$. The crude $HmCapH_2$ was purified (to remove any chlorin impurity) by the usual method[18] of refluxing a solution of the crude $HmCapH_2$ and 2,3-dichloro-5,6-dicyanobenzoquinone in benzene for 2.5 h. After the solvent was removed, the residue was dissolved in $CHCl_3$. The solution was filtered and then chromatographed on neutral alumina eluting with $CHCl_3$. The $CHCl_3$ was removed by rotary evaporator and the dark blue product was recrystallized twice from 5% pentane to yield about 5% of crude product: 95% $CHCl_3$ (v/v) after washing with hexane; yield from 1.00 g crude 265 mg; NMR ($CDCl_3$) δ −3.06 (2 H, s), ~1.25 (12 H, m), 1.59–1.90 (8 H, m), 3.87–4.22 (16 H, m), 5.66 (2 H, s), 7.24–7.68 (16 H, m), 8.70 (8 H, d). The multiplet centered at about δ 1.25 is apparently due to pentane solvate: λ_{max} ($CHCl_3$) 420, 518, 556, 595, 651 nm.

Fe(HmCap)Cl. $HmCapH_2$ (150 mg) and anhydrous $FeCl_2$ (200 mg) were dissolved in THF (100 mL) under N_2 to exclude O_2 and H_2O. 2,4,6-Trimethylpyridine (2–3 drops) was added to the solution, which was refluxed for approximately 48 h. The THF was removed by rotary evaporation and the solid washed with 5% HCl/H_2O (v/v) and recrystallized twice from $CHCl_3$/hexane: yield of Fe(HmCap)Cl 100 mg; λ_{max} 510, 575 sh nm; mol wt (mass spectrum[19]) 1146.3, $(C_{66}H_{50}O_{12}N_4)Fe$ which is minus HCl.

Fe(HmCap). Because of the extreme oxygen sensitivity of this compound in solution, the baseless Fe(HmCap) was freshly prepared and used immediately. In a typical reduction 1–10 mg of Fe(HmCap)Cl was dissolved in toluene (20 mL) and the solution was purged with N_2 to remove O_2. An equal volume of deoxygenated aqueous 0.3 M $Na_2S_2O_4$ solution was added to the Fe(HmCap)Cl solution. After vigorous shaking for 5 min the brown solution turned to an orange-red color. The aqueous layer was discarded and the toluene solution was transferred by cannula to a N_2-filled flask containing Na_2SO_4 (anhydrous) to remove any H_2O: λ_{max} (toluene) 422, 448 sh, 544 nm.

Co(HmCap). $HmCapH_2$ (350 mg) was dissolved in 100 mL of 1:1 $CHCl_3$/acetic acid (v/v). The solution was heated to reflux, after which $Co(acetate)_2{\cdot}4H_2O$ (0.5 g) was added and reflux was continued for 3 h. During this time the visible spectrum of the reaction mixture was checked for the presence of free porphyrin. If the spectrum re-

vealed the presence of free porphyrin, refluxing was continued. After complete reaction, the mixture was cooled to room temperature and the contents were washed with 3 × 150 mL of H_2O. The solvent was removed by rotary evaporation, and the dark solid was dissolved in $CHCl_3$ (50 mL). The solution was chromatographed on neutral alumina (100 g) and eluted with $CHCl_3$. The Co^{II}(HmCap) was removed from the column as a single, sharp, dark red band. Any Co^{III}(HmCap)$^+$ present could be removed from the column by eluting with methanol. The $CHCl_3$ was removed and the Co(HmCap) was recrystallized from CH_2Cl_2/heptane (1:1, v/v): yield of Co(HmCap) 300 mg; λ_{max} 416, 538, 569 sh nm.

Magnetic Susceptibilities. Magnetic susceptibilities were measured by the Evans method,[20] as adapted for metalloporphyrins by Brault and Rougee.[21] Their transformation of the Evans equation gives

$$X_M = \frac{3}{\pi}\frac{\Delta\nu}{\nu}\frac{1000}{C} + X_0M - X_D \quad (4)$$

where X_M is the molar paramagnetic susceptibility of the metalloporphyrin, $\Delta\nu$ is the frequency separation between the two resonance lines (Hz), ν is the applied field (Hz), C is the concentration (mol/L), X_0 is the mass susceptibility of the solvent, M is the molecular weight of the metalloporphyrin, and X_D is the diamagnetic susceptibility of the metalloporphyrin. Values of X_0 were calculated from the atomic diamagnetic susceptibilities.[22] Values of X_D were determined from the diagmagnetic susceptibility of Fe(TPP)[21] and the atomic diamagnetic susceptibilities. The paramagnetism of the compound is then expressed in terms of the magnetic moment, μ_{eff}:

$$\mu_{eff} = 2.84(X_M T)^{1/2} \quad (5)$$

The frequency shifts were measured by adding a reference compound (Me_4Si) to both the porphyrin solution and the solvent. The paramagnetic solution was contained in the outer tube and the solvent in an inner tube of a coaxial NMR cell. The outer tube was a standard 5-mm NMR tube and a 1-mm inner diameter capillary tube was used for the inner tube. If the outer tube contained a paramagnetic substance, two resonances were obtained for the Me_4Si peak, solvent peaks, and proton resonances of the added base. The difference between the two resonances, $\Delta\nu$, was measured with an accuracy of ±0.5 Hz.

Base Equilibria Measurements. Equilibrium constants were measured by a spectrophotometric titration method. Aliquots of deoxygenated base, either neat or diluted with toluene, were added to a toluene solution of the metalloporphyrin under N_2 in a 1-cm optical cell. The temperature of the porphyrin solution was maintained to a precision of ±0.1 °C. In general, the spectra were recorded in the 650–480- or 500–400-nm ranges.

For equilibria involving only a single ligand, B, there are two possible equilibrium expressions (eq 1 or 2 and 3). When $K_B^B = 0$, the titration shows an isosbestic point and the data can be fitted to the Hill equation[23]

$$\log y/(1-y) = n \log [B] + \log K^B \quad (6)$$

using a nonweighted linear least-squares method, where

$$y = \frac{A_{obsd} - A_0}{A_\infty - A_0}$$

and A_{obsd} = absorbance at a specific [B], A_0 = initial absorbance, where [B] = 0, and A_∞ = final absorbance, when the fully ligated porphyrin is the only species present. Values for log K^B were obtained from the y intercept of the regression line for a plot of $\log y/(1-y)$ vs. log [B].

Where $K_B^B \neq 0$ but $K_B^B \ll K^B$, the two equilibrium constants could be easily separated with high accuracy. The initial values of the titration could be fitted to the Hill equation to obtain K^B by systematically varying A_∞ and maximizing the correlation coefficient for the regression line obtained from a plot of the $\log y/(1-y)$ vs. log [B]. To obtain K_B^B, the latter values of the base titration were used. The value of A_0, assumed to be equal to the five-coordinate species M(Por)B, was allowed to vary until a maximization in the correlation coefficient for the regression line was obtained. If the equilibrium constant is small, and A_∞ is therefore difficult to obtain, the following derivation[24] of the Hill equation was used to obtain K^B:

$$\frac{1}{A_0 - A} = \frac{1}{A_0 - A_\infty} + \frac{1}{(A_0 - A_\infty)(K^B)([B])} \quad (7)$$

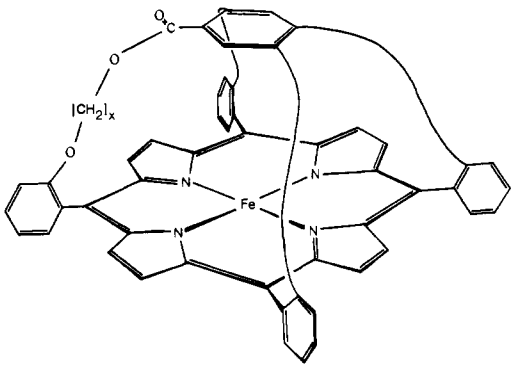

Figure 1. Schematic representations of the "Cap" (x = 2) and "homologous cap" (x = 3) porphyrin complexes.

When $K^B \simeq K_B^B$, the three species M(Por), M(Por)B, and M(Por)B_2 are present simultaneously. The equilibrium constants were obtained by measuring the absorbance at a wavelength where $\epsilon_{M(Por)} = \epsilon_{M(Por)B_2}$, and where [M(Por)B] is a function of [B]. Brault and Rougee[7] have shown that [M(Por)B] reaches a maximum concentration at some $[B]_{max}$, according to the equations

$$[M(Por)B]_{max} = [M(Por)]_T \frac{K^B[B]}{1 + K^B[B] + K^B K_B^B [B]} \quad (8)$$

$$[B]_{max} = (K^B K_B^B)^{-1/2} \quad (9)$$

Equations 8 and 9 were then used to calculate K^B and K_B^B. In those cases we investigated where $K^B \simeq K_B^B$, K_B^B was also derived from the latter stages of the base titration. Use was made of the Hill plot and satisfactory results were obtained as long as no [M(Por)] was present in this titration region.

Results

Cobalt(II) was inserted into the "capped" porphyrin and "homologous capped" porphyrin by reacting a solution of the porphyrin in 1:1 chloroform/acetic acid (v/v) with $Co^{II}(C_2H_3O_2)_2 \cdot 4H_2O$. Both porphyrins yield red Co(II) solid products, which are stable to air and water. The reduction of Fe^{III}(Cap)Cl with bis(acetylacetonato)chromium(II) in benzene solution yields the crystalline baseless Fe^{II}(Cap).[14] This brick-red solid is air stable for short periods of time, and had to be stored under an atmosphere of N_2. Solutions of Fe^{III}(HmCap)Cl in toluene were reduced in situ by reaction with an aqueous sodium dithionite solution. After removal of the aqueous layer, the toluene solution of Fe^{II}(HmCap) could be concentrated by evaporation if necessary for further experimentation. A schematic representation of the "metallocapped" porphyrins is shown in Figure 1.

Equilibrium constants, K^B, were measured for the ligation of M^{II}(Cap), where M(II) = Co(II) and Fe(II) (eq 1 and 2). Values of K^B were also obtained for corresponding M^{II}(HmCap) complexes. However, certain bases add a second ligand to Fe^{II}(HmCap) and allow determinations of K_B^B for these complexes (eq 3). The equilibrium constants were obtained by spectrophotometric titrations of toluene solutions of M^{II}(Cap) and M^{II}(HmCap) with either neat base or solutions of base in toluene under N_2 atmosphere. Plots of log $[y/(1-y)]$, where y equals $[M^{II}(Por)(B)]/[M^{II}(Por)]_{total}$, vs. log [B] gave straight lines with slopes of 1.0 ± 0.1. Adequate isobestics points, after dilution corrections, were maintained throughout the titrations. A typical base titration of the Co(Cap) complex is shown in Figure 2 and a typical base titration of the Fe(HmCap) complex is shown in Figure 3. Values for the equilibrium constants for base addition to the Co^{II}(Cap) and Co^{II}(HmCap) complexes are given in Table I. Results obtained for the Fe(II) complexes are compiled in Table II. Equilibrium constants were checked at a second wavelength, and proved to be independent of the wavelength chosen. Table III gives enthalpy and entropy parameters de-

Table I. Ligation Equilibria (eq 1) for Cobalt(II) Porphyrins

species[a]	base	$pK_a(BH^+)$	log K^B	ref
Co(Cap)	1-MeIm	7.25[e]	2.32 ± 0.05	this work
	1,2-Me_2Im	7.85[e]	1.84 ± 0.05	this work
	$(n\text{-Bu})_3P$	8.43[f]	3.48 ± 0.04	this work
	$P(OEt)_3$	3.50[g]	1.25 ± 0.03	this work
	pentamethylene sulfide	(−4)[h]	1.00 ± 0.05	this work
	methyl phenyl sulfide	(−5)[h]	0.52 ± 0.06	this work
	BuSH	(−7)[h]	<−1	this work
Co(Cap)[b]	BuS⊖	10.66[h]	3.0 ± 0.2	this work
Co(HmCap)	1-MeIm	7.25	2.28 ± 0.05	this work
	1,2-Me_2Im	7.85	1.93 ± 0.05	this work
Co(PPIXDME)[c]	1-MeIm	7.25	3.70	1
Co(T(*p*-OCH_3)PP)[d]	1-MeIm	7.25	3.37	2
	1,2-Me_2Im	7.85	2.79	2

[a] At 23.1 ± .0.1 °C in toluene unless otherwise noted. [b] Solvent is DMF. [c] At 23.0 °C. [d] At 25.0 °C. [e] Albert, A. *Phys. Methods Heterocycl. Chem.* **1963**, *1*. [f] Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. [g] Estimated value; see ref 4. [h] Estimated values from similar bases. See: Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.

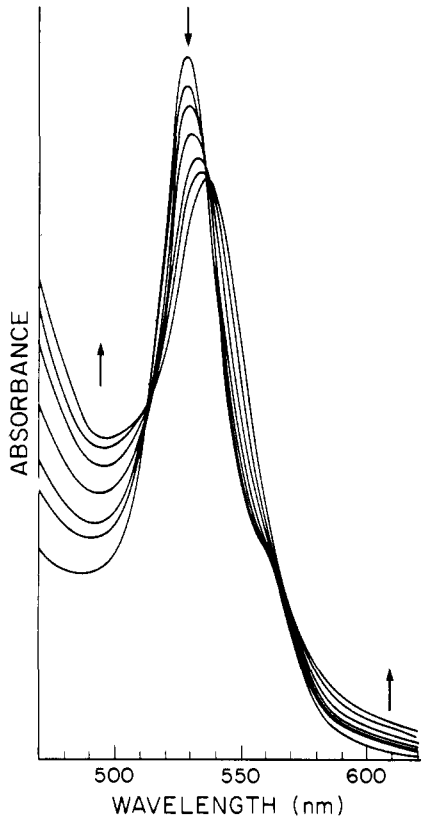

Figure 2. Spectral changes occurring upon titration of a 7.6×10^{-5} M toluene solution of Co(Cap) with 0.2146 M 1-MeIm in toluene at −5.0 °C. The final base concentration is 1.3×10^{-2} M.

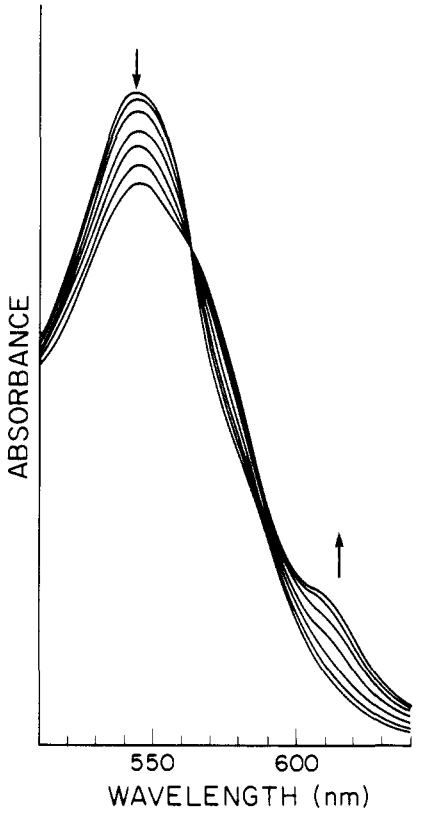

Figure 3. Spectral changes occurring upon titration of a 1.0×10^{-4} M toluene solution of Fe(HmCap) with 0.0884 M 1,2-Me_2Im in toluene at 23.1 °C. The final base concentration is 4.6×10^{-3} M.

rived from van't Hoff plots of log K^B vs. $1/T$, using titrations performed at no fewer than three different temperatures. Results reported for other porphyrin systems are included in Tables I-III for comparative purposes.

By means of the Evans' method[20] the magnetic susceptibilities of some $Fe^{II}(HmCap)(B)_x$ (x = 1, 2) complexes were obtained. The results are shown in Table IV, along with the magnetic moments of related Fe(II) porphyrin complexes.

Discussion

One unique feature of the "capped" metal porphyrins, compared to other "flat" metal porphyrins, is their ability to block the axial site inside the cap and prevent the binding of a second base at this site. However, Baldwin and co-workers[14] showed that small molecules such as carbon monoxide and dioxygen can coordinate to the position inside the cap. Since Fe(Cap) can only add one base, this complex was used to study the monoligation of ferrous porphyrins in some detail. This had not previously been possible with the flat iron(II) porphyrins, because the second base adds more strongly than the first owing to the accompanying electron spin change in going from five- to six-coordinate iron(II). Furthermore, Fe(HmCap) was investigated to determine the effect a larger cap size has on monoligation. It was even more important to determine if the larger cap size would permit the coordination of a second base inside the cap.

One expects the ligand affinity at the axial position outside the cap for Fe(II) and Co(II) capped porphyrins to be similar to that for analogous Fe(II) and Co(II) flat porphyrins. However, the data in Tables I and II show that the Fe(II) and

Table II. Ligation Equilibria (eq 2 and 3) for Iron(II) Porphyrins

species[a]	base	$pK_a(BH^+)$	log K^B	log $K_B{}^B$	ref
Fe(Cap)	1-MeIm	7.25[e]	2.90 ± 0.05		this work
	1,2-Me_2Im	7.85[e]	3.06 ± 0.05		this work
	3-Clpy	2.84[f]	1.53 ± 0.04		this work
	py	5.27[f]	1.88 ± 0.04		this work
	3,4-Me_2py	6.46[f]	2.26 ± 0.04		this work
	sec-$BuNH_2$	10.56[g]	2.16 ± 0.06		this work
	t-$BuNH_2$	10.83[g]	2.50 ± 0.06		this work
	$(n\text{-Bu})_3P$	8.43[h]	4.66 ± 0.06		this work
	$P(OEt)_3$	3.50[i]	3.24 ± 0.05		this work
	BzNC		5.44 ± 0.15		this work
Fe(Cap)[b]	BuSⓀ	10.66[j]	4.2 ± 0.2		this work
Fe(HmCap)	1-MeIm	7.25[e]	3.31 ± 0.05	0.77 ± 0.05	this work
	1,2-Me_2Im	7.85[e]	3.61 ± 0.05		this work
	py	5.27[f]	2.17 ± 0.20	0.84 ± 0.05	this work
	sec-$BuNH_2$	10.56[g]	2.79 ± 0.30	2.85 ± 0.10	this work
	t-$BuNH_2$	10.83[g]	2.23 ± 0.05		this work
	$prNH_2$	10.53[g]	3.40 ± 0.30	4.05 ± 0.10	this work
	$(n\text{-Bu})_3P$	8.43[h]	5.49 ± 0.15		this work
	$P(OEt)_3$	3.50[i]	3.58 ± 0.05		this work
Fe(Deut)	2-MeIm	7.86[e]	4.10		7
FeTPP[c]	2-MeIm	7.86[e]	4.38		7
	Im	6.95[e]	3.94	4.89	7
	py	5.27[f]	3.18	4.28	9
FeTPP[d]	CO		4.82	2.15	12
FeTpivPP	1,2-Me_2Im	7.85[e]	4.5		8
Fe(PPIXDME)	BuSⓀ	10.66[j]	4.4		32

[a] Solvent is toluene at 23.1 ± 0.1 °C unless otherwise indicated. [b] Solvent is DMF. [c] Solvent is benzene at 25.0 °C. [d] At 20 °C. [e] Albert, A. *Phys. Methods Heterocycl. Chem.* **1963**, *1*. [f] Schofield, K. "Hetero-Aromatic Nitrogen Compounds", Plenum Press: New York, 1967; p 146. [g] Albert, A.; Serjeant, E. P. "Ionization Constants of Acids and Bases"; Methuen; London, 1962; p 140. [h] Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. [i] Estimated value; see ref 4. [j] Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 233.

Table III. Thermodynamic Data for the Binding of Axial Ligands to Iron(II) and Cobalt(II) Porphyrins, M(Por) + B ⇌ M(Por)B

compd	base	ΔH, kcal/mol	ΔS, eu/mol	ref
Fe(Cap)	1-MeIm	−6.1 ± 1	−7.4 ± 2	this work
Fe(Cap)	py	−5.3 ± 1	−9.3 ± 2	this work
Co(Cap)	1-MeIm	−8.8 ± 1	−19 ± 2	this work
Co(HmCap)	1-MeIm	−8.2 ± 1	−17.2 ± 2	this work
Co(T(*p*-OCH_3)PP)	1-MeIm	−11.4	−23	2
Co(PPIXDME)	1-MeIm	−10.7	−19	1

Table IV. Magnetic Moments of Iron(II) Porphyrins

species	μ,μ_B[a]	spin state	ref
Fe(HmCap)(1-MeIm)	4.6 ± 0.2	2	this work
Fe(HmCap)(1-MeIm)$_2$	3.1 ± 0.2	1	this work
Fe(HmCap)($prNH_2$)$_2$	0	0	this work
Fe(TPP)(py)$_2$	0[b]	0	*c*
Fe(TPP)(2-MeIm)	5.2[b]	2	*c*
Fe(TPP)	4.4[b]	1	*c*

[a] Magnetic susceptibility measured by Evans' method[20] at 34 °C unless otherwise noted. [b] Magnetic susceptibility measured on solid by Faraday balance at 25 °C. [c] Collman, J. P.; Reed, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 2048.

Co(II) capped porphyrins do not bind bases as strongly as do other Fe(II) and Co(II) porphyrins. Since electronic substituent changes are known to have a relatively small effect[3] on ligation in these systems and since the substituents on the phenyl rings of the capped porphyrin are very similar to those of T(*p*-OCH_3)PP, it follows that the much smaller ligand binding of the capped metal porphyrins compared with M[T(*p*-OCH_3)PP] is not due to electronic effects.

The lower base affinity might be caused by the greater steric hindrance afforded the axial base by the tetra-*meso*-phenyl groups held rigidly in place in the metal capped porphyrins, compared with the lesser steric restrictions of the flat M(TPP)-type complexes. It is also known[25] that the metal in a five-coordinate complex is pulled out of the plane of the porphyrin toward the base. If this motion is restricted in the metal capped porphyrins, it will be reflected in smaller monoligation constants. The implication of such conformational strain in model compounds for hemoglobin cooperativity is discussed in the accompanying paper.

The data in Tables I and II show the Fe(Cap) to be a poorer base binder than is Fe(HmCap). In contrast to this, Co(Cap) and Co(HmCap) have comparable K^B (eq 1) values. This difference in monoligation of the Fe(II) and Co(II) may relate to the fact that iron is known[25] to be further out of the porphyrin plane in its five-coordinate complexes than is cobalt. The results then suggest that HmCap offers less resistance to the movement of the metal to a position outside the porphyrin plane than does the Cap porphyrin, which in turn has a greater effect on the iron than the cobalt complexes.

Another difference is observed between the monoligation of the iron and cobalt capped complexes. Both Fe(Cap) and Fe(HmCap) bind 1,2-Me_2Im more strongly than 1-MeIm, whereas the reverse is true for Co(Cap) and Co(HmCap). This has to do with their relative affinities for 1-MeIm and the sterically hindered 1,2-Me_2Im. This behavior of iron was observed earlier[24] for deuteroheme dimethyl ester. The greater binding of 1,2-Me_2Im in the iron complex is in accord with its basicity being greater than that of 1-MeIm ($pK_a(BH^+)$ = 7.85 vs. 7.25). The same relative binding tendencies of the two imidazoles would be expected for the cobalt complexes, providing that cobalt were as far out of the porphyrin plane as is iron. Since the binding in cobalt of 1,2-Me_2Im is weaker than that of 1-MeIm, it appears that the steric effect of the 2-methyl group in 1,2-Me_2Im predominates in the cobalt complex relative to iron. This is because cobalt is not far enough out of the porphyrin plane to minimize its steric interaction with the 2-methyl group of the coordinated 1,2-Me_2Im.

Previous monoligation studies of ferrous porphyrins were

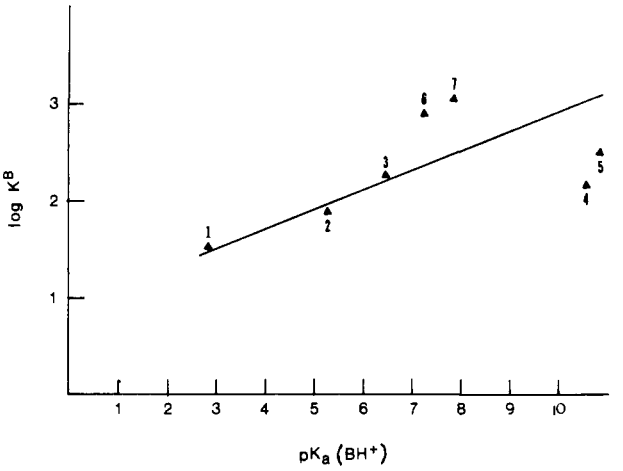

Figure 4. Correlation between pK_a for the conjugate acids (BH^+) and log K^B for the reaction Fe(Cap) + B ⇌ Fe(Cap)(B) in toluene at 23.1 °C. Bases are 1 = 3-Clpy; 2 = py; 3 = 3,4-Me_2py; 4 = *sec*-$BuNH_2$; 5 = *t*-$BuNH_2$; 6 = 1-MeIm; 7 = 1,2-Me_2Im. The straight line represents a least-squares regression line for points 1, 2, and 3.

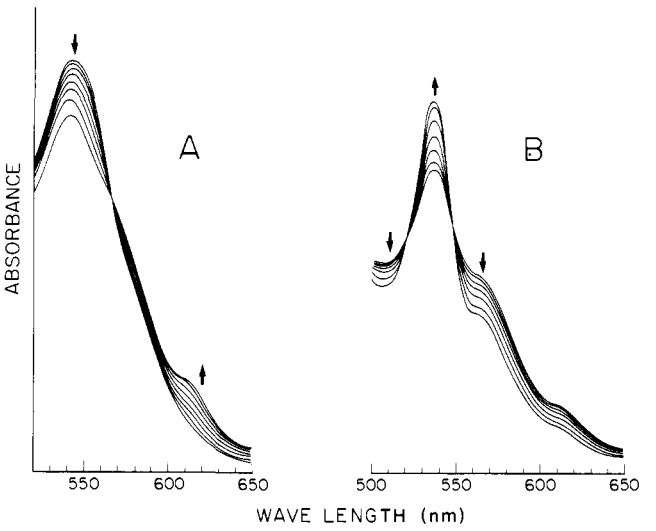

Figure 5. (A) Spectral changes occurring upon titration of a $\sim 10^{-4}$ M toluene solution of Fe(HmCap) with 0.0566 M 1-MeIm in toluene at 23.1 °C. The final base concentration is 2.8×10^{-3} M. (B) The titration of a toluene solution of Fe(HmCap)(1-MeIm) initially 0.0563 M in 1-MeIm, with neat 1-MeIm at 23.1 °C. The final base concentration is 0.701 M.

limited to sterically hindered bases[7,8] or estimates were made on unfavorable systems where $K_B^B > K^B$.[7,9-12] Now the use of Baldwin's Fe(Cap) permits a direct systematic study of the monoligation of an iron(II) porphyrin, similar to the studies reported for cobalt(II) porphyrins.[1,2,4] For cobalt(II) porphyrins, Walker[2] noted that for structurally similar bases (substituted pyridines or imidazoles) there was a linear correlation between the pK_a of the base and log K^B. This is the usual[26] ideal behavior for the formation of metal complexes. The same correlation is found for the binding of an axial base to Fe(Cap), as is shown in Figure 4 for N-donor ligands. There is a fairly linear correlation with proton basicity for the binding of structurally similar substituted pyridine ligands. However, the binding constants of *sec*-butylamine and *tert*-butylamine are smaller than expected, based on their values of pK_a in relation to the correlation for the pyridine ligands. Also 1-MeIm and 1,2-Me_2Im form more stable iron complexes than expected on the basis of their proton basicities. This behavior of the three types of ligands (pyridines, saturated amines, and imidazoles) is similar to that reported[2] for cobalt(II) porphyrins. The explanation used for cobalt also applies for iron. Thus, values of proton basicity (pK_a) of ligands only measure their σ-donor ability, which is the only way saturated amines can bind to metals. However, unsaturated ligands (pyridines and imidazoles) can also interact by π bonding with metals. This means that unsaturated ligands may bind stronger to metal porphyrins than is reflected by their proton basicities. In further support of this is the fact that strong π-acid ligands such as $(n\text{-Bu})_3$P, $P(OEt)_3$, and BzNC give the largest K^B for the Fe(Cap) system. The special bonding and magnetic properties of these strong π-acid adducts of Fe(Cap) are discussed in a separate paper.[27]

Since S-donor ligands are important in certain hemoproteins such as cytochrome P450,[28-31] it is significant that thiolate ligands have a large tendency[32] to add to the axial position of iron(II) porphyrins (Table II). Unfortunately, we were unable to get satisfactory titrations for the formation of 1:1 adducts between Fe(Cap) and thioethers or mercaptans. However, this was possible for Co(Cap) and the results (Table I) show that the S ligands decrease in their binding tendency in the order thiolates ≫ thioethers > mercaptans.[38] It is reasonable to expect the same relative binding properties of S ligands toward iron(II) porphyrins, for which there is no quantitative data to our knowledge. That thiolate ion is a much better ligand than are thioethers and mercaptans is evident from their respective $pK_a(BH^+)$ values (Table I).

Evidence for Six-Coordinate Fe(HmCap)(B)$_2$. Although Fe(Cap)(B) does not add a second base except for small molecules such as O_2 and CO, the larger cap size of HmCap does permit the formation of Fe(HmCap)$(B)_2$ with certain ligands. For example, Figure 5A shows the spectral changes which occurred during the titration of a toluene solution of Fe(HmCap) with a 0.0566 M 1-MeIm solution in toluene. A value for log K^B (23.1 °C) of 3.31 ± 0.05 was obtained, fitting the observed spectral changes to eq 2. The spectral changes shown in Figure 5B were due to further additions of neat 1-MeIm. These spectral changes are attributed to the formation of Fe(HmCap)$(1\text{-MeIm})_2$ with log K_B^B (23.1 °C) = 0.77. Consistent with this interpretation are the magnetic moments observed using the Evans[20] method. The μ_{eff} of a 0.02 M 1-MeIM solution of Fe(HmCap) in toluene, about 5×10^{-3} M in FeHmCap, is 4.6 μ_B, which is in accord with high-spin (S = 2) Fe(II). However, a 1.8 M 1-MeIm solution of Fe(HmCap) in toluene has a μ_{eff} of 3.1 μ_B for Fe(II) of intermediate spin (S = 1). Using the experimentally determined equilibrium constants, the 0.02 M 1-MeIm solution contains >90% of Fe(HmCap)(1-MeIm) and the 1.8 M 1-MeIm solution contains >90% of Fe(HmCap)$(1\text{-MeIm})_2$. Furthermore, the spectral changes in Figure 5A are similar to that for the addition of a single base such as 1,2-Me_2Im to Fe(HmCap) (see Figure 3). Note that iron(II) porphyrins are known[8] not to add a second 1,2-Me_2Im.

The intermediate spin (S = 1) state of Fe(HmCap)$(1\text{-MeIm})_2$ can be explained qualitatively by a crystal-field d-orbital splitting argument, providing that the second 1-MeIm is assumed to bind to the Fe center nonaxially through the side of the cap itself. Since the binding of the second 1-MeIm is much smaller (log K^B = 3.31, log K_B^B = 0.77), its nonaxial binding seems reasonable. The limited "pocket" size of the HmCap (3.8 Å from porphyrin plane to benzene top in $CapH_2$[33]) would prevent a normal axially bound six-coordinate complex. The crystal field splittings expected for Fe(HmCap)(1-MeIm) and for Fe(HmCap)$(1\text{-MeIm})_2$ are shown in Figure 6. This assumes a coordinate system chosen such that the second base binds along a line in the yz plane, bisecting the xy and xz planes at the origin (Fe atom). Upon this type of nonaxial coordination, the iron moves toward the porphyrin plane causing an increase in the energy of the $d_{x^2-y^2}$ orbital. The d_{z^2} energy level is also raised somewhat, since it has a component in the xy plane which experiences some repulsive

interaction. The largest effect is that on the d_{yz} orbital, which is raised in energy because one of its lobes points directly at the nonaxial base. This permits Fe(HmCap)(1-MeIm)$_2$ to be the observed intermediate spin, providing that the energy gap ΔE is smaller than the spin pairing energy.

Another possible binding site considered for the second base was that it be outside the cap adjacent (or cis) to the first base. This might be possible if the Fe atom was significantly out of the plane of the porphyrin toward the first 1-MeIm. In order to examine this possibility, Fe(HmCap) was titrated with the bidentate ligands 1,10-phenanthroline, 2,2′-bipyridine, and ethylenediamine. Only the ethylenediamine showed any spectral changes indicative of binding. However, the ethylenediamine does not behave as a bidentate ligand but binds in two distinct steps involving 2 equiv of ethylenediamine per iron(II) porphyrin. This was then tested using the monodentate propylamine, which is similar in size to ethylenediamine. Propylamine shows exactly the same spectral changes upon titration of Fe(HmCap) as does ethylenediamine. Also the two amines have similar values of K_B^B (log K_B^B = 4.98, 4.05 for en, $PrNH_2$). These results suggest that ethylenediamine binds as a monodentate ligand in a manner analogous to the monodentate propylamine. This argues against the cis binding of bases in Fe(HmCap)(B)$_2$.

Several bases form six-coordinate complexes with Fe(HmCap). Their binding strength, as measured by K_B^B, is an indication of their ability to penetrate the open walls of the cap itself and correlates well with the size of the base. Heterocyclic amines such as 1-MeIm and py bind weakly to Fe(HmCap) with log K_B^B = 0.77 and 0.84, respectively. *sec*-Butylamine, a branched alkylamine, binds stronger (log K_B^B = 2.85) than do the heterocycles, and propylamine, a linear alkylamine, binds even stronger (log K_B^B = 4.05). However, the larger ligands 1,2-Me_2Im and *t*-$BuNH_2$ do not form Fe(HmCap)(B)$_2$. This is also true of tri-*n*-butylphosphine, which is known[34] to form Fe[T(*p*-OCH_3)PP][(*n*-Bu)$_3$P]$_2$.

The smaller ligands such as propylamine bind in a normal fashion in Fe(HmCap)($PrNH_2$)$_2$. This complex, like other Fe(Por)(B)$_2$ complexes, is low spin (S = 0), has the expected optical spectrum, and does not add dioxygen in the presence of excess propylamine.[35] However, 1-MeIm and py add to Fe(HmCap) to form novel pseudo-six-coordinate complexes. These complexes are of intermediate spin (S = 1), and add dioxygen to form pseudo-seven-coordinate complexes.[35] In spite of the evidence in support of these novel iron(II) complexes, we must await X-ray structural studies in order to know more about the nature of these compounds. Nevertheless, the complexes Fe(Cap) and Fe(HmCap) do provide systems from which valuable comparative studies of and bonding effects of axial ligands can be assessed. The novel bonding found for Fe(HmCap)(B)$_2$ is interesting in itself, and it may be a model for looking at distal effects of the heme pocket of hemoglobins and myoglobins. Sperm-whale myoglobin contains a distal histidine (E7) which is believed[36] to act like a "door" allowing oxygen to enter but otherwise blocking the entrance to the heme. Instead of a distal histidine, some forms of erythrocruorin[37] have isoleucine (E11) as a distal residue which is in contact with oxygen or carbon monoxide in the heme pocket. In the abnormal human hemoglobin Zurich a valine (E11) is the only distal residue.[36] The function of the distal residue is important to the oxygenation of these hemoproteins, and the iron(II) capped porphyrins may permit modeling of hemoproteins with different distal residues.

Summary

This study shows that the ligand affinities for the monoligation of Fe(II) and Co(II) capped porphyrins are considerably smaller than those for other porphyrin systems. The lower base affinity of the metal capped porphyrins appears to be associated with steric restraints in the five-coordinate complex due to the attached cap. The ligation tendencies of the capped porphyrins vary as follows: Fe(HmCap) > Fe(Cap), and Co(Cap) ~ Co(HmCap). This behavior may be due to differing conformational effects in the Co(II) and Fe(II) porphyrins, related to iron being further out of the porphyrin plane in its five-coordinate complexes than is cobalt.

Correlations between proton basicity of the ligand (for the same ligand atom donor) and its bonding have been shown for Fe(Cap). However, π-bonding ligands such as imidazoles, pyridines, phosphines, phosphites, and isocyanide show binding greater than that expected on the basis of their proton basicity. Sulfur base binding to Co(Cap) shows a relative binding order for S-donor ligands of thiolate ≫ thioethers > mercaptans. This trend also correlates the values of pK_a(BH$^+$) of the S-donor ligands.

The large cap size of Fe(HmCap) permits the usual binding of two axial ligands, providing that they are small such as propylamine. However, intermediate-size bases such as 1-MeIm appear to weakly coordinate the second base in a nonaxial position through the side of the HmCap. Crystal field arguments are considered as an explanation for the intermediate spin (S = 1) state observed for Fe(HmCap)(1-MeIm)$_2$. This interaction of non-axially-bound bases with the Fe(HmCap) may serve as a model for distal residue interactions with bound CO and O_2 in natural hemoproteins.

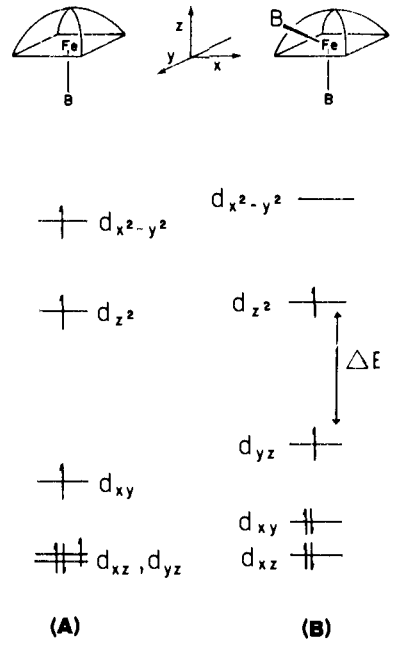

Figure 6. A qualitative crystal field splitting diagram for iron(II) in (A) Fe(HmCap)(1-MeIm) and (B) Fe(HmCap)(1-MeIm)$_2$. Figure 6B shows the postulated electronic structure for the intermediate-spin (S = 1) Fe(HmCap)(1-MeIm)$_2$, assuming nonaxial base binding to the d_{yz} orbital of the iron center. It should be noted that in the schematic representation of the capped porphyrin the pyrrole nitrogens lie at the midpoint of the lines connecting the corners of the square plane.

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References and Notes

(1) Stynes, D. V.; Stynes, H. C.; James, B. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 1796–1801.
(2) Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1150–1153.
(3) Walker, F. A.; Berioz, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3484–3489.

(4) Takayanagi, T.; Yamamoto, H.; Kwan, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2618–2622.
(5) Stynes, D. V.; Stynes, H. C.; Ibers, J. A.; James, B. R. *J. Am. Chem. Soc.* **1973**, *95*, 1142–1149.
(6) Abbreviations: Por, dianion of a natural or synthetic porphyrin; B, various donor ligands; Cap, dianion of the capped porphyrin, 5,10,15,20-[pyromellitoyl(tetrakis-*o*-oxyethoxyphenyl)]porphyrin; HmCap, dianion of the homologous capped porphyrin, 5,10,15,20-[pyromellitoyl(tetrakis-*o*-oxypropoxyphenyl)]porphyrin; TPP, dianion of *meso*-tetraphenylporphine; T(*p*-OCH_3)PP, dianion of tetra-*p*-methoxy-*meso*-tetraphenylporphine; PPIXDME, dianion of protoporphyrin IX dimethyl ester; Deut, dianion of deuteroporphyrin IX; TpivPP, dianion of "picket fence porphyrin", *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl)porphyrin; THF, tetrahydrofuran; 1-MeIm, *N*-methylimidazole; 1,2-Me_2Im, 1,2-dimethylimidazole; 2-MeIm, 2-methylimidazole; Im, imidazole; μ_{eff}, effective magnetic moment; (*n*-Bu)$_3$P, tri-*n*-butylphosphine; $P(OEt)_3$, triethyl phosphite; BuSH, 1-butanethiol; BuS Ⓚ, butyl mercaptide potassium crown ether; DMF, *N,N*-dimethylformamide; 3-Clpy, 3- chloropyridine; py, pyridine; 3,4-Me_2py, 3,4-dimethylpyridine; *sec*-$BuNH_2$, *sec*-butylamine; *t*-$BuNH_2$, *tert*-butylamine; BzNC, benzyl isocyanide; $PrNH_2$, *n*-propylamine; en, ethylenediamine; Me_4Si, tetramethylsilane.
(7) Brault, D.; Rougee, M. *Biochem. Biophys. Res. Commun.* **1974**, *57*, 654–659.
(8) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 564–568.
(9) Brault, D.; Rougee, M. *Biochemistry* **1974**, *13*, 4591–4597.
(10) Rougee, M.; Brault, D. *Biochemistry* **1975**, *14*, 4100–4106.
(11) Rougee, M.; Brault, D. *Biochem. Biophys. Res. Commun.* **1973**, *55*, 1364–1369.
(12) Wayland, B. B.; Mehne, L. F.; Swartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2379–2383.
(13) Almog, J.; Baldwin, J. E.; Dyer, R. L.; Peters, J. *J. Am. Chem. Soc.* **1975**, *97*, 226–227.
(14) Almog, J.; Baldwin, J. E.; Huff, J. *J. Am. Chem. Soc.* **1975**, *97*, 227–228.
(15) Szymanski, T. Ph.D. Thesis, Northwestern University, Evanston, Ill., 1978.
(16) Adler, A. D.; Longo, T. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.
(17) $HmCapH_2$ was previously prepared by Professor Jack E. Baldwin and coworkers, but the synthesis is unpublished. A sample from Professor Baldwin's laboratory was found to be identical with the $HmCapH_2$ prepared in this synthesis.
(18) Barnett, G. H.; Hudson, M. F.; Smith, K. M. *Tetrahedron Lett.* **1973**, 2887–2888.
(19) The mass spectrum was performed on Fe^{III}(HmCap)Cl by the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, Nebr.
(20) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.
(21) Brault, D.; Rougee, M. *Biochemistry* **1974**, *13*, 4598–4602.
(22) Figgis, B. N.; Lewis, J. In "Modern Coordination Chemistry", Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1967; p 403.
(23) Hill, A. V. *J. Physiol (London)* **1910**, 40, iv–vii.
(24) White, D. K.; Cannon, J. B.; Traylor, T. G. *J. Am. Chem. Soc.* **1979**, *101*, 2443–2454.
(25) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339–345.
(26) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; Wiley: New York, 1967; p 26.
(27) Ellis, P. E., Jr.; Jones, R. D.; Basolo, F., *J. Chem. Soc., Chem. Commun.*, in press.
(28) Stern, J. O.; Peisach, J. *J. Biol. Chem.* **1974**, *249*, 7495–7498.
(29) Chang, C. K.; Dolphin, D. *J. Am. Chem. Soc.* **1975**, *97*, 5948–5950.
(30) Collman, J. P.; Sorrell, T. N. *J. Am. Chem. Soc.* **1975**, *97*, 4133–4134.
(31) Chang, C. K.; Dolphin, D. *J. Am. Chem. Soc.* **1976**, *98*, 1607–1609.
(32) Chang, C. K.; Dolphin, D. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3338–3342.
(33) Jameson, G. B.; Ibers, J. A., *J. Am. Chem. Soc.*, in press.
(34) Conner, W. M.; Straub, D. K. *Inorg. Chem.* **1977**, *16*, 491–494.
(35) Linard, J. E.; Ellis, P. E., Jr.; Budge, J. R.; Jones, R. D.; Basolo, F. *J. Am. Chem. Soc.*, following paper in this issue.
(36) Perutz, M. F. *Br. Med. Bull.* **1976**, *32*, 195–208.
(37) Weber, E.; Steigemann, W.; Jones, T. A.; Huber, H. *J. Mol. Biol.* **1978**, *120*, 327–336.
(38) Ellis, P. E., Jr.; Jones, R. D.; Basolo, F. *Proc. Natl. Acad. Sci. U.S.A.*, **1979**, *76*, 5418–5420.

Oxygenation of Iron(II) and Cobalt(II) "Capped" Porphyrins

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Abstract: The O_2 binding constants are presented for a series of cobalt and iron complexes of the "capped" porphyrins ($CapH_2$ and $HmCapH_2$). The Cap complexes have larger O_2 affinities than the corresponding HmCap systems, despite little difference in the basic structures in the capped porphyrins. The thermodynamic values of some of these complexes are compared to those of other oxygen carriers. The O_2 affinities of the capped porphyrin complexes are considerably smaller than for other corresponding porphyrin complexes, and the major contributor to this difference is reflected in the $\Delta H°$ values. The capped porphyrins appear to inhibit oxygenation by imposing steric constraints on the movement of the metal atom from a stable, out of porphyrin plane position to an in-plane position. Evidence for the existence of a novel pseudo-seven-coordinate dioxygen complex, $Fe(HmCap)(B)_2(O_2)$, is presented. One of the bases is thought to coordinate to the metal in a nonaxial manner through the d_{xz} or d_{yz} orbitals of the metal.

Introduction

Model oxygen carriers are synthesized and studied in order to understand more fully the nature of dioxygen binding to myoglobin and hemoglobin.[1] The simplest model compound, $Fe(TPP)(B)_2$[2] in an aprotic solvent, was shown to reversibly bind dioxygen at low temperatures (−45 °C), but the reaction involves the substitution of dioxygen for one of the axially ligated bases.[3] At higher temperatures the reaction of $Fe(TPP)(B)_2$ with dioxygen results in an irreversibly oxidized product, the μ-oxo dimer (Fe(III)-O-Fe(III)). This differs from the natural hemoprotein where the iron is five coordinate, and oxygenation merely involves the addition of dioxygen to the vacant coordination site on iron. Other model oxygen carriers are made by the attachment of iron porphyrins to polymer supports.[4] The polymer supports serve to prevent dimerization, because two iron centers cannot get close enough to react. Also the polymer support system provides a five-coordinate ferrous ion, which is analogous to deoxymyoglobin and deoxyhemoglobin.

Much interest in recent years has centered on metal complexes of substituted tetraphenylporphyrins. These porphyrins are synthesized to meet specific requirements, in that substituents can be varied to provide different electronic or steric environments around the metal. The most extensively studied[5] of these are the iron(II) "picket-fence" porphyrins, which can reversibly oxygenate in aprotic solution containing excess axial ligand at room temperature. Even in excess concentrations of ligand, the metal centers of some of the complexes can exist in a state of five coordination. Unique model properties are also found[6] with chelated protoheme, having a "proximal" imid-

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