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(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.

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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 Hm$CapH_2$). 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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azole covalently attached. The iron complexes have many characteristics remarkably similar to those of myoglobin and hemoglobin.[5-7]

As part of our investigation of factors which influence the binding of dioxygen in myoglobin and hemoglobin, we are studying the characteristics of another series of substituted tetraphenylporphyrins. These are the metal "capped" porphyrins, elegantly prepared by Baldwin and co-workers.[8,9] Both $CapH_2$ and $HmCapH_2$ are ortho-substituted tetraphenylporphyrins, with the four substituents being joined together on the same side of the porphyrin plane with a tetrasubstituted benzene (Figure 1). Previous communications report the ligation and oxygenation equilibria[9,10] and the O_2 and CO stretching frequencies[11] of these metal porphyrin complexes. These studies show that a seemingly small structural change in the capped porphyrins of cobalt(II) or iron(II) results in significant differences in chemical properties. There are also large differences between the capped porphyrin complexes and the corresponding picket-fence porphyrin complexes. These facts may be important in discussing the mechanism of cooperativity in hemoglobin, because the difference between the R and T states of hemoglobin may be the result of a slight conformational change. Our results suggest that such a small change might suffice to cause a lower O_2 affinity in the T state than in the R state.

In this paper we report our data on the oxygen affinity of iron(II) and cobalt(II) Cap and HmCap complexes, and compare these values with data in the literature on related systems. The nature of O_2 binding to Fe(HmCap)(1-MeIm)$_2$ is also discussed in terms of a unique pseudo-seven-coordinate iron dioxygen complex.[9]

Experimental Section

Reagents. Toluene was reagent grade and distilled under N_2 from sodium benzophenone ketyl prior to use. Pyridine and 3,4-lutidine were reagent grade and distilled under N_2 over BaO before using. 1-MeIm was dried over KOH, vacuum distilled, and stored under N_2. 1,2-Me_2Im was vacuum distilled and stored below 0 °C. The amine bases were dried over KOH and distilled under N_2. 3-Clpy (Aldrich, 99%) was distilled under N_2. All bases except 1,2-Me_2Im were stored over molecular sieves. $P(n\text{-}Bu)_3$ and $P(OEt)_3$ were vacuum distilled under N_2. Gaseous dioxygen was Air Products Ultra-Pure Carrier Gas (containing less than 1.0 ppm H_2O) or Matheson Primary Standard 0.999% O_2 in N_2. When the temperature of the equilibrium experiment to be used was less than −70 °C, the oxygen gas was further dried by passing over molecular sieves at −130 °C.

Syntheses. The capped prophyrin compounds $CapH_2$, Fe(Cap)Cl, and Fe(Cap) were prepared and characterized according to the method of Baldwin and co-workers.[8,12] The compounds HmCap, Co(Cap), Co(HmCap), and Fe(HmCap)(Cl) were prepared by literature methods.[13] The Fe(HmCap) was prepared in situ by reduction of Fe(HmCap)(Cl) with aqueous sodium dithionite.[9] The compounds Fe(HmCap)(1-MeIm) and Fe(HmCap)($prNH_2$)$_2$ were also prepared in situ by adding 1 mL of 1-MeIm and 1 mL of $PrNH_2$, respectively, to dried samples of Fe(HmCap). The excess base was then evaporated by heating gently and reducing the pressure with a vacuum pump. The flask was heated to no more than 50 °C during this process, as excess heat will drive off all coordinated base. This method may not give the exact base-metal stoichiometry indicated, but it was suitable for the experiments conducted.

Procedure. Equilibrium constants for the oxygenation reactions were determined spectrophotometrically, using a 4.0-cm path length low-temperature visible cell.[14] A Cary 14 spectrophotometer was used in all experiments. In order to exclude water and dioxygen, all solution transfers were done with cannulas or with gas-tight syringes equipped with Luer-Lock valves. Fe(Cap) (~1 mg) was added to the visible cell, which contained a small magnetic stir bar, and flushed with N_2 for at least 1 h before the solvent solution was added. The base solution was prepared by adding a known mass of the appropriate base to a 25-mL volumetric flask, which had been stoppered with a serum cap and thoroughly flushed with N_2. Toluene was then added to make a total of 25.0 mL of base solution. After mixing, the base solution was transferred to the visible cell.

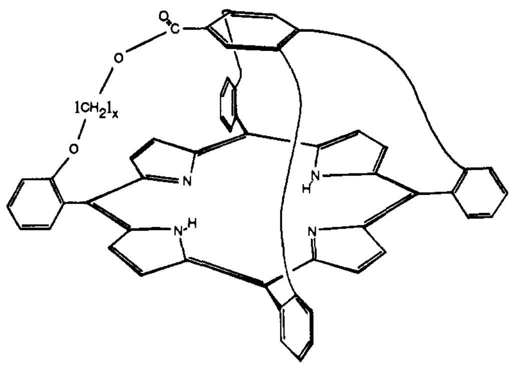

Figure 1. Schematic representation of $CapH_2$ (x = 2) and $HmCapH_2$ (x = 3).

Co(Cap) and Co(HmCap) base solutions were prepared in a manner analogous to that of the Fe(Cap) base solutions, except that extra precautions were taken to ensure that all glassware was as dry as possible. At the low temperatures needed for the titrations of the cobalt complexes, the solutions were clouded by water.

The base concentrations were chosen to give greater than 99% of the five-coordinate complex in solution. The amount of the base needed was determined from the equilibrium constant for the addition of base to the four-coordinated species.[13]

The Fe(HmCap) base solutions were prepared by first reducing 0.8–2.0 mg of Fe(HmCap)Cl in toluene or benzene with aqueous $Na_2S_2O_4$. The bright red solution was then transferred to an airless-ware flask equipped with a magnetic stir bar. The solvent was removed by heating gently under vacuum. The red residue was finally dried for a minimum of 3 h at 150 °C in vacuo. The base solution, prepared as described above for Fe(Cap), was added to the Fe(HmCap) residue, mixed, and transferred to the visible cell. Again the base concentrations were chosen to ensure more than 99% of the five-coordinated species for the respective bases 1,2-Me_2Im, t-$BuNH_2$, $P(n\text{-}Bu)_3$, and $P(OEt)_3$. These bases do not form six-coordinate complexes with Fe(HmCap).[14] The spectra of these iron(II) complexes are similar to those of other five-coordinate complexes.[15] When 1-MeIm, py, or $PrNH_2$ were the bases, concentrations were chosen to ensure greater than 96% six coordination.

Once the solution was in the visible cell, it was cooled to the chosen temperature with the appropriate slush bath. While cooling, the cell was attached to the vacuum line and degassed for a total of 1 h. The system was then shut off from the vacuum pump and allowed to equilibrate, with the pressure reading being the vapor pressure of the solution. This value was subtracted from the equilibrium pressures recorded during the titration. Once the vapor pressure was recorded, an initial spectrum was taken. Aliquots of O_2 were then added from a gas manifold[16] via a gas-tight valve to the system. When $P_{1/2}^{O_2}$ was less than 10 Torr, a mixture of 0.999% O_2 in N_2 was used as the titrant. The solution was allowed to stir until equilibrium was attained. Equilibrium was reached more quickly if the cell was also agitated by hand. Use of stainless steel flexible vacuum tubing allowed the cell to be shaken. The spectra for a typical titration of Co(Cap)(B) are shown in Figure 2. The pressure of O_2 above the solution was determined with MKS Baratron, Type 221 series, pressure gauges having a range of 0–100 and 0–1000 Torr. Pressures were obtained in a digital format from a Data Precision digital voltmeter (Model 245). Reversibility was checked after the last O_2 addition by vacuum removal of O_2 to obtain the identical initial deoxy spectrum.

When either Fe(HmCap)(1-MeIm) or Fe(HmCap)($PrNH_2$)$_2$ was used, base solutions were not added. Instead, toluene alone was added to the flask containing the sample, mixed quickly, and transferred via a cannula to the visible cell. The cell, containing a small magnetic stir bar, had been flushed thoroughly with N_2 and cooled to −63 °C prior to addition of solution. The dioxygen titration was conducted in the manner described above, except that fewer additions of O_2 were made. After the addition of sufficient dioxygen to completely oxygenate the sample, 2 mL of neat oxygen-free base was added to the solution. After mixing, a final spectrum was taken. When 1-MeIm was added, the solution had to be warmed slightly (above −60 °C) to prevent the 1-MeIm from freezing.

The oxygenation of five-coordinate complexes is illustrated by the

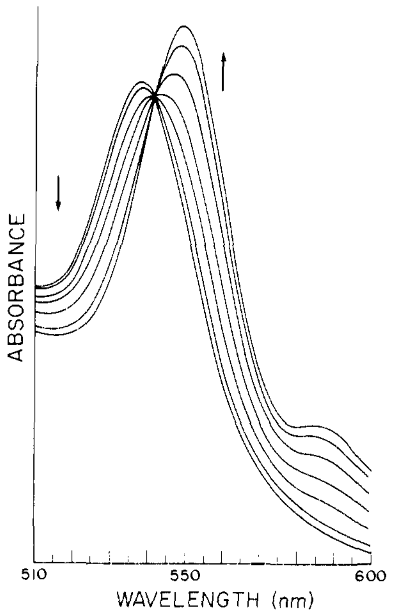

Figure 2. Spectral changes occurring upon titration of a toluene solution of ~10^{-4} M in Co(Cap)(1-MeIm), 0.03 M in 1-MeIm, with the following pressures of dioxygen at −78 °C: 0, 20.14, 51.64, 91.37, 204.71, 505.95, and 995.05 Torr.

equation

$$\mathrm{M(Por)(B)} + \mathrm{O_2} \xrightleftharpoons{K_B^{O_2}} \mathrm{M(Por)(B)(O_2)} \quad (1)$$

The data from the spectrophotometric titrations are treated in one of two ways. (1) When the absorbance of the completely (>99%) oxygenated product can be obtained, the data are fitted to the Hill equation[18]

$$\log [y/(1-y)] = n \log P_{O_2} - \log (P_{1/2}{}^{O_2}) \quad (2)$$

where y equals the fraction of the total metal porphyrin binding O_2. Values for $P_{1/2}{}^{O_2}$ were determined from the x intercept of the regression line for a plot of log $[y/(1-y)]$ vs. log P_{O_2}. For the simple additions of O_2 to five-coordinate complexes, the values of n equal 1.00. Values for $P_{1/2}{}^{O_2}$ were found to be independent of the wavelength used to monitor the extent of oxygenation. (2) If only partial oxygenation occurred at a pressure of 1000 Torr, the data were fitted to an equation employed by Collman:[7]

$$P_{O_2} = [\mathrm{M(Por)}]_T b\Delta\epsilon(P_{O_2}/\Delta A) - P_{1/2}{}^{O_2} \quad (3)$$

where $[\mathrm{M(Por)}]_T$ is the total metal porphyrin concentration, b is the cell path length, $\Delta\epsilon$ is the difference in molar absorptivity of the oxy and deoxy complexes, and ΔA is the difference between the absorbance at a particular P_{O_2} and the absorbance of the deoxy complex at the same wavelength. Since $[\mathrm{M(Por)}]b\Delta\epsilon$ is a constant, a plot of P_{O_2} vs. $P_{O_2}/\Delta A$ will give a straight line with y intercept equal to $-P_{1/2}{}^{O_2}$. Plots were made for at least two wavelengths over a pressure range of 0-1000 Torr. In several instances eq 3 was used with data originally fit to eq 2. The $P_{1/2}{}^{O_2}$'s obtained from each were the same within experimental error. All data were fitted using a nonweighted linear least-squares method. Values of $P_{1/2}{}^{O_2}$ are reproducible to better than 5%.

The data for the oxygenation of Fe(HmCap)$(B)_2$, with excess B and with B = 1-MeIm or py, were fitted to equations described previously.[9] The $P_{1/2}{}^{O_2}$ is determined from eq 2 or 3 except that the reaction is an addition of O_2 to a six-coordinate complex.

Results

Solid Fe(Cap), Co(Cap), and Co(HmCap) are moderately stable with respect to aerial oxidation, and transfers of the solid materials can be performed in contact with the atmosphere without special precautions. Because Fe(HmCap) is prepared in situ by reduction of Fe(HmCap)Cl, there is no reason to expose it to the atmosphere. It is always kept under nitrogen or in vacuo. Exposing solutions of Fe(Cap) or Fe(HmCap), in the absence of a large excess of coordinating base, to the atmosphere at room temperature results in rapid, irreversible oxidation to the μ-oxo dimers. With excess concentrations of coordinating base solutions, the complexes and their O_2 adducts are stable for several hours in contact with the atmosphere at room temperature.

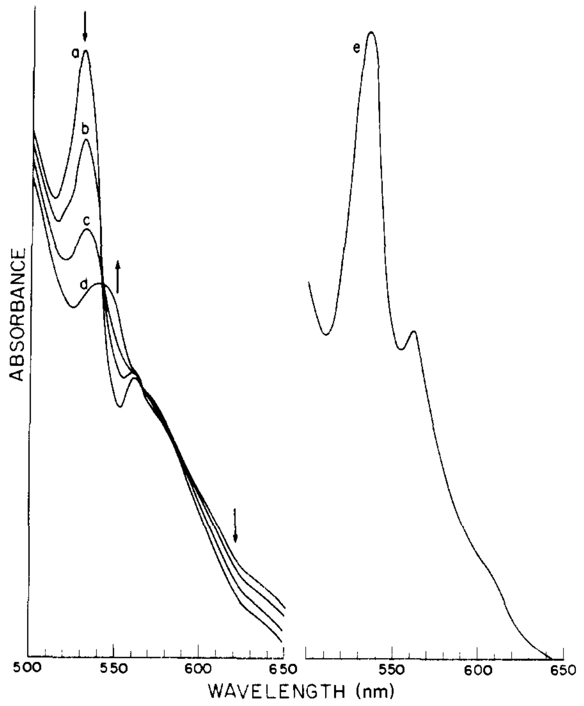

Figure 3. Spectral changes which occur upon additions of O_2 or $PrNH_2$ to a toluene solution of ~10^{-4} M in Fe(HmCap)$(PrNH_2)_2$ at −63 °C: (a) initial spectrum of Fe(HmCap)$(PrNH_2)_2$; (b) 8.12 Torr of O_2; (c) 38.60 Torr of O_2; (d) 602.1 Torr of O_2; (e) addition of 2 mL of neat $PrNH_2$ to the solution in (d). Absorbance scale is different from that for (a)-(d).

The addition of base solutions to Fe(Cap), Co(Cap), or Co(HmCap) yields solutions of the corresponding five-coordinate species. This fact is shown by the visible spectra and by estimates made using the base concentrations and equilibrium constants (K^B)[13] for the equilibria represented by the equation

$$\mathrm{M(Por)} + \mathrm{B} \xrightleftharpoons{K^B} \mathrm{M(Por)(B)} \quad (4)$$

These three metal porphyrins show no optical spectral change indicative of adding a second base. Figure 2 shows the spectra from a titration of Co(Cap)(1-MeIm) with O_2.

The addition of solutions of t-$BuNH_2$ or of 1,2-Me_2Im to Fe(HmCap) gives only five-coordinate species, even in high concentrations of base.[13] When unhindered bases such as 1-MeIm or py are used, Fe(HmCap) forms a six-coordinate species:

$$\mathrm{Fe(HmCap)(B)} + \mathrm{B} \xrightleftharpoons{K_B{}^B} \mathrm{Fe(HmCap)(B)_2} \quad (5)$$

Although for these two complexes $K_B{}^B$ is smaller than K^B, it is still too large to allow the oxygenation of a predominantly five-coordinate complex. A significant concentration of the easily oxidizable four-coordinate complex Fe(HmCap) is still present in the solution when the five-coordinate Fe(HmCap)(B) concentration is maximized. All O_2 titrations of the py and 1-MeIm adducts of Fe(HmCap) were therefore performed on the six-coordinate complexes. Base concentrations were large enough to ensure that the amounts of four- and five-coordinate complexes were negligible.

Spectrophotometric oxygen titrations of toluene solutions

Table I. Equilibrium Data for Oxygenation of Five-Coordinate Iron(II) Capped Porphyrin Complexes in Toluene (eq 1)

complex	base	$pK_a(BH^+)$	$\log K^B$ [a]	$P_{1/2}^{O_2}$, Torr[b] 0 °C	−23 °C	−45 °C	−63 °C
Fe(Cap)	1-MeIm	7.25[c]	2.90	4.5	0.78	0.10[d]	
	1,2-Me_2Im	7.85[c]	3.06	930	162	27	
	py	5.27[e]	2.17	26	4.2	0.36[d]	
	3,4-Lut	6.46[e]	2.26	34			
	3-Clpy	2.84[e]	1.53	32			
	sec-$BuNH_2$	10.56[f]	2.16	12			
	t-$BuNH_2$	10.83[f]	2.50				0.27
	$P(OEt)_3$	3.50[g]	3.24			*h*	
	$P(n\text{-}Bu)_3$	8.43[i]	4.66			*h*	
Fe(HmCap)	1-MeIm	7.25[c]	3.31[j]	120–180[k]			
	1,2-Me_2Im	7.85[c]	3.61				880
	t-$BuNH_2$	10.83[f]	2.23				575
	sec-$BuNH_2$	10.56[f]	2.79	*l*			
	$PrNH_2$	10.53[f]	3.40[j]	*l*			

[a] Equilibrium constant for eq 4 at 23 °C; values from ref 13. [b] Values are reproducible within 5%, except when noted otherwise. [c] Reference 19. [d] Value reproducible within 10%. [e] Reference 20. [f] Reference 21. [g] Estimated from values in ref 22. [h] No detectable spectral changes up to 1 atm (760 Torr). [i] Reference 22. [j] Equilibrium constants from ref 13 for addition of second base ($K_B{}^B$) are 0.77 (B = 1-MeIm), 2.85 (B = *sec*-$BuNH_2$), and 4.05 (B = $PrNH_2$). [k] For discussion see text and ref 9. [l] Value for oxygenation of the five-coordinate complex is not able to be determined directly because the complex is six coordinate, with two axially ligated bases, in solutions containing excess base. There are no detectable spectral changes up to 1 atm when the six-coordinate species in excess base solution is titrated with O_2 at 0 °C.

Table II. Equilibrium Data for Oxygenation of Cobalt(II) Capped Porphyrins in Toluene (eq 1)

complex	base	$pK_a(BH^+)$	$\log K^B$ [a]	$P_{1/2}^{O_2}$, Torr[b] −63 °C	−78 °C	−91 °C
Co(Cap)	1-MeIm	7.25[c]	2.32	790	140	45
	1,2-Me_2Im	7.85[c]	1.84		2000–4000	*d*
	py	5.27[e]	*f*		1380	
	sec-$BuNH_2$	10.56[g]	*f*		955	
Co(HmCap)	1-MeIm	7.25[c]	2.28		>5000	

[a] Equilibrium constant for eq 4 at 23 °C in text; values from ref 13. [b] Values are reproducible within 10%. [c] Reference 19. [d] No detectable spectral change up to 1000 Torr of O_2. [e] Reference 20. [f] K^B not determined; solutions were made, however, to ensure greater than 99% five coordination. [g] Reference 21.

of Fe(Cap)(B), Fe(HmCap)(B), Fe(HmCap)$(B)_2$, Co(Cap)(B), and Co(HmCap)(B), all with excess base present, were done. Adequate isosbestic points were maintained in all titrations. When eq 2 could be used on the data, plots of log $[y/(1-y)]$ vs. log P_{O_2} gave straight lines with slopes of 1.0–0.1. The value of the x intercept is equal to $-\log K_{O_2}$, where $K_{O_2} = (P_{1/2}^{O_2})^{-1}$. When eq 3 was employed, plots of P_{O_2} vs. $P_{O_2}/\Delta A$ gave straight lines with the y intercept being equal to $-P_{1/2}^{O_2}$. Values obtained for the oxygenation of the five-coordinate complexes are shown in Tables I and II.

Unexpectedly, it was found that Fe(HmCap)(1-MeIm)$_2$ binds O_2 in a manner that is independent of base concentration.[9] This fact also appears to be true when py is the base, but unfortunately Fe(HmCap)(py)$_2$ binds dioxygen very poorly ($P_{1/2}^{O_2} > 1000$ Torr at 0 °C). The values obtained for the pyridine system were not precise.

For Fe(HmCap)($PrNH_2$)$_2$, $K_B{}^B > K^B$,[13] and it does not bind O_2 when excess base concentrations are present. These properties are also characteristic of Fe(TPP)(py)$_2$, which will bind O_2 reversibly via a substitution reaction at temperatures below ~−45 °C.[3] Note that such a solution contains only stoichiometric amounts of pyridine, since only solid Fe(TPP)(py)$_2$ is dissolved in the pure solvent. However, the addition of base easily prevents oxygenation, because under such conditions pyridine successfully competes with O_2 for a coordination site. Low temperatures are needed to slow the reactions which form the μ-oxo dimer. In order to determine if the normal behavior of Fe(Por)$(B)_2$ is also shown by Fe(HmCap)($PrNH_2$)$_2$, it was prepared as the solid with approximately the stoichiometry indicated. The results of O_2 titrations of a toluene solution of Fe(HmCap)($PrNH_2$)$_2$ are shown in Figure 3. The deoxy spectrum at −63 °C is similar to those of other six-coordinate iron(II) porphyrin complexes.[24] The first O_2 addition, 8.12 Torr, gives strong evidence that oxygenation is occurring. Oxygenation was almost complete at 38.60 Torr, and at 602 Torr of O_2 it is clear that the system was completely oxygenated. The 620-Torr spectrum is similar to that of Fe(HmCap)(*t*-$BuNH_2$)(O_2), which is definitely a six-coordinate complex. Upon addition of 2 mL of $PrNH_2$ to the completely oxygenated solution, the spectrum obtained is that of deoxy species Fe(HmCap)($PrNH_2$)$_2$.

A similar experiment was performed using solid Fe(HmCap)(1-MeIm)$_2$. The deoxy spectrum (Figure 4) of its toluene solution, however, resembled that of the five-coordinate Fe(HmCap)(*t*-$BuNH_2$). The compound in solution is five-coordinate Fe(HmCap)(1-MeIm), in accordance with the small binding constant ($K_B{}^B$) for the second base.[9] At −63 °C complete oxygenation was obtained at about 20 Torr of O_2, but to be certain of this 304.2 Torr was used (Figure 4). At this pressure of O_2, a large excess of 1-MeIm was added to the solution and the spectrum changed only slightly. The spectrum still showed complete oxygenation (Figure 4d). Removal of O_2 by vacuum resulted in the six-coordinate spectrum of Fe(HmCap)(1-MeIm)$_2$.

The thermodynamic values for oxygenation of Fe(Cap)(1-MeIm), Fe(Cap)(1,2-Me_2Im), Fe(Cap(py), and Co(Cap)(1-MeIm) were obtained by determining the $P_{1/2}^{O_2}$'s at three different temperatures. Values of $\Delta H°$ and $\Delta S°$ were then determined from least-squares fits to the van't Hoff equation. The values for these and other systems are given in Table III.

Discussion

Oxygenation of Five-Coordinate Complexes. The information contained in Tables I and II has many interesting features. In accord with several iron and cobalt systems,[6,7,15] the use of

Table III. Equilibrium and Thermodynamic Values for Oxygenation of Iron(II) and Cobalt(II) Porphyrin Complexes in Toluene (eq 1)

complex	$P_{1/2}^{O_2}$, Torr[a]	$\Delta H°$, kcal/mol	$\Delta S°$, eu[b]	ref
Fe(Cap)(1-MeIm)	23[c]	−10.5 ± 0.3	−41 ± 1	this work[d]
Fe(Cap)(1,2-Me_2Im)	4.0×10^3 [c]	−9.7 ± 0.2	−49 ± 1	this work[d]
Fe(Cap)(py)	1.8×10^2 [c]	−11.8 ± 0.4	−50 ± 2	this work[d]
Fe(triPiv(4CIm)PP)	0.60	−16.8	−42	6
Fe(TpivPP)(1,2-Me_2Im)	38	−14.3	−42	6
Mb (sperm whale)[e]	0.29	−14.8	−47	25, 26
Hb (human, "T")[f]	26			28, 29
Hg (human, "R")[f]	0.17			28, 29
Co(Cap)(1-MeIm)	1.4×10^5 [c]	−7.8 ± 0.4	−50 ± 2	this work[d]
Co(T(*p*-OCH_3)PP)(1-MeIm)	1.0×10^4 [c]	−8.9	−49	30
Co(PPIXDME)-(1-MeIm)	6.1×10^3 [c]	−9.7	−51	31
Co(TpivPP)(1-MeIm)	7.0×10^1	−12.2	−51	7
CoMb (sperm whale)[e]	3.4×10^1	−13.1	−53	32, 33

[a] 25 °C for iron complexes, 15 °C for cobalt complexes. [b] Standard state is 1 Torr. [c] Calculated from thermodynamic values. [d] Error limits for $\Delta H°$ and $\Delta S°$ are standard deviations from van't Hoff plots. [e] Aqueous solution, pH 7, 0.1 M phosphate ion. [f] Aqueous solution, pH 7.4, 0.1 M NaCl, 0.05 M bis-Tris buffer.

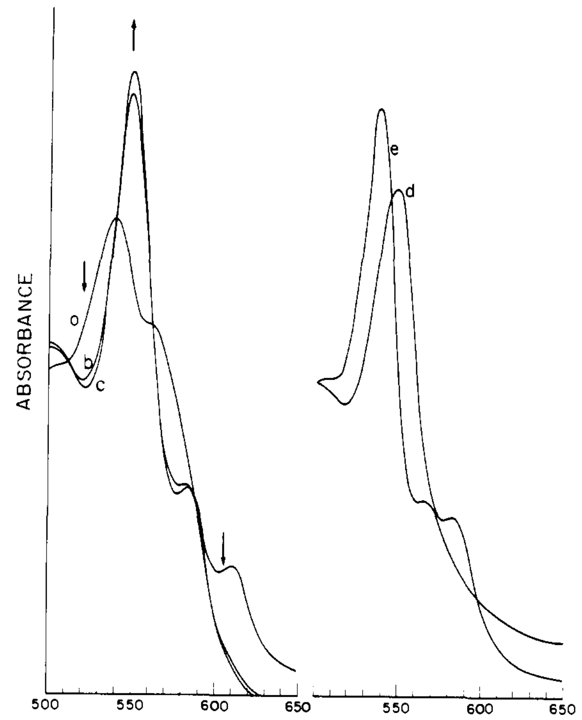

Figure 4. Spectral changes which occur upon additions of O_2 or 1-MeIm to a toluene solution of $\sim 10^{-4}$ M in Fe(HmCap)(1-MeIm) at −63 °C: (a) initial spectrum of Fe(HmCap)(1-MeIm); (b) 19.78 Torr O_2; (c) 304.2 Torr O_2; (d) addition of 2 mL of neat 1-MeIm to the solution in (c) (absorbance scale is different from that in (a)-(c)); (e) removal of O_2 by vacuum from solution (d). Absorbance scale is different from those in (a)-(d).

hindered bases such as 1,2-Me_2Im and *t*-BuNH_2 as axial ligands destabilizes the O_2 adduct. The $P_{1/2}^{O_2}$ for Fe(Cap)(1,2-Me_2Im) is 200 times larger than the $P_{1/2}^{O_2}$ Fe(Cap)(1-MeIm) at 0 °C. The accepted explanation for this behavior is that the hindered bases do not allow the ferrous ion to easily move toward the porphyrin plane because of steric interaction with the pyrrole group on the porphyrin ring.[15,34] The high-spin iron atom, as it binds O_2, becomes low spin and moves into the plane of the porphyrin. The effect of changing from 1-MeIm to 1,2-Me_2Im is to decrease the O_2 affinity by a factor of about 180, which is comparable to the average difference of values for T- and R-state iron(II) porphyrins in human hemoglobin.[29]

The difference in O_2 affinity for Co(Cap)(B) for B = 1-MeIm vs. 1,2-Me_2Im is not as large as it is for Fe(Cap)(B), as was also observed for the picket-fence complexes. This may be because cobalt(II) is not as far out of the porphyrin plane in the deoxy state as is iron(II).[35-38] A hindered base will therefore have less effect on the binding of O_2 to cobalt porphyrins than it does on the binding of O_2 to iron porphyrins.

The pK_a for a series of substituted pyridines, as axial bases, has little effect on the O_2 affinity of Fe(Cap)(B). The $P_{1/2}^{O_2}$'s for 3-Clpy (pK_a = 2.84), py (5.27), and 3,4-lut (6.46) are all about 30 Torr at 0 °C. The more electron donating a base (the higher the pK_a), the better the metal should bind O_2 because it can more readily donate electron density to the O_2 moiety. For cobalt[30,39] and manganese[40] porphyrins there is a rough correlation between the pK_a of various substituted pyridines and dioxygen binding equilibria; however, the overall effect is small. A similar study of the effect of substituted pyridines on the O_2 uptake by the Co(Cap)(B) was not done, since the O_2 affinity of Co(Cap)(py) is too small for us to determine accurately. That Fe(Cap)(1-MeIm) has the highest affinity for O_2 is expected, because 1-MeIm is a good π-electron donor.[41] The increased electron density on the metal center increases its affinity for O_2, since charge transfer is an essential part of M-O_2 bonding. In contrast, the low O_2 affinity of these systems when the axial base is a phosphine or phosphite is a result of the π-electron acceptor characteristics of these ligands.[42]

We originally believed that the small O_2 affinity of M(Cap)(B) relative to M(Por)(B) might be due to the small "cap size" placing constraints on O_2 inside the cap. In order to test this we prepared M(HmCap)(B), which we think has a larger cap size, and if this were the important factor then its O_2 affinity should be larger than that for M(Cap)(B). The results (Tables I and II) show that just exactly the opposite happens.

The deoxy state of a flat cobalt porphyrin would be better solvated by nonpolar solvents such as toluene, especially at low temperature. A polar bond such as Co(III)-O_2^- would not be stabilized in such solvents. Since the O_2 moiety of the picket-fence analogues is effectively shielded from the solvent by virtue of the "pickets", the solvation effect would be minimized. This would lead to the observed[7,33] greater stability of the oxygenated species. Yet the results presented here appear to negate this solvation hypothesis, since the bound O_2 in the capped porphyrin systems is even more protected from solvent influence than in the corresponding picket-fence porphyrin complexes. The highly shielded cobalt(II) capped porphyrins, Co(HmCap)(B) and Co(Cap)(B), have a lower O_2 affinity than the corresponding highly solvated flat porphyrin complexes, Co(PPIXDME)(B) and Co(T(*p*-OCH_3)PP)(B). The same trend follows with iron porphyrins, where Fe(Cap)(1-MeIm) binds O_2 about 40 times less than Fe(triPiv(4CImP)-PP). The conclusion is that the solvolysis hypothesis[7,33] may be valid in accounting for the differences in O_2 affinity between CoMb and Co(PPIXDME)(1-MeIm)[33] and between the cobalt(II) picket-fence porphyrins and Co(T(*p*-OCH_3)PP)(B),[7] but for the capped porphyrin systems solvolysis must play a minor role in determining O_2 affinity. The invariance of O_2 affinity to the pK_a of the axially substituted pyridines also suggests that some other factor(s) predominates in determining the O_2 affinity of the capped metal porphyrins.

The low O_2 affinity of the capped porphyrin systems could be the result of several factors: (1) unfavorable steric interactions between the bound dioxygen and the porphyrin cap, (2) an increase in the conformational strain energy of the capped porphyrin complexes upon oxygenation, and (3) electronic substituent effects. In going from M(Cap)(B) to the corresponding M(HmCap)(B) the steric interactions between bound dioxygen and the porphyrin cap should decrease because the cap size is larger. This predicts that M(HmCap)(B) should have a larger O_2 affinity than M(Cap)(B), but since the contrary is found factor (1) is ruled out. Electronic effects (3) are expected to be small from previous studies,[40,45] and our studies of the capped porphyrin systems show that electronic changes have little effect on the O_2 affinity of the complexes. Therefore, of the three factors considered, it appears that the conformational strain energy (2) must play a major role.

The low O_2 affinities displayed by the capped porphyrins suggest that the conformational strain energy in M(capped)(B) is enhanced upon oxygenation to M(capped)(B)(O_2). The metal is out of the plane of the porphyrin, which may be "domed",[46] in the deoxy species, and movement of the metal into the porphyrin plane upon oxygenation may be hindered owing to steric restraints imposed by the porphyrin cap. Consequently, the capped porphyrins would tend to "lock" the metal into the out-of-plane position. Thus the major difference between the various systems (Table III) may be the energy needed to undome the porphyrin and to bring the ferrous ion into the porphyrin plane. For natural systems and the various picket-fence porphyrin complexes, this energy would be smaller than that for the corresponding capped porphyrin complexes. Since the O_2 affinities for the HmCap systems are less than for the corresponding Cap systems (and the smallest of any system in Table III) it follows that the former systems lock the metal even more rigidly into the five-coordinated conformation.

This five-coordinate conformation of the capped porphyrins need not necessarily have more strain than do other deoxy metal porphyrin systems. Gelin and Karplus[47] have found from energy calculations that the unliganded, or deoxy, heme is not subject to any significant steric strain. The iron atom is in the optimal position for a five-coordinate high-spin ferrous ion, and this position is not significantly farther from the mean plane of the porphyrin than in five-coordinate model compounds.[49] In the deoxy state there may be some doming of the porphyrin ring, but the energy difference between a domed and planar structure is slight, not enough to store considerable amounts of strain energy.[47] Even the porphyrin ring itself in hemoglobin is very flexible, since an expansion of the ring to accommodate a high-spin ferrous ion in the plane is estimated[28] to require less than 0.5 kcal. The capped porphyrin complexes have K_B values that are about ten times smaller than other corresponding metal porphyrins.[13] These data suggest that the deoxy capped porphyrin complexes have similar or slightly smaller conformational stabilities than do the other systems. The major difference between the capped porphyrins and other systems must then result from the actual oxygenation process. If the porphyrin caps, owing to steric interactions with atoms in the porphyrin ring, prevent the porphyrin from undoming and/or the metal from entering the mean porphyrin plane, the O_2 affinity of the complex would be quite small.

Energy calculations by Warshel[50] and later by Baldwin and Chothia[28] have pointed to a conformational difference between R-state and T-state hemes in hemoglobin. In R-state hemoglobin, it was concluded[28] that the imidazole of the proximal histidine is in a symmetric position relative to the heme. This supposedly lessens the steric interactions with the porphyrin ring and allows the heme to easily oxygenate. In the T state the imidazole of the proximal histidine is coordinated to the ferrous ion in an asymmetric conformation which causes steric interaction between the imidazole and the porphyrin nitrogens. Thus, the O_2 affinity is lowered considerably because steric interaction prevents the iron atom from going into the porphyrin plane. This is similar to the conformational strain effect which we propose is responsible for the low O_2 affinity of the capped porphyrin complexes.

The change in axial bases for porphyrin complexes from 1-MeIm to 1,2-Me_2Im produces decreases in O_2 affinity which are similar to those for going from R-state to T-state hemoglobins[6] and cobalt-reconstituted hemoglobin.[51] This effect of 1,2-Me_2Im is due to the steric interaction of the 2-methyl substituent which resists the metal entering the porphyrin plane on oxygenation. In going from 1-MeIm to 1,2-Me_2Im for Fe(Cap)(B) or Co(Cap)(B), the O_2 affinity also decreases by amounts similar to that for changes from R- to T-state Hb and CoHb. For example (Table III), the $P_{1/2}{}^{O_2}$ for Fe(Cap)(1,2-Me_2Im) is about 180 times higher than that for Fe(Cap)(1-MeIm). For hemoglobin, the $P_{1/2}{}^{O_2}$ for the T state is 150 times higher than for the R state. Thus, the steric interactions which cause the lowering of O_2 affinity in going from 1-MeIm to 1,2-Me_2Im are virtually independent of those interactions which cause the low O_2 affinity of the capped porphyrin complexes.

The thermodynamic values in Table III show that the major differences in binding O_2 by the metal complexes are manifested in the enthalpy term. If the capped porphyrins are constrained to a five-coordinate configuration, the process of binding O_2 to form a six-coordinate system would require more energy than if these constraints were smaller. The values of $\Delta H°$ are higher for the more constrained capped porphyrin systems than for the other metalloporphyrins of lesser strain. However, the values of $\Delta S°$ are all much the same because the major factor contributing to $\Delta S°$, the loss of degrees of freedom in binding O_2, is similar for all systems. It should also be noted that the enthalpy terms reflect the added steric restraint of the 1,2-Me_2Im systems compared with the corresponding 1-MeIm systems. Thus Fe(Cap)(1,2-Me_2Im) has the highest $\Delta H°$ and the highest $P_{1/2}{}^{O_2}$ of the iron systems in Table III.

Oxygenation of Fe(HmCap)($B)_2$. In an earlier communication[9] it was suggested that the oxygenation of Fe(HmCap)(1-MeIm)$_2$ occurs by a simple addition reaction:

$$\mathrm{Fe(HmCap)(1\text{-}MeIm)_2} + \mathrm{O_2} \xrightleftharpoons{K_{B_2}{}^{O_2}} \mathrm{Fe(HmCap)(1\text{-}MeIm)_2(O_2)} \quad (6)$$

This result requires the formation of a most unusual pseudo-seven-coordinate complex. The addition of dioxygen would be dependent on the base concentration if it proceeded by the usual substitution reaction, represented here by the oxygenation of Fe(TPP)(py)$_2$:[3]

$$\mathrm{Fe(TPP)(py)_2} + \mathrm{O_2} \xrightleftharpoons{K_{eq}} \mathrm{Fe(TPP)(py)(O_2)} + \mathrm{py}$$

$$\text{where } K_{eq} = (K_B{}^{O_2})(K_B{}^B)^{-1} = \frac{[\mathrm{Fe(TPP)(py)(O_2)}][\mathrm{py}]}{[\mathrm{Fe(TPP)(py)_2}]P_{O_2}} \quad (7)$$

From eq 7 the apparent $P_{1/2}{}^{O_2}$ would be a function of base concentration, and the following relationship may be derived:

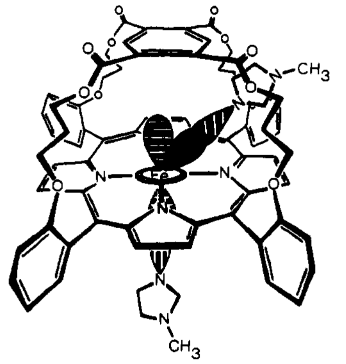

Figure 5. Schematic representation of nonaxial base, 1-MeIm, in Fe(HmCap)(1-MeIm)$_2$. Horizontally lined orbital is iron d_{z^2}, vertically lined orbitals are sp^2 lobes of imidazole nitrogens, and solid orbital is a lobe of the iron d_{yz} (or d_{xz}) orbital.

$$P_{1/2}^{O_2}\text{ (apparent)} = (1 + K_B{}^B[B])P_{1/2}^{O_2}, \text{ where } P_{1/2}^{O_2} = (K_B{}^{O_2})^{-1} \quad (8)$$

The measurement of dioxygen affinities was made at 0 °C, where $K_B{}^B = 8.3 \pm 0.7$. If the base concentration is raised from 0.5 to 2.0 M 1-MeIm (B = 1-MeIm), the $P_{1/2}^{O_2}$ (apparent) should increase by a factor of 3.4 according to eq 8. The results, however, show that $P_{1/2}^{O_2}$ (apparent) is constant. Thus, the reaction of Fe(HmCap)(1-MeIm)$_2$ with O_2 is independent of the base concentration and is most likely an addition reaction.

The $P_{1/2}^{O_2}$ for the addition reaction, eq 6, can be determined from eq 2 or 3. The $P_{1/2}^{O_2}$ values for the formation of the pseudo-seven-coordinate complex are 200 ± 10 Torr at 0 °C and 22 ± 2 Torr at −45 °C. In order to compare the oxygenation with that for the five-coordinate systems, however, an estimate of 120–180 Torr is made for the reaction of O_2 to form Fe(HmCap)(1-MeIm)(O_2).[9]

Further work on this novel system gives added credence to the reaction represented by eq 6. Solid Fe(HmCap)(1-MeIm) was dissolved in toluene and titrated with O_2 at −63 °C (Figure 4). The deoxy spectrum (Figure 4a) is typical of a five-coordinate iron(II) porphyrin complex. The addition of O_2 oxygenates more than half of the complex at 11.2 Torr and most of it at 19.8 Torr. To ensure complete oxygenation, the solution spectrum was determined at greater than 300 Torr of O_2. This spectrum (Figure 4c) has a peak at 549 nm and resembles the spectrum of Fe(Cap)(1-MeIm)(O_2). When a large excess of 1-MeIm is added, the spectrum changes little (Figure 4d). The maximum is now at 546 nm, and this is believed to be the spectrum of Fe(HmCap)(1-MeIm)$_2$(O_2). It is significant that the addition of excess 1-MeIm does not replace the dioxygen from the molecule. However, when O_2 is removed by vacuum, the reverse of eq 6 occurs and the spectrum of Fe(HmCap)(1-MeIm)$_2$ is obtained (Figure 4e).

For the addition of 1-MeIm to Fe(HmCap), $K_B{}^B \ll K^B$.[13] The second base only weakly binds to the iron atom. This is in marked contrast to the behavior[13] of the smaller base $PrNH_2$, which, upon addition to Fe(HmCap), shows the well-known relationship of $K_B{}^B > K^B$ for the ligation of iron(II) porphyrins.[15] That the coordination of $PrNH_2$ with Fe(HmCap) shows normal behavior is confirmed by much experimental evidence. For example, Fe(HmCap)($PrNH_2$)$_2$ will not oxygenate in excess base, because the second base binds too strongly. At low base concentration, the usual reversible oxygenation occurs. The results show (Figure 3) that the deoxy spectrum is similar to that of Fe(TPP)(B)$_2$.[23] Upon the addition of 10 Torr of O_2 the complex is approximately half-oxygenated, and at 80 Torr of O_2 adduct formation is almost complete. At −63 °C and an O_2 pressure of 602 Torr, the complex Fe(HmCap)($PrNH_2$)(O_2) was converted to Fe(HmCap)($PrNH_2$)$_2$ on the addition of 2 mL of neat $PrNH_2$ (Figure 3e). Unlike the addition of O_2 to Fe(HmCap)(1-MeIm)$_2$, Fe(HmCap)($PrNH_2$)$_2$ oxygenates via a substitution reaction.

Since Fe(HmCap)($PrNH_2$)$_2$ shows normal behavior toward oxygen addition, the second $PrNH_2$ is believed to occupy the axial coordination position inside the cap. The abnormal behavior of Fe(HmCap)(1-MeIm)$_2$ (and corresponding py) toward oxygen addition suggests that the second 1-MeIm does not occupy the normal axial coordination site. We believe that it is coordinated at an off angle (Figure 5) inside the cap. We tested[13] the possibility of bonding the second base cis to the first outside the cap by using ethylenediamine. The results show that ethylenediamine does not behave as a bidentate ligand, but functions as a monodentate to form Fe(HmCap)(en)$_2$. Therefore, cis coordination of the second base outside the cap does not seem very likely. Also in support of this is the fact that Fe(HmCap) will not bind a second large base such as 1,2-Me_2Im or t-BuNH_2.

On the premise that 1-MeIm adds to Fe(HmCap)(1-MeIm) in a nonaxial position, it follows that the d_{z^2} orbitals of iron in both Fe(HmCap)(1-MeIm) and Fe(HmCap)(1-MeIm)$_2$ should be of comparable energy and available for interaction with the dioxygen molecule. Also, either the d_{xz} or d_{yz} orbital has a lobe directed toward the nonaxial base in Fe(HmCap)(1-MeIm)$_2$, and consequently will be raised in energy. Thus the relative iron(II) d orbital energy order for such a distorted bis base complex is d_{xy}, $d_{xz} < d_{yz} < d_{z^2} < d_{x^2-y^2}$ (Figure 6), if the d_{yz} orbital is directed toward the nonaxial base. Provided that the spin-pairing energy is greater than the energy gap between the d_{yz} and d_{z^2} levels, the intermediate-spin state[9,13] ($S = 1$) of Fe(HmCap)(1-MeIm)$_2$ may be rationalized. The spin state of Fe(HmCap)(1-MeIm) is the normal $S = 2$, known for most other five-coordinate iron(II) porphyrin complexes. The pseudo-seven-coordinate complex is diamagnetic.[52]

The resonance Raman spectrum of Fe(HmCap)(1-MeIm)$_2$ further confirms the uniqueness of this complex.[53] Several vibrational modes of the porphyrin ring have been shown to shift frequency in a manner which reflects the coordination number and oxidation state of the metal center.[54] Raman spectra of naturally occurring porphyrins are different in appearance from the tetraphenylporphyrin systems. Only with the synthesis of the picket-fence porphyrins and the capped porphyrins was it possible to make a systematic study[53,54] of these structure-sensitive frequencies for iron tetraphenylporphyrins. The iron picket-fence porphyrins, tetraphenylporphyrins, and capped porphyrins have similar (usually within 3 cm^{-1}) frequencies for these marker bands when the same spin states and oxidation states are compared.

As shown in Table IV, the 1538-cm^{-1} band (band A) for Fe(HmCap)(1-MeIm)$_2$ is similar in value to those of the high-spin, five-coordinate complexes Fe(Por)(B). Since studies have shown[55] that the frequencies for band A are correlated to the porphyrin core size, the presence of this band in Fe(HmCap)(1-MeIm)$_2$ suggests that the porphyrin core is of comparable size of the five-coordinate complexes, even though it is pseudo-six-coordinate and of intermediate spin. The values of the other two structure-sensitive frequencies (B and C in Table IV) support the possibility of a nonaxial base, since there are two distinct bands in each frequency range, one corresponding to five coordination and the other to six coordination. Because the concentration of 1-MeIm gives greater than 90% of the six-coordinate complex, the origin of the double peaks cannot be due to an equilibrium mixture of the five- and six-coordinate species. Bands B and C are generally associated with vibrational modes of the pyrrole groups in the porphyrin ring.[54-56] If the second base is bonded nonaxially to a d_{yz} or d_{xz} orbital, it will be situated above only one of the four pyrrole groups. This imposed degeneracy may cause some of the vi-

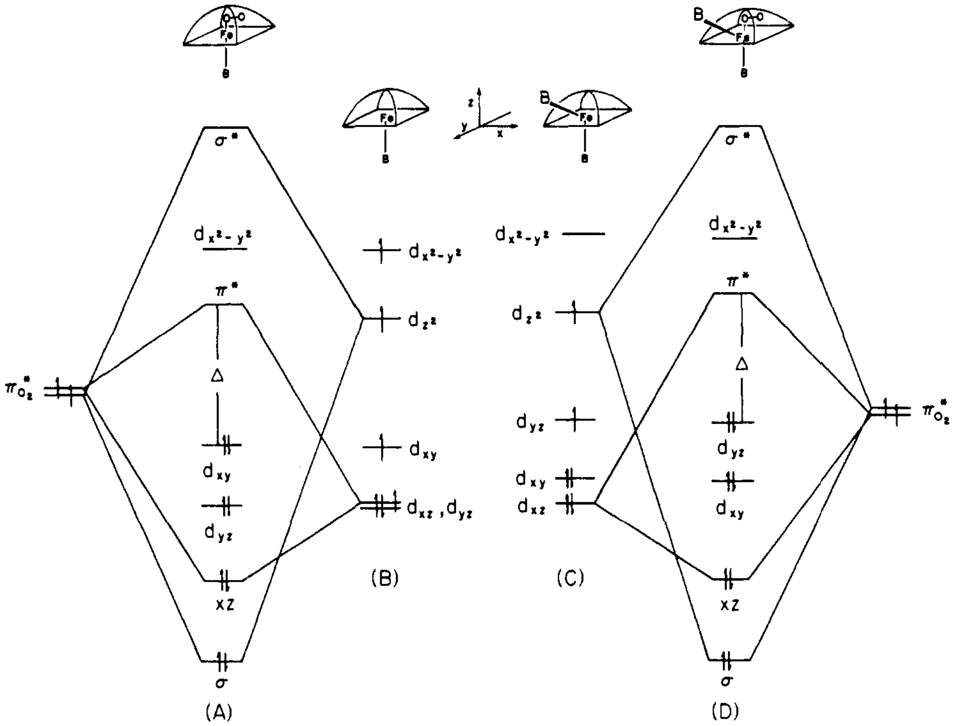

Figure 6. A qualitative MO scheme for the bonding in iron capped porphyrin dioxygen complexes, showing both σ and π interactions between the iron and coordinated O_2. (A) and (B) represent Fe(Cap)(B)(O_2) and Fe(Cap)(B), respectively. (C) is the hypothesized electronic structure for the pseudo-six-coordinate complex, Fe(HmCap)$(B)_2$, showing intermediate spin and the nonaxial base binding to the d_{yz} orbital of the iron center. (D) is the scheme for Fe(HmCap)$(B)_2(O_2)$. This scheme is analogous to the $Fe^{II}(O_2) \leftrightarrow Fe^{IV}(O_2)^{-II}$ valence bond resonance hybrid when Δ > pairing energy. Scheme taken in part from ref 57. It should be noted that in the schematic representations of the capped porphyrin complexes the porphyrin nitrogens lie, not at the corners of the square, but at the midpoints of the lines connecting the corners. They are still situated along the x and y axes.

Table IV. Resonance Raman Structure-Sensitive Bands for Synthetic Iron(II) Porphyrin Complexes

complex	coordination no.	structure-sensitive bands, cm^{-1}			ref
		A	B	C	
Fe(Cap)(1-MeIm)	5	1540	1345	371	this work[a]
Fe(TpivPP)(2-MeIm)	5	1540	1344	366	54
Fe(TPP)(2-MeIm)	5	1337	1342	372	54
Fe(HmCap)$(1\text{-MeIm})_2$	6 (pseudo)	1538	1348 1356[b]	380 371[b]	this work[a]
Fe(HmCap)$(prNH_2)_2$	6	1559	1356	382	this work[a]
Fe(TpivPP)$(1\text{-MeIm})_2$	6	1560	1355	384	54
Fe(Tpp)$(1\text{-MeIm})_2$	6	1557	1354	382	54

[a] See ref 53. [b] Shoulder.

brational modes to split, some to the six-coordinate frequency and the rest to that of the five coordinate. The pyrrole group under the nonaxial base may resemble the pyrrole groups in six-coordinate species, whereas the other three pyrroles approach five-coordinate status because they have little interaction with the second base.

Investigations of the IR spectra of solutions of the O_2 and of the CO adducts of Fe(HmCap)$(1\text{-MeIM})_2$ also support the formation of the pseudo-seven-coordinate species Fe(HmCap)$(1\text{-MeIm})_2(O_2)$ and Fe(HmCap)$(\text{MeIm})_2$(CO), respectively. In the presence of excess 1-MeIm to assure coordination of the second base, the dioxygen adduct has an IR band at ν_{O_2} 1160 cm^{-1} and the carbon monoxide adduct has a band at ν_{CO} 1979 cm^{-1}. These values are both in the approximate region for corresponding iron(II) porphyrins, and this suggests that the weakly bound nonaxial 1-MeIm has little effect on the binding of O_2 and of CO in this system. In spite of all the evidence in support of these pseudo-seven-coordinate species, the exact structures of the complexes will have to await a complete single-crystal X-ray study. We continue our efforts to obtain suitable crystals for such a study.

Summary

The O_2 affinities of iron and cobalt complexes of the capped porphyrins are considerably smaller than those of the natural proteins and the corresponding synthetic oxygen carriers. This lower O_2 affinity of the capped porphyrins appears to be associated with the greater conformational strain which accompanies the formation of the six-coordinate dioxygen adducts. The effect of the porphyrin cap on the ligation of an axial base[13] to form five-coordinate complexes is much smaller than the effect on oxygenation. It is proposed that these steric interactions constrain the five-coordinate metal center in a tetragonal pyramid complex to a position out of the porphyrin plane, thereby preventing it from easily entering the porphyrin ring upon oxygenation. The exact nature of this steric interaction remains a mystery, and it is noteworthy that the homologous cap affords even a greater amount of strain in the system.

Evidence is presented for the formation of the novel pseudo-seven-coordinate complex Fe(HmCap)$(1\text{-MeIm})_2(O_2)$. Unlike the normal behavior of iron(II) porphyrins, Fe(HmCap)(1-MeIm)$_2$ adds dioxygen and carbon monoxide to form the pseudo-seven-coordinate complexes. It is believed that this pseudo-seven-coordinate system is possible because the binding of the second base is thought to be nonaxial, binding to a d_{xz} or d_{yz} orbital, leaving the d_{z^2} orbital for binding to dioxygen and to carbon monoxide.

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(1) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979,** *79,* 139–179, and references cited therein.

(2) Abbreviations: TPP, dianion of *meso*-tetraphenylporphine; T(*p*-OCH$_3$)PP, dianion of tetra-*p*-methoxy-*meso*-tetraphenylporphine; TpivPP, dianion of "picket-fence porphyrin", *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl)-porphyrin; triPiv(4CIm)PP, dianion of *meso*-tri(α,α,α-*o*-pivalamidophenyl)-β-*o*-3-(*N*-imidazolylpropylamidophenyl)porphyrin; Cap, dianion of the capped porphyrin 5,10,15,20-[pyromellitoyl(tetrakis-*o*-oxypropoxyphenyl)]porphyrin; Mb, myoglobin; Hb, hemoglobin; CoMb, cobalt reconstituted myoglobin; CoHb, cobalt reconstituted hemoglobin; Por, dianion of any porphyrin; PPIXDME, dianion of protoporphyrin IX dimethyl ester; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; 1,2-Me$_2$Im, 1,2-dimethylimidazole; py, pyridine; 3,4-Lut, 3,4-lutidine; 3-Clpy, 3-chloropyridine; *sec*-BuNH$_2$, *sec*-butylamine; *t*-BuNH$_2$, *tert*-butylamine; PrNH$_2$, propylamine; P(*n*-Bu)$_3$ tri-*n*-butylphosphine; P(EtO$_3$), triethyl phosphite; M, metal; $P_{1/2}^{O_2}$, pressure of oxygen necessary to oxygenate 1/2 of the available sites; P_{O_2}, pressure of O$_2$.

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(17) $P_{1/2}^{O_2}$ is defined as the pressure of oxygen at which one-half of the available bonding sites are oxygenated. For a simple addition reaction, with equilibrium constant K_{O_2}, X + O$_2$ $\rightleftharpoons$ X(O$_2$), $P_{1/2}^{O_2} = 1/K_{O_2}$. For a discussion of comparison of equilibrium constants for various solvents, see ref 7.

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