phosphorescent and the reactive triplet states need not necessarily be identical, the above features can serve as a first guideline for the investigation of the photochemical properties of 6-NB, which is currently under way.

Acknowledgment. We thank Professor Dr. H. Rau from the University of Stuttgart-Hohenheim for valuable discussions. A grant to M.G. from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Ligand, Oxygen, and Carbon Monoxide Affinities of Iron(II) Modified "Capped" Porphyrins

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Abstract: Ligand, O_2, and CO binding constants are presented for iron(II) modified "capped" porphyrins. Steric effects at the axial position outside the cap were altered by changing a tetraphenyl-type cap to a corresponding tetranaphthalene-type cap. The steric hindrance caused by the peri hydrogens of the naphthalene groups is believed to be responsible for the decrease in ligation in the order *n*-propylamine > isobutylamine > *sec*-butylamine > *tert*-butylamine. Inductive effects in the porphyrin plane were altered by introducing a nitro group. Such an electron-withdrawing group enhances ligation but retards oxygenation. The solvent effect on O_2 binding by the capped complexes is small, presumably because the environment of the O_2 bound inside the cap is not greatly changed by changes in solvent. The CO affinities of iron(II) capped porphyrins and of corresponding iron(II) flat-open porphyrins are similar. In contrast, the O_2 affinities of the capped systems are lower than their flat-open counterparts, which means the iron(II) capped porphyrin complexes discriminate against O_2 but not CO. This is discussed in terms of distal steric effects on the stable structures of Fe–O–O (bent) and Fe–C–O (linear).

Coordination chemists had been frustrated for many years due to their inability to prepare an iron complex capable of carrying oxygen in a manner akin to the natural proteins myoglobin and hemoglobin.[2] This frustration ended a few years ago with the discoveries that synthetic iron(II) complexes of "chelated-heme",[3] "picket-fence",[4] and "capped"[5] porphyrins reversibly add dioxygen. Since there are severe restrictions on studies that can be made on natural proteins, it is extremely important now to have these model oxygen carriers which can be subjected to the desired investigations. Extensive work has been done on the bonding and the structure of $Fe–O_2$ and of Fe–CO in these models[2,6] and on the kinetics and thermodynamics of ligation,[7-11] oxygenation,[6,8,11-14] and carbonylation.[11,14-16]

Our previous publications presented thermodynamic data on ligand[9] and on oxygen[13] affinities of iron(II) "capped" porphyrins. The data showed that ligand affinities are smaller relative to the corresponding "flat-open" porphyrin Fe(TPP),[17] and oxygen affinity is smaller than that of the picket-fence complex and the hemoproteins. This was rationalized in terms of conformational strain present in the capped systems. The data also reported the effect of axial ligation on oxygen affinity as well as the effect of cap size ($n = 2$ vs. 3 in Figure 1) on ligation and on oxygenation.

This paper reports the effect of electronic and of steric changes in the equatorial plane of the porphyrin ring on the addition of axial ligands, of oxygen, and of carbon monoxide in iron(II) modified capped porphyrins. The data reported show that the oxygen affinities of the capped porphyrin systems are less than those of the corresponding flat-open porphyrins, whereas the carbon monoxide affinities of both systems are similar. This

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(17) Abbreviations: Por, dianion of porphyrin; C_2-Cap, dianion of the C_2-capped porphyrin 5,10,15,20-[pyromellitoyltetrakis[*o*-(oxyethoxy)phenyl]]porphyrin; C_3-Cap, dianion of the C_3-capped porphyrin 5,10,15,20-[pyromellitoyltetrakis[*o*-(oxypropoxy)phenyl]]porphyrin; NapC_2-Cap, dianion of the naphthyl C_2-capped porphyrin (see Figure 1); C_2-Cap-NO_2, dianion of the β-nitro C_2-capped porphyrin (see Figure 1); TPP, dianion of *meso*-tetraphenylporphine; T(*p*-OCH_3)PP, dianion of *meso*-tetrakis(*p*-methoxyphenyl)porphine; TpivPP, dianion of the "picket-fence" porphyrin *meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis[*o*-(pivalamido)phenyl]porphyrin; Piv_3-(5CImP)Por, dianion of the "tailed picket-fence" porphyrin *meso*-(α,α,α-tris[*o*-(pivalamido)phenyl]-β-[*o*-[5-(*N*-imidazolyl)valeramido]phenyl]-porphyrin; PocPivP, dianion of "picket-pocket" porphyrin (see ref 11 and structure in following paper); chelated protoheme (mesoheme), see ref 3; 6,6-cyclophane and 7,7-cyclophane, see ref 10 and structure in following paper; Mb, myoglobin; Hb, hemoglobin; B, monodentate ligand; 1-MeIm, 1-methylimidazole; 1,2-Me_2Im, 1,2-dimethylimidazole; 2-MeIm, 2-methylimidazole; 1,5-DCIm, 1,5-dicyclohexylimidazole; *n*-$PrNH_2$, *n*-propylamine; *i*-$BuNH_2$; isobutylamine; *sec*-$BuNH_2$, *sec*-butylamine; *t*-$BuNH_2$; *tert*-butylamine; THF, tetrahydrofuran; DMF, *N,N*- dimethylformamide; K^B, the equilibrium constant for the base addition $Fe(Por) + B \rightleftharpoons Fe(Por)B$; $K_B{}^B$, the equilibrium constant for the base addition $Fe(Por)B + B \rightleftharpoons Fe(Por)B_2$; $P_{1/2}{}^{O_2}$, the O_2 pressure at half-saturation; $P_{1/2}{}^{NH_3}$, the NH_3 pressure at half-saturation; CTAB, cetyltrimethylammonium bromide.

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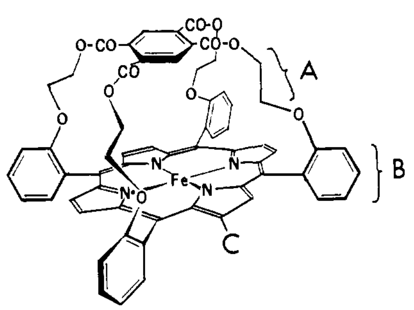

	A (-(CH$_2$)-$_n$	B	C
C$_2$-Cap	n=2	phenyl	H
C$_3$-Cap	n=3	phenyl	H
NapC$_2$-Cap	n=2	naphthyl	H
C$_2$-CapNO$_2$	n=2	phenyl	NO$_2$

Figure 1. Iron(II) "capped" porphyrins.

difference is explained in terms of distal steric effects, although it is recognized that there are pro[11,18–22] and con[14,16] proponents as to the importance of steric factors for the discriminatory binding of O_2 and of CO to metal complexes.

Experimental Section

Reagents. Toluene, CH_2Cl_2, THF, and DMF were reagent grade. Toluene was distilled under N_2 from sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled over P_2O_5. THF was distilled over sodium metal. MeOH was distilled over $Mg(OMe)_2$. All these solvents were distilled under N_2 before use. DMF was stored over activated 4-Å molecular sieves for several days, stirred over KOH at room temperature for 2 days, decanted, and then distilled under N_2. The distillate was pumped for 4 h at room temperature under vacuum. 1-MeIm was dried over KOH, distilled under vacuum, and stored under N_2. 1,2-Me$_2$Im was dried over KOH, distilled under vacuum, and stored below 0 °C. All aliphatic amines were dried over KOH, distilled, and stored under N_2. 1,5-DCIm was synthesized by the method of Traylor and co-workers.[14]

N_2 gas was Matheson prepurified grade and was passed through Ridox and molecular sieve columns to remove residual O_2 and water. Gaseous dioxygen was Air Products ultrapure carrier gas (containing less than 1.0 ppm H_2O) or Matheson primary standard 0.999% O_2 in N_2. Gaseous ammonia was Matheson anhydrous. Dilute ammonia gas was Matheson certified standard, 206.5 ppm NH_3 in N_2. Gaseous CO was Matheson Primary Standard 15.1 ppm, 190.3 ppm, and 1.002% CO in N_2.

Analyses. Elemental analyses of C, H, and N wereperformed by H. Beck of this department.

Syntheses. Fe(C$_2$-Cap)Cl was prepared by the method described earlier.[23,24] Fe(C$_3$-Cap)Cl was prepared as described in a previous paper.[9]

Fe(NapC$_2$-Cap)Cl. NapC$_2$-CapH$_2$ was prepared by the method used for the corresponding C$_2$-CapH$_2$.[5,23] NapC$_2$-Cap (1.3 g) and anhydrous $FeCl_2$ (5.0 g) were dissolved in $LiAlH_4$-dried THF (700 mL). The mixture was refluxed with stirring under dry argon for 6 days. The THF was removed by rotory evaporation and the solid was triturated with $CHCl_3$ until all the porphyrin was extracted. The crude porphyrin was chromatographed on neutral alumina with $CHCl_3$ as solvent. The porphyrin was collected and evaporated to dryness, giving a purple solid: yield of Fe(NapC$_2$-Cap)Cl 1.48 g; λ_{max} (toluene) 419, 515, 586, 567 nm. Anal. Calcd for $C_{78}H_{50}N_4O_{12}FeCl$: C, 70.62; H, 3.80; N, 4.22. Found: C, 69.96; H, 4.20; N, 4.19.

Fe(C$_2$-Cap-NO$_2$)Cl. C$_2$-CapH$_2$-NO$_2$ was prepared by the method described earlier.[24] The synthesis of Fe(C$_2$-Cap-NO$_2$)Cl was based on the general procedure published by Adler and co-workers.[25] The porphyrin C$_2$-CapH$_2$-NO$_2$ (50 mg) and anhydrous $FeCl_2$ (60 mg) were dissolved in DMF (100 mL). The mixture was refluxed with stirring under N_2. During this time a visible spectrum in toluene of an aliquot taken from the reaction mixture was checked for the presence of free porphyrin. After 30 h of reflux, the mixture was allowed to cool to room temperature, 100 mL of water was added to the mixture, and the aqueous mixture was extracted with $CHCl_3$. The extract was washed with 5% HCl and water and then evaporated to dryness. The resulting solid was recrystallized from CH_2Cl_2/hexane to yield 37 mg of Fe(C$_2$-Cap-NO$_2$)Cl; λ_{max} (toluene) 438, 513 (sh), 555 (sh), 630 (sh). Anal. Calcd for $C_{62}H_{41}N_5O_{14}FeCl$: C, 63.58; H, 3.53; N, 5.98. Found: C, 63.57; H, 3.65; N, 6.24. Fe(TPP)Cl and Fe(T(*p*-OCH$_3$)PP)Cl were prepared by the method of Adler and co-workers.[25]

Fe(Por). Because of the extreme oxygen sensitivity of these compounds in solution, the baseless Fe(Por) was freshly prepared and used immediately. In a typical reduciton, 1–10 mg of Fe(Por)Cl was dissolved in toluene (20 mL) and the solution was purged with N_2 to remove O_2. An equal volume of deoxygenated aqueous 0.3 M $Na_2S_2O_4$ solution was added to the Fe(Por)Cl solution. After vigorous shaking for 5 min, the brown solution turned to an orange-red color. The aqueous layer was discarded and the toluene solution was transferred by cannula to a N_2-filled flask containing Na_2SO_4 (anhydrous) to remove any H_2O. λ_{max} in visible region (toluene): Fe(C$_2$-Cap), 543 nm; Fe(C$_3$-Cap), 544 nm; Fe(C$_2$Nap-Cap), 545 nm; Fe(C$_2$-Cap-NO$_2$), 549, 585 (sh); Fe(TPP), 538 nm; Fe(T(*p*-OCH$_3$)PP), 541 nm.

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

For equilibria involving only a single ligand, B, there are two possible equilibrium expressions (eq 1 and 2). Data were treated in one of three different ways, depending on the relative values of K^B and $K_B{}^B$ as described earlier.[9]

$$\mathrm{Fe(Por)} + \mathrm{B} \overset{K^B}{\rightleftharpoons} \mathrm{Fe(Por)(B)} \quad (1)$$

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

Oxygen Affinity Measurements. Equilibrium constants for the oxygenation reaction were also determined spectrophotometrically by using a 4.0-cm path length, low-temperature visible cell.[26] A Cary 14 spectrophotometer was used in all experiments. In general, the spectra were recorded in the 650–480-nm range. The Fe(Por)(B) solution was prepared as described previously.[13] The base concentrations were chosen to give greater than 99% of the five-coordinate complex in "capped" porphyrin complexes and 98% of that in a "flat-open" porphyrin complex such as Fe(T(*p*-OCH$_3$)PP)(1,2-Me$_2$Im). The concentration of the base solution was determined from the equilibrium constants K^B and $K_B{}^B$ in Table I. Spectral changes were recorded, with isosbestic points, by the addition of aliquots of O_2 from a gas manifold[27] via a gastight valve to the porphyrin complex solutions.[13] A mixture of 0.999% O_2 in N_2 or pure O_2 was used, depending on the value of $P_{1/2}{}^{O_2}$. Reversibility was checked after the last O_2 addition by vacuum removal of O_2 to obtain the identical initial spectrum.

The oxygenation of five-coordinate complexes is illustrated by eq 3.

$$\mathrm{Fe(Por)(B)} + \mathrm{O_2} \overset{K_B{}^{O_2}}{\rightleftharpoons} \mathrm{Fe(Por)(B)(O_2)} \quad (3)$$

$$\text{where } P_{1/2}{}^{O_2} = (K_B{}^{O_2})^{-1}$$

The data from the spectrophotometric titrations were treated in one of two ways as described earlier.[13] The values of $P_{1/2}{}^{O_2}$ obtained from each were the same within experimental error.

The ammonia affinities for five-coordinate complexes were determined by the same method as that described here for oxygen affinity measurements. Because of the high affinity, a dilute mixture of 206.5 ppm NH_3 in N_2 was used as the titrant, as well as pure ammonia gas.

The dioxygen complex of a flat-open iron porphyrin such as Fe(T(*p*-OCH$_3$)PP) is unstable at temperatures above −25 °C.[28] At lower temperatures (−45 °C) it is sufficiently stable that reversible oxygenation was observed. Under these conditions it was possible to collect the data

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Table I. Ligation Equilibria for Iron(II) Porphyrins (Eq 1 and 2)

species[a]	base	pK_a(BH$^+$)	log K^B	log $K_B{}^B$
Fe(C_2-Cap)	1-MeIm	7.25[b]	2.90 ± 0.05[e]	
	1,5-DCIm	7.64[c]	3.17 ± 0.05	
	1,2-Me_2Im	7.85[b]	3.06 ± 0.05[e]	
	n-$PrNH_2$	10.56[h]	2.25 ± 0.20	0.32 ± 0.07
	i-$BuNH_2$	10.42[d]	2.07 ± 0.15	*f*
	sec-$BuNH_2$	10.56[d]	2.15 ± 0.06[e]	
	t-$BuNH_2$	10.45[d]	2.50 ± 0.06[e]	
Fe(C_3-Cap)	1-MeIm	7.25[b]	3.31 ± 0.05	0.77 ± 0.05
	1,5-DCIm	7.64[c]	3.00 ± 0.05	
	1,2-Me_2Im	7.85[d]	3.61 ± 0.05[e]	
	n-$PrNH_2$	10.56[h]	3.40 ± 0.30[e]	4.05 ± 0.10
	sec-$BuNH_2$	10.56[d]	2.79 ± 0.30[e]	2.85 ± 0.10
	t-$BuNH_2$	10.45[d]	2.23 ± 0.05[e]	
Fe(NapC_2-Cap)	1-MeIm	7.25[b]	2.87 ± 0.04	
	1,5-DCIm	7.64[c]	3.22 ± 0.07	
	1,2-Me_2Im	7.85[b]	2.32 ± 0.04	
	n-$PrNH_2$	10.56[h]	2.58 ± 0.20	1.33 ± 0.07
	i-$BuNH_2$	10.42[d]	1.54 ± 0.15	*f*
	sec-$BuNH_2$	10.56[d]	1.18 ± 0.05	
	t-$BuNH_2$	10.45[d]	0.90 ± 0.05	
Fe(C_2-Cap-NO_2)	1-MeIm	7.25[b]	3.68 ± 0.05	
	1,2-Me_2Im	7.85[b]	3.89 ± 0.05	
Fe(TPP)	1,2-Me_2Im	7.85[b]	4.43 ± 0.05	0.39 ± 0.10
Fe(T(*p*-OCH_3)PP)	1,2-Me_2Im	7.85[b]	4.40 ± 0.05	0.31 ± 0.10[g]

[a] Solvent is toluene at 23.1 ± 0.1 °C unless otherwise indicated. [b] Albert, A. *Phys. Methods Heterocycl. Chem.* 1963, 1. [c] Measured in 1:1 $MeOH/H_2O$ solution at 25 °C. [d] Hall, N. F.; Sprinkle, M. R. *J. Am. Chem. Soc.* 1932, *54*, 3469. [e] Reference 9. [f] Reaction rates were too small to measure the $K_B{}^B$ values; in all other cases equilibrium was reached in a few minutes. [g] At −45 °C log $K_B{}^B$ was 2.19 and 2.09 in toluene and in DMF, respectively. [h] Bates, R. G. *Ann. N.Y. Acad. Sci.* 1961, *92*, 341.

needed to determine O_2 affinities. At this temperature the value of $K_B{}^B$ is large enough that dioxygen and 1,2-Me_2Im are competing for the sixth coordination site on the complex (eq 4 and 5). In this case the apparent

$$\text{Fe(T}(p\text{-OCH}_3\text{)PP)(1,2-Me}_2\text{Im)} + 1\text{,2-Me}_2\text{Im} \overset{K_B{}^B}{\rightleftharpoons} \text{Fe(T}(p\text{-OCH}_3\text{)PP)(1,2-Me}_2\text{Im)}_2 \quad (4)$$

$$\text{Fe(T}(p\text{-OCH}_3\text{)PP)(1,2-Me}_2\text{Im)} + \text{O}_2 \overset{K_B{}^{O_2}}{\rightleftharpoons} \text{Fe(T}(p\text{-OCH}_3\text{)PP)(1,2-Me}_2\text{Im)(O}_2\text{)} \quad (5)$$

$P_{1/2}{}^{O_2}$ is a function of base concentration, and eq 6 may be derived.

$$P_{1/2}{}^{O_2}(\text{apparent}) = (1 + K_B{}^B[\text{B}])P_{1/2}{}^{O_2} \quad (6)$$

$$\text{where } P_{1/2}{}^{O_2} = (K_B{}^{O_2})^{-1}$$

According to this equation, values of $P_{1/2}{}^{O_2}$ were obtained from the *y* intercept of the regression line from a plot of $P_{1/2}{}^{O_2}$(apparent) vs. [B]. Also, values of $K_B{}^B$ were obtained by dividing the slope of the plot by th *y*-intercept value.

Carbon Monoxide Affinity Measurements. The experimental procedures used for these studies were similar to those described above for oxygen affinity measurements. Once the iron(II) complex solution was in the visible cell, it was brought to the chosen temperature and then attached to the solution–CO equilibrium apparatus. This apparatus was equipped with gas inlet and outlet tubes, by which N_2 gas containig varying partial pressures of CO was bubbled through the porphyrin solution. The partial pressure of CO in the gas was adjusted by mixing pure N_2 with commercially prepared CO in N_2 (15.1 ppm, 190.3 ppm 1.002%) with two Matheson 600 rotameters and two precision needle valves. The rotameters were individually calibrated throughout their ranges with both N_2 and CO in N_2. By use of this apparatus, partial pressures of CO could be continuously varied from 1 × 10^{-3} to 7.6 torr.

In order to prevent concentration changes during bubbling, the gas mixtures were saturated with the solvent at the same temperature as the porphyrin solution, and a large amount of Fe(Por)B solution (20 mL) was used. Each gas mixture was passed through the solution until equilibrium was attained, as indicated by constant measurement of absorbance. This method is essentially the same as that used by Collman and co-workers[29] for the measurement of O_2 affinity. The method in which aliquots of CO are added to the solution by changing the pressure, used for O_2 affinity measurements,[13] could not be used. This is because it took a very long time (>5 h) for equilibrium to be attained, especially when low concentrations of CO gas (~1 × 10^{-3} torr) were used. Reversibility was checked after the last CO addition by purging with N_2 gas for ~12 h to obtain the identical initial spectrum. The CO binding to five-coordinate complexes is illustrated by eq 7.

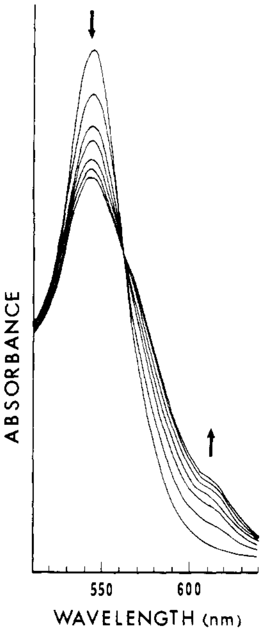

Figure 2. Spectral changes occurring upon titration of a 6.315 × 10^{-5} M toluene solution of Fe(NapC_2-Cap) with 1.1157 M 1-MeIm in toluene at 23.1 °C. The final base concentration is 8.12 × 10^{-2} M.

$$\text{Fe(Por)(B)} + \text{CO} \overset{K_B{}^{CO}}{\rightleftharpoons} \text{Fe(Por)(B)(CO)} \quad (7)$$

$$\text{where } P_{1/2}{}^{CO} = (K_B{}^{CO})^{-1}$$

Data from the spectrophotometric titrations were treated in one of two ways, as described above for oxygenation. The $P_{1/2}{}^{CO}$ values obtained in each way were the same within experimental error. All data were fitted by using a nonweighted linear least-squares method.

Infrared Spectra Measurements. Toluene solutions of Fe(Por)(1,2-Me_2Im) were prepared by the method previously described.[13] Transfer of solutions to the cell, which had been flushed with N_2 before the solution was added, was performed by using gastight syringes. Concentrations of the iron porphyrin solutions were approximately 1 × 10^{-2} M. Samples of these solutions were then exposed to an atmosphere of CO at room temperature.

Infrared spectral data were collected between 4000 and 400 cm^{-1} on a Perkin-Elmer 283 spectrometer at 2-cm^{-1} resolution using NaCl cells with a light path length of 0.5 mm.

Results

Equilibrium constants, K^B and $K_B{}^B$, were measured for the ligation of Fe(Por) (eq 1 and 2). The equilibrium constants were obtained by spectrophotometric titrations of toluene solutions of the iron(II) complex with base under nitrogen. Isosbestic points, after dilution corrections, were maintained throughout the titrations (Figure 2). Values for the equilibrium constants for base addition to complexes of the type Fe(Por) are given in Table I. Equilibrium constants were checked at a second wavelength and proved to be independent of the wavelength chosen.

It was not convenient to determine K^B and $K_B{}^B$ for the addition of ammonia to Fe(Por), but values of $P_{1/2}{}^{NH_3}$ were determined (eq 8). These values are given in Table II.

$$\text{Fe(Por)(B)} + \text{NH}_3 \overset{K_B{}^{NH_3}}{\rightleftharpoons} \text{Fe(Por)(B)(NH}_3\text{)} \quad (8)$$

$$\text{where } P_{1/2}{}^{NH_3} = (K_B{}^{NH_3})^{-1}$$

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(29) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Hayes, S. E.; Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 2761–2766.

Table II. Ammonia Addition Equilibria to Five-Coordinate Iron(II) Capped Porphyrin Complexes in Toluene (Eq 7)

complex[a]	$P_{1/2}^{NH_3}$,[b] torr
Fe(C_2-Cap)(1-MeIm)	1.0×10^{-2}
Fe(C_2-Cap)(1,2-Me_2Im)	4.6×10^{-1}
Fe(NapC_2-Cap)(1-MeIm)	6.4×10^{-3}
Fe(NapC_2-Cap)(1,2-Me_2Im)	1.1×10^{-1}

[a] Solutions are 1.0 M base in toluene. [b] At 23.1 ± 0.1 °C. Values are reproducible within 10%.

Table III. Equilibrium Data for Oxygenation of Five-Coordinate Iron(II) Capped Porphyrin Complexes in Toluene (Eq 3)

		$P_{1/2}^{O_2}$,[b] torr				
complex	base[a]	25 °C	0 °C	−23 °C	−45 °C	−63 °C
Fe(C_2-Cap)	1-MeIm[e]	23	4.5	0.78	0.10[e]	
	1,2-Me_2Im[e]	4000	930	162	27	
Fe(C_3-Cap)	1-MeIm[c]		120–180			
	1,5-DCIm[d]		54.2			
	1,2-Me_2Im[c]					880
Fe(NapC_2-Cap)	1-MeIm		2.3	0.28		
	1,2-Me_2Im		613			
Fe(C_2-Cap-NO_2)	1-MeIm		7.1			
	1,2-Me_2Im			413		
Fe(T(*p*-OCH_3)PP)	1,2-Me_2Im				5.3[e,f]	

[a] Solutions are 1.0 M base in toluene, except when noted otherwise. [b] Values are reproducible within 5%, except when noted otherwise. [c] Reference 13. [d] Solution is 0.1 M 1,5-DCIm in toluene. [e] Values reproducible within 10%. [f] See experimental section.

Spectrophotometric oxygen titrations of toluene solutions of Fe(Por)(B) complexes were carried out. Isosbestic points were maintained in all titrations (Figure 3). Values of $P_{1/2}^{O_2}$ were obtained for the first time for simple flat-open complexes such as Fe(T(*p*-OCH_3)PP)(1,2-Me_2Im). This had to be done at −45 °C to prevent irreversible oxidation, and the data were treated for competing equilibria (eq 4 and 5). Values of $P_{1/2}^{O_2}$ obtained for oxygenation of the five-coordinate complexes are shown in Table III.

Most of the oxygenation data were obtained in toluene solutions, but other solvents were also employed in order to study the effect of solvent (Table IV). Unfortunately, we were unable to obtain data using protonic solutions such as methanol, methanol/toluene, and water/CTAB suspension. In methanol, the spectra did not show the typical spectrum of the five-coordinate complex obtained in toluene solutions at the same conditions. In aqueous solution, the solubility was too low to get a visible spectrum.

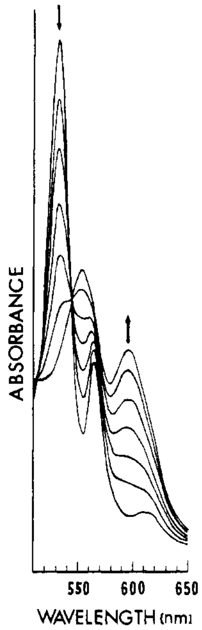


Figure 3. Spectral changes occurring upon titration of a ~10^{-5} M toluene solution of Fe(T(*p*-OCH_3)PP)(1,2-Me_2Im)$_x$, 4.60×10^{-2} M in 1,2-Me_2Im, with the following pressures of dioxygen at −45 °C: 0, 9.98, 21.51, 43.56, 84.69, 204.83, and 764.08 torr.

Earlier studies[13] report $P_{1/2}^{O_2}$ for the oxygenation of Fe(C_3-Cap)(1-MeIm)$_x$, and it was desired to have this value for a five-coordinate complex containing an axial imidazole without an alkyl group in the 2- or 4-position of the imidazole. This was achieved by using 1,5-DCIm, and the data are reported in Table III.

The titration with CO of solutions of five-coordinate iron(II) capped porphyrins gave optical spectral changes (Figure 4) with isosbestic points in accord with equilibria of the type represented by eq 7. Experimental data obtained from such spectra allow estimates of values of $P_{1/2}^{CO}$, which are recorded in Table V. The solvent effects on values of $P_{1/2}^{CO}$ are given in Table VI.

Data in Table VII permit a comparison of O_2 and of CO affinities of some iron(II) porphyrins. Table VIII contains the IR C–O stretching frequencies, ν_{CO}, compared with other model compounds and with the hemoproteins.

Discussion

Ligation. Steric effects on axial ligation of groups attached to the equatorial porphyrin plane were investigated by using Fe(NapC_2-Cap). The use of this tetranaphthalene derivative in

Table IV. Solvent Effect on Equilibria for Oxygenation of Five-Coordinate Iron(II) Capped Porphyrin Complexes

				$P_{1/2}^{O_2}$,[h] torr			
complex	base[a]	solvent	ϵ[g]	25 °C	0 °C	−23 °C	−45 °C
Fe(C_2-Cap)[b]	1-MeIm	toluene[c]	2.4	23	4.5	0.78	0.10[i]
		CH_2Cl_2	8.9		6.5	0.82	
		THF	7.6		5.0	0.35	
		DMF	36.7		3.3	0.23	
Fe(T(*p*-OCH_3)PP)	1,2-Me_2Im	toluene	2.4				5.3[i,j]
		DMF	36.7				0.41[i,j]
Fe(Piv_3(5CImP)Por)		toluene[d]	2.4	0.58			
		1:1 toluene/MeOH[e]	17.6[m]	0.059			
chelated mesoheme		90% (v/v) toluene/CH_2Cl	3.1[m]	3×10^4 M^{-1} [l]			
		2% aqueous CTAB[f] suspension	80.4[k]	1×10^6 M^{-1} [l]			

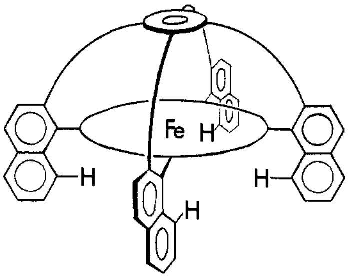
[a] Solutions are 1.0 M base in solvents, except when noted otherwise. [b] Data could not be obtained in MeOH and Toluene/MeOH solution because the five-coordinate complex could not be obtained in these solutions nor in CTAB suspension because of low solubility. [c] Reference 13. [d] Reference 8. [e] Reference 33. [f] Reference 12. [g] Dielectric constant at 25 °C. [h] Values are reproducible within 5%, except when noted otherwise. [i] Value reproducible within 10%. [j] See Experimental Section. [k] Value for H_2O. [l] Value for $K_B^{O_2}$ at 22 °C. [m] In solvent mixtures, it was assumed that dielectric constants are a linear function of the composition.

Table V. Equilibrium Data for Carbonylation of Five-Coordinate Iron(II) Capped Porphyrin Complexes in Toluene (Eq 7)

complex	base[a]	$P_{1/2}^{CO}$(25 °C),[b] torr
Fe(C_2-Cap)	1-MeIm	5.4×10^{-3} (7.6×10^{-4})[c]
	1,2-Me_2Im	2.0×10^{-1} [d] (1.7×10^{-2})[c]
Fe(C_3-Cap)[e]	1,5-DCIm	4.1×10^{-3}
	1,2-Me_2Im	1.4×10^{-1} (3.0×10^{-2})[c]
Fe(NapC_2-Cap)	1-MeIm	2.9×10^{-3}
	1,2-Me_2Im	1.0×10^{-1}
Fe(C_2-Cap-NO_2)	1-MeIm	7.0×10^{-3}
	1,2-Me_2Im	5.1×10^{-1}
Fe(TPP)	1,2-Me_2Im[f]	1.4×10^{-1}
Fe(T(*p*-OCH_3)PP)	1,2-Me_2Im[f]	8.0×10^{-2}

[a] Solutions are 1.0 M base in toluene, except when noted otherwise. [b] Values are reproducible within 10%, except when noted otherwise. [c] At 0 °C. [d] When solution is 2.75×10^{-2} M 1,2-Me_2Im in toluene, value is 2.8×10^{-1} torr. [e] The values of $P_{1/2}^{CO}$(apparent) for Fe(C_3-Cap)(1-MeIm)$_x$ at 0 °C were 1.1×10^{-3}, 1.4×10^{-3}, and 2.2×10^{-3} torr at the base concentrations 0.28, 0.99, and 3.02 M, respectively. [f] Solutions are 3.1×10^{-3} M 1,2-Me_2Im in toluene.

place of the corresponding tetraphenyl derivative places the peri hydrogens in what would appear to be a strategic position to hinder axial ligation (see I). Yet the experimental results (Table I) show that the steric effect need not be large and may even be contrary to what one expects. Thus 1-MeIm binds as strongly with Fe(NapC_2-Cap) as it does with Fe(C_2-Cap), whereas $PrNH_2$ even binds slightly stronger with the naphthalene derivative than with the phenyl analogue. In spite of this, it is clear that steric factors are operative in the naphthalene derivative because for Fe(NapC_2-Cap) the ligation tendency decreases with increasing size



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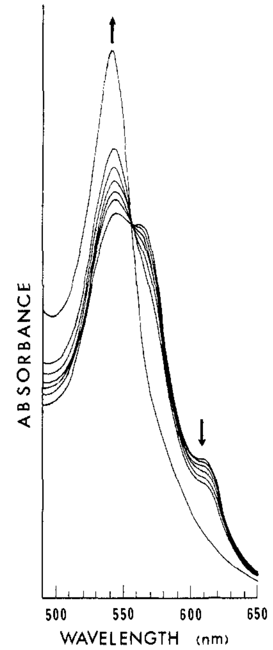


Figure 4. Spectral changes occurring upon titration of a ~10^{-5} M toluene solution of Fe(C_2-Cap)(1,2-Me_2Im), 2.75×10^{-2} M 1,2-Me_2Im, with the following pressures of carbon monoxide at 25 °C: 0, 1.97×10^{-2}, 3.44×10^{-2}, 6.13×10^{-2}, 9.31×10^{-2}, 1.45×10^{-1}, and 7.6 torr.

Table VI. Solvent Effect on the Carbonylation Equilibria of Five-Coordinate Iron(II) Porphyrin Complexes

complex	base[a]	solvent	ε[c]	$P_{1/2}^{CO}$(25 °C),[d] torr	ref
Fe(C_2-Cap)[b]	1-MeIm	toluene	2.4	7.6×10^{-4} [e]	this work
		THF	7.6	3.0×10^{-4} [e]	this work
		DMF	36.7	2.8×10^{-4} [e]	this work
	1,2-Me_2Im	toluene[f]	2.4	2.8×10^{-1}	this work
		DMF[g]	36.7	1.3×10^{-1}	this work
Fe(Piv_3(5CImP)Por)		toluene	2.4	2.2×10^{-5}	33
		1:1 toluene/MeOH	17.6[j]	3.0×10^{-6}	33
chelated mesoheme		toluene/H_2O (2% CTAB suspension)	2.4	4×10^{-4} [i]	12a
			80.4[h]	9×10^{-4} [i]	12a

[a] Solutions are 1.0 M base, unless otherwise noted. [b] Data could not be obtained in MeOH and toluene/MeOH solutions because of irreversible spectra changes nor in MTAB suspension because of low solubility. [c] Dielectric constant at 25 °C. [d] Value reproducible within 10%, except when noted otherwise. [e] At 0 °C. [f] In 2.75×10^{-2} M 1,2-Me_2Im solution. [g] In 6.42×10^{-2} M 1,2-Me_2Im solution. [h] For H_2O at 20 °C. [i] At 20 °C. [j] In solvent mixture, it was assumed the ε is a linear function of composition.

Table VII. Comparison of Oxygen and Carbon Monoxide Affinities of Iron(II) Porphyrins and Hemoproteins at 25 °C

complex	solvent	$P_{1/2}^{O_2}$, torr	$P_{1/2}^{CO}$, torr	ref
Fe(C_2-Cap)(1-MeIm)	toluene	2.3×10	5.4×10^{-3}	this work
Fe(C_3-Cap)(1,5-DCim)	toluene	5.4×10[a]	4.1×10^{-3}	this work
Fe(Piv_3(5CImP)Por)	toluene	5.8×10^{-1}	2.2×10^{-5}	8, 33
Fe(PocPivP)(1-MeIm)	toluene	3.6×10^{-1}	1.5×10^{-3}	11
chelated protoheme	benzene	5.6[b]	2.5×10^{-4}	14
Fe(7,7-cyclophane)(1,5-DCIm)	benzene	1.4	9.1×10^{-4}	10, 14
Fe(6,6-cyclophane)(1,5-DCIm)	benzene	6.9×10^{2}	8.4×10^{-2}	10, 14
Mb (sperm whale)	water (pH ~7)	2.9×10^{-1}	~2×10^{-2}	42–44
Hb (human "R")	water (pH ~7)	1.7×10^{-1}	~2.5×10^{-3}	44–48
Fe(C_2-Cap)(1,2-Me_2Im)	toluene	4.0×10^{3}	2.0×10^{-1}	this work
Fe(TPP)(1,2-Me_2Im)	toluene		1.4×10^{-1}	this work
Fe(T(*p*-OCH_3)PP)(1,2-Me_2Im)	toluene	5.3[c]	8.0×10^{-2}	this work
Fe(TpivPP)(1,2-Me_2Im)	toluene	3.8×10	8.9×10^{-3}	8, 33
Fe(PocPivP)(1,2-Me_2Im)	toluene	1.3×10	6.7×10^{-2}	11
Hb (human "T")	water pH ~7)	2.6×10	~1.5×10^{-1}	44–46

[a] At 0 °C. [b] At 2.0 °C. [c] At −45 °C.

Table VIII. Carbonyl Stretching Frequencies of CO Complexes

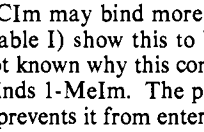
complex[a]	ν_{CO}, cm^{-1}	ref
$Fe(C_2\text{-}Cap)(1,2\text{-}Me_2Im)(CO)$	1999	this work
$Fe(C_2\text{-}Cap)(1\text{-}MeIm)(CO)$[b]	2002	36
$Fe(NapC_2\text{-}Cap)(1,2\text{-}Me_2Im)(CO)$	1998	this work
$Fe(C_3\text{-}Cap)(1,2\text{-}Me_2Im)(CO)$	1984	this work
$Fe(TPP)(1,2\text{-}Me_2Im)(CO)$	1972	this work
Fe(TpivPP)(1-MeIm)(CO)[c]	1969	49
Fe(OEP)(1-MeIm)(CO)[c]	1970	15, 50
MbCO[d]	1945	18, 47, 48
HbCO[d]	1951	18, 47, 48

[a] Solvents are 1.0 M base in toluene, except when noted otherwise. [b] Solvent is 5% 1-MeIm in toluene. [c] Solvent is benzene. [d] In aqueous solution.

of similar ligands as per $n\text{-}PrNH_2 > i\text{-}BuNH_2 > sec\text{-}BuNH_2 > t\text{-}BuNH_2$. In contrast, for $Fe(C_2\text{-}Cap)$ these alkylamines all bind to about the same extent.

Inductive effects on axial ligation of groups attached to the equatorial porphyrin plane were tested by using $Fe(C_2\text{-}Cap\text{-}NO_2)$. It is expected that electron-withdrawing groups will enhance ligation, whereas it will be retarded by electron-donating groups. The experimental results (Table I) are in accord with this, with the axial ligation of both 1-MeIm and $1,2\text{-}Me_2Im$ being larger for $Fe(C_2\text{-}Cap\text{-}NO_2)$ than for $Fe(C_2\text{-}Cap)$. However, $1,2\text{-}Me_2Im$ binds as well to $Fe(T(p\text{-}OCH_3)PP)$ as it does to Fe(TPP). This may be because the *p*-methoxyphenyl groups are not in the porphyrin plane and may not contribute resonance electron density to the porphyrin complex. Note also that reported for the first time is the log $K_B{}^B$ value for the reaction of Fe(TPP) with $1,2\text{-}Me_2Im$. It had been shown[30] that the sterically hindered axial base 2-MeIm does not form a solid bis(2-MeIm)–iron(II) porphyrin complex. This was verified[7a,15] for iron(II) deuteroporphyrin by solution equilibrium studies which show that for 2-MeIm $K^B = 1.3 \times 10^4$ M^{-1} and $K_B{}^B$ is too small to measure at 25 °C in benzene solution. Because of the low solubility of 2-MeIm in benzene, its concentration is not high enough to drive the equilibrium sufficiently toward the formation of the bis(2-MeIm) complex. Since $1,2\text{-}Me_2Im$ is appreciably more soluble, its concentration in solution can be high enough to permit formation of the bis($1,2\text{-}Me_2Im$) complex and the determination of $K_B{}^B$ (Table I). Also contributing to this difference in bis(imidazole) complex formation is perhaps the greater basicity of $1,2\text{-}Me_2Im$ than 2-MeIm.

Ligand constants are reported for the bulky ligand 1,5-DCIm, 1,5-dicyclohexylimidazole (see II). Since 1,5-DCIm is a stronger base than 1-MeIm and since the cyclohexyl groups are some distance removed from the coordinating nitrogen in position 3, it follows that 1,5-DCIm may bind more strongly than does 1-MeIm. The data (Table I) show this to be true except for $Fe(C_3\text{-}Cap)$, and it is not known why this complex binds 1,5-DCIm slightly less than it binds 1-MeIm. The primary interest in 1,5-DCIm is that its size prevents it from entering the C_3-Cap to give a pseudo-six-coordinate system of the type observed[9] for 1-MeIm. This then enables the measurement of oxygen binding to the five-coordinate imidazole complex $Fe(C_3\text{-}Cap)(1,5\text{-}DCIm)$ instead of just either the pseudo-six-coordinate $Fe(C_3\text{-}Cap)(1\text{-}MeIm)_2$ or the strained five-coordinate $Fe(C_3\text{-}Cap)(1,2\text{-}Me_2Im)$. As shown in Table I, small amines such as $n\text{-}PrNH_2$ and even $i\text{-}BuNH_2$ can coordinate with $Fe(C_2\text{-}Cap)(B)$ to form the bis(B) complexes. The equilibrium constant $K_B{}^B$, however, could not be obtained for $i\text{-}BuNH_2$, because the reaction rates are so small that equilibration is difficult to achieve.

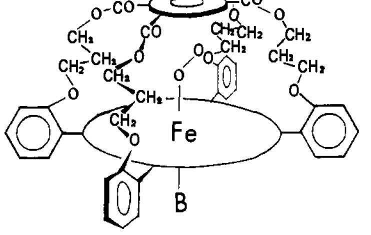


1,5-DCIm

II

The binding of the small molecule NH_3 was determined for five-coordinate Fe(Por) complexes containing either 1-MeIm or $1,2\text{-}Me_2Im$ in the axial position (Table II). This was done to see if the two different imidazoles have the same effect on the relative binding of NH_3, which can only σ bond to iron, as they have on the relative binding of O_2 and of CO, which can both σ bond and π bond to iron. All three of these small molecules are bound more strongly by the 1-MeIm than by the $1,2\text{-}Me_2Im$ complexes, and the relative difference in binding for each of the three is similar. This may suggest that in the Fe–O_2 and Fe–CO complexes, σ bonding is more important than is π bonding.

Oxygenation. Values of $P_{1/2}{}^{O_2}$ for the oxygenation of five-coordinate iron(II) capped and open-flat porphyrin complexes are shown in Table III. The results show that the O_2 affinities with changes in porphyrin decrease in the order $T(p\text{-}OCH_3)PP > NapC_2\text{-}Cap > C_2\text{-}Cap > C_2\text{-}Cap\text{-}NO_2 \gg C_3\text{-}Cap$. The larger O_2 affinity of $NapC_2$-Cap is not understood, and it is not in accord with the smaller axial ligand binding of the respective ligands. A tentative interpretation of the low O_2 affinity of the capped relative to the open-flat complexes was that it is due to conformational strain in the capped system.[13] Recent studies[31] on the shift of the Soret bands of zinc capped porphyrins suggest that the C_3-Cap may be in a squashed configuration with the aromatic ring at the top of the cap nearer the porphyrin plane than it is in the C_2-Cap complex. Should this be true, then the bent structure of Fe–O–O would possibly be interfered with by the methylene groups of the squashed C_3-Cap, causing it to have a smaller O_2 affinity (see III). This could be responsible for its lower O_2 affinity than that of the corresponding C_2-Cap complexes.



III

The C_2-capped complexes of iron(II) all have very similar O_2 affinities. In general, the O_2 affinities of these systems increase slightly with increasing ligation constants (K^B) for the axial ligands. This is understood in terms of the greater electron density placed on iron, which in turn transfers it to the O_2 moiety. One exception seems to be $Fe(C_2\text{-}Cap\text{-}NO_2)$, which has a higher ligand affinity but lower O_2 affinity than does the analogous $Fe(C_2\text{-}Cap)$ complex. This suggests that for some reason oxygenation responds more to inductive effects in the porphyrin plane than in the axial position.

Investigations of cobalt(II) complexes show[26,32] that O_2 affinity increases with increasing solvent polarity. The explanation given for this is that the dioxygen complex formed, formalized as $Co^{III}(O_2^-)$, is more polar than are the reactants and reaction is favored by polar solvents. The same behavior has been observed[28] for iron(II) "flat-open" porphyrin complexes such as Fe(TPP). Data in Table IV show that there is a tenfold increase in O_2 affinity in going from toluene to DMF solution for $Fe(T(p\text{-}OCH_3)PP)(1,2\text{-}Me_2Im)$. The same is true for the picket-fence system[33] $Fe(Piv_3(5CImP)Por)$ in toluene vs. 1:1 toluene/methanol solution. The iron(II) chelated mesoheme system[12] shows a similar enhancement in O_2 affinity in going from 90% (v/v) toluene–CH_2Cl_2 to a 2% CTAB/water suspension. Note that all of these model compounds are of the "flat-open" porphyrin type which permit

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(30) Collman, J. P.; Reed, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 2048–2049.

(31) Venkatasubramanian, P. N.; Basolo, F., unpublished results.

(32) Stynes, H. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 5125–5127.

(33) Collman, J. P.; Brauman, J. I.; Doxsee, K. .; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6035–6039.

the solvation of the Fe–O–O moiety of the dioxygen complexes. Assuming these can be formalized as $Fe^{III}(O_2^-)$, then the formation of these polar products will be favored by polar solvents.

In our hands, all attempts to measure reversible oxygenation equilibria of iron(II) capped porphyrins in protonic solvents failed. We observed only irreversible oxidation similar to that previously reported.[5,34] The results of studies with aprotic solvents of varying dielectric strengths are shown in Table IV. The point of particular interest here is that the solvent effect on O_2 binding is small, less than a factor of 2. This result is in accord with the likelihood that the Fe–O–O formed inside the cap has the "same" environment, regardless of the solvent. If the solvent does not readily enter the cap and effectively solvate the polar Fe–O–O moiety, then polar solvents lose the advantage over less polar solvents observed with the flat-open systems.

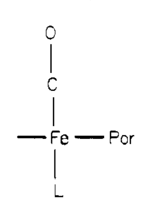
It is further of interest to compare the O_2 affinity of Fe(C_2-Cap)(1-MeIm) with other model compounds and with the natural protein. Comparative data are gathered in Table VII. Because the experimental conditions used often differ, it is not always possible to make a direct quantitative comparison. Yet it appears that a reasonable qualitative order for decreasing O_2 affinity is Hb (human "R") > Mb (sperm whale) > Fe(PocPivP(1-MeIm)) > Fe(Piv$_3$(5ClImP)Por) > Fe(7,7-cyclophane)(1,5-DCIm) ≥ Fe(chelated protoheme) > Fe(C_2-Cap)(1-MeIm) > Fe(C_3-Cap)(1,5-DCIm) > Fe(6,6-cyclophane)(1,5-DCIm). This qualitative order of O_2 affinity for the model comopunds is believed to be reliable because it is based on values of $P_{1/2}^{O_2}$ determined with toluene or benzene solutions. Much less certain is where the natural proteins fit with respect to the model compounds. The $P_{1/2}^{O_2}$ values for the proteins were determined in water solution. Assuming that the earlier discussion of solvent effect applies, then in water solution there would be about a tenfold enhancement of O_2 affinity. Applying a tenfold adjustment to the values of $P_{1/2}^{O_2}$ for the proteins puts them in the ballpark with the chelated protoheme and the C_2-Cap complexes. This would mean that for some reason the iron(II) picket-fence porphyrin has an enormously high O_2 affinity. Alternatively, it can be argued that the proteins with their hydrophobic pocket surrounding the Fe–O_2 moiety give values of $P_{1/2}^{O_2}$ in aqueous solution which can be compared with such values for model compounds in toluene. Comparing the model compounds alone, it is clear that except for 6,6-cyclophane, the capped complexes have the smallest O_2 affinity. This is believed to be due to steric effects which may lower the O_2 affinity of the capped complexes.

Carbonylation. Values of $P_{1/2}^{CO}$ for the carbonylation of five-coordinate iron(II) capped and flat-open porphyrins are shown in Table V. The results show that the CO affinities with changes in porphyrins are all about the same, varying less than a factor of 2. This contrasts the O_2 affinities, which are as much as 50-fold less for iron(II) capped vs. flat-open porphyrins. An attempt is made in the next section to explain the difference between CO and O_2 binding in these systems on the basis of their linear (Fe–C–O) and bent (Fe–O–O) structures.

Unlike the sizeable solvent effects on O_2 binding (Table IV), solvent effects on CO binding (Table VI) to iron(II) porphyrins are known[14] to be small. This difference is attributed to the nonpolar nature of the CO complex, relative to the more polar O_2 complex, whose formation is favored by polar solvents. An exception is the solvent effect on the capped systems which is small for both coordinated CO and O_2 because the environment inside the cap is not greatly altered by solvent.

It is also of interest to note the C–O stretching frequency, ν_{CO}, in the IR spectra for the capped complexes compared with those for other iron(II) porphyrins (Table VIII). Inorganic chemists[35] often use ν_{CO} as an indication of relative M–C bond strengths in analogous metal carbonyls. In terms of the valence bond theory, this is readily explained on the basis of the resonance structures $M—C{\equiv}O \leftrightarrow M{=}C{=}O$. The higher the value of ν_{CO}, the lower the metal–carbon multiple bonding and the weaker the M–C bond. On this basis, the capped systems with ν_{CO} ~2000 cm^{-1} are expected to form the weakest complexes. Yet HbCO, with ν_{CO} ~1950 cm^{-1}, has values of $P_{1/2}^{CO}$ for Hb(R) of (1–4) × 10^{-3} vs. 1-MeIm capped of (3–7) × 10^{-3} and Hb(T) of (1–2.8) × 10^{-1} vs. 1,2-Me$_2$Im capped of (1–5) × 10^{-1}. For some reason, the correlation of M–C bond strength with ν_{CO} which applies for simple metal carbonyls does not apply to the CO adducts of iron(II) porphyrins. It has been suggested that the low values[18-20] of ν_{CO} in hemoproteins are due to the bent or slanted structure of Fe–CO and that the high values[36] of ν_{CO} in the capped systems are due to the interaction of the aromatic ring at the top of the cap with the coordinated CO. These explanations are consistent with the observations that other model compounds have intermediate values of ν_{CO} ~1970 cm^{-1}.

Comparison of O_2 and of CO Binding by Iron(II) Porphyrins. Our studies on O_2 and on CO binding to five-coordinate iron(II) capped porphyrins show these to be the first systems (model or natural) where the bonding of O_2 is discriminated against, relative to CO, when compared with the bonding of O_2 and of CO to a flat-open iron(II) porphyrin. Before attempting to explain this, let us put in perspective the salient points relating to the problem. First, the stable unperturbed structures[6] for the moieties Fe–C–O and Fe–O–O are linear (IV) and bent (V). These structures were determined by X-ray studies on models for Fe–C–O[37] and on both models[38] and natural proteins[39] for Fe–O–O. Both X-ray[40] and IR[18] studies suggest that in hemoproteins Fe–C–O is either bent or slanted. Thus, the reason given[18-20] for some hemoproteins relatively binding CO less than O_2 is that distal steric requirements force CO to bind in a strained bent and/or slanted fashion, whereas the normal bent stable structure remains possible for Fe–O–O.



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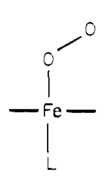
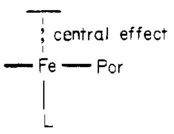
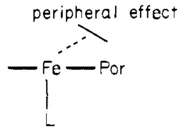


V

Distal steric effects on small molecules coordinated to iron(II) porphyrins have been discussed[10b] in terms of central steric effect (VI) and of peripheral steric effect (VII). The central effect occurs primarily along the axial position, whereas the peripheral effect is more at an angle of about 45° with the plane of the porphyrin. Considering these two steric effects, we can now explain why the iron(II) capped porphyrins discriminate against the binding of O_2 relative to CO.



VI



VII

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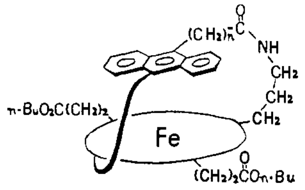
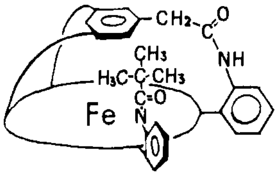
The recent X-ray study of Jameson and Ibers[41] on H_2Cap shows that the distance between the porphyrin plane and its aromatic top of the cap is about 3.9 Å. Earlier studies[37b] show the Fe–C–O distance is 2.89 Å in the Fe(TPP)(Py)(CO) complex. This may suggest that CO can bind with C_2-Cap and C_3-Cap porphyrins in its stable normal linear structure without any marked steric hindrance. However, it has been pointed out[41] that CO cannot be accommodated under such a cap in a linear and perpendicular geometry. This is true in the solid state but may not apply for a possibly more expanded system in solution. Thus the values of $P_{1/2}{}^{CO}$ (Table V) for the capped porphyrins of iron(II) are almost the same as they are for the corresponding "flat-open" porphyrins of iron(II) such as Fe(TPP) and Fe(T(*p*-OCH_3)PP), which are devoid of distal steric effects. In contrast, Fe(T(*p*-OCH_3)PP)(1,2-Me_2Im) binds O_2 about 5 times more strongly than does Fe(C_2-Cap)(1,2-Me_2Im), e.g., $P_{1/2}{}^{O_2}(-45\ °C) = 5.3$ and 27, respectively. This is attributed to peripheral steric effects experienced by bent Fe–O–O in the capped system III.

If this explanation for CO and O_2 affinities of the capped systems is valid, then it should be possible to account for CO and O_2 binding data reported by others on "pocket" and "strapped" porphyrin complexes of iron(II). The model compounds of concern are the Traylor[14] "cyclophane" (VIII) and the Collman[11] "pocket" (IX) systems. Also shown is the "cap" system X. Next to each name or symbol is given, in parentheses, the number of atoms which link the porphyrin ring to the central aromatic group. Now if we assume that discrimination against CO binding, in different systems relative to a flat-open iron(II) porphyrin, is a result of central steric effects and note that this happens for 6,6-cyclophane and perhaps for the pocket systems but not for 7,7-cyclophane and the capped systems, it may follow that the cutoff point for the number of atoms holding the porphyrin ring to the central aromatic group is seven. A system with seven or more atoms will not experience a central steric effect, whereas systems with less than seven atoms will. This means that systems such as the 6,6-cyclophane and the pocket complexes will discriminate against CO binding relative to analogous central sterically unhindered systems. Systems such as 7,7-cyclophane and capped complexes with no central steric hindrance will not effect CO binding.



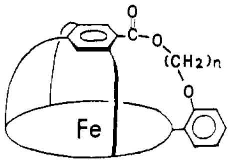
VIII

$n = 1$, 6,6-cyclophane (6)
$n = 2$, 7,7-cyclophane (7)



IX

pocket (5)



X

$n = 2$, C_2-Cap (7)
$n = 3$, C_3-Cap (8)

Discrimination against O_2 binding by iron(II) capped porphyrins is believed to result from peripheral steric effects. This readily accounts for the observation that the pocket system does not discriminate against O_2 binding.[11] In this case the tripod cap has one side open and free from peripheral steric effects. That the 6,6-cyclophane system also discriminates against O_2 binding[14] is perhaps because the flexible strap flops back and forth, putting the anthracene group in positions which create peripheral steric effects. Traylor[14] does state that since 6,6-cyclophane discriminates about equally against O_2 and CO relative to 7,7-cyclphane, steric factors will affect about equally the binding of O_2 and of CO to metal complexes. However, this is not true for the iron(II) capped porphyrins, which discriminate against O_2 but not CO binding.

Although our assessment seems grossly successful in accounting for relative O_2 and CO affinities of model iron(II) porphyrins, some anomalies remain. One is that the picket-fence iron(II) complexes bind CO more strongly than do other corresponding complexes (in private correspondence with Traylor he states this is due to an ortho steric effect). In fact, the discrimination against CO binding in the pocket system is in comparison with the picket-fence system, which approximates the polarity of the pocket system. Note (Table VII) that compared with Fe(TPP)(1,2-Me_2Im) there is no discrimination against CO binding by Fe(PocPivP)(1,2-Me_2Im). Another is the qualitative observation[21] that an anthracene strap system of type X involving nine atoms is said to discriminate against CO binding. If correct, this suggests that beyond a certain number of atoms there is enough flexibility in the strap to allow it to squash down toward the porphyrin plane and offer central steric resistance to CO binding. Yet it is somewhat reassuring that Busch[22] finds that the number of methylene groups in the strap plays an important role in the selective binding of O_2 and CO of some nonporphyrin iron(II) macrocyclics which resemble the cyclophane complexes. Also important is the X-ray structural evidence that steric effects cause Fe–C–O to be bent in one of the complexes which discriminates against CO binding.

Summary

Steric effects on the addition of ligands to the axial coordination site outside the cap were investigated by using Fe(NapC_2-Cap) vs. Fe(C_2-Cap). The effect is small, but it does discriminate between analogous alkylamines of different size. The steric hindrance is believed to be due to the peri hydrogens on the four naphthalene groups in the system. Ligation and oxygenation of Fe(C_2-Cap-NO_2) were studied in order to determine the effect of an electron-withdrawing group in the porphyrin plane. As expected, the results show that flow of electron density away from the system enhances ligation and retards oxygenation. Although there is a pronounced solvent effect on O_2 binding in iron(II) flat-open porphyrins, the capped systems show only a small solvent effect. Oxygenation is generally favored in polar solvents perhaps because of the polar formalism $Fe^{III}(O_2^-)$, but the O_2 moiety inside the cap may experience only small changes in the environment regardless of solvent.

The lower O_2 affinities of the cap systems relative to the flat complexes may be caused by the peripheral steric hindrance of the methylene groups on the bent Fe–O–O structure. In contrast, CO binding by capped systems is similar to that of flat complexes. This selective discrimination against O_2 binding but not CO binding appears to be unique for capped systems.

Acknowledgment. We thank the National Institutes of Health for support of this research. We also are grateful to Ube Industries Ltd. for support of T.H., their employee. We thank Professor T. G. Traylor for help with the synthesis of 1,5-DCIm and for generous and helpful comments.

Registry No. Fe(C_2-Cap), 55106-64-4; Fe(C_3-Cap), 80964-63-2; Fe(C_2Nap-Cap), 80964-64-3; Fe(C_2-Cap-NO_2), 80964-65-4; Fe(TPP), 16591-56-3; Fe(T(*p*-OCH_3)PP), 57715-41-0; Fe(C_2-Cap)(1-MeIm),

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Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 10.[1] Diastereoisomerism and Metallotropic Behavior in Polyindenyl Derivatives of Germanium and Tin. Facile Stereomutation

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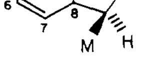
Abstract: Variable-temperature ^{1}H and ^{13}C NMR data have been recorded for Ge(ind)$_4$ (I), Sn(ind)$_4$ (II), *n*-BuSn(ind)$_3$ (III), Ph_3Sn(ind) (IV), Ph_2Sn(ind)$_2$ (V), and PhSn(ind)$_3$ (VI) (ind = η^1-indenyl). For I–III and VI, slow-limiting spectra demonstrate the existence of diastereoisomerism resulting from chirality at the indenyl C^1 atom and are consistent with the presence of all possible stereoisomers. Correlation of experimental data with results of conformational analysis leads to the conclusion that for each system the diastereoisomer distribution is approximately statistical. The ground-state configuration for the meso form of II coincides with the highest symmetry molecular conformation, which belongs to the point-group S_4. Metallotropic behavior leading to temperature dependence of the NMR data results in simultaneous stereomutation having estimated $\Delta G^{\ddagger}$ near 60–70 kJ mol^{-1}.

Dynamic stereochemistry gives rise to the temperature-dependent NMR spectra which are a well-known and characteristic property of *monohapto*cyclopentadienyl (η^1-C_5H_5) metal systems.[2-4] Much of the information now available concerning this intriguing behavior has been provided by examination of appropriate derivatives of silicon, germanium, and tin. We have demonstrated recently[1,5] that the rapid degenerate intramolecular rearrangement in such compounds proceeds with retention of configuration at the migrating metal center. Thus 1,2-metallotropic migratory pathway in a fluxional η^1-C_5H_5 organometallic molecule can be closely associated with a [1,5] sigmatropic shift as defined by Woodward and Hoffmann.[6] Metallotropism is also found to occur in some related (η^1-cyclopolyenyl)metal systems, including (a) methylcyclopentadienyls (η^1-C_5H_4Me) and (b) indenyls (η^1-C_9H_7); in these compounds molecular nonrigidity may involve facile, reversible isomerization, i.e., *nondegenerate* intramolecular rearrangement.[7,8] We have shown[7] that such a description is correct for mono(η^1-C_5H_4Me) silanes, germanes, and stannanes belonging to category a, although for (η^1-C_5H_4Me)$_4$ analogues steric restrictions may reduce the complexity of the dynamic pathway to a two-site fluxional exchange.[8] Here we address the temperature-dependent NMR phenomena exhibited by polyindenyl derivatives of germanium and tin, which are representative of the second group (b) above. We find that a full analysis of ^{1}H and ^{13}C data introduces a new dimension into the description of these systems and also supplements our view[7,8] of the behavior of compounds of type a.

Rearrangement of a 1-silyl-, 1-germyl-, or 1-stannylindene results[9] in the metal-containing group M relocating to C^3 of the indene skeleton (**1** → **2**). The higher activation energies (about 60 kJ mol^{-1} for M = Sn, 90 for Ge, and 105 for Si) for these processes compared with those occurring in η^1-C_5H_5 analogues (30 kJ mol^{-1} for Sn, 50 for Ge; and 60 for Si) are consistent[4] with the intermediacy of the energetically less favorable isoindenyl structure (**3**) in a consecutive 1,2 pathway. This is further suggested (though not proven) by[10] coalescence of the silylmethyl ^{1}H resonances in the NMR spectrum of 1,2-bis(trimethylsilyl)indene. It has been pointed out that the C^1 carbon atom in a 1-metalloindene is asymmetric;[10] hence structures **1** and **2** are enantiomorphic if interconverted by metallotropic shifts which are confined to one face of the C_5 ring (i.e., are suprafacial). Existence of stereoisomerism in bis(η^1-indenyl)mercury has also been briefly mentioned,[11] but no evidence for its incidence was



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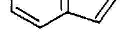

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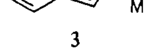

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