Cobalt Complexes of Octaethyloxophlorin. Metal-Centered Redox Chemistry in the Presence of a Redox-Active Ligand

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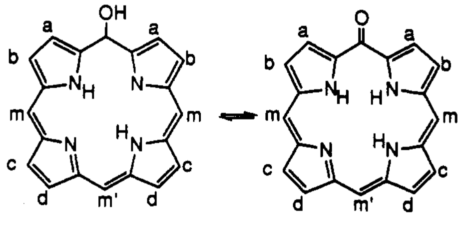
Two cobalt complexes of octaethyloxophlorin (H_2OEPOH), which are related by one-electron oxidation and proton transfer, have been characterized by X-ray diffraction. Deep orange {(py)Co^{II}(OEPOH··py)} crystallizes in the triclinic space group $P\bar{1}$ with a = 9.267(3) Å, b = 14.007(4) Å, c = 15.816(6) Å, α = 101.70(2)°, β = 92.41(3)°, and γ = 101.51(2)° at 130(2) K with $Z = 2$. Refinement of 4615 reflections with $F > 4.0\sigma(F)$ and 490 parameters yielded $R = 0.053$, $R_w = 0.055$. The structure involves a five-coordinate cobalt ion with the axial Co–N distance (2.204(3) Å) longer than the in-plane Co–N distances (average 1.988 Å). This elongation is consistent with the presence of a low-spin ($S = {}^1/_2$) d^7 ion with the d_{z^2} orbital filled. The macrocycle has an ordered structure with a second pyridine participating in a hydrogen bond to the meso hydroxyl group. Lime-green solutions of {(py)$_2$Co^{III}(OEPO)} produce blue crystals that form in the monoclinic space group $P2_1$ with a = 19.177(4) Å, b = 20.039(4) Å, c = 10.547(2) Å, and β = 100.36° at 130(2) K with $Z = 4$. Refinement of 4874 reflections with $I > 2\sigma(I)$ and 973 parameters yielded $R = 0.054$. The structure was refined as a racemic twin. There are two independent molecules in the unit cell. Each contains a six-coordinate cobalt with short in- and out-of-plane Co–N distances, which average 1.958 Å for the Co–N(pyrrole) and 1.961 Å for the Co–N(pyridine) distances, and a severely saddle-shaped macrocycle. In both molecules the meso keto groups show some disorder, and in the second molecule three of the ethyl groups are disordered. The electronic spectrum of {(py)Co^{II}(OEPOH··py)} shows a typical porphyrin-like spectrum (λ_{max}, nm: 404 (Soret), 530) while the spectrum of {(py)$_2$Co^{III}(OEPO)} shows characteristic low-energy absorption (λ_{max}, nm: 442 (Soret), 532, 622, 676) that distinguishes this trianionic macrocycle from oxophlorin radical complexes like {(py)Zn^{II}(OEPO·)}.

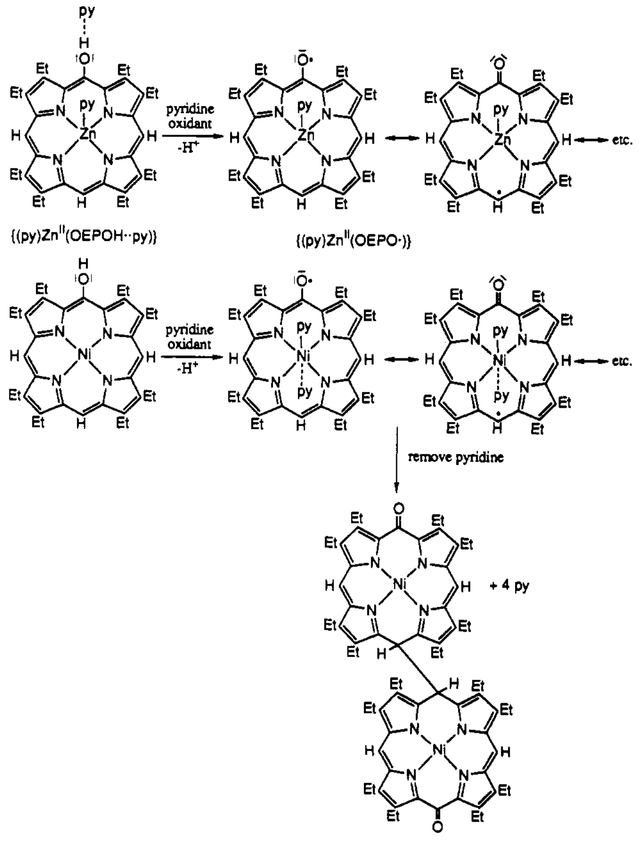
Introduction

Meso-hydroxylation of metalloporphyrins is a key step in the degradation of this macrocycle both in model systems[1,2] and in heme catabolism where heme oxygenase is the enzyme which initiates the process.[3–5] The resulting meso hydroxyporphyrins or oxophlorins, **1**,[6] and their metal complexes are considerably more easily oxidized than are their porphyrin counterparts.[7,8] The oxidation of octaethyloxophlorin (H_2OEPOH, **1**; a–d = Et; m, m′ = H) to form a free radical was demonstrated some time ago,[7,9] and recently this laboratory showed that oxidation of the zinc(II) and nickel(II) complexes of H_2OEPOH produce air-stable, isolable free radicals as shown in Scheme I.[10,11] When the axial pyridine ligands are removed, the nickel radical readily



1a **1b**

Scheme I



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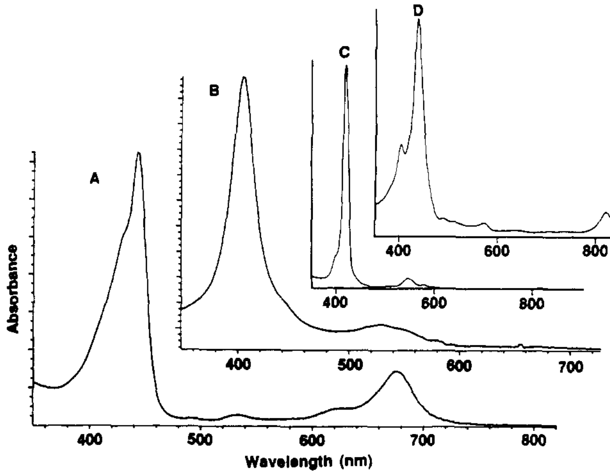


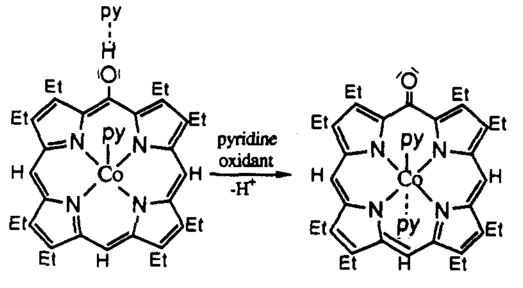
Figure 1. Electronic absorption spectra, pyridine solutions [λ_{max}, nm (ϵ, $M^{-1} cm^{-1}$)]: A, $\{(py)_2Co^{III}(OEPO)\}$ [430 sh (1.6×10^5), 442 (2.3×10^5), 532 (1.2×10^4), 622 sh (1.6×10^4), 676 (4.6×10^4)]; B, $\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$ [404 (1.6×10^4), 530 (1.4×10^3)]; C, $\{(py)Zn^{II}(OEPOH{\cdot\cdot}py)\}$ [420 (2.8×10^5), 546 (1.6×10^4), 568 (1.0×10^4)]; D, $\{(py)Zn^{II}(OEPO^{\cdot})\}$ [404 (5.1×10^4), 438 (1.2×10^5), 489 (9.8×10^3), 547 (7.5×10^3), 637 (3.6×10^3), 709 (3.2×10^3), 743 (3.3×10^3), 819 (1.4×10^4)]. Traces C and D were adapted from ref 10.

(and reversibly) dimerizes through the formation of a new C–C bond.[12]

As part of the systematic examination of the properties of metal complexes of H_2OEPOH, the behavior of the cobalt complexes has been examined. Bonnett and Dimsdale reported that treatment of $Co^{II}(OEP)$ (OEP is the dianion of octaethylporphyrin) with hydrogen peroxide in pyridine produces a green solution of $\{(py)_2Co^{III}(OEPO)\}$ which can be isolated as deep blue crystals.[2] Here we report the structure of this complex, which contains the ligand in the keto tautomeric form, **1b**, and its reduction to form the previously unknown cobalt(II) complex.

Results

Solution Characterization of $\{(py)_2Co^{III}(OEPO)\}$ and $\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$. Blue crystals of $\{(py)_2Co^{III}(OEPO)\}$, which dissolve in pyridine to produce a lime-green solution, were obtained by oxidation of $Co^{II}(OEP)$ with hydrogen peroxide in pyridine. The procedure of Bonnett and Dimsdale was followed,[2] but we found that the chromatography step was unnecessary and that it reduced the yield. Treatment of a green pyridine solution of $\{(py)_2Co^{III}(OEPO)\}$ with aqueous sodium dithionite gives a red-orange solution of $\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$, from which red crystals of the complex can be isolated by the addition of water. This cobalt(II) complex is very air sensitive. Treatment with dioxygen or iodine in pyridine results in its oxidation back to form $\{(py)_2Co^{III}(OEPO)\}$, as shown in eq 1. Thus, the redox couple, $\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}/\{(py)_2Co^{III}(OEPO)\}$, is related to the previously described couples, $\{(py)Zn^{II}(OEPOH{\cdot\cdot}py)\}/\{(py)Zn^{II}(OEPO^{\cdot})\}$[10] and $\{Ni^{II}(OEPOH)\}/\{(py)_2Ni^{II}(OEPO^{\cdot})\}$.[11] In each case, the pair of complexes is related by the loss of one electron and one proton. However, the site of redox activity is different for the cobalt complexes where it is the metal, not the ligand, that is involved.



$\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$ $\{(py)_2Co^{III}(OEPO)\}$ (1)

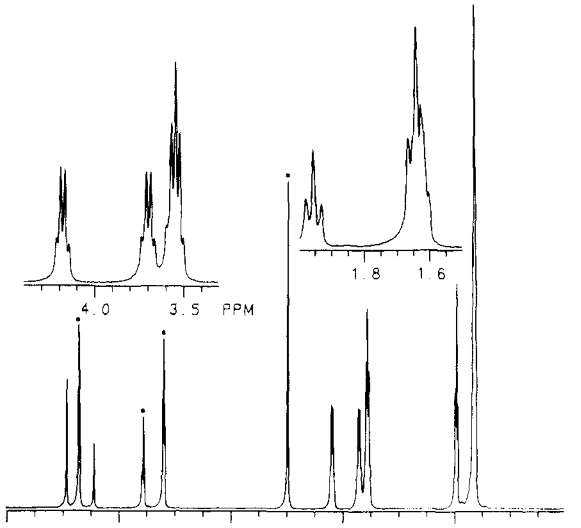


Figure 2. 300-MHz ^1H NMR spectrum of $\{(py)_2Co^{III}(OEPO)\}$ in pyridine-d_5 at 23 °C. Resonances denoted by asterisks result from residual undeuterated pyridine and from water.

Figure 1 compares the electronic absorption spectra of $\{(py)_2Co^{III}(OEPO)\}$ (trace A) and $\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$ (trace B) with those of $\{(py)Zn^{II}(OEPOH{\cdot\cdot}py)\}$ (trace C) and $\{(py)Zn^{II}(OEPO^{\cdot})\}$ (trace D).[10] The spectra of $\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$ and $\{(py)Zn^{II}(OEPOH{\cdot\cdot}py)\}$ are similar and follow the pattern that is typical for porphyrins. The spectra of $\{(py)_2Co^{III}(OEPO)\}$ and $\{(py)Zn^{II}(OEPO^{\cdot})\}$, however, are distinctly different from one another and from their reduced counterparts. The low-energy absorption at 819 nm in trace D is indicative of the formation of an oxophlorin radical.[10] A similar spectrum (with λ_{max} at 825 nm) is seen for $\{(py)_2Ni^{II}(OEPO^{\cdot})\}$.[11] For $\{(py)_2Co^{III}(OEPO)\}$ the spectrum is quite distinct with an intense, low-energy absorption at 675 nm. This spectrum agrees well with that reported by Bonnett and Dimsdale for this complex in pyridine solution.[2]

The ^1H NMR spectrum of $\{(py)_2Co^{III}(OEPO)\}$ in pyridine-d_5 solution is shown in Figure 2. In contrast to previous reports that describe the ^1H NMR spectra of oxophlorins and their complexes as broad or poorly resolved, this spectrum consists of narrow lines with good resolution. The two meso protons are observed at 8.4 and 8.95 ppm. The methylene resonances appear as two, clearly resolved quartets and one overlapping pair of quartets. One distinct methyl triplet probably results from the ethyl groups (a) adjacent to the meso keto group while the other three methyl triplets overlap one another. This spectrum establishes the nature of the cobalt spin state as low-spin ($S = 0$) d^6. Careful examination of the region from 14 to 9 ppm shows that no resonances are present. This is the region where the resonance of the meso hydroxyl proton of $\{(py)Zn^{II}(OEPOH{\cdot\cdot}py)\}$ is observed, but since $\{(py)_2Co^{III}(OEPO)\}$ lacks this functional group, no resonance is found.

Crystal and Molecular Structure of $\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$. The structure of this complex has been examined by X-ray crystallography. A drawing of the molecule, which has no crystallographically imposed symmetry, is shown in Figure 3. Atomic coordinates are given in Table I, and Table II contains selected bond distances and angles.

The cobalt ion is five-coordinate. The four Co–N(pyrrole) distances have nearly equal lengths (average 1.988 Å) while the axial Co–N(py) distance (2.203(3) Å) is longer. This situation

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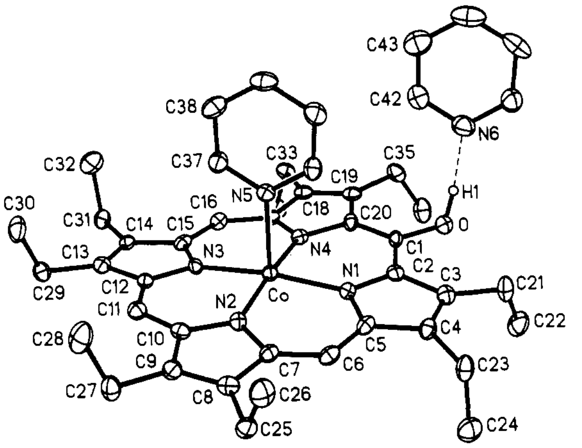

Figure 3. Perspective view of {(py)Co^{II}(OEPOH··py)} with 50% thermal contours.

is typical for low-spin ($S = {}^1/_2$) cobalt(II) porphyrins[13,14] (e.g., {(1-methylimidazole)Co(OEP)}[15]) in which occupancy of the d_{z^2} orbital by a single electron results in elongation of the bond along the z axis. The hydroxyporphyrin itself is nearly planar. Figure 4 shows a drawing that gives the out-of-plane distances for each atom within the core of the macrocycle.

Crystals of {(py)Co^{II}(OEPOH··py)} are isostructural with those of {(py)Zn^{II}(OEPOH··py)}.[10] However, the Co–N(pyrrole) distances are shorter than the Zn–N (pyrrole) distances (average 2.079 Å), but the Co–N(py) distance is slightly longer than the Zn–N(py) distance (2.183(8) Å). This lengthening of the Co–N(py) bond may be the result of steric interaction of the axial ligand with the macrocycle. The cobalt ion is 0.13 Å out of the N$_4$ plane, whereas the zinc ion is 0.31 Å out of that plane. Thus, in the cobalt structure, the axial ligand is drawn in toward the macrocycle relative to the zinc complex. This is compensated by elongation of the Co–N(py) bond. In general the structural parameters for {(py)Co^{II}(OEPOH··py)} are consistent with the presence of low-spin ($S = {}^1/_2$) Co^{II}. This is the common spin state observed for Co^{II} in porphyrin complexes.[13] In both structures there is a second pyridine molecule which is hydrogen bonded to the meso hydroxy group. In the cobalt complex, the hydrogen atom involved in this was located on a difference map. The refined O–H distance is 0.92(6) Å and the N(6)–H distance is 1.75(6) Å. The presence of this hydrogen-bonded pyridine is an important factor in the production of an ordered structure for both the cobalt and zinc oxophlorin complexes. Many porphyrin derivatives like the oxophlorins, which have sterically small perturbations to the core of the macrocycle, show varying degrees of disorder in the solid state (*vide infra*), but that is clearly not the case for these cobalt and zinc complexes.

The axial pyridine ligand is oriented so that it is nearly eclipsed with regard to the N(1)–Co and N(3)–Co bonds. The dihedral angles between the plane of the pyridine ligand and the Co–N(1) and Co–N(3) bonds are 8 and 9°, respectively. This situation, in which the plane of the axial ligand nearly eclipses two of the Co–N bonds within the macrocycle, is characteristic of five-coordinate cobalt(II) porphyrin complexes.[14,15]

Crystal and Molecular Structure of {(py)$_2$Co^{III}(OEPO)}. Atomic coordinates are given in Table III, and selected interatomic distances and angles are presented in Table IV. There are two independent molecules within the unit cell. Both suffer from some degree of disorder which involves the location of the meso keto substituent.

Table I. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for {(py)Co^{II}(OEPOH··py)}

	x	y	z	U(eq)[a]
Co	2260(1)	2095(1)	2901(1)	15(1)
O	1447(3)	5171(2)	2291(2)	24(1)
N(1)	2166(4)	3421(2)	3606(2)	17(1)
N(2)	2608(4)	1598(2)	3968(2)	17(1)
N(3)	2677(4)	841(2)	2205(2)	15(1)
N(4)	2157(4)	2647(3)	1843(2)	16(1)
N(5)	−154(3)	1538(2)	2742(2)	17(1)
C(1)	1697(4)	4296(3)	2468(3)	17(1)
C(2)	1924(4)	4257(3)	3332(3)	18(1)
C(3)	1909(5)	5076(3)	4064(3)	20(1)
C(4)	2157(5)	4718(3)	4789(3)	20(1)
C(5)	2292(5)	3700(3)	4501(3)	19(1)
C(6)	2536(5)	3092(3)	5059(3)	21(1)
C(7)	2674(5)	2118(3)	4819(3)	18(1)
C(8)	2897(5)	1490(3)	5419(3)	20(1)
C(9)	2932(5)	582(3)	4931(3)	20(1)
C(10)	2776(4)	662(3)	4031(3)	18(1)
C(11)	2839(4)	−97(3)	3342(3)	20(1)
C(12)	2815(4)	−14(3)	2485(3)	16(1)
C(13)	3004(4)	−798(3)	1764(3)	18(1)
C(14)	2997(4)	−396(3)	1042(3)	16(1)
C(15)	2780(4)	602(3)	1317(3)	17(1)
C(16)	2613(4)	1228(3)	773(3)	17(1)
C(17)	2297(4)	2166(3)	1014(3)	17(1)
C(18)	2030(4)	2758(3)	398(3)	18(1)
C(19)	1696(4)	3611(3)	854(3)	20(1)
C(20)	1804(4)	3537(3)	1756(3)	17(1)
C(21)	1775(5)	6123(3)	4064(3)	27(2)
C(22)	3193(6)	6773(3)	3861(3)	36(2)
C(23)	2350(5)	5278(3)	5715(3)	25(2)
C(24)	3973(6)	5729(4)	6016(3)	36(2)
C(25)	3007(5)	1804(3)	6386(3)	23(1)
C(26)	1496(5)	1733(3)	6755(3)	31(2)
C(27)	3043(5)	−358(3)	5221(3)	25(2)
C(28)	1553(6)	−1071(3)	5156(3)	36(2)
C(29)	3087(5)	−1831(3)	1836(3)	21(1)
C(30)	1590(5)	−2465(3)	1927(3)	32(2)
C(31)	3083(5)	−914(3)	121(3)	22(1)
C(32)	1562(5)	−1399(4)	−344(3)	35(2)
C(33)	2137(5)	2466(3)	−556(3)	22(2)
C(34)	3726(5)	2592(4)	−806(3)	31(2)
C(35)	1352(5)	4442(3)	466(3)	24(2)
C(36)	2689(5)	5280(3)	483(3)	31(2)
C(37)	−787(5)	595(3)	2358(3)	25(2)
C(38)	−2295(5)	237(4)	2194(3)	30(2)
C(39)	−3221(5)	894(4)	2449(3)	29(2)
C(40)	−2597(5)	1875(3)	2837(3)	30(2)
C(41)	−1082(5)	2152(3)	2972(3)	24(2)
N(6)	−1468(4)	4873(3)	1958(3)	33(2)
C(42)	−2120(6)	3912(4)	1655(3)	35(2)
C(43)	−3610(6)	3571(4)	1480(3)	39(2)
C(44)	−4501(6)	4251(5)	1627(3)	44(2)
C(45)	−3858(6)	5249(4)	1937(3)	40(2)
C(46)	−2349(6)	5520(4)	2095(3)	34(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Figure 5 shows a drawing of one of the molecules of the complex. The cobalt ion has an octahedral structure, and the oxophlorin ligand is ruffled.[14,16] In this molecule there are two sites for the meso keto substituent. In the major form, that group is present at site O(1a) with 0.69(1) occupancy, while the minor site, O(1b), has a fractional occupancy of 0.31(1). The other, independent molecule has a six-coordinate cobalt and a ruffled oxophlorin core. However, for the second molecule, the meso keto substituent is disordered over three sites. In all cases, however, the C–O bond distances are ~1.25 Å, a value which is appropriate for a keto, rather than a hydroxy, substituent. Molecule 2 also suffers from disorder in the positions of two entire ethyl groups and the methyl portion of another ethyl group.

Despite the differences in the disorder, the two molecules have similar geometries. In both cases, the in-plane and out-of-plane Co–N distances are nearly equal and fall in a narrow range: 1.948(7)–1.969(7) Å for molecule 1, 1.948(7)–1.972(7) Å for

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Table II. Bond Lengths (Å) and Angles (deg) for $\{(py)Co^{II}(OEPOH\cdot\cdot py)\}$

	Bond Lengths		
Co–N(1)	1.983(3)	Co–N(2)	1.990(4)
Co–N(3)	1.993(3)	Co–N(4)	1.987(4)
Co–N(5)	2.203(3)	O–C(1)	1.372(6)
N(1)–C(2)	1.383(6)	N(1)–C(5)	1.383(5)
N(2)–C(7)	1.387(5)	N(2)–C(10)	1.373(6)
N(3)–C(12)	1.384(6)	N(3)–C(15)	1.388(5)
N(4)–C(17)	1.371(5)	N(4)–C(20)	1.381(6)
N(5)–C(37)	1.340(5)	N(5)–C(41)	1.343(6)
C(1)–C(2)	1.387(6)	C(1)–C(20)	1.405(5)
C(2)–C(3)	1.458(6)	C(3)–C(4)	1.370(7)
C(6)–C(7)	1.373(6)	C(4)–C(5)	1.438(6)
C(8)–C(9)	1.354(6)	C(5)–C(6)	1.385(7)
C(9)–C(10)	1.454(6)	C(7)–C(8)	1.454(7)
C(10)–C(11)	1.371(6)	C(11)–C(12)	1.385(6)
C(12)–C(13)	1.457(6)	C(13)–C(14)	1.372(6)
C(16)–C(17)	1.385(6)	C(14)–C(15)	1.435(6)
C(18)–C(19)	1.363(6)	C(15)–C(16)	1.372(7)
C(19)–C(20)	1.451(6)	C(17)–C(18)	1.445(6)
	Bond Angles		
N(1)–Co–N(2)	90.8(1)	N(1)–Co–N(3)	171.5(1)
N(2)–Co–N(3)	88.7(1)	N(1)–Co–N(4)	88.9(1)
N(2)–Co–N(4)	173.6(1)	N(3)–Co–N(4)	90.7(1)
N(1)–Co–N(5)	94.5(1)	N(2)–Co–N(5)	96.1(1)
N(3)–Co–N(5)	94.0(1)	N(4)–Co–N(5)	90.3(1)
Co–N(1)–C(2)	128.9(3)	Co–N(1)–C(5)	126.6(3)
C(2)–N(1)–C(5)	104.5(3)	Co–N(2)–C(7)	127.1(3)
Co–N(2)–C(10)	128.1(3)	C(7)–N(2)–C(10)	104.8(4)
Co–N(3)–C(12)	127.8(3)	Co–N(3)–C(15)	127.4(3)
C(12)–N(3)–C(15)	104.6(3)	Co–N(4)–C(17)	126.2(3)
Co–N(4)–C(20)	128.8(3)	C(17)–N(4)–C(20)	104.8(3)
Co–N(5)–C(37)	122.6(3)	Co–N(5)–C(41)	121.3(2)
C(37)–N(5)–C(41)	116.0(3)	O–C(1)–C(2)	117.5(3)
O–C(1)–C(20)	117.0(4)	C(2)–C(1)–C(20)	125.3(4)
N(1)–C(2)–C(1)	123.8(4)	N(1)–C(2)–C(3)	111.4(4)
C(1)–C(2)–C(3)	124.8(4)	C(2)–C(3)–C(4)	105.6(4)
C(3)–C(4)–C(5)	107.2(4)	N(1)–C(5)–C(4)	111.3(4)
N(1)–C(5)–C(6)	125.1(4)	C(4)–C(5)–C(6)	123.6(4)
C(5)–C(6)–C(7)	125.9(4)	N(2)–C(7)–C(6)	124.4(4)
N(2)–C(7)–C(8)	110.7(4)	C(6)–C(7)–C(8)	124.8(4)
C(7)–C(8)–C(9)	106.7(4)	C(8)–C(9)–C(10)	106.6(4)
N(2)–C(10)–C(9)	111.2(3)	N(2)–C(10)–C(11)	125.1(4)
C(9)–C(10)–C(11)	123.6(4)	C(10)–C(11)–C(12)	124.7(4)
N(3)–C(12)–C(11)	124.4(4)	N(3)–C(12)–C(13)	111.1(4)
C(11)–C(12)–C(13)	124.4(4)	C(12)–C(13)–C(14)	105.9(4)
C(13)–C(14)–C(15)	107.1(4)	N(3)–C(15)–C(14)	111.3(4)
N(3)–C(15)–C(16)	123.8(4)	C(14)–C(15)–C(16)	124.7(4)
C(15)–C(16)–C(17)	125.9(4)	N(4)–C(17)–C(16)	125.9(4)
N(4)–C(17)–C(18)	111.0(4)	C(16)–C(17)–C(18)	123.1(4)
C(17)–C(18)–C(19)	107.2(4)	C(18)–C(19)–C(20)	105.6(4)
N(4)–C(20)–C(1)	123.0(4)	N(4)–C(20)–C(19)	111.4(3)
C(1)–C(20)–C(19)	125.4(4)		

molecule 2. These Co–N distances are all significantly shorter than the Co–N distances in $\{(py)Co^{II}(OEPOH\cdot\cdot py)\}$. In particular, the out-of-plane Co–N(py) distances have contracted as a result of the emptying of the d_{z^2} orbital in the d^6 Co(III) complex. The in-plane Co–N distances are at the short end of the range of Co–N distances that are seen in six-coordinate cobalt(III) porphyrins (1.949–1.993 Å). However, they are consistent with the Co–N distances in low-spin complexes with monodentate ligands.[17] To accommodate such short distances, the oxophlorin macrocycles in the two molecules are severely ruffled. This can be best appreciated by turning to Figure 6, which shows the out-of-plane displacements for the atoms within the macrocyclic core of each molecule. The extent of this distortion is paralleled by the cobalt(III) complex $\{(3,5\text{-lutidine})(NO_2)Co^{III}(TPP)\}$, which also has short Co–N(pyrrole) distances of 1.949(2) and 1.958(2) Å and a severely ruffled porphyrin core.[18]

In both molecules of $\{(py)_2Co^{III}(OEPO)\}$, the two pyridine ligands are nearly perpendicular to one another. The angle between the two pyridine planes in molecule 1 is 77° while it is 75° in molecule 2. In contrast to the arrangement in $\{(py)Co^{II}(OEPOH\cdot\cdot py)\}$, the planes of the pyridine ligands in $\{(py)_2Co^{III}(OEPO)\}$ are staggered with respect to the Co–N(pyrrole) bonds. In molecule 1, the angle between the pyridine with N(5) and the Co–N(1) bond is 53° while the angle between the other pyridine containing N(6) and the Co–N(1) bond is 49°. In molecule 2, the angle between the pyridine that contains N(11) and the Co–N(7) bond is 40° while the angle between the pyridine that contains N(12) and the Co–N(7) bond is 35°. These orientations of the pyridine ligands minimize contact between the ortho hydrogens of the pyridine ligands and the pyrrole nitrogens of the oxophlorin ligand and place the axial ligands in the least sterically congested position within the complex. Nevertheless, in order to accommodate the short axial Co–N bonds, the macrocycle is forced to undergo S_4 ruffling.

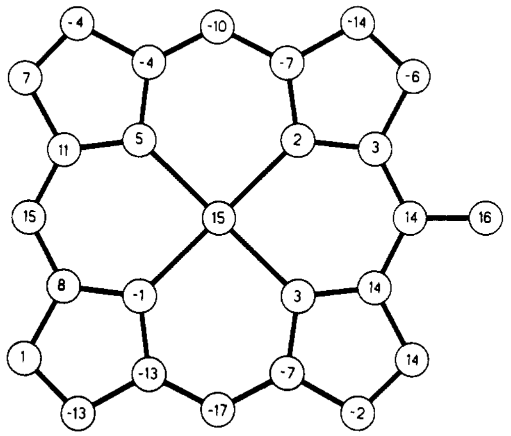

Figure 4. Diagram of the macrocyclic core of $\{(py)Co^{II}(OEPOH\cdot\cdot py)\}$ in which each atom label has been replaced by a number that represents the perpendicular displacement, in units of 0.01 Å, of that atom from the plane of the core of the macrocycle.

Discussion

This work on the cobalt complexes of H_2OEPOH offers some interesting similarities and contrasts with that on zinc(II)[10] and nickel(II)[11] complexes. Clearly the cobalt(II) and zinc(II) complexes $\{(py)Co^{II}(OEPOH\cdot\cdot py)\}$ and $\{(py)Zn^{II}(OEPOH\cdot\cdot py)\}$ are similar in structure. These two complexes contain a porphyrin-like core and a peripheral meso hydroxyl group. Both $\{(py)Zn^{II}(OEPOH\cdot\cdot py)\}$ and Ni(OEPOH) are oxidized in pyridine to stable radicals, as shown in Scheme I. In contrast, the cobalt(II) complex, $\{(py)Co^{II}(OEPOH\cdot\cdot py)\}$, undergoes metal-centered oxidation to produce $\{(py)_2Co^{III}(OEPO)\}$, in which the ligand coordinates as the trianion of tautomeric structure **1b** of the macrocycle.

It has become clear that trivalent metal ions can coordinate to the trianion of H_2OEPOH in two distinct fashions. In the five-coordinate Fe^{III},[19,20] Mn^{III},[21] In^{III},[22] and Ga^{III}[23] complexes, the ligand acts as a bridging group and the cofacial dimers **2** are

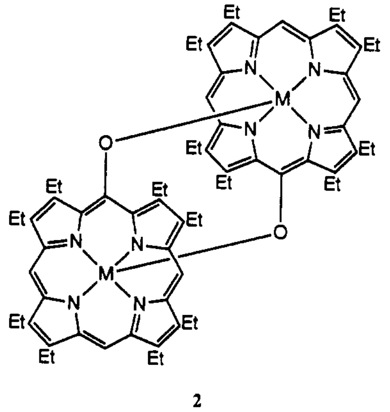

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Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $\{(py)_2Co^{III}(OEPO)\}^a$

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Co(1)	8778(1)	640(1)	4933(1)	26(1)	O(2C)	13122(6)	384(6)	619(10)	42(3)
O(1A)	9501(5)	775(5)	9345(9)	57(3)	N(7)	13921(3)	1325(3)	6253(6)	25(4)
O(1B)	6969(12)	203(12)	1662(22)	57(3)	N(8)	14440(3)	41(4)	6338(6)	25(4)
N(1)	9364(3)	66(4)	6185(6)	29(4)	N(9)	13710(3)	−182(4)	3829(6)	33(4)
N(2)	8585(3)	−106(3)	3730(6)	26(4)	N(10)	13216(3)	1121(3)	3756(6)	29(4)
N(3)	8182(3)	1204(3)	3672(6)	28(4)	N(11)	12996(3)	274(4)	5733(6)	32(4)
N(4)	8974(4)	1395(3)	6137(6)	29(4)	N(12)	14666(3)	878(3)	4387(6)	25(4)
N(5)	7939(3)	417(4)	5662(6)	33(4)	C(47)	12992(5)	2062(5)	5128(9)	49(6)
N(6)	9617(3)	884(3)	4197(6)	27(4)	C(48)	13502(4)	1888(5)	6177(8)	33(5)
C(1)	9432(5)	773(5)	8141(8)	44(7)	C(49)	13722(5)	2306(4)	7298(8)	36(5)
C(2)	9577(5)	177(5)	7497(8)	35(6)	C(50)	14292(4)	2004(4)	8027(7)	30(5)
C(3)	10017(5)	−347(5)	8027(8)	38(6)	C(51)	14405(4)	1382(4)	7381(7)	20(5)
C(4)	10097(4)	−790(4)	7048(8)	33(5)	C(52)	14911(4)	912(4)	7916(8)	30(5)
C(5)	9676(4)	−512(5)	5900(8)	35(5)	C(53)	14873(4)	250(4)	7433(7)	25(5)
C(6)	9528(4)	−850(5)	4719(8)	31(5)	C(54)	15242(4)	−293(4)	8126(7)	27(5)
C(7)	8985(4)	−673(4)	3727(7)	27(5)	C(55)	14999(4)	−864(4)	7483(7)	25(5)
C(8)	8709(4)	−1091(4)	2645(8)	30(5)	C(56)	14510(4)	−663(4)	6344(8)	27(5)
C(9)	8120(4)	−779(4)	2001(8)	29(5)	C(57)	14214(5)	−1068(5)	5363(9)	39(6)
C(10)	8052(4)	−141(4)	2677(8)	28(4)	C(58)	13850(5)	−841(4)	4162(9)	41(6)
C(11)	7574(4)	347(4)	2246(8)	30(5)	C(59)	13662(7)	−1248(5)	3030(11)	76(10)
C(12)	7685(4)	1012(5)	2657(8)	27(5)	C(60)	13440(5)	−828(5)	2042(8)	55(7)
C(13)	7336(4)	1596(5)	1986(8)	32(5)	C(61)	13469(5)	−159(5)	2534(8)	39(6)
C(14)	7662(4)	2134(4)	2589(8)	30(5)	C(62)	13218(4)	414(5)	1820(7)	37(5)
C(15)	8181(4)	1893(4)	3675(8)	27(5)	C(63)	13040(5)	997(5)	2445(8)	37(6)
C(16)	8525(4)	2313(4)	4644(8)	30(5)	C(64)	12600(6)	1532(6)	1806(9)	71(9)
C(17)	8878(4)	2047(4)	5839(8)	30(5)	C(65)	12480(7)	1942(6)	2811(12)	106(12)
C(18)	9054(4)	2460(4)	6986(8)	30(5)	C(66)	12885(5)	1712(5)	3948(9)	47(6)
C(19)	9262(5)	2015(5)	7978(9)	40(5)	C(67)	13397(5)	2977(4)	7518(9)	40(6)
C(20)	9203(5)	1370(5)	7454(8)	35(6)	C(68)	13684(6)	3548(5)	6830(10)	63(9)
C(21)	10399(6)	−399(6)	9466(8)	68(9)	C(69)	14688(5)	2210(4)	9329(8)	43(6)
C(22)	9922(8)	−627(7)	10252(12)	94(12)	C(70)	14435(7)	1861(6)	10429(8)	64(10)
C(23)	10513(5)	−1433(5)	7130(9)	45(6)	C(71)	15755(5)	−252(5)	9356(8)	51(8)
C(24)	10054(6)	−2041(6)	7108(11)	68(9)	C(72)	15420(8)	−246(7)	10555(8)	94(14)
C(25)	9008(5)	−1739(5)	2330(9)	39(6)	C(73)	15235(4)	−1568(4)	7804(8)	27(5)
C(26)	8813(6)	−2331(5)	3119(12)	63(8)	C(74)	15828(5)	−1793(4)	7125(9)	39(6)
C(27)	7651(5)	−979(5)	778(9)	39(5)	C(75)	13649(7)	−2038(6)	3075(13)	95(11)
C(28)	7832(6)	−627(6)	−392(8)	57(8)	C(76)	14368(7)	−2253(7)	2967(13)	108(12)
C(29)	6743(5)	1587(6)	868(8)	47(6)	C(77)	13212(6)	−1012(7)	637(10)	86(10)
C(30)	6966(6)	1478(7)	−414(9)	65(7)	C(78A)	13793(8)	−1025(10)	−61(14)	42(5)
C(31)	7512(5)	2862(5)	2293(9)	42(5)	C(78B)	12478(8)	−880(12)	83(17)	58(6)
C(32)	6983(6)	3163(6)	3077(12)	71(8)	C(79A)	12368(7)	1620(8)	326(12)	53(4)
C(33)	8980(5)	3192(5)	7032(10)	48(6)	C(79B)	12118	1459	689	53(4)
C(34)	8239(5)	3420(6)	7130(12)	58(6)	C(80A)	11666(7)	1272(8)	−49(13)	53(4)
C(35)	9459(5)	2194(5)	9384(8)	44(6)	C(80B)	12559	1743	−275	53(4)
C(36)	8847(5)	2097(7)	10088(9)	64(7)	C(81A)	11851(8)	2429(7)	2877(16)	45(4)
C(37)	7741(5)	−229(5)	5760(9)	40(6)	C(81B)	12373	2692	2395	45(4)
C(38)	7127(6)	−380(7)	6181(10)	65(7)	C(82A)	12132(11)	3114(7)	2621(21)	72(5)
C(39)	6683(6)	97(7)	6502(10)	64(7)	C(82B)	11525	2862	2522	72(5)
C(40)	6896(5)	748(7)	6437(9)	62(6)	C(83)	12422(4)	37(5)	4970(9)	39(5)
C(41)	7524(5)	901(6)	6000(8)	45(6)	C(84)	11827(5)	−171(5)	5419(10)	50(6)
C(42)	10221(4)	1063(5)	4952(8)	32(5)	C(85)	11803(5)	−111(6)	6698(10)	52(6)
C(43)	10831(5)	1177(5)	4465(9)	45(6)	C(86)	12397(5)	127(5)	7504(10)	47(7)
C(44)	10820(5)	1103(6)	3134(9)	51(6)	C(87)	12983(5)	305(5)	7002(8)	40(5)
C(45)	10190(5)	938(5)	2359(9)	43(6)	C(88)	14809(4)	1524(5)	4317(7)	33(5)
C(46)	9603(5)	834(4)	2912(8)	34(5)	C(89)	15423(4)	1758(5)	3965(8)	35(6)
Co(2)	13826(1)	573(1)	5049(1)	22(1)	C(90)	15988(5)	1319(6)	3630(8)	45(5)
O(2A)	15485(17)	1072(17)	8608(32)	42(3)	C(91)	15753(4)	636(5)	3674(8)	38(5)
O(2B)	14309(12)	−1684(12)	5410(22)	42(3)	C(92)	15130(4)	436(4)	4055(7)	29(5)

[a] Occupancies for disordered atoms are as follows: C(79A), C(80A), 0.67(1); C(79B), C(80B), 0.33(1); C(78A), C(78B), 0.5 (fixed); C(81A), C(82A), 0.57(1); C(81B), C(82B), 0.43(1); O(1A), 0.69(1); O(1B), 0.31(1); O(2A), 0.18(1); O(2B), 0.27(1); O(2C), 0.55(1).

formed. Recent crystallographic work on the In^{III} complex $\{In^{III}(OEPO)\}_2$ has produced the first thorough structural information on a dimer of this sort.[22] Additionally, six-coordinate, monomeric complexes, like $\{(py)_2Co^{III}(OEPO)\}$ and $\{(py)_2Mn^{III}(OEPO)\}$,[21] exist in which the oxophlorin ligand does not use the meso oxo substituent in coordination to the metal ions.

Comparison of the structures of $\{(py)_2Co^{III}(OEPO)\}$ and $\{(py)_2Mn^{III}(OEPO)\}$[21] shows that the oxophlorin ligand retains the degree of flexibility that is also shown by porphyrin ligands. The cobalt complex has a severely ruffled core, while that of the manganese complex is essentially flat. These differences can be traced to differences in the metal–ligand distances. For the high-spin ($S = 2$) d^4 manganese(III) complex, the Mn–N distances (in-plane, 2.020 Å; out-of-plane, 2.376 Å) are significantly longer than the Co–N distances in the low-spin d^6 complex. Additionally, in the manganese complex, the out-of-plane Mn–N distance is sufficiently elongated, due to the population of the d_{z^2} orbital, that pyridine ligands can eclipse a trans N–Mn–N unit. Thus, in $\{(py)_2Mn^{III}(OEPO)\}$, the two pyridine ligands adopt the coplanar arrangement that is very common for complexes of this type. In distinct contrast, the two pyridine ligands in $\{(py)_2Co^{III}(OEPO)\}$ are arranged in nearly perpendicular planes and are staggered with respect to the Co–N(pyrrole) bonds. This

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Table IV. Bond Lengths (Å) and Angles (deg) for {$(py)_2Co^{III}(OEPO)$}

Bond Lengths							
Molecule 1							
Co(1)–N(1)	1.948(7)	Co(1)–N(2)	1.954(8)	C(1)–C(2)	1.427(14)	C(1)–C(20)	1.427(14)
Co(1)–N(5)	1.956(7)	Co(1)–N(3)	1.950(7)	C(2)–C(3)	1.399(14)	C(3)–C(4)	1.391(13)
Co(1)–N(6)	1.969(7)	Co(1)–N(4)	1.967(8)	C(6)–C(7)	1.383(12)	C(4)–C(5)	1.441(13)
O(1A)–C(1)	1.253(14)	O(1B)–C(11)	1.25(2)	C(8)–C(9)	1.360(13)	C(5)–C(6)	1.401(13)
N(1)–C(5)	1.363(13)	N(1)–C(2)	1.389(12)	C(9)–C(10)	1.481(14)	C(7)–C(8)	1.437(13)
N(2)–C(7)	1.370(11)	N(2)–C(10)	1.370(11)	C(10)–C(11)	1.360(13)	C(11)–C(12)	1.406(14)
N(3)–C(12)	1.355(11)	N(3)–C(15)	1.381(12)	C(12)–C(13)	1.465(13)	C(13)–C(14)	1.347(14)
N(4)–C(17)	1.349(12)	N(4)–C(20)	1.380(12)	C(16)–C(17)	1.423(12)	C(14)–C(15)	1.459(13)
N(5)–C(41)	1.343(13)	N(5)–C(37)	1.358(13)	C(18)–C(19)	1.379(14)	C(15)–C(16)	1.395(13)
N(6)–C(42)	1.332(11)	N(6)–C(46)	1.355(11)	C(19)–C(20)	1.402(15)		
Molecule 2							
Co(2)–N(8)	1.948(7)	Co(2)–N(11)	1.957(7)	C(47)–C(66)	1.411(14)	C(48)–C(49)	1.448(12)
Co(2)–N(9)	1.972(7)	Co(2)–N(7)	1.959(7)	C(49)–C(50)	1.359(12)	C(52)–C(53)	1.418(13)
Co(2)–N(12)	1.964(7)	Co(2)–N(10)	1.965(7)	C(50)–C(51)	1.456(12)	C(54)–C(55)	1.369(12)
O(2A)–C(52)	1.25(4)	O(2B)–C(57)	1.25(3)	C(51)–C(52)	1.397(12)	C(55)–C(56)	1.441(12)
O(2C)–C(62)	1.248(14)	N(7)–C(51)	1.377(11)	C(53)–C(54)	1.425(12)	C(56)–C(57)	1.357(13)
N(7)–C(48)	1.379(11)	N(8)–C(53)	1.361(11)	C(57)–C(58)	1.406(14)	C(58)–C(59)	1.44(2)
N(8)–C(56)	1.416(12)	N(9)–C(61)	1.362(12)	C(59)–C(60)	1.35(2)	C(60)–C(61)	1.435(14)
N(9)–C(58)	1.380(13)	N(10)–C(66)	1.375(12)	C(61)–C(62)	1.409(14)	C(62)–C(63)	1.414(14)
N(10)–C(63)	1.386(11)	N(11)–C(83)	1.329(11)	C(63)–C(64)	1.453(14)	C(64)–C(65)	1.39(2)
N(11)–C(87)	1.344(12)	N(12)–C(88)	1.330(12)	C(65)–C(66)	1.39(2)		
N(12)–C(92)	1.346(11)	C(47)–C(48)	1.383(13)				
Bond Angles							
Molecule 1							
N(1)–Co(1)–N(2)	90.4(3)	N(1)–Co(1)–N(5)	90.7(3)	N(1)–C(2)–C(1)	124.1(9)	C(4)–C(3)–C(2)	108.7(8)
N(2)–Co(2)–N(5)	90.4(3)	N(1)–Co(1)–N(3)	179.1(3)	C(3)–C(4)–C(5)	104.9(8)	N(1)–C(5)–C(6)	125.5(9)
N(2)–Co(1)–N(3)	88.9(3)	N(5)–Co(1)–N(3)	88.8(3)	N(1)–C(5)–C(4)	110.2(8)	C(6)–C(5)–C(4)	123.6(9)
N(1)–Co(1)–N(6)	90.1(3)	N(2)–Co(1)–N(6)	90.4(3)	C(7)–C(6)–C(5)	123.6(9)	N(2)–C(7)–C(6)	123.8(8)
N(5)–Co(1)–N(6)	178.9(4)	N(3)–Co(1)–N(6)	90.4(3)	N(2)–C(7)–C(8)	111.0(7)	C(6)–C(7)–C(8)	124.8(8)
N(1)–Co(1)–N(4)	89.8(3)	N(2)–Co(1)–N(4)	179.7(3)	C(9)–C(8)–C(7)	106.4(8)	C(8)–C(9)–C(10)	107.1(8)
N(5)–Co(1)–N(4)	89.8(3)	N(3)–Co(1)–N(4)	90.9(3)	C(11)–C(10)–N(2)	126.5(9)	C(11)–C(10)–C(9)	124.9(8)
N(6)–Co(1)–N(4)	89.4(3)	C(5)–N(1)–C(2)	107.0(7)	N(2)–C(10)–C(9)	108.4(8)	O(1B)–C(11)–C(10)	120.7(15)
C(5)–N(1)–Co(1)	125.1(6)	C(2)–N(1)–Co(1)	127.7(6)	O(1B)–C(11)–C(12)	116.6(14)	C(10)–C(11)–C(12)	121.5(8)
C(7)–N(2)–C(10)	107.1(7)	C(7)–N(2)–Co(1)	126.6(6)	N(3)–C(12)–C(11)	123.9(8)	N(3)–C(12)–C(13)	110.6(8)
C(10)–N(2)–Co(1)	126.2(6)	C(12)–N(3)–C(15)	106.5(8)	C(11)–C(12)–C(13)	125.3(8)	C(14)–C(13)–C(12)	106.1(8)
C(12)–N(3)–Co(1)	128.2(6)	C(15)–N(3)–Co(1)	125.3(6)	C(13)–C(14)–C(15)	107.4(8)	C(13)–C(14)–C(31)	128.5(8)
C(17)–N(4)–C(20)	105.9(8)	C(17)–N(4)–Co(1)	126.3(6)	N(3)–C(15)–C(14)	109.3(8)	N(3)–C(15)–C(16)	127.2(8)
C(20)–N(4)–Co(1)	127.7(7)	C(41)–N(5)–C(37)	118.7(8)	C(15)–C(16)–C(17)	120.6(9)	C(16)–C(15)–C(14)	122.8(8)
C(41)–N(5)–Co(1)	120.5(7)	C(37)–N(5)–Co(1)	120.6(7)	N(4)–C(17)–C(18)	110.8(8)	N(4)–C(17)–C(16)	126.4(9)
C(42)–N(6)–C(46)	118.4(8)	C(42)–N(6)–Co(1)	121.1(6)	C(19)–C(18)–C(17)	104.8(8)	C(16)–C(17)–C(18)	121.7(8)
C(46)–N(6)–Co(1)	120.4(6)	O(1A)–C(1)–C(2)	119.4(10)	N(4)–C(20)–C(19)	110.7(9)	C(18)–C(19)–C(20)	107.7(8)
O(1A)–C(1)–C(20)	118.6(10)	C(2)–C(1)–C(20)	122.0(8)	C(19)–C(20)–C(1)	125.2(8)	N(4)–C(20)–C(1)	123.7(9)
C(3)–C(2)–N(1)	109.1(8)	C(3)–C(2)–C(1)	126.4(9)				
Molecule 2							
N(8)–Co(2)–N(9)	91.1(3)	N(8)–Co(2)–N(11)	90.3(3)	C(52)–C(51)–C(50)	122.7(7)	N(7)–C(51)–C(50)	109.9(7)
N(8)–Co(2)–N(7)	89.7(3)	N(11)–Co(2)–N(9)	90.1(3)	O(2A)–C(52)–C(53)	116.0(2)	O(2A)–C(52)–C(51)	123.0(2)
N(9)–Co(2)–N(7)	178.9(3)	N(11)–Co(2)–N(7)	89.1(3)	N(8)–C(53)–C(52)	125.3(8)	C(51)–C(52)–C(53)	119.9(8)
N(11)–Co(2)–N(12)	179.2(3)	N(8)–Co(2)–N(12)	89.3(3)	C(52)–C(53)–C(54)	122.7(8)	N(8)–C(53)–C(54)	111.8(8)
N(7)–Co(2)–N(12)	90.3(3)	N(9)–Co(2)–N(12)	90.6(3)	C(54)–C(55)–C(56)	106.9(7)	C(55)–C(54)–C(53)	106.9(7)
N(11)–Co(2)–N(10)	90.3(3)	N(8)–Co(2)–N(10)	179.1(4)	C(57)–C(56)–C(55)	126.1(9)	C(57)–C(56)–N(8)	124.4(9)
N(7)–Co(2)–N(10)	89.6(3)	N(9)–Co(2)–N(10)	89.6(3)	O(2B)–C(57)–C(56)	122.0(2)	N(8)–C(56)–C(55)	109.2(8)
C(51)–N(7)–C(48)	106.1(7)	N(12)–Co(2)–N(10)	90.2(3)	C(56)–C(57)–C(58)	124.5(10)	O(2B)–C(57)–C(58)	113.6(15)
C(48)–N(7)–Co(2)	127.4(6)	C(51)–N(7)–Co(2)	126.4(6)	N(9)–C(58)–C(59)	108.8(9)	N(9)–C(58)–C(57)	125.5(10)
C(53)–N(8)–Co(2)	128.6(6)	C(53)–N(8)–C(56)	105.0(7)	C(60)–C(59)–C(58)	106.6(9)	C(57)–C(58)–C(59)	125.1(10)
C(61)–N(9)–C(58)	107.7(8)	C(56)–N(8)–Co(2)	126.4(6)	N(9)–C(61)–C(62)	125.8(9)	C(59)–C(60)–C(61)	108.5(8)
C(58)–N(9)–Co(2)	125.0(6)	C(61)–N(9)–Co(2)	127.3(7)	C(62)–C(61)–C(60)	125.5(8)	N(9)–C(61)–C(60)	108.4(9)
C(66)–N(10)–Co(2)	127.8(6)	C(66)–N(10)–C(63)	105.4(8)	O(2C)–C(62)–C(61)	118.5(10)	O(2C)–C(62)–C(63)	120.6(10)
C(83)–N(11)–C(87)	117.3(8)	C(63)–N(10)–Co(2)	126.8(6)	N(10)–C(63)–C(62)	125.3(8)	C(63)–C(62)–C(61)	120.8(8)
C(87)–N(11)–Co(2)	121.0(6)	C(83)–N(11)–Co(2)	121.8(6)	C(62)–C(63)–C(64)	124.2(8)	N(10)–C(63)–C(64)	110.3(8)
C(88)–N(12)–Co(2)	120.9(6)	C(88)–N(12)–C(92)	118.3(8)	C(79B)–C(64)–C(63)	124.5(10)	C(79B)–C(64)–C(65)	122.7(10)
C(48)–C(47)–C(66)	123.4(9)	C(92)–N(12)–Co(2)	120.7(6)	C(64)–C(65)–C(66)	108.7(10)	C(65)–C(64)–C(63)	104.1(9)
C(47)–C(48)–C(49)	124.6(8)	C(47)–C(48)–N(7)	124.9(8)	N(10)–C(66)–C(47)	124.0(9)	N(10)–C(66)–C(65)	111.1(9)
C(50)–C(49)–C(48)	106.9(8)	N(7)–C(48)–C(49)	110.1(7)	C(65)–C(66)–C(47)	124.7(10)	C(78B)–C(77)–C(60)	116.1(11)
N(7)–C(51)–C(52)	127.2(8)	C(49)–C(50)–C(51)	106.8(7)				

arrangement minimizes contact between the pyridine hydrogens and the pyrrole nitrogens, but in order to accommodate the very short axial Co–N(pyridine) bonds, it does cause the oxophlorin to undergo a ruffled distortion. This distortion minimizes contact between the ortho pyridine hydrogens and the meso carbons of the oxophlorin. Notice that the core distorts so that the meso carbon atoms are on opposite sides of the axial pyridine ligand that lies over those meso carbon atoms.

The relative orientations of two axial ligands such as pyridine and imidazole have received considerable attention in regard to their effect on the electron structure and physical properties of porphyrin complexes, especially iron(III) complexes.[14,24–29] The arrangement seen in {$(py)_2Co^{III}(OEPO)$} with the two pyridine ligands nearly perpendicular and staggered over the Co–

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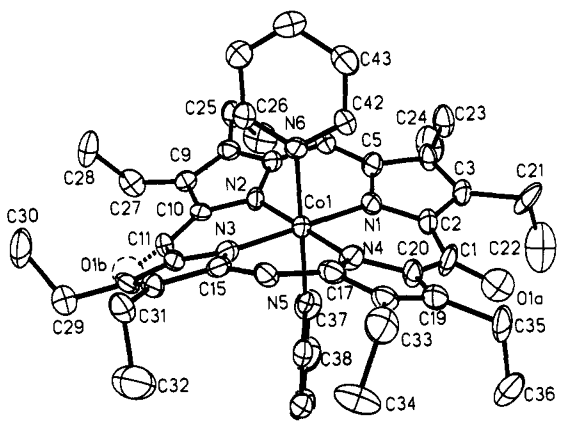

Figure 5. Perspective view of molecule 1 of $\{(py)_2Co^{III}(OEPO)\}$ with 50% thermal contours.

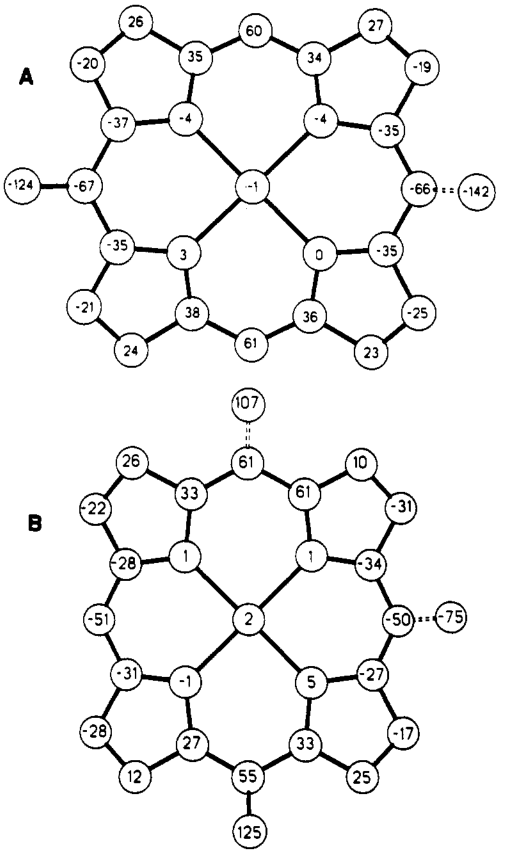

Figure 6. Diagrams of the core of the two molecules of $\{(py)_2Co^{III}(OEPO)\}$ with the displacement of each atom (in units of 0.01 Å) from the plane of the macrocycle: A, molecule 1; B, molecule 2.

N(pyrrole) bonds is characteristic of a number of complexes such as $[(py)_2Fe^{III}(TPP)]^+$ [27] and $[(L)Fe^{III}(TMP)]^+$ (TMP is the dianion of tetramesitylporphyrin; L is 4-(dimethylamino)pyridine,[28] 3-ethylpyridine,[29] 3-chloropyridine,[29] or 4-cyanopyridine[24]), which have short axial metal–ligand distances. Some time ago it was suggested that the ruffled porphyrin geometry in $\{(3,5\text{-lutidine})(NO_2)Co^{III}(TPP)\}$ was a consequence of crystal packing forces.[18] We have examined the crystal packing in $\{(py)_2Co^{III}(OEPO)\}$, but do not find any evidence of crowding between molecules. Thus, we conclude that the S_4 ruffling within $\{(py)_2Co^{III}(OEPO)\}$ is a consequence of internal pressure of the axial pyridine ligands upon the oxophlorin core.[16]

The electronic absorption spectrum shown in trace A of Figure 1 is a useful diagnostic marker for metal complexes that contain the oxophlorin trianion in the simple, nonbridging form. The characteristic feature is the low-energy absorption at ca. 700 nm with a prominent shoulder at lower wavelengths. Thus for $\{(py)_2Co^{III}(OEPO)\}$ these occur at 676 and 622 nm, respectively, while for $\{(py)_2Mn^{III}(OEPO)\}$ they appear at 743 and 678 nm (see trace i of Figure 3 in ref 2) and for $\{(py)_2Ga^{III}(OEPO)\}$ they are found at 692 and 636 nm.[23] In contrast, complexes that contain the oxophlorin radical have a single absorption that occurs above 800 nm.[10,11]

Table V. Crystallographic Data

	$\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$	$\{(py)_2Co^{III}(OEPO)\}$
empirical formula	$C_{46}H_{54}CoN_6O$	$C_{46}H_{53}CoN_6O$
fw	765.9	764.9
space group	$P\bar{1}$, triclinic	$P2_1$, monoclinic
a, Å	9.267(3)	19.177(4)
b, Å	14.007(4)	20.039(4)
c, Å	15.816(6)	10.547(2)
α, deg	101.70(2)	
β, deg	92.41(3)	100.36(1)
γ, deg	101.51(2)	
V, Å	1960.4(10)	3987.0(14)
Z	2	4
T, K	130(2)	120(2)
λ, Å	0.710 73 (Mo Kα)	1.541 78 (Cu Kα)
μ, mm^{-1}	0.482	3.703
d_{calc}, Mg/m^3	1.297	1.274
transm coeff	0.92–0.97	0.55–0.72
R^a	0.053 ($I > 2\sigma(I)$)	0.054 ($I > 2\sigma(I)$)
$R_w{}^b$ or $R_{w2}{}^c$	0.056^b	0.144^c

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$. [c] $R_{w2} = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

Experimental Section

Preparation of Compounds. $\{(py)_2Co^{III}(OEPO)\}$. This was obtained by a modification of the procedure of Bonnett and Dimsdale.[2] Under a dinitrogen atmosphere, a 0.3-mL portion (0.086 mmol) of 1% hydrogen peroxide in pyridine was added to a red solution of 30 mg (0.05 mmol) of $Co^{II}(OEP)$ in 15 mL of pyridine. The solution was heated to 60 °C for 20 min. Water (5 mL) was added to the resulting lime-green solution. The microcrystalline blue precipitate was collected by filtration and washed with water. The solid was dried under vacuum; yield 35 mg, 92%.

$\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$. Under a dinitrogen atmosphere, a 5-mL portion of a saturated solution of sodium dithionite in water was added to a green solution of 10 mg (0.014 mmol) of $\{(py)_2Co^{III}(OEPO)\}$ in 10 mL of pyridine. The reaction mixture, which immediately turned deep orange, was stirred overnight. Upon addition of 10 mL of water to the orange solution, a red-orange solid formed. This was collected by filtration, washed with water, and dried under vacuum for 12 h to give 9 mg (92%) of the product. The product is very air sensitive, and prolonged vacuum drying produces a product whose solubility in dichloromethane is reduced, presumably due to the loss of pyridine.

X-ray Data Collection. $\{(py)Co^{II}(OEPOH{\cdot\cdot}py)\}$. Dark orange plates were obtained by addition of water to a pyridine solution of the complex and then allowing the mixture to stand for several days. A suitable crystal was coated with a light hydrocarbon oil and mounted in the 130 K dinitrogen stream of a Siemens R 3 m/V diffractometer that was equipped with a locally modified low-temperature apparatus. Two check reflections showed only random (<2%) variation in intensity during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are collected in Table V.

$\{(py)_2Co^{III}(OEPO)\}$. Deep blue crystals were obtained by addition of water to a pyridine solution of the complex and allowing the mixture to stand. The crystal selected for data collection was mounted in the cold stream (120 K) of a Siemens P4 diffractometer that was equipped with a locally modified LT-2 low-temperature apparatus. Nickel-filtered Cu Kα radiation from a rotating-anode source that operated at 15 kW was used. Two check reflections showed only random fluctuations of less than 0.5% in intensity during data collection. Relevant information is contained in Table V.

Solution and Structure Refinement. Calculations were performed on a DEC microVAX workstation 3200 with SHELXTL Plus v. 4.00 or SHELXL-92, γ-test version. Scattering factors and corrections for

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anomalous dispersion were taken from a standard source.[30] The solution for each compound was accomplish by direct methods with subsequent cycles of least-squares refinement and calculation of difference Fourier maps. Hydrogen atoms were included with the use of a riding model with a fixed isotropic thermal parameter 1.2 times the value of the adjacent carbon atom.

{(py)Co^{II}(OEPOH··py)}. Refinement proceeded smoothly in the space group $P\bar{1}$. An absorption correction was applied.[31] All non-hydrogen atoms were refined with anisotropic thermal parameters. The largest peak in the difference map was 0.33 e Å^{-3}, and the largest hole was −0.35 e Å^{-3}.

{(py)$_2$Co^{III}(OEPO)}. The structure was solved in the space group $P2_1$ using direct methods (SHELXS). Although the systematic absences are also consistent with the space group $P2_1/m$, the structure could not be solved in this space group. There are two molecules in the asymmetric unit, and each displays some disorder. Molecule 1 has two alternate positions for the oxygen atom in the meso position. Thus, the thermal parameters for oxygen atoms O(1A) and O(1B) were tied together and occupancies required to sum to 1.0. Refinement resulted in a U value of 0.057(3) Å^2 and occupancies of 0.69(1) and 0.31(1), respectively. Molecule 2 showed the presence of three alternate positions, and refinement of occupancies for O(2A), O(2B), and O(2C) yielded values of 0.18(1), 0.27(1), and 0.55(1), respectively, with a common thermal parameter of 0.042(3) Å^2. In addition, three of the ethyl groups of molecule 2 are disordered. Two terminal methyl groups of equal weight, C(78A) and C(78B), were assigned to one of these, while the occupancies of the ethyl groups C(79)–C(80) and C(81)–C(82) were determined by refinement. However, the positional parameters of their minor components ("B" atoms) were fixed after their location on a final difference map in order to smooth the convergence of the model. An attempt to determine the handedness was not entirely successful, resulting in a Flack x parameter of 0.126(8) (expected values are 0 (within 3 esd's) for correct and +1 for inverted absolute structure). The original hand yielded a R_{w2} value of 0.1638. Refinement was by full-matrix least-squares methods, based on F^2, using a γ-test version of the program SHELXL-92, with anisotropic thermal parameters for all non-hydrogen atoms except those that were disordered. The final difference map was featureless. After the structure was fully refined, there were large discrepancies in Co–N bond distances that could not be explained. Most notably, two of the in-plane Co–N distances were 0.14 Å shorter than the other two. This pattern also occurred in the refinement of the structure in the opposite hand. Refinement of the structure as a racemic twin[32,33] (as suggested by the SHELXL-92 software) markedly improved the Co–N bond distances, lowered the R values, and eliminated a problem with a few non-positive definite atoms. Further, the disorder in the two ethyl groups C(79)–C(80) and C(81)–C(82) became resolved. R_{w2} decreased to 0.1437; the conventional R based on data with $I > 2\sigma(I)$ decreased from 0.0717 to 0.0542. The twin parameter converged to 0.58(1). Other evidence for twinning was noted earlier by the crystal morphology in which each crystal in the sample is shaped like a chunky butterfly.

Instrumentation. ^{1}H NMR spectra were recorded on a General Electric QE 300 Fourier transform spectrometer. Electronic spectra were obtained through the use of a Hewlett Packard diode array spectrometer.

Acknowledgment. We thank the National Institutes of Health (Grant GM 26226) for financial support.

Supplementary Material Available: Tables of bond distances, angles, anisotropic thermal parameters, hydrogen atom coordinates, and crystal data for {(py)Co^{II}(OEPOH··py)} and {(py)$_2$Co^{III}(OEPO)} and a view of molecule 2 of the latter which shows the disorder (20 pages). Ordering information is given on any current masthead page.

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