Synthesis and Characterization of Models for the Bilin Catabolites of Chlorophylls Using Metallo-β-oxochlorins and -benzo[at]chlorins: Comparison of Macrocycle Cleavage versus meso-Oxochlorin Formation †

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Synthetic studies on meso-substitution and subsequent macrocycle ring-opening reactions have been performed on a 3-oxochlorin 7 and benzo[at]chlorin 19 to obtain access to bilins related to the natural chlorophyll catabolites 2 and 3. The zinc oxochlorin 8 could be trifluoroacetoxylated with thallium(III) trifluoroacetate in the 5-, 15- or 20-meso-positions. The 15-trifluoroacetoxy derivative 10 spontaneously ring-opened to give a bilintrione 13, which exhibited the same basic structural characteristic found in natural chlorophyll catabolites, namely macrocycle cleavage at a meso-position distant from (rather than adjacent to) the pyrrolenine ring. A single crystal structure analysis of 13 showed a linear conformation, indicating that a Z to E isomerization had taken place. This result is in contrast to most known bilin structures derived from macrocycles, which exhibit a helical conformation. meso-Oxygenated derivatives (related to compounds formerly termed oxo-phlorins) were obtained upon acid hydrolysis of the 5-(11) and 20-trifluoroacetoxy-3-oxochlorin 9. Attempts to ring-open 9 or 11 under basic or photochemical reaction conditions were unsuccessful. Trifluoroacetoxylation of the nickel(II) β-benzochlorin 19 yielded regioselectively the 5-substituted derivative 20, which could be ring-opened under mildly basic conditions to give the 19-methoxybenzobilin-1-ones 21 and 22. Here macrocycle cleavage occurred at the substituted meso-position neighbouring the reduced ring. Application of a similar strategy to the nickel(II) β-oxochlorin 23 gave similar results with formation of only the 20-trifluoroacetoxylated derivative 24, which upon basic hydrolysis reacted to give the corresponding meso-oxo-derivative 25/26. Thus, selective meso-substitution, a requirement for regioselective macrocycle cleavage, giving access to model compounds for the natural chlorophyll catabolites depends strongly on the central metal in the macrocyclic precursor.

The synthesis of bilins from chlorins has attracted interest in past years due to the possible involvement of such open-chain tetrapyrroles in the degradation of naturally occurring chlorins, namely the chlorophylls.[1] Recently, two intermediates of chlorophyll a 1 catabolism after macrocycle cleavage have been identified. One class of compounds, originally termed 'rusty pigments', was isolated from senescing barley leaves. The main chlorophyll catabolite found, a 1-formyl-19-oxobilane 2, showed that extensive hydroxylation, reduction of meso-bridges, and oxidation of the pyrroline ring had occurred.[2] The other, related compound, was first detected by Oshio and Hase[3a] in *Chlorella protohecoides* and its structure was elucidated in 1991 by Engel *et al.* and identified as a 7,8-dihydrobiladiene-a,b 3.[3b,c] Although several significant differences between 2 and 3 exist, in both cases macrocycle cleavage had (surprisingly) taken place at C(5) instead of the 'chemically more reactive' C(20).

The site of macrocycle cleavage in the tetrapyrrole ring system is of central importance for understanding the catabolic processes involved in chlorophyll degradation. Ring-opening in chlorins at C(5), *i.e.* two meso-positions removed from the pyrrolenine ring (as found in 2 and 3), was unexpected since most known chlorin ring-opening reactions lead to macrocycle cleavage at the meso-bridge neighbouring the reduced ring. Examples for this are the photooxygenation of zinc(II) octaethylchlorin,[4] and photochemical ring-opening of meso-substituted zinc(II) chlorins such as 20-chloro-[5] or 20-trifluoro-acetoxy-derivatives[6] of chlorophyll a and derivatives of the bacteriochlorophylls c.[7] An example of a naturally occurring

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2

3

4
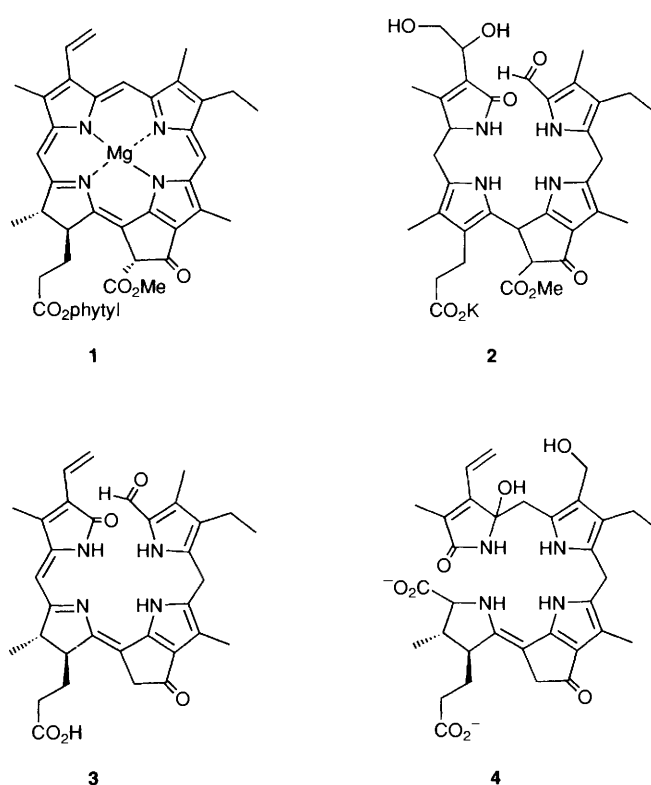
chlorin catabolite 4 (a 2,3-dihydro-bilene-a) with its precursor ring-opened next to the reduced ring was isolated[8a] from *Euphausia pacifica*; it has a structure simillar to dinoflagellate

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luciferin.[8b] Most of the published model studies were based on the observation that, when compared with porphyrins, chlorins show a high reactivity towards electrophilic attack at the C(5) and C(20) positions (*i.e.* next to the reduced ring), whereas the C(10) and C(15) positions did not react under similar conditions.[9a] In accord with these results the *meso*-carbons adjacent to the reduced pyrrole ring were found to have higher calculated electron densities, thus making them more susceptible to attack by electrophilic agents.[9b] Numerous examples of regioselective substitution of the *meso*-carbon next to the reduced ring have been given in the literature.[10] The substituents thus introduced then promoted preferential ring-opening at the substituted *meso*-positions next to the pyrrolenine ring(s). The ease of ring-opening at the substituted *meso*-position might be interpreted as being due to the steric strain introduced by the substituent.[11] On the basis of these results it was also reasoned that *meso*-substitution might be a preliminary step to ring-opening in chlorophyll catabolism.[12]

The only ring-opening reaction of a chlorin leading to macrocycle cleavage at a *meso*-position not neighbouring the reduced ring was described by Iturraspe and Gossauer.[13] They found that photooxidative ring cleavage of the chlorophyll macrocycle is dependent on the central metal. While photochemical ring-opening of the zinc(II) complex of methyl 13²-demethoxycarbonylpheophorbide a gave macrocycle cleavage at C(20) (*i.e.* next to the reduced ring), the corresponding cadmium(II) complex ring-opened at C(5), leading to a bilin similar to **2** and **3**. In this context we were interested to see if model bilins related to **2** and **3** are also accessible by chemical oxidation. In line with the results described above this involves selective introduction of a substituent at a *meso* position distant from the reduced ring [C(10) or C(15)], followed by opening the macrocycle at that particular *meso*-position where substitution occurs.

Results and Discussion
Earlier studies on porphyrin reactivity had shown the versatility of thallium(III) trifluoroacetate (TTFA) for electrophilic aromatic substitution at *meso*-carbons. TTFA can be used to produce either directly *meso*-trifluoroacetylated metalloporphyrins or, in the presence of trifluoroacetic acid (TFA), to yield *meso*-oxidized derivatives like *meso*-oxoporphyrins (formerly oxophlorins), *meso*-dioxoporphyrins (formerly dioxoporphodimethenes), and xanthoporphyrinogens.[14] For example, treatment of the zinc(II) complex of *trans*-octaethylchlorin with 1 equiv. of TTFA afforded the corresponding zinc(II) 5- trifluoro-acetoxyoctaethylchlorin, which, upon basic hydrolysis in the presence of oxygen, yielded the corresponding ring-opened dihydrobilin.[15] Similarly, treatment of zinc(II) methyl 13²-demethoxycarbonylpheophorbide a with TTFA produced solely the 20-substituted trifluoroacetoxychlorin. Hydrolysis of this chlorin in the presence of ascorbic acid afforded again the corresponding dihydrobilins.[16] Earlier studies had shown that the reactivity of the *meso*-positions towards electrophilic attack increases with the degree of saturation. In order to develop synthetic methods for the preparation of simple bilin models of **2** and **3** we decided to study the reactivity of chlorins (such as oxochlorins and benzochlorins) towards trifluoroacetylation.

A simple synthesis of oxochlorins is available by oxidation of octaethylporphyrin **5** to dihydroxychlorin **6**, which undergoes an acid-catalysed pinacol–pinacolone rearrangement to yield geminal-dialkyl-β-oxochlorins. Initial studies in this area were performed by Fischer *et al.*,[17a] Inhoffen *et al.*,[17b] and by Bonnett *et al.*[17c] An improved synthesis of **6** and **7** was recently described by Chang and Sotiriou;[17d] this method utilizes oxidation of octaethylporphyrin **5** with osmium tetraoxide to give **6** and rearrangement in acidic media to the geminal ketone **7**. A
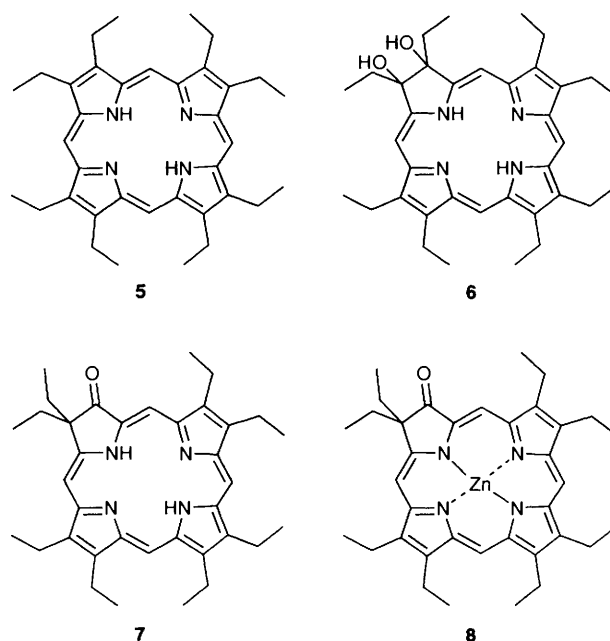
prerequisite for our attempted trifluoroacetylation is a suitable metal complex, necessary for activation of the porphyrin ligand towards electrophilic attack.[18] Zinc(II) is the most suitable metal ion in this respect, and we first attempted metallation of the dihydroxychlorin **6** by refluxing with a saturated solution of methanolic zinc(II) acetate. The product formed, however, was found to be the zinc complex of the pinacol-rearranged product, the zinc β,β'-diethyl ketone **8**. No zinc(II) oxochlorin could be isolated under the standard methods used for zinc insertion.[19] The zinc(II) oxochlorin **8** was readily prepared in high yield by treating the green diol **6** with concentrated sulfuric acid[17d] and refluxing the resulting octaethyloxochlorin **7** with a methanolic solution of zinc(II) acetate for 30 min; we decided to proceed with this compound for studies on the trifluoroacetylation reaction and subsequent ring-opening studies.

The zinc(II) oxochlorin **8** was treated with 1.1 equiv. of TTFA to give two stable trifluoroacetylated products **9** and **11** in 49 and 14% yield, respectively. The products were separated by preparative TLC and characterized (*vide infra*) as the 20- and 5-*meso*-substituted oxochlorins, respectively. Inhoffen and Gossauer earlier performed a similar acetoxylation reaction but used the free-base oxochlorin **7** and lead tetraacetate.[20] They obtained the 5-, 10- and 20-substituted acetoxychlorins in yields in the range 1–10%. In order to assign unambiguously the structure of the different zinc(II) trifluoroacetoxychlorins we employed NMR shift reagent techniques[21] using [Eu(fod)₃].[21b] Detailed analysis of the NMR spectra of **8** and the two trifluoroacetoxylated fractions led to the unambiguous assignment of the structures **9** and **11** for the reaction products.[21e]

Three green bands were observed by TLC upon treating **8** with TTFA. The least polar band was identified as (2,2', 7,8,12,13,17,18-octaethyl-20-trifluoroacetoxy-3-oxochlorinato)zinc(II) **9** (14% yield), followed by (2,2',7,8,12,13,17,18-octaethyl-5-trifluoroacetoxy-3-oxochlorinato)zinc(II) **11** (49%), and then followed by another darker green band, presumably (2,2',7,8,12,13,17,18-octaethyl-15-trifluoroacetoxy-3-oxochlorinato)zinc(II) **10**, which decomposed upon exposure to air to give a blue pigment **13** in 10% yield based on zinc oxochlorin **8**. The yield of the blue compound was increased to 49% by performing the trifluoroacetoxylation under the same conditions but using 4 equiv. of TTFA. The electronic absorption spectrum of this compound is presented in Fig. 1 and shows strong absorbance at 608 nm and the absence of a Soret band,
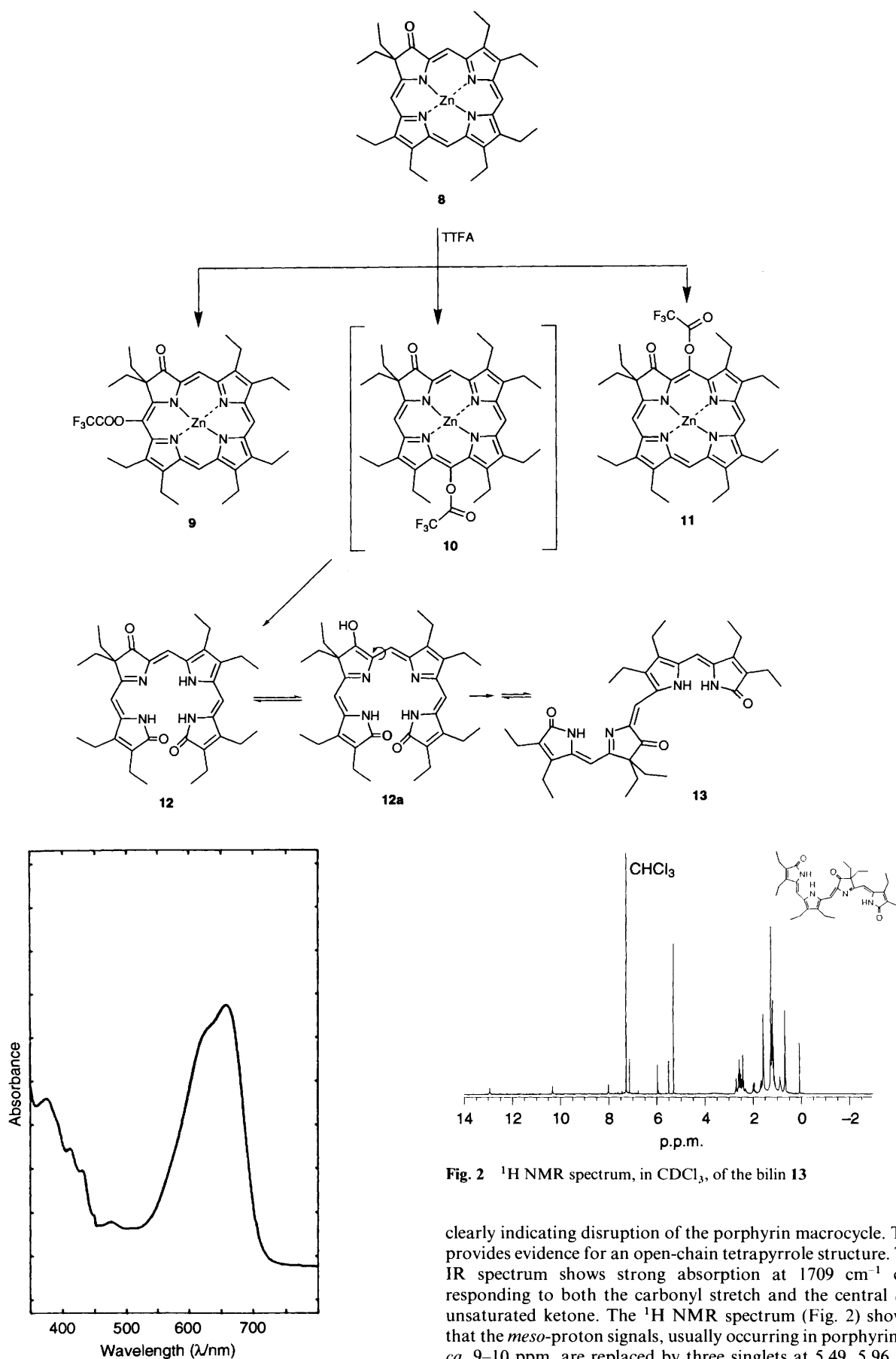
8

TTFA

9

10

11

12

12a

13

Fig. 1   Electronic absorption spectrum of the extended bilin **13** in dichloromethane

Fig. 2   ¹H NMR spectrum, in CDCl₃, of the bilin **13**

clearly indicating disruption of the porphyrin macrocycle. This provides evidence for an open-chain tetrapyrrole structure. The IR spectrum shows strong absorption at 1709 cm⁻¹ corresponding to both the carbonyl stretch and the central α,β-unsaturated ketone. The ¹H NMR spectrum (Fig. 2) showed that the *meso*-proton signals, usually occurring in porphyrins at *ca*. 9–10 ppm, are replaced by three singlets at 5.49, 5.96 and 7.12 ppm, characteristic of conjugated methine protons. The mass spectrum indicated a molecular weight of 570 and the
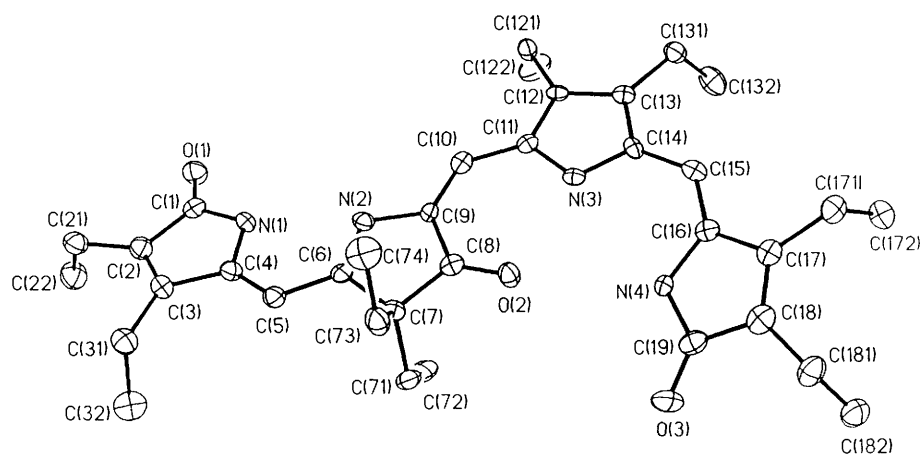
Fig. 3 View of the molecular structure of the bilin 13 in the crystal. Ellipsoids are drawn for 50% occupancy; hydrogen atoms have been omitted for clarity.

molecular formula $C_{35}H_{46}N_4O_3$ was confirmed by elemental analysis. An unambiguous structure determination of the blue compound as the octaethylbilin-1,12,19(21H,24H)-trione 13 was made by single crystal X-ray analysis.

The molecular structure, shown in Fig. 3, indicates strikingly that macrocycle cleavage has taken place at the 10-position, thus inferring C(10) as the place of trifluoroacetoxylation in the unstable intermediate 12. The molecule has an extended linear conformation, with an almost co-planar arrangement of the pyrrole units. The average deviation from the least-square of the 23 bilin atoms is 0.18 Å, with the largest deviations being observed in the reduced and oxidized pyrrole rings. The planes of individual pyrroles form angles with each other of: (ring)A–B 10.4°, B–C 1.3° and C–D 22.9°. Because of the linear arrangement of the tetrapyrrole these angles are much smaller than those observed in biliverdins or, for example, in the crystal structure of 3.[3c] The compound crystallizes with a half molecule of solvation (water) per asymmetric unit. The water molecule is hydrogen bonded to the carbonyl oxygen in ring D [O(3)–O(1S) = 2.804 Å]. Individual water molecules are connected by contacts of 2.581 Å, indicating the formation of a hydrogen bonded network in the crystal. No intramolecular hydrogen bonds were observed.

The observation of macrocycle cleavage at C(10) is contrary to the usual result of substitution and subsequent macrocycle cleavage at *meso*-positions neighbouring the reduced pyrrole ring.[9a,10] Additionally, the linear conformation of 13 was surprising and implies bond isomerization along C(10)–C(11). This is in contrast to most known open-chain bilin-type tetrapyrroles from macrocyclic ring-opening, which normally have a helical structure, like 12.[3c,22a,b] Notably, both the natural chlorophyll catabolite 3,[3c] and the C(20)-ring-opened dihydrobilin from [3-ethyl]-bacteriopheophorbide c methyl ester[22c] from *Chloroflexus aurantiacus* have a helical macrocycle arrangement. A structure with non-helical arrangement has also been described, but here the helical conformation was prevented by steric hindrance due to a C(10)-*tert*-butyl group.[22d] 1,19-Dioxobiladienes were found to have a ridge-tile structure stabilized by intramolecular hydrogen bonding.[22e] Similar intramolecular hydrogen bonding and stabilization of helical structures was found in 3-oxo-2,3-dihydrobilatrienes-abc, which are closely related to the present compound, the only differences being different peripheral substituents and ring opening at C(5).[22f]

The Z-to-E isomerization may be due to either a photo-chemical reaction during work-up or, more likely, a keto–enol tautomerism, thereby converting the helical product 12 of the

ring-opening reaction, *via* 12a, into the (presumably) thermo-dynamically more stable *trans* form 13. A related Z-to-E isomerization was observed during photochemical studies of phytochrome model compounds. Kufer *et al.* reported that treatment of dihydrobilindiones with 2-mercaptoethanol and irradiation with light lead to Z-to-E isomerization.[23a] Another comparable reaction is the photochemical cyclization of pterobilin dimethyl ester to phorcabilin dimethyl ester.[23b] The spectroscopic differences between the Z and E form described by these authors agree well with those obtained upon com-parison of compound 13 (*i.e.* E form) with the bilin derived from zinc(II) methyl 13²-demethoxycarbonylpheophorbide a, which is known to be helical (*i.e.* Z form) (data not shown).[16]

Both the corresponding 20- 9 and 5-trifluoroacetoxyocta-ethyloxochlorin 11 were subjected to mild basic hydrolysis following the procedure of Huster and Smith.[16] No reaction was observed for either compound and the starting materials were recovered. The present trifluoroacetoxyoxochlorin series 9, 10 and 11 thus constitutes a unique series where only the 15-substituted derivative can be ring-opened, leading to a product where macrocycle cleavage occurred at a *meso*-bridge *not* adjacent to the reduced ring. With the exception of Gossauer's photochemical ring-opening of cadmium(II) chlorophyll deriva-tives,[13] this represents the first example of a chemical oxidation providing, in reasonable yields, model compounds for the natural chlorophyll degradation products 2 and 3. A possible reason for the spontaneous ring-opening of the C(15) derivative might be found in steric considerations. Of the three structures 9, 10 and 11, both 9 and 11 have the *meso*-substituent next to the reduced ring, a conformationally 'relaxed' part of the macrocycle and thus these should experience less steric strain than 10, where the TFA-group is located in-plane between two ethyl groups. The related crystal structure of chloro(5-acetoxy-octaethylporphyrinato)iron(III) shows some crowding around the acetoxy substituent.[24]

Acid hydrolysis of (2,2',7,8,12,13,17,18-octaethyl-20-trifluo-roacetoxy-3-oxochlorinato)zinc(II) 9 led to the formation of the corresponding 3,20-dioxo derivative 14, which is related to the class of compound formerly named oxophlorins.[25] Octaethyl-*meso*-oxoporphyrins have been prepared in good yields using acid hydrolysis of metallo-*meso*-trifluoroacetoxyporphyrins[25b] and *meso*-acetoxyporphyrins.[20] 3,20-Dioxochlorin 14, assumed to be the enol form, was found to be more polar than the start-ing 20-trifluoroacetoxyoxochlorin 9. Upon column chrom-atography and exposure to air the enol form interconverts, presumably into the keto form 15, which is less polar and observed to be the more stable tautomer. Separation of the

9

14

15

HCl
H₂O

11

16

HCl
H₂O
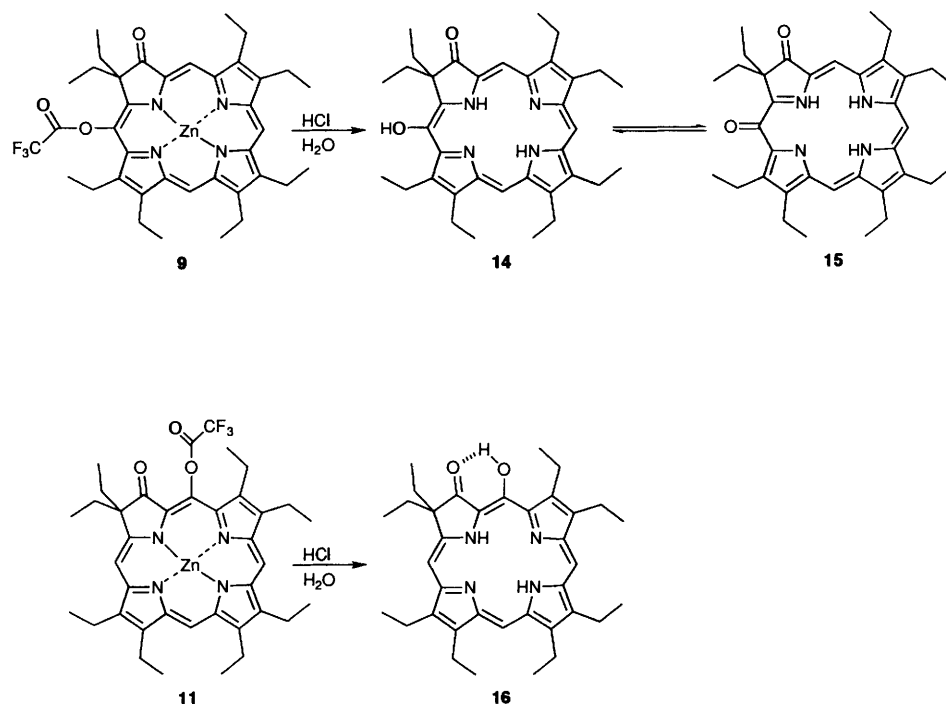
tautomers could not be achieved; contamination with the other tautomer was always observed, although the keto form 15 predominated upon exposure to air. Both compounds show significantly different electronic absorption spectra[25c] which might be attributed to the higher degree of macrocycle distortion in the distorted keto form compared to the planar enol form.[25d] ESR spectroscopy showed both dioxochlorins 14 and 15 to be at least partially paramagnetic, with the intensity of the ESR signal being temperature dependent. Apparently, there is more radical character formed upon heating of the solution at *ca.* 40 °C, whereas at −60 °C almost no ESR signal was observed. Similar results regarding the temperature dependence have been described for the corresponding *meso*-oxooctaethyl-porphyrins,[26] indicating that the properties of such species are similar in both the porphyrin and chlorin series. The isomeric 5-trifluoroacetoxy compound 11 was likewise subjected to acidic hydrolysis to form a purple product 16. No ESR signal could be detected for the hydrolysed product upon exposure to air. This has been explained by the formation of a strong intramolecular hydrogen bond between the *meso*-hydroxy group and the β-keto group which stabilizes the *meso*-hydroxy (enol-form) and prevents formation of the *meso*-oxo (keto-form).[18,20] Similar behaviour was found for *meso*-oxygenated furan and thiophene porphyrin analogues, where tautomerization to the *meso*-oxo(keto)porphyrin is prevented by the bivalent hetero-atoms.[27]

Since chemical ring-opening of the 20- and 5-trifluoro-acetoxyoxochlorins 9 and 11 was unsuccessful we attempted photochemical macrocycle cleavage. Following the procedure of Iturraspe and Gossauer[13] a solution of 9 in dichloromethane was irradiated for 2.5 h with 20 fluorescence lamps whilst oxygen was bubbled through it. No change in the absorption spectrum was observed even upon more prolonged irradiation. Alternatively, we attempted to prepare the corresponding *meso*-chlorinated oxochlorin derivatives for photochemical ring-opening.[5] Treatment of 8 with aqueous HCl and hydrogen peroxide[9a] gave a mixture of four compounds in yields so low as to discourage continuation of this avenue of research.

The octaethylbenzo[*at*]porphyrin derivative 19 was chosen as the second compound for studies on bilin formation from

chlorins. This compound is easily prepared from octaethyl-porphyrin 5 by metallation with nickel(II) acetate to give nickel(II) octaethylporphyrin 17, which then was subjected to a Vilsmeier-type formylation with 3-(dimethylamino)acrolein and phosphoryl chloride to yield the (2-formylvinyl)derivative 18.[28] Treatment of 18 with acid led to formation of the nickel(II) 3,3′,7,8,12,13,17,18-octaethylbenzo[*at*]porphyrin 19. The benzochlorin was then treated with TTFA to give the 5-trifluoroacetoxy derivative 20 in good yield. The reaction was regioselective with the 5-substituted derivative being the only reaction product. When 20 was subjected to mild basic hydrolysis in the presence of oxygen and ascorbic acid a brown compound was formed, which exhibited a main absorption maximum at 454 nm. Bonnett and co-workers described a variety of metal complexes of octaethylbilindione, with the Mn, Co, Cu and Co complexes being green, while the Ni complex exhibited a brownish colour.[29] The ^{1}H NMR spectrum of our reaction product showed disruption of the macrocycle and methine-H signals which are shifted upfield to 4.84 and 6.62 ppm. A signal at 3.53 ppm corresponds to a methyl ether indicating that upon ring disruption a methoxy group was introduced from the methanol used to dissolve the sodium acetate. Thus, the product of the basic hydrolysis of 20 is the nickel(II) complex of a 19-methoxybenzobilin-1-one ring-opened at C(20). Two isomeric forms 21 and 22 are possible.

Attempts to demetallate the nickel(II) benzobilin isomer 21 or 22 proved to be futile. Neither simple stirring or refluxing in concentrated sulfuric acid led to demetallation. Treatment with acid induced, however, a 50 nm hypsochromic shift of the absorption maximum. Similar observations were made by Fuhrhop *et al.* upon trituration of (1′-deoxo-1′-formyl-1,2-dihydrooctaethylbiliverdinato)zinc(II) with HCl.[30] The reaction was fully reversible indicating protonation at ring III.

After successful trifluoroacetoxylation of the nickel complex 19 we prepared the corresponding nickel(II) complex 23 of the oxochlorin 7. Treatment of 7 with nickel(II) acetylacetonate and subsequent reaction with TTFA gave the trifluoroacetoxylated product 24. Compared to the zinc(II) complex 8 the reaction of 23 was much slower and gave lower yields. Similar to the behaviour of the nickel(II) benzochlorin 19, upon reaction
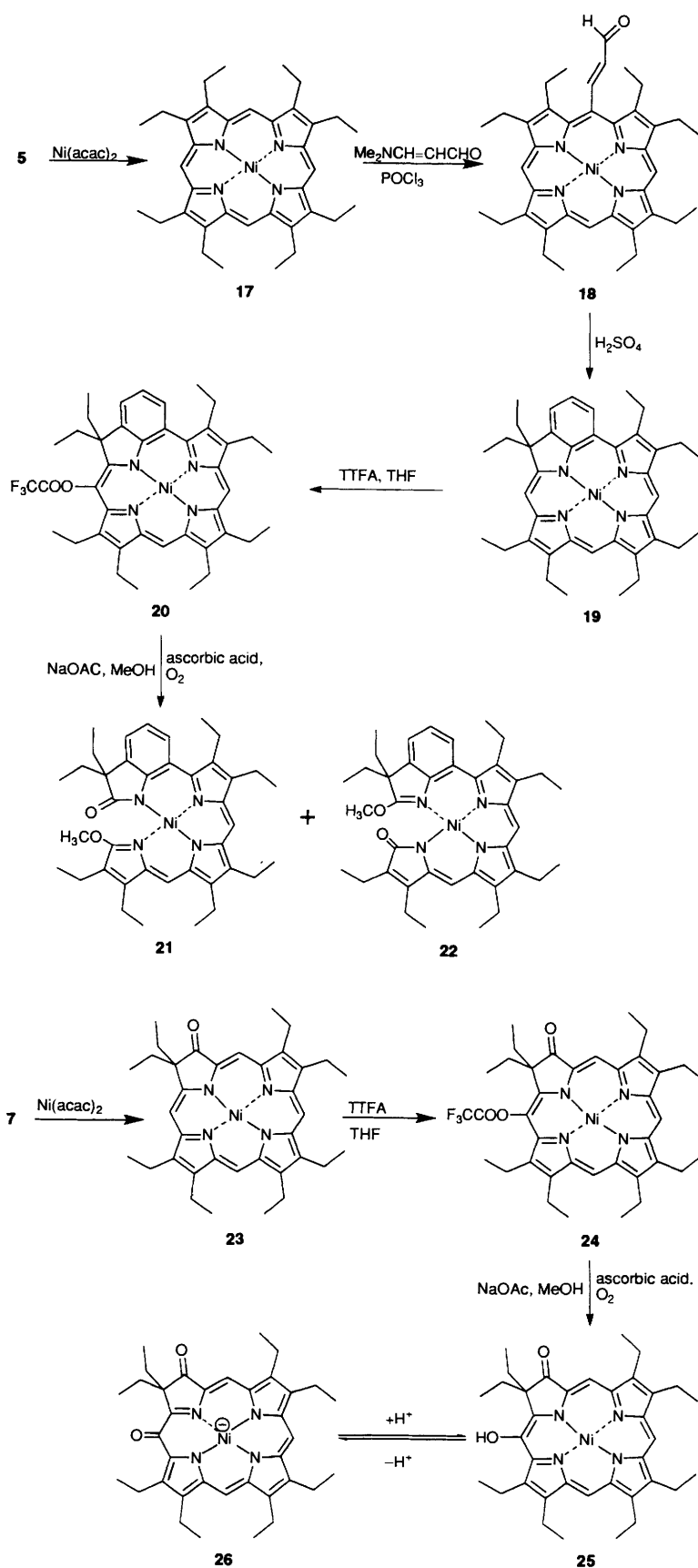
with TTFA only one product, the 20-trifluoroacetoxylated derivative **24**, was obtained regioselectively. Mild basic hydrolysis of **24** with methanolic sodium acetate in the presence of ascorbic acid and air gave one product more polar than the

starting material. The product, obtained in 30% yield, exhibited broad lines in its ^{1}H NMR spectrum and the ESR spectrum showed an isotropic signal with a g value of 2.001. The electronic absorption spectrum still exhibited typical metal-

lochlorin characteristics with maxima at 428 and 618 nm. The spectroscopic results confirmed the presence of partial radical character of the molecule and the structure was assigned to be the 20-oxo/hydroxy-derivative **25/26**. The nickel(II) π-cation radical obtained by facile one-electron oxidation of **26** is stable at room temperature in dichloromethane and no interconversion to another form was observed. Many porphyrin radicals are found to be stable due to conjugation of the aromatic rings; in general, a higher stability of the metal complexes was observed compared with free-base porphyrin radicals.[31]

While the variation of redox properties with central chelated metal of tetrapyrroles has long been realized,[32] the present results show clearly that considerable differences exist in the *meso*-reactivities of metallo-β-oxochlorins. Under suitable conditions the zinc(II) complex **8** undergoes *meso*-trifluoroacetoxylation to yield up to 49% yield of the bilin **13** with the desired ('natural') point of ring-opening the corresponding nickel(II) complex **23** becomes substituted at the 'classical' C(20) position to yield ultimately **25**. A similar result was obtained with the nickel(II) benzochlorin **19**, further illustrating how finely tuned are the reactivities of these various metallotetrapyrroles.

Experimental

General.—All reagents were of analytical grade, usually obtained from Aldrich. Reactions were monitored by analytical TLC, which was performed on cut-strips of precoated plastic-backed sheets (Merck silica gel 60 F254, 0.25 mm thickness). Preparative TLC was performed on self-prepared silica gel plates (20 × 20 cm, 1 mm thickness) using Merck silica gel GF 254 and 60 G. Plates were activated prior to use by heating at 110 °C for at least 8 h. Column chromatography was performed using Merck silica gel 60. Melting points are uncorrected and were measured on a Thomas/Bristoline microscopic hot-stage apparatus. Electronic absorption spectra were recorded in dichloromethane with a Hewlett-Packard 8450A spectrophotometer. ^{1}H and ^{19}F NMR spectra were obtained on a General Electric QE-300 spectrometer; for ^{1}H spectra chemical shifts are reported relative to chloroform at 7.258 ppm and for ^{19}F spectra signals are reported relative to dichlorodifluoromethane at 0 ppm. IR spectra were recorded with an IBM FT-IR spectrometer. Mass spectra were obtained in the electron ionization mode at the UC San Francisco Mass Spectrometry resource. ESR spectra were obtained either on a V-4540 Varian E-4 EPR spectrometer or a Bruker ER 200D spectrometer. 2,2-Di(4-*tert*-octylphenyl)-1-picrylhydrazyl free radical was used as standard. Elemental analyses were determined by Midwest Microlab., Indianapolis, IN.

Starting Materials.—2,3,7,8,12,13,17,18-Octaethylporphyrin **5** was prepared according to the method reported by Ono and Maruyama.[33] 2,3,7,8,12,13,17,18-Octaethyl-2,3-dihydroxyporphyrin **6** and the rearranged geminal monoketone **7** were synthesized according to the procedure described by Chang and Sotiriou.[17d] The octaethylcyclobenzo[at]porphyrin **19** was prepared by Vilsmeier formylation and acid rearrangement as described earlier.[28]

(2,2',7,8,12,13,17,18-*Octaethyl-3-oxochlorinato*)*zinc*(II) **8**.—Octaethyloxochlorin **7** (85.4 mg, 0.154 mmol) was dissolved in CH_2Cl_2 (30 cm³) and mixed with a saturated solution of zinc(II) acetate in methanol (10 cm³). The mixture was refluxed for 30 min under nitrogen, diluted with water, washed with sat. aqueous $NaHCO_3$, dried (Na_2SO_4) and evaporated to provide compound **8** (80 mg, 0.131 mmol, 85%) after crystallization from CH_2Cl_2-MeOH, mp 268–270 °C (Found: C, 70.6; H, 7.3; N, 9.2%; M⁺, 612.2817. $C_{36}H_{44}N_4OZn$ requires C, 70.41; H, 7.22; N, 9.12%; *M*, 612.280 63); λ_{max}/nm (CH_2Cl_2) 414 (ε/dm³

mol⁻¹ cm⁻¹ 116 000), 570 (16 400) and 618 (43 100); δ_H(CDCl₃) 0.39 (6 H, t, geminal CH_2CH_3), 1.85 (18 H, m, CH_2CH_3), 2.61 (4 H, m, geminal CH_2CH_3), 3.76–3.94 (12 H, m, CH_2CH_3), 8.95 (1 H, s, 5-H), 9.61 (1 H, s, *meso*-H), 9.66 (1 H, s, *meso*-H) and 9.73 (1 H, s, 10-H); *m/z* 612.3 (100%, M⁺) and 583.2 (21%, M − CH_2CH_3).

Trifluoroacetylation of 2,2',7,8,12,13,17,18-Octaethyl-3-oxochlorinato)zinc(II).—To a solution of (octaethyloxochlorinato)zinc(II) **8** (85 mg, 0.139 mmol) in dry THF (15 cm³) stirred under N_2 was added a solution of TTFA (75 mg) in dry THF (10 cm³) *via* a syringe. The mixture was stirred for 10 min and then poured into a mixture of dichloromethane–dilute aq. sodium bisulfite (200 cm³). The organic layer was washed several times with aqueous $NaHSO_3$ and then with aqueous $NaHCO_3$, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by silica gel preparative TLC using 1% THF in CH_2Cl_2 as eluent to yield the 20-trifluoroacetoxy derivative **9** (49.4 mg, 49%), the 5-isomer **11** (14.5 mg, 14%) and the blue bilin derivative **13** (8 mg, 10%). Note that the yield of **13** is increased to 49% by using 4 equiv. of TTFA in the above reaction.

(2,2',7,8,12,13,17,18-*Octaethyl-3-oxo-20-trifluoroacetoxychlorinato*)*zinc*(II) **9**; mp 294–295 °C (Found: C, 63.1; H, 6.2; N, 7.7%; M⁺, 724.2596. $C_{38}H_{43}F_3N_4O_3Zn$ requires C, 62.85; H, 5.97; N, 7.72%; *M*, 724.2578); ν_{max}/cm⁻¹ 2968 (CH stretch), 1797 (CF₃COO) and 1716 (ring ketone); λ_{max}/nm (CH_2Cl_2) 331 (ε/dm³ mol⁻¹ cm⁻¹ 27 000), 416 (166 000), 574 (14 000) and 622 (51 000); δ_H(CDCl₃) 0.19 (3 H, t, geminal CH_2CH_3), 0.43 (3 H, t, geminal CH_2CH_3), 1.78 (18 H, m, CH_2CH_3), 2.27 (1 H, q, geminal CH_2CH_3), 2.56–2.65 (2 H, m, geminal CH_2CH_3), 3.13 (1 H, q, geminal CH_2CH_3), 3.92 (11 H, m, CH_2CH_3), 9.62 (1 H, s, *meso*-H), 9.77 (1 H, s, *meso*-H) and 9.81 (1 H, s, *meso*-H); δ_F(CDCl₃) −66.53 (3 F, s, CF_3COO); *m/z* 724.3 (100%, M⁺), 695.2 (5%, M − CH_2CH_3) and 627.3 (5%, M − CF_3COO).

(2,2',7,8,12,13,17,18-*Octaethyl-3-oxo-5-trifluoroacetoxychlorinato*)*zinc*(II) **11**; mp 60 °C (hygroscopic) (Found: M⁺, 724.2566. $C_{38}H_{43}F_3N_4O_3Zn$ requires *M*, 724.2578); ν_{max}/cm⁻¹ 2966 (CH stretch), 1799 (CF₃COO) and 1707 (ring ketone); λ_{max}/nm (CH_2Cl_2) 332 (ε/dm³ mol⁻¹ cm⁻¹ 29 500), 424 (150 000), 574 (15 000) and 622 (42 000); δ_H(CDCl₃) 0.35 (6 H, t, geminal CH_2CH_3), 1.82 (18 H, t, geminal CH_2CH_3), 2.67 (4 H, m, geminal CH_2CH_3), 3.90 (12 H, m, CH_2CH_3), 8.91 (1 H, s, *meso*-H), 9.68 (1 H, s, *meso*-H) and 9.88 (1 H, s, *meso*-H); δ_F(CDCl₃) −67.77 (3 F, s, CF_3COO); *m/z* 724.3 (100%, M⁺) and 628.2 (45%, M − CF_3COO).

2,3,7,8,13,13',17,18-*Octaethylbilin*-1,12,19(21H,24H)-*trione* **13**; mp 203–206 °C (Found: M⁺, 570.3572. $C_{35}H_{46}N_4O_3$ requires *M*, 570.3570); ν_{max}/cm⁻¹ 2968–2930 (CH stretch) and 1709 (C=O); λ_{max}/nm (CH_2Cl_2) 328 (ε/dm³ mol⁻¹ cm⁻¹ 27 500), 363 (20 700), 381 (17 800) and 608 (40 500); δ_H(CDCl₃) 0.66 (6 H, t, geminal CH_2CH_3), 1.16 (18 H, m, CH_2CH_3), 1.98 (4 H, q, geminal CH_2CH_3), 2.40–2.68 (12 H, m, CH_2CH_3), 5.50 (1 H, s, methine-H), 5.96 (1 H, s, methine-H), 7.12 (1 H, s, methine-H), 7.99 (1 H, s, NH), 10.31 (1 H, s, NH) and 12.92 (1 H, s, NH).

2,2',7,8,12,13,17,18-*Octaethyl-3,20-dioxochlorin* **14**.—A suspension of 2,2',7,8,12,13,17,18-octaethyl-3-*oxo*-20-*trifluoroacetoxychlorinato*)*zinc*(II) **9** (20 mg, 0.028 mmol) in 10 mol dm⁻³ HCl (5 cm³) was heated for 2 h at 100 °C and then cooled to room temperature and diluted with CH_2Cl_2 (100 cm³). The organic phase was separated, washed with aq. $NaHCO_3$ until it became neutral, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography using 2% methanol in (CH_2Cl_2) as eluent. The major green band was collected and, after exposure to air, was spontaneously converted into a less polar but more stable compound (14 mg, 75% yield); mp 128–130 °C; λ_{max}/nm (CH_2Cl_2) 404 (ε/dm³

mol^{-1} cm^{-1} 101 500), 646 (9900) and 690 (13 400); ESR (in toluene using DPPH as standard) g = 2.002.

2,2',7,8,12,13,17,18-*Octaethyl-3,5-dioxochlorin* **16**.— A suspension of (2,2',7,8,12,13,17,18-octaethyl-3-oxo-5-trifluoroacetoxychlorinato)-zinc(II) **11** (13 mg, 0.018 mmol) in 10 mol dm^{-3} HCl (3 cm^3) was heated for 2 h at 100 °C and then cooled to room temperature and diluted with CH$_2$Cl$_2$ (100 cm^3). The organic phase was separated, washed with water and aq. sodium hydrogen carbonate until it became neutral, dried (Na$_2$SO$_4$) and evaporated. The residue was purified by silica gel column chromatography with 2% methanol in CH$_2$Cl$_2$ as eluent. The major band was collected to yield **16** (5 mg, 41%); mp 240–242 °C; amounts of material available were insufficient for full characterization; λ_{max}/nm (CH$_2$Cl$_2$) 402 (ε/dm^3 mol^{-1} cm^{-1} 102 600), 509 (78 900), 581 (86 000), 592 (84 700) and 643 (89 200); δ_H(CDCl$_3$) −0.75 (2 H, d, NH), 0.37 (6 H, t, geminal CH$_2$CH_3), 1.74 (18 H, m, CH$_2$CH_3), 2.63 (4 H, m, geminal CH_2CH$_3$), 3.70–3.94 (12 H, m, CH_2CH$_3$), 8.48 (1 H, s, *meso*-H), 9.05 (1 H, s, *meso*-H), 9.45 (1 H, s, *meso*-H) and 9.73 (1 H, s, 10-H).

(3,3',7,8,12,13,17,18-*Octaethyl-5-trifluoroacetoxycyclobenzo-*[at]*porphyrinato*)*nickel*(II) **20**.—To a solution of (benzo-chlorinato)nickel(II) **19** (100 mg, 0.159 mmol) in dry THF (20 cm^3) was added TTFA (100 cm^3) in dry THF (10 cm^3). The solution was stirred at room temperature for 20 min and then poured into a separatory funnel containing a mixture of CH$_2$Cl$_2$ and sat. aq. sodium bisulfite (v/v, 2:1). The organic phase was separated, washed with aq. NaHCO$_3$ and water, dried (Na$_2$SO$_4$) and evaporated. The residue was purified by silica gel column chromatography using 60% light petroleum (bp 40–60 °C fraction) in dichloromethane as eluent. The fast moving green band was collected to yield, after crystallization from CH$_2$Cl$_2$–hexane the title compound **20** (55 mg, 46%), mp 200–202 °C (Found: C, 66.4; H, 6.2; N, 7.6. C$_{41}$H$_{45}$F$_3$N$_4$NiO$_2$ requires C, 66.41; H, 6.12; N, 7.56%); λ_{max}/nm (CH$_2$Cl$_2$) 428 (ε/dm^3 mol^{-1} cm^{-1} 71 500), 578 (11 400) and 686 (35 900); δ_H(CDCl$_3$) 0.01 (3 H, t, geminal CH$_2$CH_3), 0.27 (3 H, t, geminal CH$_2$CH_3), 1.54 (18 H, overlapping t, CH$_2$CH_3), 2.18 (2 H, m, geminal CH_2CH$_3$), 2.45 (1 H, m, geminal CH_2CH$_3$), 2.96 (1 H, m, geminal CH_2CH$_3$), 3.66–3.28 (14 H, overlapping q, CH_2CH$_3$), 7.76–7.74 (2 H, dd, CH benzene ring), 8.53 (1 H, s, *meso*-H), 8.80 (1 H, dd, CH benzene ring) and 8.82 (1 H, s, *meso*-H); δ_F(CDCl$_3$) −67.06 (3 F, s, CF$_3$COO).

(3,3',7,8,12,13,17,18-*Octaethyl-19-methoxycyclobenzobilin-1-onato*)*nickel*(II) **21** [*or* (3,3',7,8,12,13,17,18-*Octaethyl-1-meth-oxycyclobenzobilin-19-onato*)*nickel*(II) **22**].—To (2,2',7,8,12,13, 17,18-octaethyl-20-trifluoroacetoxybenzochlorinato)nickel(II) **20** (9 mg, 0.012 mmol) dissolved in THF (0.5 cm^3) was added 0.25 mol dm^{-3} methanolic sodium acetate (4 cm^3) and 1 mol dm^{-3} aq. ascorbic acid (6 drops). The mixture, exposed to the air, was stirred for 1.5 h after which it had turned slightly greenish brown. The solution was then washed with water and the product extracted with dichloromethane (200 cm^3). The organic phase, exposed to the air, was stirred for a further 2 h after which it was evaporated and the residue purified by silica gel column chromatography eluting with 1% methanol in dichloromethane. The major brown band was collected to yield the product **21** or **22** (7 mg, 87%), mp 93–95 °C; λ_{max}/nm (CH$_2$Cl$_2$) 454 (ε/dm^3 mol^{-1} cm^{-1} 23 700); δ_H(CDCl$_3$) 0.40 (6 H, overlapping t, geminal CH$_2$CH_3), 1.10–1.11 (18 H, overlapping t, CH$_2$CH_3), 2.43–2.27 (12 H, m, CH$_2$CH$_3$), 1.87 and 2.71 (4 H, m, geminal CH_2CH$_3$), 3.53 (3 H, s, OCH_3), 4.84 (1 H, s, methine-H), 6.62 (1 H, s, methine-H), 7.01 (1 H, s, methine-H), 7.33 (1 H, t, CH benzene ring) and 7.54 (1 H, d, CH, benzene ring).

(2,2',7,8,12,13,17,18-*Octaethyl-3-oxochlorinato*)*nickel*(II) **23**. —A mixture of the oxochlorin **7** (88 mg, 0.159 mmol), *o*-xylene (20 cm^3) and Ni(acac)$_2$ (100 mg) was refluxed at 150 °C for 1 h. After cooling, the solution was washed with water (× 3), dried (Na$_2$SO$_4$) and evaporated under vacuum. The metallated product was obtained after crystallization from CH$_2$Cl$_2$– MeOH (90 mg, 93%); mp 196–198 °C (Found: C, 71.2; H, 7.3; N, 9.1. C$_{36}$H$_{44}$N$_4$NiO requires C, 71.18; H, 7.30; N, 9.22%); λ_{max}/nm (CH$_2$Cl$_2$) 412 (ε/dm^3 mol^{-1} cm^{-1} 99 100), 506 (8500), 544 (10 500), 570 (13 200) and 616 (50 800); δ_H(CDCl$_3$) 0.44 (6 H, t, geminal CH$_2$CH_3), 1.70 (12 H, overlapping t, CH$_2$CH_3), 2.53 (4 H, q, geminal CH_2CH$_3$), 3.76 (12 H, overlapping q, CH_2 CH$_3$) and 8.56, 9.30, 9.37 and 9.44 (1 H each, each s, *meso*-H).

(2,2',7,8,12,13,17,18-*Octaethyl-3-oxo-20-trifluoroacetoxy-chlorinato*)*nickel*(II) **24**.—Nickel(II) octaethyloxochlorin **23** (50 mg, 0.082 mmol) was dissolved in dry THF (10 cm^3) and to the solution was added *via* a syringe a solution of TTFA (100 mg) in (10 cm^3) dry THF. The solution was stirred for 2 h at room temperature and then poured into a separatory funnel containing a mixture of dichloromethane and aq. NaHSO$_3$ (v/v, 1:1). The organic phase was separated, washed with aq. NaHCO$_3$ and then by water, dried (Na$_2$SO$_4$) and evaporated. The residue was purified by silica gel column chromatography using 40% light petroleum (bp 40–60 °C fraction) in dichloromethane as eluent. The fast moving green band was collected to yield the title product **24** (27 mg, 46%), mp 199–200 °C (Found: M$^+$, 718.2631. C$_{38}$H$_{43}$F$_3$N$_4$NiO$_3$ requires M, 718.2641); λ_{max}/nm (CH$_2$Cl$_2$) 416 (ε/dm^3 mol^{-1} cm^{-1} 88 300), 516 (11 400), 580 (14 000) and 622 (39 300); δ_H(CDCl$_3$) 0.07 (3 H, t, geminal CH$_2$CH_3), 0.67 (3 H, t, geminal CH$_2$CH_3), 1.68 (18 H, overlapping t, CH$_2$CH_3), 1.95, 2.34 and 2.71 (3 H, each m, geminal CH_2CH$_3$), 3.06–3.17 (2 H, overlapping m, geminal CH_2CH$_3$ and CH_2CH$_3$), 3.69 (11 H, overlapping q, CH_2CH$_3$) and 9.09, 9.29 and 9.31 (3 H, each s, *meso*-H); δ_F(CDCl$_3$) −67.08 (3 F, CF$_3$COO).

(2,2',7,8,12,13,17,18-*Octaethyl-20-hydroxy-3-oxochlorinato*)-*nickel*(II) **25**.—To the trifluoroacetylated Ni^{II} complex **24** (15 mg, 0.021 mmol) in THF (1.5 cm^3) was added a 0.25 mol dm^3 methanolic solution of sodium acetate and 0.1 mol dm^{-3} ascorbic acid (8 drops). The solution, exposed to the air, was stirred at room temperature for 2.5 h after which it was poured into water. The organic phase was separately diluted with dichloromethane (100 cm^3), dried (Na$_2$SO$_4$) and stirred for a further 3 h exposed to the air. After evaporation of the reaction mixture, the residue was chromatographed on silica gel eluting with 40% light petroleum (bp 40–60 °C fraction) in dichloromethane. The major green band was collected to yield the product **25** (5 mg, 38%). Mp 191–193 °C (Found: M$^+$, 622.2830. C$_{36}$H$_{44}$N$_4$NiO$_2$ requires M, 622.2818); λ_{max}/nm (CH$_2$Cl$_2$) 378 (ε/dm^3 mol^{-1} cm^{-1} 35 600), 428 (92 800), 538 (10 800), 572 (12 300) and 618 (32 400); ESR (in toluene, using DPPH as standard) g = 2.001.

Crystal Structure Determination of **13**.—Crystals, grown by slow diffusion of methanol into a concentrated solution of the bilin in dichloromethane, were immersed in hydrocarbon oil. A suitable single crystal was selected, mounted on a glass fibre and inserted in the low-temperature nitrogen stream of the diffractometer.[34]

Crystal data. C$_{35}$H$_{46}$N$_4$O$_3$·1/2H$_2$O. M = 579.8, monoclinic, a = 8.537(2), b = 14.537(2), c = 26.184(2) Å, β = 98.45(2)°, U = 3214.2(9) Å^3 (by least-squares refinement on diffractometer angles for 22 automatically centred reflections, λ = 1.541 78 Å), space group $P2_1/n$, Z = 4, D_c = 1.213 mg m^{-3}, $F(000)$ = 1264. Dark blue parallelepiped. Crystal dimensions: 0.35 × 0.15 × 0.06 mm, μ(Cu-Kα) = 0.633 mm^{-1}.

Data collection and processing. Siemens P4 diffractometer with attached Siemens rotating anode and equipped with a locally modified Siemens LT device, 2θ–θ mode with a scan width of $2.0°$ plus $K\alpha$-separation, scan speed const. $14.28°$ min^{-1}, Cu–$K\alpha$ radiation; 3904 independent reflections ($0 < 2\theta \leqslant 108.5°$, $\pm h$, $+k$, $+l$) giving 3103 reflections with $I > 2\sigma(I)$. Reflections were corrected for Lorentz, polarisation and absorption effects.[35]

Structure analysis and refinement. Direct methods followed by least-squares refinement on $|F|$ with all non-hydrogen atoms refined with anisotropic thermal parameters (except for the solvent oxygen) and hydrogens in calculated positions (C–H = 0.96, N–H = 0.9 Å, U_{iso} = 0.03 Å^2). The weighting scheme used was $w = 1/[\sigma^2(F) + 0.1494F^2]$, 383 parameters refined. Final R and R' values are 0.059, 0.076. The SHELXTL-PLUS program package was used for all calculations.[36]

Full data on the crystal structure determination have been deposited and are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW on giving the full literature citation of this paper.†

† See Instructions for Authors (1995), *J. Chem. Soc., Perkin Trans. 1,* 1995, Issue 1.

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