Formation of a *meso*-Tetraphenylsecochlorin and a Homoporphyrin with a Twist

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The osmium tetroxide-mediated dihydroxylation of *meso*-tetraphenylporphyrin leads to the formation of the *vic*-diol *meso*-tetraphenyl-2,3-*vic*-diol-2,3-chlorin. The corresponding Ni(II) complex was converted by lead tetraacetate into (*meso*-tetraphenyl-2,3-secochlorinato-2,3-dialdehyde)nickel(II). This novel pigment undergoes an almost quantitative, intramolecular double acetal formation when treated with methanol in the presence of acid to produce a porphyrinoid in which one pyrrolic unit is formally replaced by a six-membered ring. An X-ray crystal structure determination, the first for such a homoporphyrin, reveals the severely twisted conformation of its chromophore.

Research on chlorin-type pigments, porphyrins in which one β,β'-bond of a porphyrin is formally reduced, is exceedingly rich.[1] This is due to the fundamental importance chlorins play in photosynthesis and, in part, to recent developments in which chlorins have been utilized as photosensitizers in photodynamic therapy (PDT).[2] Despite the wealth of knowledge on chlorins, examples of secochlorins, porphyrins in which a β,β'-bond has been cleaved, are rare.[3] Porphyrinoids in which one pyrrolic unit has been replaced by, for instance, a six-membered ring are similarly rare.[4]

Flitsch reported in 1986 a step-by-step synthesis of two “bisnorporphyrins”, which were bacterio- and isobacteriochlorin-like molecules in which two sets of β,β'-carbon atoms were removed relative to the parent compounds.[5] The first example of a secochlorin was described by Chang et al. as recently as 1992.[6] Their fortuitous synthesis is based on a complex rearrangement of an (octadehydrocorrinato)nickel(II) salt and is not a general route. The same is true for the serendipitous formation of a porphyrazine-based secochlorin.[7] The first, and until now the only, reported synthesis of a secochlorin with the potential for generality was reported in 1993 by Bonnett and co-workers.[8] Their synthesis was based on the lead tetraacetate cleavage of an octaethyl-2,3-dihydroxy-2,3-chlorin to form a bisketone, octaethyl-2,3-secochlorin-2,3-dione. This secochlorin underwent an intramolecular aldol condensation when treated with bases to form a homoporphyrin containing a six-membered ring.

Attempts to modulate the photophysical properties of porphyrins (or the electrochemical properties of their metallocomplexes) have been directed at distortion of the normally essentially planar porphyrin moiety by, for example, the introduction of bulky external substituents, causing the macrocycle to adopt various types of nonplanar conformations. The molecular structures and the ground- and excited-state conformations of nonplanar porphyrins were reviewed in 1995.[9]

In our own search for novel PDT agents, we made a preliminary report on the osmium tetroxide-mediated dihydroxylation of *meso*-tetraphenylporphyrins to produce *vic*-diol-substituted chlorins and their metal complexes, such as **1**−**3** (Scheme 1).[10] Here we detail the synthesis of diol chlorin **1**, its Ni(II) complex **2**, and Zn(II) complex **3**, and for the first time, we report on the facile

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(5) (a) Flitsch, W. *Pure. Appl. Chem.* **1986**, *58*, 153−160. (b) Bohusch, M.; Flitsch, W.; Kneip, H. G. *Liebigs Ann. Chem.* **1991**, 67−70.

(6) Chang, C. K.; Wu, W.; Chern, S.-S.; Peng, S.-M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 70−72. Interestingly, this rearrangement was first reported in 1969 by Johnson and co-workers but was misinterpreted: Grigg, R.; Johnson, A. W.; Shelton, K. W. *J. Chem. Soc. C* **1969**, 655−666. Hamilton, A.; Johnson, A. W. *J. Chem. Soc. C* **1971**, 3879−3882.

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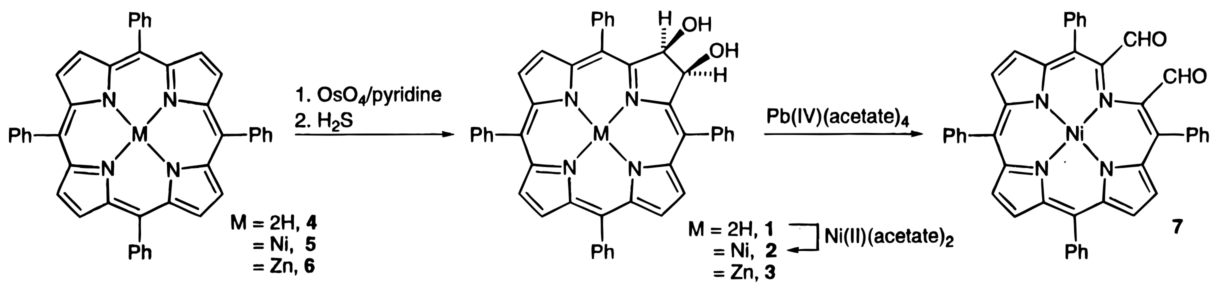
Scheme 1



conversion of **2** into a novel secochlorin. Furthermore, this secochlorin was utilized in the quantitative formation of a porphyrinoid incorporating a partially saturated six-membered ring. An X-ray crystal diffraction study of this unusual pigment is presented. We believe this is the first report of a TPP-based secochlorin, the first X-ray crystal structure reported for porphyrinoids containing six-membered rings, which is, incidentally, one of the most severely distorted porphyrinoids structurally characterized.

Discussion

A CHCl$_3$–pyridine solution of *meso*-tetraphenylporphyrin (TPP, **4**) or its Zn(II) complex **6**, when treated with OsO$_4$, followed by a reductive workup, produced over the course of several days one major product that was identified as the *cis*-diol chlorin **1** or **3** (Scheme 1).[10] Although the dihydroxylation of TPP has not been reported prior to our paper, the osmylation of octaalkylporphyrins has been studied in some detail.[11] Standard porphyrin metalation procedures could be applied to insert Ni(II) into this chlorin to yield metallochlorin **1**.[12] Both reaction steps proceed smoothly with little or no decomposition, and the reaction can be followed by TLC and UV–vis spectroscopy. Unlike the facile hydroxylation of the Zn(II) porphyrin **6** (in fact, its dihydroxylation produces a higher yield than that for **4**), the direct hydroxylation of (*meso*-tetraphenylporphyrinato)Ni(II) (**5**) to produce **2** is very inefficient. The solubility of this metalloporphyrin is low and thus the dihydroxylation prohibitively slow.

We have found that the diol moiety in **2** allows access to the novel dialdehyde **7** when treated with a stoichiometric amount of lead tetraacetate in THF. This reaction proceeds cleanly, within minutes, to produce the beige-brown pigment **7** in high yields (Scheme 1). ^{1}H- and proton-decoupled ^{13}C NMR (singlet at 9.7 and 188.7 ppm) and IR spectroscopy (C═O stretch at 1684 cm^{-1}) readily identify this product as the (*meso*-tetraphenyl-2,3-dicarboxaldehyde-2,3-secochlorinato)nickel(II) (**7**). Its optical spectrum, in comparison to that of the starting compound, is shown in Figure 1. Its metallochlorin-type spectrum is, presumably by virtue of the two electron-withdrawing substituents on the chromophore, considerably different from that of the starting material **2** and, compared to the parent diol, bathochromically shifted. This finding is analogous to Bonnett's dione.[8]

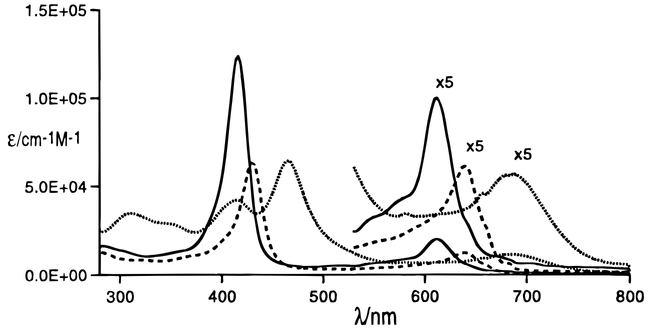


Figure 1. UV/Vis spectrum of **2** (CH$_2$Cl$_2$/0.5% MeOH) (–), of **7** (CH$_2$Cl$_2$) (···), and **9** (CH$_2$Cl$_2$) (- - -).

Treatment of a solution of **7** in CH$_2$Cl$_2$ or CHCl$_3$ containing MeOH with a trace of gaseous HCl resulted in complete consumption of **7** and rapid appearance of two compounds, labile **8** and stable **9**. Further treatment with acid resulted, at the expense of **8**, in the formation of **9** as the sole product. The optical spectra of **8** and **9** are almost identical. The optical spectrum of **9** is also shown in Figure 1. Its spectrum is reminiscent of metallochlorins but is considerably bathochromically shifted compared to a regular metallochlorin such as **2**. The formation of **8**, as seen in the mass spectrum, is associated with an increase in mass corresponding to the addition of methanol to the starting compound, and **9** has gained an additional 14 mass units, corresponding to the additional uptake of a methylene group. These changes are, under the present reaction conditions, best explained by the uptake of 2 equiv of methanol with a concomitant loss of water (Scheme 2). Hence, these mass spectral results suggest the formation of an acetal. Dialdehyde **7** is ideally set up for an intramolecular double acetal formation. Acid-catalyzed reaction of one aldehyde group with methanol forms hemiacetal **10**. The alcohol functionality of this hemiacetal reacts immediately with the second aldehyde functionality to form the isolable intermediate **8**, thereby establishing the oxazine-like six-membered ring. Upon further acid treatment, **8** is converted into the double acetal **9**. The ^{1}H NMR spectra of **8** and **9** support these conversions. The expected overall symmetry of the compounds **8** (no symmetry) and **9** (2-fold symmetry) can be seen from the coupling patterns of the β-protons (**8**: six doublets $J = 4.5$ Hz, each integrating for 1H; **9**: two doublets $J = 4.5$ Hz and one singlet, each integrating for 2H). In addition, the presence of one or two methoxy groups and the hydrogens attached to the nonaromatic part of the molecule are

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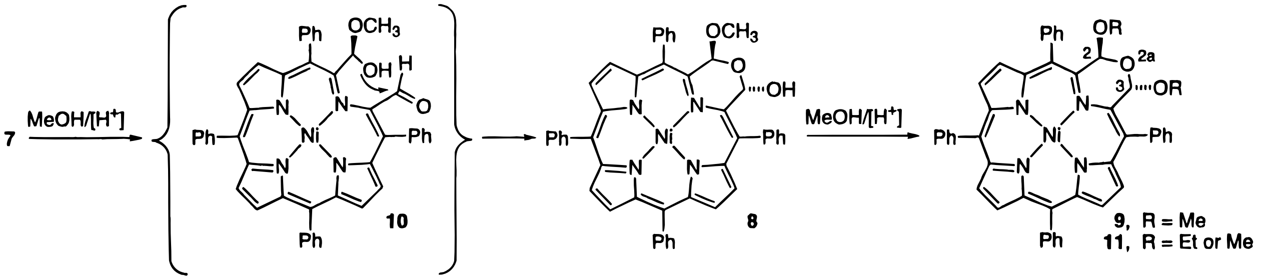
(11) (a) Fischer, H.; Eckoldt, H. *Liebigs Ann. Chem.* **1940**, *543*, 138–162. (b) Fischer, H.; Pfeiffer, H. *Liebigs Ann. Chem.* **1944**, *556*, 131–153. (c) Chang, C. G.; Sotiriou, C.; Weishih, W. *J. Chem. Soc., Chem. Commun.* **1986**, 1213–1215. (d) Bonnett, R.; Nizhnik, A. N.; Berenbaum, M. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1822–1823. (e) Pandey, K. R.; Shiau, F. Y.; Isaac, M.; Ramaprasad, S.; Dougherty, T. J.; Smith, K. M. *Tetrahedron Lett.* **1992**, *33*, 7815–7818. (f) Adams, K. R.; Berenbaum, M. C.; Bonnett, R.; Nizhnik, A. N.; Salgado, A.; Asunción Vallés, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1465–1470.

(12) Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1; Chapter 10.

Scheme 2



clearly visible in the ^{1}H NMR spectra of **8** and **9**, respectively.

In one particular experiment, **7** was dissolved in CHCl$_3$, a drop of MeOH was added, and the solution was treated with HCl gas. Petroleum ether 40−60 was allowed to diffuse into the solution. Dark green crystals of **11**, suitable for X-ray crystal structure analysis, were deposited. The optical spectrum of the crystalline material was identical to that for **9**. Surprisingly, though, mass spectral analysis of the crystals showed that in addition to the expected peak (m/e = 748), two more peaks with m/e = 762 and 776 were present, corresponding to compounds containing one or two more methylene groups. The ^{1}H NMR spectrum was also unexpectedly complex and indicated the presence of a mixture of closely related compounds, some of which contained ethyl groups. Reinvestigation of the experiment revealed that CHCl$_3$ stabilized with EtOH was used. As a result, the formation of a mixture of ethyl and methyl double acetals (methyl methyl, methyl ethyl, as well as ethyl ethyl) was possible, thus explaining the spectroscopic findings for **11** (Scheme 2). Fortunately, despite the presence of three species in the crystalline material, it was possible to solve the crystal structure.[13] All three compounds crystallized in the same lattice and largely in the same orientation. The presence of the methoxy-bearing compounds was noticeable only by a partial occupancy for the terminal carbon of the ethoxy side chains. This conservation of one lattice for TPP-based structures is not unusual.[9c,14] An ORTEP representation and a side view of the molecular structure of **11** is shown in Figure 2. The crystal structure establishes the final proof for the double acetal structure of **9** (and **11**).[15]

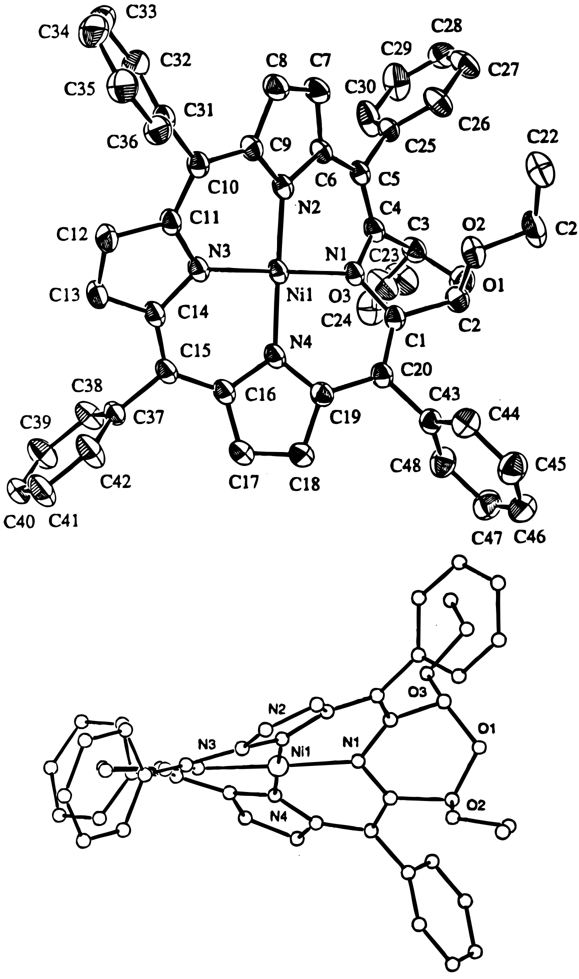


Figure 2. Top: ORTEP representation of the molecular structure of **11**. Thermal ellipsoids are scaled to the 33% probability level. Hydrogen atoms have been omitted for clarity. The partially occupied positions have been assigned by the use of nonshaded spheres. Bottom: side view (view along the axis formed by the $\beta-\beta$ bond opposite of the oxazepin ring) of **11**. The relevant distances (Å) are as follows: Ni(1)−N(1) 1.900(2); Ni(1)−N(2) 1.892(2); Ni(1)−N(3) 1.898(2); Ni(1)−N(4), 1.887(2). For a quantification of the observed distortion see ref 17.

The alkoxy groups of the double acetal functionality are exclusively arranged transoid to each other. This can be rationalized using steric and stereoelectronic arguments.[16] The observed conformation maximizes the number of antiperiplanar relationships between nonbonded electron pairs of the ring oxygen and the C−OCH$_3$ bonds (anomeric interactions) and, at the same time, minimizes the steric interaction of the methoxy substituents with the phenyl groups. Of great significance is the fact that the presence of the partially saturated six-membered ring in **11** results in a spectacular distortion of the porphyrin "plane". This distortion is best described by a roughly 40° twist along the axis passing through N1−Ni−N3.[17] Despite this, the central nickel atom is still coordinated in a square planar fashion and the median Ni−N bond length of 1.895 Å is shorter than that

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[13] Experimental details of the crystal structure investigation, including tables atom coordinates, B_{eq} values, tables of bond lengths, angles and torsion angles, and tables of least-squares planes are available upon request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW, U.K., on quoting the full journal citation.

[14] Byrn, M. P.; Curtis, C. J.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Tendick, S. K.; Terzis, A.; Strouse, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 9480−9497.

[15] Crystals of pure **9** of high quality could also be grown; however, due to the high quality of the structure analysis of **11** and the isomorphous appearance of both crystals, their study by X-ray diffraction was not persued.

[16] (a) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin, 1983. (b) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983.

found in (porphyrinato)Ni(II) complexes (bond lengths 1.929(4) Å).[18] We attribute the bathochromically-shifted features of the UV−vis spectra of **8** and **9** (and **11**) and the reduction of the extinction coefficient, as compared to the diol metallochlorin **2**, to the observed distortion of the macrocycle.

Attempted demetalations of the pigments **7**−**9** invariably led, as judged by the UV−vis spectrum of the reaction mixtures, to complete destruction of the porphyrinoid chromophore. We, therefore, attempted the preparation of the free base secochlorin by oxidative cleavage of the diol chlorin **1**, but the resulting products were highly unstable and could not be analyzed. Evidently, the metal plays a stabilizing role in secochlorin **7**. We then pursued the oxidation of the Zn(II) diol chlorin **3**, hoping to be able to take advantage of the stabilizing effect of a central metal and the fact that Zn(II) can be removed from porphyrinoid macrocycles under much milder conditions than Ni(II),[12] however, to no avail. Again, the oxidation products of **3** proved to be very unstable, and also attempts to react the assumed (secochlorinato)Zn(II) in situ to the corresponding homoporphyrin failed. This inability to prepare the free bases or Zn(II) complexes of this type of compounds is precedented.[8]

In closing, we have shown that a secochlorin derived from (*meso*-tetraphenylporphyrinato)Ni(II) is accessible in two simple and high-yielding steps. Moreover, this secochlorin can be converted by acid-catalyzed reaction with methanol into a metallohomoporphyrin in which one pyrrolic unit of a porphyrin is formally being replaced by a partially saturated six-membered ring. The X-ray crystal structure of this unique compound revealed its severely distorted conformation. Mostly, such homoporphyrins have been synthesized through de novo syntheses.[4] The work presented here and preliminary results from our laboratories show that the approach of modifying the β,β'-bond of a porphyrin in a stepwise manner allows a more facile generation of such and related compounds. We anticipate that further research will provide access to the free base compounds that, presumably, will have largely bathochromic shifted UV−vis spectra and that, therefore, will be of interest for their use as photosensitizers in PDT.

Experimental Section

General Information. All solvents and chemicals were of reagent-grade quality. The chloroform used for the dihydroxylations was EtOH stabilized. The silica gel used in the flash chromatographies was Merck silica gel 60, 230−400 mesh, while R_f values were measured on Merck silica TLC aluminum sheets (silica gel 60 F_{254}). Elemental analyses and mass spectroscopy were performed by the departmental Microanalysis and Mass Spectroscopy Laboratories. The NMR spectra were recorded on a Bruker WH-400 or a Varian XL-300 spectrometer in the solvents indicated and were referenced to residual solvent peaks.

***meso*-Tetraphenyl-2,3-*cis*-dihydroxy-2,3-chlorin (1).** TPP **4** (1.0 g, 1.63×10^{-3} mol) was dissolved/suspended in freshly distilled, ethanol-stabilized $CHCl_3$/10% pyridine (200 mL) and was treated with OsO_4 (540 mg, 1.3 equiv). (CAUTION: Fumehood and eye protection!) The reaction flask was stoppered and stirred at ambient temperature for 4 days and was shielded from ambient light with aluminum foil. The reaction was then quenched by purging with gaseous H_2S for 5 min (CAUTION: Fumehood, trapping of excess H_2S!) (washing the organic reaction mixture with dilute base solutions to extract the H_2S tends to form very stable emulsions). Following the addition of MeOH (20 mL), the precipitated black OsS was filtered off through Celite. The filtrate was evaporated to dryness by a stream of N_2 or *in vacuo*. The resulting residue was loaded onto a silica gel column (25 × 7 cm) and eluted with CH_2Cl_2. The first fraction was starting material (400 mg, 40% recovery). MeOH/CH_2Cl_2 (1.5%) then eluted **1**. Slow evaporation from a MeOH/CH_2Cl_2 mixture gave **1** (520 mg, 8.02×10^{-4} mol, 49% yield) as a bright purple crystalline material: mp >300 °C dec; R_f (silica−CH_2Cl_2/1.5% MeOH) 0.68; ^1H NMR (400 MHz, $CDCl_3$) δ −1.78 (br s, 2H), 3.14 (s, exchangeable with D_2O, 2H), 6.36 (s, 2H), 7.68−7.80 (m, 12H), 7.92 (d, $J = 8.5$ Hz, 2H), 8.09 (br s, 4H), 8.15 (d, $J = 8.5$ Hz, 2H), 8.33 (d, $J = 4.5$ Hz, 2H), 8.48 (s, 2H), 8.63 (d, $J = 4.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.9, 113.2, 123.1, 124.2, 126.7, 127.5, 127.7, 127.9, 128.1, 132.2, 132.7, 133.9, 134.1, 135.5, 140.6, 141.2, 141.8, 153.2, 161.4; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 408 (5.27), 518 (4.19), 544 (4.19), 592 (3.85), 644 (4.38) nm; fluorescence (CH_2Cl_2) at 649 nm (excitation 512 nm); MS (EI, 300 °C) *m/z* 648 (0.5, M^+), 646 (0.9, $M^+ - 2H$), 630 (100, $M^+ - H_2O$), 614 (42.7); HRMS (EI, 300 °C) *m/e* calcd for $C_{44}H_{32}N_4O_2$ 648.2525, found 648.2525. Anal. Calcd for $C_{44}H_{32}N_4O_2 \cdot {}^1/_2H_2O$: C, 80.34; H, 5.06; N, 8.52. Found: C, 80.26; H, 4.93; N, 8.46.

(*meso*-Tetraphenyl-2,3-*cis*-dihydroxy-2,3-chlorinato)nickel(II) (2). A solution of **1** in as little solvent ($CHCl_3$/MeOH 9:1) as possible and containing a 3-fold molar excess of nickel acetate tetrahydrate was refluxed under N_2 for 24 h. Crystallization by slow solvent exchange from $CHCl_3$ to MeOH quantitatively gave green crystals of analytical purity: mp >250 °C dec; R_f (silica−CH_2Cl_2/0.5% MeOH) 0.48; ^1H NMR (400 MHz, $CDCl_3$) δ 2.85 (s, 2 H, exchangeable with D_2O), 5.81 (s, 2 H), 7.55−7.65 (m, 12 H), 7.70 (m, 4 H), 7.82 (m, 4 H), 8.22 (overlapping s and d = ^3J (H,H) = 4.5 Hz, 4 H), 8.38 (d, ^3J (H,H) = 4.5 Hz, 2 H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 76.0, 111.4, 123.2, 127.3, 127.5, 128.2, 128.5, 132.2, 132.6, 137.5, 139.1, 139.4, 140.4, 145.8, 148.6; UV−vis (CH_2Cl_2/0.5% MeOH) λ_{max} (log ϵ) 416 (5.10), 516 (3.66), 552 (sh), 572 (sh), 612 nm (4.30); MS (FAB, thioglycerol) *m/e* 705 (25.5, MH^+), 704 (20.2, M^+), 687 (18.0, $M^+ - OH$); HRMS (FAB, thiogycerol) *m/e* calcd for $C_{44}H_{31}N_4O_2{}^{58}Ni$ 705.180 05, found 705.179 45. Anal. Calcd for $C_{44}H_{30}N_4NiO_2 \cdot CH_3OH \cdot {}^1/_3H_2O$: C, 74.29; H, 4.34; N, 7.88. Found: C, 74.33; H, 4.06; N, 7.59.

(*meso*-Tetraphenyl-2,3-*cis*-dihydroxy-2,3-chlorinato)zinc(II) (3). Compound **3** was prepared in 72% yield from **6** following the procedure outlined for the dihydroxylation of **4**. Alternatively, refluxing of a solution of diol chlorin **1** in $CHCl_3$/MeOH 9:1 containing excess zinc acetate converts the free base quantitatively into its metalated form within 2 h. Slow evaporation of a $CHCl_3$/MeOH solution containing a drop of pyridine produces blue-green crystals of **3** as its pyridine adduct. Washings of a $CHCl_3$ solution of **3** with dilute aqueous acetic acid removes coordinated pyridine: mp > 300 °C dec; R_f (1.5% MeOH/CH_2Cl_2) 0.62; ^1H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 2H, exchangeable with D_2O), 6.12 (s, 2H), 7.55−7.72 (m, 12H), 7.81 (d, $^3J = 7$ Hz, 2H), 7.94 (d, $^3J = 7$ Hz, 2H), 7.96−8.06 (m, 6H), 8.37 (s, 2H), 8.46 (d, $^3J = 4.5$ Hz, 2H) (pyridine adduct: additional signals at δ, 3.8 (m, 2H), 5.9 (br tr, 2H), 6.69 (tr, $^3J = 2.5$ Hz, 1H)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.63, 126.48, 126.59, 126.63, 127.23, 127.35, 127.48, 127.68, 127.77, 127.82, 129.31, 132.11, 132.52, 133.63, 133.68, 133.79, 141.73, 142.57, 146.52, 148.04, 154.22, 156.28; UV−vis (CH_2Cl_2/0.5% MeOH) λ_{max} (log ϵ) 418 (5.41), 524, 564, 596 (sh), 614 (4.71) nm; MS (FAB, 3-NBA) *m/e* 710 (29.2, M^+), 693 (7.0, $M^+ - OH$), 676 (3.7, $M^+ - 2OH$); HRMS (FAB, 3-NBA) *m/e* calcd for $C_{44}H_{30}N_4O_2{}^{64}Zn$ 710.166 02, found 710.165 95. Anal. Calcd

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[17] Atoms defining plane (mean deviation, ψ^2). **1**: N(1), N(2), N(3), N(4) (0.0350, 913). **2**: N(2), C(6), C(7), C(8), C(9) (0.0176, 174); 2: N(3), C(11), C(12), N(13), N(14) (0.0109, 74.1). **3**: N(4), C(16), C(17), C(18), C(19) (0.0135, 103.4). Dihedral angle (deg) between planes: 1/2 (156.3); 1/3 (21.6); 1/4 (24.2); 1/5 (84.8); 2/3 (152.8); 2/4 (132.9); 2/5 (73.9); 3/4 (30.8); 3/5 (98.8); 4/5 (68.1).

[18] For (octaethylporphyrinato)Ni(II). Collins, D. M.; Buchler, J. W.; Schmidt, W. R. *J. Am. Chem. Soc.* **1972**, *94*, 6689−6698.

for $C_{44}H_{30}N_4O_2Zn \cdot C_5H_5N$: C, 74.38; H, 4.46; N, 8.85. Found: C, 74.50; H, 4.25; N, 8.9.

(*meso*-Tetraphenyl-2,3-secochlorinato-2,3-dialdehyde)-nickel(II) (7). **2** (170 mg, 9.94×10^{-5} mol) dissolved in dry THF (10 mL) was treated with Pb(IV)(acetate)$_4$ (120 mg, moist). Within 10 min at rt the solution turned from green to dark beige. When no starting material was detectable by TLC (~20 min), the solution was evaporated to dryness in vacuo and the resulting residue was purified by flash chromatography (silica, 3 × 7 cm, $CHCl_3$). The first yellow fraction was collected and evaporated to dryness and dissolved in CH_2Cl_2 and the solvent exchanged with hexane to give **7** in 80% yield as a dark purple-brown powder of analytical purity: mp >250 °C; R_f (silica$-CHCl_3$) 0.88; ^1H NMR (400 MHz, DMSO-d_6) δ 7.55$-$7.60 (m, 12 H), 7.70$-$7.75 (m, 8 H), 7.85 (d, ^3J (H,H) = 4.8 Hz, 2 H), 7.98 (s, 2 H), 8.18 (d, ^3J (H,H) = 4.8 Hz), 9.50 (s, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 120.0, 126.7, 127.4, 127.8, 128.2, 128.6, 130.8, 131.4, 132.9, 133.4, 134.0, 134.6, 135.7, 138.8, 140.8, 144.1, 146.9, 188.7; IR (film) $\nu = 1684$ cm^{-1} (C=O); UV$-$vis (CH_2Cl_2) λ_{max} (log ϵ) 312 (4.55), 344 (sh), 414 (4.63), 466 (4.78), 686 nm (4.04); MS (EI, 70 eV, 280 °C) *m/z* 702 (4.0, M$^+$), 700 (3.5, M$^+ - 2$H), 686 (33.6, M$^+ -$ O), 684 (8.1, M$^+ - H_2O$), 673 (100, M$^+ -$ CHO); HRMS (FAB, 3-NBA/$CHCl_3$) *m/e* calcd for $C_{44}H_{29}N_4{}^{58}NiO_2$ 703.1644, found 703.1639. Anal. Calcd for $C_{44}H_{28}N_4NiO_2$: C, 75.13; H, 4.01; N, 7.96. Found: C, 75.04; H, 4.34; N, 7.34.

(*meso*-Tetraphenyl-3-hydroxy-2-methoxy-2a-oxa-2a-homoporphyrinato)nickel(II) (8) and (*meso*-Tetraphenyl-2,3-methoxy-2a-oxa-2a-homoporphyrinato)nickel(II) (9). **7** (100 mg, 1.42×10^{-4} mol) dissolved in $CHCl_3$/MeOH (10 mL, pentene stabilized, 5% MeOH) was carefully treated with some gas from the headspace of a concd HCl bottle, applied through a pipet. Compounds **8** and **9** appeared immediately. The mixture was separated on a preparative TLC plate (silica 1 mm, $CHCl_3$). Depending on the amount of acid, variable yields of the two green products were produced. Exhaustive acid treatment of **7** (or **8**) produced, after recrystallization from CH_2Cl_2-petroleum ether 30:60, analytically pure purple crystals of **9** in 90% yield. **8**: mp >150 °C dec; R_f (silica$-CHCl_3$) 0.45; ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (d, ^3J (H,H) = 7.6 Hz, 1 H), 3.12 (s, 3H), 6.12 (s, 1 H), 6.47 (d, ^3J (H,H) = 7.6 Hz, 1 H), 7.50$-$7.65 (m, 20 H), 7.78 (d, ^3J (H,H) = 4.6 Hz, 1 H), 7.84 (d, ^3J (H,H) = 4.6 Hz, 1 H), 8.06 (two overlapping d, 2 H), 8.22 (dd, ^3J (H,H) = 4.6, 1.2 Hz, 2 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 54.1, 89.2, 96.7, 110.5, 111.1, 125.3, 125.4, 127.4, 127.7, 127.8, 127.9, 128.0, 128.1, 128.8, 128.8, 129.0, 132.4, 133.1, 137.7, 137.8, 137.9, 138.5, 138.7, 140.8, 141.3, 141.4, 145.5, 145.6; UV$-$vis (CH_2Cl_2) λ_{max} (log ϵ) 430 (4.82), 640 (4.10); MS (EI, 3-NBA/$CHCl_3$) *m/z* 734 (20, MH$^+$); HRMS (EI, 3-NBA/$CHCl_3$) *m/e* calcd for $C_{45}H_{32}N_4{}^{58}NiO_3$ 734.182 79, found 734.183 14. **9**: mp >200 dec; R_f (silica$-CHCl_3$) 0.8; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 3.03$ (s, 6 H), 6.08 (s, 2 H), 7.5$-$7.65 (m, 20 H), 7.81 (d, ^3J (H,H) = 4.5 Hz, 2 H), 8.06 (s, 2 H), 8.22 (d, ^3J (H,H) = 4.5 Hz, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 54.6, 97.4, 111.9, 122.6, 124.4, 125.9, 126.0, 126.2, 127.1, 127.6, 127.7, 127.8, 128.9, 129.2, 132.8, 132.9, 133.3, 138.7, 138.8, 139.0, 139.7, 142.4, 146.5; UV$-$vis (CH_2Cl_2) λ_{max} (log ϵ) 430 (4.81), 640 (4.09); MS (EI, 3-NBA/$CHCl_3$) *m/e* 748 (18, MH$^+$), 717 (8, M$^+ - OCH_3$); HRMS (EI, 3-NBA/$CHCl_3$) *m/e* calcd for $C_{46}H_{34}N_4{}^{58}NiO_3$ 748.198 44, found: 748.199 38. Anal. Calcd for $C_{46}H_{34}N_4NiO_3$: C. 73.72; H, 4.56; N, 7.48. Found: C, 73.81; H, 4.63; N, 7.52.

Mixture of 9, (*meso*-Tetraphenyl-2-ethoxy-3-methoxy-2a-oxa-2a-homoporphyrinato)nickel(II), and (*meso*-Tetraphenyl-2,3-ethoxy-2a-oxa-2a-homoporphyrinato)nickel(II) (11). The compounds were prepared in a manner analogous to the method as to make **9** from **7** but in $CHCl_3$/MeOH/EtOH. The three components present could be separated by analytical TLC. Their presence was also indicated by three strong molecular ion peaks at *m/e* 748 (corresponding to $C_{46}H_{34}N_4{}^{58}NiO_3$), 762 (corresponding to $C_{47}H_{36}N_4{}^{58}NiO_3$), and 776 (corresponding to $C_{48}H_{38}N_4{}^{58}NiO_3$). The ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) are complex. Compared to the spectrum of **9**, additional signals at δ 0.8 (two overlaying t) and at 3.5 (m) and at $\delta = 14.8$ and 62.4 indicated the presence of ethyl groups.

X-ray Experimental Data for [$C_{47}H_{36}N_4NiO_3$] (11). Crystals of this compound grew as dark green prisms by vapor diffusion of petroleum ether 40:60 into a $CHCl_3$ solution of **11**. The datum crystal, triclinic space group $P\bar{1}$ (#2), had dimensions of 0.2 × 0.25 × 0.3 mm. The data were collected on a Rigaku AFC6S diffractometer at 21 ± 1 °C using Cu Kα radiation ($\lambda = 1.541\,78$ Å) with a graphite monochromator and using the $\omega - 2\theta$ scan technique ($2\theta_{max} = 155°$). The data were processed and corrected for Lorentz and polarization effects. No decay correction was applied. The structure was solved by the heavy atom Patterson method and expanded using Fourier techniques. Hydrogens were fixed in calculated positions. Final R value is 0.044 (Rw = 0.042). The crystal of **11** is a solid solution of four different compounds differing only in the alkoxy groups OR and OR′: R = R′ = Me (33%); R = Me, R′ = Et (17%); R = Et, R′ = Me (17%); R = R′ = Et (33%). The β-positions of the two OR groups are partially occupied, and the carbon atoms of one of the groups are both 2-fold disordered. All but one of the non-hydrogen atoms were refined anisotropically; the low occupancy atom C(24a) was refined isotropically.[19]

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Supporting Information Available: ORTEP, side view, and stereoscopic view of the molecular structure of **11** and experimental details of the crystal structure investigation, including tables of atomic coordinates, B_{eq} values, bond lengths, angles, torsion angles, and least-squares planes (36 pages). This material is contained in 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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(19) *teXsan: Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1995.