

Biladienones from the Photooxidation of a *meso-gem*-Disubstituted Phlorin: Crystal and Molecular Structures of the 3N + O Coordinated Nickel(II) and Copper(II) Complexes

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The photooxidation of a *meso-gem*-disubstituted phlorin gave two isomeric biladienones in an equilibrium involving a *Z-E* double bond photoisomerism. The structures of these bile pigments were elucidated using NMR techniques and show terminal benzoyl and pyrrolone moieties. Complexation with divalent cations (nickel(II), copper(II)) gave stable compounds whose crystal and molecular structure could be determined by X-ray diffraction. The metal is coordinated with three pyrrole nitrogen atoms and one oxygen atom of a terminal benzoyl group. In the crystal, the molecules are arranged in pairs through hydrogen bonds between the free terminal pyrrolones.

Introduction

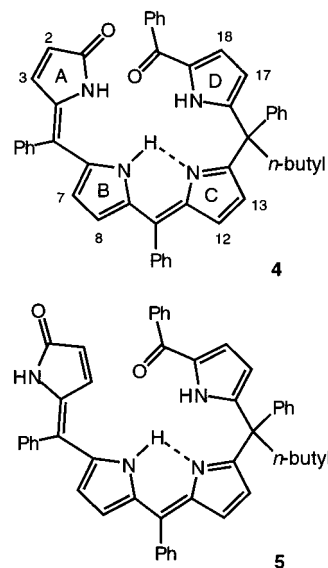
Phlorins are nonaromatic isomers of chlorins and are produced after reduction or addition of nucleophiles to the porphyrins macrocycle.^{1–10} The stability of most phlorins is limited. Only in a few favorable cases, when stabilized by steric hindrance, ring deformation, or complexation by high valent metals, can these compounds be isolated in a pure state.^{5–10} The general decomposition process is a simple oxidation to the parent porphyrin, but the irreversible meso addition of a carbon nucleophile, viz., an alkyl group, does not allow this reaction to proceed. We isolated such a phlorin (**1**) by addition of *n*-butyllithium to *meso*-tetraphenylporphyrin, and although highly unstable toward oxidation, it could be fully characterized. Here, we report the reactivity of **1** under photooxidation conditions and describe the major products of the reaction. The corresponding metal complexes have been subjected to crystallographic study and revealed original features such as 3N + O coordination and hydrogen-bond pairing of molecules.

Results and Discussion

Photooxidation of Phlorin 1. **1** was obtained⁹ after addition of 3 equiv of *n*-butyllithium to H₂TPP (**2**), concurrently with chlorin **3**. **1**, although of moderate stability in the crystalline

state, decomposed rapidly in solution when exposed to daylight and air, the blue-green solution turning purple. From the resulting mixture, two purple products, **4** and **5**, in a 3:1 ratio could be isolated (Scheme 1). They showed similar spectral data and identical molecular weight, suggesting the presence of the same conjugated system with at most a diastereoisomeric relationship or a double bond isomerism.

The UV–visible data of **4** (λ_{\max} = 326, 352, and 538 nm) and **5** (λ_{\max} = 324, 358, and 526 nm) are close to those of purple pigments such as **6** (λ_{\max} = 368 and 565 nm), obtained on photooxidation of porphyrin dianions,¹¹ suggesting a similar oxidative cleavage of the macrocycle. The NMR data (Table 1) measured for **4** and **5** show four distinct pairs of pyrrolic protons, all at high field (**4**: 6.22–6.92; **5**: 5.96–7.47 ppm) with respect to the pyrrole protons of porphyrins. In both **4** and



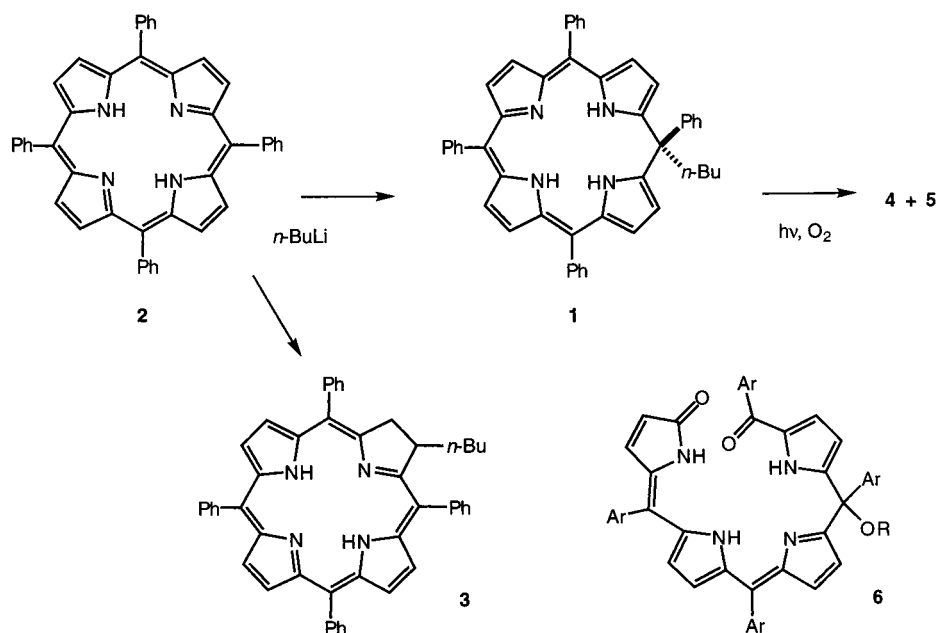
5, four pyrrolic protons are coupled with N–H protons,

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- (1) (a) Woodward, R. B. *Angew. Chem.* **1960**, *72*, 651. (b) *Ind. Chim. Belge* **1962**, *27*, 1293. (c) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 818.
- (2) Mauzerall, D. *J. Am. Chem. Soc.* **1962**, *84*, 2437.
- (3) Mauzerall, D.; Hong, F. T. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 17, pp 704–705.
- (4) Inhoffen, H. H.; Jäger, P.; Mählpoh, R.; Mengler, C. D. *Annalen* **1967**, *704*, 188.
- (5) (a) Sugimoto, H. *J. Chem. Soc., Dalton Trans.* **1982**, 1169. (b) Segawa, H.; Azumi, R.; Shimidzu, T. *J. Am. Chem. Soc.* **1992**, *114*, 7564.
- (6) (a) Setsune, J.-i.; Ikeda, T.; Iida, T.; Kitao, T. *J. Am. Chem. Soc.* **1988**, *110*, 6572. (b) Setsune, J.-i.; Ishimaru, Y.; Kitao, T. *Chem. Lett.* **1990**, 1351. (c) Setsune, J.-i.; Wada, K.; Igashino, H. *Chem. Lett.* **1994**, 213.
- (7) (a) Liddell, P. A.; Olmstead, M. M.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 2038. (b) Swanson, K. L.; Snow, K. M.; Jeyakumar, D.; Smith, K. M. *Tetrahedron* **1991**, *47*, 685. (c) Holmes, R. T.; Lin, J. J.; Khoury, R. G.; Jones, C. P.; Smith, K. M. *Chem. Commun.* **1997**, 819. (d) Lin, J. J.; Gerzveske, K. R.; Liddell, P. A.; Senge, M. O.; Olmstead, M. M.; Khoury, R. G.; Weeth, B. E.; Tsao, S. A.; Smith, K. M. *J. Org. Chem.* **1997**, *62*, 4266.

- (8) (a) Krattinger, B.; Callot, H. J. *Tetrahedron Lett.* **1996**, *37*, 7699. (b) Krattinger, B.; Callot, H. J. *Tetrahedron Lett.* **1998**, *39*, 1165.
- (9) Krattinger, B.; Callot, H. J. *Eur. J. Org. Chem.* **1999**, 1857, 7.
- (10) Ruppert, R.; Jeandon, C.; Sgambati, A.; Callot, H. J. *Chem. Commun.* **1999**, 2123.

Scheme 1

**Table 1.** Selected Proton Resonances of **4** and **5**

	4	5	$\Delta\delta$ (4 – 5)
H-2	6.19	5.94	+0.25
H-3	6.93	7.47	–0.54
H-7	6.33	6.18	+0.15
H-8	6.63	6.48	+0.15
H-12	6.65	6.75	–0.10
H-13	6.36	6.34	+0.02
H-17	6.30	6.05	+0.25
H-18	6.79	6.76	+0.03
ring A NH	9.1	6.9	+2.2
	(coupled with H-2+H-3)	(coupled with H-2+H-3)	
ring D NH	9.9	10.1	–0.2
	(coupled with H-17+H-18)	(coupled with H-17+H-18)	
rings B + C NH	12.3 (v br)	12.9 (v br)	–0.7

themselves appearing as broad singlets at 9.2 and 9.9 ppm, respectively, for **4** and 6.9 and 10.1 ppm for **5**. Additionally, very broad signals were detected at 12.3 and 12.9 ppm for **4** and **5**, respectively.

All signals corresponding to pyrrole, *o*-phenyl, butyl, and N–H protons could be assigned and correlated by homonuclear decoupling and nuclear Overhauser enhancement spectroscopy. It was noticed that the chemical shifts of all but three protons were in the same range (± 0.25 ppm) for both compounds (see Table 1). Two protons, one C–H and one N–H, both located on pyrrolone A, show opposite effects, suggesting a permutation of their respective positions and thus a double bond isomerism between this unit and the next meso carbon. This was further confirmed by the fact that the pyrrolone N–H proton in **5** showed a nuclear Overhauser effect correlation with the ortho protons of the adjacent phenyl group. These data are in contrast with those measured for a diastereoisomeric pair represented by **6**, whose NMR data¹² are almost identical ($\Delta\delta \leq 0.1$ ppm for the pyrrolic protons; Ar = 3,4,5-trimethoxyphenyl). Accordingly, we formulated the purple oxidation products of **1** as

double bond isomers **4** and **5**. Two N–H hydrogens are clearly located on the terminal pyrrolone and benzoylpyrrole units. The very low field shift and the absence of observable coupling with pyrrolic protons, themselves showing a significant broadening, suggest that the last N–H hydrogen is shared by pyrroles B and C.

Compound **5** is a secondary product that may arise from a photoisomerization of the C(4)–C(5) double bond. This was confirmed by the fact that solutions of **4** or **5** isomerize when illuminated with visible light to give the same equilibrated mixture containing a 3:1 **4** vs **5** ratio. Control experiments in the dark confirmed the stability of **4** and **5** in the absence of light.

The oxidative cleavage of the porphyrinic ring is well-documented^{11–20} and has often been studied as a model for the catabolism of chlorophylls.^{13–15} Simple porphyrin bases, like octaalkyl- or tetraarylporphyrins are rather stable and require an activating procedure to be efficiently photooxidized: complexation with cations of electropositive metals (Mg, Zn) or treatment with bases to form the reactive dianion. The initial ring opening is often followed by solvent addition. Examples of this sequence have been described in the tetraarylporphyrin series,^{11,12,17–19} and open chromophores such as **6** have been characterized by NMR. In the case of **1**, the base itself is highly reactive, as one would expect from a reduced macrocycle, but the products are similar. The difficulties generated by the reversible addition of solvent in structures such as **6**¹⁹ are

- (11) Cavaleiro, J. A. S.; Neves, M. G. P. M. S.; Hewlins, M. J. E.; Jackson, A. H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1937.
 (12) Silva, A. M. S.; Neves, M. G. P. M. S.; Martins, R. R. L.; Cavaleiro, J. A. S.; Boschi, T.; Tagliatesta, P. *J. Porphyrins Phthalocyanines* **1998**, 2, 45.

- (13) Fuhrhop, J.-H.; Mauzerall, D. *Photochem. Photobiol.* **1971**, 13, 453.
 (14) Struckmeier, G.; Thewalt, I.; Fuhrhop, J.-H. *J. Am. Chem. Soc.* **1976**, 98, 278.
 (15) Fuhrhop, J.-H.; Wasser, P. K. W.; Subramanian, J.; Schrader, U. *Annalen* **1974**, 1450.
 (16) (a) Smith, K. M.; Unsworth, J. F. *Tetrahedron* **1975**, 31, 367. (b) Brown, S. B.; Smith, K. M.; Bisset, G. M. F.; Troxler, R. F. *J. Biol. Chem.* **1980**, 255, 8063. (c) Risch, N.; Schormann, A.; Brockmann, H. *Tetrahedron Lett.* **1984**, 25, 5993. (d) Smith, K. M.; Bisset, G. M. F.; Bushell, M. J. *Bioorg. Chem.* **1980**, 9, 1.
 (17) Smith, K. M.; Brown, S. B.; Troxler, R. F.; Lai, J. *Photochem. Photobiol.* **1982**, 36, 147.
 (18) Cavaleiro, J. A. S.; Hewlins, M. J. E.; Jackson, A. H.; Neves, M. G. P. M. S. *J. Chem. Soc., Chem. Commun.* **1986**, 142.
 (19) Cavaleiro, J. A. S.; Hewlins, M. J. E.; Jackson, A. H.; Neves, M. G. P. M. S. *Tetrahedron Lett.* **1992**, 33, 6871.
 (20) Rüdiger, W.; Thümmel, F. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 1216.

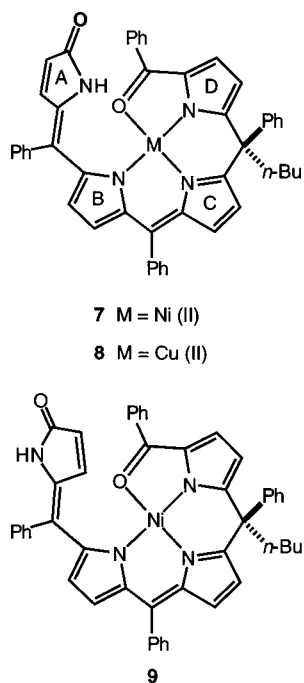
avoided in the phlorin case. Products **4** and **5** are stable in the dark as solids and in solution, while illumination induces the photoisomerization but no side reactions.

The photoequilibrium involving **4** and **5** recalls a similar reaction of phytochrome: the terminal pyrrolone of this morphogenetic pigment, also derived from the oxidation of a porphyrinic precursor, shows the same *Z-E* isomerism under illumination.²⁰

Recently, a stable ring oxidation of a tetra-*N*-substituted isophlorin was also obtained and could be characterized by X-ray diffraction (XRD).²¹ For comparison with the structures of the various pigments obtained in the oxidation of porphyrins or isophlorin, we wished to obtain a X-ray structure determination of **4** and **5** but failed to obtain suitable crystals of the bases and thus turned to the corresponding metal complexes.

Metal Complexes of Biladienones 4 and 5. Complex formation occurred rapidly with divalent cations such as zinc, copper, or nickel to give deep blue solutions. The zinc complex of **4** ($\lambda_{\max} = 644$ nm) could be observed in the presence of a large excess of zinc acetate but could not be isolated. Its long wavelength absorption is in agreement with that of a zinc complex of **6** ($R = H$; $\lambda_{\max} = 624$ nm).¹⁹

The nickel complexes of **4** and **5**, respectively **7** and **9** ($\lambda_{\max} = 358$ and 594 nm for **7**; 357 and 592 nm for **9**), are stable and could be fully characterized by NMR and XRD. The copper(II) complex **8** was also characterized by its XRD structure and showed similar features.



In addition to the expected pyrrolic and phenyl protons, the NMR spectra of **7** and **9** showed one broad singlet typical for NH groups. This feature suggested the coordination of the nickel atom to three N atoms and one O atom, instead of the more classical four N atom arrangement.

The NH proton and one pyrrolic proton coupled to this NH show a major chemical shift modification on going from **7** to **9** ($\Delta\delta = -1.8$ and $+1.84$ ppm, respectively). It strongly suggested that the pyrrolone remained uncomplexed and that the pyrrolone NH and CH protons adjacent to the C—C exocyclic double bond exchanged their relative positions. The enhancement of the shifts observed in **7** and **9** vs **4** and **5** might

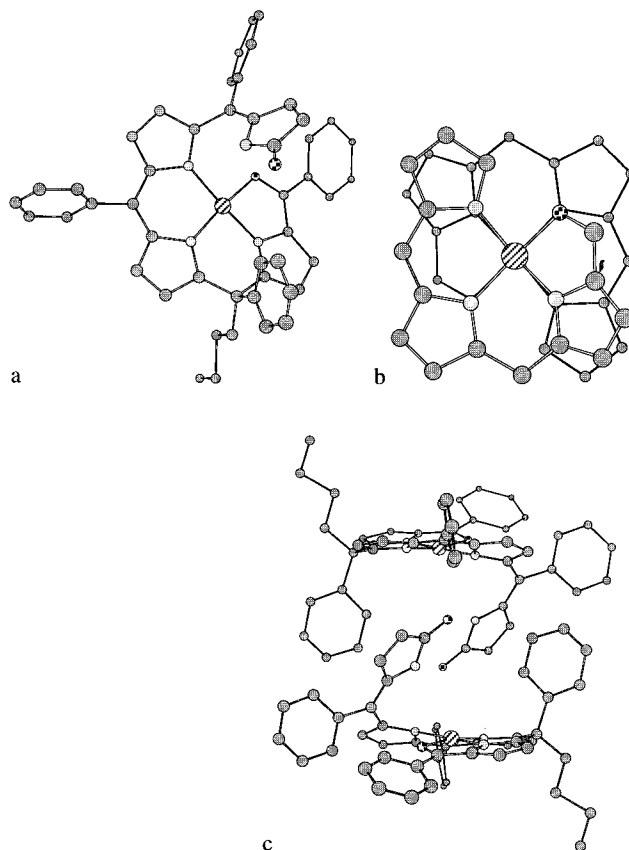


Figure 1. Nickel complex **7**: (a) viewed perpendicularly to the coordination plane, (b) molecule pair viewed along the Ni...Ni axis (benzoyl and phenyl groups omitted), and (c) edge-on view of the same pair (H omitted).

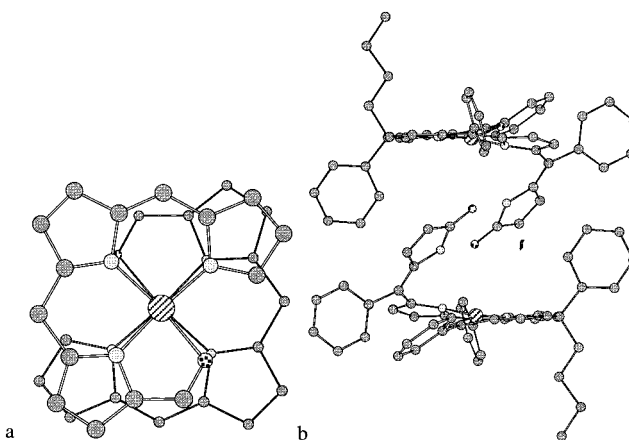


Figure 2. Copper complex **8**: (a) molecular pair viewed along the Cu...Cu axis (benzoyl and phenyl groups omitted) and (b) edge-on view of the same pair (H omitted).

reflect the higher rigidity of the metal-bound tripyrrolic framework.

Crystal and Molecular Structures of Metal Complexes 7–9. The crystal structures (Figures 1–3; Table 2) of **7–9** confirmed a 3N + O coordination, the pyrrolone being almost perpendicular to the metal coordination plane in **7** and **8** and making a 45° angle in **9**. The structures also confirmed the double bond isomerism between **4** and **5** but in addition showed that in the solid, the noncoordinated pyrrolone ring and the butyl

(21) Setsune, J.-i.; Kashihara, K.; Wada, K. *Chem. Lett.* **2001**, 72.

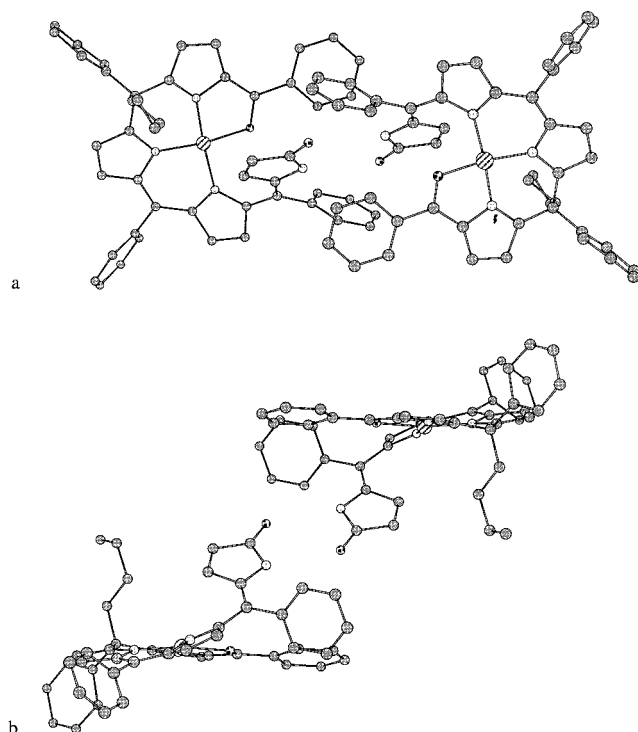


Figure 3. Nickel complex **9**: (a) molecule pair viewed perpendicularly to the coordination plane and (b) edge-on view of the same pair (H omitted).

Table 2. Selected Bond Lengths and Angles for **7–9**

	7	8	9
Bond Lengths (Å)			
M—N _B	1.916(3)	2.047(3)	1.900(6)
M—N _C	1.909(3)	1.927(3)	1.886(6)
M—N _D	1.876(3)	1.944(3)	1.865(7)
M—O	1.831(3)	1.888(3)	1.822(6)
benzoyl C=O	1.296(5)	1.275(5)	1.283(9)
pyrrolone C=O	1.234(5)	1.225(5)	1.240(9)
C(4)—C(5)	1.361(6)	1.362(6)	1.35(1)
C(5)—C(6)	1.466(6)	1.480(5)	1.47(1)
Angles (Deg)			
N _B —M—N _C	94.6(1)	94.9(1)	94.4(3)
N _C —M—N _D	89.7(2)	89.9(1)	90.1(3)
N _D —M—O	83.6(1)	80.9(1)	83.2(3)
O—M—N _B	92.3(1)	96.4(1)	92.6(3)

group are on opposite sides of the coordination plane in **7** and **8**, both derived from **4**, but are on the same side in **9**. Finally, the pyrrolone rings of two molecules are hydrogen bonded to form enantiomeric pairs of **7–9**.

The coordination of the metal is realized by three M—N bonds and one M—O bond, this last bond being longer than the M—N bonds, while among the M—N bonds, the one with pyrrole D is significantly shorter in all cases. The angles around the metal are in the 81–96° range, the smallest corresponding to the five-membered ring. The coordinated tripyrrolic unit and the benzoyl group are slightly displaced from the coordination plane in **7** and **8**. They are in a saddlelike arrangement for the nickel complex **7**, and are like tweezers (in edge-on view) for the copper complex **8**. The three remaining phenyl groups and the butyl chain are located in near-perpendicular planes with regard to the metal coordination plane.

The pyrrolone is attached to the tripyrrolic unit by an unsymmetrical meso bridge with the short double bond corresponding to the one that isomerizes in the bases. The proximity of the

pyrrolone NH (in **7**) or H-3 (in **9**) and the tripyrrolic unit is confirmed: in **7**, the H of the NH group is close to the ring D nitrogen atom (2.44 Å) and Ni (2.86 Å); the same holds for the pyrrolone H-3 (respectively, 2.62 and 2.71 Å to the same atoms).

Molecules of **7–9** form dimers bound by hydrogen bonds between N and O atoms of two pyrrolones (N—O' = 2.91, 2.90, and 2.96 Å for **7–9**, respectively). The average distance between the tetrapyrrolic units is close to 8 Å in **7** and **8** (Ni···Ni' = 8.00 Å; Cu···Cu' = 7.59 Å); the shortest atom—atom distance (Ni···N = 7.56 Å; Cu···N = 7.75 Å) was measured between the metal of one molecule and the N atom of ring B of the other molecule. The metal—ligand bonds are eclipsed and rotated by half a turn. The pair of molecules of **9** shows a very different arrangement, the tetrapyrrolic units being shifted by ca. 10 Å (Ni···Ni = 12.84 Å). However, the distance separating the tetrapyrrolic units is similar (minimal distance 8.81 Å, measured between the benzoyl groups).

A literature survey showed that fully unsaturated bile pigments coordinate metal ions using the four N atoms, either as helicoidal monomeric units or as binuclear extended helices.^{14,22–28} Coordination to additional metal atoms may involve a pyrrolone oxygen atom²⁶ or the π system.²⁸ Bases often show distorted structures, the steric hindrance between terminal rings being avoided by the rotation of one pyrrolic unit.^{29–31} Meso addition of solvent clearly favors this rotation. The terminal and rotated unit is often a pyrrolone, when resulting from the oxidation of a meso bridge, and it couples with that of a second bile pigment molecule via hydrogen bonds.^{29,31}

The 3N + O coordination around the metal in **7–9** may be favored by two facts: (i) the presence of a carbonyl group (benzoyl in our case) able to participate with the neighboring pyrrole in a chelate effect and the coplanar phenyl group having a stabilizing effect and (ii) the low nucleophilicity of the fourth pyrrolic ligand, the pyrrolone. The insertion of a sp³ carbon in the bile pigment framework might also be of importance by allowing the free rotation of the benzoyl-bearing pyrrole. This is illustrated in one literature example:²⁶ a simple helix (4N coordination) opens to a binuclear complex (3N + O coordination of the first metal ion) after addition of a nucleophile to a meso position. In this last example, the resulting geometry and distances around the 3N + O coordinated copper atom are very similar to those found in **8**. Similar 3N + O coordination is known in a few additional cases: a tripyrene³² and a ketobiladiene,²⁷ both possessing a carbonyl group available for coordination. Finally, these results suggest that earlier structural

- (22) Sheldrick, W. S. *Isr. J. Chem.* **1983**, *23*, 155.
 (23) Balch, A. L.; Latos-Grazinski, L.; Noll, B. C.; Olmstead, M. M.; Safari, N. *J. Am. Chem. Soc.* **1993**, *115*, 9056.
 (24) Balch, A. L.; Mazzanti, M.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1994**, *116*, 9114.
 (25) Koerner, R.; Olmstead, M. M.; Ozarowski, A.; Phillips, S. L.; Van Calcar, P. M.; Winkler, K.; Balch, A. L. *J. Am. Chem. Soc.* **1998**, *120*, 1274.
 (26) Koerner, R.; Olmstead, M. M.; Ozarowski, A.; Balch, A. L. *Inorg. Chem.* **1999**, *38*, 3262.
 (27) Khoury, R. G.; Senge, M. O.; Colchester, J. E.; Smith, K. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3937.
 (28) Lord, P.; Olmstead, M. M.; Balch, A. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2761.
 (29) Sheldrick, W. S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1457.
 (30) (a) Bonfiglio, J. V.; Bonnett, R.; Hursthouse, M. B.; Abdul Malik, K. M.; Naithani, S. C. *J. Chem. Soc., Chem. Commun.* **1977**, 829. (b) Bonfiglio, J. V.; Bonnett, R.; Buckley, D. G.; Hamzesh, D.; Hursthouse, M. B.; Abdul Malik, K. M.; Naithani, S. C.; Trotter, J. J. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1291.
 (31) Cullen, D. L.; Van Opendenbosch, N.; Meyer, E. F., Jr; Smith, K. M.; Eivazi, F. *J. Chem. Soc., Perkin Trans. 2* **1982**, 307.
 (32) Sessler, J. S.; Gebauer, A.; Král, V.; Lynch, V. *Inorg. Chem.* **1996**, *35*, 6636.

hypotheses¹⁹ regarding the metal coordination in porphyrin oxidation products should be questioned.

Experimental Section

General. UV–visible spectra: Hewlett-Packard 8453 (CH₂Cl₂). NMR (CDCl₃, unless otherwise stated): Bruker AC 300, AM 400, and ARX 500. Elemental analyses were performed at the Service de Microanalyse, Université Louis Pasteur, Strasbourg. HRMS were measured by LSMBO, Université Louis Pasteur (FAB). X-ray structures were determined by the Service de Cristallographie, Université Louis Pasteur, Strasbourg. Chromatographic separations were obtained using Merck 9385 silica gel or Merck 1076 alumina.

Photooxidation of Phlorin 1. A solution of **1** (282 mg) in CH₂Cl₂ (1500 mL) was stirred at daylight or illuminated with a tungsten lamp under an atmosphere of air for 15 h. The blue-green solution slowly turned light purple. After consumption of the starting material, the solvent was evaporated, and the residue was chromatographed on silica gel (400 mL) and eluted with a solvent gradient (CH₂Cl₂–AcOEt, 9:1) to give two purple fractions in a 3:1 ratio. Both bases **4** (102 mg; 35%) and **5** (9 mg; 3%) were obtained as amorphous solids from hexane at 0 °C, the losses being due to the high solubility.

Base 4. UV–Vis λ_{\max} , nm (ϵ): 326 (33 300), 352 (33 000), 538 (22 600). NMR: δ 12.3 (br s, 1H, NH), 9.9 and 9.1 (2 br s, 1 + 1H, NH), 7.79 (m, 2H, benzoyl-Ph *o*-H), 7.55–7.25 (m, 18H, *meso*-Ph), 6.93 (dd, 1H, $J = 5.8$ and 1.2 Hz, pyrrole H), 6.79 (dd, 1H, $J = 4$ and 2.4 Hz, pyrrole H), 6.65 (d, 1H, $J = 4.4$ Hz, pyrrole H), 6.63 (d, 1H, $J = 4.4$ Hz, pyrrole H), 6.36 (dd, 1H, $J = 4$ and 2.8 Hz, pyrrole H), 6.33 (d, $J = 4.4$ Hz, pyrrole H), 6.30 (d, $J = 4.4$ Hz, pyrrole H), 6.19 (dd, 5.8 and 1.5 Hz, pyrrole H), 2.55 (t, 2H, butyl CH₂), 1.25 (m, 4H, butyl 2 CH₂), 0.80 (t, 3H, butyl CH₃). HRMS (m/z): calcd, 704.315; found, 704.315.

Base 5. UV–vis λ_{\max} , nm (ϵ): 324 (33 000), 358 (25 700), 526 (28 300). NMR: δ 12.9 (v br, 1H, NH), 10.1 and 6.9 (2 br s, 1 + 1H, NH), 7.68 (m, 2H, benzoyl-Ph *o*-H), 7.7–7.2 (m, 18H, *meso*-Ph), 7.47 (dd, 1H, $J = 5.6$ et 1.6 Hz, pyrrole H), 6.76 (dd, 1H, $J = 4.0$ and 2.8 Hz, pyrrole H), 6.75 (d, 1H, $J = 4.4$ Hz, pyrrole H), 6.48 (d, 1H, $J = 4.1$; pyrrole H), 6.34 (d, 1H, $J = 4.4$, pyrrole H), 6.18 (d, 1H, $J = 4.1$, pyrrole H), 6.05 (dd, 1H, $J = 4.0$ and 2.8 Hz, pyrrole H), 5.94 (dd, 1H, $J = 5.6$ and 1.9 Hz, pyrrole H), 2.50 (br s, 2H, butyl CH₂), 1.25 (m, 4H, butyl 2CH₂), 0.83 (t, 3H, butyl CH₃). HRMS (m/z): calcd, 704.315; found, 704.315.

Nickel Complexes of Bases 4 and 5. Base **4** (10 mg) and nickel acetylacetonate (10 mg) were refluxed in benzene–methanol, 10:1 (2.2 mL), for 5 min. The solution was evaporated, and the residue was chromatographed on alumina (20 mL in CH₂Cl₂). Complex **7** was eluted with the same solvent and crystallized from hexane at 0 °C (10 mg). Crystals suitable for XRD were obtained by slow diffusion of hexane into a concentrated CH₂Cl₂ solution of **7**. Starting from base **5**, the same method afforded the nickel complex **9**.

7. UV–vis λ_{\max} , nm (ϵ): 358 (34 200), 594 (30 300). NMR: δ 8.8 (br s, 1H, NH), 7.64 (d, 2H, benzoyl *o*-H), 7.1–7.55 (m, 18H, phenyl H), 7.00 (d, 2H, $J = 4.4$ Hz, 2 pyrrole H), 6.64 (d, 1H, $J = 4.2$ Hz, pyrrole H), 6.58 (d, 1H, $J = 4.4$ Hz, pyrrole H), 6.50 (d, 1H, $J = 4.2$ Hz, pyrrole H), 6.17 (dd, 1H, $J = 5.6$ and 1.8 Hz, pyrrole H), 6.03 (br s, 1H, pyrrole H coupled with H at 6.58), 5.85 (br s, 1H, pyrrole H coupled with H at 7.00), 2.4 (br s, 2H, butyl CH₂), 1.3 (m, 4H, butyl 2CH₂), 0.88 (t, 3H, butyl CH₃). Anal. Calcd for C₄₈H₃₈N₄O₂Ni: C, 75.70; H, 5.03; N, 7.36. Found: C, 75.59; H, 5.04; N, 7.24.

9. UV–vis λ_{\max} , nm (ϵ): 357 (38 800), 592 (30 600). NMR (C₂D₂Cl₄, 348 K): due to the low resolution of most signals at 298 K,

Table 3. Crystal Data and Data Collection Parameters for **7–9**

	7	8	9
empirical formula	C ₄₉ H ₄₀ Cl ₂ N ₄ NiO ₂	C ₄₈ H ₃₈ CuN ₄ O ₂	C ₄₈ H ₃₈ N ₄ NiO ₂
mol wt	846.51	766.40	761.57
cryst syst	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 12/ <i>c</i> 1
<i>a</i> , Å	12.384(1)	11.7163(8)	41.726(3)
<i>b</i> , Å	13.484(1)	12.5811(6)	9.1582(3)
<i>c</i> , Å	14.285(1)	14.4254(8)	20.275(1)
α , deg	66.612(8)	86.335(5)	
β , deg	71.521(8)	66.244(5)	101.546(5)
γ , deg	79.266(8)	79.738(5)	
<i>V</i> , Å ³	2071.5(2)	1915.0(2)	7591(1)
<i>Z</i>	2	2	8
cryst dimns, mm ³	0.2 × 0.2 × 0.2	0.2 × 0.14 × 0.02	0.16 × 0.14 × 0.10
ρ (calcd) g/cm ⁻³	1.36	1.33	1.33
abs coeff μ , mm ⁻¹	0.643	0.616	0.557
temp, K	173	173	294
radiation (λ , Å)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
θ limits (deg)	2.5/27.55	2.5/27.45	2.5/27.54
no. of data collected	22739	13057	15403
no. with $I > 3\sigma(I)$	6751	4212	2748
R	0.070	0.050	0.065
Rw	0.081	0.066	0.086

the data reported here were obtained in C₂D₂Cl₄ at 348 K. δ 9.16 (dd, 1H, $J = 5.6$ and 1.6 Hz, pyrrole H), 7.66 (d, 2H, benzoyl *o*-H), 7.2–7.55 (m, 18H, phenyl H), 7.04 (d, 1H, $J = 4.5$ Hz, pyrrole H), 6.95 (br s, 1H, NH), 6.69 (d, 1H, $J = 4.5$ Hz, pyrrole H), 6.66 (d, 1H, $J = 4.2$ Hz, pyrrole H), 6.30 (d, 1H, $J = 4.2$ Hz, pyrrole H), 6.2 (br s, 2H, pyrrole H), 6.0 (br s, 1H, pyrrole H), 2.46, 1.40, 1.28 (3m, 3 × 2H, butyl CH₂), 0.96 (t, 3H, butyl CH₃).

Copper Complex 8. Base **4** in boiling CH₂Cl₂ was treated with excess copper acetate in warm MeOH. The solution immediately turned blue-violet and was washed with water and dried (Na₂SO₄). Copper complex **8** formed quantitatively (TLC) and was characterized by its X-ray structure. Suitable crystals were obtained by slow diffusion of hexane into a concentrated CH₂Cl₂ solution.

Photoisomerization of Bases 4 and 5. Base **4** or **5** (1 mg) in CH₂Cl₂ was left on a bench (sunlight or W bulb) for 48 h to give a clean 3:1 mixture of **4** and **5**, as analyzed by UV–visible spectroscopy after separation on silica gel TLC or after NMR measurement on the isomeric mixture. Solutions of **4** or **5** are stable when kept in the dark (see Table 3).

Crystal data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, under the deposition numbers CCDC 141313 (**7**), 141314 (**8**), and 151196 (**9**).

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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