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Comparison of the Structures of the Five-Coordinate Cobalt(II) Pyridine, Five-Coordinate Cobalt(III) Methyl, and Six-Coordinate Cobalt(III) Methyl Pyridine Complexes of Octaethylporphyrin

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Abstract: The molecular structures of the complexes of Co(OEP)CH_3, Co(OEP)(CH_3)(Py), and Co(OEP)(DMAP) were determined by X-ray diffraction. The complexes are related to each other and to coenzyme B_{12} by a reaction sequence that involves coordination of pyridine to the five-coordinate alkyl–Co(III) porphyrin complex to afford a six-coordinate alkyl–Co(III) porphyrin pyridine complex followed by homolysis of the alkyl–cobalt bond to afford a five-coordinate Co(II) porphyrin pyridine complex. The compound (2,3,7,8,12,13,17,18-octaethylporphyrinato)(4-(*N,N'*-dimethylamino)pyridine)cobalt(II), Co(OEP)(DMAP), crystallized in the monoclinic space group $P2_1/n$ (Z = 4) with unit cell dimensions a = 14.392(6) Å, b = 14.864(6) Å, c = 18.217(5) Å, β = 95.60(3)°, and V = 3878.4(2.6) Å^3. The structure was refined to R = 0.050 on F_o^2 on the basis of 5122 reflections with $I > 0$. The 1.982(2)-Å Co—N$_{eq}$ distance and the 0.12-Å displacement of the cobalt atom from the porphyrin nitrogen plane are typical of five-coordinate, square-pyramidal complexes of cobalt(II) porphyrins with nitrogenous bases, but the 2.191(2)-Å Co—N$_{ax}$ distance is longer than previously observed for a pyridine axial ligand. The compound (2,3,7,8,12,13,17,18-octaethylporphyrinato)(methyl)cobalt(III), Co(OEP)CH_3, crystallized with two independent molecules per asymmetric unit in the triclinic space group $P\bar{1}$ (Z = 4) and had unit cell dimensions a = 13.776(1) Å, b = 14.038(2) Å, c = 16.593(2) Å, α = 99.20(1)°, β = 90.07(1)°, γ = 95.67(1)°, and V = 3151.6(6) Å^3. The structure refined to R = 0.061 on F_o on the basis of 4699 reflections with $I > 2\sigma(I)$. The agreement of structural details between the two independent molecules was excellent, despite some disordering of ethyl groups. The cobalt atom has square pyramidal geometry and mean displacement of 0.10 Å from the plane of the four nitrogen atoms. The average Co—C and Co—N$_{eq}$ distances are 1.973 and 1.966 Å, respectively. The compound (2,3,7,8,12,13,17,18-octaethylporphyrinato)(methyl)(pyridine)cobalt(III), Co(OEP)(CH_3)(Py), crystallized in the triclinic space group $P\bar{1}$ (Z = 2) with unit cell dimensions a = 10.667(2) Å, b = 10.902(2) Å, c = 16.119(3) Å, α = 97.51(3)°, β = 97.67(3)°, γ = 99.96(3)°, and V = 1808.5(6) Å^3. The structure was refined to R = 0.065 on F_o on the basis of 2320 reflections with $F_o > 4\sigma(F_o)$. The cobalt atom has octahedral geometry and is centered in the plane of the porphyrin. The Co—C, Co—N$_{eq}$, and Co—N$_{ax}$ distances are 2.018, 1.983, and 2.214 Å, respectively. A strong mutual *trans* influence of the methyl and pyridine axial ligands is evident from the structures. Coordination of pyridine to five-coordinate Co(OEP)(CH_3) results in a 0.045-Å elongation of the Co—C bond. The Co—N$_{ax}$ distance in the six-coordinate, formally d^6 cobalt(III) complex Co(OEP)(CH_3)(Py) is between 0.17 and 0.24 Å longer than that in other six-coordinate Co(III) porphyrin pyridine X complexes. It is also significantly longer than the Co—N$_{ax}$ distance in five-coordinate, d^7 cobalt(II) porphyrin pyridine complexes. The porphyrin core size (Co—N$_{eq}$ distance) of Co(OEP)(CH_3)(Py) is slightly larger than that of Co(OEP)CH_3 but is essentially identical to that of Co(OEP)(DMAP). The centering of the cobalt atom in the porphyrin plane in the six-coordinate complex increases the steric interactions of both the axial methyl and pyridine ligand with the porphyrin. Overall, the data help rationalize the "base-on" effect, the acceleration of the homolysis rate of Co—C bonds that accompanies ligand binding in B_{12} and B_{12} model compounds.

The discovery of a cobalt—carbon bond in coenzyme B_{12} sparked extensive development of the chemistry of both alkyl–cobalt macrocycle and alkyl–cobalt porphyrin complexes.[1] In several enzymes, the adenosylcobalamin prosthetic group functions as a source of adenosyl radicals by reversible homolysis of the Co—C bond.[2,3] Consequently, measurements of the Co—C bond dissociation energies of coenzyme B_{12} and of model complexes have received considerable attention.[4–10] Two coordination equilibria markedly affect the bond dissociation energies. Complexation of adenosylcobalamin by apoenzyme results in a dramatic acceleration of the homolysis of the Co—C bond by $\geq 10^{10}$ relative to free coenzyme.[5b,c] The "base-on" effect, which results from coordination of an axial ligand, accelerates the homolysis of the Co—C bond by a factor of 10^2–10^3.[5b–d,8–12] A seemingly contradictory observation, though, is that for axial bases of similar steric size increasing the strength of the base

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increases the strength of the Co—C bond.[4a,h] Although the manner in which these accelerations occur is not understood, they are thought to involve steric interactions and distortions induced by coordination of the axial ligand or the coenzyme to the enzyme. Clearly, a thorough understanding of the relationship between coordination state and structural features of B_{12} and its model complexes is important.

Despite great interest, few five-coordinate alkyl–cobalt macrocycle complexes have been structurally characterized.[13-15] Structures of simple alkyl–cobalt porphyrin complexes are not known. This situation limits the opportunities to compare structures of closely related five- and six-coördinate alkyl–cobalt complexes, which serve respectively as models of the "base-off" and "base-on" forms of coenzyme B_{12}.

We are currently investigating the effect of modified porphyrins on the ligand-binding equilibria of Co(II) and alkyl–Co(III) porphyrin complexes.[16] As part of this investigation, we determined and report here the structures of Co(OEP)CH_3, Co(OEP)(CH_3)(Py), and Co(OEP)(DMAP).[17] The compounds are related by a reaction series in which coordination of pyridine to a five-coordinate alkyl–Co(III) porphyrin complex affords a six-coordinate pyridine alkyl–Co(III) porphyrin complex, eq 1, which then undergoes homolysis of the alkyl—cobalt bond to afford a five-coordinate pyridine Co(II) porphyrin complex, eq 2. Differences between the isosteric bases DMAP and pyridine are not expected to affect significantly the structural features that are of interest here (see below).

$$\mathrm{Co^{III}(Por)R + Py \rightarrow Co^{III}(Por)(R)(Py)} \qquad (1)$$

$$\mathrm{Co^{III}(Por)(R)(Py) \rightarrow Co^{II}(Por)Py + R^{\bullet}} \qquad (2)$$

Experimental Section

The compounds H_2(OEP),[18] Co(OEP),[19] and Co(OEP)CH_3[20] were prepared by literature methods. Co(OEP)CH_3 was purified by chromatography on basic alumina that was deactivated with tetrahydrofuran (3 mL per 100 g of alumina). Elution was with a 4:6 benzene/hexane mixture. Crystals of Co(OEP)CH_3 were obtained by slow cooling of a hot toluene solution. Crystals of Co(OEP)(CH_3)(Py) were obtained by vapor diffusion of a 10:1 ethanol/pyridine mixture into a 10:1 toluene/pyridine solution of Co(OEP)CH_3. Crystals of Co(OEP)(DMAP) were obtained by layering hexane over a chloroform solution of Co(OEP) and excess DMAP. Because of the air sensitivity of the complexes, all manipulations and recrystallizations were conducted under a nitrogen atmosphere. Alkyl complexes were handled under subdued lights.

X-Ray Data Collection, Structural Analysis, and Refinement for Co(OEP)(DMAP). A crystal of the complex was sealed in a glass capillary tube under nitrogen and then optically aligned on a Picker goniostat operated by a Krisel Control diffractometer automation system. Following a low-angle ($5° \leq 2\theta \leq 10°$) peak search, the orientation angles (ω, χ, and 2θ) for 12 intense reflections were used by an autoindexing algorithm[21] to calculate preliminary values for the cell constants. The angles for 20 higher order reflections ($30° \leq 2\theta \leq 35°$) were then optimized by an automatic peak-centering routine[22] and least-squares fit to give the refined lattice parameters, Table 1, and the orientation matrices. The space group was uniquely determined to be $P2_1/n$ by the systematic absences of $\{0\ k\ 0\}$, $k = 2n + 1$, and $\{h\ 0\ l\}$, $h + l = 2n + 1$.

Intensity data were measured with Zr-filtered Mo X-ray radiation at a take-off angle of 2°. The θ–2θ scan mode was employed with a fixed scan rate and variable scan width. The intensities of three standard reflections were measured after every 90 min of exposure time. No crystal decay was observed. The integrated intensity, I, and its standard deviation, $\sigma_c(I)$, for each measured peak were calculated from the expressions $I = w(S/t_s - B/t_b)$ and $\sigma_c(I) = w(S/t_s^2 + B/t_b^2)^{1/2}$, where S represents the total scan count measured in time t_s, B is the combined background count in time t_b, and the weighing factor $w = 0.00063$. The intensity data were corrected for Lorentz-polarization effects, and equivalent reflections were averaged. The standard deviation of the square of each structure factor, $F_o^2 = I/\mathrm{Lp}$, was calculated from the expression $\sigma(F_o^2) = [\sigma_c(F_o^2)^2 + (0.025F_o^2)^2]^{1/2}$. Further details of the data collection are summarized in Table 1.

The initial position of the Co atom was determined from an analysis of the Harker vectors from an unsharpened Patterson map. The remaining non-hydrogen atoms were obtained by Fourier methods and refined anisotropically. All of the hydrogen atoms were located on a subsequent difference Fourier map, which was calculated using only low-angle data with ($\sin \theta/\lambda$) < 0.40 Å. Full-matrix refinement (based on F_o^2) of the positional and anisotropic thermal parameters for the non-hydrogen atoms with fixed contributions for the hydrogen atoms converged with the final discrepancy indices listed in Table 1. The final difference Fourier map was essentially featureless.

X-Ray Data Collection, Structural Analysis, and Refinement of Co(OEP)(CH_3)(Py). A single crystal of Co(OEP)(CH_3)(Py) was sealed under nitrogen in a capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The corresponding lattice parameters and orientation matrix for the triclinic unit cell were determined from a least-squares fit of the orientation angles for 25 reflections at 22 °C. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 1.

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and variable ω scans. Background counts were measured at the beginning and end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured periodically during data collection and gave no indication of crystal decay or sample movement. The data were corrected for Lorentz-polarization, and the symmetry equivalent reflections were averaged.

The X-ray structure was solved by direct methods (SHELXTL PLUS operating on a St. Clair 486 workstation). All non-hydrogen atoms were revealed by successive difference Fourier syntheses. Following anisotropic refinement of the non-hydrogen atoms, idealized positions for the hydrogen atoms were included as fixed contributions using a riding model. Full-matrix least-squares refinement, based upon the minimization of $\sum w_i|F_o - F_c|^2$, with $w_i^{-1} = \sigma^2(F_o) + 0.0010F_o^2$, converged with the final discrepancy indices listed in Table 1.

X-Ray Data Collection, Structural Analysis, and Refinement for Co(OEP)CH_3. Data were collected on the Siemens P4 diffractometer as described above for Co(OEP)(CH_3)(Py). No systematic absences were observed. Details of the collection and other pertinent information are presented in Table 1.

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(17) Abbreviations: OEP, dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; TPP, dianion of 5,10,15,20-tetraphenylporphyrin; Py, pyridine; DMAP, 4-(*N*,*N'*-dimethylamino)pyridine; 1-MeIm, 1-methylimidazole; 1,2-Me_2Im, 1,2-dimethylimidazole; 3,5-Me_2Py, 3,5-lutidine; acacen, dianion of *N*,*N'*-ethylenebis(acetylacetonimine); DH, monoanion of dimethylglyoxime; (DO)(DOH)pn, N^2,$N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime); saloph, dianion of disalicylidene-*o*-phenylenediamine; TC-*n*,*n*; dianion of tropocoronand ligand with —$(CH_2)_n$— and —$(CH_2)_m$— linkages (see ref 15).

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Table 1. Data for X-ray Diffraction Studies of Co(OEP)(DMAP), Co(OEP)CH_3, and Co(OEP)(CH_3)(Py)

	Co(OEP)(DMAP)	Co(OEP)CH_3	Co(OEP)(CH_3)(Py)
		Crystal Data at 22(1) °C	
formula	$C_{43}H_{54}CoN_6$	$C_{37}H_{47}CoN_4$	$C_{42}H_{52}CoN_5$
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/n$[a]	$P\bar{1}$	$P\bar{1}$
α, Å	14.392(6)	13.776(1)	10.667(2)
b, Å	14.864(6)	14.038(2)	10.902(2)
c, Å	18.217(5)	16.593(2)	16.119(3)
α, deg		99.20(1)	97.51(3)
β, deg	95.60(3)	90.07(1)	97.67(3)
γ, deg		95.67(1)	99.96(3)
V, Å^3	3878.4(2.6)	3151.6(6)	1808.5(6)
Z	4	4	2
fw, amu	713.88	606.72	685.84
ρ_{calc}, g/cm^3	1.223	1.279	1.259
crystal size, mm	0.45 × 0.30 × 0.65	0.12 × 0.30 × 0.50	0.04 × 0.10 × 0.40
μ, cm^{-1}	5.01	5.77	5.11
		Data Collection and Refinement	
radiation	Zr-filtered Mo Kα	Mo Kα, graphite monochromator	Mo Kα, graphite monochromator
scan type	θ–2θ	ω	ω
2θ range of measd reflns	5–45°	2.5–50.0°	2.0–50.0°
reflns measd	$\pm hkl$	$-h\pm k\pm l$	$h\pm k\pm l$
scan speed	2°/min	2–5°/min	2–5°/min
scan range, deg	1.1 + 0.9 tan θ	–0.37°(Kα_1); 0.37°(Kα_2)	–0.60°(Kα_1); 0.60°(Kα_2)
no. of reflns measd	5288	12524, 11032 unique	5515, 4630 unique
agreement between equivalent data, $R_{av}(F_o)$	0.023	0.0307	0.024
standard reflns		variations $\leq\pm3\sigma(I)$ for each of three standard reflns	
no. unique data used to refine	5122 [$I > 0$]	8649 [$I > 0$]	2320 [$F_o > 4\sigma(F_o)$]
transmission coeff	0.81–0.87	1.0	0.87–0.95
$R(F_o)$[b]	0.053	0.061[c]	0.065
$R_w(F_o)$[d]			0.073
$R(F_o^2)$[e]	0.050		
$R_w(F_o^2)$[f]	0.088	0.114[c]	
σ_1	1.94[g]	1.04[g]	1.41[h]
no. of variables	451	792	433
data to parameters	11.31:1	10.9:1	5.4:1

[a] This is a nonstandard setting of space group $P2_1/c$; equivalent positions are $\pm(x,y,z)$; $(1/2 + x, 1/2 - y, 1/2 + z)$; $(1/2 - x, 1/2 + y, 1/2 - z)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] *R* value for 4699 reflections with $I > 2\sigma(I)$. [d] $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. [e] $R(F_o^2) = \sum||F_o^2 - F_c^2||/\sum F_o^2$. [f] $R_w(F_o^2) = \{\sum w_i[|F_o^2 - F_c^2|]^2/\sum w_i F_o^4\}^{1/2}$. [g] The standard deviation of an observation of unit weight (GOF) or $\sigma_1 = [\sum(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where *n* is the number of relections and *p* is the number of parameters varied during the last refinement cycle. [h] $\sigma_1 = [\sum(w_i[|F_o| - |F_c|]^2)/(n - p)]^{1/2}$, where *n* and *p* are defined as before.

The X-ray structure was solved by direct methods (SHELXTL IRIS operating on a Silicon Graphics Iris Indigo workstation). All non-hydrogen atoms were revealed by successive difference Fourier syntheses. During the anisotropic refinement of the non-hydrogen atoms, it became apparent that two of the ethyl groups of the second independent molecule were disordered between two different sites in a roughly 2:1 ratio. The atoms of the major site (C58, C59, C68, and C69) were refined anisotropically, and those of the minor site (C58′, C59′, C68′, and C69′) were refined isotropically. The occupancy factor refined to 0.674. The C—C distances within the disordered ethyl groups were restrained to 1.51 ± 0.02 Å. The hydrogen atom positions were idealized and included as fixed contributions using a riding model with the isotropic temperature factors set at 1.2 times the corresponding value of the isotropic temperature factor of the adjacent carbon. Full-matrix least-squares refinement, based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$, with $w_i^{-1} = [\sigma^2(F_o^2) + (0.0500P)^2 + 0.410P]$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$, was performed with SHELXL-93 and converged with the final discrepancy indices listed in Table 1. The agreement between the two independent molecules in the asymmetric unit was good. The structure also was consistent with a preliminary structural analysis performed on a crystal of Co(OEP)CH_3 whose lesser quality did not permit the collection of sufficient data to resolve the disorder.

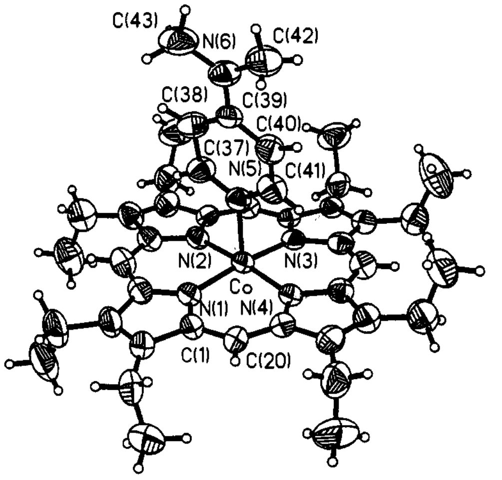

Figure 1. ORTEP diagram of the molecular structure of Co(OEP)(DMAP), $C_{43}H_{54}CoN_6$. The labeling of the OEP atoms, which has been omitted for sake of clarity, is the same as in Figure 2. Thermal ellipsoids are scaled to enclose 50% probability.

Results and Discussion

ORTEP drawings of Co(OEP)(DMAP), molecule 1 of Co(OEP)CH_3, and Co(OEP)(CH_3)(Py) are shown in Figures 1–3, respectively. The numbering scheme for the atoms of OEP is shown in Figure 2. For sake of clarity, the labels of most OEP atoms are omitted in Figures 1 and 3. The average bond lengths and bond angles of the complexes are presented in Table 2. The esd's reported in Table 2 were calculated for averages of populations assuming idealized D_{4h} symmetry. (This may not be appropriate for all the populations, as is clearly the case for N_{eq}—Co—N_{ax} in Co(OEP)(DMAP).) Tables of atomic coordinates of the non-hydrogen atoms, refined thermal parameters, the hydrogen atom coordinates, interatomic distances and bond angles, and equations of pertinent least-squares planes and their dihedral angles are available as supplementary material.

Table 2. Average Bond Lengths (Å) and Bond Angles (deg)[a]

type	Co(OEP)(DMAP)	Co(OEP)CH$_3$ molecule 1	Co(OEP)CH$_3$ molecule 2	Co(OEP)(CH$_3$)(Py)
Co—N$_{eq}$[b]	1.982(2)	1.966(14)	1.967(12)	1.983(19)
Co—N$_{ax}$	2.191(2)			2.214(9)
Co—C		1.976(6)	1.970(6)	2.018(12)
Co—Ct[c]	0.123(1)	0.094(3)	0.105(3)	0.008[d]
N—C$_a$	1.376(14)	1.381(30)	1.383(30)	1.376(23)
C$_a$—C$_m$	1.374(9)	1.373(31)	1.368(30)	1.379(45)
C$_a$—C$_b$	1.443(16)	1.441(18)	1.443(32)	1.446(51)
C$_b$—C$_b$	1.351(9)	1.353(18)	1.340(31)	1.346(13)
c-N$_{eq}$—Co—N$_{eq}$	89.8(3)	89.9(5)	89.8(2)	90.0(8)
t-N$_{eq}$—Co—N$_{eq}$	172.9(7)	174.5(7)	173.9(11)	179.3(3)
c-N$_{eq}$—Co—N$_{ax}$	93.6(50)			90.2(24)
c-N$_{eq}$—Co—C$_{ax}$		92.8(16)	93.1(16)	89.8(18)
N$_{ax}$—Co—C$_{ax}$				176.9(4)
Co—N—C$_a$	127.7(9)	128.1(19)	127.7(10)	127.7(27)
C$_a$—N—C$_a$	104.5(4)	103.7(8)	104.3(10)	104.6(18)
N—C$_a$—C$_m$	124.1(10)	123.7(20)	124.3(19)	124.4(40)
N—C$_a$—C$_b$	111.1(4)	111.7(26)	110.8(18)	111.0(45)
C$_m$—C$_a$—C$_b$	124.9(9)	124.6(19)	124.8(15)	124.6(22)
C$_a$—C$_m$—C$_a$	126.3(6)	126.2(12)	125.6(6)	125.8(28)
C$_a$—C$_b$—C$_b$	106.6(10)	106.5(18)	107.0(18)	106.7(26)
Py rotation[e]	19.8			14.3
Py cant[f]	81.5			87.6

[a] For bonds and angles that are not of a unique type, the esd's in parentheses were calculated for averages of populations assuming idealized D_{4h} symmetry. Esd's of individual light atom distances (C—C and N—N) were typically 0.005, 0.008, and 0.015 Å, respectively, in the DMAP, CH$_3$, and (CH$_3$)(Py) complexes. [b] Abbreviations: eq, equatorial; ax, axial; a, pyrrole α-carbon; b, pyrrole β-carbon; m, meso-carbon; Ct, center. [c] Displacement of Co atom from the least-squares plane of the four equatorial nitrogen atoms. [d] Displaced toward N$_{ax}$. [e] Dihedral angle between pyridine plane and plane defined by N$_{ax}$ and two *trans* N$_{eq}$. [f] Dihedral angle between pyridine plane and the least-squares plane of the four equatorial nitrogen atoms.

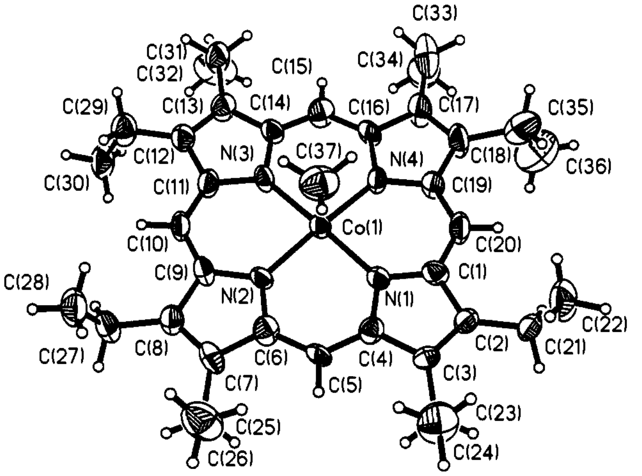

Figure 2. ORTEP diagram of the molecular structure of molecule 1 of Co(OEP)CH$_3$, C$_{37}$H$_{47}$CoN$_4$, labeled with the atom-numbering scheme. Thermal ellipsoids are scaled to enclose 50% probability.

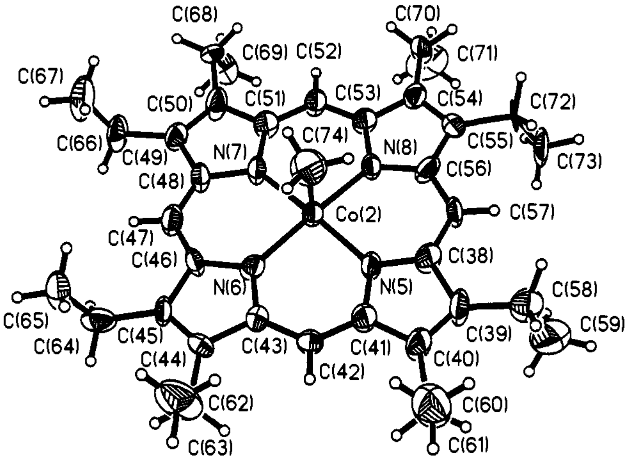

Figure 3. ORTEP diagram of the molecular structure of Co(OEP)(CH$_3$)(Py), C$_{42}$H$_{52}$CoN$_5$. The labeling of the OEP atoms, which has been omitted for sake of clarity, is the same as in Figure 2. Thermal ellipsoids are scaled to enclose 50% probability.

Description of Structures. Co(OEP)(DMAP). The cobalt atom of Co(OEP)(DMAP) is five-coordinate and has a distorted square-pyramidal stereochemistry. The four equatorial nitrogen atoms that form the basal plane are coplanar within ±0.014 Å. The cobalt atom is displaced 0.123(1) Å from this plane toward the nitrogen atom of the DMAP axial ligand. The equatorial Co—N lengths are 1.982(2) Å. The N—Co—N angles between adjacent nitrogen atoms in the equatorial plane average 89.8°. The axial Co—N bond is 2.191(2) Å long and is tipped slightly from the normal to the basal plane toward a direction between N1 and N4.

The individual bond lengths and angles in the porphyrin skeleton depart trivially from 4-fold symmetry. The average bond lengths and angles, Table 2, are unremarkable. The porphyrin is distorted from planarity in a manner that combines a shallow S_4 ruffle and a slight bending of the pyrrole ring that contains N1 away from the axial ligand. Among the carbons with the largest displacements from the equatorial nitrogen mean plane are C2 and C3, the β-carbons of the bent-back pyrrole ring, which have deviations of −0.231 and −0.177 Å, respectively. The mean plane of the 20 porphyrin carbon atoms is displaced 0.048 Å from the plane of the equatorial nitrogen atoms in the direction away from cobalt.

The plane of the DMAP ring is inclined at an angle of 81.5° with respect to the equatorial nitrogen mean plane and is rotated 19.8° from the N2—Co—N5 plane. The later angle, ϕ, is significantly smaller than 45°, the value which corresponds to the orientation with minimal nonbonded contacts between the hydrogen atoms bonded to C37 and C41 and the atoms of the porphyrin core. The structural details of the coordinated DMAP ligand are similar to those of DMAP[23] and of 4-(dimethylamino)-pyridinium cations in two different salts.[24] The N6—C39 bond

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Table 3. Comparisons of Metrical Features and Formation Constants of Structurally Characterized Five-Coordinate Cobalt(II) Porphyrin Complexes

complex	Co—N_{eq}[a,b]	Co—N_{ax}	Co—Ct	ϕ[c]	log K_f[d]	ref
Co(TPP)(1-MeIm)	1.977(3)	2.157(3)	0.13	0.0	3.37[e]	25
Co(TPP)(1,2-Me_2Im)	1.985(2)	2.216(2)	0.15	20	2.79[f]	26
Co(TPP)(3,5-Me_2Py)	2.000(3)	2.161(5)	0.14	41.1	3.03[g]	27
Co(OEP)(1-MeIm)[h]	1.96(1)	2.15(1)	0.13	10	3.37	28
Co(OEP)(DMAP)	1.982(2)	2.191(2)	0.12	19.8	3.62[i]	tw

[a] Abbreviations are defined in Table 2 and ref 17. [b] Bond lengths in angstroms. [c] Degrees. [d] For purposes of comparison, all data in this column are log K_f for coordination of the ligand to reference metalloporphyrin (tetra(*p*-methoxyphenyl)porphinato)cobalt(II) in toluene at 25 °C. See ref 29. When available, actual values for log K_f of the specific complex listed in the table are indicated by a footnote. [e] log $K_f = 3.38$ for Co(TPP); see ref 29. [f] log $K_f = 2.91$ for Co(TPP); see ref 30. [g] Tabulated value is for 3,4-Me_2Py. [h] Errors in this structure are relatively large because of disorder. [i] log $K_f = 3.31$ for Co(OEP); see ref 16a.

between the dimethylamino group and the pyridine ring has substantial double-bond character. In particular, the 1.354(4) Å N6—C39 bond length is relatively short, the three angles about N6 sum to 360°, which suggests sp^2 hybridization, and the C42—N6—C43 plane of the 4-dimethylamino group is nearly coplanar (4.3° dihedral angle) with the plane of the DMAP ring.

The structure of Co(OEP)(DMAP) resembles the structures of four other characterized five-coordinate cobalt(II) porphyrins. Comparisons of specific features and of formation constants are presented in Table 3. The displacements of the cobalt atom out of the equatorial nitrogen mean plane are quite similar in all five complexes. With the exception of Co(TPP)(3,5-lut),[27] the equatorial Co—N distances agree within error. The axial Co—N bond of Co(OEP)(DMAP), which has the largest stability constant of the five complexes, seems anomalously long. The bond is minimally 0.03 Å longer than the corresponding bonds in Co(TPP)(1-MeIm),[25] Co(OEP)(1-MeIm),[28] and Co(TPP)(3,5-lut) yet is 0.025 Å shorter than the axial Co—N bond of Co(TPP)(1,2-Me_2Im).[26] The latter is thought to be stretched by unfavorable steric interactions between the methyl groups of the ligand and the porphyrin core. Although ϕ for Co(OEP)(DMAP) is smaller than optimal, it is substantially larger than observed for the imidazole complexes. There is no evidence that unusually short nonbonded contacts elongate the axial Co—N bond in the DMAP complex. Thus, the data show that axial Co—N bond lengths (all Co—N(sp^2)) and formation constants do not correlate with each other. Because the greater electron-donating properties of DMAP do not affect the structure in any obvious manner, we expect that the structure of the complex formed with the isosteric but weaker base Py (log $K_f = 2.69$ for Co(OEP)(Py) vs 3.31 for Co(OEP)(DMAP)[16a]) should not be significantly different.

Co(OEP)CH_3. It is a nontrivial task to grow crystals of Co(OEP)CH_3 suitable for X-ray studies. Decomposition to Co(OEP) by homolysis of the alkyl—cobalt bond can occur during crystallization. The complex crystallizes with two independent molecules per asymmetric unit, which increases the number of parameters to be found and the size of the data set required. Furthermore, at least two of the ethyl groups (in molecule 2) are disordered. Despite these difficulties, the agreement of structural details between two independent determinations of the structure and between the two independent molecules in the asymmetric unit was quite good.

The cobalt atoms of both independent molecules of Co(OEP)CH_3 have square-pyramidal coordination geometries. The four nitrogen atoms are coplanar within ±0.012(3) Å in molecule 1 and ±0.018(3) in molecule 2. Cobalt atoms lie 0.094(3) and 0.105(3) Å, respectively, above these planes. The average Co—N bond length is 1.966 Å, and N—Co—N angles are 89.9°. The axial Co—C bonds are 1.976(6) and 1.970(6) Å long, respectively, and are essentially normal to the nitrogen mean planes.

Table 4. Comparisons of Five-Coordinate Organocobalt(III) Complexes.

complex	Co—N_{eq}[a,b]	Co—C_{ax}	Co—Ct	ref
Co(TPP)(CH_2CHO)	1.969	1.976(7)	0.14	31
Co(TPP)($CH_2C(O)CH_3$)	1.948[c]	2.028(3)	0.11	32
Co(acacen)CH_3		1.95(2)	0.12	13
Co(saloph)$CH_3\cdot 0.5H_2O$[d]		1.957(13)	0.11	14
Co(saloph)(*i*-Pr)$\cdot 1.5H_2O$		2.031(8)	0.16	14
Co(TC-3,3)(C_2H_5)		1.963(6)	0.19	15
Co(TC-3,3)(*n*-C_3H_7)		1.976(7)	0.21	15
Co(TC-4,4)CH_3		1.940(8)	0.11	15
Co(OEP)CH_3[e]	1.966	1.976(6)	0.094	tw
Co(OEP)CH_3[f]	1.967	1.970(6)	0.105	tw

[a] Abbreviations are defined in Table 2 and ref 17. [b] Distances in angstroms. [c] This distance is shortened by ruffling of the porphyrin core. [d] Contains two independent molecules per unit cell. Data is for molecule B, which unlike molecule A is monomeric and five-coordinate. [e] Molecule 1. [f] Molecule 2.

The average bond lengths and angles of the porphyrin macrocycles are typical. The porphyrin skeletons of the two independent molecules are essentially planar. The largest displacements from the 24-atom plane are 0.074(6) and 0.083(7) Å, respectively.

Co(OEP)CH_3 and the small set of other structurally characterized five-coordinate organocobalt(III) complexes[13-15,31,32] are compared in Table 4. The substantial conformity in coordination geometry, short Co—C bond distances, and displacement of Co toward the alkyl, despite the differences in equatorial ligation to cobalt, support the suggestion by Jaynes et al. that these features are general characteristics of five-coordinate Co(III) alkyl complexes.[15] All complexes are square-pyramidal with the alkyl group in the unique axial coordination site. The cobalt atoms of the five independent methyl-containing complexes are displaced 0.110 ± 0.016 Å from the plane of their equatorial donor set. The Co—C bond lengths of the methyl-containing complexes are indistinguishable (at the 3σ level) and are among the shortest Co—C(sp^3) bonds known. Complexes with bulkier axial groups than methyl generally have both larger cobalt displacements and Co—C bond lengths.[33,34] This is consistent with the expected increase in steric interactions between the axial group and the macrocycle. Comparisons of Co—N_{eq} are only meaningful with the two other porphyrin complexes, which have a fifth ligand that contains a carbonyl group β to cobalt rather than a simple alkyl. The average Co—N distance in Co(TPP)(CH_2CHO)[31] agrees with that in Co(OEP)CH_3. The shorter Co—N distance in Co(TPP)($CH_2C(O)CH_3$) is a consequence of ruffling of the porphyrin core.[32] The formylmethyl and acetonyl ligands in these complexes are both oriented such that the C_α—C_β bond of the ligand and a Co—N bond are nearly eclipsed. In addition, the C_α—C_β distances in these complexes of 1.426(14) and 1.468(4) Å, respectively, are significantly shorter than the normal C—C single-bond distance of 1.51 Å in C—C═O compounds. These features and the short contacts between the β-carbonyl carbon and the porphyrin nitrogen suggest both that the carbonyl group may interact with the metal and/or porphyrin[31] and that these ligands are poor models for alkyls.

Co(OEP)(CH_3)(Py). The cobalt atom of Co(OEP)(CH_3)(Py) has distorted octahedral coordination geometry. The 24

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macrocycle atoms of the porphyrin ligand, which occupies the equatorial coordination sites, are coplanar within ±0.05 Å. The cobalt atom is displaced by at most a trivial amount from this plane toward the nitrogen atom of the axial pyridine ligand. The axial Co—N bond is 2.214(9) Å long and is tipped 2° from the normal to the porphyrin plane toward N4. The Co—C bond is 2.018(12) Å long and is tipped roughly 1° from the normal to the porphyrin plane toward a direction between N1 and N4. As a result, the N5—Co—C37 angle is reduced to 176.9° from the idealized value of 180°. The plane of the pyridine ligand is inclined at an angle of 87.6° with respect to the equatorial nitrogen mean plane and has $\phi = 14.3°$ with respect to the N2—Co—N5 plane.

The Co—C and Co—N_{ax} distances in Co(OEP)(CH_3)(Py) are indistinguishable from those in methylcobalamin, given the significant esd's of the methylcobalamin structure.[35] Comparisons with other six-coordinate alkyl–Co(III) porphyrin complexes are not possible because none were structurally characterized prior to this report. Other characterized six-coordinate Co(III) porphyrin complexes have N, N;[36-38] N, O;[39,40] N, Cl;[41] O, O;[42] O, Cl;[43] and S, S[44] donor groups in the two axial ligands. Although these combinations differ from the C, N donor pair in Co(OEP)(CH_3)(Py), some structural similarities are apparent. The average equatorial Co—N distances, which range between 1.976(4) and 1.98(2) Å in complexes that have nonruffled porphyrin macrocycles,[36,37,44] are comparable to the 1.983-Å distance in Co(OEP)(CH_3)(Py). The cobalt atom lies in the plane of the porphyrin in all of the complexes, excluding [Co(TPP)Cl(H_2O)].[43] In marked contrast, the axial Co—N distances to pyridine ligands in these compounds range between 1.978 and 2.04 Å,[38-41] or 0.17 to 0.24 Å shorter than the corresponding distance in Co(OEP)(CH_3)(Py). The axial Co—N distance in Co(OEP)(CH_3)(Py) is also substantially longer than those in octahedral cobaloximes, $Co^{III}(DH)_2$; Costa-type complexes, Co^{III}[(DO)(DOH)pn]; and Co(III) Schiff-base complexes.[33,34] One exception is (Py)[Co(saloph)](C_2H_5), whose Co—N distance of 2.215(4) Å was noted to be the longest known in a B_{12} model compound.[45] However, the long Co—N distance in this compound is attributed to a large folding distortion of the saloph ligand toward the axial pyridine. An analogous interaction of porphyrin and pyridine is not present in Co(OEP)(CH_3)(Py).

Comparison of the Structures. Co(OEP)CH_3, Co(OEP)(CH_3)(Py), and Co(OEP)(DMAP) model cobinamide, alkyl–cobalamin, and cob(II)alamin complexes, respectively. Both series of complexes are related by reaction sequences that involve coordination of base to a five-coordinate alkyl–Co(III) complex to afford a six-coordinate alkyl–Co(III) base complex, which then homolyses to afford a five-coordiante Co(II) base complex.

The Co—C bond elongates 0.045 Å on coordination of pyridine to Co(OEP)CH_3. Concurrently, the cobalt atom moves into the plane of the porphyrin, a displacement of 0.10 Å. These changes result in a net decrease in the distance of the alkyl carbon atom from the porphyrin plane. Thus, steric interactions between the alkyl group and the porphyrin increase upon coordination of the axial base. The increase in coordination number also may be accompanied by a slight expansion of the porphyrin core.

The structures of Co(OEP)(CH_3)(Py) and Co(OEP)(DMAP) establish that the major structural change that occurs upon homolysis of the alkyl—cobalt bond is a 0.12-Å displacement of the cobalt atom from the porphyrin plane in the direction toward the axial base. The Co—N_{eq} distances and the core size of the porphyrin remain unchanged. The Co—N_{ax} bond length determined for Co(OEP)(DMAP) is 0.023 Å smaller than that of Co(OEP)(CH_3)(Py), but the difference may not be statistically significant (only about 2σ). Because the Co—N_{ax} bond length for this compound seemed anomalously long (see above), comparisons with the other five-coordinate cobalt(II) porphyrin complexes, Table 3, is appropriate. These suggest that the Co—N_{ax} distance could decrease by as much as 0.05 Å upon homolysis. In any event, homolysis results in a significant net increase in the distance of the pyridine from the porphyrin plane. The lessening of steric interactions between the pyridine and porphyrin is further enhanced by an increase in the pyridine rotation angle, ϕ. The combined effect of these changes is evident in the distances between the porphyrin nitrogen atoms and the idealized positions of the pyridine α-hydrogen atoms. These increases from 2.43 Å (N4 to H42A) and 2.61 Å (N2 to H38A) in Co(OEP)(CH_3)(Py) to 2.55 Å (N4 to H48) and 2.70 Å (N2 to H45) in Co(OEP)(DMAP). The shorter distances appear to be less than the sum of the van der Waals radii of nitrogen and hydrogen.

The strong mutual electronic *trans* influence of the axial methyl and pyridine ligands is evident from the structures. The elongation of the Co—C bond is striking, as is the effect on the Co—N bond. The Co—N_{ax} distance in the six-coordinate, formally d^6 cobalt(III) Co(OEP)(CH_3)(Py) complex is one of the longest Co—N distances known. Comparisons made above show that this bond is 0.17–0.24 Å longer than in other six-coordinate Co(III) porphyrin pyridine complexes. Moreover, the distance is longer than that in five-coordinate, d^7 cobalt(II) porphyrin pyridine complexes, which have a singly occupied Co-pyridine N antibonding MO. Calculations for six-coordinate B_{12} models establish that the σ-MO responsible for Co—C bonding has some Co—N antibonding character.[46-49]

The three OEP complexes are the only set of structurally characterized complexes that constitute a complete reaction sequence of the type involved in B_{12}. The absence of other sets is a consequence of the tendency of five-coordinate B_{12} compounds and model compounds to dimerize or coordinate an additional ligand and become six-coordinate. Nonetheless, where comparisons can be made, the features and trends observed in the OEP series are consistent with earlier observations. We have already noted the constancy of the displacements of the cobalt atom as a function of the structure type. Thus, the net 0.22-Å displacement of the cobalt atom across the porphyrin plane that occurs during the above reaction sequence is anticipated by previous results. The out-of-plane movement of the cobalt atom, the decrease in Co—N_{ax} distance, and lack of change in the Co—N_{eq} distance upon "homolysis" in the OEP complexes mirror the structural differences between the methylcobalamin and cob(II)alamin.[35,50] Moreover, structural data for cob(II)alamin permit one to determine that the distance between the benzimidazole nitrogen and the corrin plane increases by 0.06 and 0.01 Å, respectively, upon homolysis of coenzyme B_{12} and methylcobalamin.[50] The electronic *trans* influence of the axial ligands

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is well established from the structural changes that occur in six-coordinate complexes when axial ligands are varied.[33,34,51] Prior to this report, though, no reliable data were available that established the magnitude of the effect of coordination of an axial base on the cobalt—alkyl bond distance in a closely related pair of complexes. The only other pair of five-coordinate alkyl–Co(III) and six-coordinate alkyl–Co(III) base complexes that have been structurally characterized are Co(acacen)CH$_3$ and Co(acacen)(CH$_3$)(Py).[13,52] Unfortunately, the respective Co—C distances of 1.95(2) and 1.99(1) Å are indistinguishable because of their large standard deviations.

Conclusions. Several of the structural changes observed in the series of OEP complexes reported here contribute to and help rationalize the "base-on" effect in which coordination of an axial ligand accelerates homolysis of the Co—C bond. The significant elongation of the Co—C bond distance in Co(OEP)(CH$_3$)(Py) relative to Co(OEP)(CH$_3$) reflects both the electronic *trans* influence of the pyridine and the increased steric interactions of the alkyl ligand with the porphyrin. In addition, the steric interaction of the pyridine with the porphyrin is more extensive in Co(OEP)(CH$_3$)(Py) than in Co(OEP)(DMAP), the homolysis product.[53] It should be noted that these increased steric interactions occur regardless of whether the equatorial ligand is sufficiently flexible to transmit mechanically the steric bulk of the axial base to the alkyl group. These observations might support Brown's suggestion that the base-on effect in B$_{12}$ compounds is due to a substantial entropic stabilization of the base-off form.[9] The entropic stabilization is proposed to result from conformation changes that decrease the steric interactions between the corrin and the axial ligands and consequently increase the range of side-chain thermal motions.

On the other hand, our results lead us to question the explanation proposed for the direct correlation of the Co—C bond strength and the electron donor strength of the base. More basic ligands are expected to stabilize higher oxidation states and therefore to favor the six-coordinate alkyl–Co(III) complex over the five-coordinate Co(II) complex.[4a,h] However, the cobalt ion of the six-coordinate alkyl complex appears relatively electron rich. The Co—N$_{ax}$ distance in Co(OEP)(CH$_3$)(Py) is tremendously longer than expected for a true six-coordinate Co(III) porphyrin pyridine complex and is even significantly longer than most five-coordinate Co(II) porphyrin pyridine complexes. Thus, the Co(III) oxidation state of the six-coordinate complex could be more formal than real. The decrease in the Co—N$_{ax}$ distance upon homolysis suggests that ligand binding could be substantially stronger in the five-coordinate complex than in the six-coordinate complex. Given that the transition state for homolysis is known to be very product-like,[4] stronger coordination in the five-coordinate complex will stabilize the transition state for homolysis relative to the reactant and will thereby increase the rate of homolysis. We are currently investigating this issue in our laboratory.

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Supplementary Material Available: Tables S-I through S-XVI, giving atomic coordinates, thermal parameters, hydrogen atom coordinates, bond lengths and angles, and least-squares best planes for Co(OEP)(DMAP); atomic coordinates, thermal parameters, hydrogen atom coordinates, isotropic thermal parameters, bond lengths and angles, and least-squares best planes for Co(OEP)-CH$_3$; and atomic coordinates, thermal parameters, hydrogen atom coordinates, interatomic distances, bond angles, and least-squares best planes for Co(OEP)(CH$_3$)(Py) (36 pages); listings of observed and calculated structure factors for Co(OEP)(DMAP), Co(OEP)-CH$_3$, and Co(OEP)(CH$_3$)(Py) (55 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(53) The long Co—N$_{ax}$ bond length in Co(OEP)(CH$_3$)(Py) and the very much shorter Co—N$_{ax}$ bond length in other six-coordinate nonalkyl Co(III) porphyrin complexes that also have the Co atom in the plane of the porphyrin led one reviewer to question how important the relief of steric strain was in the present case. An example of the latter type of complex is Co(TPP)-(NO$_2$)(3,5-Me$_2$Py), which has Co—N$_{ax}$ = 2.036(4) Å (see ref 38). The lutidine ligand in this complex has a pyridine rotation angle $\phi = 36.4$ °, which is favorable for reducing steric interactions. The contact distances between the porphyrin nitrogen atoms and the lutidine α-hydrogen atoms are 2.55 and 2.76 Å, which are substantially greater than the analogous contacts of 2.43 and 2.61 Å in Co(OEP)(CH$_3$)(Py). Thus, despite a much shorter Co—N$_{ax}$ distance in the lutidine complex, the steric interactions appear to be less significant than in Co(OEP)(CH$_3$)(Py).