Scheme II

$$M^- + *M_s^+e_s^- \qquad *M_s^+ + M^-$$

$$M_s^+e_s^- \quad [7] \qquad [8] \quad M_s^+$$

$$\boxed{*M^-}$$

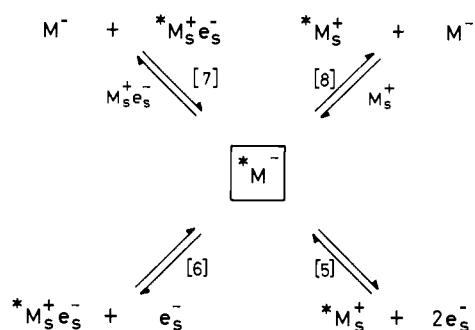$$[6] \qquad\qquad [5]$$

$$*M_s^+e_s^- + e_s^- \qquad *M_s^+ + 2e_s^-$$

paramagnetically (e.g., by e_s^-) or by exchange.

The exchange processes which effectively limit the lifetime of M^- in solutions, and hence may cause NMR broadening, are equilibria 5–8 given in Scheme II. We have already ruled out (7) as a contender for fast exchange in sodium solutions. Our ESR spectra show the concentration of e_s^- in Na–DPA solutions to be relatively low, suggesting equilibria 5 and 6 lie to the left as found previously for Na^- in other systems.[24] Equilibrium 8 involves a M_s^+–M^- exchange process, perhaps in a binuclear complex M_s^+–M^-, and this is likely to be the rate-limiting step which results in lifetime broadening of the NMR.[25,26] A detailed analysis of nuclear spin relaxation in Na^- is currently under way.

Results on Rb^- and Cs^- in other systems (e.g., 12-crown-4[17] and three-component systems[11]) indicate a greater solvent involvement in the ground-state wave function of these larger alkalide ions.[14] This appears to result in more efficient nuclear relaxation, giving rise to extremely broad NMR resonances. Clearly, in the present system, a substantial "solvation" of the heavier anions may be occurring, resulting in rapid electron/cation exchange (eq 2, 3, 5, and 6).

E. Reduction Mechanisms. In an elegant study of the reduction of *N,N*-dimethylacetamide (DMA) by sodium in liquid ammonia Young and Dewald[27] found a fourth-order rate law to be obeyed:

$$-d(e_s^-)/dt = [e_s^-][Na_s^+][e_s^-][\text{amide}]$$

Within the overall context of Scheme I, this could implicate the triple-ion, $e_s^-Na_s^+e_s^-$, as one of the reducing species in Na–NH₃ solutions. However, this might imply that the rates of all Na–NH₃ reductions are sodium ion dependent, which does not seem to be the case. Young and Dewald[27] suggest that the reaction sequence envisaged for the M–NH₃ reduction of the amide may also be responsible for the decomposition of the metal–amide solutions. In the amide-like solvents the corresponding reducing species may now be the sodium anion, Na^-. Clearly in TMU the decomposition reaction is facile; in certain of the other tertiary amides the identification of Na^- as a stable, long-lived entity suggests a relative inertness of the solvents toward concerted electron/anion attack at the carbonyl group. This is also demonstrated from the pulse radiolysis studies in these systems.[4,5]

Attempts to reduce DEA in Na–NH₃ solutions and to study Na/DMA and Na/DEA systems have shown DEA to be more resistant to reduction than the dimethyl analogue.[27] Whether the relative inertness of DEA results from steric[28] or electronic[29] effects is not clearly understood at present. The inertness of DEA to Na–NH₃ solutions is reminiscent of the behavior of HMPA which is not readily cleaved by e_s^-, either in Na–NH₃ or in HMPA itself.[30] The stability of HMPA solutions increases by a factor of 3–4 when the temperature is lowered from 298 to 283 K. Likewise, certain metal–amide solutions are stable at reduced temperatures but decompose more rapidly at room temperature. It is interesting to note the corresponding changes in behavior of e_s^- via pulse radiolysis studies.[5] Lowering the temperature increases both the lifetime and the radiolytic yield of solvated electrons in neat DEA.

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Structural Differentiation of CO and O₂ Binding to Iron Porphyrins: Polar Pocket Effects

T. G. Traylor,* Noboru Koga, and Larrie A. Deardurff

Contribution from the Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093. Received March 18, 1985

Abstract: A new iron porphyrin, 3,5-pyridine-5,5-hemecyclophane, has been prepared, and its dioxygen and carbon monoxide binding studied. In contrast to other "strapped" pyridines with larger cyclophane links, this compound shows no tendency to bind its attached pyridine. With use of 1,5-dicyclohexylimidazole as proximal base, a five-coordinated heme is obtained. This heme shows severe steric hindrance toward both dioxygen and carbon monoxide binding. It displays a ratio of carbon monoxide to dioxygen affinities as low as 5, a much lower binding ratio than those shown by any other model systems, by hemoglobin, or by myoglobin. This suggests ways of preparing artificial dioxygen-binding materials which preferentially bind dioxygen.

The relative affinities of carbon monoxide and dioxygen to hemes and hemoproteins is of great current interest, both with respect to the understanding of those factors which govern these affinities in biological systems[1–12] and in regard to the preparation

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of synthetic dioxygen transporting materials.[13,14]

In hemoproteins the ratio of the binding constants for CO and O_2 ($K_B^{CO}/K_B^{O_2} = M$) is variable, ranging from 0.03 in Ascaris hemoglobin[15] through 17 in myoglobin[16] to 6000 in glycera hemoglobin.[17] Synthetic heme compounds have M values from

(1) (a) Abbreviations: DClm, 1,5-dicyclohexylimidazole; MTAB, myristyltrimethylammonium bromide. K^Y and K_Z^Y represent equilibrium constants for addition of Y to the four- and five-coordinated hemes, respectively. Kinetic association and dissociation rates for ligand Y are similarly represented as k_Z^Y and k_Z^{-Y}, respectively. FePiv 5Clm, FePocPiv, FeMedPocPiv, see ref 4d; cyclophane nomenclature: porphyrins having groups covalently strapped over the porphyrin face are labeled *n*-, *n,n*-, *n,n,n*-, or *n,n,n,n*-cyclophanes to indicate a single methylene strap or a more complex group such as an arene or adamantane group attached to the porphyrin by two (*n,n*), three (*n,n,n*), or four (*n,n,n,n*) chains, respectively. The value of *n* represents the number of atoms between the porphyrin ring and either the other group or the other side of the porphyrin. Thus compounds with the same *n* should have pockets of similar size. (b) The relevant figures are in the supplementary material.

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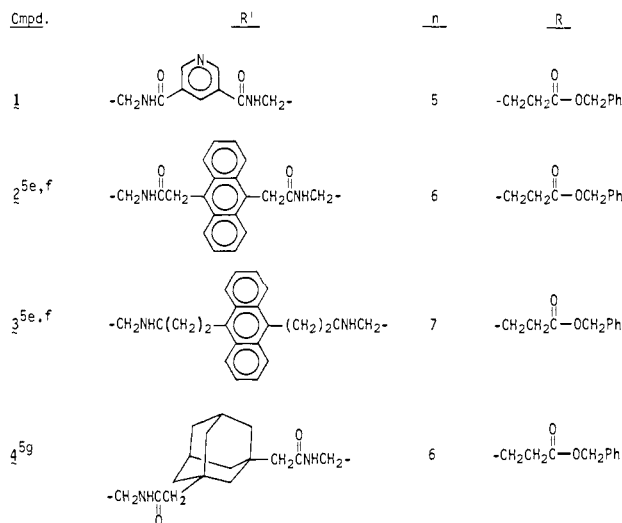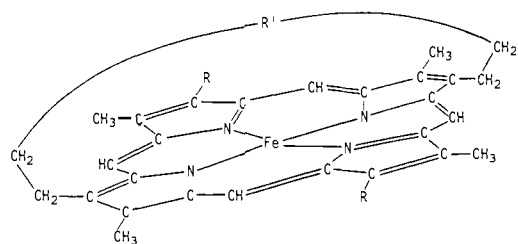(17) Parkhurst, L. J.; Sims, P.; Goss, D. J. *Biochemistry* **1980**, *19*, 2688.

Figure 1. Cyclophane heme compounds.

~300 in polar environments[5a-c] to ~50000 in toluene or benzene.[4a-c,9e,18] Therefore, it has not yet been possible to prepare synthetic heme model compounds which mimic the binding properties of all the heme proteins.

We have previously shown that electron donation to the heme,[5a,19a] increased basicity in the base, B,[19b] or increased polarity of the solvent[5a-d] increases dioxygen affinities but have little affect

$$-\underset{\underset{O_2}{|}}{\overset{\overset{B}{|}}{Fe}}- + CO \underset{M}{\rightleftharpoons} -\underset{\underset{CO}{|}}{\overset{\overset{B}{|}}{Fe}}- + O_2$$
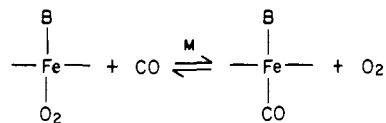
on carbon monoxide affinities. On the basis of these findings we proposed a "local polar effect" for increased dioxygen affinity in orthoamide-substituted tetraphenylhemes.[5j] More recently others have elaborated on this idea.[9,18,20,21]

The introduction of a cyclophane strap or cap across the face of the heme, to provide steric interference to ligand binding, has been variously reported to decrease both carbon monoxide and dioxygen affinities to similar extents,[5e,f,h] to decrease carbon monoxide affinity somewhat more than that of dioxygen,[5g,12] or to decrease CO affinity and slightly increase dioxygen affinity.[4f,g] These variations in the consequences of presumed steric effects have been attributed either to a polar effect of the connecting amide groups[5e,9f,11,13] or to steric differentiation of the linearly bound CO and angularly bound dioxygen.[4f,g,20]

Several recent studies of local polar effects[9,18,22] on dioxygen affinities seem to support the former interpretation involving the well-established polar differentiation of CO and O_2 binding.[5c] To further clarify the relationships between polar and steric effects we have considered the preparation of cyclophane heme compounds having very polar cyclophane straps. Such a strap might

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provide steric hindrance to dioxygen, carbon monoxide, and other ligands, but, due to the proximity of the polar group, it would also retard the dissociation of dioxygen and thus provide polar differentiation between CO and O_2 binding.

We now report the preparation of dioxygen and carbon monoxide binding to a new pyridine cyclophane heme (Figure 1) having increased local polarity near the binding site and a remarkably low value of M.

Experimental Section

Reagents. Toluene (Mallinckrodt AR) was purified by the literature[23] method, except that it was distilled from calcium hydride (Aldrich) and stored over 4 Å molecular sieves. Methylene chloride (Mallinckrodt AR), triethylamine (Aldrich), and pyridine (Mallinckrodt AR) were distilled from calcium hydride prior to use. Ferrous sulfate (Matheson-Coleman-Baker), 3,5-pyridinedicarboxylic acid (Aldrich), sodium dithionite (Fischer), sodium phosphate (Baker), and all other reagents (Mallinckrodt, analytical reagent) were used without futher purification. Carbon monoxide gas (Matheson, 99.9%) and oxygen (Linde Products, commercial grade) were used directly while argon (Linde Products, commercial grade) was passed through an oxygen scrubber (American Scientific Products) prior to use. 1,5-Dicyclohexylimidazole was synthesized as previously described.[24]

Spectrophotometers. The reported UV–vis spectra were digitally recorded on a Kontron Uvicon 810 spectrophotometer. NMR spectra were recorded on either a Varian EM-390 90 MHz or a 360 MHz spectrometer.[24]

Pyridine-porphyrin-5,5-cyclophane, [8,18-Bis(2-carbobenzyloxyethyl)-2,7,12,17-tetramethylporphyrin-3,13-pyridine-3,5-[5(1-oxo-2-aza),5(1-oxo-2-aza)]cyclophane, 1P. For 1 h 3 mL of thionyl chloride and 32.1 mg of 3,5-pyridinedicarboxylic acid were heated at reflux, the excess thionyl chloride removed under vacuum, the residue taken up in 5 mL of CH_2Cl_2, this removed under vacuum, and the residue dissolved in 10 mL of CH_2Cl_2. An 8.9-mL aliquot was combined with 11.1 mL of CH_2Cl_2 and placed into a 20-mL syringe of a two-syringe drive unit. Into the other syringe was added, under argon, 0.138 g (0.17 mmol) of 3,13-bis(3-aminopropyl)-8,18-bis(2-carbobenzyloxyethyl)-2,7,12,17-tetramethylporphyrin[24] and 1 mL of triethylamine in 19 mL of methylene chloride. Both solutions were added at 1 mL/min to 100 mL of deoxygenated methylene chloride under argon and stirred for 3.5 h. The solution was washed twice with 30 mL of water, dried over sodium sulfate, and evaporated to dryness. The residue was chromatographed on silica gel by eluting with methanol–chloroform (5:95 v/v). The desired porphyrin was collected in the first 200 mL of eluent to give 30.2 mg of the pyridine capped porphyrin, **1P** (17.5%). Mass spectrum: calcd 935; found 935. UV–vis (MeOH) 401, 501, 539, 568, 621. NMR ($CDCl_2$) δ 10.15 (s, 5 H, meso), 10.0 (s, 2 H, meso), 7.41–7.25 (m, 10 H, phenyl), 7.20 (m, 2 H, 2,6-pyridine H), 6.48 (s, 1 H, 4-pyridine), 5.2 (s, 4 H, CH_2-Ph), 3.7 (s, 6 H, CH_3), 3.63 (s, 6 H, CH_3), [δ 4.5 (m), 4.1 (m), 3.3 (m), 3.2 (m), 2.7 (m), 2.3 (m)] (side arm protons).

Pyridine Hemin 5,5-Cyclophane Chloride, 1^+Cl^-. Iron was inserted into the capped porphyrin, **1P**, by the standard ferrous sulfate method.[25] The product was purified by chromatography on silica gel by eluting with 200:1, 100:1, and finally 95:1 chloroform/methanol to yield 6.1 mg (20%) of 1^+Cl^-. UV–vis (toluene) 380,402, 505, 534, 634 nm.

Preparation of Pyridine Heme 5,5-Cyclophane, 1. Into a 50 mm × 5 mm test tube was added a small portion (<1 mg) of 1^+Cl^- dissolved in 1 drop of methylene chloride. The resultant solution was diluted with 0.1 to 0.2 mL of toluene. A few crystals of 1,5-dicyclohexylhexylimidazole were added, then the test tube was equipped with a serum cap. Carbon monoxide gas was bubbled through the solution for ca. 1 min. Reduction of the heme was accomplished by adding ca. 0.2 mL of saturated aqueous sodium dithionite in pH 9, 0.1 M sodium phosphate buffer and shaking vigorously until the bright red color of 1-DCIm(CO) was observed. After the layers were separated by centrifugation, the desired heme complex was transferred to a tonometer[5k] with a microliter syringe.

Kinetics were obtained with a 140-mL gas tonometer. Unless a base concentration study was being performed, the tonometer was charged with 2.9 mL of 0.7 M DCIm in toluene. An additional 0.5 mL of toluene then added and the resulting solution deoxygenated by bubbling CO gas through it for 30 min. The desired amount of reduced heme (above) was then added. Carbon monoxide gas was bubbled through until the volume
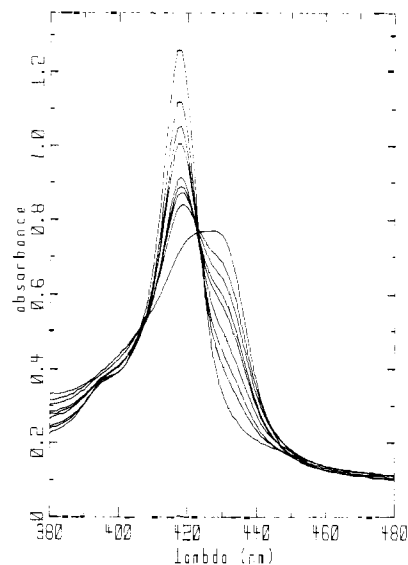
Figure 2. Titration of 1-DCIm (ca. 7 μM) with CO gas in toluene at 20 °C. Increasing absorbance at 417 nm corresponds to the following CO partial pressures (torr): 0.0, 10.2, 15.3, 20.3, 25.4, 61.0, 86.4, 137.3, and 700.0.

was reduced back to 2.9 mL. During this time, the W-10 septum (Applied Science), attached to the side of the tonometer and used to introduce the heme solution, was replaced. If the data at less than 1 atm of carbon monoxide were to be gathered, the tonometer was degassed by 3 freeze–evacuate–thaw cycles. Aliquots of either carbon monoxide or dioxygen gas were added to the tonometer via gas-tight syringes and equilibrated by stirring the solution in the large portion of the tonometer at 20 °C for 15 min prior to determining rates.

Determination of Rate Constants. The tonometer was placed into a water-jacketed cell holder at 20 ± 0.1 °C. The sample was photolyzed with either a Sunpak 611 flash gun (pulse width 0.6 ms) or a Phase-R Model DL-2100A tunable dye laser (pulse width 600 ns) rated at 1.0 J/pulse. Rhodamine 590 dye (Exciton) in absolute ethanol gave a pulse centered at 584 nm. When the flash gun was used, its output in the UV region was excluded from the sample with a yellow filter (444-nm cutoff). A Kodak 35 Wratten filter (flash gun only) and second monochromator were used to exclude the photolysis beam from the photomultiplier tube (PMT).

The monitoring beam was selected by a Zeiss PMQ-II monochromator with a 30-W tungsten bulb. Transient changes in the beam were monitored as previously described.[5k] When a rate constant is reported as being dependent on ligand concentration, at least four different concentrations were used. All rates were determined from three or more duplicate samples, unless otherwise stated.

Titration of 1 with DCIm. Approximately 10–20 μL of a ca. 1 mM solution of 1^+Cl^- in chloroform was added to a cuvette containing 3 mL of toluene and equipped with a septum. The resultant solution (ca. 8 μM) was bubbled with argon gas (saturated with toluene vapor) for 1 h. After addition of 0.25 mL of saturated aqueous sodium dithionite (0.1 M phosphate buffer) the solution was vigorously shaken for 1 min, and the layers were separated by centrifuging the cuvette. The initial UV–vis spectrum was recorded at 20 ± 0.1 °C, then aliquots of 0.127 M DCIm in deoxygenated toluene were added. The cuvette was shaken and centrifuged before intermediate spectra were recorded. All spectra were stored on a computer and analyzed by fitting the initial and final spectra (1 and 1-DCIm) to the intermediate ones. The resulting relative compositions were used to determine the binding constant, K^B.[1b]

Titration of 1-DCIm with Carbon Monoxide. The low ligand affinity of 1-DCIm made its direct titration with carbon monoxide possible. A 3-mL sample of 0.1 M DCIm in toluene was prepared and transferred to a tonometer equipped with an optical cell. Carbon monoxide gas, saturated with toluene vapor, was bubbled through the solution for 30 min. To this was added a few microliters of a concentrated (ca. 1 mM) 1-DCIm-CO solution, prepared as above, to give an absorbance at the Soret maximum of ca. 1.3 ($\sim7 \times 10^{-6}$ M). The carbon monoxide gas was removed by 5 freeze–evacuate–thaw cycles, which resulted in the formation of the five-coordinated 1-DCIm species. The tonometer was then filled partially with argon gas. Aliquots of CO gas were added via a gas-tight syringe, and the sample was stirred at 20 °C for 15 min. Spectra were recorded after each addition and stored on a computer. The titration was driven to completion by passing CO gas, saturated with

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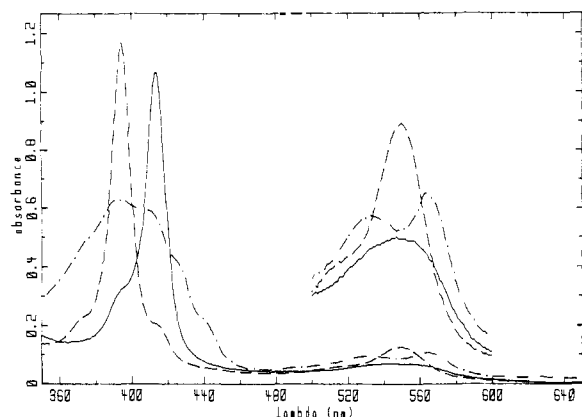
Figure 3. UV–vis spectra of **1** in toluene at ambient temperature: (–·–) **1**, four-coordinated heme; (– –) **1**-CO, under 730 torr of CO gas; (—) py-**1**-CO, 0.11 M pyridine. The latter two spectra are at the same concentrations. Insets are 7-fold expanded.
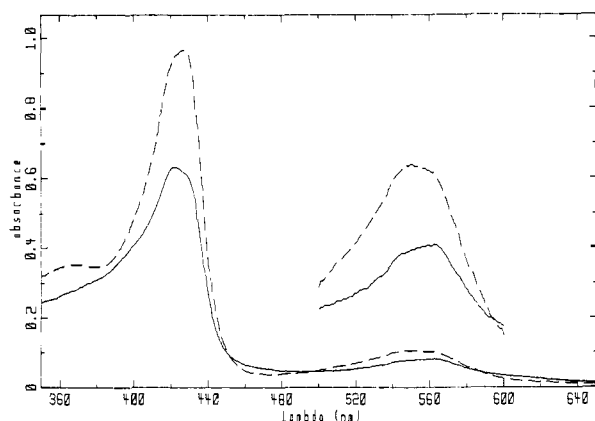
Figure 4. UV–vis. spectra of **1**: (– –) in toluene containing 0.18 M DCIm; (—) in pure 1-methylimidazole.

toluene vapor, for 10 min. A typical set of spectra are shown in Figure 2. Analysis of the data was done by the same curve-fitting procedure described for the base titration.
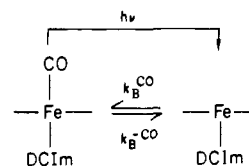
Results

Absence of Binding of the Internal Pyridine. A solution of about 5×10^{-6} M **1**$^+$Cl$^-$ in toluene was carefully degassed and reduced as described above. The spectrum, shown in Figure 3, is typical of four-coordinated iron porphyrins with this type of substitution pattern[26] and shows no sign of five-coordination. Addition of 1 atm of CO resulted in a spectrum which is essentially identical with that of mesoheme mono-CO complex. Thus, even with CO present, the pyridine is not bound. Addition of pyridine to the mono-CO adduct produced a spectrum typical of six-coordinated complexes (B–Hm–CO).

Steric Hindrance to External Base Binding. The spectrum of a solution of ca. 8 μM **1** and 0.7 M DCIm in toluene, prepared as described above, is shown in Figure 4. This spectrum is essentially identical with the spectrum of five-coordinated adamantane heme cyclophane, **4**, reported previously. The spectrum of **1** in pure 1-methylimidazole is also shown in this figure for comparison. It is clear that very little binding of the second base occurs even at this high concentration.

Binding of DCIm and Carbon Monoxide to 1. The low affinity of **1** toward imidazole and carbon monoxide allowed their binding constants to be determined by direct titration. Addition of aliquots of a solution of DCIm to **1** in toluene resulted in isosbestic

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(26) (a) Rougee, M.; Brault, D. *Biochemistry* **1975**, *14*, 4100. (b) Brault, D.; Rougee, M. *Biochem. Biophys. Res. Commun.* **1974**, *57*, 654. (c) Rougee, M.; Brault, D. *Ibid.* **1973**, *56*, 1364.

Scheme I

changes.[1b] Rather than analyze the titration data at one wavelength, the spectra were analyzed by fitting the entire initial four- and five-coordinate spectra to the intermediate spectra with a program adapted for this purpose. Hill plots of the data resulted in a value of $K^B = 6.2 \pm 0.4 \times 10^3$ M^{-1} (slopes: 0.91 and 1.0). A kinetic method, discussed below, of determining K^B gave a value of 2.8×10^3 M^{-1}, in fair agreement with the direct titration results. The K^Bs reported for anthracene-7,7-cyclophane, **3** (6.6 $\times$ 10^3 M^{-1}), and anthracene-6,6-cyclophane, **2** (6.0 $\times$ 10^3 M^{-1}), are in good agreement with that reported here.

Aliquots of carbon monoxide added to a 0.1 M DCIm toluene solution of **1**-DCIm resulted in isosbestic spectral changes (Figure 2). These data were analyzed by the same spectra-fitting procedure used above. Hill plots of the data from three runs (slopes: 1.07, 1.02, and 0.96) gave an average value of K_B^{CO} of 0.07 $\pm$ 0.002 torr^{-1} (2.7 $\pm$ 0.2 $\times$ 10^3 M^{-1}).

Kinetics of Carbon Monoxide Binding to 1-DCIm. The direct interpretation of carbon monoxide binding rates requires that Scheme I be obeyed. If the base concentration is not high enough, a second "base-off" mechanism competes for return of DCIm-heme-CO.[27] This situation has been discussed in detail.[24,27] A plot[1b] of DCIm concentration vs. the observed k_B^{CO} shows that the observed rate becomes constant above 0.6 M DCIm indicating the mechanism Scheme I attains. The average value of k_B^{CO} is 630 $\pm$ 33 M^{-1} s^{-1}.

A kinetic analysis including both base-on and base-off mechanisms,[24] and assuming that the rate of formation of DCIm-**1**-CO is the sum of k_B^{CO}[CO] and k_{CO}^{CO}[CO] and rapid preequilibria, gives eq 1. A nonlinear least-squares fit of the base concentration

$$\frac{k_{obsd}}{[CO]} = \frac{k_B^{CO}[B] + 1/2k_{CO}^{CO}K^{CO}[CO]}{K^B[B] + K^{CO}[CO]} \quad (1)$$

vs. k_{obsd} data gave reasonable values for the rate and binding constants. The value of 3400 M^{-1} s^{-1} for k_{CO}^{CO} was obtained from k_B^{CO} observed at low concentrations of base. At concentrations less than 0.04 M, the rate constant appeared to be leveling off at 3400 M^{-1} s^{-1}. The value of K^{CO}, calculated from eq 1, is 5.3 $\pm$ 0.8 $\times$ 10^4 M^{-1}, which compares well with the value of 3.7 $\times$ 10^4 M^{-1} for adamantane cyclophane **4**. Because steric hindrance differentiates the insides of these cyclophanes, these similar K^{CO} values, also similar to that of deuteroheme (2 $\times$ 10^4 M^{-1}),[26c] refer to outside binding of CO. This result further documents the conclusion that these cyclophanes are not strained.

The observed k_B^{CO} was also determined as a function of carbon monoxide concentration at high but constant DCIm concentration (0.7 M). Unlike most other hemes having high CO affinities, this heme displayed pseudo-first-order rate constants which, when plotted against CO concentration, revealed a nonzero intercept.[1b] A least-squares fit of the data to eq 2 resulted in k_B^{CO} of 549 $\pm$

$$k_{obsd}^{CO} = k_B^{CO}[CO] + k_B^{-CO} \quad (2)$$

5 M^{-1} s^{-1} and an intercept of 0.21 $\pm$ 0.02 s^{-1}. The equilibrium constant, calculated by dividing the slope by the intercept, is 2.6 $\times$ 10^3 M^{-1}, in excellent agreement with the 2.7 $\times$ 10^3 found by direct titration. The internal consistency of these methods of determining the carbon monoxide binding constants indicates that, at 0.7 M DCIm, the observed kinetics can be approximated by Scheme I. This simplification allows dioxygen kinetics to be studied with confidence.

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6508 *J. Am. Chem. Soc., Vol. 107, No. 23, 1985*

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Table I. Rate Constants for Hemes and Heme Proteins for the Binding of Carbon Monoxide and Dioxygen[a]

compound	solvent	k_B^{CO}, M^{-1} s^{-1}	k_B^{-CO}, s^{-1}	$k_B^{O_2}$, M^{-1} s^{-1}	$k_B^{-O_2}$, s^{-1}	$P_{1/2}^{O_2}$, torr	$P_{1/2}^{CO}$, torr	M	ref
chelated	H$_2$O/MTAB	3.6×10^6	0.009	2.6×10^7	47	1.0	0.002	500	5b
protoheme	benzene	1.1×10^7	0.025	6.2×10^7	4000	5.6	0.00025	22000	5i
chelated mesoheme	toluene, 10% CH$_2$Cl$_2$	8×10^6	0.05	5.3×10^7	1700	2.8	0.0005	5600	5k
	toluene	1.1×10^7		8.4×10^7	4800	4.9			5g
7,7-anthracene cyclophane heme	benzene	6×10^6	0.05	6.5×10^7	1000	1.4	0.0009	1500	24
6,6-anthracene cyclophane heme	benzene	3×10^4	0.05	1×10^5	800	700	0.17	4100	24
6,6-adamantane cyclophane heme	toluene	9.2×10^3	0.05	1.5×10^5	690	300	0.57	530	5g
5,5-pyridine cyclophane heme	toluene	6×10^2	0.24	1.1×10^4	68	540	37	14	this work
	o-C$_6$H$_4$Cl$_2$					290	62	5	this work
FePiv$_3$5ClIm	toluene	3.6×10^7	0.0078	4.3×10^8	2900	0.58	2.2×10^{-5}	27000	4g
FePocPiv-1-MeIm	toluene	5.8×10^5	0.0086	2.2×10^6	9	0.36	1.5×10^{-3}	270	4g

[a] Data at 20 or 25 °C, see original references for conditions and gas solubility.

Table II. Binding and Kinetics of **1** in Different Solvents

solvent	k_B^{CO}, torr^{-1} s^{-1}	k_B^{-CO}, s^{-1}	$k_B^{O_2}$, torr^{-1} s^{-1}	$k_B^{-O_2}$, s^{-1}	k_B^{CO}, torr^{-1}	$K_B^{O_2}$, torr^{-1}	M^a
toluene	7.56×10^{-3}	0.24	0.126	68	0.0268	0.0019	14
o-dichlorobenzene	4.09×10^{-3}	0.25	0.119	35	0.0162	0.0034	5
1-MeIm	1.17×10^{-3}	0.14			0.00842	0.0022	4

[a] These M values are determined in units of pressure.

Dioxygen Binding and Kinetics. The heme **1** rapidly and irreversibly oxidizes in the presence of dioxygen at room temperature. Thus, determination of the oxygen affinity by traditional titration is precluded.[4] However, the binding constant can be determined by a kinetic method used successfully for the anthracene and adamantane cyclophane hemes.[24] A partial pressure of at least 730 torr of carbon monoxide over a solution of DCIm-1-CO was required to prevent oxidation due to the low CO affinity.

In the presence of dioxygen, the two observed rates are dependent upon O$_2$ concentration. The slower rate is defined by eq 3 and can be used to determine the dioxygen affinity.[5g,24] A

$$k_B^{CO}[CO]/k_{obsd}^{slow} = K_B^{O_2}[O_2] + 1 \qquad (3)$$

plot of the partial pressures of dioxygen vs. k_{obsd}^{slow} is shown in Figure 5. This plot is the result of eight independent experiments. Equation 3, fitted by least squares to this data, afforded a slope ($K_B^{O_2}$) of $1.86 \pm 0.06 \times 10^{-3}$ torr^{-1} (155 M^{-1}) and an intercept of 1.01.

The fastor process was measured at the deoxy (428 nm) maximum and the carbonmonoxyheme/deoxy isosbestic point (407 nm). At both wavelengths it was possible to measure the fast rate without interference from the slow rate. This rate at 407 nm was found to be due to the appearance of absorbance and assigned to the formation of DCIm-1-O$_2$. The 428-nm datum was due to the loss of deoxy absorbance as O$_2$ bound to the five-coordinated heme. Under the conditions of the experiment, the formation of DCIm-1-O$_2$ is the approach to the equilibrium rate constant given in eq 4. The plot of dioxygen pressure vs. k_{obsd}^{fast} for six independent

$$k_{obsd}^{fast} = k_B^{O_2}[O_2] + k_B^{-O_2} \qquad (4)$$

experiments[1b] afforded $k_B^{O_2}$ (determined from the slope) of 0.13 $\pm$ 0.007 torr^{-1} s^{-1} (1.05×10^4 M^{-1} s^{-1}). The intercept is 46 $\pm$ 3 s^{-1}.

In order to better determine the value for the dioxygen dissociation rate, two additional methods of calculation were used. First the slope of the fast rate plot was divided by the slow rate slope ($k_B^{O_2}/K_B^{O_2}$) to give $k_B^{-O_2}$ of 67.7 s^{-1}. Secondly, the method of Momenteau and Lavalette,[9] given in eq 5, was used. The parameters k_B^{CO}, k_{obsd}^{fast}, and k_{obsd}^{slow} have the same meaning as discussed

$$k_B^{-O_2} = k_{obsd}^{slow} (k_{obsd}^{fast}/k_B^{CO}[CO]) \qquad (5)$$

above and are measurable for each data point. This allows the
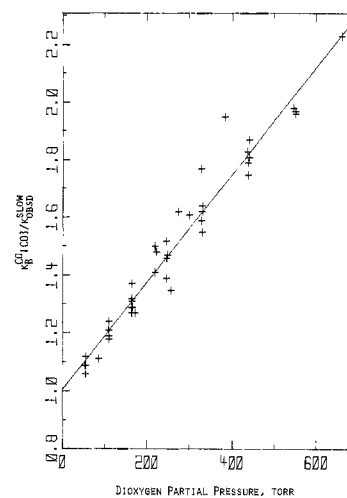
Figure 5. Plot of $k_B^{CO}[CO]/k_{obsd}^{slow}$ as a function of the dioxygen partial pressure over toluene (0.7 M DCIm) at 20 °C; composite of eight runs. The partial pressure of CO is ca. 730 torr. The slope is 1.86×10^{-3} torr^{-1} s^{-1}, and the intercept is 1.01.

value of $k_B^{-O_2}$ to be calculated at each point and gives 53 $\pm$ 5 s^{-1} as the dissociation rate. Thus all three methods gave essentially the same value, indicating that the dioxygen dissociation rate of **1** has been substantially reduced relative to adamantane[5g] and anthracene[24] cyclophane hemes. These results are listed in Table I.

Solvent Effects on Carbon Monoxide and Dioxygen Binding to 1. The above kinetic studies were repeated with 1-MeIm, o-dichlorobenzene (DCB),[18] and DMF as solvents. The carbon monoxide affinities were determined kinetically, using eq 2. The slope[1b] was divided by the intercept from plots of k_{obsd}^{CO} vs. CO pressure to give K_B^{CO}. Values of 0.008 $\pm$ 0.001 and 0.02 $\pm$ 0.009 torr^{-1} were found for the solvents 1-MeIm and o-dichlorobenzene, respectively. These values are ca. 2–3 times lower than that found for **1** in toluene (0.03 torr^{-1}). No affinity constant was measured in DMF as it was observed that DMF binds to **1** and displaces DCIm, even at 0.7 M concentration of the latter.

The association and dissociation rates are listed in Table II. It was found that most of the lowering of the CO affinity resulted from decreases in the association rate constant. Little change in

the CO dissociation rate was observed on going to more polar solvents. The pressure units for the binding constants were chosen because the solubilities of CO and O_2 are not known in 1-MeIm or DCB.

Accurate measurement of the dioxygen affinity in 1-MeIm was not possible for two reasons. First, 1 atm partial pressure of CO was required to keep DCIm-1-CO reduced in the presence of O_2; hence, more than 1 atm total pressure was present in the tonometer. Secondly, even under 1 atm of CO gas, fairly rapid oxidation occurred. However, comparison of the values among themselves should be valid. Dioxygen affinity in 1-MeIm was found to be 0.0022 ± 0.00015 torr^{-1},[1b] similar to the 0.0019 torr^{-1} found in toluene. Moreover, because the CO affinity is reduced, the M value (K^{CO}/K^{O_2}) decreases from 14 to 4. In DCB, the O_2 affinity is $3.4 \pm 0.8 \times 10^{-3}$ torr^{-1},[1b] and the corresponding M value is 5.

An attempt to measure the approach to equilibrium rate for O_2 in DCB was made difficult by the presence of more than one fast rate. However, an analysis by eq 5 with two data points give an O_2 dissociation rate of 35 ± 2 s^{-1}. With use of the observed $K_B^{O_2}$ and $k_B^{-O_2}$, a value of 0.12 torr^{-1} s^{-1} for the association rate was calculated. These data are summarized in Table II.

Discussion

The first remarkable property of the pyridine, 5,5-cyclophane heme **1**, the ferrous derivative, is the failure to form either an internal or external iron–pyridine complex. The pyridine-strapped

$$(6)$$

$$(7)$$
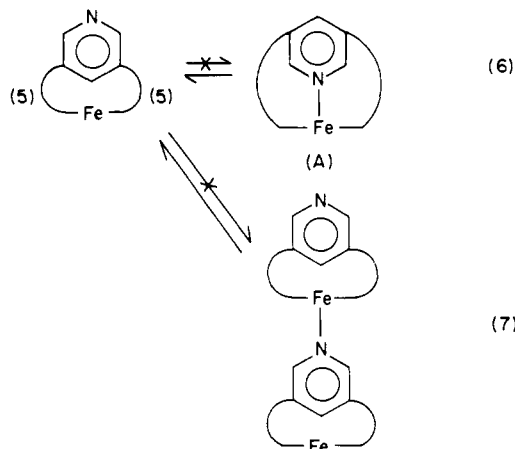
heme compounds reported by Momenteau et al.,[9] having as little as six atoms connecting the pyridine to the porphyrin ring on each side, showed complete internal binding as represented in A. Our cyclophane **1** has five atoms making this connection on either side. It is even more remarkable that carbon monoxide binds, presumably to the outside of the heme, without inducing pyridine binding. It is well-known that the binding of CO and bases to
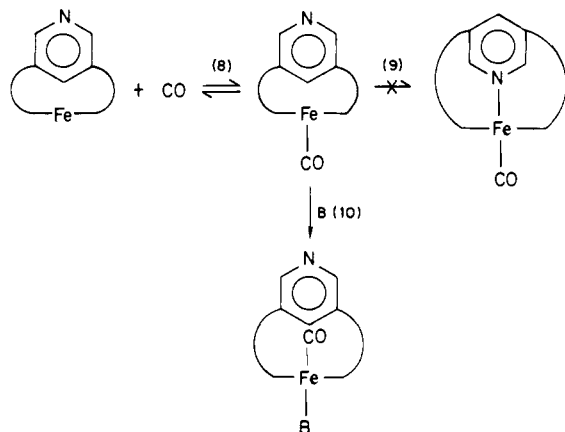
iron(II) porphyrins is synergistic, each increasing the affinity of the other by several orders of magnitude.[26] We can therefore conclude that the pyridine-bound form (chelated form) of **1** or 1-CO encounters sufficient strain to prevent internal binding.

Therefore, this compound is not a "hanging base"[9] or chelated heme,[5] but an interesting member of the class of porphyrin cyclophanes.[24] We can therefore study the steric and polarity effects of the pyridine dicarboxamide group as a cyclophane cap in comparison to previously reported anthracene and adamantane cyclophanes shown in Figure 1.
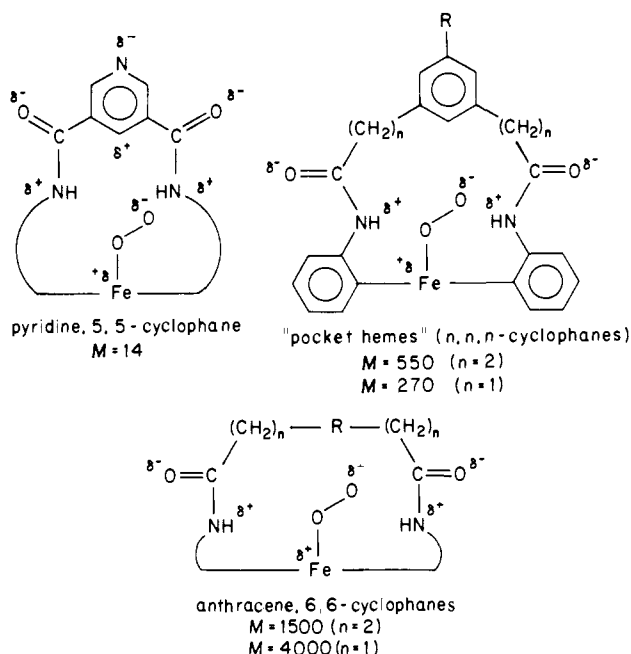
The Polar Pocket Effect. The principal discovery presented here is the rather spectacular decrease in the M value ($K_B^{CO}/K_B^{O_2}$) from about 20 000 for simple type hemes to a value of 14 for 1-DCIm in toluene and 5 in o-dichlorobenzene. All the previous cyclophanes studied contained amide groups in the connecting side chains as does **1**, and all have values of M (270–4000) which are less than the values for simple hemes such as chelated protoheme in benzene (~ 20000, Table I). However, chelated protoheme has an M value of ~ 500 in the polar environment of aqueous cetyltrimethylammonium bromide. We therefore conclude that the low M value for 1-DCIm results from the introduction of the two amide groups and the polar pyridine ring, in *direct* contact with bound dioxygen. This group reduces the dioxygen association rate constant ($k_B^{O_2}$) by 7600 through steric repulsion. This same proximity reduces the dioxygen dissociation rate ($k_B^{-O_2}$) by 70 times, through polar effects,[28] with the result that $K_B^{O_2}$ decreases 110 times. However, since the polar effect does not reduce k_B^{-CO} (rather some strain actually increases it slightly), and k_B^{CO} is reduced by 17 500, the K_B^{CO} is reduced 75 000 times, the full effect of steric hindrance. It is therefore the canceling of steric effects on dioxygen binding by polar reduction of $k_B^{-O_2}$ which brings about the reduction in M. Further reduction of $M = 5$ in more polar solvents confirms this postulate (Table II). We can now rationalize the discrepancies in M values and their interpretations as applied to various cyclophanes. In all cases steric effects reduce the association rates approximately the same for O_2 and CO, indicating similar steric effects. Dissociation rates for CO and isonitriles are little affected as the size of the pockets decrease, indicating that the bending of the Fe–CO bond has little or no affect on binding and thus no affect on CO vs. O_2 differentiation.

The figures below, along with the examination of molecular models, reveal interesting changes in pocket polarity as the pocket size decreases. As is especially clear with the n,n,n-cyclophanes (pocket porphyrins), the amide groups are brought closer and aligned better for dipole interaction with the Fe^+–O–O^- dipole as the pocket size decreases. In the case of **1**, the amide groups are brought closer and the dipole is increased by the pyridine group as compared to the anthracene cyclophane. In some cases, the possibility of improved hydrogen bonding to bound dioxygen also exists.[9,21]

These results appear to confirm our earlier conclusions that *solvent or local polarity effects* are the principal factors in the determination of M values, the differentiation of O_2 and CO binding. Steric differentiation, being determined by association rates, is controlled by the size and shape of the ligand and not by the geometry (bent vs. linear) of the bound state as is so often suggested.

Applications to Heme Proteins. In view of these conclusions we should reconsider the control of dioxygen and carbon monoxide bonding in heme proteins. The heme pockets in hemoglobin and myoglobin are often referred to as being hydrophobic and sterically conjested.[3] Interestingly, the amino acid side chain, to which steric hindrance to ligand approach is commonly attributed, is an imidazole which is *very polar*. Thus the pocket in these heme proteins, having a very polar group within van der Waals distance (and, in fact, hydrogen-bonding distance) of the bound ligand in an environment of rather low dielectric constant, presents a very polar environment for dioxygen binding. Additionally, movement of this imidazole, under the influence of protein conformational change, can greatly alter the dipole–dipole interaction between

(28) A referee has suggested that the reduction of O_2 dissociation rate might be due to a hindrance of O_2 escape from the heme:O_2 cage. Recent studies of NO and RNC quantum yields (J. Marsters, unpublished) show that, on the contrary, steric hindrance *increases* quantum yields. These studies, which will be discussed elsewhere, provide futher and more definitive evidence for a common mechanism of operation of steric effects on O_2, CO, and NO.

pyridine, 5, 5 - cyclophane
M = 14

"pocket hemes" (n, n, n - cyclophanes)
M = 550 (n = 2)
M = 270 (n = 1)

anthracene, 6, 6 - cyclophanes
M = 1500 (n = 2)
M = 4000 (n = 1)

Heme Protein
Dioxygen Complex

this imidazole and the $Fe^{\delta+}$–$OO^{\delta-}$ dipole of bound dioxygen. Thus, the proteins afford pocket environments similar to that provided by the "polar pocket porphyrin" described here.

We propose that both heme proteins and model compounds sometimes control the absolute affinities for both carbon monoxide and dioxygen using steric effects and differentiate carbon monoxide and dioxygen with "local polar effects" as previously discussed.[5a,9,18,21]
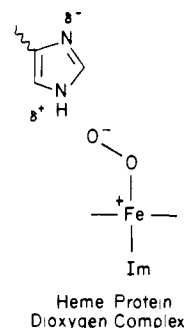
It now appears that the affinities of CO and O_2 for heme compounds can be controlled independently and therefore materials could be designed to preferentially carry either CO or O_2.

Supplementary Material Available: Eight figures comprising a titration of **1** with 1,5-dicyclohexylimidazole and seven plots of the rates of reaction of carbon monoxide or dioxygen with **1** (after carbon monoxide photolysis) as functions of concentrations of carbon monoxide, dicyclohexylimidazole, or dioxygen; slopes and intercepts of these plots are discussed in the text (9 pages). Ordering information is given on any current masthead page.

A Complex Containing a Ni–O Unit at the Center of a Porphyrin. The X-ray Crystal and Molecular Structure of the Nickel(II) Complex of Octaethylporphyrin N-Oxide Dianion

Alan L. Balch,* Yee-Wai Chan, and Marilyn M. Olmstead

Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received March 26, 1985

Abstract: The structure of the nickel(II) complex of octaethylporphyrin N-oxide dianion has been determined by X-ray crystallography. The complex, $C_{36}H_{44}N_4NiO$, crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with two molecules per unit cell of dimensions $a = 10.610$ (2) Å, $b = 13.203$ (2) Å, $c = 13.199$ (1) Å, $\alpha = 115.49$ (1)°, $\beta = 102.33$ (1)°, $\gamma = 102.85$ (1)° at 140 K. The structure was refined to $R = 0.068$ for 518 parameters and 3639 reflections. The molecule contains a nickel ion bound to three of the four nitrogens and the oxygen in a somewhat distorted planar array (Ni–N: 1.922 (4), 1.929 (5), 1.900 (4) Å; Ni–O: 1.788 (4) Å). The distance from nickel to the remaining nitrogen of 2.489 (5) Å indicates there is no direct bond between these atoms. The N–O distance is 1.363 (6) Å. The oxygen atom lies 0.65 (1) Å above the porphyrin, and the pyrrole ring to which it is attached is tilted by 38.3 (4)° out of the porphyrin plane. The structure is disordered as a result of packing of pairs of major (82.6%) and minor (17.4%) forms. The basic structural features of the porphyrin core in the two forms are similar.

Experimental[1–4] as well as theoretical studies[5,6] have suggested that the reactive forms of highly oxidized heme proteins involved in oxygen activation and heme destruction may contain structure

1 (M = Fe) in which an oxygen atom is inserted into a N–Fe bond

1   2

as an alternate to the more conventional oxo structure **2**. Although a number of stable oxo metalloporphyrins that can serve as models for **2** (M = Fe) have been structurally characterized,[7–10] no ex-

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