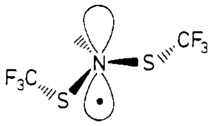
G[17] for $(CH_3)_2\dot{N}$, where $\angle = 117°$.[22]

Another aspect is the decrease in $a(^{14}N)$ that occurs on replacing CF_3 or CF_3S groups in $(CF_3S)_2\dot{N}$ by phenyl groups (Table II).[23] The decrease reflects delocalization of the unpaired spin into the phenyl system. The increase in *g* factor in going from $(C_6H_5)_2\dot{N}$ to $(C_6H_5S)_2\dot{N}$ probably results from the larger spin-orbit coupling due to the S atoms.[24,25]

From molecular models the following W-shaped structure is suggested for $\dot{N}(SCF_3)_2$. For $(CH_3)(CH_3O)\dot{N}$ this type of structure has also been suggested, based on INDO calculations.[20]



The C-S-N-S-C skeleton together with the lone electron pair are assumed to be approximately in the nodal plane of the p-orbital occupied by the unpaired electron. This is supported by the low coupling constants for $^{33}S_\beta$ and $^{13}C_\gamma$. The S-N-S angle is assumed to be <119 °C based on analogy with $(CF_3S)_3N$, where the S-N-S angle is 118.8°[26] together with theoretical calculations,[27] which indicate that this angle decreases on elimination of a $CF_3S\cdot$ group to form $(CF_3S)_2\dot{N}$.

As a conclusion, from the above discussion it appears that $(CF_3S)_2\dot{N}$ is not stabilized significantly by spin delocalization. In support of this are the very small (<0.8 G) coupling constants for $^{13}C_\gamma$ and $^{33}S_\beta$. For this reason, the extremely small N-N bond energy in **1** cannot be related to the stability of the resulting radicals. It must therefore be due to destabilization of **1**. This is clearly shown by the extremely low value for the N-N bond dissociation energy in **1** (32 kJ/mol) which may be compared with 296 kJ/mol[28] for N-N bond dissociation in hydrazine. The low value (5 J K^{-1}/mol) found for the activation entropy for N-N bond homolysis in **1** demonstrates that the transition state for bond homolysis strongly resembles the ground state.

2. Nature of the N-N bond. The principal reason for the extremely low N-N bond energy in **1** is suggested to be a combination of steric and electronic factors. As a result of the strong electron withdrawing properties of SCF_3 (Hammett $\sigma(SCF_3) = 0.64$), SCF_3 groups are expected to reduce the N-N bond distance. This type of effect is seen with F_2NNF_2 (N-N bond distance 1.25 Å) as compared to H_2NNH_2 (bond distance 1.45 Å). A decrease of the N-N bond distance will, however, be prevented by strong steric interaction between the bulky SCF_3 groups. The lone electron pairs on the nitrogens also contribute to steric repulsion.[27] In the analogous case $(CF_3S)_3CC(SCF_3)_3$, the C-C bond distance is 1.7 Å,[11] to be compared with a C-C bond distance of 1.54 Å for ethane. This shows that the steric effect, which tends to widen the bond length, predominates over the electronic effect, which tends to decrease the bond distance. In the case of F_2NNF_2 the N-N bond strength (88 kJ/mol)[29] is strongly reduced as compared to that in H_2NNH_2, *although* the N-N bond length of 1.25 Å in F_2NNF_2 is considerably smaller than the 1.45 Å for H_2NNH_2. The combination of small bond length and low bond energy in F_2NNF_2 may be explained by assuming that the bond length results as a compromise between bond shortening effects due to the electronegative fluorines and steric effects that prevent the further approach of the two NF_2 moieties. With this bond length, the bond energy is only 88 kJ/mol. If analogous arguments are applied to $(CF_3S)_2NN(SCF_3)_2$, it is clear that steric effects prevent the N-N bond from reaching the low distance required by the electron-withdrawing effect of the SCF_3 groups. As a result, the N-N bond is very weak, as shown by the extremely low bond energy of 32 kJ/mol.

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Registry No. **1**, 80653-51-6; $(CF_3S)_3N$, 4317-00-4; $(CF_3S)_2N\cdot$, 80653-52-7; galvinoxyl, 2370-18-5; Koelsch radical, 2152-02-5.

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Laser Photodissociation of Nitrogenous Bases from Pentacoordinated Cobalt(II) Porphyrins

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Abstract: Pentacoordinated complexes of cobalt(II)-deuteroporphyrin IX dimethyl ester with nitrogenous bases ($(L)Co^{II}DPDME$) can be photodissociated by a laser pulse. The rate constants for ligand binding and dissociation are found to decrease upon increasing the pK_a of the external base. The kinetic results are compared to those previously found for the binding of the same ligands to pentacoordinated iron(II)-5,10,15,20-tetraphenylporphyrin-base$_2$ complexes ($Fe^{II}TPP$-B). The compared pK_a dependence of the "on" rates in both systems confirms the role of an electrostatic repulsion barrier between ligand and $Fe^{II}TPP$-B dipole moments, and its absence in the cobalt(II)-porphyrin case. Except for this term, the association rates are not very different in both systems. On the contrary, the dissociation rates are about two orders of magnitude larger for $(L)Co^{II}DPDME$ complexes than for the hexacoordinated iron(II) porphyrins (hemochromes). The results are discussed in terms of the relative metal orbital occupancies. The comparison also suggests that the contribution of π bonding in pentacoordinated Co(II) complexes is smaller than in hemochromes.

Introduction

Ligand photodissociation from low-spin hexacoordinated iron(II) porphyrins is well documented. Extensive studies have been devoted to natural complexes of biological importance and to synthetic heme models. Among the compounds which have been reported to be photosensitive are oxy- and carboxyhemoproteins,[1,2] carboxyhemochromes,[3] and hemochromes.[4,5] Pho-

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todeligation thus appears as a general property of hexacoordinated ferrohemes. It is also a powerful tool for investigating the dynamics of ligand binding. Thus we have reported previously that the binding and dissociation rate constants of the second axial base in hemochromes ($k_{\pm 2}$) decrease upon increasing the pK_a of the external ligand.[5] The relation was interpreted in terms of long- and short-distance interactions which respectively control the "on" and the "off" rate. In particular, examination of the potential energy terms governing the reaction rate (k_2) suggested that electrostatic repulsion between ligand and pentacoordinated porphyrin dipole moments might account for the lesser reactivity of the stronger nitrogenous bases.

In the present work we investigate the consequences of replacing Fe(II) by Co(II) upon the binding properties of nitrogenous bases. Ligand binding to metalloporphyrins generally proceeds in two steps leading to the formation of 1:1 and eventually 2:1 complexes

$$\mathrm{P} + \mathrm{L} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathrm{PL} \qquad (K_1 = k_{+1}/k_{-1}) \tag{1}$$

$$\mathrm{PL} + \mathrm{L} \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} \mathrm{PL}_2 \qquad (K_2 = k_{+2}/k_{-2}) \tag{2}$$

where P denotes the metalloporphyrin and L a nitrogenous base. While the hexacoordinated hemochromes are the dominant species obtained with ferroporphyrins ($K_2 \gg K_1$), Co(II) porphyrins are characterized by a low affinity for the second axial ligand ($K_2 \ll K_1$).[6-9] Therefore only pentacoordinated Co(II) complexes are generally present in solution.

Although synthetic Co(II) porphyrins have received considerable attention,[6] the photodeligation of their pentacoordinated complexes has not been reported previously.[10] We have observed that the nitrogenous bases could be photodissociated from pentacoordinated Co(II) porphyrins and we have investigated the kinetics of ligand rebinding according to reaction 1.

Experimental Section

Cobalt(II)–deuteroporphyrin IX dimethyl ester (Co^{II}DPDME) was synthesized and purified according to the procedure of Caughey et al.[11] Toluene and liquid ligands were redistilled before use. Toluene solutions of Co^{II}DPDME (10^{-4} M) were deaerated by bubbling argon. In the range of ligand concentrations used (5×10^{-4} to 3×10^{-3} M) at least one-third of the porphyrin was present as the pentacoordinated species.

The apparatus and the techniques used in the laser photolysis experiments have been described in details in a previous paper.[5] The photodissociation was triggered using the 530-nm harmonics of a Q-switched neodymium laser (pulse width = 20 ns). Transient absorbance changes were monitored at the maximum of the α-band of the tetracoordinated porphyrin near 550 nm. The minimum absorbance change which could be detected was $\approx 10^{-3}$ with a time constant of $\approx$50 ns. The transient spectrum and the quantum yields were obtained from the initial absorbance changes and corrected for the fluctuations of the laser output. Ferrohemochromes were used as a reference for the quantum yield measurements.[4] All experiments were performed at 25 °C.

Results and Discussion

Upon photolysis of the pentacoordinated base–Co^{II}DPDME complexes the absorption near 550 nm transiently increased. No signal was observed in the absence of ligand. The difference spectrum recorded at $t = 0$ was found to reproduce reasonably well the static difference spectrum between pentacoordinated and free Co^{II}DPDME (Figure 1). It can therefore be concluded that photolysis simply removes the nitrogenous base of the pentacoordinated species.

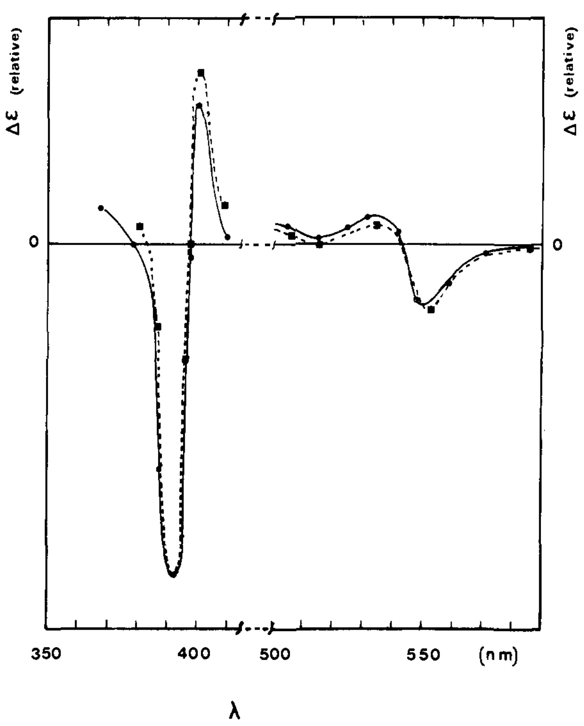

Figure 1. Initial difference spectrum following laser photolysis of (piperidine)Co^{II}DPDME (–●–) and calculated difference spectrum between (piperidine)Co^{II}DPDME and Co^{II}DPDME (--■--). The spectra have been normalized for easier comparison.

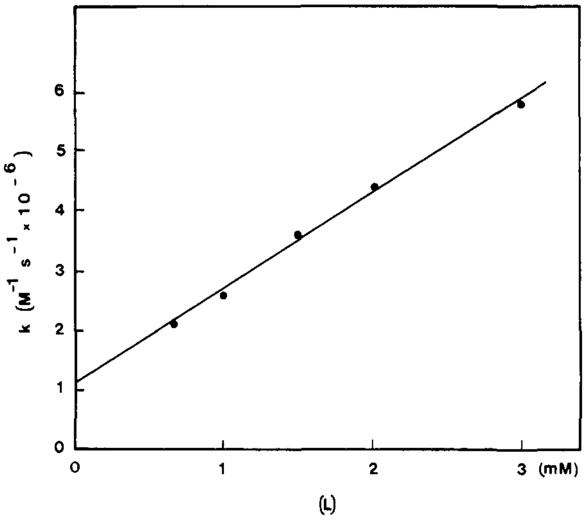

Figure 2. Recombination rates of L = 4-methylpyridine with Co^{II}DPDME after photolysis: porphyrin concentration, 10^{-4} M in toluene; temperature, 25 °C.

The photodissociation quantum yields were in the range 0.01–0.1, i.e., of the same order of magnitude as those reported previously for hemochromes.[4] No systematic dependence on the base pK_a could be noticed. Typical values were 0.03, 0.03, and 0.05 for 4-cyanopyridine, 4-dimethylaminopyridine, and piperidine, respectively.

The recombination reaction was exponential and the relaxation rate was a linear function of the concentration of ligand (L) (Figure 2). Provided that (L) ≫ (P), the relaxation rate of equilibrium 1 is given by

$$k = k_1(\mathrm{L}) + k_{-1} \tag{3}$$

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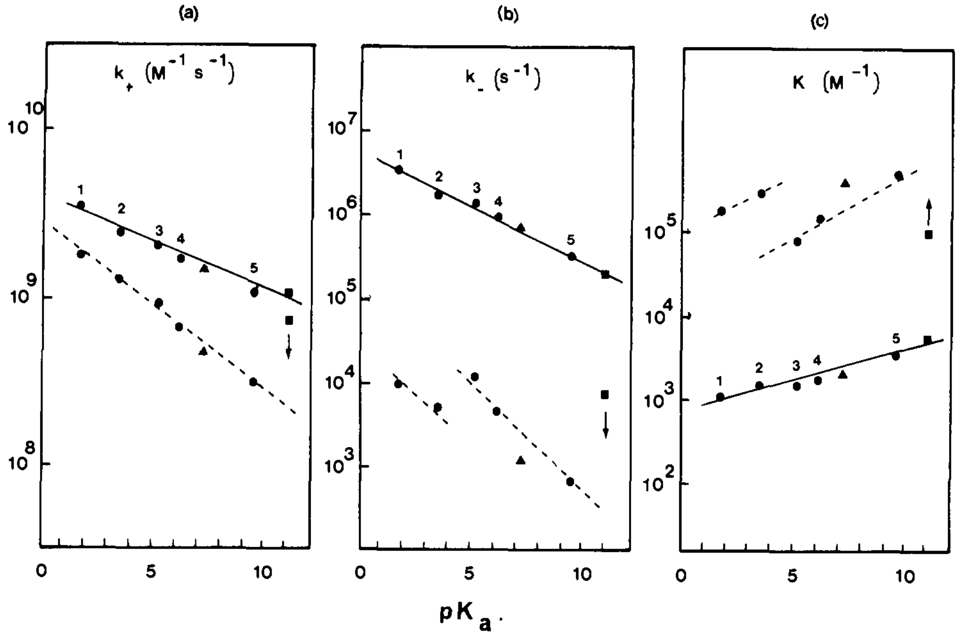

Figure 3. Association (a) and dissociation (b) rate constants and equilibrium constants (c) as a function of ligand basicity: full lines, k_1, k_{-1}, and K_1 (Co^{II}DPDME): dotted lines, $2k_2$, k_{-2}, and $2K_2$ for Fe^{II}TPP–Py (data from ref 5). k_1 has to be compared to $2k_2$ (and K_1 to $2K_2$) since ligand binding to Co^{II}DPDME and Fe^{II}TPP–Py proceeds respectively on two and one of the porphyrin faces. The ligands are (●) 4-cyanopyridine (1); 4-acetylpyridine (2); pyridine (3); 4-methylpyridine (4); 4-dimethylaminopyridine (5); (▲) 1-methylimidazole; (■) piperidine.

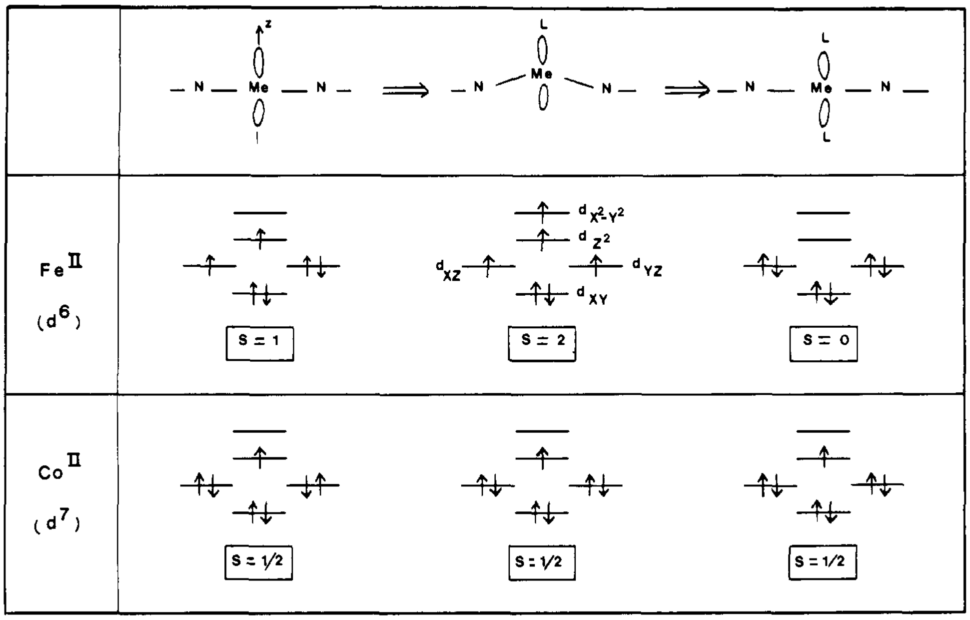

Figure 4. Metal orbitals occupancy and spin state of the various Fe(II) and Co(II) porphyrin complexes considered in the text.

The situation encountered with Co(II) complexes was particularly favorable since, contrary to the hemochromes,[5] k_{-1} was of an order of magnitude comparable to k_1(L); the association and dissociation rate constants could thus be obtained directly from the slope and intercept of the linear plots of k against (L) (Figure 2). Their ratio yielded the equilibrium constant K_1 (eq 1). The results are presented graphically in Figure 3 in which log $k_{\pm1}$ and log K_1 are plotted against the pK_a of the reacting base.

Similar correlations have been already reported for the equilibrium constant K_1 and for the enthalpy of ligand binding to various Co(II)-porphyrins.[7,8] As in the case of hemochromes,[5] the kinetic data give a still better insight into the factors which govern the reactivity ("on"-rates) or the intrinsic stability ("off"-rates). For the sake of comparison, our previous results for the binding of the second axial base in hemochromes (reaction 2) are also shown in dotted lines in Figure 3.

Remembering that pentacoordinated cobalt(II) and hexacoordinated iron(II) porphyrins respectively follow reaction schemes 1 and 2, their differences and similarities are more conveniently discussed in terms of the metal orbital occupancy diagram displayed in Figure 4. Although the porphyrin and the metal atom differ in (L)Fe^{II}TPP–B hemochromes[12] and in the present (L)Co^{II}DPDME complexes, the situation immediately following photodissociation is similar: one ligand molecule binds to a complex in which the d_{z^2} metal orbital is occupied by a single electron (respectively the high-spin pentacoordinated Fe^{II}TPP–B complex and the tetracoordinated Co^{II}DPDME). However, the position of the metal atom with respect to the porphyrin plane is opposite in the reactants and in the products. The cobalt atom, which is in the plane in the reacting tetracoordinated Co^{II}DPDME, is displaced out of plane in the final pentacoordinated (L)-Co^{II}DPDME; on the contrary, the iron atom is out of plane in the initial pentacoordinated (L)Fe^{II}TPP but becomes coplanar

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[12] Abbreviation: (L) denotes an external ligand, and –B a covalently linked base, as defined in ref 5.

in the final hexacoordinated hemochrome (L)Fe^{II}TPP–B (Figure 4).

The pK_a dependence of the binding constant of hemochromes (k_2) has been attributed in part to the repulsion at long distance between the base dipole moment and the dipole of the pentacoordinated porphyrin resulting from the out of plane displacement of the iron.[5] As the base dipole moment varies linearly with pK_a, this repulsion term in the energy barrier for reaching the transition state increases with the ligand basicity. In this respect, a remarkable exception is piperidine, which has a small dipole moment in spite of its high pK_a and which accordingly reacts faster with iron(II) than expected and deviates significantly from the correlation (Figure 3a). As tetracoordinated Co(II) porphyrins are expected to be devoid of dipole moment, this repulsion term should vanish. Indeed the pK_a dependence of k_1 in the cobalt complexes is much less pronounced than that of k_2 in hemochromes. The fact that piperidine now also follows the same correlation as other ligands further confirms the role of dipole repulsion terms in hemochromes and their absence in the cobalt system (Figure 3a). In the region of low pK_a (where the dipole repulsion term is the smallest) cobalt(II) k_1 and iron(II) k_2 values approach each other and are close to diffusion control; thus the reactivity of both systems is not very different, but for the additional dipole–dipole energy barrier in the hemochromes. This might seem surprising in view of the fact that the iron atom is displaced roughly 0.5 Å out of the porphyrin plane in the pentacoordinated Fe(II) complexes,[13] while the cobalt atom remains virtually coplanar with the macrocycle in Co^{II}DPDME (Figure 4). However, the critical Fe–N(base) distance in the transition state can be as high as 5–7 Å,[5] and the field experienced at long distance by the approaching ligand might not be very sensitive to the small displacement of the metal atom. The direct repulsion between the lone pair electrons of the base and the single d_{z^2} metal electron might then constitute the leading part of the energy barrier and account for the residual pK_a dependence observed in the cobalt complexes.

The pK_a dependence observed for k_{-1} and K_1 indicates that the stability of the final complexes increases with the σ-donor strength of the ligand (Figures 3b and 3c). The lesser affinity of ligands toward tetracoordinated Co^{II}DPDME as compared to pentacoordinated Fe^{II}TPP–B (Figure 3c) can be almost entirely attributed to a better stabilization of the final hexacoordinated iron complex. The dissociation rates k_{-1} for (L)Co^{II}DPDME are about two orders of magnitude higher than the k_{-2} rates in hemochromes (Figure 3b). The greater stability of hemochromes has been rationalized in terms of occupation of the metal orbitals;[7] after going to the final low-spin hexacoordinated complex, the d_{z^2} orbital becomes vacant, while it remains occupied and destabilized on formation of the pentacoordinated cobalt complex (Figure 4). This destabilization has been invoked to account for the small values of K_2 in cobalt[7] and is likely to be at the origin of the high dissociation rates as well. Another consequence is a longer bond distance (Co–N(base) = 2.16 Å)[14] in (L)Co^{II} porphyrins as compared to (L)Fe^{II} porphyrin–base (Fe–N(base) = 2.02 Å).[15] Furthermore, the cobalt atom is slightly displaced by 0.14 Å above the porphyrin. As the "off" rates are predominantly governed by short-distance interactions, the longer bond is relatively favorable for sterically hindered ligands such as piperidine. This ligand was found previously to deviate from the k_{-2} vs. pK_a correlation presumably because of the interaction of its hydrogen atoms with the porphyrin.[5] Due to the reduced interaction in the cobalt complexes, piperidine no longer remains an exception (Figure 3b). It is the strongest ligand because it is the best σ donor. Another consequence of the longer cobalt–base bond is the reduction of eventual π interactions. This is also shown in Figure 3b, where 4-cyano- and 4-acetylpyridine now follow the cobalt correlation, contrary to the situation in hemochromes where additional charge transfer at short distance is probably at the origin of their greater stability as compared to other ligands.[5] In short, both the longer metal–N(base) distance and the absence of exceptions in the k_{-1} vs. pK_a correlation point to minimal (if any) contribution of π bonding in pentacoordinated complexes of Co^{II}DPDME.

Registry No. (L)Co^{II}DPDME (L = 4-cyanopyridine), 84081-86-7; (L)Co^{II}DPDME (L = 4-acetylpyridine), 84081-87-8; (L)Co^{II}DPDME (L = 4-methylpyridine), 84081-88-9; (L)Co^{II}DPDME (L = 4-dimethylaminopyridine), 84081-89-0; (L)Co^{II}DPDME (L = pyridine), 29130-56-1; (L)Co^{II}DPDME (L = 1-methylimidazole), 84081-90-3; (L)Co^{II}DPDME (L = piperidine), 84081-91-4; Co^{II}DPDME, 15892-11-2.

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