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# Synthesis of a Fused Bis-Chlorin

**Claire K.** Johnson and David Dolphin*

**Department of Chemistry, The University** of British Columbia, Vancouver, B.C., Canada V6T 1Z1.

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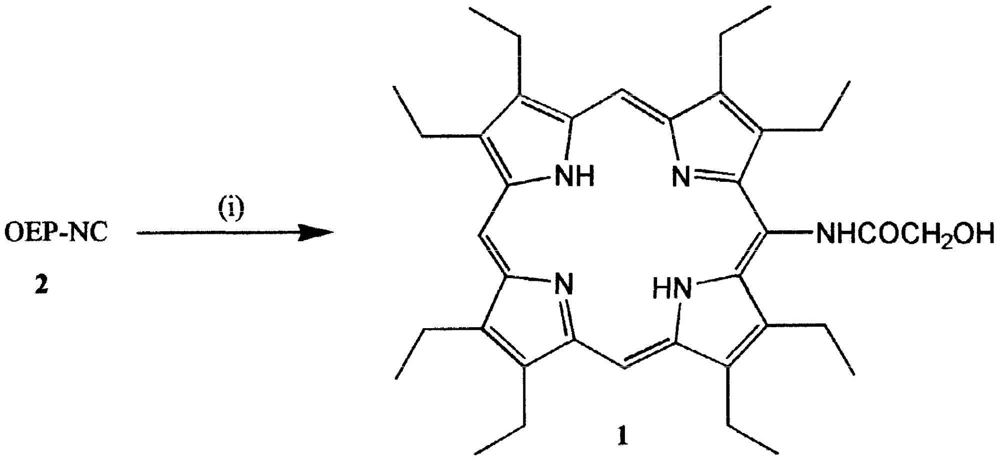
***Abstract:*** A dimeric pyridochlorin was formed by Lewis acid treatment of the nickel complex of *meso*-isocyanooctaethylporphyrin.

The recent interest in dimeric porphyrin compounds as models for the special pair in the photosynthetic reaction centre,[1] and in particular, a communication detailing the preparation of a planar bis-chlorophyll derivative,[2] prompts us to report the serendipitous synthesis of a fused bis-chlorin.

Our investigations into the intramolecular cyclization of various *meso*-substituted octaethylporphyrins led us to prepare the hydroxymethylated formamide **1**. This was formed in 28% yield by alkylation of *meso*-isocyanooctaethylporphyrin **2**[3] with paraformaldehyde under Lewis acidic conditions (Scheme 1).



(i) $(CHO)_n$, $BF_3.OEt_2$, toluene

**Scheme 1.** Alkylation of isocyanooctaethylporphyrin, **2**

When the nickel-complexed isocyanide **Ni-2** was subjected to identical treatment[4] in an attempt to prepare **Ni-1**, none of the desired product was isolable. Instead, a brown compound with low polarity was obtained in approximately 50% yield. Further studies demonstrated that this product was formed in similar yield

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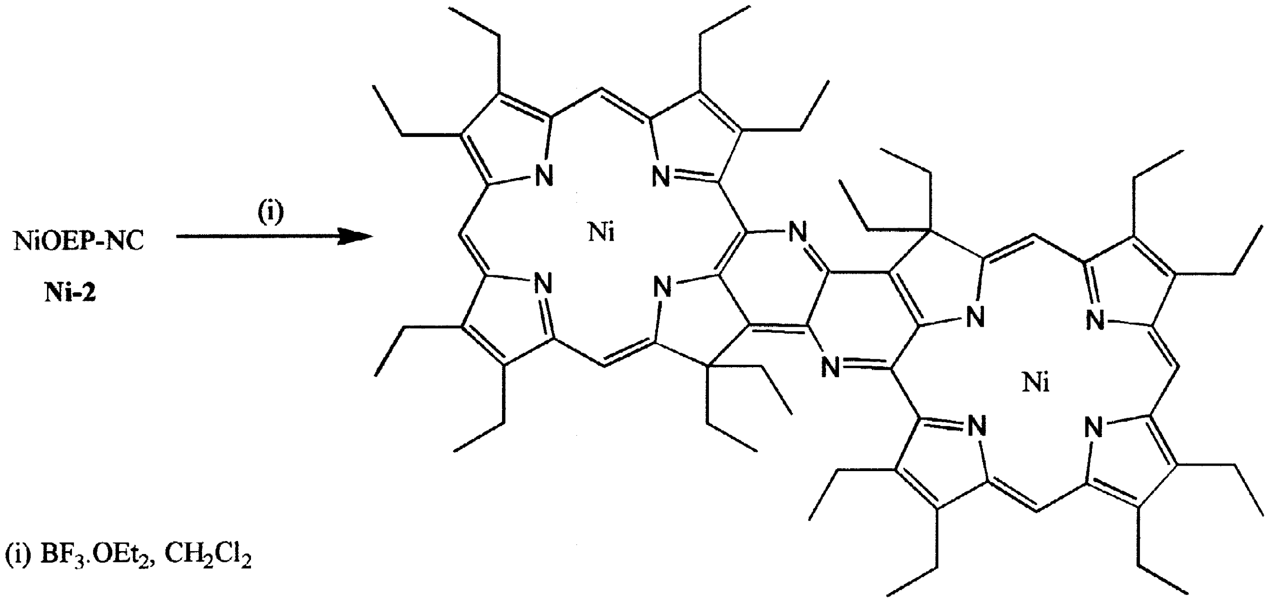
independently of paraformaldehyde. Mass spectral and $^1$H NMR data indicated that the compound was a dimer with a high degree of symmetry.[5] X-ray crystallography[6] established the structure to be that of the dimeric pyridochlorin **Ni-3**, the two monomers being joined by a common framework (Scheme 2).



NiOEP-NC
**Ni-2**

(i) $BF_3.OEt_2$, $CH_2Cl_2$

**Ni-3**

**Scheme 2.** Dimerization of nickel isocyanooctaethylporphyrin, **Ni-2**

The X-ray structure (Figure 1) shows the two chlorin rings to be held in an approximately coplanar S-shaped arrangement.

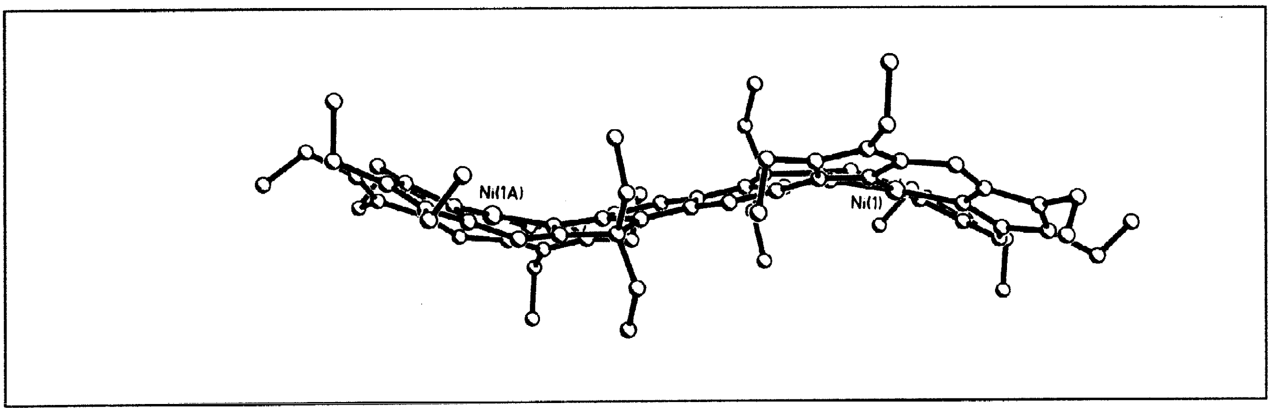


**Figure 1.** X-ray structure of **Ni-3**

The planarity and rigidity of the molecule allows electronic interaction between the aromatic systems of the two chlorins. This is reflected in the visible absorption spectrum (Figure 2), with a Soret band at 500 nm which is significantly red shifted compared to that of a typical nickel chlorin (at 410-430 nm), and a weak absorption at 816 nm which is absent in the spectra of conventional chlorins.

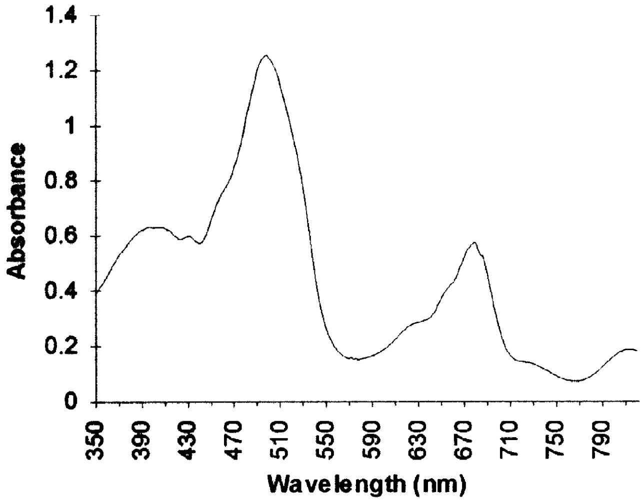


**Figure 2.** Visible absorption spectrum of **Ni-3** in dichloromethane

The free base dimer **3** was prepared in 77% yield by treatment of **Ni-3** with concentrated sulfuric acid. Metallation of **3** with zinc acetate led to quantitative formation of **Zn-3**.The visible absorption spectra of these compounds were similar to those of the nickel dimer.

**Acknowledgements:**

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4. **Ni-2** (25 mg) in $CH_2Cl_2$ (3 mL) and $BF_3.Et_2O$ (25 μL) was stirred overnight. Pyridine (1 drop) was added and the solvent evaporated. Product purified over silica ($CH_2Cl_2$:hexanes 1:1).

5. **Ni-3**: $^{1}$H NMR ($CDCl_3$) $\delta$: -0.05 (t, J=7.5Hz, 12H), 1.40-1.60 (m, 36H), 2.64-2.76 (m, 4H), 3.10-3.30 (m, 16H), 3.42 (q, J=7.3Hz, 4H), 3.64-3.76 (m, 4H), 4.17 (q, J=7.3Hz, 4H), 7.64 (br. s, 2H), 7.96 (s, 2H), 8.49 (br. s, 2H); UV-Vis ($CHCl_3$) $\lambda_{max}$ nm (log $\varepsilon$): 408 (4.69), 500 (4.99), 680 (4.64), 816 (4.13); MS (FAB) (3-NBA + $CHCl_3$ matrix): *m/e* calc'd for $C_{74}H_{87}N_{10}{}^{58}Ni{}^{60}Ni$: 1233.5757, found: 1233.57831; Analysis calc'd for $C_{74}H_{86}N_{10}Ni_2.HCl$: C, 70.02; H, 6.91; N, 11.03. Found: C. 69.98, H, 6.85; N, 10.93.

6. **Ni-3.2CH$_2$Cl$_2$**: $C_{76}H_{90}Cl_4N_{10}Ni_2$, MW = 1402.80, purple prism from $CH_2Cl_2$/hexanes, crystal size 0.30x0.29x0.25 mm, triclinic, space group $P\bar{1}$, a = 10.6420(1), b = 11.9025(1), c = 14.9759(2) Å, $\alpha$ = 98.388(1), $\beta$ = 100.603(1), $\gamma$ = 106.754(1)°, V = 1745.07(3) Å$^3$, Z = 1, $\rho_{calcd}$ = 1.335 Mg/m$^3$, Siemens SMART diffractometer, $\theta$ range 1.42-25.09°, radiation $\lambda$ = 0.71073 Å, T = 173(2) K, structure solution with direct methods, refinement on $F^2$, 6016 independent reflections, 4818 with $I > 2\sigma(I)$, observed data R1 = 0.0686, wR2 = 0.1751, all data R1 = 0.0885, wR2 = 0.1929.