temperature is lowered. The temperature dependence of the proton line widths also supports a monotonic increase in the effective axial ligand field strength as the temperature is lowered.

The present analysis suggests that a detailed study of the g tensor as a function of solvent and temperature is likely to lead to an elucidation of the electronic nature and the thermodynamic characteristics of the axial solvation once a precise theory relating g values to the spacings in the d orbital energy manifold is developed. The temperature-dependent dipolar shifts reported here suggest a novel and particularly simple method for monitoring the magnetic anisotropy, although a more sophisticated description of the isotropic shifts in low-spin, planar d^7 ions may be desirable for obtaining more quantitative values for the magnetic anisotropy. Furthermore, the average g value would have to be determined before obtaining an adequate description of the g tensor at any temperature.

A single-crystal determination of the components of the bulk susceptibility tensor as a function of temperature would be particularly illuminating, inasmuch as the deviation of the temperature dependence of the dipolar shift in solution from that predicted from the solid-state data would necessarily reflect only the change in susceptibility tensor due to variable solvation. Attempts are in progress to obtain the required single crystal of a cobalt(II) porphyrin.

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Thermodynamics of Ligand and Oxygen Binding to Cobalt Protoporphyrin IX Dimethyl Ester in Toluene Solution

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Abstract: Thermodynamic data for the binding of ligands to cobalt(II) protoporphyrin IX dimethyl ester (CoP) are presented. Data for formation of the five-coordinate complex LCoP are compared with thermodynamic data for the reversible binding of oxygen (1:1) to LCoP. Enhanced oxygen binding to LCoP for L = imidazole, 1-methylimidazole, and *N,N*-dimethylformamide is discussed in terms of the π-donor properties of these ligands. Spectral data for the formation of five- and six-coordinate Co(II) complexes are presented, as well as data for the 1:1 oxygen adducts and peroxo-bridged complexes.

The binding of ligands to metal porphyrins has been the subject of considerable interest in recent years.[3-5] Thermodynamic data are now available for ligand binding to divalent Fe,[6,7] Ni,[8,9] Cu,[9] Zn,[8,10] Cd,[10] Hg,[10] and Mg[11] porphyrins. Both five- and six-coordinate complexes have been reported. Although visible spectroscopic data for Co(II) and Co(III) porphyrins in coordinating solvents have been reported, changes in spectra for Co(III) species have been interpreted in terms of changes in coordination number[12] and changes in oxidation state[13] (Co(III) $\rightleftarrows$ Co(II)). Esr spectral evidence for five- and six-coordinate cobalt porphyrin complexes at $-196°$ has been presented,[14] but no definitive data on equilibrium constants or visible spectral changes accompanying changes from four- to five- to six-coordinate cobalt(II) porphyrins have been reported.[14a]

We were particularly interested in ligand binding to cobalt(II) protoporphyrin IX dimethyl ester (CoP) in connection with our studies of reversible oxygenation of cobalt porphyrins.[15-17] Since an initial five-coordinate complex is typically required for oxygen binding to cobalt to occur, it is important to know quantitatively the conditions under which the five-coordinate complex, LCoP, forms. Comparison of the thermodynamics of ligand binding to CoP and oxygen binding to LCoP should provide insight into the factors which stabilize the coablt–oxygen bond and also should increase our knowledge of the donor–acceptor properties of the oxygen in these complexes.

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Table I. Thermodynamic Data for Ligand Binding to CoP in Toluene Solution

Ligand	Temp, °C	log K_1, M^{-1}	ΔH,[a] kcal/mol	ΔS,[a] eu	pK_a
DMF	23	1.18			
	0	1.63 ± 0.1	−7.9	−21	−2.0[b]
	−23	2.25			
4-CNpy	23	3.24			
	0	3.88 ± 0.1	−10.0	−19	1.86[c]
	−23	4.60			
py	23	3.78			
	0	4.03 ± 0.1	−6.9	−6	5.27[c]
	−23	4.70			
4-*t*-Bupy	23	3.85			
	0	4.40 ± 0.1	−9.0	−13	5.99[c]
	−23	5.07			
Imidazole	23	3.64			
	0	4.00 ± 0.1	−7.9	−10	6.95[d]
	−23	4.70			
CH_3-Im	23	3.70			
	0	4.40 ± 0.1	−10.7	−19	7.25[d]
	−23	5.15			
4-NH_2py	23	4.00			
	0	4.48 ± 0.1	−8.1	−9	9.30[c]
	−23	5.10			
Piperidine	23	3.83			
	0	4.61 ± 0.1	−10.4	−17	11.30[c]
	−23	5.25			

[a] The values of ΔH and ΔS were obtained from a weighted least-squares analysis of the data points. Since error estimates are not very meaningful for such a small number of data points, we have estimated the standard deviations derived from the least-squares analysis for all of the above data sets. We conclude that $\sigma(\Delta H) = 0.6$ kcal/mol and $\sigma(\Delta S) = 2$ eu and that errors within two standard deviations seem reasonable. [b] Estimated from data given in J. T. Edward, H. S. Chang, K. Yates, and R. Stewart, *Can. J. Chem.*, **38**, 1518 (1960). [c] K. Schofield, "Hetero-Aromatic Nitrogen Compounds," Plenum Press, New York, N. Y., 1967, p 146. [d] K. Hoffman, *Chem. Heterocycl. Compounds*, **6**, 3 (1953).

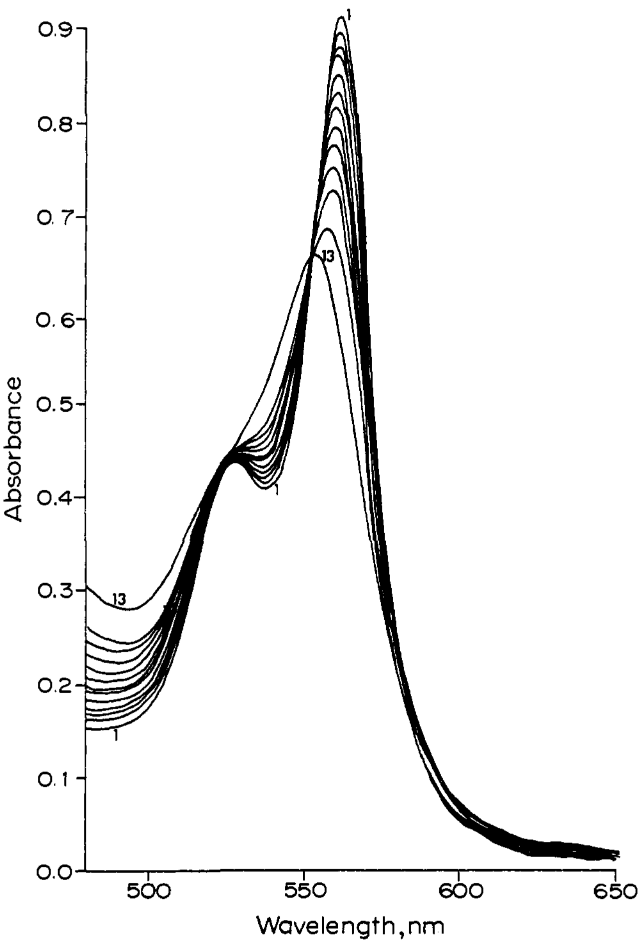

Figure 1. Typical spectrophotometric titration for the determination of the equilibrium constant for the formation of LCoP at 23°. Spectrum 1 is that of 4 × 10^{-6} *M* CoP. The subsequent spectra, with decreasing maximum intensities (2–13), are at various added concentrations of 1-methylimidazole: 0.97, 1.94, 2.92, 4.86, 6.80, 8.75, 12.5, 16.4, 20.9, 28.4, 37.8, and 2200 × 10^{-5} *M*, respectively.

Experimental Section

Materials. Protoporphyrin IX dimethyl ester, grade 1, lot 100 C-2680, was purchased from Sigma Chemical Co. and used without further purification. Co(II) protoporphyrin IX dimethyl ester (CoP) was prepared by the method described by Falk[18] and recrystallized from benzene.

Toluene was refluxed over, and distilled from, CaH_2 prior to use and degassed three times by the freeze–thaw method.

Pyridine, piperidine, 4-*tert*-butylpyridine, and 1-methylimidazole (CH_3-Im) were distilled from KOH prior to use. Imidazole (Im), 4-aminopyridine, and 4-cyanopyridine were recrystallized from benzene and dried *in vacuo*. *N*,*N*-Dimethylformamide (DMF) was distilled from CaO prior to use.

The low-temperature visible cell and procedure for measurement of the equilibrium constant for reversible oxygenation of LCoP have been described previously.[15] Concentrations of L used in these determinations were 3.5 × 10^{-5}–1.0 × 10^{-4} *M* for the nitrogen donor bases and 4.5 × 10^{-2}–4.5 × 10^{-1} *M* for DMF, sufficient to give greater than 90% LCoP formation under the conditions of the experiments in all cases.

Ligand-Binding Measurements. Equilibrium constants for ligand binding to CoP were determined by a spectrophotometric titration procedure. Aliquots of ligand solution (10^{-2}–10^{-3} *M* in toluene, except for DMF which was added neat) were added to 50 ml of a toluene solution of CoP (5 × 10^{-6} *M*) under N_2 from a calibrated syringe. Complete spectra from 700 to 450 nm were recorded. Equilibrium constants were calculated as described by Marzilli and coworkers[19] from the change in absorption at λ = 560 nm. Values of K_1 were found to be independent of the wavelength used. Data points were confined to concentrations of L where the ratio LCoP/CoP ranged between 0.25 and 4.0. Measurements were made at ambient (23°), ice–slush bath (0°), and CCl_4-slush bath temperatures (−23°).[20] Dilution corrections were kept small, and good isosbestic points resulted. Ligand concentrations were adjusted for volume contraction of toluene at lower temperatures, but the corrections were very small.

Results

CoP + L $\rightleftarrows$ LCoP, K_1. Addition of ligand (~10^{-3} *M*) to a toluene solution of CoP in the absence of air results in a decrease in the intensity of the Soret peak (404 nm) and the α peak (563 nm), accompanied by a small blue shift (8 nm) of the latter (Figure 1). No observable shift of the Soret band occurs.

Equilibrium constants (K_1) were obtained at 23, 0, and −23° by following the change in visible spectrum with ligand concentration. Plots of log [LCoP/CoP] *vs.* log [L] gave straight lines with slope 1.0 ± 0.2 consistent with 1:1 complex formation for each of the ligands investigated. Assignment of the LCoP species was further indicated from esr spectra at −196°. N superhyperfine splittings, ^{59}Co splittings, and *g* values, similar to those reported[14] for five-coordinate amine complexes of cobalt tetraphenylporphyrins, were observed. Equilibrium constants obtained from the log: log plots, and thermodynamic functions obtained from van't Hoff plots, are given in Table I.

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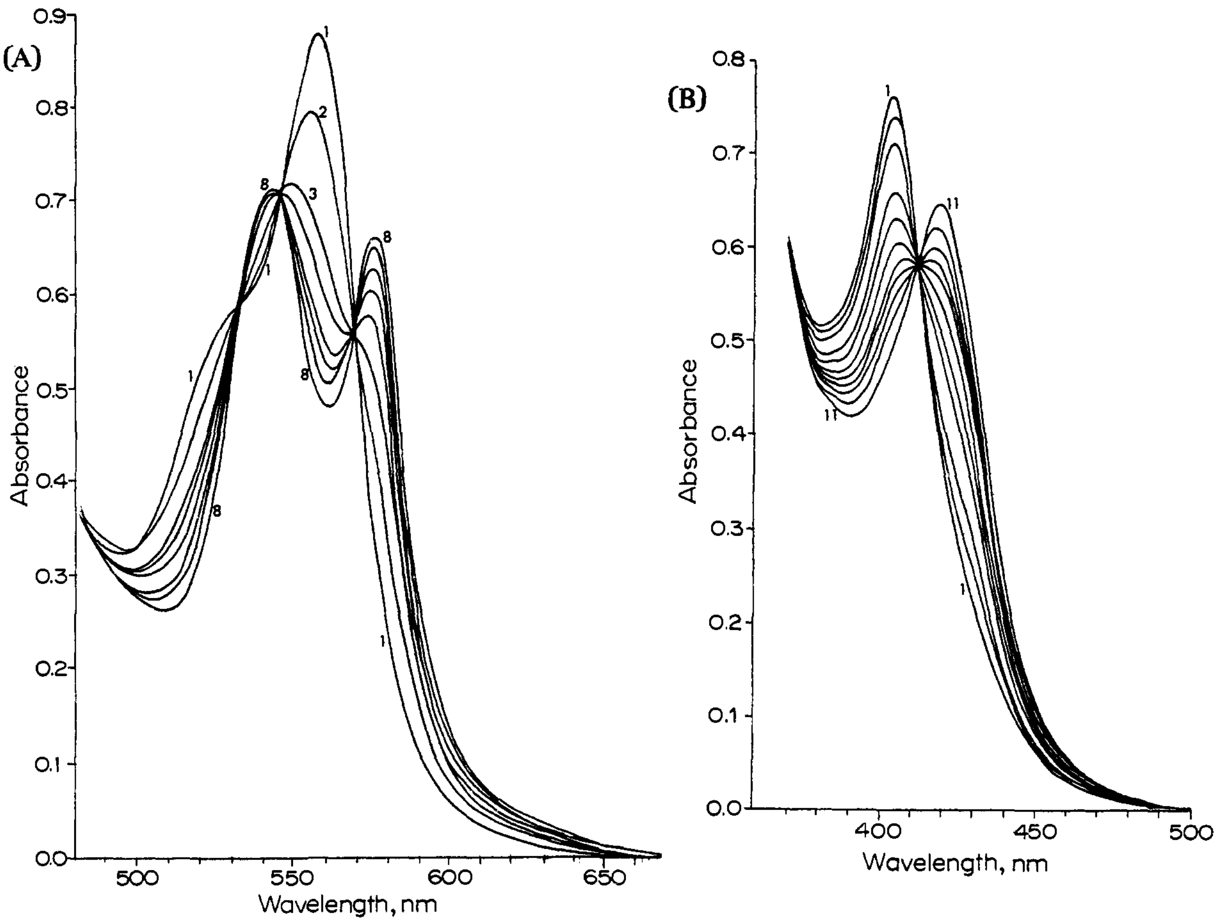

Figure 2. Typical spectrophotometric data for determination of the equilibrium constant for 1:1 O_2 binding to LCoP: (A) in visible region at −45°; [CoP] = 4.35×10^{-6} *M*, [Im] = 3.3×10^{-6} *M*; the O_2 pressures (Torr) for spectra 1–8 are 0.0, 20.4, 55.5, 103.6, 159.2, 195.7, 355.5, and 747.2, respectively; (B) in Soret region at −45°; [CoP] = 6×10^{-7} *M*, [Im] = 1.7×10^{-5} *M*; the O_2 pressures (Torr) for spectra 1–11 are 0.0, 17.5, 31.4, 48.6, 57.6, 72.4, 87.2, 106.7, 141.0, 301.2 and 760.0, respectively.

$LCoP + O_2 \rightleftarrows LCoP(O_2)$, K_{O_2}. On exposure to oxygen at low temperatures, solutions of LCoP exhibit a change in visible spectrum, which is a function of the oxygen pressure and which is reversible, *i.e.*, pumping off the oxygen restores the spectrum of LCoP (Figure 2). We have previously assigned this spectral change to the formation of a 1:1 oxygen adduct.[15] Upon formation of the oxygen complexes, a splitting of the single maximum of LCoP at 555 nm occurs, giving two peaks at 540 and 573 nm. In the Soret region, a new peak appears at 420 nm with a corresponding disappearance of the peak at 404 nm assigned to LCoP. The formation of the 1:1 oxygen complex has been corroborated by esr measurements in toluene at −196° and in fluid dimethylformamide solution[16] at −44° up to +18°.

The method used for evaluation of the equilibrium constants and thermodynamic functions for the reversible oxygenation has been described previously.[15] The data are presented in Table II. Thermodynamic data are not presented for the 4-cyanopyridine system because of the large estimated errors in log K_{O_2}. These large errors are a result of our inability to obtain an accurate estimate of the spectrum of the fully oxygenated complex, since the 4-cyanopyridine system has a very poor affinity for oxygen even at very low temperatures. In all other cases we were able to obtain the $LCoP(O_2)$ spectrum by cooling to ∼−70° and correcting for temperature effects.

$LCoP(O_2) + LCoP \rightarrow LCoP(O_2)PCoL$. Although toluene solutions of LCoP do not form measurable amounts of the 1:1 oxygen complex at room temperature, under some conditions a slow irreversible reaction with oxygen may take place. A detailed study of the kinetics of this reaction, which we assign to the formation of a μ-peroxo-bridged Co(III) dimer or possibly to the formation of a Co(III) hydroxy complex, is described elsewhere.[17] The formation of the Co(III) species is accompanied by a spectral change in the visible region similar to that observed for the 1:1 oxygen adduct, and the Soret band now appears at 428 nm. The position of the Soret band clearly distinguishes the 1:1 oxygen complex from the μ-peroxo or hydroxy complex.

$LCoP + L \rightleftarrows L_2CoP$, K_2. At high concentrations of piperidine (>1 *M*), an additional change in spectrum is observed which is a function of the piperidine concentration. A new band in the Soret region at 420 nm appears with a corresponding decrease in the intensity of the band at 404 nm assigned to LCoP; an increase in the intensity ratio β/α, relative to the CoP spectrum, is observed in the visible region. We assign these changes in spectrum to the formation of the six-coordinate complex L_2CoP. The intensities of the two Soret peaks indicate that about 60% of the cobalt is present as the six-coordinate complex at room temperature in pure piperidine (Figure 3). On dilution of the solution with

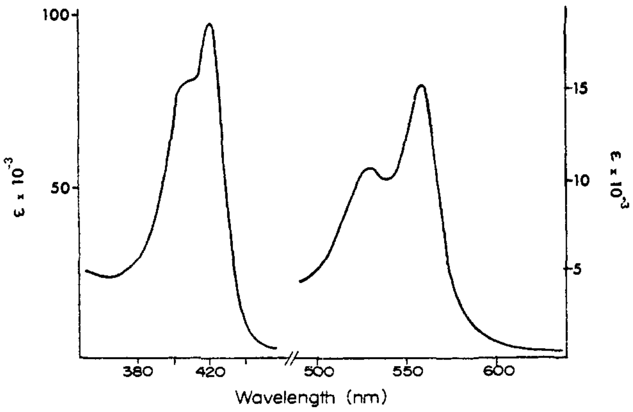

Figure 3. Spectrum of CoP in piperidine at room temperature. The Soret region shows peaks due to five- and six-coordinate complexes.

Table II. Thermodynamic Data for Reversible O_2 Binding to Cobalt(II) Protoporphyrin IX Dimethyl Ester–Ligand in Toluene Solution

Compound	Temp, °C	log K_{O_2} (mm^{-1})	ΔH,[a,b] kcal/mol	ΔS,[a,b] eu
DMF·CoP	−31	−2.88[e]		
	−45	−2.27	−11.0	−59
	−63.5	−1.34		
4-CNpy·CoP[c]	−45	−3.8		
	−63.5	−3.3		
py·CoP[d]	−45	−2.84		
	−57.5	−2.25	−9.2	−53
	−63.5	−2.09		
4-*t*-Bupy·CoP[d]	−37.4	−3.12		
	−45	−2.77	−9.8	−56
	−63.5	−1.97		
Im·CoP	−31	−2.50		
	−45	−1.84	−11.3	−58
	−57.5	−1.25		
CH_3-Im·CoP[d]	−31	−2.36		
	−37.4	−2.04	−11.8	−59
	−45	−1.70		
4-NH_2py·CoP	−31	−2.58		
	−37.4	−2.34		
	−45	−2.05	−9.9	−53
	−63.5	−1.20		
pip·CoP	−31	−2.92		
	−45	−2.35	−9.0	−50
	−63.5	−1.65		

[a] Standard state of 1 Torr. [b] See footnote *a* of Table I. [c] Thermodynamic data cannot be calculated with any accuracy due to large errors in K_{O_2} because of low oxygen affinity (<half oxygenated at −63.5° with 760 Torr O_2 pressure). [d] The values of ΔH and ΔS and their standard deviations differ slightly from those quoted in ref 15 and 17 because of the application of a more rigorous analysis in the present case. [e] Estimated errors in log *k* are ±0.06 except for 4-CNpy where the errors are ±0.3; the errors differ slightly from those quoted in ref 15 and 17 because of the application of a more rigorous analysis in the present case.

toluene, the peak at 420 nm, resulting from the six-coordinate complex, decreases relative to the peak at 404 nm. Similarly, raising the temperature results in an increase in the 404-nm peak and a corresponding decrease in the 420-nm peak. The intensities of the two peaks in this system at room temperature are unaffected by the presence of oxygen. From the variation of the spectrum with piperidine concentration, log K_2 is estimated to be $-0.7 \pm 0.3\ M^{-1}$ at room temperature; the temperature effect shows that the formation of L_2CoP from LCoP is an exothermic process.

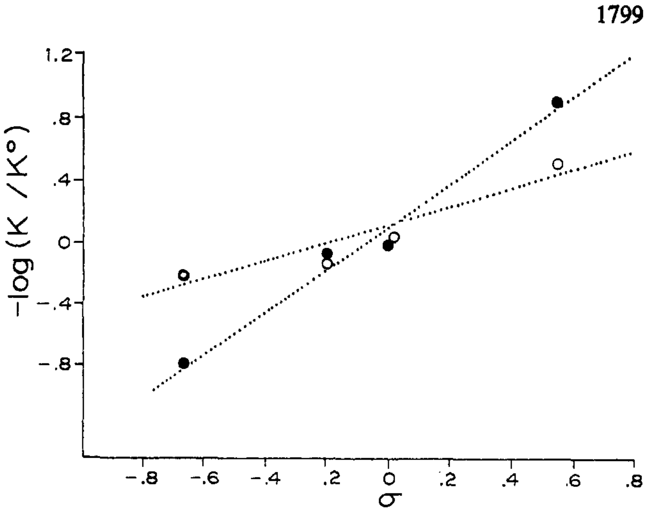

Figure 4. Hammett plots for the para-substituted pyridine systems: ○, ligand binding; ●, oxygen binding; K° refers to py·CoP; K refers to (substituted-py)CoP.

No appreciable amounts of the six-coordinate complex are formed at room temperature with the weaker coordinating solvents, pyridine and 4-*tert*-butylpyridine. At −40°, formation of the six-coordinate complex is observed for 4-*tert*-butylpyridine.[21]

Walker[14] has reported esr evidence at −196° for six-coordinated complexes of cobalt(II) tetraphenylporphyrins. Esr spectral parameters, obtained at −196° in our studies with the protoporphyrin system in 1 *M* piperidine or neat *tert*-butylpyridine, are very similar to those reported by Walker.

At the high ligand concentration required for the formation of the six-coordinate complexes, solvent effects are likely to play an important role, and thus no attempt was made to obtain thermodynamic data for the $LCoP + L \rightleftarrows L_2CoP$ equilibrium.

Discussion

The thermodynamic data presented in this work are limited to cobalt protoporphyrin IX dimethyl ester in toluene solution. Large effects resulting from changes in solvent and porphyrin have been reported in similar studies.[6–8,16] Therefore, comparison of the data presented here with those on different systems must be made with some caution. We will restrict our attention to data obtained for benzene or toluene solutions. Although some differences between protoporphyrin IX dimethyl ester and tetraphenylporphyrin are expected, comparison of general trends in ligand binding for these porphyrins may be valid.[22]

Ligand Binding. A comparison of log K_1, ΔH, and ΔS in Table I clearly demonstrates that no simple correlation exists between any of these parameters and the pK_a of the protonated ligand. Such a correlation is not expected for such a diverse set of ligands. If we restrict our attention to the set of structurally related para-substituted pyridine ligands, where Hammett relationships are known to exist,[23,24] a reasonable correlation is observed (Figure 4).

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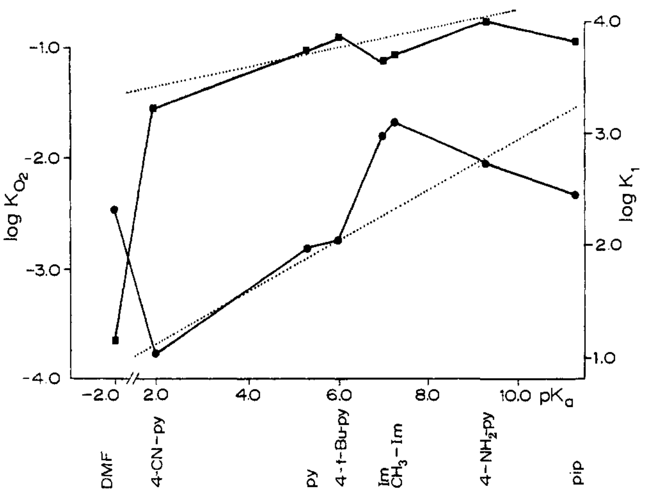

Figure 5. Comparison of ligand and oxygen binding data as a function of the pK_a of the coordinated ligand: ●, data for oxygen binding (left hand ordinate); ■, data for ligand binding (right hand ordinate); dashed lines show correlation of log K_{O_2} and log K_1 with pK_a for the pyridine systems.

The observed linear free energy relationship (LFER) may be compared with similar LFER's reported for 1:1 pyridine binding to Zn, Cd, and Hg tetraphenylporphyrins.[23] These Hammett plots give ρ values of +1.5, +2.2, and +3.1 for Zn(II), Cd(II), and Hg(II), respectively, compared with the value of +0.6 obtained from Figure 4 for the present Co(II) system. The positive ρ values indicate that the reaction is favored by electron-donating substituents on the pyridine. The trend for Zn, Cd, and Hg parallels the σ polarizability of the metal ion.[23] The behavior of the Co systems would be expected to be similar to that of the Zn systems.

Although various stoichiometries have been reported for the reaction of pyridines with nickel(II) porphyrins,[3,8] it is clear that the stability constants also increase with increasing basicity of the pyridine, and the six-coordinate complex is formed only at high ligand concentration.[25] The small K_2 values for Ni(II) and Co(II) may be understood in terms of destabilization of the d_{z^2} orbital on formation of the six-coordinate complex. For Fe(II) porphyrin systems, where the d_{z^2} orbital is vacant after going to a six-coordinate low spin complex, K_2 is much larger;[6,7] the destabilization of the d_{z^2} orbital likely confers the low-spin configuration on the six-coordinate Fe(II) complexes.

Spectral changes, similar to those we assign to six coordination in our cobalt(II) protoporphyrin IX dimethyl ester systems, have been interpreted in terms of Co(II) $\rightleftarrows$ Co(III) equilibria in a corresponding mesoporphyrin IX system.[13] The spectral changes do not appear to be consistent with changes in oxidation state: the esr measurements readily show that the Soret band at 420 nm is due to six-coordinate $L_2Co^{II}P$ and not to Co(III). Our observed spectral changes are in good agreement with studies by Datta-Gupta on the spectra of cobalt tetraphenylporphyrins in coordinating and noncoordinating solvents.[12] Formation of a six-coordinate from a five-coordinate Co(III) complex was accompanied by a shift of the Soret band to about 20 nm longer wavelength; this may be compared to a corresponding shift of 16 nm in our Co(II) systems.

It should be noted also that our observed spectral changes in the Soret region are very similar to those reported by Baker and coworkers[9] for formation of the bis(piperidine) complex of nickel(II) mesoporphyrin IX, although these workers did not observe the intermediate five-coordinate complex.

The spectral changes accompanying change in coordination number of cobalt porphyrins are of interest. Any theoretical attempt to explain metal porphyrin spectra must take coordination effects into account. The spectrum of CoP undergoes only small changes on forming the five-coordinate adduct LCoP, but much more pronounced changes occur on formation of the six-coordinate L_2CoP. The observed change in the position of the Soret band is not consistent with the proposed rule that two ligands shift the Soret band twice as much as one ligand.[26] We observe no shift in the Soret band on formation of the five-coordinate adduct while a shift of 16 nm occurs on formation of the six-coordinate complex.

Oxygen Binding. As with the binding of a ligand L to CoP, no simple, general relationship exists between ΔG, ΔH, or ΔS of the oxygenation of LCoP and the basicity of the ligand L. Again, however, a good correlation is found between log K_{O_2} and the pK_a of the protonated pyridine bases, and the Hammett plot shown in Figure 4 gives an ρ value of +1.47. This is much larger than the value for ligand binding to CoP and supports an $LCo^{III}P \cdot O_2 \cdot^-$ formulation for the oxygen complex, in which substantial transfer of electron density from cobalt to oxygen occurs. Such a formulation is suggested by (a) esr studies on the oxygen complexes of cobalt(II) porphyrins[14] and cobalt(II) Schiff base species[27] and (b) a crystal structure of py·Co(bzacen)O_2 (bzacen = *N,N'*-ethylenebis(benzoylacetoniminide)), which shows[28] the oxygen bound in a bent manner with an O–O distance of 1.26 Å, within 0.02 Å of the reported O–O bond length of the superoxide ion.[29]

A comparison of equilibrium constants for oxygenation and ligand binding is shown in Figure 5, in which log K_{O_2} at −45°, and log K_1 at 23°, are plotted against

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(25) Our findings that the K_1 values for tetraphenylporphyrin systems and protoporphyrin IX systems are of comparable magnitude (ref 22) lead us to believe that the magnitude of the binding constants of nitrogen-donor axial ligands are similar for Co(II) and Ni(II) porphyrins. The first ligand is added at low ligand concentrations ($K_1 \sim 10^3$–10^4 M^{-1} at 25° for Ni(tetraphenylporphyrin)), and this process results in very little spectral change.[8] Apparent discrepancies in the literature can be accounted for if, at higher ligand concentrations ($\sim$1 *M*), a diamagnetic LNi(porphyrin) complex forms a paramagnetic L_2Ni(porphyrin) complex. Abraham and Swinton (*J. Chem. Soc. B*, 903 (1969)) and McLees and Caughey (*Biochemistry*, 7, 642 (1968)), studying mesoporphyrin- and protoporphyrin IX dimethyl ester systems, report overall formation constants β_2 of $\sim 10^{-2}$ M^{-2}, but both groups are studying possibly the LNi(porphyrin) + L $\rightleftarrows$ L_2Ni(porphyrin) equilibrium. The $n = 2$ value, observed by McLees and Caughey in plots of log (NiL_n/Ni) :log L, may arise from neglect of solvent–ligand ($CHCl_3$–piperidine) interactions which were noted by Abraham and Swinton. Using a quoted value of $\sim$0.2 M^{-1} for the formation constant of the chloroform–piperidine complex changes the free ligand concentration markedly; for example, the log L range for 4–10 *M* total piperidine is approximately doubled after correcting for formation of the solvent complex, and this could lead to a measured *n* value twice the true one. We have been unable to observe any significant spectral change on adding piperidine at low concentrations to solutions containing the nickel complex of protoporphyrin IX dimethyl ester.

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pK_a of the protonated base. The lines drawn serve only as a visual aid (similar profiles are observed throughout the temperature ranges studied, and the different temperatures for the two K values were chosen for convenience). The reasonably linear correlations for the log K_{O_2} and log K_1 values with pK_a of the substituted pyridines are represented by the dashed lines, and such trends hold for all the temperatures studied. Consideration of the data at each of the temperatures shows the significant finding that the log K_{O_2} values for the DMF, imidazole, and methylimidazole systems are much greater than that expected from the relative basicities of these ligands. Such differences are attributed to the π-donor properties of these ligands. The bonding of the oxygen molecule in the cobalt complexes has been explained in terms of σ donation from a nonbonding sp^2 lone pair on oxygen to the d_{z^2} orbital on cobalt, accompanied by synergistic π back-bonding from the filled cobalt d_{xz} (or d_{yz}) orbitals into the empty π^* orbitals of oxygen.[30,31] Since ligands coordinated trans to the oxygen will compete for π-electron density on the cobalt, the binding of O_2 to LCoP will be sensitive to the π-donating or -accepting ability of the axial ligand L. Good π acceptors will decrease π-electron density on the metal, resulting in a weaker Co–O_2 bond; while good π donors will promote oxygenation by increasing the electron density available for back-bonding. Imidazoles are much better π donors than pyridines[32,33] and the strong π-donor properties of DMF have been demonstrated[34] in studies of carbonyl-stretching force constants in LMo(CO)$_5$. The relatively large values of log K_{O_2} for these ligand systems may be understood then in terms of their π-donor properties, and this is reflected in more negative ΔH values. Walker[35] has noted also that oxygenation of LCoP (where CoP is the cobalt(II) complex of tetra(*p*-methoxyphenyl)porphyrin) is much more favorable when L is *N*-methylimidazole rather than para-substituted pyridines. Other workers have shown that in molecular oxygen complexes, the greater the electron density on a metal, the stronger the metal oxygen bond.[36,37]

The log K_{O_2} for the piperidine system appears almost 1 order of magnitude less than expected from a consideration of its basicity. This essentially non-π-bonding ligand would also be expected to favor O_2 coordination compared with a π-accepting pyridine ligand of similar basicity. The reason for the low log K_{O_2} values is not clear, but steric effects could play a role.

Considering the nature of the LCoP(O_2) complex in terms of a $Co^{II} + O_2 \rightleftarrows Co^{III}O_2\cdot^-$ equilibrium, the oxidation–reduction potential of the cobalt, and its dependence on the ligand L and the porphyrin, should be related directly to the ease of formation of the oxygen complexes. The LCoP systems with the lowest standard reduction potentials would be expected to have the greatest affinity for molecular oxygen; or, in other words, ligands which stabilize cobalt(III) relative to cobalt(II) would give systems with the highest affinity for oxygen. It would be of interest to determine the standard reduction potentials of the LCoP systems studied in the present work; data available[38] for some cobalt(II) mesoporphyrin IX systems are too limited for any comparisons to be made between reduction potentials and K_{O_2}. More extensive data on iron[39] and manganese porphyrin[40-42] complexes do indicate that increased basicity of the axial ligand leads to more negative reduction potentials.

Imidazole is reported to bind to Mn(III) more strongly than to Mn(II) and is more effective than pyridine in stabilizing Mn(III) against reduction to Mn(II).[41] Mössbauer studies on pyridine, piperidine, and imidazole complexes of ferric and ferrous porphyrins have shown that of these ligands imidazole forms the least stable complex with the ferroporphyrin and the most stable complex with the ferriporphyrin.[32] The imidazole is thought to have the greater capacity to stabilize high positive charge by dissipation of this charge over the imidazole ring.[4]

Thus, the greater affinity of the imidazole complexes for oxygen can be rationalized either in terms of the π-acceptor properties of the coordinated oxygen, or the stabilization of cobalt(III) in the oxygen complex. The former tends to emphasize the π-donor properties of the ligand, while the latter is likely to include both σ and π effects.

In view of the ability of the very weakly basic DMF ligand to promote oxygenation equally as well as the strongly basic piperidine ligand, it appears that the π-donor properties of the axial ligand play the dominant role in oxygen binding to cobalt. This is of interest since the axial ligands involved in natural reversible oxygen carriers are known to be good π donors (imidazole in hemoglobin[43] and myglobin,[44] and probably sulfur ligands in hemocyanin[45]).

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