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# Cleavage of (octaethyl-2,3-dihydroxychlorinato)nickel(II) to give the novel 2,3-dioxo-2,3-secochlorin system

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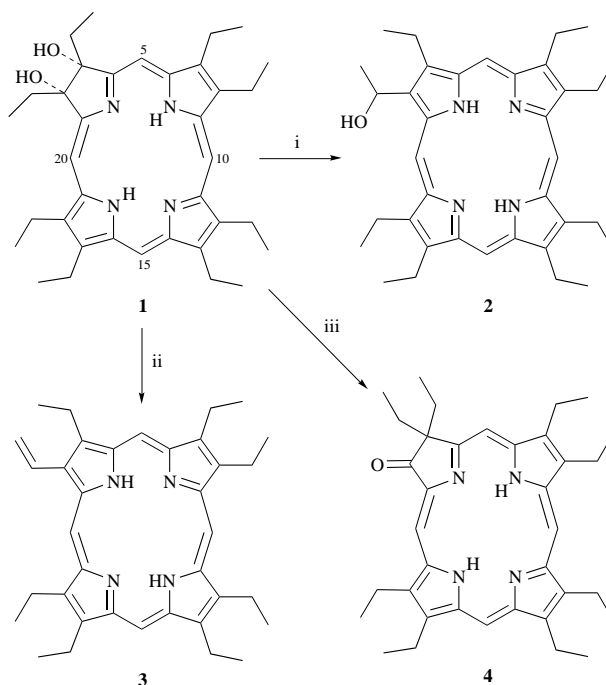
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Treatment of (octaethyl-2,3-dihydroxychlorinato)nickel(II) with lead tetraacetate in benzene causes cleavage of the 2–3 bond to give the nickel(II) 2,3-secochlorin-2,3-dione system **7**, a previously unknown structural type. The structure is established by elemental analysis and spectroscopic methods, and confirmed by X-ray analysis. The dione gives a bis(2,4-dinitrophenylhydrazone). Treatment with base causes an aldol-type condensation to occur to give the (2-oxo-2a-homoporphyrinato)nickel(II) **8**. This substance is rather unreactive, and it has not been possible to prepare carbonyl derivatives. This lack of reactivity is rationalised in terms of charge delocalisation which reduces carbonyl double-bond character. These novel pathways are discussed in relation to the known (and different) pathways of chlorophyll catabolism which have recently been uncovered.

The *cis*-hydroxylation of a  $\beta\beta'$ -bond of the porphyrin system *via* osmylation was introduced by Fischer and Eckoldt,<sup>1</sup> who studied a number of naturally derived porphyrins. The reaction was observed to be slow (several days, room temperature) and presumably gave mixed regioisomers: in the case of phylloporphyrin two such isomers were isolated. More recently it has been shown (for example, in the synthesis of the prosthetic group of haem *d*, which is a 12,13-dihydroxyprotohaem) that such isomers can, with some effort, be effectively isolated by preparative thin layer chromatography and identified by two-dimensional NMR techniques.<sup>2</sup> Because they have strong absorption in the red region of the visible spectrum, the 2,3-dihydroxychlorins (and the corresponding tetrahydroxybacteriochlorins) have also attracted attention as potential photosensitisers for photodynamic therapy (PDT).<sup>3,4</sup>

Model  $\beta\beta'$ -dihydroxychlorins have also been important. The *cis* configuration of the diol is evident from its method of preparation, and has been confirmed for the octaethyl derivative **1** by X-ray analysis,<sup>5</sup> which also indicates that the tautomeric imino hydrogens are on opposite non-reduced rings (shown here as 22*H*,24*H*). Acid treatment of **1** gives a variety of useful products depending on conditions, as shown in Scheme 1. The pinacol–pinacolone rearrangement in this series **1**→**4** was first established for model systems,<sup>8</sup> where it was noted that it generated the *gem*- $\beta$ -dialkylation pattern found in the natural corrinoids. Migratory aptitude studies<sup>9</sup> have indicated for common natural  $\beta$ -substituents the order alkyl groups, propionate, H > methyl > acetate. The formation of dioxobacteriochlorins and dioxoisobacteriochlorins by repeated reaction<sup>10</sup> has recently become of particular interest with the discovery of natural products with these structures (e.g. tolporphyrin is a dioxobacteriochlorin,<sup>11</sup> and haem *d*<sub>1</sub> is a dioxoisobacteriochlorin<sup>12</sup>). The dioxo compounds, and sulfido, imino and methide derivatives of them, have also been considered as PDT photosensitisers.<sup>13</sup>

Our interest in the cleavage of the *vic*-diol system of **1** originated with the suggestion<sup>14</sup> that such cleavage might be involved in the catabolism of chlorophyll *a* and *b* (Scheme 2). On chemical grounds the major reactive sites of the chlorophylls **5** are expected to be (a) C-13<sup>2</sup>, a pseudobenzylic acidic ( $\beta$ -keto ester) position; (b) the metal- $\pi$  system, readily oxidised and readily demetallated; (c) the ring A–C-3 vinyl system; (d) the unsubstituted *meso*-positions, particularly C-20; and (e) the tertiary

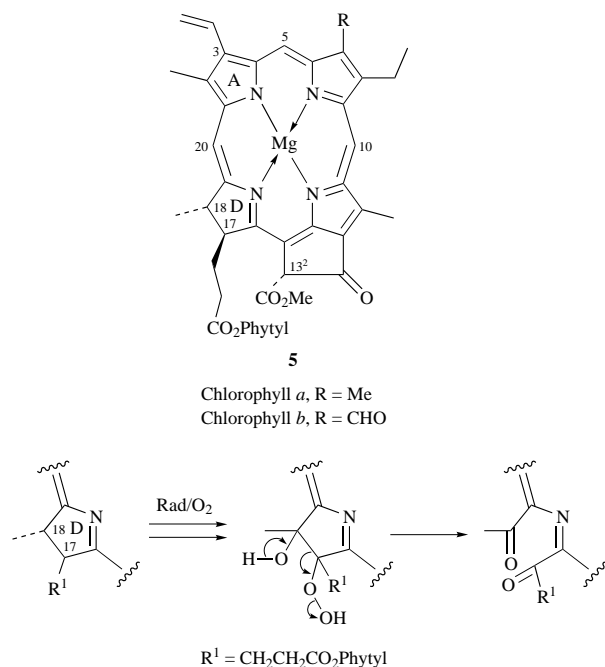


**Scheme 1** Acid catalysed modifications of octaethyl-2,3-*cis*-dihydroxychlorin **1**. Reagents and conditions: i, HCl, aq. dioxane, 100 °C, 30 min, 49%;<sup>6</sup> ii, PhH, HCl, reflux, 3 h, 90%;<sup>6</sup> iii, 70% HClO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 30 min, 20 °C, 72%<sup>3,7</sup> or H<sub>2</sub>SO<sub>4</sub>–SO<sub>3</sub>, 20 °C, 75%.<sup>3</sup>

pseudobenzylic C-17 and C-18 positions.<sup>15</sup> Recently, various catabolites from reactions at the C-5 bridge (oxidative cleavage of the C-4–C-5 bond) have been recognised by Gossauer and co-workers<sup>16</sup> and by Kräutler and co-workers.<sup>17</sup> Reaction at both C-17 and C-18 has not yet been detected, but the possibility remains that radical reactions could lead to ring D cleavage as indicated in Scheme 2.

Osmylation of octaethylporphyrin in dichloromethane–pyridine (72 h, Ar), followed by cleavage of the cyclic osmate with H<sub>2</sub>S–MeOH gave octaethyl-*cis*-2,3-dihydroxychlorin **1**.<sup>3,6,18</sup> Attempts to devise a procedure in which catalytic amounts of osmium tetroxide could be used were not successful.

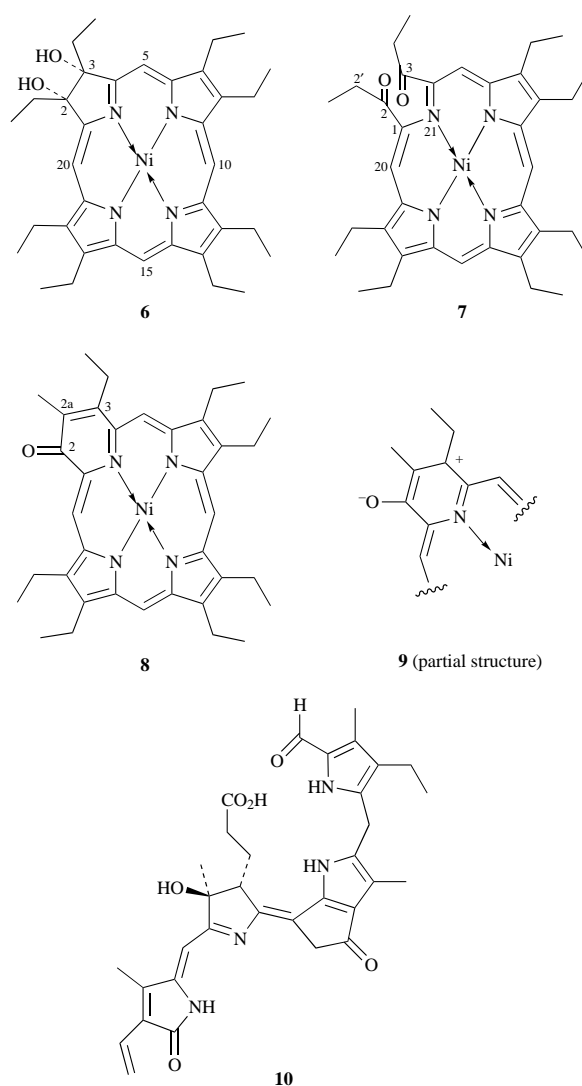
Treatment of **1** with lead tetraacetate in pyridine or in ben-



Scheme 2

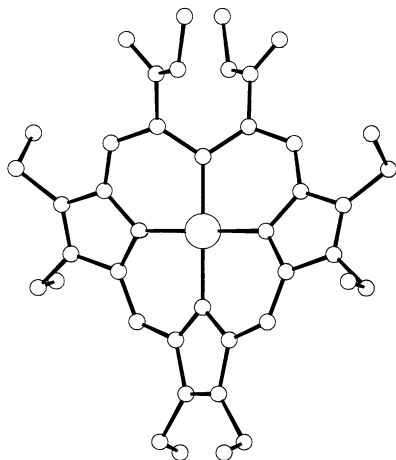
zene produced a mixture of products. It was therefore decided to protect the imino functions (which formally offered a vicinal amino alcohol centre) by preparing the nickel(II) complex **6**. This was accomplished using nickel acetate in dimethylformamide. A slight difficulty arose here, since Grigg *et al.* had reported that attempted metallation of *cis*-2,3-dihydroxyetiochlorin I with nickel acetate in methanolic ammonium hydroxide had generated nickel(II) 2(3)-oxoetiochlorin I.<sup>19</sup> In order to be certain that a similar rearrangement had not occurred in the present instance, a small sample of nickel(II) octaethyl-2-oxochlorin<sup>20</sup> was prepared for comparison, and proved to be spectroscopically and chromatographically distinct from the product obtained here. (We attribute the earlier result to the protracted reaction period (24 h) and the use of inappropriate conditions, since 43% of the starting material was recovered.<sup>19</sup>) The structure **6** rests on elemental analysis, an accurately measured molecular ion (albeit in low abundance on electron impact ionisation), the observation in the IR spectrum of hydroxy stretching and not carbonyl stretching [ $\nu_{\max}$  1711 cm<sup>-1</sup> in nickel(II) octaethyl-2-oxochlorin<sup>20</sup>] and the <sup>1</sup>H NMR spectrum which showed that the molecule must have a plane of symmetry perpendicular to the plane of the macrocycle [two *meso*-signals at  $\delta$  9.12 (C-10, 15) and  $\delta$  8.25 (C-5, 20)]. The methylene protons of the ethyl groups at C-2, 3 were non-equivalent and formed part of an AMX<sub>3</sub> system with  $J_{\text{gem}}$  15 Hz and  $J_{\text{vic}}$  7.5 Hz. Interestingly this effect was much clearer in the metal complex than in the free base: possibly this reflects the increased rigidity of the complex.

The nickel(II) dihydroxychlorin **6** in benzene was treated with freshly recrystallised dried lead tetraacetate. Over 15 min at room temperature the solution changed in colour (dark green → leaf green): **6** was no longer detectable and ethylene glycol was added to quench the reaction. The product was obtained as tiny green needles, and is formulated as the novel 2,3-secochlorin-2,3-dione **7** (76% yield). Elemental analysis and accurate measurement of the molecular ion (12% abundance in electron impact) established the molecular formula C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>NiO<sub>2</sub> (although the carbon analysis was low). The UV-VIS spectrum showed strong broad bands at 444 ( $\epsilon$  49 000) and 648 nm ( $\epsilon$  13 300), while in the IR the carbonyl groups appeared as a single band at 1676 cm<sup>-1</sup>. The NMR spectra (<sup>1</sup>H and <sup>13</sup>C) again accorded with a system of C<sub>2</sub> symmetry: the *meso*-protons appeared at  $\delta$  9.03 (s) and  $\delta$  8.17 (s), showing only



marginal changes compared with the corresponding signals ( $\delta$  9.12, 8.25) in the precursor **6**. Both the <sup>1</sup>H and <sup>13</sup>C NMR spectra supported structure **7**, which was confirmed by X-ray crystal analysis.<sup>21</sup> The resulting structure is shown in Fig. 1. In the crystal the carbonyl groups point in different directions, one above, one below, the macrocyclic mean plane: thus the C-2 carbonyl lies in a plane (C-1, C-2, C-2', O) which makes a dihedral angle of 62° with the plane determined by C-1, C-2, C-20 and N-21. As a consequence the carbonyl is partially conjugated ( $\nu_{\max}$  1676 cm<sup>-1</sup>; <sup>13</sup>C NMR  $\delta$  201.6 for C-2, 3). Each of the ethyl groups of the *seco* system lies above the opposite carbonyl group and hence the two hydrogens of each methylene group adjacent to the carbonyl experience restricted rotation and are inequivalent, and appear as double quartets in the <sup>1</sup>H NMR spectrum.

It is interesting that under different conditions the reaction of lead tetraacetate with  $\beta$ -oxochlorin **4** has been shown to give products of *meso*-acetoxylation at C-10, C-15 and C-20.<sup>22</sup> Although such product types may occur in the (more complex) reaction of the free base **1**, they have not been detected amongst the reaction products of the nickel complex **6**. The secochlorindione **7** shows some normal carbonyl reactions. Thus it gave a bis(2,4-dinitrophenylhydrazone) which was characterised by mass spectrometry and <sup>1</sup>H NMR spectroscopy. Treatment of **7** with potassium *tert*-butoxide in *tert*-butyl alcohol at 40 °C resulted in an aldol condensation between the adjacent ethyl ketone functions to give the novel homoporphyrinone system **8**, which was also obtained on treating the secochlorindione with methylamine or ethylenediamine. Compound **8** was obtained as small blue prisms in 64% yield. It analysed for C<sub>36</sub>H<sub>42</sub>N<sub>4</sub>NiO,



**Fig. 1** Molecular structure of the 2,3-secochlorin-2,3-dione **7** viewed at right angles to the five atoms of former ring A and with the two-fold axis vertical<sup>21</sup>

and showed a broadened spectrum of a chlorin type [ $\lambda_{\max}$  437 ( $\epsilon$  128 000) and 612 nm ( $\epsilon$  27 700)] in chloroform. The IR spectrum showed absorption at 1636  $\text{cm}^{-1}$ , consistent with a highly conjugated carbonyl group, as is the location of the  $^{13}\text{C}$  signal for C-2 at  $\delta$  191.2 (*cf.*  $\delta$  201.6 for **7**). The  $^1\text{H}$  NMR spectrum showed loss of symmetry in the system with respect to the precursor, with four *meso*-signals appearing at  $\delta$  9.253, 9.035, 9.028 and 8.810, while the isolated methyl group (at C-2a) appeared as a singlet at  $\delta$  2.725. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were consistent with structure **8**.

The chemical properties of this complex were investigated, but studies were frustrated by its kinetic stability. The complex could not be demetallated by refluxing 5 M  $\text{HCl}-\text{CF}_3\text{CO}_2\text{H}$ , and even the addition of thiols [as in  $\text{CF}_3\text{CO}_2\text{H}-(\text{CH}_2\text{SH})_2$ ]<sup>23</sup> had no effect. The carbonyl group of **8** was found to be unreactive. Derivatives of common carbonyl reagents were not formed, nor did it react with lithium dibutylcuprate.<sup>24</sup> Attempted Diels–Alder reaction with 2,3-dimethylbuta-1,3-diene in the presence of boron trifluoride–diethyl ether failed to occur. We attribute the lack of carbonyl reactivity to the dominance of the delocalised system **9**, which arises because of its pseudobenzylic carbocation character.

Returning to the question of chlorophyll catabolism, it seems evident that if a secochlorindione system were first formed, it would fairly readily undergo an internal aldol condensation to give the corresponding homoporphyrin-2-one. It seems to us that the robustness of this system, even if it is overemphasised in the nickel complex, makes it rather unlikely that it is formed during chlorophyll breakdown, otherwise surely it would have been detected long ago. However now that the model system is known, this supposition is the more open to experimental investigation. At any event, the recent report<sup>25</sup> of a 17-hydroxy derivative formulated as **10** as a chlorophyll degradation product in *Chlorella protothecoides* suggests that radical reactions at C-17/C-18 may indeed play a part in the catabolic process.

## Experimental

### General

The following spectroscopic equipment was used.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra: Bruker AM250 or WH400, chemical shifts ( $\delta$ ) being relative to tetramethylsilane and  $J$  values in Hz, the DEPT sequence being used to distinguish  $\text{CH}$ ,  $\text{CH}_2$  and  $\text{CH}_3$  in the  $^{13}\text{C}$  spectra; IR spectra: Perkin-Elmer 1600FT; UV–VIS spectra: Perkin-Elmer Lambda 2, extinction coefficients ( $\epsilon$ ) being given in  $\text{l mol}^{-1} \text{cm}^{-1}$ ; electron impact mass spectra: Kratos MS50; FAB mass spectra: VG Autospec with 3-nitrobenzyl alcohol dispersant. Thin layer chromatography was carried out on Merck Kieselgel 60H. Microanalysis was done by Alfred Bernhardt, Mülheim or by Butterworth Micro-

analytical Consultancy, Teddington. Melting points were determined on a Kofler block and are not corrected.

### (2,3,7,8,12,13,17,18-Octaethyl-2,3-*cis*-dihydroxychlorinato)-nickel(II) **6**

2,3,7,8,12,13,17,18-Octaethyl-2,3-*cis*-dihydroxy-22*H*,24*H*-chlorin<sup>3,6</sup> (39 mg) and nickel acetate tetrahydrate (60 mg, excess) were stirred under argon in dimethylformamide (15 ml, previously Ar flushed) at 90 °C for 14 h. To the cooled solution was added dichloromethane (100 ml), and the organic phase was washed with water ( $4 \times 50$  ml), dried over  $\text{Na}_2\text{SO}_4$ , filtered and taken to dryness. The residue was chromatographed (silica gel 60, 19 cm  $\times$  3 cm) with chloroform and the main fraction (blue) was collected and crystallised from dichloromethane–hexane to give (2,3,7,8,12,13,17,18-octaethyl-2,3-*cis*-dihydroxychlorinato)nickel(II) (**6**) (30 mg, 70%) as blue–green prisms, mp 205–206 °C;  $R_f$  (silica gel,  $\text{CHCl}_3$ ) 0.46 (Found: C, 69.3; H, 7.2; N, 9.15.  $\text{C}_{36}\text{H}_{46}\text{N}_4\text{NiO}_2$  requires C, 69.15; H, 7.4; N, 8.95%);  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  ( $\epsilon$ ) 385 (sh, 58 000), 399 (79 500), 491 (4000), 525 (2800), 575 (sh 6800) and 618 (38 000);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3445 (br s), 2963, 2920, 2860, 1654 (br), 1458, 1262, 1217 and 1018;  $\delta_{\text{H}}$  (250 MHz,  $\text{CDCl}_3$ ) 9.12 (s, *meso*-H at C-10, 15), 8.25 (s, *meso*-H at C-5, 20), 3.63, 3.52 (overlapping q,  $J$  7.5, 7.5,  $\text{CH}_2$  at 8, 12, 13, 17 and at 7, 18, respectively), 3.18 (s, exchangeable  $\text{D}_2\text{O}$ , OH at 2, 3), 2.47, 2.19 (dq and dq,  $J_{\text{vic}}$  7.5,  $J_{\text{gem}}$  15, AM part of  $\text{AMX}_3$  system,  $\text{CH}_2\text{CH}_3$  on ring A), 1.56–1.72 (m, overlapping t,  $J$  7.5,  $\text{CH}_2\text{CH}_3$  on rings B, C, D), 1.06 (t,  $J$  7.5,  $\text{CH}_2\text{CH}_3$  on ring A);  $m/z$  (FAB) 626 (100%,  $\text{M} + 2$ ); (EI) 624.3040 (2%,  $\text{C}_{36}\text{H}_{46}\text{N}_4^{58}\text{NiO}_2$  requires 624.2974), 606 (100,  $\text{M} - \text{H}_2\text{O}$ ), 588 (16,  $\text{M} - 2\text{H}_2\text{O}$ ), 577 (19,  $\text{M} - \text{H}_2\text{O} - \text{Et}$ ); peaks of diminishing abundance at 562, 547, 532, 517 attributed to sequential loss of methyl groups (benzylic cleavage).

### (3,3,7,8,12,13,17,18-Octaethyl-2-oxochlorinato)nickel(II) **20**

In a similar way 3,3,7,8,12,13,17,18-octaethyl-2-oxo-22*H*,24*H*-chlorin<sup>26</sup> (4.6 mg) and nickel acetate tetrahydrate (15 mg) in dimethylformamide (1 ml) were stirred at 90 °C in the dark under nitrogen for 12 h. The solvent was removed, and the residue was subjected to preparative TLC (silica gel, 20%  $\text{CHCl}_3$  in light petroleum, bp 60–80 °C). The green component was separated to give the title compound as an amorphous solid,  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  372, ~410 (Soret), 508sh, 546, 574 and 620;  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  2965, 2930, 2870, 1717 and 1460;  $R_f$  (silica gel, 15% acetone in light petroleum 60–80 °C) 0.75 (vivid green); under the same conditions the nickel diol had  $R_f$  0.41 (sea green).

### (2,3,7,8,12,13,17,18-Octaethyl-2,3-dioxo-2,3-secochlorinato)-nickel(II) **7**

The nickel(II) *cis*-diol (**6**, 75 mg) dissolved in anhydrous benzene (8 ml) was stirred with freshly crystallised (HOAc), dried (KOH pellets *in vacuo*, dark) lead tetraacetate (54 mg, excess) for 15 min at room temperature. Ethylene glycol (0.5 ml) was added, and stirring was continued for 2 min. Chloroform (50 ml) was added, and the mixture was washed with water ( $2 \times 25$  ml), the organic phase was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and taken to dryness. The residue was chromatographed on silica gel 60 (12 cm  $\times$  3 cm) with chloroform. The leaf-green fraction was collected, taken to dryness, and crystallised from dichloromethane–methanol to give small green needles (57 mg, 76%) of (2,3,7,8,12,13,17,18-octaethyl-2,3-dioxo-2,3-secochlorinato)-nickel(II), mp 180–185 °C;  $R_f$  (silica gel,  $\text{CHCl}_3$ ) 0.48 (Found: C, 68.65; H, 7.4; N, 9.3.  $\text{C}_{36}\text{H}_{44}\text{N}_4\text{NiO}_2$  requires C, 69.35; H, 7.1; N, 9.0%);  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  ( $\epsilon$ ) 444 (49 000), 514 (sh, 6300) and 648 (13 300);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2966, 2932, 2869, 1676, 1560, 1267, 1217, 1189, 1020 and 964;  $\delta_{\text{H}}$  (250 MHz,  $\text{CDCl}_3$ ) 9.03 (s, *meso*-H at C-10, 15), 8.17 (s, *meso*-H at C-5, 20), 3.37–3.68 (m, overlapping q,  $J$  7.5,  $\text{CH}_2\text{CH}_3$  on rings B, C, D), 2.74 and 2.03 (both dq,  $J_{\text{vic}}$  7.5,  $J_{\text{gem}}$  17, AM part of  $\text{AMX}_3$  system,  $2 \times \text{COCH}_2\text{CH}_3$  at 2, 3), 1.60–1.72 (m, overlapping t,  $J$  7.5,

CH<sub>2</sub>CH<sub>3</sub> on rings B, C, D), 0.85 (t, *J* 7.5, 2 × COCH<sub>2</sub>CH<sub>3</sub>); δ<sub>C</sub>(100.6 MHz, CDCl<sub>3</sub>) 201.6 (C-2, 3), 145.3, 145.1, 144.2, 143.0, 142.9, 141.8, 139.6 (aromatic quaternary carbons of 7 sorts), 103.0, 93.7 (*meso*-carbons of 2 sorts), 32.5 (CH<sub>2</sub>CH<sub>3</sub> at C-2, 3), 19.3, 19.2, 19.1 (CH<sub>2</sub>CH<sub>3</sub> on rings B, C, D), 17.7 (CH<sub>2</sub>CH<sub>3</sub> on rings B, C, D) and 9.1 (CH<sub>2</sub>CH<sub>3</sub> at C-2, 3); *m/z* (FAB) 626 (11%, *M* + 4), 564 (100, *M* – COEt – H); (EI) 622.282 (12, *M*, C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>NiO<sub>2</sub> requires 622.282), 565.247 (100, *M* – COEt, C<sub>33</sub>H<sub>39</sub>N<sub>4</sub>NiO requires 565.248).

### Carbonyl reactions of the 2,3-dioxo-2,3-secochlorin 7

(i) **Bis(2,4-dinitrophenylhydrazone)**. The nickel(II) complex **7** (2 mg) was warmed with 1% 2,4-dinitrophenylhydrazine in 1% HCl in ethanol (1 ml) for 5 min, and then kept at room temperature. After 2 h a brown precipitate had formed which was purified by TLC (silica gel 60, 20 × 20 × 0.1 cm) using chloroform as irrigant. [2,3-Bis(dinitrophenylhydrazono)-2,3,7,8,12,13,17,18-octaethyl-2,3-secochlorinato]nickel(II) was obtained as an amorphous green powder (*ca.* 1 mg), *R*<sub>f</sub> (silica gel, CHCl<sub>3</sub>) 0.16; *m/z* 983 (22%, *M* + 1), 745 [100, *M* – C(C<sub>2</sub>H<sub>5</sub>)=NNHC<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>]; δ<sub>H</sub>(250 MHz, CDCl<sub>3</sub>) 11.28 (br s, 2 × NH, hydrazone groups), 9.01 (s, *meso*-H at C-10, 15), 8.93 (d, *J*<sub>3,5</sub> 2.5, 2 × C-3H of phenyl), 8.47 (dd, *J*<sub>5,3</sub> 2.5, *J*<sub>5,6</sub> 9.5, 2 × C-5H of phenyl), 8.27 (d, *J*<sub>6,5</sub> 9.5, 2 × C-6H of phenyl), 7.91 (s, *meso*-H at C-5, 20), 3.40–3.67 (m, overlapping q, *J* 7.6, CH<sub>2</sub>CH<sub>3</sub> on rings B, C, D), 2.61 and 1.82 [2 × *m* AMX<sub>3</sub> system, 2 × C(=N)CH<sub>2</sub>CH<sub>3</sub>], 1.60–1.75 (m, overlapping t, *J* 7.6, CH<sub>2</sub>CH<sub>3</sub> on rings B, C, D) and 0.14 [t, *J* 7.6, 2 × C(=N)CH<sub>2</sub>CH<sub>3</sub>].

(ii) **2a-Homoporphyrin-2-one 8**. Treatment of the secochlorindione **7** with primary amines (methylamine, ethylenediamine) gave the 2a-homoporphyrin-2-one **8** as the only product detected.

### (3,7,8,12,13,17,18-Heptaethyl-2a-methyl-2-oxo-2a-homoporphyrinato)nickel(II) 8

(2,3,7,8,12,13,17,18-Octaethyl-2,3-dioxo-2,3-secochlorinato)-nickel(II) (63 mg) and potassium *tert*-butoxide (69 mg) dissolved in *tert*-butyl alcohol (20 ml) were stirred (N<sub>2</sub>) for 15 h at 40 °C. The solution was then diluted with chloroform (70 ml), washed with water (3 × 25 ml), the organic phase being dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and taken to dryness. The residue was chromatographed over silica gel 60 (23 × 3 cm, CHCl<sub>3</sub>). The major green fraction was collected and crystallised from CH<sub>2</sub>Cl<sub>2</sub>–MeOH to give 39 mg (64%) of (3,7,8,12,13,17,18-heptaethyl-2a-methyl-2-oxo-2a-homoporphyrinato)nickel(II), as small blue prisms, mp 292–296 °C; *R*<sub>f</sub> (silica gel, CHCl<sub>3</sub>) 0.34 (Found: C, 71.5; H, 7.15; N, 9.35. C<sub>36</sub>H<sub>42</sub>N<sub>4</sub>NiO requires C, 71.4; H, 7.0; N, 9.25%); λ<sub>max</sub>(CHCl<sub>3</sub>)/nm (ε) 437 (128 000), 568 (11 000) and 612 (27 700); ν<sub>max</sub>(KBr)/cm<sup>–1</sup> 2960, 2928, 2867, 1636, 1614, 1533, 1463, 1221, 1055, 1017 and 958; δ<sub>H</sub>(400 MHz, CDCl<sub>3</sub>) 9.253 (s, C-20H), 9.035, 9.028 (2 × s, H at C-10, 15 not necessarily respectively), 8.810 (s, H at C-5), 3.65–3.7 (m, overlapping q, *J* 7.6, CH<sub>2</sub>CH<sub>3</sub> on rings B, C, D), 3.449 (q, *J* 7.6, CH<sub>2</sub>CH<sub>3</sub> at C-3), 2.725 (s, CH<sub>3</sub> at C-2a) and 1.6–1.8 (m, overlapping t, 7 × CH<sub>2</sub>CH<sub>3</sub>); δ<sub>C</sub>(100.6 MHz, CDCl<sub>3</sub>) 191.2 (C-2), 157.1 (C-2a), 145.0, 144.8, 144.7, 143.9, 140.7, 139.9, 139.7, 138.6, 136.5, 133.5, 129.9 (quaternary unsaturated C), 103.4, 99.1, 97.8, 97.5 (*meso*-C), 26.3 (CH<sub>2</sub>CH<sub>3</sub> at C-3), 19.4, 19.3, 19.2 (CH<sub>2</sub>CH<sub>3</sub> on rings B, C, D), 17.9, 17.8 (CH<sub>2</sub>CH<sub>3</sub> on rings B, C, D), 15.6 (CH<sub>3</sub> at C-2a) and 12.3 (CH<sub>2</sub>CH<sub>3</sub> at C-3); *m/z* (FAB) 605 (98%, *M*), 604 (100, *M* – H), 589 (10, *M* – Me), 575 (11, *M* – Et) and 547(13).

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