redox orbital model, which predicts the existence of three spatially isolated (intrinsically C_{2v}) portions of the molecular structure with, at most, minimal interaction. These conclusions are further substantiated by Heath's observation of the intervalence charge-transfer transitions in the reduction products of $[Ru(bpy)_3]^{2+}$, and both results appear consistent with the predictions of the vibronic coupling model of Schatz. Thus, a principal question remaining to be answered for the single ring model (both redox and optical orbitals) concerns the origin of the minimal interaction.

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Registry No. $[Ru(Me_2\text{-phen})_3](PF_6)_2$, 85185-55-3; $[Ru(Me_2\text{-bpy})_3](PF_6)_2$, 83605-44-1; $[Fe(Me_2\text{-phen})_3](PF_6)_2$, 85202-31-9; $[Fe(Me_2\text{-bpy})_3](PF_6)_2$, 85185-57-5; FMP^+, 85185-58-6; FMP^0, 85185-59-7; FMB^+, 71619-84-6; RMB^+, 65605-26-7; RMB^0, 83605-52-1; RMB^-, 83605-53-2; RMP^+, 85185-60-0; RMP^0, 85185-61-1; RMP^-, 85185-62-2.

Synthesis and Characterization of the "Pocket" Porphyrins[1a]

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Abstract: The synthesis of the "pocket" series is described. The iron(II) complexes have been extensively characterized by ^1H NMR, MCD, Mössbauer, direct axial ligand titrations, and magnetic susceptibility determinations. The results of these experiments indicate that in toluene, regimes of axial base concentration can be found in which iron(II) derivatives of the "pocket" porphyrins remain predominantly five-coordinate in the absence of gaseous ligand. Further, these five-coordinate complexes form stable and reversible oxygen adducts. The resonance Raman spectra of five-coordinate iron(II) "pocket" porphyrins are discussed as well as studies based on interactions with CO.

Recent attention has focused on developing synthetic iron(II) porphyrin complexes which are capable of reversibly binding O_2[2-6] in a manner analogous to hemoglobin (Hb)[7] and myoglobin (Mb). Many such models have been prepared[8-20] and their interactions with various ligands described.[14-25] To date, our own contributions

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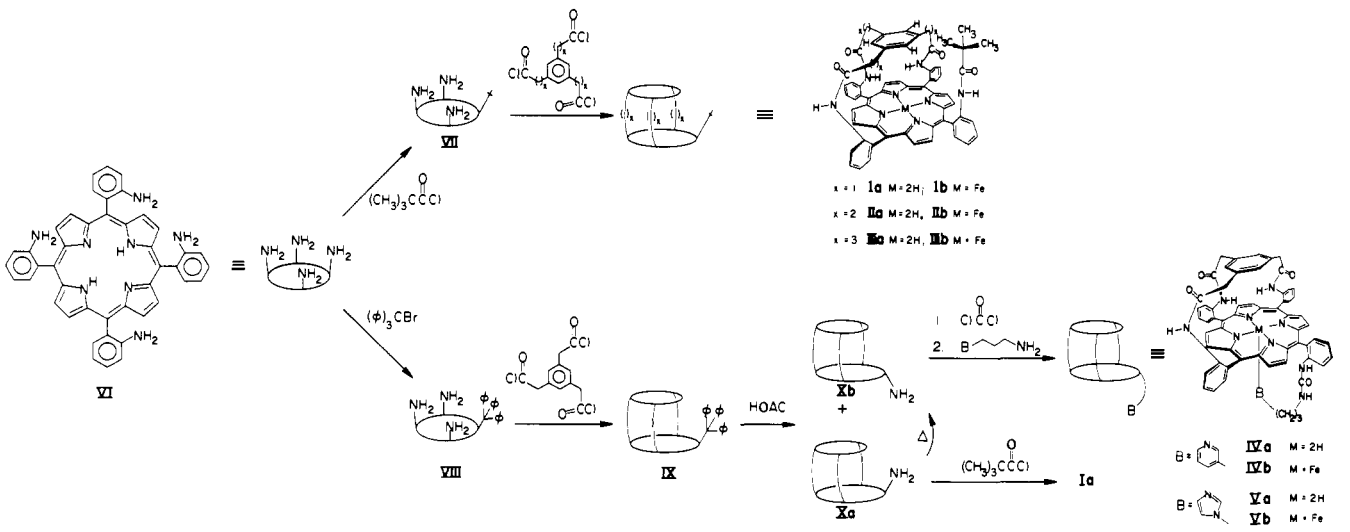
0002-7863/83/1505-3038$01.50/0

Scheme I



in this area have been primarily concerned with the synthesis,[9,26] structural characterization,[26-28] and gaseous ligand-binding properties[22,23,29,30] of the "picket fence" and "tailed" "picket fence" prophyrins. Dilute toluene solutions of iron(II) derivatives of the "picket fence" series have been shown capable of mimicking the O_2 binding behavior of both the high affinity, relaxed (Hb(R)) and low affinity, tense (Hb(T)) forms of hemoglobin.[22] By contrast, the "picket fence" complexes were found to bind CO with ca. 100-fold greater affinity than the natural systems.[23] This was considered as being consistent with the proposal[31-34] that steric effects within the heme cavity serve to lower selectively the CO binding affinities in hemoproteins. Structural studies are consistent with this proposal. Whereas O_2 has been found to bind in an intrinsically bent fashion in both models[27,28] and hemoproteins,[35] the CO ligand binds in a linear fashion only in simple iron(II) porphyrin complexes.[36] The FeCO unit is forced to adopt a nonlinear binding geometry in hemoproteins[37] by virtue of interactions with various distal side residues, particularly histidine,[37a] valine,[37b] leucine,[37c] or isoleucine.[37d]

This paper reports the synthesis and characterization of a new series of hemoprotein models, the iron(II) "pocket" porphyrins. These compounds were specifically designed so as to investigate[20,22] more fully the influence that nonbonded steric effects may have on O_2 and CO binding in well-characterized model systems. Throughout this series of congurent models, the "pockets" are expected to accommodate the formation of unhindered, bent FeO_2 units, while providing steric hindrance which should, to various extents, interfere with the normally linear binding of CO. It might therefore be expected that the O_2 affinities of the "pocket" porphyrin complexes should be similar to those of the "picket fence" complexes while the CO affinities should be reduced. The following paper[20b] consists of a detailed comparison between the O_2 and CO binding behavior of the iron(II) "pocket" and "picket fence" porphyrin models. The results described therein suggest that steric encumbrance may indeed reduce CO affinities relative to those of O_2. Other groups have also synthesized sterically encumbered models[11,15-17,19] with the objective of studying the effect of distal-side steric interactions on ligand affinities. The results obtained in, and conclusions drawn from, these studies are not necessarily in agreement with ours. Several reasons for the apparent disparities are discussed in the following paper.[20b]

Only model iron(II) porphyrin complexes which remain five-coordinate about iron in the absence of gaseous ligands and which form stable O_2 complexes can be used to measure directly both O_2 and CO affinities under equilibrium conditions.[2b] It is important to verify that these two criteria are satisfied by the "pocket" porphyrins. We have found that as dilute toluene solutions, stable oxygen adducts are formed from the iron(II) "pocket" porphyrins Ib, IIb, and IIIb (Scheme I), provided sufficiently high concentrations of coordinating base (1-MeIm or 1,2-Me_2Im) are present. Unfortunately, when O_2 is admitted to solutions of the "tailed" "pocket" porphyrins IVb or Vb, rapid oxidation to the μ-oxo dimer occurs. This is in contrast to previous findings with the "tailed" "pickel fence" systems which form stable O_2 complexes.[2a,9b,23] In light of the limited utility of IVb and Vb as models, the bulk of our attention has focused on the more encumbered systems Ib and IIb. Since the "pocket" porphyrins Ib–IIIb requires large excess concentrations of axial base to stabilize the formation of the O_2 adducts, we felt it important to characterize thoroughly the coordination chemistry of the iron(II) "pocket" porphyrin complexes in the absence of gaseous ligand, so as to be assured that five-

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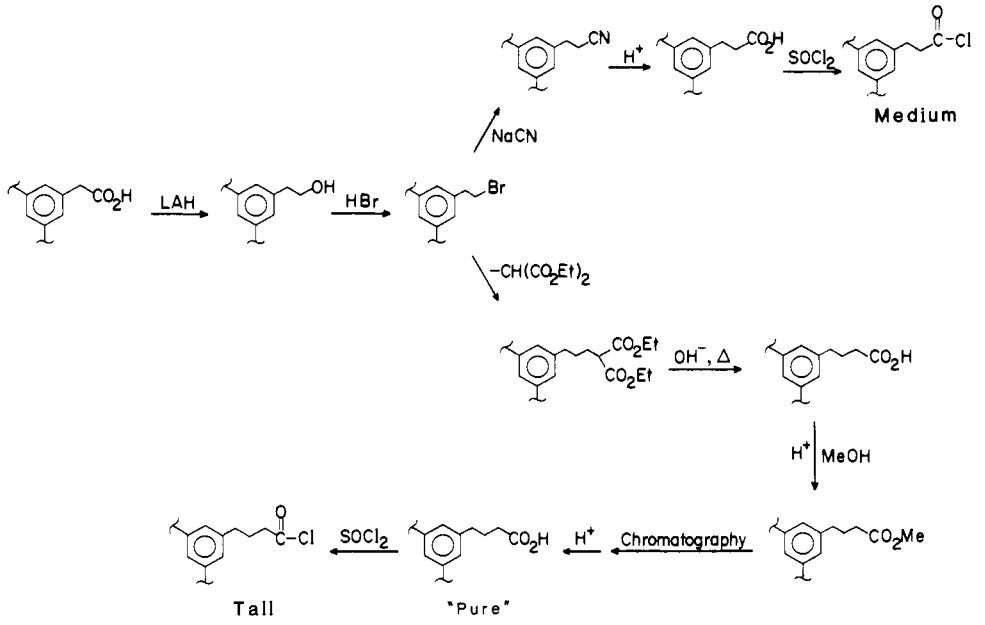
Scheme II. Synthesis of Medium and Tall Pocket Acid Chlorides



coordination pertains about iron. This is important since for simple, sterically unemcumbered iron(II) porphyrins formation of the bis-ligated, six-coordinate species is favored in the presence of excess unhindered nitrogenous bases (e.g., 1-MeIm). Equations 1 and 2 illustrate the equilibria of interest.[21a,b] Here FeP represents

$$\mathrm{FeP} + \mathrm{B} \overset{K_B}{\rightleftharpoons} \mathrm{FeP(B)} \quad (1)$$

$$\mathrm{FeP(B)} + \mathrm{B} \overset{K_B^B}{\rightleftharpoons} \mathrm{FeP(B)_2} \quad (2)$$

an unligated, four-coordinate, iron(II) porphyrin, B an axial base, and FeP(B) and $FeP(B)_2$ the mono-ligated and bis-ligated species, respectively. For these unprotected systems K_B^B exceeds K_B. As such, attempts[21c,38] to measure gaseous ligand affinities in the presence of an unhindered nitrogenous base would yield a value for the equilibrium constant associated with base displacement. What is desired, however, is the value of the equilibrium constant representing the direct addition of the gaseous ligand to the five-coordinate iron(II) porphyrin complex, FeP(B), to produce the ligated species FeP(B)(L). It has been known[21,39] for some time that the use of sterically hindered bases (e.g., 1,2-Me_2Im) serves to lower the value of K_B^B, permitting the generation of five-coordinate iron(II) porphyrin complexes. Since, however, the value of K_B^L is also lowered[21,23] this approach is limited in scope with regard to hemoprotein modeling studies.[2b]

In this paper we present a wide variety of spectroscopic evidence concerning the coordination chemistry of Ib–Vb. The results suggest that, in analogy to the "capped" porphyrins of Baldwin and Basolo et al.,[10,18,19] the iron(II) "small pocket" and "medium pocket" complexes, Ib and IIb, have distal side steric hindrance sufficient to ensure that five-coordination predominates over a wide range of imidazole and 1-methylimidazole concentrations. The range of base concentrations investigated include those used for the quantitative CO and O_2 binding studies described in the next paper.[20b]

The "pocket" porphyrins also provide a convenient system with which to explore other interesting phenomena. Since five-coordination predominates around iron in the imidazole-type complexes of Ib, the low-frequency resonance Raman spectra could be measured and Fe–N_ϵ(imidazole) stretching frequencies easily assigned. The changes in ν(Fe–N_ϵ) observed can be discussed in terms of changes in the equilibrium constant for monoligation, K_B. The "pocket" porphyrins also provide a set of models with which to test the recent hypotheses that the values of ν(CO) in the IR[31,33b,34,40] or $J(^{13}C–^{57}Fe)$ in the ^{13}C NMR[41] may be directly correlated with CO binding affinities and/or sterically induced distortions of the FeCO unit in iron(II) porphyrin carbonyl complexes.

Results

The common precursor to all of the "pocket" porphyrins, *meso*-tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphyrin, VI, was prepared in the usual manner.[26] This was treated with slightly over 1 equiv of pivaloyl chloride to give the "mono-picket" compound VII in 60% yield after chromatography (Scheme I). Compound VII could be treated with the appropriate benzene triacid chloride to yield the "small", "medium", or "tail" "pocket" porphyrin compounds designated as H_2PocPiv, Ia, H_2MedPoc, IIa, or H_2TalPoc, IIIa, respectively. The acid chlorides were prepared by treating the appropriate benzene triacid with thionyl chloride. The three-prong amide coupling to the "mono-picket" porphyrin was carried out at high dilution under a nitrogen atmosphere. These reactions routinely proceeded with yields of 65% or better after chromatography. Benzene-1,3,5-triacetic acid[42] and 1,3,5-tris-(2′-carboxyethyl)benzene[43] were prepared according to the literature. 1,3,5-Tris(3′-carboxypropyl)benzene was prepared from the reaction of 1,3,5-tris(2′-bromoethyl)benzene with sodium diethylmalonate (Scheme II). This chain-extension step proved most difficult and only a mixture of apparently mono-, di-, and trimalonate addition products could be obtained. The crude product was therefore deesterified, decarboxylated, converted to the corresponding mixture of methyl esters which were separated by chromatography to yield the pure trimethyl ester in an overall yield of 28%. The pure triacid was obtained in essentially quantitative yield following hydrolysis.

Treatment of VI with 1 equiv of trityl bromide led to the "monotrityl" compound VIII in 65% yield after chromatography (Scheme I). The protected precursor VIII was treated with 1,3,5-benzenetriacetyl chloride in the usual way to produce IX in 33% yield. The triphenylmethyl protecting group was removed by stirring in 90% acetic acid. The resulting "α-amino" "pocket" Xa was heated at reflux in toluene yielding a 1:1 mixture of the α-amino and β-amino atropisomers, Xa and Xb. Compound Xb

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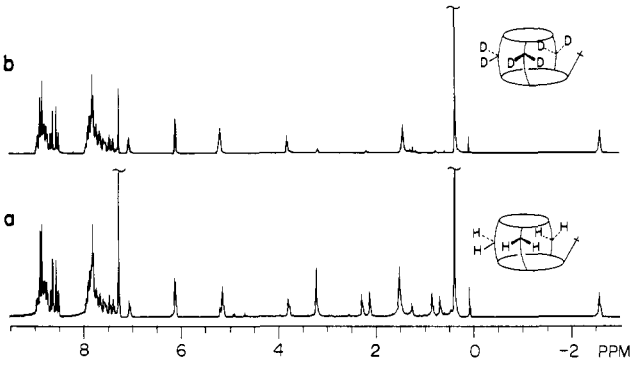

Figure 1. 100-MHz ^1H NMR spectra in $CDCl_3$ of H_2PocPiv, Ia (spectrum a) and a specifically deuterated analogue (spectrum b).

was isolated by chromatography and the recovered Xa was reequilibrated and rechromatographed to increase the overall yield of conversion to Xb. Solutions of Xb were exposed to phosgene gas and then either 3-(1-imidazolyl)propylamine[44] or 3-(3-pyridyl)propylamine[45] was added to give the "tailed" "pocket" compounds Va or IVb in good yield. Because analogous "tailed" compounds bearing appended imidazole units are sensitive to light and oxygen,[9b] the phosgene reactions and subsequent purification steps were carried out under N_2 and in the dark.

The metal-free porphyrins Ia–Va were characterized by ^1H NMR and mass spectroscopy. Elemental analysis was performed on Ia–IIIa. The ^1H NMR spectra proved especially informative for the simpler members of the "pocket" porphyrin series. In the ^1H NMR spectra of compounds Ia, IVa, and Va, it was possible to identify the signals arising from the porphyrin skeleton, the pivaloyl "picket", the benzene cyclophane, and the methylene bridges. The methyl bridge signals are particularly diagnostic and could be assigned on the basis of spin-decoupling experiments. For instance, in compounds derived from benzene triacetic acid (e.g., Ia, Va, IVa) a characteristic doublet of doublets was observed at ca. 0.8 and 2.2 ppm. Irradiation of one of the doublets caused the other to collapse to a singlet. This AB system derives from the diastereotopic protons of the two equivalent bridging methylenes. In order to support this assignment, benzenetriacetic acid specifically deuterated in the α positions was used to prepare an analogue of Ia in which the six protons of methylene bridges were replaced by deuterons. Figure 1 shows the ^1H NMR spectra of both Ia and the specifically deuterated analogue. As expected, the signals assigned to the methylene bridges were not observed in the deuterated complex.

The iron(II) derivatives (Ib, IIb, IIIb, IVb, Vb) were prepared under N_2 from the metal-free porphyrins by means of the previously reported direct iron(II) insertion reaction using $FeBr_2$.[9b] When possible, characterization studies were carried out immediately following insertion of Fe(II). If necessary, the iron(II) porphyrin complexes were stored as either the four- or five-coordinate solids. These were obtained by the slow addition of heptane to toluene solutions containing, when necessary, excess of the appropriate axial base. The crystalline solids were washed with heptane then dried in vacuo.

The iron(II) complexes of the "pocket" series of porphyrins Ib–Vb and particularly their adducts with externally provided ligands (e.g., 1-MeIm, 1,2-Me_2Im, O_2, CO) have been characterized by a wide variety of spectroscopic techniques (optical spectroscopy, ^1H NMR, Mössbauer, magnetic susceptibility, resonance Raman spectroscopy, IR, ^{13}C NMR). Importantly, similar solution conditions were used for these spectroscopic characterizations as were used for the gaseous ligand-binding studies discussed in the following paper.[20b] Since we found that IVb, Vb, and pyridine complexes of Ib–IIIb oxidized in the presence of O_2, useful gaseous ligand-binding studies on these complexes could not be performed under equilibrium conditions.

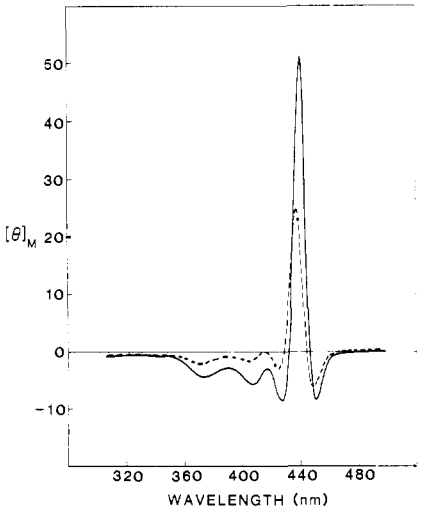

Figure 2. MCD spectra of FePocPiv in 1-MeIm (2.0 M) (–); in Im (0.03 M) (--).

Therefore, the spectroscopic characterization studies focused on complexes of Ib–IIIb with various imidazole ligands. The results from each of the characterizations are considered separately in the ensuing Discussion section.

Discussion

Optical Spectroscopy. Both the electronic absorption and magnetic circular dichroism spectra of all new iron(II) "pocket" porphyrin complexes were routinely recorded and compared with those of standard iron(II) tetraarylporphyrins. Recent work from our laboratory has served to establish a standard set of both UV/visible absorption and Soret MCD spectral data for iron(II) tetraarylporphyrins in various spin states and coordination geometries.[9,46] Several general trends have emerged. Four-coordinate iron(II) tetraarylporphyrins have two bands of nearly equal intensity in the Soret region (350–500 nm) of the electronic absorption spectra, as well as a broad peak at roughly 540 nm in the visible region (500–700 nm). Addition of nitrogenous base to a four-coordinate iron(II) porphyrin produces high-spin five- or low-spin six-coordinate complexes (eq 1 and 2), both of which exhibit spectra in the visible region with major bands at ca. 535 and 565 nm. In the Soret region, the absorption spectra of both the mono- and bis-ligated species appear qualitatively similar with λ_{max} for six-coordinate complexes appearing 5–10 nm further to the blue. Since these differences are slight, in situations where a possible mixture of five- or six-coordinate complexes may exist, we have preferred not to rely on electronic spectra in assigning coordination geometries or spin states for the various "pocket" porphyrin complexes. Once the coordination geometries are established by other means (vide infra), then the absorption spectra can serve as a useful "fingerprint" for the various complexes. Electronic spectra are therefore given for representative complexes of Ib, IIb, and IIIb in the Experimental Section.

In contrast to the electronic absorption spectra, we have found that the shape and sign (but not the intensity) of the MCD bands in the Soret region are a sensitive qualitative probe for spin state (and hence, coordination geometry) in complexes of iron(II) porphyrins.[46] In complexes derived from iron(II) tetraarylporphyrins and various imidazole ligands, dramatic differences are observed in the Soret MCD between the five-coordinate, high-spin form and the bis-ligated, low-spin form. The Soret region of the five-coordinate complexes shows a strong positive band at ca. 440 nm, while the MCD spectra of the six-coordinate bis-ligated species show an inverted bell-shaped form at ca. 425 nm.

While MCD has previously been used to explore the coordination characteristics of the "small" "pocket" complex, FePocPiv,

(44) Schwan, T. J. *J. Heterocycl. Chem.* **1967**, *4*, 633–634.
(45) Hawes, E. M.; Davis, H. L. *J. Heterocycl. Chem.* **1973**, *10*, 39–42.
(46) Collman, J. P.; Basolo, F.; Bunnenberg, E.; Collins, T. J.; Dawson, J. H.; Ellis, P. E., Jr.; Marrocco, M. L.; Moscowitz, A.; Sessler, J. L.; Szymanski, T. *J. Am. Chem. Soc.* **1981**, *103*, 5636–5648.

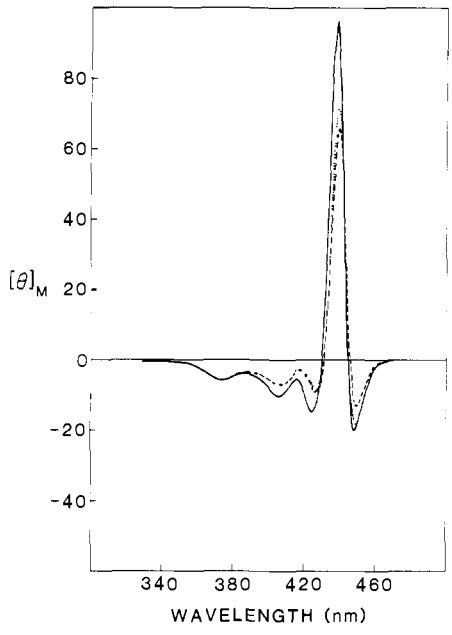

Figure 3. MCD spectra of FeMedPoc in 1-MeIm (2×10^{-3} M) (–); in 1-MeIm (0.02 M) (···); in 1-MeIm (0.13 M) (--).

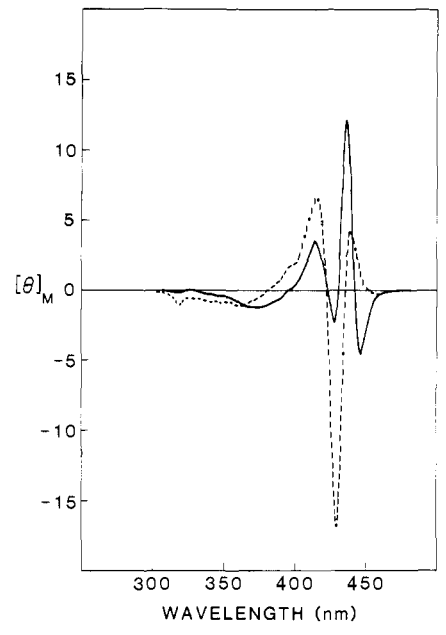

Figure 4. MCD spectra of FeTalPoc in 1,2-Me_2Im (5×10^{-3} M) (–); in 1-MeIm (5×10^{-4} M) (--).

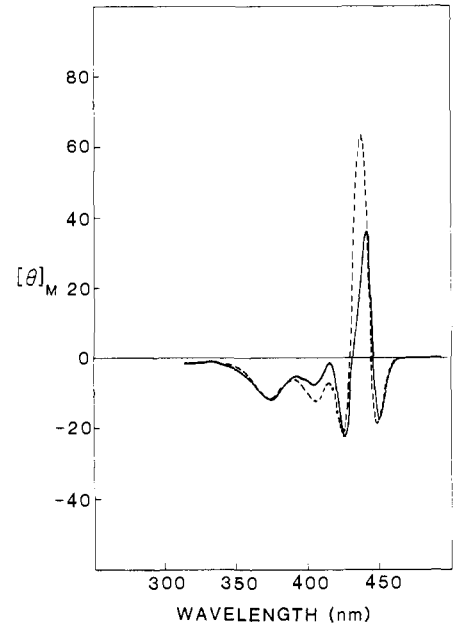

Figure 5. MCD spectra of FePoc3CuIm (--); in 1-MeIm (excess) (—).

Ib,[46] it has not hitherto been applied to the study of other members of the "pocket" series. Moreover, since MCD serves as a form of characterization with which to compare the results of other studies (NMR, Mössbauer, magnetic susceptibility), an abbreviated discussion of the MCD spectral properties of complexes derived from Ib is appropriate here. Figure 2 shows that the Soret MCD spectra for dilute toluene solutions (ca. 5×10^{-5} M) of Ib containing excess imidazole or 1-methylimidazole are characterized by the presence of a positive band at 440 nm. This spectral feature is qualitatively similar to that of the well-characterized high-spin complex FeTPP(1,2-Me_2Im) and in strong contrast to the six-coordinate complexes FeTPP(1-MeIm)$_2$.[19,46] This comparison suggests that even in 2 M 1-methylimidazole (porphyrin-to-ligand ratio of ca. 1:40 000) five-coordination predominates about iron in the "pocket" complexes. In fact, no discernible change in the Soret MCD spectra was seen as the concentration of 1-methylimidazole was increased from 0.001 to 2 M. Figure 3 shows the effect on the MCD spectra of adding increasing quantities of 1-methylimidazole to dilute toluene solutions of FeMedPoc, IIb. The loss of band intensity at 438 nm suggests that although five-coordination predominates at 1-methylimidazole concentrations of 0.13 M, some conversion to the bis-ligated six-coordinate complex has occurred. The Soret region MCD of IIIb indicates that no unusual control of coordination is accomplished by the "tall" "pocket". In fact, in the presence of excess ($\gtrsim$3 equiv) 1-methylimidazole, IIIb shows a typical six-coordinate spectra indicating that FeTalPoc(1-MeIm)$_2$ is the dominant species in solution (Figure 4). In the presence of 0.005 M 1,2-Me_2Im, solutions of IIIb appear to be five-coordinate. Soret region MCD spectra of the "tailed" "pocket" compound FePoc3CuIm, Vb, both in neat toluene and in the presence of added imidazole, are reproduced in Figure 5. It is interesting to note that some slight differences in the band features are discernible, suggesting that a quantity of bis-ligated complex is being formed as the result of adding 1-methylimidazole. If true, this interpretation suggests that the pivaloyl group in compounds Ib and IIb (absent in IVb and Vb) serves an important ancillary role in controlling ligand binding. Qualitative measurement of ligand binding using UV/visible spectroscopy can complement the qualitative trends observed in the MCD spectra.

Equilibrium constants for the coordination of axial ligands to the "small" "pocket" complex, Ib, were measured spectrophotometrically. Aliquots of axial base, prediluted with toluene, were added anaerobically to toluene solutions of the initially four-coordinate iron(II) porphyrin. The changes in the electronic absorption spectra were then recorded in either the 650–480-nm or 500–400-nm ranges. The temperature was in all cases maintained at 25.0 ± 0.3 °C and to ±0.1 °C during the course of any given run.

For Ib, K_B^B is negligible and the binding of an axial base occurs exclusively according to eq 1, with good isosbestic behavior. Figure 6 shows the typical spectral changes which occur during the course of a base-binding titration. Values for the monoligation constant, K_B, could be obtained by using the simple equilibrium expression

$$K_B = \frac{[\mathrm{FeP(B)}]}{[\mathrm{FeP}][\mathrm{B}]} \tag{3}$$

where $[\mathrm{FeP(B)}] = [\mathrm{FeP_{TOT}}]y$, $[\mathrm{FeP}] = [\mathrm{FeP_{TO_T}}] - [\mathrm{FeP(B)}]$, $[\mathrm{B}] = [\mathrm{B_{TOT}}] - [\mathrm{FeP(B)}]$, and $[\mathrm{FeP_{TOT}}]$ and $[\mathrm{B_{TOT}}]$ are the total concentrations of metalloporphyrin and base, respectively. At any given wavelength λ,

$$y = \frac{[\mathrm{FeP(B)}]}{[\mathrm{FeP_{TOT}}]} = \frac{A_\lambda - A_{0\lambda}}{A_{\infty\lambda} - A_{0\lambda}} \tag{4}$$

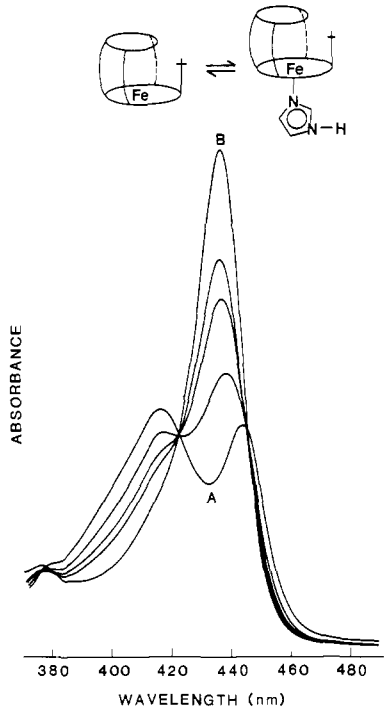

Figure 6. Spectral changes occurring upon titration of a toluene solution of FePocPiv, Ib, with Im. Curve A is four-coordinate; curve B is five-coordinate.

where A_λ is the absorbance at a specific [B] for a given wavelength λ, $A_{0\lambda}$ is the absorbance of the four-coordinate species at λ, and $A_{\infty\lambda}$ is the absorbance at λ of the fully ligated form.[47] A second, algebraically equivalent approach to data reduction involved using the Hill equation:[48]

$$\log \frac{y}{1-y} = n \log [B] + \log K_B \qquad (5)$$

Values of log K_B were obtained as the y intercept from plots of $\log y/(1-y)$ vs. log B, using standard linear least-squares analysis. In all cases, linear plots were obtained with $n = 1.0 \pm 0.1$, indicating that the equilibria being monitored spectrophotometrically was indeed the monoligation reaction of eq 1. Values for log K_B obtained with these two methods matched to within ±10%. In all cases equilibrium constants were calculated at a second wavelength, and the value of log K_B always proved independent of wavelength. Results are summarized in Table I.

A comparison among the K_B values shown in Table I suggests that increasing basicity within a series of imidazole-type ligands leads to greater affinities for base binding to iron(II) porphyrins. Furthermore, increased steric hindrance at the 2-position of the imidazole ligand appears to have a relatively small effect on the affinity for monoligation, K_B. This is in marked contrast to the severe reduction of binding affinity for the second ligand resulting from such steric hindrance.[21,23,28,39] It is possible that steric effects serve to lower slightly the value of K_B from what would be expected solely on the basis of ligand basicity. These conclusions are similar to those reached by Basolo and co-workers based on studies with the iron(II) "capped" porphyrins.[18] Interestingly, the values for K_B obtained in the "capped" systems are significantly lower than those observed in simple iron(II) porphyrins.[21] Distortions of the porphyrin macrocycle (e.g., "doming"[7] effects) were considered responsible for this unusual behavior in the "capped" systems.[18] The similarity of K_B for the binding of 1,2-Me_2Im to Ib and the open cavity "picket fence" model complex,[23] FeTPivP suggests that either these effects do not substantially influence the values for K_B or that porphyrin distortions upon base binding occur to a similar extent in the "pocket" and "picket fence" porphyrins.

(47) We assume in all cases that Beer's law is obeyed.
(48) Hill, A. V. *J. Physiol. (London)* **1910**, *40*, iv–vii.

Table I. Frequencies (cm^{-1}) of the Iron–Imidazole Stretching Vibrations in Five-Coordinate Hemes[a]

	ν(Fe–N_ϵ)	log K_B	pK_a (BH^+)	ref
FePocPiv(Im)	236	4.18 (±0.05)	6.95[b]	this work
FePocPiv(1-MeIm)	227	4.46	7.25[b]	this work
FePocPiv(2-MeIm)	215	4.53	7.86[b]	this work
FePocPiv(1,2-Me_2Im)	193	4.73	7.85[b]	this work
FeTPivP(2 MeIm)	209			68
FeTPP(2-MeIm)[c]	206			
FePPIX(2-MeIm)[d]	206-215			68
FeTPivP(1,2-Me_2Im)	200	4.57	1.85[b]	68

[a] In CH_2Cl_2 or benzene solution at 25 °C. [b] Reference 76. [c] Data taken from ref 63a and assigned on the basis of present work. [d] Aqueous suspension, various concentrations of cetyltrimethylammonium bromide used.

The K_B values in Table I also provide a set of data with which to correlate the resonance Raman results (vide infra).

When solutions of FeMedPoc, IIb, are titrated with dilute solutions of 1-methylimidazole in toluene, initial spectral changes are observed which are similar to those obtained in the analogous titrations of Ib. Some deviation from isosbestic behavior is, however, observed for IIb at higher concentrations of 1-MeIm. This suggests that $K_B^B > 0$ in accord with the MCD results given above. Little change in the absorption spectra are seen as solutions of FeMedPoc(1-MeIm) are steadily titrated with 1-MeIm provided $5 \times 10^{-4} \leq [B] \leq 0.1$ M. As the concentration of base is further increased, however, a new set of isosbestic spectral changes occur, corresponding to the conversion of FeMedPoc(1-MeIm) to FeMedPoc(1-MeIm)$_2$. An estimated value of $K_B^B = 0.2$ M^{-1} was obtained, using the Hill equation and the extrapolation procedures of Basolo and co-workers.[18]

The spectral changes occurring upon addition of 1,2-Me_2Im to toluene solutions of FeTalPoc, IIIb, are qualitatively similar to those seen upon the addition of 1-MeIm to IIb. Apparently, as suggested by the MCD results, just one base binds to IIIb to yield the five-coordinate complex, FeTalPoc(1,2-Me_2Im) at low 1,2-Me_2Im concentrations. This is followed by complexation of a second base and conversion to the six-coordinate complex FeTalPoc(1,2-Me_2Im)$_2$ at higher base concentrations. Poor isosbestic behavior was observed and no quantitative analyses have been made. This result does, however, suggest that although a regime can be found where five-coordination predominates, K_B^B is appreciably larger for FeTalPoc than for other simple iron(II) porphyrins, such as FeTPP[19] or iron deuteroheme.[21]

Both electronic absorption and MCD spectroscopy have been used to monitor the interactions of the "pocket" porphyrin complexes with O_2 and CO. Previous work[9] has shown that in general, CO and O_2 adducts of other iron(II) tetraarylporphyrin imidazole complexes display bands at ca. 425 nm in the Soret absorption spectra, with the molar extinction coefficients for the carbonyl adducts being approximately twice those of the oxygen complexes. Similar observations are seen in the Soret MCD spectra.[46] In general, both the CO and O_2 adducts give rise to S-shape bands similar in character to the A term band observed in oxy or carbonmonoxymyoglobin, with the molar ellipticities of the carbonyl complexes being twice that of the oxygen adducts. Figure 7 shows the changes in the Soret MCD spectra occurring when O_2 or CO is added to a solution of IIb containing 0.13 M 1-MeIm. Similar spectral changes are observed with the "small" and "tall" "pocket" complexes FePocPiv(1-MeIm) and FeTalPoc(1,2-Me_2Im) so these MCD spectra are not reproduced here. Significantly, the CO and O_2 MCD spectra for the well-characterized "tailed" "picket fence" system[9b] shows behavior perfectly analogous to that of the FeMedPoc(1-MeIm) complex (Figure 7). It has been previously shown that the "picket fence" complexes form stable O_2 and CO adducts.[9] Therefore, the MCD spectra can be interpreted as being evidence supporting the conclusion that, just as with the iron(II) "picket fence" porphyrins, stable O_2 and CO complexes are formed in the iron(II) "pocket" porphyrin series. It should be noted that the iron(II) derivatives of both the "picket fence" and "pocket"

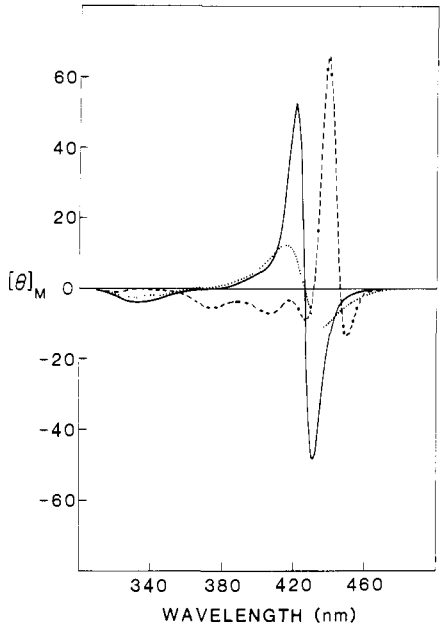

Figure 7. MCD spectra of FeMedPoc in 1-MeIm (0.13 M) (--); $+O_2$ (···); +CO (-).

porphyrins form not only stable, but also reversible, O_2 complexes in toluene solution at room temperature. The five-coordinate iron(II) porphyrin, FeP(B) can be exposed to O_2 (forming FeP(B)(O_2)) then extensively bubbled with N_2 to regenerate the initial five-coordinate species FeP(B) (P = PocPiv, MedPoc, TPivP, etc.).

Although the general features of the Soret absorption and Soret MCD spectra of the six-coordinate carbonyl and oxygen adducts of the various iron(II) "pocket" porphyrin imidazole complexes are similar to those for other analogous systems (e.g., FeTPivP(1,2-Me_2Im)), this is not the case in the visible region of the electronic absorption spectra. In the visible, both the O_2 and CO adducts of the "picket fence" systems show predominantly a single weak band in the 540–550-nm region.[9] By contrast, the carbonyl and oxygen complexes derived from five-coordinate complexes of Ib, IIb, or IIIb show bands at about 520 and 560 nm, respectively.

It is important to stress that only at high excess concentrations of axial base (1-MeIm, 1,2-Me_2Im) do the iron(II) "pocket" complexes Ib, IIb, IIIb form oxygen adducts which are sufficiently stable kinetically so as to allow determinations of O_2 binding affinities under equilibrium conditions.

At low base concentration, oxidation to the μ-oxo iron(III) porphyrin dimer occurs. A similar observation has been made with regard to the iron(II) "capped" porphyrin complexes.[10] Apparently, large concentrations of axial bases serve to reduce the concentration of the rapidly oxidized,[49] four-coordinate species.[10] Since the nitrogenous bases bind with much greater affinity to the *unencumbered* side of the "capped" and "pocket" porphyrins, high concentrations of axial base also serve to effect regioselective gaseous ligand binding within the protected cavity, as the axial base competitively inhibits O_2 or CO from binding on the unencumbered side.[50] Table II shows the half-lives of various iron(II) "pocket" O_2 complexes obtained in the usual way.[10] Although the rates of oxidation are extremely sensitive to impurities, these data show that the sterically protected iron(II) "pocket" porphyrins form long-lived oxygen complexes under conditions where the bimolecular oxidation[49] to the μ-oxo dimer is suppressed. In fact, the "pocket" porphyrins are among the more stable of the known hemoprotein models. It is of interest to note that at a given concentration of 1-MeIm, the oxygen complex derived from FePocPiv, Ib, is kinetically less stable than that derived from FeMedPoc, IIb. The reasons for this are as yet not entirely understood. A complete analysis of the rates of both base and O_2[20b] binding is needed to clarify this point.

Table II. Stabilities of Selected Iron(II) Porphyrin O_2 Adducts

complex	base concn, M	half-lives at 25 °C	ref
FeTPivP(1,2-Me_2IM)	10^{-41} [a]	1 month	2a
$FePiv_3$5CIm	"tailed"[a,b]	3 days	2a
FePocPiv(1,2-Me_2Im)	0.1[a]	1 day	this work
FePocPiv(1-MeIm)	1.0[a]	36 h	this work
FePocPiv(1-MeIm)	0.1[a]	7 h	this work
FeMedPoc(1-MeIm)	0.1[a]	2 days	this work
Fe4Cu(1-MeIm)	0.2[c]	≳12 h	17
"chelated protoheme"	"tailed"[b,d]	≳10 s	25a
FePoc3Cu(py)	"tailed"[a,e]	~10 min	this work
FePF3Cu(py)	"tailed"[a,e]	1 day	this work
FeC_2-cap(1-MeIm)	0.64[c]	5 h	10b

[a] Toluene. [b] Covalently attached imidazole ligand. [c] Benzene. [d] Aqueous cetyltrimethylammonium bromide suspension (2%). [e] Covalently attached pyridine ligand.

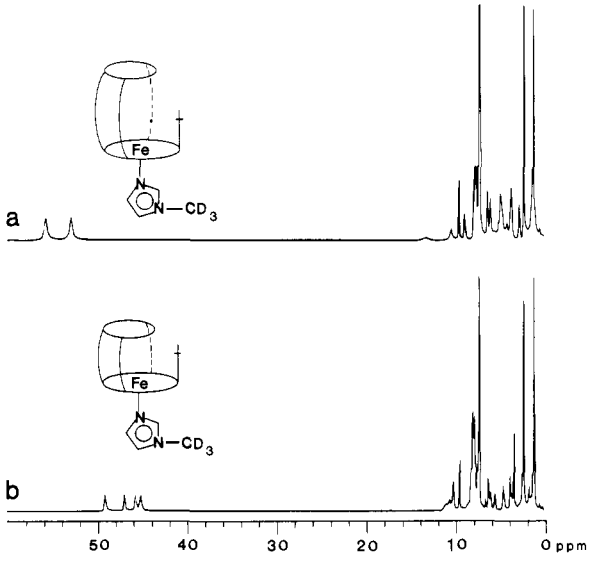

Figure 8. 100-MHz ^{1}H NMR spectra in toluene-d_8 of FeMedPoc(1-MeIm-d_6) (upper trace, a) and FePocPiv(1-MeIm-d_6) (lower trace, b).

Proton Nuclear Magnetic Resonance. Proton nuclear magnetic resonance has been widely used to characterize both hemoproteins and simple iron(II) porphyrin model complexes.[51] In tetraarylporphyrins, the degree of isotropic shift of the pyrrole β protons serves as a convenient probe for both oxidation and spin state.[52-54] In five-coordinate high-spin iron(II) porphyrins at or near room temperature, these resonances generally appear as sharp, well-resolved signals in the 45–60-ppm region (downfield from Me_4Si according to the diamagnetic convention). Perdeuterated 1-MeIm was synthesized and used for several ^{1}H NMR studies. Figure

(49) (a) Alben, J. D.; Fuchsman, W. H.; Beaudreau, C. H.; Caughey, W. S. *Biochemistry* **1968**, *7*, 624–635. (b) Cohen, I. A.; Caughey, W. S. *Ibid.* **1968**, *7*, 636–641. (c) Hammond, G. S.; Wu, C.-H. S. *Adv. Chem. Ser.* **1968**, *77*, 186–207. (d) Chin, D.-H.; LaMar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344–4349.

(50) We have generally found (cf. ref 20b) that for complexes derived from Ib and IIb the CO and O_2 affinities are independent of base concentration provided $0.1 \lesssim [B] \lesssim 1$ M. In contrast to the behavior with imidazole-type ligands, we have found that toluene solutions of Ib and pyridine do not support the reversible binding of O_2 at room temperature. This probably reflects the low K_B for pyridine rather than some intrinsic property of the pyridine base. Pyridine supports reversible oxygenation in the "picket fence" series of complexes.[56]

(51) (a) LaMar, G. N.; Walker, F. A. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. IV, Chapter 2, and references therein. (b) LaMar, G. N.; Horrocks, W., Jr.; Holm, R. H., Eds. "NMR of Paramagnetic Molecules"; Academic Press: New York, 1973, and references therein.

(52) LaMar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63–75.

(53) LaMar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1782–1790.

(54) (a) Goff, H.; LaMar, G. N.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 3641–3646. (b) Goff, H.; LaMar. G. N. *Ibid.* **1977**, *99*, 6599–6606.

Table III. Observed NMR Shifts of Pyrrole Protons in Selected Iron(II)/(III) Tetraarylporphyrin Complexes

complex	spin state	chemical shift[a]	ref
FeTPP(Cl)	2.5	78.95	52
$(FeTPP)_2O$	*b*	13.48	52
$[FeTPP(Im)_2]^+Cl^-$	0.5	−16.65	53
FeTPP	1	4.65	54a
FeTPP(2-MeIm)	2	52.2	54b
$FePiv_34CIm$	2	52–60	9
FePoc3CuIm	2	47.5–50.5	this work
FePocPiv(1-MeIm)	2	45.5–49.0	this work
FePocPiv(Im)		52.5–57.0	this work
FeMedPoc(1-MeIm)	2	53.0–56.0	this work
FePocPiv(py)	*c*	24.5–27.5	this work
Fe3CuPoc(py)	2	34.5–40.0	this work
FePF3Cu(py)	2	47	55

[a] Vs. Me_4Si; downfield designated as positive shift. [b] Antiferromagnetically coupled, $S = 2.5$. [c] Exact nature of species formed upon addition of pyridine to Ib is not known.

8 shows the ^1H NMR spectra of FeMedPoc(1-MeIm-d_6) and FePocPiv(1-MeIm-d_6) at room temperature under conditions of excess axial base. The central position of the pyrrole β proton signals at 54 and 47 ppm are similar to those seen for other high-spin five-coordinate iron(II) porphyrins (Table III). When the relative concentration of 1-MeIm-d_6 is increased from 20 to 100 equiv, the pyrrole β signals of FeMedPoc, IIb, become broadened and less well resolved. This again suggests that under these conditions a quantity of the six-coordinate, bis-ligated $FeMedPoc(1\text{-}MeIm)_2$ complex exists in rapid equilibrium with the predominant five-coordinate species, FeMedPoc(1-MeIm). By contrast, no evidence of behavioral changes dependent on 1-MeIm-d_6 concentration are seen with FePocPiv(1-MeIm). When CD_2Cl_2 solutions of FePocPiv(Im-d_4) (containing ~20 equiv of axial base) are cooled, the pyrrole β peaks are broadened and shifted to lower field by the Curie effect.[55] In the temperature range investigated ($-20 \le t \le 30$ °C), no evidence of the formation of six-coordinate species could be detected. Moreover, Curie plots of $\Delta\nu$ vs. 1/temp proved linear where $\Delta\nu$ is the shift difference of a pyrrole β peak at a given temperature relative to that observed for the diamagnetic complex (pyrrole β protons at 8.7 ± 0.2 ppm vs. Me_4Si). In contrast to the imidazole complexes, well-defined ^1H NMR behavior is not exhibited when pyridine-d_5 is used as axial base with Ib. At low ligand to porphyrin ratios (≤20 equiv), signals at 24–27 ppm are observed which are ascribed to the pyrrole β protons. At higher concentrations of pyridine-d_5, these signals broaden beyond recognition and the spectrum resembles that of the diamagnetic complex. This behavior indicates that a mixture of five-coordinate ($S = 2$) and six-coordinate ($S = 0$) complexes probably pertains at high pyridine-d_5 concentration either due to binding of a second pyridine ligand or adventitious coordinating impurities. The formation of an $S = 1$ six-coordinate species[18a] cannot be ruled out. The fact that at high relative concentrations of pyridine-d_5 a typical diamagnetic spectrum is observed suggests strongly that the latter explanation is not valid. It is worth noting that the pyrrole β proton signals occur at lower field for the rigorously five-coordinate pyridine "tailed" "picket fence"[56] and pyridine "tailed" "pocket" porphyrin complexes (cf., Table III) than they do for Ib with low concentrations of pyridine-d_5.

Proton nuclear magnetic resonance was also used to determine magnetic susceptibilities in toluene solution. The Evans method as adapted for iron(II) porphyrins by Brault and Rougee was employed,[57] and specific results are given in the Experimental Section. In general, it was found that $\mu_{eff} \sim 5\mu_B$ for compounds assigned to be high-spin, $S = 2$, five-coordinate complexes on the basis of ^1H NMR and MCD experiments. This is as expected on the basis of work with other five-coordinate systems.[9,57b] When O_2 or CO was admitted, no detectable paramagnetic shifts were seen. With the concentrations used and the estimated minimum noticeable shift (ca. 0.5 Hz on a 100-Hz instrument), the smallest detectable μ_{eff} would be ca. 1.2 μ_B. Therefore, this value is reported in the Experimental Section when no paramagnetic shift was seen. The above results are similar to those obtained with the iron(II) "picket fence" porphyrins.[9] They indicate that presumably diamagnetic $S = 0$ O_2 and CO complexes are formed from the iron(II) "pocket" porphyrin complexes Ib and IIb.

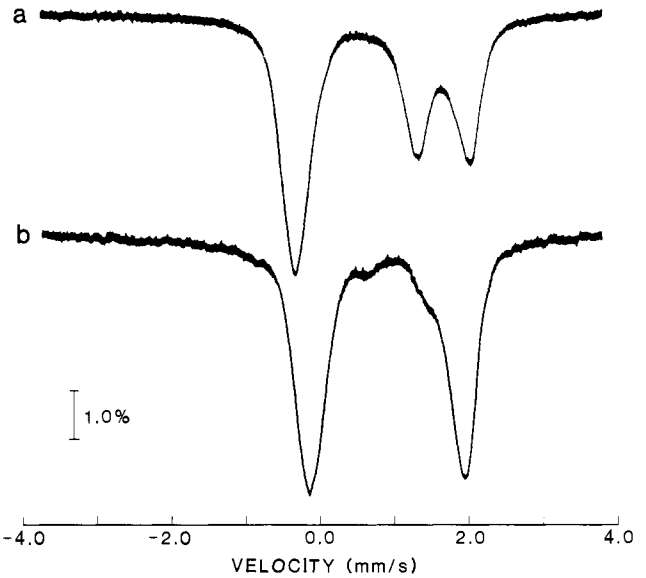

Figure 9. Mössbauer spectra of FePocPiv(1-MeIm) and FePocPiv(1-MeIm)$_2$ (curve a) and FePocPiv(1,2-Me_2Im) (curve b), obtained at 77 K. Frozen toluene solutions containing 100 equiv of axial base were used.

Table IV. Mössbauer Spectral Parameters of Selected Iron(II) Tetraarylporphyrins[a]

complex	δ, mm/s	δE, mm/s	spin state	ref
FeTPP[d]	0.50	1.50	1	59b
FeTPP(2-MeIm)[d]	0.92	2.26	2	59b
$FeTPP(piperidine)_2$[d]	0.50	1.44	0	59b
$FeTPivP(1\ MeIm)(O_2)$[d]	0.27	2.04	0	59a
FePocPiv(1-MeIm)[b,c]	0.81	2.36	2	this work
FePocPiv(1-MeIm)[d]	0.81	2.19	2	this work
$FePocPiv(1\ MeIm)_2$[b,c]	0.46	1.65	0	this work
$FePocPiv(1\text{-}MeIm)(O_2)$[b]	0.23	2.23	0	this work
FePocPiv(1,2-Me_2Im)[b]	0.92	2.27	2	this work
$FePocPiv(1,2\text{-}Me_2Im)(O_2)$[b]	0.24	2.32	0	this work
FeMedPoc(1-MeIm)[d]	0.88	1.88	2	this work
$FeMedPoc(1\text{-}MeIm)_2$[e]	0.48	1.37	0	this work
FeMedPoc(1,2-Me_2Im)[e]	1.01	2.15	2	this work
FeMedPoc(1,2-Me_2Im)[d]	1.11	2.13	2	this work

[a] 77 K, frozen benzene or toluene solution unless noted otherwise. [b] 100 equivalents of axial base used. [c] Observed as 1:1 mixture of mono- and bis-ligated. [d] 77 K, solid sample. [e] 10 equiv of axial base used.

Mössbauer Spectroscopy. Mössbauer spectroscopy has been used extensively to study the electronic nature of iron(II) hemoproteins as well as the simple porphyrin complexes which serve as models for them.[58] In order to probe the coordination geometry of the encumbered "pocket" porphyrins, we have prepared samples of FePocPiv, Ib, and FeMedPoc, IIb, 90% enriched with ^{57}Fe. The 1-MeIm, 1,2-Me_2Im, and O_2 complexes of these systems have been examined. Their zero-field Mössbauer spectra have been deter-

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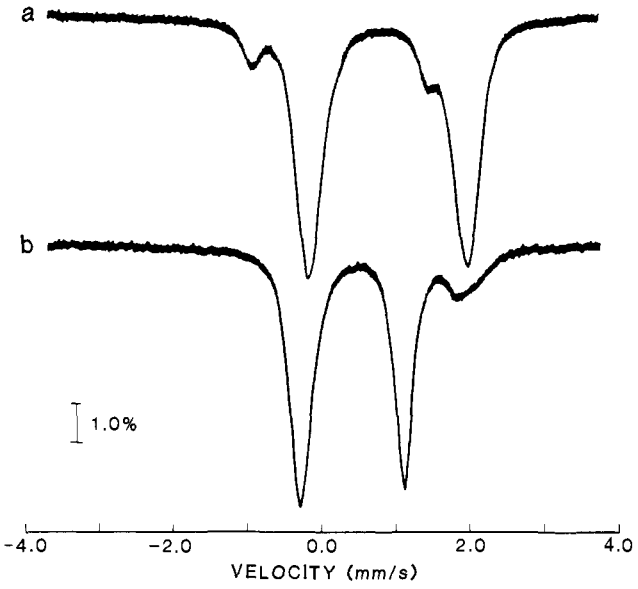

Figure 10. Mössbauer spectra of FeMedPoc(1,2-M_2Im) (curve a) and FeMedPoc(1-MeIm)$_2$ (curve b), 77 K, frozen toluene solutions, 10 equiv axial base.

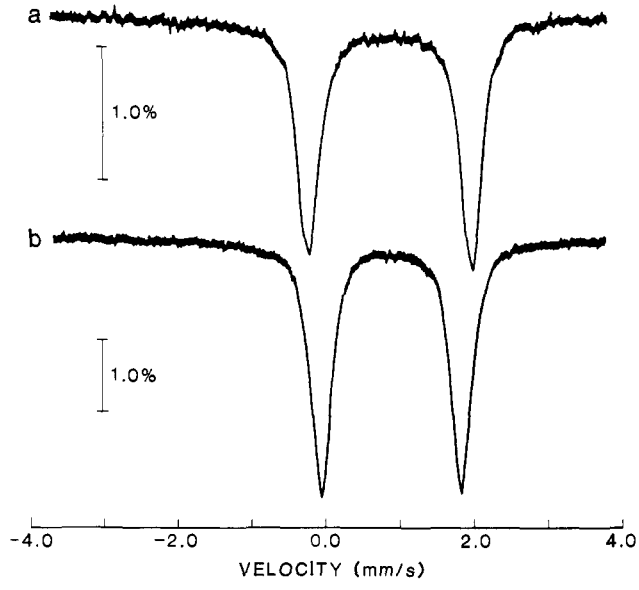

Figure 11. Mössbauer spectra of FePocPiv(1-MeIm) (curve a) and FeMedPoc(1-MeIm) (curve b) at 77 K, solid powder.

mined both as frozen toluene glasses and as solid powder samples at 4.2 and 77 K. Representative results obtained at 77 K are given in Table IV. Figure 9 shows the Mössbauer spectra at 77 K for a toluene glass obtained by freezing ca. 1 mM solutions of Ib containing 100 equiv of either 1-MeIm or 1,2-Me_2Im. The spectra of the glass obtained from Ib + 1,2-Me_2Im consists of primarily one component. This is easily assigned to the high-spin, five-coordinate species FePocPiv(1,2-Me_2Im). By contrast, the spectra of Ib + 1-MeIm consists of two components. A comparison of the experimental δ and ΔE values with those from the literature[9,59] suggests that a ca. 1:1 mixture of FePocPiv(1-MeIm) and FePocPiv(1-MeIm)$_2$ pertains under these conditions. Interestingly, when analogous glasses are prepared from solutions containing only 10 equiv of base, an approximately 3:2 ratio of five-coordinate ($S = 2$) and six-coordinate ($S = 0$) complexes is formed. These results show that although 1-MeIm is indeed capable of entering into the "pocket", a fair degree of coordination control is achieved even at the low temperatures existing in the solution just prior to congealment into a glass. It is well-known[60,61] that K_B^B is greatly enhanced at these low temperatures. In fact, under conditions where five-coordination predominates at room temperature (i.e., 10 equiv of base), Mössbauer spectroscopy shows that FeMedPoc(1-MeIm)$_2$ is the major species (Figure 10) existing in frozen toluene glasses derived from solutions of IIb + 1-MeIm.

Solid samples of FePocPiv(1-MeIm), FeMedPoc(1-MeIm), and FeMedPoc (1,2-Me_2Im) were also examined. Toluene solutions of Ib or IIb with excess axial base were treated with heptane at 25 °C to precipitate out the solid porphyrin complexes. The resulting powders were studied at 77 K. These Mössbauer spectra (Figure 11) reflect but one major component which can indeed be ascribed to the respective high-spin, five-coordinate complexes: FeMedPoc(1-MeIm), FeMedPoc(1,2-Me_2Im), and FePocPiv(1-MeIm). Of course, the porphyrin species precipitated is that which is least soluble, so caution must be used before assuming the precipitate is necessarily representative of all species existing in solution. Nevertheless, these solid-state Mössbauer studies seem to suggest further that good control of coordination is achieved at room temperature for these systems.

The ability of the iron(II) "pocket" porphyrin complexes to bind O_2 was confirmed by Mössbauer. Toluene glasses were prepared by freezing solutions of FePocPiv(1,2-Me_2Im)(O_2) or FePocPiv(1-MeIm)(O_2) containing excess axial base. The resulting Mössbauer spectra are nearly identical with those of FeTPivP(1-MeIm)(O_2) and show only one component. This result, in conjunction with the spectroscopic studies discussed above, again suggests that the "pocket" porphyrins are indeed capable of forming O_2 complexes.

Low-Frequency Resonance Raman Spectroscopy. Certain of the porphyrin-related vibrational modes in heme systems have been shown to be sensitive to changes in spin and oxidation state,[62,63a] and as such resonance Raman spectroscopy has been used extensively to probe the coordination characteristics of both hemoproteins[62] and model metalloporphyrin complexes.[63] Resonance Raman spectroscopy is also capable of detecting the low-frequency (<600 cm^{-1}) vibrations associated with motions of the iron atom.[64f,65] Since vibrational frequencies can often be correlated with bond strengths, monitoring changes in these modes can serve as a probe for protein- or ligand-induced changes in iron–ligand interactions.[65] In hemoglobin, recent interest has focused on whether the conformational changes associated with the T- and R-state transition are reflected in differing strengths of the Fe–O_2 and Fe–N_ϵ (HisF8) bonds.[40,64-66] In that quaternary structural changes accompanying O_2 binding are, in part, transmitted through the Fe–N_ϵ bond,[67] particular interest has centered on assessing the extent to which changes in the strength of this bond might contribute to the free energy of cooperativity.[64f,g,65] As such, it is of interest to assess the extent to which changes in the Fe–N_ϵ

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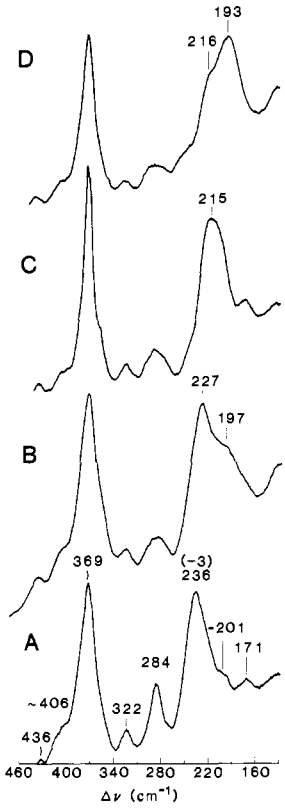

Figure 12. Low-frequency resonance Raman spectra of FePocPiv(B) in CH_2Cl_2 or benzene at 25 °C: (A) B = Im; (B) B = 1-MeIm; (C) B = 2-MeIm; (D) B = 1,2-Me_2Im. Spectra were obtained with 454.5-nm excitation, 10-cm^{-1} spectral band-pass, and 50.0-s time constant. The value in parentheses shows shift in this peak observed when Im-d_4 is used as axial ligand.

bond strength might be correlated with changes in the Fe–N_ϵ stretching frequency in model iron(II) porphyrin complexes.[68]

The "pocket" porphyrins offer a unique system with which to probe changes in ν(Fe–N_ϵ) as the result of changes in axial ligation. Substantial evidence has now been presented which shows that in derivatives of Ib the "pocket" sterically enforces five-coordination about iron in the presence of an excess of various imidazole ligands. Therefore, with Ib the axial base can be systematically varied and the changes in ν(Fe–N_ϵ) observed.

The results of the present resonance Raman study indicate that for five-coordinate iron(II) porphyrins, the Fe–imidazole stretching frequencies lie in the 190–240-cm^{-1} region (Figure 12). For each member of the series of compounds of the general formula Fe^{II}PocPiv(B), where B = Im, 1-MeIm, 2-MeIm, and 1,2-Me_2Im, we observe a set of bands 436, 369, 322, and 284 cm^{-1} common to each of the spectra. These are assigned to porphyrin modes which are insensitive to axial base characteristics.[69] In addition to these, there is an envelope of bands centered about 200 cm^{-1} which varies in both frequency and intensity distribution as a function of axial base substitution.

We observe a band at 236 cm^{-1} in the spectrum of Fe^{II}PocPivIm which shifts to 227 cm^{-1} in the spectrum of Fe^{II}PocPiv(1-MeIm), whereas a band at ~200 cm^{-1} that occurs in both spectra gains intensity in the latter. The high-frequency bands are assigned to ν(Fe–N_ϵ) on the basis of 3 ± 1 cm^{-1} downshift in the 236-cm^{-1} band in the spectrum of Fe^{II}PocPiv(Im-d_4). These assignments are congruent with those made earlier by Hori and Kitagawa in their study of "picket fence" porphyrins.[68] The frequency shift on going from Im to 1-MeIm may be predicted on the basis of mass ratios alone, assuming a diatomic oscillator model.

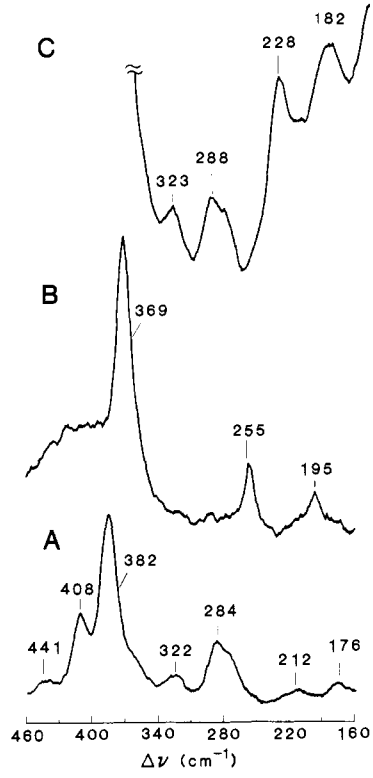

Figure 13. Low-frequency resonance Raman spectra of iron(II) "pocket" porphyrin compounds in CH_2Cl_2 at 25 °C, same conditions as Figure 12: (A) Fe^{II}PocPiv; (B) $[Fe^{III}PocPiv]_2O$; (C) Fe^{II}PocPiv(py).

A comparison of the Fe(II) "pocket" complex formed with the unhindered ligand 1-MeIm with that formed with 2-MeIm, a hindered ligand of the same mass, reveals that ν(Fe–N_ϵ) is 12 cm^{-1} lower for the 2-MeIm adduct. Although this shift probably has its origin in the increased hindrance of the 2-methyl unit, it does not necessarily reflect a decreased Fe–N_ϵ bond strength. A decrease in frequency on going from 1-MeIm to 2-MeIm is expected neither on the basis of K_B nor mass ratios. In the 200-cm^{-1} region no relative change of intensity is observed.

A detailed rationalization of the 12-cm^{-1} difference in ν(Fe–N_ϵ) for the 2-methyl and 1-methyl adducts is not currently possible. The most likely explanation is that in the 2-MeIm adduct, off-perpendicular "stretching" or "rocking" motions contribute substantially to the Fe–N_ϵ normal mode. These effects should be less pronounced in the unhindered 1-MeIm adduct. Structural studies[28] of FeTPivP(2-MeIm)·EtOH indicate that the imidazole unit is in fact tilted off the normal to the porphyrin plane, so as to accommodate the sterically demanding 2-MeIm ligand. Currently, no structural information is available for the analogous "pocket" porphyrins.

In the spectrum of Fe^{II}PocPiv(1,2-Me_2Im) an intense band is observed at 193 cm^{-1}. The band at 215 cm^{-1} in the spectrum of Fe^{II}PocPiv(2-MeIm) is calculated to shift down to 209 cm^{-1} in the spectrum of the 1,2-Me_2Im adduct. A downshift of 22 cm^{-1} instead of 6 cm^{-1} might be explained as due to the extra steric hindrance arising from the mutual repulsion of the methyl groups of the disubstituted imidazole, the so-called "buttressing" effect.[30,70] However, the frequency-intensity patterns of the ν(Fe–N_ϵ) band and the ~200-cm^{-1} band of the preceding three compounds suggests the occurrence of a Fermi resonance. In such a scheme, the 200-cm^{-1} band would increase in intensity and shift to lower frequency as is observed, perhaps due to the proximity of a hidden ν(Fe–N_ϵ) band at 209 cm^{-1} in the Fe^{II}PocPiv(1,2-Me_2Im) complex.

Figure 13 shows the low-frequency resonance Raman spectra for FePocPiv(py). As was observed in the ^{1}H NMR, the pyridine systems show anomalous behavior as compared to imidazole

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(70) Similarly, in toluene solution, FeTPP(1,2-Me_2Im) has a 2-fold lower CO affinity than FeTPP(2-MeIm) (cf. ref 21b).

Table V. CO Stretching Frequencies (IR) and $P_{1/2}^{CO}$

compd	ν(CO), cm^{-1}	$P_{1/2}^{CO}$, torr	ref
Mb(CO)[a]	1945	0.014–0.025	33b, 77
Hb(CO)[a]	1951	0.004, 0.035[b]	33b, 77, 78, 79
FeMedPoc(1-MeIm)[c,f]	1954 (1909)[e]	6.5×10^{-4}	this work
Fe4Cu(1-MeIm)	1960[d]	0.1[c]	17
FeTalPoc(1-MeIm)[c]	1963		this work
FePocPiv(1-MeIm)[c]	1964[f]	1.5×10^{-3}	this work
FeTPivP(1-MeIm)[c]	1969	"irreversible"	31
FeTPP(1,2-Me$_2$Im)[c]	1970	0.15	19
FePPIXDMe(1-MeIm)[c]	1970		80
Fe(C$_2$cap)(1-MeIm)[c]	2002	5.4×10^{-3}	73

[a] Hemoproteins in aqueous media. [b] Values for the binding of the fourth CO and for the overall equilibrium, respectively. [c] Benzene or perdeuterated benzene. [d] In neat 1-methylimidazole. [e] Obtained with ^{13}CO. [f] $\nu_{(CO)}$ was found independent of 1-methylimidazole concentration when between 3 and 300 equiv of base were used.

systems. Since the coordination properties of pyridine are not yet defined, unambiguous assignment of ν(Fe–N$_\epsilon$) is not currently possible. The use of py-d_5 led to small changes ($\lesssim$2 cm^{-1}) in both the 182- and 228-cm^{-1} bands.

In the stretching frequency assigned to ν(Fe–N$_\epsilon$), Nagai and Kitagawa[65] have recently observed a 6-cm^{-1} shift between deoxy T-state HbA (ν(Fe–N$_\epsilon$) = 215 cm^{-1}) and deoxy R-state NES des-ARG$^{141\alpha}$-Hb (ν(Fe–N$_\epsilon$) = 221 cm^{-1}). Valency hybrids were used[66] to ascertain that the shift (ca. 15–20 cm^{-1}) is greater for the α subunit than for the β subunit (ca. 4–7 cm^{-1}). These workers concluded that the Fe(II)–N$_\epsilon$ bond is stretched in the process of an R to T transition, producing greater strain energy along the Fe–N$_\epsilon$ bond in the α subunit than in the β subunit. Results obtained with the "picket fence" model complexes were used to support the assignment of ν(Fe–N$_\epsilon$) in these hemoprotein systems.[68] Unlike the "pocket" porphyrins, the "picket fence" system constitutes only a limited arena in which axial base effects can be studied, since the iron(II) "picket fence" porphyrins favor six-coordination in the presence of excess 1-MeIm.[9]

In the new "pocket" model compounds, our ligand binding studies have suggested that factors other than lowered bond strengths can account for decreases in ν(Fe–N$_\epsilon$). Neither the "picket fence" nor the "pocket" complexes are direct analogues of the "active site" for Hb. They are ortho-substituted tetraphenyliron(II) porphyrins, and as such, monomers free of site–site interactions and other protein related effects. Furthermore, the hindrance from the 2-methyl of an imidazole-type ligand has no exact biological counterpart. It is, however, of interest that similar differences in ν(Fe–N$_\epsilon$) were observed between the R-state model FePocPivP(1-MeIm) and the T-state models FePocPiv(2-MeIm) ($\Delta\nu$(Fe–N$_\epsilon$) = 12 cm^{-1}) and FePocPiv(1,2-Me$_2$Im) ($\Delta\nu$(Fe–N$_\epsilon$) = 27 cm^{-1}, after correction for mass differences) as were seen in hemoglobin.[65,66] To the extent that an analogy exists between Hb and its model compounds, these findings indicate that, in the analysis of hemoprotein resonance Raman spectra, caution must be exercised in associating changes in Fe–N$_\epsilon$ frequencies with an increase in strain energy or the lowering of bond order in the Fe–N$_\epsilon$(HisF8) linkage.

Interactions with CO. The CO affinities of complexes derived from the "pocket" porphyrins Ib and IIb are substantially lower than those of the analogous "picket fence" complexes.[20] This reduction in affinity is ascribed to the steric encumbrance afforded by the protecting "pocket". As yet, we have been unsuccessful in our attempts to grow crystals suitable for X-ray diffraction experiments.[71] We have therefore considered spectroscopic probes which might be used to correlate CO affinities with putative steric distortions of the FeCO unit. Both CO stretching frequencies[31,33b,34,40] and ^{13}C–^{57}Fe coupling constants[41] in iron(II) porphyrin carbonyl complexes have been suggested as being suitable probes for this task. The CO complexes of several iron(II) "pocket" porphyrins have been investigated by these techniques and these results are now discussed.

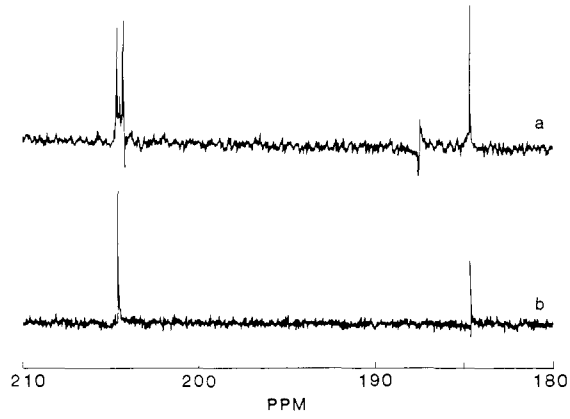

Figure 14. Low-field region of ^{13}C NMR spectra recorded in 1:1 toluene-d_8:THF, at a field strength of 75 Hz; (spectrum a) ^{57}FeMedPoc(1-MeIm)(^{13}CO); (spectrum b) ^{56}FeMedPoc(1-MeIm)(^{13}CO).

The values of the CO stretching frequencies and CO affinities for FePocPiv(1-MeIm)(CO), FeMedPoc(1-MeIm)(CO), and FeTalPoc(1-MeIm)(CO), as well as those for several compounds in the literature are collected in Table V. It is clear from these data that, at present, *no* simple correlations can be made between CO affinities, structure, and CO stretching frequencies in iron(II) porphyrin carbonyl complexes.[72] Of particular interest is the observation that the stretching frequency of FeMedPoc(1-MeIm)(CO) is lower than that of either the more encumbered FePocPiv(1-MeIm)(CO) model or the totally unemcumbered FeTPivP(1-MeIm)(CO) complex. The CO affinities of the "medium" "pocket" system are, however, intermediate between those of the "small" "pocket" and "picket fence" complexes.[20b] Surprisingly, the ν(CO) values are reduced in the "pocket" complexes as compared to simple iron(II) systems, whereas those of the various "capped" porphyrin carbonyl complexes are increased.[19,73] It has been suggested that no distortion of the intrinsically linear FeCO unit occurs in the "capped" porphyrins.[19] The high CO stretching frequencies were ascribed to electronic interactions with the aromatic "cap".[19,73] Both aromatic electronic interactions and steric hindrance effects might contribute to the nature of the FeCO unit in carbonyl adducts of complexes derived from the "pocket" porphyrins Ib, IIb, and IIIb. Therefore, the behavior of ν(CO) in the "pocket" series of porphyrins might reflect an admixture of these effects.

LaMar and co-workers[41] have recently reported the values for the ^{57}Fe–^{13}CO coupling constants obtained for ^{57}PPIX(1-MeIm)(^{13}CO) and ^{57}Mb(^{13}CO) obtained by ^{13}C NMR spectroscopy. These workers suggested that J(^{13}C–^{57}Fe) might be a convenient probe for assessing the extent to which an FeCO unit is distorted (i.e., bent and/or tilted) from the normal linear binding geometry. It was further suggested that the similarity in J(^{13}CO–^{57}Fe) values obtained in both the unhindered model, ^{57}PPIX(1-MeIm)(^{13}CO), and ^{57}FeMb(^{13}CO) indicates that no distortion of the FeCO unit pertains in Mb(CO) *in solution*. This proposal is in direct contrast to the substantial deviations from linearity seen in the solid state.[37]

The "pocket" and "picket fence" series of porphyrins offer an opportunity to test whether J(^{13}CO–^{57}Fe) correlates with CO affinities in iron(II) porphyrin carbonyl complexes. The low-field ^{13}C NMR spectra for FeTPP(1-MeIm)(^{13}CO), FeTPivP(1-MeIm)(^{13}CO), FeMedPoc(1-MeIm)(^{13}CO), and FePocPiv(1-MeIm)(^{13}CO) were measured at 75 Hz, using both normal ^{56}Fe

(71) A preliminary analysis of EXAFS data indicates that CO unit is bound in a nonlinear fashion in FePocPiv(Im)(CO). These results will be published later (by Linda Powers, Bell Labs).

(72) This finding supports a recent proposal to this effect by Chang.[17]

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and 90% ^{57}Fe-enriched samples. Data were obtained at 23 °C in standard 5-mm tubes, using 1:1 THF:toluene-d_8 solutions of ca. 5 mM in metalloporphyrin. All spectra were proton decoupled and typically 5000–10000 transients were recorded. Figure 14 shows the ^{13}C NMR spectra in the downfield region for both FeMedPoc(1-MeIm)(^{13}CO) and the analogous complex prepared with 90% enriched ^{57}Fe. Since ^{57}Fe has a spin of $I = 0.5$ (^{56}Fe has a spin of $I = 0$), a doublet is observed upon isotopic substitution. This allows the assignment of the peak at 204 ppm (downfield relative to tetramethylsilane) as being due to bound CO. The peak at 184 ppm is assigned to free CO in solution. The higher field region of the spectra contains the multitude of peaks arising from solvents, 1-MeIm, etc. and is not shown.

The data in Table V allow for the following observations. Firstly, $J(^{13}C–^{57}Fe)$ values do *not*, within error, correlate with CO affinities. Thus, to the extent that the lowered CO affinities observed in the "pocket" complexes are ascribable to differences in steric encumbrance, values for $J(^{13}CO–^{57}Fe)$ do not correlate with the degree to which the CO unit is distorted from its normal linear binding configuration. This suggests that little information can be garnered by this technique with regard to the geometry of the Fe–CO unit in Mb(CO), in solution. It is interesting to note further that a clear trend in chemical shifts is observed in Table III. The higher chemical shifts in the "pocket" porphyrins most probably reflect interactions between the ring current of the aromatic "pocket" and the bound carbonyl ligand, rather than any particular distortions of the CO moiety. This observed trend nonetheless indicates that the environment of the bound CO is different in the "pocket" complexes than in the unencumbered analogues, providing further evidence that gaseous ligands such as CO are bound in a regioselective manner inside the protecting "pocket".

Experimental Section

General Information. Proton magnetic resonance spectra were recorded on either a Varian Instruments XL-100 or Brucker HX-360 pulsed Fourier transform NMR spectrometer interfaced with a Nicolet 1180 data system. Carbon magnetic resonance spectra were recorded on a Nicolet 300 spectrometer interfaced with a Nicolet 1180E data system. Infrared spectra were obtained in benzene or benzene-d_6 solution in CaF_2 cells, using a Nicolet 7199 Fourier transform IR spectrometer interfaced with a Model 1180 data system.

Electronic spectra were recorded on a Cary 219 spectrophotometer thermostated to 25.0 ± 0.3 °C with a FormaScientific Model 2095 constant-temperature bath and circulator. MCD for toluene solutions were measured on a JASCO J-40 circular dichrometer fitted with a 15-kG electromagnet. The spectra were recorded, manipulated, and smoothed on a Data General Nova Model 840 computer and stored on magnetic diskettes. $[\theta]_m$ is in units of deg cm^2 dmol^{-1} G^{-1}.

Mössbauer spectra were recorded on ^{57}Fe-enriched porphyrin complexes. Samples were prepared under N_2 at Stanford either as solids diluted 1:1 in BN or as frozen toluene glasses of ca. mM concentration in metalloporphyrin and shipped to University Park under liquid N_2, where the usual[59] apparatus and techniques were used for data collection.

Resonance Raman spectra were recorded at 25 °C in benzene or CH_2Cl_2 solutions sealed in 9-in. NMR tubes, using irradiation at 454.5 nm in the back-scattering geometry. A 10-cm^{-1} spectral band-pass and 50.0-s time constant were employed. Low laser power levels and line focusing of the laser light were used to minimize possible artifacts due to laser heating. The frequencies were measured to ±1 cm^{-1} by using the 703-cm^{-1} line of CH_2Cl_2 or the 606-cm^{-1} line of benzene as internal frequency standards.

Solution magnetic susceptibilities were measured on a Varian XL-100 NMR spectrometer, using a concentric tube arrangement consisting of a 1.7-mm inner diameter capillary tube nestled in a standard 5-mm NMR tube. The inner tube contained the metalloporphyrin in toluene, and the outer tube contained a 4:1 mixture of toluene-d_8 and toluene. The differences in the toluene methyl resonances $\Delta\nu$ could be measured to an accuracy of ±0.5 Hz.

Chromatographic separations were made by using either gravity columns or a medium-pressure liquid chromatograph consisting of a Cheminert metering pump, Altex glass column, and an Instrumentation Specialties Co. Model 328 fraction collector.

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by the Stanford Microanalytical Laboratory or by the Analytische Laboratorien (Engelskirchen, W. Germany). Mass spectral analyses were performed at either the Stanford Mass Spectrometry Laboratory, the Midwest Center for Mass Spectrometry (Lincoln, NE), or the Middle Atlantic Mass Spectrometry Laboratory (Baltimore, MD).

Iron insertions and subsequent manipulations requiring the exclusion of oxygen were carried out in a Vacuum Atmospheres drybox equipped with an MO-40 Dri-Train capable of maintaining an N_2 atmosphere of under 2 ppm O_2 or H_2O. The atmosphere was monitored with a Vacuum Atmospheres AO-316-C oxygen analyzer.

Materials. All solvents and reagents were purchased commercially and further purified as follows. DMF was distilled at reduced pressure from BaO under an N_2 atmosphere and stored over degassed 3-Å molecular sieves. CH_2Cl_2 was distilled from CaH_2 under N_2. THF was distilled from sodium benzophenone ketyl under N_2. Benzene and toluene were distilled from sodium or potassium metal under N_2. Heptane was stirred with 6 N H_2SO_4 and then 0.5 M $KMnO_4$ in 6 N H_2SO_4, washed with dilute $NaHCO_3$ and H_2O, dried over $MgSO_4$, and distilled from CaH_2 under N_2. Thionyl chloride was distilled twice from triphenyl phosphite under N_2 immediately prior to use. 2,6-Lutidine was passed through alumina and then distilled from BF_3·Et_2O. 1-MeIm was heated at reflux with and distilled under reduced pressure from first phthalic anhydride (one time) and then KOH (two times), stored over activated 4-Å molecular sieves for 1 month, and then trap-to-trap distilled under reduced pressure (ca. 5×10^{-6} torr). 1,2-Me_2Im was distilled twice from Na metal at reduced pressure and subjected to 100 cycles of zone refining. Im and 2-MeIm were recrystallized from benzene. Pyridine was distilled from KOH under N_2. The $^{57}Fe_2O_3$ (90% enriched) was purchased from Oak Ridge National Laboratories and reduced to ^{57}Fe powder, and the Fe and ^{57}Fe powders were converted to $FeBr_2$ and ^{57}-$FeBr_2$ by literature procedure.[74] The ^{13}CO gas (90% enriched) was purchased from Monsanto Stable Isotopes. Imidazole-d_3 and imidazole-d_4 were obtained by the exchange of imidazole with D_2O; imidazole-d_4 was also purchased commercially (Stohler Isotopes). The 1-methylimidazole-d_6 was prepared from imidazole-d_4 by treatment with CD_3I according to the procedure of Wallach.[75] Silica gel type 62 was purchased from W. R. Grace, Inc. Silica gel type 60 was purchased from E. Merck & Co. Both were dried for 24 h at 55 °C prior to use. Woelm activity grade I neutral alumina was evacuated for 24 h and stored under N_2 prior to use. The TLC was performed on commercially prepared silica gel plates purchased from Analtech, Inc.

Synthesis. 1,3,5-Tris(3′-(methyoxycarbonyl)propyl)benzene. Sodium hydride (0.85 g as a 60% dispersion in oil) was put in a dry 500-mL three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, and nitrogen bubbler. After the NaH was washed with dry hexanes, 100 mL of dry DMF was added followed by the slow, dropwise addition of 4.5 cm^3 of freshly distilled diethyl malonate; 1,3,5-tris(2′-bromoethyl)benzene (0.2 g, 0.56 mmol) was added and the mixture heated at reflux for 14 h. After cooling, the resulting emulsion was extracted with ether (4 × 100 mL). The combined ether extracts were washed with brine (3 × 100 mL) and dried over Na_2SO_4, and the solvent was removed to yield a pale yellow oil. TLC (silica, EtOAc:hexanes 1:3 v/v) showed three spots. This crude oil was heated at reflux overnight in 80 cm^3 of 2 N KOH_{aq} containing 20 cm^3 of EtOH. After cooling, the solution was acidified with dilute aqueous HCl and taken to dryness in vacuo. The resulting salts were extensively extracted with acetone:ether:MeOH 1:1:1. After filtration and removal of the solvent, the resulting gum-like material was heated for 4 h at 180 °C. After the mixture cooled, 100 mL of MeOH containing 1 drop of H_2SO_4 was added and the solution heated at reflux overnight. After cooling and removal of the solvent, the material was loaded onto a 0.5 × 8 in. column of grade 62 silica. After elution with EtOAc:hexanes 1:3 (v/v), the leading band was taken to dryness yielding the pure triester (30 mg, 28% yield): NMR ($CDCl_3$) δ 1.90 (q, 6 H, CH_2), 2.28 (t, 6 H, CH_2), 2.55 (t, 6 H, CH_2), 3.68 (s, 9 H, OCH_3), 6.83 (s, 3 H, aromatic); mass spectrum (m/e) calcd for $C_{21}H_{30}O_6$, 378, found, 378.

1,3,5-Tris(3′-carboxypropyl)benzene. The above triester (20 mg, 53 mmol) was dissolved in 20 mL of 2 N NaOH and heated at reflux overnight. After cooling, dilute HCl was added until precipitation was complete (pH ca. 4). The resulting slurry was taken to dryness in vacuo

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at room temperature. The solids were washed with acetone:EtOH 1:1 (3 × 5 mL). The solution was filtered and taken to dryness, yielding the desired acid (17 mg, 95%): mp 93–95 °C; mass spectrum (m/e) calcd for $C_{18}H_{24}O_6$, 336, found, 336.

The acid was treated with $SOCl_2$ in the usual way to yield the triacid chloride which was used both to generate IIIa (vide infra) and to regenerate the trimethyl ester described above.

1,3,5-Tris(carboxymethyl-α,α-d_2)benzene. 1,3,5-Benzenetriacetic acid (0.5 g, 1.6 mmol) was treated with 2 mL of 1 N NaOD in D_2O and heated at reflux for 1 week. The solution was taken to dryness in vacuo and redissolved in 2 mL of 1 N NaOD and the above exchange process repeated. The solution was then neutralized with DCl (generated by adding D_2O to $AlCl_3$) and extracted with ether (3 × 15 mL). The combined ether extracts were then taken to dryness to yield 0.35 g of the deuterated product; NMR (D_2O) δ 4.5 (s, 3 H, aromatic).

1,3,5-Benzenetriacetyl Chloride. 1,3,5-Benzenetriacetic acid (1.35 g, 5.3 mmol) was stirred at room temperature for 24 h under N_2 with 50 cm^3 of twice distilled (from triphenyl phosphite) thionyl chloride containing 1 drop of DMF. The excess $SOCl_2$ was pumped off and dry CH_2Cl_2 was added and removed by pumping. The resulting crude triacid chloride was pumped at 10^{-5} torr for 24 h and then used directly without further purification. This same procedure was used for the generation of all the benzenetriacid chlorides required in this study.

***meso*-Mono(α-*o*-pivalamidophenyl)tris(α,α,α-*o*-aminophenyl)porphyrin (VII).** *meso*-Tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphyrin, VI (1.0 g, 1.5 mmol), was dissolved in 700 mL of CH_2Cl_2 with 0.80 mL of pyridine. Pivaloyl chloride (0.22 g, 1.8 mmol) was dissolved in 50 mL of CH_2Cl_2 and 0.85 mL of pyridine and this solution was added dropwise. The resulting porphyrin solution was stirred under N_2 in an ice bath for 2 h. Then, 10% NH_4OH (150 mL) was added and the solution stirred for 0.5 h. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic portion was stripped to dryness, washed with hexanes then dried in vacuo. Two such preparations were combined and chromatographed by MPLC on a 2.5 × 50 cm column packed with silica gel 60 using 5:1 CH_2Cl_2:ether as eluent. The second band was collected and stripped to dryness at room temperature. Any remaining *meso*-mono($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphyrin was similarly collected as the third band. Average yields were 735 mg (VII) and 670 mg of recovered *meso*-mono($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphyrin for an overall yield of 60%, based on VI consumed. VII was identified by its NMR spectrum and its conversion to the known H_2TPivPP: NMR ($CDCl_3$) δ 2.6 (s, 2 H, pyrrole), 0.2 (s, 9 H, $(CH_3)_3C$), 3.6 (s, br, 6 H, HN–), 7.9 (m, 25 H, pyrrole β, phenyl, amide NH).

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-(α-*o*-pivalamidophenyl)porphyrin, H_2PocPiv (Ia). *meso*-Mono(α-*o*-pivalamidophenyl)tris(α,α,α-*o*-aminophenyl)porphyrin (VII) (400 mg, 0.53 mmol) was dissolved in 2.0 L of dry CH_2Cl_2 containing 5.0 mL of pyridine. Excess 1,3,5-benzenetriacetyl chloride (1.62 g, 5.3 mmol) was dissolved in 20 mL of CH_2Cl_2 and loaded onto 1.5 g of activity 1 neutral alumina. The solution coming off the alumina was dripped directly into the porphyrin solution. The reaction was stirred under N_2 in an ice bath until judged complete by TLC. (When the run was deemed complete, an additional 400-mg sample of VII could be added into the same flask and further quantities of the acid chloride added. This procedure allowed for large-scale preparations under high dilution conditions while conserving solvent.) Ten-percent NH_4OH (200 mL) was added and the solution was stirred for 0.5 h. The organic layer was separated and the aqueous layer extracted with $CHCl_3$. The combined organic portion was stripped to dryness, washed with hexanes, and then dried in vacuo. The crude product was dissolved in 50 mL of $CHCl_3$ and filtered through 1 g of type 62 silica to remove polymer. The filtered solution was evaporated to dryness, dissolved in 4:1 $CHCl_3$:acetone (40 mL), and chromatographed by MPLC on a 2.5 × 20 cm column packed with silica gel 60. The column was eluted with 4:1 $CHCl_3$:acetone, yielding an average of 320 mg (63%) of pure Ia which could be recrystallized from $CHCl_3$/EtOH to give purple needles: ^{1}H NMR ($CDCl_3$) δ −2.60 (2 H, s, pyrrole H), 0.35 (9 H, s, $C(CH_3)_3$), 0.75 (2 H, d, J_{gem} = 30 Hz, methylene bridges), 1.50 (impurity), 2.22 (2 H, d, J_{gem} = 30 Hz, methylene bridges), 3.20 (2 H, s, methylene bridges), 3.85 (1 H, s, triacetylphenyl moiety), 5.10 (2 H, s, amide NH), 6.10 (2 H, s, triacetylphenyl moiety), 7.10 (1 H, s, amide NH), and 7.75–8.90 (25 H, m, aromatic); UV λ_{max} ($CHCl_3$) 421 nm (ϵ 261 000), 516 (12 900), 547 (2790). 588 (4180), and 644 (1230); mass spectrum (m/e) calcd, 956.37985; found, 956.38127. Anal. Calcd for $C_{61}H_{48}N_8O_4 \cdot H_2O$: C, 75.14; H, 5.17; N, 11.49. Found: C, 74.88; H, 5.15; N, 11.43.

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-(β-*o*-pivalamidophenyl)porphyrin. Pure Ia could be converted to a 1:1 mixture of Ia and the "β-picket pocket" compound by refluxing in toluene for 2 h. The mixture was chromatographed on type 62 silica with 3:1:0.25 $CHCl_3$:hexane:CH_3CN as the eluent and the second band was collected. The "β-picket pocket" compound was identified by its thermal equilibration back to Ia and ^{1}H NMR spectroscopy ($CDCl_3$) δ 0.1 (s, 9 H, CH_3C), other features same as for Ia.

5,10,15-(1,3,5-Tris(carbamoylmethylbenzene-α,α-d_2)tris(α,α,α-*o*-aminophenyl)-20-(α-*o*-pivalamidophenyl)porphyrin. "Deuteropocket" was made from VII (100 mg, 0.13 mmol) in a manner similar to Ia except using 1,3,5-tris(chloroformyl)benzene-α,α-d_2 (0.43 g, 1.4 mmol) in place of 1,3,5-benzenetriacetyl chloride. ^{1}H NMR ($CDCl_3$) δ 2.6 (s, 2 H, pyrrole, H), 0.35 (s, 9 H, $(CH_3)_3C$), 3.85 (s, 1 H, triacetylphenyl moiety), 5.10 (s, 2 H, amide NH), 7.75–8.90 (m, 25 H, pyrrole β, phenyl, amide NH).

***meso*-Mono(α-*o*-((triphenylmethyl)amino)phenyl)tris(α,α,α-*o*-aminophenyl)porphyrin (VIII).** *meso*-Tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)-porphyrin (1.0 g, 1.5 mmol) was dissolved in 1.2 L of CH_2Cl_2 and 2.8 mL of triethylamine. Trityl bromide (480 mg, 1.5 mmol) was dissolved in 40 mL of CH_2Cl_2 and added to the porphyrin solution dropwise. The resulting mixture was stirred under N_2 in an ice bath for 2 h. The solution was washed twice with 50 mL of H_2O, dried with $MgSO_4$, and then evaporated to dryness. Two such preparations were combined, dissolved in 40 mL of $CHCl_3$, and chromatographed by MPLC on a 2.5 × 50 cm column packed with silica gel 60. The column was eluted with 3:7 ethyl acetate:hexane (v/v). The second to the last band was collected and stripped to dryness in vacuo at room temperature. Any remaining *meso*-tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphyrin was collected as the last band. Average yields were 1.12 g of VIII and 0.75 g of VI for an overall yield of 65%, based on starting material consumed. Compound VIII was identified by its conversion to IX and ^{1}H NMR (CD_3Cl_3) δ −2.65 (s, 2 H, pyrrole), 3.6 (s, br, 6 H, H_2N–), 7–9.5 (m, 40 H, pyrrole β, phenyl, amide NH).

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-(α-*o*-((triphenylmethyl)amino)phenyl)porphyrin (IX). *meso*-Mono(α-*o*-((triphenylmethyl)amino)phenyl)tris(α,α,α-*o*-aminophenyl)-porphyrin (350 mg, 0.38 mmol) was dissolved in 750 mL of CH_2Cl_2 and 1.0 mL of pyridine. Excess 1,3,5-benzenetriacetyl chloride (1.16 g, 3.8 mmol) was dissolved in 10 mL of CH_2Cl_2 and added dropwise to the porphyrin solution via a 1.5-g plug of activity 1 neutral alumina. The solution was stirred under N_2 in an ice bath until the reaction was judged complete by TLC. The procedure was repeated twice more in the same flask in order to conserve solvent. Ten-percent NH_4OH (200 mL) was added and the solution stirred for 30 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic portion was stripped to dryness, washed with hexanes, and then dried in vacuo. Two such preparations were combined, dissolved in 30 mL of 1:4 acetone:CH_2Cl_2 and filtered through 5 g of type 62 silica to remove polymer. The filtered solution was chromatographed by MPLC on a 2.5 × 25 cm column packed with silica gel 60 and eluted with 1:9 acetone:CH_2Cl_2. Average yields were 880 mg (33%) of pure IX. Compound IX was identified by its conversion to Xa and NMR spectrum ($CDCl_3$) δ −2.65 (s, 2 H, pyrrole), 0.20 (d, 2 H, methylene bridges), 1.50 (impurity), 1.81 (d, 2 H, methylene bridges), 3.15 (s, 2 H, methylene bridges), 3.40 (s, 1 H, triacetylphenyl moiety), 4.90 (s, 2 H, amide NH), 5.27 (s, 7 H, amide NH), 5.95 (s, 2 H, triacetylphenyl moiety), 6.75–9.1 (m, 40 H, pyrrole β, phenyl, amide NH).

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-(α-*o*-aminophenyl)porphyrin, H_2AmPoc (Xa). 5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-amidophenyl))-20-(α-*o*-((triphenylmethyl)amino)phenyl)porphyrin (880 mg, 0.79 mmol) was dissolved in 90% aqueous acetic acid and stirred overnight. The solution was neutralized by careful addition of NH_4OH and extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and then stripped to dryness, yielding Xa quantitatively. Compound Xa was identified by conversion to Ia and ^{1}H NMR spectroscopy. Compound Xa (1 mg, 1 × 10^{-3} mmol) was dissolved in 4 mL of toluene and excess pivaloyl chloride (2 mg, 1.6 × 10^{-2} mmol) added. The product was shown by TLC to be identical with Ia. Compound Xa was fairly insoluble in most organic solvents and as such the ^{1}H NMR spectrum was poorly resolved: ($CDCl_3$) δ 2.65 (s, 2 H, pyrrole), 0–2.2 (impurity), 3.25 (s, 2 H, methylene bridges), 3.75 (s, 1 H, triacetylphenyl moiety), 4.0–4.5 (impurity), 5.2 (s, 1 H, amide NH), 6.25 (s, 2 H, triacetylphenyl moiety), 6.75–9.1 (m, 24 H, pyrrole β, phenyl).

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-(β-*o*-aminophenyl)porphyrin (Xb). The α-amino compound Xa (690 mg, 0.79 mmol) was dissolved in 100 mL of toluene and heated at reflux for 5 h. The porphyrin was stripped to dryness, dissolved in 25 mL of 1:9 MeOH:CH_2Cl_2, and chromatographed by MPLC on a 2.5 × 25 cm column packed with silica gel 60. The column was eluted with 1:19 MeOH:CH_2Cl_2 and the first band collected, yielding 311 mg (45%) of pure Xb. Compound Xa was also collected and recycled. Compound Xb was identified by its thermal equilibration back to a 1:1 mixture of Xa and Xb. Furthermore, when Xb was treated with excess pivaloyl chlo-

ride, the "β-picket pocket" compound was generated quantitatively.

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-β-*o*-3-(*N*-imidazolyl)propylureidophenyl)porphyrin, H_2Poc3CuIm (Va). The "β-amino pocket" porphyrin Xb (200 mg, 0.23 mmol) was dissolved in 75 mL of THF in a three-necked round-bottom flask equipped with two stopcocks and a rubber septum. Phosgene (CAREFUL!) was blown over the solution for 20 min, and the excess was bubbled through aqueous base. Solvent was removed in vacuo and then 30 mL of THF was added with a N_2 purge and removed in vacuo. The dark green residue was dissolved in 200 mL of THF with 1 mL of pyridine. The following steps were carried out in a darkroom illuminated by a 40-W red light bulb. 3-(*N*-Imidazolyl)propylamine (500 mg, 3.98 mmol) was dissolved in 10 mL of THF with a trace of pyridine and injected via syringe dropwise into the purple-brown porphyrin solution. The solution was stirred for 2 h and the solvent removed in vacuo. The residue was dissolved in CH_2Cl_2, washed twice with H_2O, and chromatographed on a 3 × 22 cm column of type 62 silica gel. The column was eluted with 3:17 MeOH:$CHCl_3$ and the first major band was collected yielding 144 mg (63%) pure Va: NMR (2:1 $CDCl_3$:CD_3OD) δ 2.65 (s, 2 H, pyrrole), 1.2 (m, 6 H, methylene, cyclophane, tail), 2.15 (d, 2 H, methylene bridge), 2.40 (t, 2 H, methylene, tail), 3.00 (m, 3 H), 3.80 (m, 3 H), 5.95 (s, 2 H), 6.20 (s, 1 H), 6.45 (s, 1 H), 6.75 (s, 1 H), 7.20 (s, 2 H), 7.3–9.0 (m, 24 H, pyrrole β, phenyl); mass spectrum (*m/e*) calcd for $C_{63}H_{49}N_{11}O_4$, 1023.396; found, 1023.417 ± 0.05 amu.

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-(β-*o*-3-(3-pyridyl)propylureidophenyl)porphyrin, H_2Poc3Cu(py) (IVa). The same procedure as for Va except 3-(3-pyridyl)propylamine (500 mg, 3.7 mmol) was used in place of 3-(*N*-imidazolyl)propylamine. The same chromatography conditions were used, but IVa proved to be the second major band: NMR (2:1 $CDCl_3$:CD_3OD) δ 2.65 (s, 2 H, pyrrole), 0.80 (m, 2 H, CH_2 tail), 1.4 (m, 4 H), 1.80 (m, 2 H, CH_2 tail), 2.30 (d, 2 H, methylene bridges), 2.40 (t, 2 H, CH_2 tail), 3.15 (s, 2 H, methylene bridge), 3.55 (s, 1 H), 4.20 (m, 2 H), 6.05 (s, 2 H, triacetylphenyl moiety), 6.80–9.00 (m, 29 H); mass spectrum (*m/e*) calcd for $C_{65}H_{50}N_{10}O_4$ 1034.5, found, 1034.5; for $C_{65}H_{50}N_{10}O_4{\cdot}H^+$, 1035.5, found 1035.5.

5,10,15-(1,3,5-Tris(benzenetripropionyl)tris(α,α,α-*o*-aminophenyl))-20-(α-*o*-pivalamidophenyl)porphyrin, H_2MedPoc (IIa). This was prepared from VII (400 mg, 0.53 mmol) by the same procedure as that used for Ia, except 1,3,5-tris(2′-chloroformylethyl)benzene (1.85 g, 5.3 mmol) was used in place of 1,3,5-benzenetriacetyl chloride. Average yields of 400 mg (75%) were obtained after chromatography and recrystallization from $CHCl_2$/heptane: ^1H NMR (2:1 $CDCl_3$:C_2D_5OD) δ 2.65 (s, 2 H, pyrrole H), −0.5 (m, br, 4 H, methylene bridge), 0.5 (s, 9 H, $(CH_3)_3C$), 0.80 (m, 2 H, methylene bridge), 1.50 (m, 2 H, methylene bridge), 1.70 (impurity), 2.4 (m, 4 H, methylene bridge), 3.70 (s, 1 H, cyclophane), 5.20 (s, 2 H, amide NH), 5.90 (s, 2 H, cyclophane), 7.25–9.0 (m, 26 H, pyrrole β, phenyl, amide NH); mass spectrum (*m/e*) calcd for $C_{64}H_{54}N_8O_4{\cdot}H^+$, 999.4; found, 999.4.

Anal. Calcd for $C_{64}H_{54}N_8O_4{\cdot}H_2O$: C, 75.57; H, 5.55; N, 11.00. Found: C, 75.58; H, 5.61; N, 11.03.

5,10,15-(1,3,5-Tris(benzenetributyryl)tris(α,α,α-*o*-aminophenyl))-20-(α-*o*-pivalamidophenyl)porphyrin, H_2TalPoc (IIIa). This was prepared from VII (36 mg, 0.047 mmol) in the same manner as Ia except 1,3,5-tris(3′-chloroformylpropyl)benzene (18 mg, 0.048 mmol) was used in place of 1,3,5-benzenetriacetyl chloride. The yield of IIIa was 42 mg (85%) after chromatography: ^1H NMR ($CDCl_3$) δ 2.65 (s, 2 H, pyrrole H), 0.42 (s, 9 H, $(CH_3)_3C$), 0.50–1.65 (m, 16 H, methylene bridge), 2.05 (m, 2 H, methylene bridge), 4.65 (s, 1 H, cyclophane), 5.70 (s, 2 H, cyclophane), 6.45 (s, 2 H, amide NH), 7.10–9.00 (m, 26 H, pyrrole β, phenyl, amide NH); mass spectrum (*m/e*) calcd for $C_{67}H_{60}N_8O_4{\cdot}H^+$, 1041.43; found, 1041. Anal. Calcd for $C_{67}H_{60}N_8O_4{\cdot}H_2O$: C, 75.97; H, 5.90; N, 10.58. Found: C, 75.30; H, 5.91; N, 10.47.

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-((α-*o*-pivalamidophenyl)porphyrinato)iron(II), FePocPiv (Ib). All iron insertions and subsequent manipulations were carried out in an N_2 drybox with less than 2.0 ppm of O_2.

Ia (100 mg, 0.11 mmol) was dissolved in 10 mL of 1:1 THF:benzene with 0.25 mL of 2,6-lutidine. The solution was brought to reflux and excess $FeBr_2$ (100 mg, 0.5 mmol) was immediately added. The solution was heated at reflux for 1 min and then the solvent was removed in vacuo. The orange-brown residue was redissolved and chromatographed on 10 g of activity 1 neutral alumina. Elution with 10:1:1 toluene:THF:MeOH produced Ib in essentially quantitative yield: UV–vis λ_{max} (toluene) 417 nm (ε, 143.9), 443 (129.6), 538 (21.0). Anal. Calcd for $C_6H_{48}N_8O_4Fe{\cdot}THF$: C, 72.08; H, 5.03; N, 10.35; Fe, 5.16. Found: C, 72.22; H, 5.46; N, 9.28; Fe, 5.27.

FePocPiv(Im). Solutions were generated by the addition of 2–20 equiv of imidazole to the four-coordinate Fe^{II}PocPiv solution. Five-coordinate Fe^{II}PocPiv(Im) was obtained in CH_2Cl_2 toluene, etc. FePocPiv(Im): UV–vis λ_{max} (toluene) 438 nm (ε 224.6), 541 (14.3), 561 (13.6); ^1H NMR (CD_2Cl_2 with 20 equiv of imidazole-d_4) δ 0.2–12.0 (m, ~38 H), 52.5 (d, 4 H, pyrrole β), 54.5 (s, 2 H, pyrrole β), 57.0 (s, 2 H, pyrrole β).

FePocPiv(1-MeIm). FePocPiv with $2–10^4$ equiv of 1-MeIm yielded five-coordinate FePocPiv(1-MeIm): UV–vis λ_{max} (toluene) 439 nm (ε 320.1), 541 (21.4), 563 (19.6); ^1H NMR (toluene-d_8 with 100 equiv of 1-MeIm-d_6) δ 0–10 (m, ~38 H), 45.5 (d, 4 H, pyrrole β), 47.0 (s, 2 H, pyrrole β), 49 (s, 2 H, pyrrole β); μ_{eff} (toluene, 29 °C) = 5.03 μ_B. +CO: λ_{max} 427 nm (ε 209), 519 (16.6); ν(CO) 1965 ± 2 cm^{-1} (C_6D_6); μ_{eff} (toluene, 29 °C) <1.2 μ_B. +O_2: λ_{max} (toluene) 424 nm (ε 80.4), 559 (11.7); μ_{eff} (toluene, 29 °C) < 1.2 μ_B.

FePocPiv(2-MeIm). FePocPiv with $2–10^4$ equiv of 2-MeIm yielded five-coordinate FePocPiv(2-MeIm): λ_{max} (toluene) 438 nm (ε 331), 536 (14.9), 562 (18.0).

FePocPiv(1,2-Me_2Im). FePocPiv with $2–10^4$ equiv of 1,2-Me_2Im yielded five-coordinate FePocPiv(1,2-Me_2Im): λ_{max} (toluene) 438, 535 nm (ε 16.0), 562 (19.3). μ_{eff} = 5.02 μ_B. +CO: λ_{max} (toluene) 439, 519. +O_2: λ_{max} (toluene) = 422, 561; μ_{eff} (toluene, 29 °C) < 1.2 μ_B.

FePocPiv(py). FePocPiv with $2–10^2$ equiv of pyridine yielded FePocPiv(py): λ_{max} (toluene) 436 nm (ε 249), 534 (17.3), 561 (sh) (13.5); μ_{eff} (toluene with 20 equiv of pyridine, 29 °C) = 4.05 μ_B; ^1H NMR (toluene-d_8 with 20 equiv of pyridine-d_5) δ 0–10 (m, ~38 H), 24.5 (s, 2 H, pyrrole β), 25.5 (s, 2 H, pyrrole β), 27.5 (s, 4 H, pyrrole β). +CO: ^1H NMR has features similar to H_2PocPiv (Ia); ^1H NMR (pyridine-d_5) features similar to Ia.

5,10,15-(1,3,5-Tris(benzenetripropionyl)tris(α,α,α-*o*-aminophenyl))-20-((α-*o*-pivalamidophenyl)porphyrinato)iron(II), FeMedPoc (IIb). Fe(II) was inserted into IIa in the usual way to produce FeMedPoc (IIb): λ_{max} (toluene) 418, 443, 539.

FeMedPoc(1-MeIm). FeMedPoc with 2–100 equiv of 1-MeIm produced FeMedPoc(1-MeIm): λ_{max} (toluene) 439, 542, 561; μ_{eff} (toluene with 20 equiv of 1-MeIm, 29 °C) = 4.88 μ_B, μ_{eff} (toluene with 100 equiv of 1-MeIm) = 4.68 μ_B; ^1H NMR (toluene-d_8 with 20 equiv of 1-MeIm-d_6) δ 0–10.5 (m, ~44 H), 53 (s, 4 H, pyrrole β), 56 (s, 4 H, pyrrole β). +CO: ^1H NMR had features similar to IIb; ν(CO) 1954 ± 2 cm^{-1} (C_6D_6). +O_2: λ_{max} (toluene): 425, 554; μ_{eff} (toluene, 29 °C) < 1.2 μ_B. FeMedPoc with ≥10^5 equiv of 1-MeIm produced FeMedPoc(1-MeIm)$_2$: λ_{max} (toluene) 440, 545.

FeMedPoc(1,2-Me_2Im). FeMedPoc with $2–10^4$ equiv of 1,2-MeIm produced FeMedPoc(1,2-Me_2Im): λ_{max} (toluene) 440, 543, 533 (sh). +CO: λ_{max} (toluene) 423, 526. +O_2: 424, 557.

5,10,15-(1,3,5-Tris(benzenetributyryl)tris(α,α,α-*o*-aminophenyl))-20-((α-*o*-pivalamidophenyl)porphyrinato)iron(II), FeTalPoc (IIIb). Fe(II) was inserted into H_2TalPoc (IIIa) in the usual way to yield FeTalPoc (IIIb): λ_{max} (toluene) 515, 441, 530 (br), 564 (br).

FeTalPoc(1-MeIm)$_2$. FeTalPoc with ≳3 equiv of 1-MeIm yielded FeTalPoc(1-MeIm)$_2$: λ_{max} (toluene) 428, 533; ^1H NMR had features similar to that of IIIa. +CO: ν(CO) 1964 ± 2 cm^{-1} (C_6D_6).

FeTalPoc(1,2-Me_2Im). FeTalPoc with 2–120 equiv of 1,2-Me_2Im produced predominantly FeTalPoc(1,2-Me_2Im): λ_{max} (toluene) 437, 531, 562. +CO: λ_{max} (toluene) 422, 512. +O_2: λ_{max} (toluene) 420, 551. FeTalPoc with ≥0.1 M 1,2-Me_2Im produced appreciable FeTalPoc(1,2-Me_2Im)$_2$: λ_{max} (toluene) 433, 533, 562, 580 (sh).

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-(β-*o*-3-((3-pyridyl)propylureidophenyl)porphyrinato)iron(II), FePoc3Cu(py) (IVb). Fe(II) was inserted into IVa in the usual manner to yield FePoc3Cu(py) (IVb): λ_{max} (THF) 433, 533; ^1H NMR (THF-d_8) δ 0–12 (m, ~37 H), 16.2 (s, 1 H), 17.5 (s, 1 H), 34.5 (s, 2 H, pyrrole β), 36.5 (s, 2 H, pyrrole β), 40.0 (d, 4 H, pyrrole β), 61.5 (s, 1 H, pyridine H).

5,10,15-((1,3,5-Benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl))-20-(β-*o*-3-((*N*-imidazolyl)propylureidophenyl)porphyrinato)iron(II), FePoc3CuIm (Vb). Fe(II) was inserted into Va in the usual manner to yield FePoc3CuIm (Vb): λ_{max} (THF) 434, 534, 561 (sh); ^1H NMR (THF-d_8) δ 0–10 (m, ~38 H). 47.5 (s, 2 H, pyrrole β), 48.5 (s, 2 H, pyrrole β), 49.5 (s, 2 H, pyrrole β), 50.5 (s, 2 H, pyrrole β), 58.5 (s, 7 H, imidazole H).

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O_2 and CO Binding to Iron(II) Porphyrins: A Comparison of the "Picket Fence" and "Pocket" Porphyrins[1a]

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Abstract: Kinetic and equilibrium O_2 and CO binding behavior for various iron(II) porphyrin systems are reported. Compared to the "picket fence" complexes, unprotected iron(II) porphyrins have both lowered ligand affinities and lowered ligand association rates. This is explained in terms of a solvation effect which stabilizes the five-coordinate form in the unprotected iron(II) porphyrins. Five-coordinate iron(II) complexes of the sterically encumbered "medium" and "small" "pocket" porphyrins show substantially reduced CO affinities as compared to the analogous open-cavity "picket fence" complexes. Kinetic data indicate that the lowered CO affinities in the "pocket" complexes are primarily reflected in decreased association rates. By contrast, the "pocket" models show both decreased O_2 dissociation and association rates as compared to the "picket fence" analogues. As such, the O_2 affinities are virtually identical throughout the series of "pocket" and "picket fence" complexes. These results are discussed in terms of distal-side steric interactions.

Understanding the role the protein plays in regulating the binding of small ligands to hemoproteins continues to be a topic of active interest.[2-6] In particular, recent attention has focused on whether the heme cavity sterically discriminates between small ligands such as CO and O_2, thereby affecting their relative binding affinities.[4-6] Structural analyses in carbonylated hemoproteins reveal that the CO unit is bent and/or tilted from the perpendicular to the porphyrin plane, owing to interactions with the distal residues.[7] In structures of oxygenated hemoproteins the O_2 unit is found to be bent.[8] In Fe(II) porphyrin systems, free from protein effects, the FeCO unit is linear and normal to the porphyrin plane,[9] whereas O_2 binds in a bent fashion.[10] We[11,12] and others[13,14] have proposed that in hemoproteins distortion of the FeCO unit reduces CO affinities without affecting the O_2 affinity of the intrinsically bent FeO_2 group.[2b-d,8,10] This so-called "distal-side steric effect"[15] could serve as an important detoxification mechanism for CO.[11]

Studies with iron(II) porphyrins offer the possibility of modeling various aspects of hemoprotein reactivity[16-18] as well as exploring specific structure-function relationships in well-characterized systems.[19,20] In order to explore the role of distal steric effects

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