Steric and Electronic Effects in the Coordination of Amines to a Cobalt(II) Porphyrin[1a,b]

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Abstract: The equilibrium constants and free energies of formation of a series of 1:1 complexes between amines and $\alpha,\beta,\gamma,\delta$-tetra($p$-methoxyphenyl)porphinatocobalt(II) in toluene were measured by spectral methods. Equilibrium constants were also measured as a function of temperature for some amines in order to obtain ΔH and ΔS values. The results show cobalt–nitrogen bond strengths in the range of 8–10 kcal/mol. A plot of log K *vs.* the pK_a of the conjugate acid of the amine shows a linear relationship within each type of amine (pyridines, imidazoles, aliphatic amines). Complexes with imidazoles were found to be most stable, suggesting that imidazoles are better π acceptors from the d_π orbitals of the cobalt. Steric interactions, as evidenced by the equilibrium constants when the amine is γ-collidine, quinoline, acridine, benzimidazole, and 1,2-dimethylimidazole, give some feeling for the distance the cobalt must lie out of the plane of the porphyrin ring. The relationship of this work to present theories of the heme–heme interaction in hemoglobin is discussed.

In an earlier epr investigation of cobalt(II) porphyrins and their amine and molecular oxygen complexes,[2] the following species were identified by their characteristic epr spectra: the four-coordinate complex CoP in the solid state and in toluene solution, the 1:1 amine adduct CoP·B, the 2:1 amine adduct $\text{CoP}\cdot\text{B}_2$, and the oxygen adduct $\text{CoP}\cdot\text{B}\cdot\text{O}_2$. The equilibria involved are summarized in the following reactions

$$\text{CoP} + \text{B} \overset{K_1}{\rightleftarrows} \text{CoP}\cdot\text{B} \qquad \text{“five-coordinate amine adduct”} \quad (1)$$

$$\text{CoP}\cdot\text{B} + \text{B} \overset{K_2}{\rightleftarrows} \text{CoP}\cdot\text{B}_2 \qquad \text{“six-coordinate amine adduct”} \quad (2)$$

$$\text{CoP}\cdot\text{B} + \text{O}_2 \overset{K_3}{\rightleftarrows} \text{CoP}\cdot\text{B}\cdot\text{O}_2 \qquad \text{“O}_2\text{ adduct”} \quad (3)$$

$$\text{CoP}\cdot\text{B}_2 + \text{O}_2 \overset{K_4}{\rightleftarrows} \text{CoP}\cdot\text{B}\cdot\text{O}_2 + \text{B} \qquad \text{“O}_2\text{ adduct”} \quad (4)$$

where P represents a series of para-substituted *meso*-tetraphenylporphyrins ((p-X)TPP) and B represents some Lewis base. The slow disappearance of the epr signal in samples containing a mixture of CoP·B and $\text{CoP}\cdot\text{B}\cdot\text{O}_2$ has been interpreted[2] as evidence of the reaction

$$\text{CoP}\cdot\text{B} + \text{CoP}\cdot\text{B}\cdot\text{O}_2 \overset{K_5}{\rightleftarrows} \text{B}\cdot\text{CoP}\cdot\text{O}_2\cdot\text{COP}\cdot\text{B} \quad (5)$$
$$\text{“binuclear complex”}$$

Since the epr signal disappears very slowly at room temperature,[3] it does not interfere with the investigation of reaction 1 in air at room temperature or with investigation of reactions 3 and 4 at low temperatures.[3]

Considerable interest has recently been shown in regard to the nature of the bond between cobalt and oxygen in the reversibly formed monomeric oxygen adducts. The Co(II) analog of hemoglobin, “coboglobin,” shows the same sort of cooperative binding of oxygen as does hemoglobin.[4] Also, some reactions of coenzyme B_{12} have been postulated to proceed through a Co(II) “free radical” intermediate.[5] Therefore it appeared that an investigation of the thermodynamics of equilibria 1–4, as a function of amine and porphyrin ring substituents, might shed some light on the electronic and steric factors which influence these reactions. In this report[1a,b] is presented a detailed study of steric and electronic effects for reaction 1; the following paper[3] describes electronic and steric effects on reactions 2–4.

Experimental Section

The cobalt porphyrin used for the work described below was $\alpha,\beta,\gamma,\delta$-tetra($p$-methoxyphenyl)porphinatocobalt(II), Co(p-OCH_3)-TPP, which was prepared according to the procedure described in ref 2. It was found necessary to chromatograph the cobalt porphyrin within a few days of when it was to be used, in order to avoid a catalytic decomposition to a Co(II) complex.[3,6]

Liquid amines were distilled from zinc dust and barium oxide; solid amines were recrystallized twice from benzene. Toluene was freshly distilled from sodium hydride.

Reaction 1 was investigated in the temperature range of 20–50° by measuring the visible absorption spectra of a series of solutions in which the concentration of amine was varied. The visible peak at 5320 Å decreases in extinction coefficient and shifts very slightly to longer wavelength as the concentration of amine is increased, as shown in Figure 1. Good isosbestic points for the formation of this five-coordinate complex were observed until the concentration of amine reaches approximately 0.1 *M;* above this concentration nonisosbestic behavior was often observed. This nonisosbestic behavior was probably due to the formation of molecular complexes between the aromatic amine and the π system of the porphyrin. An alternate explanation could have been the formation of the six-coordinate amine complexes, but these compounds are not generally observed at room temperature in amine concentrations of 0.1–1 *M.*[3] The equilibrium constants for reaction 1 were measured at three or four temperatures within the 20–50° range, and ΔH_1 was determined from the slope of the van't Hoff plots. It was not necessary to protect the samples used for measuring K_1 from air, since equilibrium 3 is not favorable at room temperature; in each case, it is estimated that less than 0.8% of the five-coordinate amine adduct will be coordinated to O_2 at room temperature in air.[3]

Results and Discussion

The thermodynamic data for reaction 1 at 25° are presented in Table I for some typical amines of different basicities, π-bonding capabilities, and steric factors. The values of ΔH_1 and ΔS_1 are presented for a representative group of amines. The values of log K_1 from Table I are plotted against the pK_a values of the conjugate acids of the amines in Figure 2.

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[1] (a) Preliminary report presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1, 1971, No. INOR 146. (b) Presented at the XIV International Conference on Coordination Chemistry, Toronto, Canada, June 27, 1972.

[2] F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970).

[3] F. A. Walker, *ibid.*, **95**, 1154 (1973).

[4] (a) B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Soc. U. S.*, **67**, 637 (1970); (b) B. M. Hoffman, C. A. Spilburg, and D. H. Petering, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 343 (1971).

[5] B. Babior and D. C. Gould, *Biochem. Biophys. Res. Commun.*, **34**, 411 (1969); B. M. Babior, *J. Biol. Chem.*, **245**, 6125 (1970).

[6] F. A. Walker and R. F. Trecartin, unpublished results.

Table I. Thermodynamic Data for Reaction 1 at 25°

Amine[a]	pK_a (BH$^+$)	K_1, M^{-1}	$-\Delta G_{298}$, kcal/mol (±0.05)	$-\Delta H_{298}$, kcal/mol (±1)	$-\Delta S_{298}$, cal/(mol deg) (±4)
Py	5.22	485 ± 29	3.66	8.5	16
4-MePy	5.98	794 ± 64	3.95	7.3	11
3,4-Me$_2$Py	6.46	1083 ± 122	4.14	9.0	16
4-Me$_2$NPy	9.70	4124 ± 301	4.93		
3,5-Cl$_2$Py	<2.84	191 ± 8	3.11		
4-MeO$_2$CPy	4.8	503 ± 38	3.68		
2,4,6-Me$_3$Py	7.43	68 ± 5	2.50		
IsoQ	5.14	644 ± 20	3.83		
Quin	4.94	15.9 ± 1.2	1.64	~0	−6
Acr	5.58	<0.1			
Im	6.65[b]	1400 ± 150	4.28		
N-MeIm	7.06	2370 ± 218	4.60	11.4	23
5-Cl-N-MeIm	5.45	1244 ± 125	4.22		
N-AcIm	3.6	785 ± 120	3.98	10.1	20
1,2-Me$_2$Im	7.85	617 ± 39	3.80		
BzIm	5.18[b]	275 ± 26	3.33		
N-SiMe$_3$Im	*c*	1387 ± 153	4.29		
Pip	11.12	2430 ± 238	4.61	6.8	7
Mor	8.70	1583 ± 176	4.36		
Quinuc	10.60	1546 ± 134	4.35		

[a] Abbreviations: Py = pyridine, 4-MePy = 4-picoline, 3,4-Me$_2$Py = 3,4-lutidine, 4-Me$_2$NPy = 4-dimethylaminopyridine, 3,5-Cl$_2$Py = 3,5-dichloropyridine, 4-MeO$_2$CPy = methyl isonicotinate, 2,4,6-Me$_3$Py = γ-collidine, IsoQ = isoquinoline, Quin = quinoline, Acr = acridine, Im = imidazole, N-MeIm = 1-methylimidazole, 5-Cl-N-MeIm = 5-chloro-1-methylimidazole, N-AcIm = *N*-acetylimidazole, 1,2-Me$_2$Im = 1,2-dimethylimidazole, BzIm = benzimidazole, N-SiMe$_3$Im = 1-trimethylsilylimidazole, Pip = piperidine, Mor = morpholine, Quinuc = quinuclidine (1,4-ethylenepiperidine). [b] Corrected for the fact that ImH$^+$ (and BzImH$^+$) can lose H$^+$ from either of its two nitrogens (log 2). [c] pK_a (BH$^+$) not known.

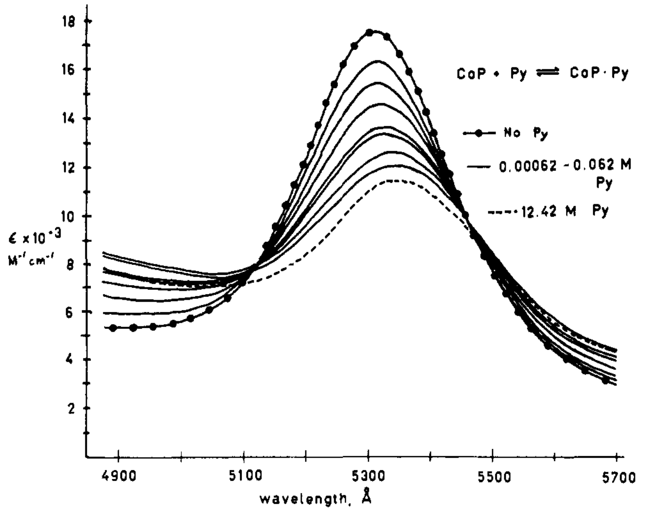

Figure 1. Visible spectral changes upon addition of pyridine to Co(p-OCH$_3$)TPP. Top line is for Co(p-OCH$_3$)TPP in the absence of pyridine. Solvent is toluene. Nonisosbestic behavior of the 12.42 *M* pyridine trace probably indicates spectral changes due to solvation of the five-coordinate pyridinate complex by excess pyridine, since K_2 is much less than 1.[3]

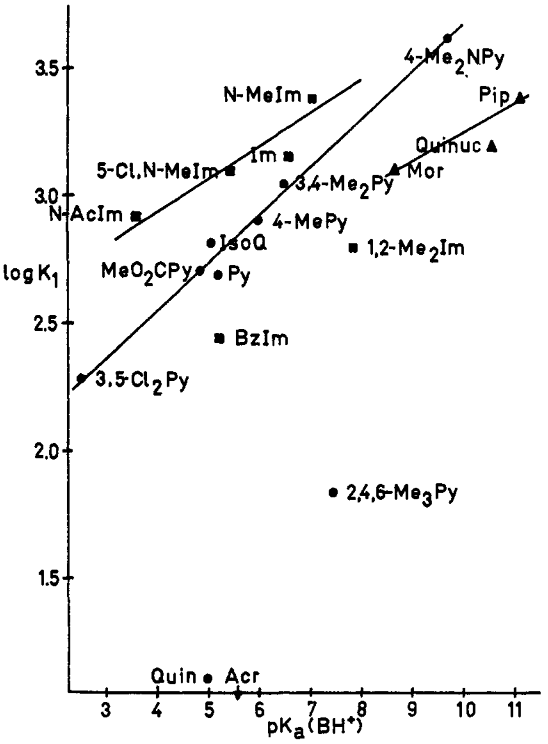

Figure 2. Relationship between amine basicity (σ-donor strength) and log K_1. Abbreviations are as given in footnote *a* of Table I.

The enthalpies of reaction 1 appear, from the data of Table I, to parallel roughly the free energies of the reactions; however, the parallelism is not perfect, as may be seen by the variation in the entropy of the reaction. Typically one might expect that for a reaction such as 1, ΔS_1 would be similar in each case where similar steric and solvation effects operate. The data of Table I indicate that aromatic amines generally show more negative ΔS_1 values than the aliphatic amine, which is probably due to different types of solvation of the complex when B is an aliphatic amine. The entropies of solvation of Co(p-OCH$_3$)TPP, Co(p-OCH$_3$)TPP·B, and B are all expected to be large and negative in toluene solution,[7] particularly when B is an aromatic

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(7) The nmr spectra of diamagnetic and paramagnetic transition metal tetraphenylporphyrins show significantly different chemical shifts for the pyrrole protons in benzene or toluene than in other solvents, such as CDCl$_3$, CH$_2$Cl$_2$, and CS$_2$.[8,9] This probably indicates a change in the ring current deshielding effects due to molecular complex formation between the aromatic porphyrin ring and the aromatic ring of the solvent molecules.

(8) F. A. Walker and G. L. Avery, *Tetrahedron Lett.*, 4949 (1971).

(9) G. N. LaMar and F. A. Walker, *J. Amer. Chem. Soc.*, in press.

amine, and it is difficult to estimate what the contribution to ΔS_1 from solvation effects will be.

ΔS_1 varies linearly with ΔH_1, giving an isoequilibrium temperature of about 360 ± 10°K. (The isoequilibrium temperature is the slope of the plot of ΔS_1 *vs.* ΔH_1. It represents the temperature at which each reaction would have the same ΔG_1.[10]) Thus, room temperature (298°K) is far enough away from the isoequilibrium temperature that log K_1 is a sensitive measure of pK_a (BH$^+$) dependence (Figure 2). The experimental error in the determination of K_1 was generally about 10%, and the slopes of the van't Hoff plots gave rise to errors in ΔH_1 of ± 1 kcal/mol, leading to errors of ± 4 eu in ΔS_1. Thus, only general conclusions concerning ΔH_1 and ΔS_1 may be reached.

The enthalpies of reaction 1 for aromatic amines (pyridines and imidazoles) are more negative than for the aliphatic amine (piperidine). The extra stabilization of the cobalt–nitrogen bond may arise from involvement of the π^* orbitals of the aromatic amines in some degree of π back-bonding. This same effect is observed more clearly in the linear free energy plot of Figure 2, where it is seen that in the absence of steric interactions, imidazoles generally form more stable complexes with Co(p-OCH$_3$)TPP than do pyridines of the same σ-donor strength; aliphatic amines form less stable complexes than either type of aromatic amine. Since the π-symmetry orbitals of the low-spin Co(II) (d^7) ion are completely filled, this would suggest that imidazoles are better π acceptors from Co(II) in Co(p-OCH$_3$)TPP than are pyridines. The results for this system are in contrast to the conclusions reached from investigation of iron(II) and iron(III) porphyrin–amine complexes[11] and several aqueous Cu(II) amine complex systems.[12] (The results also suggest that isoquinoline has similar energy π^* orbitals to the pyridines.) Since the direction and the extent of π bonding depend critically on the energies of the metal d$_\pi$ and ligand π and π levels, it is possible that the strong-field nature of the porphyrin ligand may shift the π-symmetry orbitals of Co(II) to the proper energy so that they are more similar to the energy of the imidazole than to the pyridine π^* orbitals. Further experiments are underway to test this hypothesis. It is interesting that such a π-bonding effect should be noted in this system, since it is generally expected that π back-bonding to an axial ligand should be relatively weak when the metal is bonded to a porphyrin.

In addition to the effects of π bonding on the stability of the five-coordinate amine complex, Figure 2 also shows steric effects on the stability of the amine complex. Molecular space-filling models (Corey, Pauling, Koltun) indicate that if the cobalt atom remains in the plane of the porphyrin ring when the amine is bonded, serious van der Waals repulsions will occur between the π system of the porphyrin and the hydrogen atoms bonded to the carbons α to the nitrogen of the amine when the amine is one of the pyridines or the secondary and tertiary aliphatic amines (piperidine, morpholine, and quinuclidine) but less when the amine is an imidazole. Molecular models also show that when methyl groups are substituted on the carbons α to the bonding nitrogen, serious steric repulsions result in forming the cobalt–nitrogen bond unless the cobalt moves significantly out of the plane. The values of K_1 for sterically hindered amines provide some suggestion of how far the cobalt atom is out of the plane. For the hindered substituted amines considered, 1,2-dimethylimidazole shows the smallest lowering of K_1 (relative to nonhindered imidazoles), probably both because of the more favorable geometry of the five-membered ring and also because only one methyl group is adjacent to the bonding site. On the other hand, γ-collidine (2,4,6-trimethylpyridine) shows a larger decrease in K_1 (as compared to pyridines of similar basicity but no steric hindrance). For γ-collidine to bond to cobalt with a Co–N bond length of 2.05 Å to relieve the van der Waals repulsions between the methyl groups and the π system of the porphyrin, the cobalt would have to be about 1.3 Å out of the plane of the porphyrin ring. Since the epr spectra of all of the five-coordinate amine complexes are almost identical,[2] it is likely that the hybridization of the Co atom is nearly the same in each case, which suggests that the position of cobalt is very similar in each of the five-coordinate complexes and is thus probably close to that required for bonding of γ-collidine. Of course, the only geometric quantity that can be estimated from molecular models is the approximate distance from the plane of the porphyrin ring to the nitrogen of the amine, which for γ-collidine is about 3.3 Å. If the Co–N bond is longer than 2.05 Å, as it is in the six-coordinate bis(piperidine)cobalt(II) tetraphenylporphyrin (2.44 Å),[13] then the cobalt may not be as far out of the plane as 1.3 Å. However, it is clear from the epr parameters[2] that the hybridization of cobalt is different in the five-coordinate amine complexes than it is in the four- or six-coordinate cobalt porphyrins,[14] which strongly suggests that the cobalt is significantly out of the plane.

Quinoline also falls far below the other aromatic amines in the stability of its 1 : 1 complex with Co(p-OCH$_3$)TPP and has an extremely weak Co–N bond, which is probably due to approximately the same degree of steric repulsion as that found for γ-collidine. Interestingly, benzimidazole shows significantly less lowering of K_1 due to steric repulsion than does quinoline. This is undoubtedly due to the more favorable bond angles of the five-membered imidazole ring, which act to remove much of the steric interaction with the hydrogen of the carbon of the adjacent ring (8-H for quinoline, 4-H for benzimidazole).

When a second ring is fused onto the quinoline to form acridine, no coordination of acridine to Co(p-OCH$_3$)TPP is evidenced by changes in the visible spectrum. Serious distortion of the visible spectrum did occur at high concentrations ($\gg$0.1 *M*) of these amines, which suggests that they may be involved in molecular complex formation with the π system of the porphyrin. Epr investigations of toluene solutions containing Co(p-OCH$_3$)TPP and an excess of acridine

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[10] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 324–326; S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *J. Amer. Chem. Soc.*, **92**, 299 (1970).

[11] L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967).

[12] P. R. Huber, R. Griesser, and H. Siegel, *ibid.*, **10**, 945 (1971); W. J. Eilbeck, F. Holmes, G. G. Phillips, and A. E. Underhill, *J. Chem. Soc. A*, 1161 (1967).

[13] W. R. Scheidt, *J. Amer. Chem. Soc.*, submitted for publication.

[14] D. Kivelson and F. A. Walker, unpublished work.

at low temperatures show evidence of some sort of complex formation, although the epr spectrum observed is different from that of a typical five-coordinate amine complex[2] ($g_{\parallel} = 2.024$, $g_{\perp} = 2.413$, $|A_{\parallel}| = 0.00903$ cm^{-1}, and $|A_{\perp}| = 0.00507$ cm^{-1} for the Co-acridine sample, as contrasted with the typical five-coordinate amine complexes:[2] $g_{\parallel} = 2.027$, $g_{\perp} \geq 2.324$, $|A_{\parallel}| = 0.0078$ cm^{-1}, $|A_{\perp}| \leq 0.0011$ cm^{-1}). In fact, the type of epr spectrum observed resembles that of Co(p-OCH$_3$)TPP in toluene glasses (ref 2, Figure 2), except that it is more compressed; the g and A values are intermediate between those of the Co(II) porphyrins in toluene and those of the corresponding amine complexes.[2] This suggests either a very tight molecular complex between the π systems of acridine and Co(p-OCH$_3$)TPP or a very weak Co–N bond. No nitrogen superhyperfine structure is observed in the Co–acridine spectrum, which indicates extremely weak complex formation, if any; this suggests that acridine forms a molecular π complex. Further discussion of such complexes will be presented elsewhere.[15]

Molecular models indicate that the distance required from the nucleus of the amine nitrogen to the center of the plane of the porphyrin is 3.9 Å in order to minimize van der Waals repulsions between the 4- and 5-H of acridine and the π system. In comparison, the value for the γ-collidine complex is 3.3 Å (*vida supra*). This strongly suggests that for Co–N bond formation, the critical distance between the nucleus of the nitrogen and the center of the plane of the porphyrin is of the order of 3.3–3.5 Å. Thus, if the five-coordinate amine complexes do all have the same geometry with respect to the Co–N bond length and the distance the Co is out of the plane, then this geometry must include the critical distance of about 3.3 Å. If the Co–N bond length in the five-coordinate amine complexes is as long as it is in the bispiperidine–CoTPP complex (2.44 Å),[13] then the cobalt may be as much as 0.9 Å out of plane.

Although molecular models may tend to overemphasize the importance of van der Waals interactions, it is clear from the stability, particularly of the γ-collidine complex (Table I, Figure 2), and the similarity of its esr spectrum to those of less sterically hindered five-coordinate amine complexes,[2] that the cobalt atom is significantly farther out-of-plane than assumed by Hoffman, *et al.*,[4b] in their discussion of the relationship between "coboglobin" and hemoglobin. They have assumed that since Co(II) is in the low-spin state in the porphyrin complexes studied so far, the cobalt ion is clearly small enough to fit within the space available in the center of the plane of the porphyrin ring (in contrast to high-spin Fe(III)[16] as well as high-spin Fe(II) as found in deoxyhemoglobin[17]). Thus, because "coboglobin" does show a "heme–heme interaction," Perutz's model[17] for this interaction in hemoglobin is seriously questioned,[4b] since it requires the proximal histidine to move between 0.45 and 0.65 Å upon coordination of O$_2$.[17] In order for such significant movement of the fifth ligand to take place upon further coordination, the M–N bond length must be very much longer in the five-coordinate than in the six-coordinate complexes of interest and/or the metal must be significantly out of the plane in the five-coordinate complex. The out-of-plane distance of Fe(II) in deoxyhemoglobin is estimated to be 0.75 Å.[17]

Arguments as to out-of-plane distance of a metal based only on the spin state of the metal do not take into account the distorting effects of a fifth ligand. We suggest that, from the thermodynamic data presented herein, the distance of the ligand nitrogen from the plane of the porphyrin ring probably does fall within the "allowable bounds" of the Perutz model[17] for Co(II) as well as Fe(II). Thus, we feel that "coboglobin"[4] is probably able to undergo the same sorts of changes in tertiary and quaternary structure upon coordination of oxygen as has been proposed for hemoglobin.[17] Clearly, the final word on the out-of-plane position of Co(II) in the five-coordinate amine complexes will come from structure determinations of such complexes. To date, the only structure of a monomeric Co–O$_2$ complex is that if the [N,N'-ethylenebis(benzoylacetoniminido)]-(pyridine)(dioxygen)cobalt(III).[18] Unfortunately, the absence of a rigid ring system prevents direct comparsion of this system and the porphyrins.

A rough measure of the electronic effects exerted by para-substituted pyridines may be obtained from a plot of the Hammett σ constants[19] for the four para-substituted pyridines of Table I against log K_1. The plot gives a slope of $\rho \approx -1.0$, with rather large uncertainty, since only four substituents were studied. This may be contrasted to the larger effect of a para substituent on the phenyl rings of Ni(p-X)TPP on the formation constant of its bispiperidine complex, where $\rho = 1.3$.[20] Data available at the present time on the effect of para substituents on the phenyl rings of Co(p-X)TPP on the equilibrium constant for reaction 1 where B = pyridine show a very similar slope to that observed for the nickel–piperidine reaction.[21] Thus it appears that the cobalt atom is more sensitive to electronic effects within the porphyrin ring than it is to the basicity of the substituted pyridine. This is in line with the fact that the porphyrin is a strong-field ligand which is a good π acceptor. Thus, the cobalt atom and its π symmetry orbitals are very sensitive to changes in electronic factors (electron donating *vs.* electron accepting) in the porphyrin macrocycle.[22] The substituted pyridines do not compete equally with the porphyrin for a share in the π back-bonding tendencies of the cobalt.

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(19) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 173.

(20) F. A. Walker and E. Hui, manuscript in preparation.

(21) F. A. Walker and E. Poulson, unpublished work.

(22) That this is indeed a π-electronic effect is discussed in detail elsewhere.[20,23,24]

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