Bis-porphyrin Derivatives. Part 1. Reaction of *meso*-Hydroxymethylporphyrinatometal Derivatives with Acids

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Treatment of the nickel(II) or copper(II) derivative of octaethyl-*meso*-hydroxymethylporphyrin with sulphuric acid in dimethyl-formamide or -acetamide gives mainly the *meso.meso'*-ethylenebis(porphyrinatometal) derivative by reactions involving electron transfer from the metal. In the absence of metal, only disproportionation reactions occur. Vilsmeier formylation of the nickel dimer yields mono- and di-substitution products.

meso-HYDROXYMETHYL derivatives of etioporphyrin I [1] and octaethylporphyrin [2] (OEP) have been prepared from the corresponding *meso*-formyl derivatives by reduction with borohydride. In the present investigation of certain reactions of *meso*-hydroxymethylporphyrins we have used the nickel complex of *meso*-hydroxymethyl-OEP (1; R = CH_2·OH), formed by reduction of the corresponding *meso*-formyl compound. Attempts to form the corresponding tosylate (tosyl chloride in pyridine), mesylate (mesyl chloride in the presence of triethylamine), and acetate have been unsuccessful to date. However, when a solution of (1; R = CH_2·OH) containing ethanol was warmed with a trace of acid, the ethyl ether (1; R = CH_2·OEt) was obtained, as red plates after crystallisation. When the reaction was carried out with dimethylformamide as solvent in the presence of sulphuric acid under reflux there was obtained in *ca.* 50% yield a crystalline nickel-containing product which has been formulated as the *meso,meso'*-ethylenebis(porphyrinatonickel) derivative (2). Analysis indicated loss of oxygen and the molecular formula $C_{37}H_{44-46}N_4Ni$. The initial mass spectral determination gave a base peak at *m/e* 604 ($C_{37}H_{46}N_4Ni$) thus eliminating the possibility of an additional ring as in (3) (*cf.* ref. 3), and later determinations showed a molecular ion at *m/e* 1206—1210.

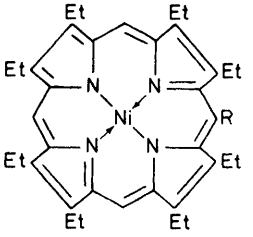
Originally it was considered possible that the new product was the nickel(II) derivative of *meso*-methyl-OEP (1; R = Me), *m/e* 604, which was unknown at that time. However, this possibility was eliminated by direct comparison when that compound was prepared by reduction of the *meso*-formyl analogue (1; R = CHO) with lithium aluminium hydride at 65 °C, which gave a separable mixture of the *meso*-methyl and *meso*-hydroxymethyl derivatives as well as the 'dimer' (35%). Although the overall shape of the electronic spectrum of (2) did suggest a nickel(II) *meso*-alkyl-OEP derivative, there were distinct differences between the spectra of (1; R = Me) and (2). Thus the breadth of the Soret band of (2) and its position (420.5 nm) were anomalous, as were the ratios of intensities of the Soret band and the α- and β-bands in the visible region.

Likewise, the ^1H n.m.r. spectrum of (2), in comparison with those of nickel(II) *meso*-alkyl-OEP derivatives,[4] contained several anomalous features. It was clear that three *meso*-positions remained free and one was substituted. The signals for the *meso*-protons were at

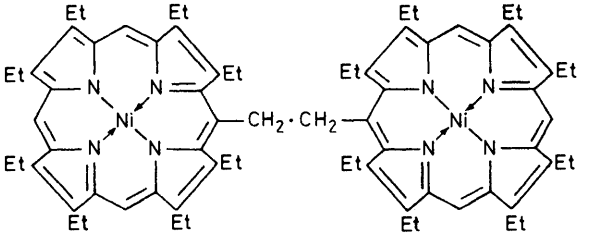
[1] A. W. Johnson and D. Oldfield, *J. Chem. Soc.*, 1966, 794.
[2] H. H. Inhoffen, J.-H. Fuhrhop, H. Voight, and H. Brockmann, jun., *Annalen*, 1966, **695**, 133.
[3] M. E. Flaugh and H. Rapoport, *J. Amer. Chem. Soc.*, 1968, **90**, 6877.
[4] 'Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Amsterdam, 1975, p. 431.

δ *ca.* 9.3 as usual, but whereas in most nickel(II) *meso*-substituted OEP derivatives [*e.g.* (1; R = CH_2·OH, Me, or Et)] the signal for the three *meso*-protons was a singlet (usually somewhat broadened), and in the *meso*-formyl compound two singlets were obtained but only narrowly separated (by 0.03 p.p.m.), in the spectrum of (2) two singlets were observed (2 : 1) with a separation of 0.18 p.p.m. The ethylene bridge signal (integration ratio to *meso*-protons 2 : 3) appeared as a singlet at δ 3.91. The signals in the δ 3—4 range (CH_2) were ill-defined, but there was a large upfield shift (*ca.* 0.9 p.p.m.) of one 6 H triplet (2 × β-CH_2·CH_3), presumably a result of interaction with the other porphyrin ring. This is the reaction of α-hydroxymethylferrocene (4) with strong acids to give 1,2-diferrocenylethane; possible mechanisms for the dimerisation have been discussed briefly.[5] Under reductive conditions, *e.g.* Clemmensen reduction,[6] acylferrocenes are readily converted into dimers of the same type, and related reactions are known in other series, *e.g.* reduction of 9-formylanthracene to 1,2-di-9-(anthryl)ethane with lithium aluminium hydride.[7] The formation of the ' dimer ' (2), along with other products, from the reduction of nickel *meso*-formyl-OEP with lithium aluminium hydride is referred to above.

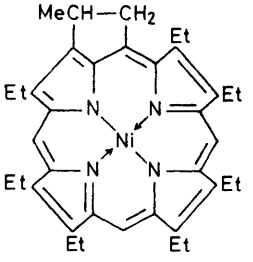
For the acid-catalysed dimerisations the presence of



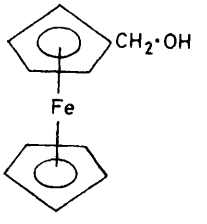
(1)



(2)



(3)



(4)

difference was unlike anything previously encountered. It appeared, therefore, that there existed appreciable interactions between the porphyrin rings.

The action of sulphuric acid on the ether (1; R = CH_2·OEt) in dimethylformamide under similar conditions also gave the ' dimer ' (2) (25%). Moreover the hydroxymethylporphin (I; R = CH_2·OH) could be converted into (2) by acid in 1,2-dimethoxyethane or dimethylacetamide as solvent (30 and 25%, respectively). Sulphuric acid could be replaced by toluene-*p*-sulphonic acid. We have also carried out a similar sequence of reactions with the copper(II) derivative of *meso*-hydroxymethyl-OEP,[2] although the yield (12%) of dimer was appreciably lower.

Treatment of the ' dimer ' (2) with concentrated sulphuric acid at room temperature removed the metal and gave the corresponding free base, which could be reconverted into (2) by treatment with acetylacetonatonickel in refluxing benzene. A close analogy for the formation of (2) from nickel *meso*-hydroxymethyl-OEP the metal was essential. A metal-free sample of *meso*-hydroxymethyl-OEP was obtained by demetallation of nickel *meso*-formyl-OEP with sulphuric acid, followed by reduction with sodium borohydride. Treatment of this product with sulphuric acid in dimethylformamide as before gave no dimeric product, and there was obtained a mixture of OEP together with its *meso*-formyl and *meso*-methyl derivatives. Thus in the absence of metal, disproportionation occurs giving both oxidation and reduction products. The involvement of the metal in the dimerisation leads us to view the reaction as an electron transfer from the metal to the carbocation, leading to the primary carbon radical which then dimerises. Reduction of the intermediate nickel(II) species may be brought about either by the solvent or by disproportionation.

The dimer(2) has been subjected to Vilsmeier formylation; the 10-monoformyl derivative (16.6%) was obtained together with a mixture of the 15,15′-diformyl

[5] K. L. Rinehart, C. J. Michejda, and P. A. Kittle, *J. Amer. Chem. Soc.*, 1959, **81**, 3162.

[6] S. J. Goldberg, W. D. Bailey, and M. L. McGregor, *J. Org. Chem.*, 1971, **36**, 761.

[7] K. C. Schreiber and W. Emerson, *J. Org. Chem.*, 1966, **31**, 95.

(1.9%), 10,10′-diformyl (32.5%), and 10,15′-diformyl (16.2%) derivatives, the orientation of the formyl substituents being decided on the basis of the n.m.r. signals of the remaining *meso*-protons, which also provided clear evidence for the existence of two porphin rings. Thus, in the 15,15′-isomer all the *meso*-proton signals appeared as one singlet (δ 8.71). In the 10,10′ and 10,15′-isomers, the *meso*-proton signals formed two singlets [δ 8.94 and 9.09 (1 : 1) and 8.87 and 9.09 (1 : 3), respectively]. In the 10-monoformyl compound the *meso*-proton signals formed four singlets [δ 8.83, 9.15, 9.26, and 9.45 (1 : 1 : 2 : 1)]. 10-Formyl protons corresponded to a signal at δ *ca.* 11.55 and 15-formyl protons to a signal at *ca.* 11.7. Reduction of the 10,10′-diformyl compound with sodium borohydride gave the corresponding 10,10′-bis-hydroxymethyl derivative.

Informative ^{13}C signals for the various compounds described are listed in the Table. Signals corresponding to pyrrole ring carbon atoms and peripheral β-ethyl substituents, which were almost constant throughout the series, have not been included.

^{13}C N.m.r. spectral data (δ_C)

Compound	*meso*-C	Substituents
(1; R = H)	96.78	
(1; R = CHO)	105.76 (C-5), 99.94 (C-15), 99.02 (C-10, 20)	189.49 (CHO)
(1; R = CH_2·OH)	110.76 (C-5), 96.74 (C-10, 20), 96.44 (C-15)	60.90 (CH_2·OH)
(1; R = CH_2·OEt)	108.19 (C-5), 96.54 (C-10, 20), 96.20 (C-15)	67.95 (CH_2·OEt) 65.28 (CH_2·O·CH_2Me)
(2)	112.75 (C-5), 96.49 (C-10, 20), 95.71 (C-15)	36.94 (CH_2·CH_2)
10,15′-$(CHO)_2$-(2)	119.34, 116.97 (C-5,5′)	188.45 (CHO)
	105.81, 104.05 (C-10,15′)	187.66 (CHO) 35.80 (CH_2·CH_2)
	100.96 (C-20) (?) 100.05 (C-10′, 20′) (?) 98.65 (C-15) (?)	

EXPERIMENTAL

Electronic spectra were determined with a Unicam SP 8000 (solvent $CHCl_3$), mass spectra with an AEI MS-30, ^1H n.m.r. spectra with a Varian EM-360, Perkin-Elmer R32, or JEOL PS-100 (solvent $CDCl_3$), ^{13}C and FT ^1H n.m.r. spectra with a JEOL PFT-100 (solvent $CDCl_3$) (internal standard Me_4Si), and i.r. spectra with a Perkin-Elmer 577 instrument (KBr disc). For t.l.c. Kieselgel PF_{254} (Merck) was used; for columns Spence type H alumina was employed. Hexane refers to light petroleum (b.p. 60—80 °C) distilled over the range 64—68 °C; chloroform for chromatography and electronic spectroscopy was distilled from anhydrous K_2CO_3. 'Acid-free' chloroform and dichloromethane were obtained by percolation through a column of basic alumina immediately before use.

meso-*Formyloctaethylporphyrinatonickel*(II) (1; R = CHO).—Nickel(II) OEP was subjected to Vilsmeier formylation by following literature directions for the similar reaction with nickel(II) etioporphyrin I.[1] The product (85—90%) was obtained as dark violet *needles* (from methylene chloride–methanol) (Found: C, 71.7; H, 7.1; N, 9.05. $C_{37}H_{44}N_4NiO$ requires C, 71.75; H, 7.15; N, 9.05%), $\lambda_{max.}$ 323, 404, 426, 531, 562, and 653 nm (ε 11 860, 69 700, 75 700, 4 130, 6 590, and 8 090), $\lambda_{max.}$ (KBr) 1 697 and 1 655 cm^{-1} (in CH_2Cl_2 solution the 1 697 band was almost absent), δ_H 1.70(t) and 1.75(t) (CH_3 of peripheral Et) 3.72 and 3.76 (q, CH_2 of peripheral Et), 9.27 (2 H, s, 10- and 20-H), 9.30 (1 H, s, 15-H), and 11.86 (1 H, s, CHO).

meso-*Hydroxymethyl- and* meso-*Ethoxymethyl-octaethylporphyrinatonickel*(II)- (1; R = CH_2·OH or CH_2·OEt).—Compound (1; R = CHO) (210 mg) was reduced with sodium borohydride (150 mg) in tetrahydrofuran (80 ml) containing water (1%). The green colour of the aldehyde and changed to deep red within 1 h, and when t.l.c. showed the absence of starting material, water and ether were added and the porphyrin was extracted into the organic layer. Drying, evaporation, and crystallisation from acid-free dichloromethane–methanol gave red *needles* (180 mg, 85%) (Found: C, 71.3; H, 7.55; N, 9.15. $C_{37}H_{46}N_4NiO$ requires C, 71.5; H, 7.45; N, 9.0%), $\lambda_{max.}$ 302, 349, 407, 536, and 574 nm (ε 8 900, 12 390, 134 900, 6 300, and 11 650), $\nu_{max.}$ (CCl_4) 3 647 cm^{-1} (OH), δ_H 1.36 (exchangeable with D_2O, OH), 1.70 and 1.76 (both t, CH_3 of peripheral Et), 3.82 and 3.95 (both q, CH_2 of peripheral Et), 6.40 (d, CH_2OH, collapses to s in presence of D_2O), and 9.41 (s, 3 *meso*-H).

Crystallisation of the product from chloroform containing a trace of acid and ethanol gave the meso-*ethoxymethyl derivative*, which was separated readily from the hydroxymethyl compound on t.l.c. (silica; 25% chloroform–hexane). It was crystallised from dichloromethane–methanol and formed red plates (Found: C, 72.5; H, 7.9; N, 8.8. $C_{39}H_{50}N_4NiO$ requires C, 72.15; H, 7.75; N, 8.8%), $\lambda_{max.}$ 348, 409, 537, and 574 nm (ε 16 280, 185 300, 10 330, and 17 780), *m/e* 648 (80%) and 604 (100), δ_H 1.11 (t, O·CH_2·CH_3), 1.72 and 1.75 (both t, CH_3 of peripheral Et), 3.26 (q, O·CH_2·CH_3), 3.81 (q, CH_2 of peripheral Et), 5.92 (s, CH_2·OEt), and 9.39 (s, 3 *meso*-H).

meso,meso′-*Ethylenebis*[*octaethylporphyrinatonickel*(II)] (2) *and* meso,meso′-*Ethylenebis*(*octaethylporphyrin*).— *meso*-Hydroxymethyloctaethylporphyrinatonickel(II) (120 mg) in dimethylformamide (20 ml) containing concentrated sulphuric acid (3 mol. equiv) was heated under reflux for 1 h. The red colour had changed to brown after *ca.* 15 min. The mixture was poured into ice–water (200 ml) and the brown precipitate separated and washed with water. The solid was dissolved in chloroform; the solution was dried, concentrated, and chromatographed on alumina (50% chloroform–hexane for elution). The fastest moving red band containing the major product together with some nickel OEP was collected. Elution with more polar solvents yielded numerous red, green, and brown fractions but no single compound was present in an amount sufficient for identification other than the *meso*-formyl derivative, which was compared by chromatography with an authentic sample. The major red fraction was purified by t.l.c. on silica (10% chloroform–hexane for elution); nickel OEP (10 mg) was obtained as a pink fraction and meso,meso′-*ethylenebis*[*octaethylporphyrinatonickel*(II)] as a red fraction. This product was isolated and precipitated from dichloromethane–methanol as a dark violet powder (60 mg, 50%), which crystallised from chloroform–benzene or chloroform–methanol to yield shining violet prisms (however a crystal suitable for *X*-ray analysis could not be obtained) (Found: C, 73.35; H, 7.7; N, 9.15. $C_{74}H_{90}N_8Ni_2$ requires C, 73.5; H, 7.5; N, 9.25%), $\lambda_{max.}$ 301, 347, 421, 539, and 575 nm (ε 26 400, 31 000, 276 600, 25 400, and 28 600), $\lambda_{infl.}$ 416 nm

(ε 258 800), *m/e* 1 206—1 210 (<5%), 618 (10), 604 (100), and 590 (40), δ_H 1.05, 1.56, 1.76, and 1.84 (all t, 16 × CH_3 of peripheral Et), 2.7—3.2br (m), 3.45br (q), and 3.87br (m) (16 × CH_2 of peripheral Et + 2 × *meso*-CH_2, 9.24 (s, 4 *meso*-H), and 9.46 (s, 2 *meso*-H) (even at 220 MHz the broad methylene signals were unresolved).

The dimer (15 mg) was stirred in concentrated sulphuric acid (5 ml) for 2 h at room temperature, then poured into ice–water, and the product was neutralised with aqueous sodium hydrogen carbonate. Extraction with dichloromethane and evaporation yielded a dark violet solid which was crystallised from dichloromethane–methanol. T.l.c. on silica (acid-free chloroform for elution) showed a single orange-red spot (the free base). A satisfactory analysis was not obtained; *m/e ca.* 1 094 (<5%), 548 (100), and 533 (17), $\lambda_{max.}$ 416br, 516, 551, 586, and 638 nm (ε 192 200, 22 170, 9 890, 10 260, and 2 630), $\lambda_{infl.}$ 368 nm (ε 121 700 $\lambda_{max.}$ ($CHCl_3$ containing 0.5% trifluoroacetic acid) 534sh, 568, and 613 nm, δ_H −2.8vbr (NH), 1.10, 1.64, and 1.91 (all br, t, CH_3 of peripheral Et), 3.4—3.9vbr (m) and 4.07br (q) (CH_2 of peripheral Et), 4.99br (s, CH_2 of bridge), and 9.74 and 9.85 (s, *meso*-H).

Treatment of this metal-free dimer (5 mg) with acetylacetonatonickel(II) (18 mg) in refluxing benzene for 24 h followed by aqueous washing, drying, and chromatography on alumina, gave the nickel-containing dimer (2) (3 mg), identical with an authentic specimen (t.l.c. and n.m.r. spectrum).

meso,meso′-*Ethylenebis*[*octaethylporphyrinatocopper*(II)].—*meso*-Formyloctaethylporphyrinatocopper(II) was reduced with sodium borohydride [2] to the corresponding meso-*hydroxymethyl derivative* (Found: C, 71.05; H, 7.25; N, 9.25%; M^+, 625.296 6. $C_{37}H_{46}{}^{63}CuN_4O$ requires C, 70.95; H, 7.4; N, 8.95%; *M*, 625.296 7), $\lambda_{max.}$ 333, 408, 537, and 575 nm (ε 16 060, 300 000, 10 980, and 15 310), $\nu_{max.}$ 3 560 cm^{-1} (OH).

The foregoing *meso*-hydroxymethylporphyrin (30 mg) in dimethylformamide (20 ml) containing concentrated sulphuric acid (2 drops) was heated at *ca.* 140 °C with stirring for 1½ h. The brown solution was poured into water (150 ml) and the precipitate separated and thoroughly washed with water. The solid was dissolved in chloroform and the solution dried and evaporated. The residue was chromatographed on alumina (50% chloroform–hexane for elution) and the first red band was separated. The product was further purified by t.l.c. on silica (10% chloroform–hexane for elution). The main product was crystallised from dichloromethane–methanol to give the *copper complex* of the dimer as fine violet needles (3.5 mg, 12%) (Found: C, 72.55; H, 7.25; N, 9.35. $C_{74}H_{90}Cu_2N_8$ requires C, 72.95; H, 7.45; N, 9.2%), *m/e* 1 216—1 220 (<5%), 623 (30), 609 (40), and 595 (100), $\lambda_{max.}$ 329, 400, 409, 426sh, 548, and 579br nm (ε 37 300, 273 000, 255 000, 143 000, 21 800, and 19 300).

Reaction of meso-*Hydroxymethyloctaethylporphyrin with Sulphuric Acid.*—The starting material was obtained by reduction of the corresponding *meso*-formyl compound with borohydride; [2] the *meso*-formyl compound was obtained by demetallation of the corresponding nickel complex (1; R = CHO) with concentrated sulphuric acid at room temperature for 24 h. The *meso*-hydroxymethyl derivative (50 mg) in dimethylformamide (35 ml) containing concentrated sulphuric acid (2 drops) was heated under reflux for 1 h. The product was poured into water and extracted with dichloromethane; the extract was dried and evaporated. The residue was dissolved in dichloromethane and chromatographed on alumina (dichloromethane for elution); a fast-moving red band was obtained together with a series of minor red, green, and brown bands. The major red band was subjected to t.l.c. on silica (25% chloroform–dichloromethane for elution) and was separated into two major red bands, the first of which was shown to consist of OEP and the second (4.5 mg) to consist of *meso*-methyl-OEP on the basis of n.m.r.[4] and mass spectra: *m/e* 548 (100%, *M*) and 533 (20, *M* − CH_3). The more polar products proved to be a complex mixture but small quantities of both starting material and *meso*-formyl-OEP were shown to be present by comparison of visible spectra and R_F values with those of authentic samples.

10-*Mono- and* 10,10′-, 10,15′-, *and* 15,15′-*Diformyl Derivatives of the Dimer* (2).—Compound (2) (206 mg) was dissolved in dry 1,2-dichloroethane (250 ml) and added dropwise with vigorous stirring to a previously prepared mixture of phosphoryl chloride (1.52 ml) and dry dimethylformamide (1.28 ml). The mixture was maintained at 80 °C during the addition and for a further 1 h. The resulting green solution was stirred at 50 °C with saturated aqueous sodium acetate (250 ml) for 2 h, and the organic layer was then separated, dried, and evaporated. The residue was dissolved in chloroform and chromatographed on alumina (chloroform for elution). Two major fractions were collected separately. The first, green-brown, less polar fraction was subjected to t.l.c. on silica (75% chloroform–hexane for elution); several minor green components were obtained together with the major green-brown product, which was shown by n.m.r. (below) to be the 10-*monoformyl derivative*. It formed fine brown needles (35 mg, 16.6%) (from dichloromethane–methanol) (Found: C, 72.8; H, 7.25; N, 9.35. $C_{75}H_{90}N_8Ni_2O$ requires C, 72.85; H, 7.35; N, 9.05%), $\lambda_{max.}$ 345, 414, 544, 580, and 666 nm (ε 28 470, 180 350, 15 350, 17 940, and 10 240), $\lambda_{infl.}$ 440 nm (ε, 130 060), $\nu_{max.}$ 1 650 cm^{-1} (C=O), δ_H 0.9—1.1 and 1.5—1.8 (overlapping t, CH_3 of peripheral Et), 2.5—4.0vbr (unresolved m, CH_2 of peripheral Et), and 8.83 (H-15), 9.15 (H-20), 9.26 (H-10′ and -20′), 9.45 (H-15′), and 11.51 (CHO) (all s).

The more polar broad green band from the column was also subjected to t.l.c. on silica (75% chloroform–hexane for elution); three green bands were separated. The least polar fraction was still impure (n.m.r.) and was therefore chromatographed further to yield the 15,15′-*diformyl derivative* (4 mg, 1.9%). In the n.m.r. spectrum, the methylene bridge signal appeared as a singlet, δ 3.69, that of the remaining four *meso*-protons as a singlet, δ 8.71, and that of the aldehyde protons as a further singlet, δ 11.66. The second green component was crystallised from dichloromethane–methanol to form dark green needles (70 mg, 32.5%), shown (n.m.r.) to be the 10,10′-*diformyl derivative* (Found: C, 72.15; H, 7.15; N, 9.15. $C_{76}H_{90}N_8Ni_2O_2$ requires C, 72.15; H, 7.15; N, 8.85%), $\lambda_{max.}$ 308, 342, 444br, 560sh, 602sh, and 668 nm (ε 25 000, 29 600, 165 000, 10 800, 13 300, and 19 600), $\nu_{max.}$ 1 650 cm^{-1} (C=O), δ_H 0.98, 1.07, 1.49, and 1.78 (overlapping t, CH_3 of peripheral Et), 2.79vbr, 3.34br (q), and 3.70br (q) (CH_2 of peripheral Et), 3.66 (s, bridge CH_2), 8.94 (s, 15- and 15′-H), 9.09 (s, 20- and 20′-H), and 11.55 (s, 2 × C*H*O).

The third green compound was crystallised from dichloromethane–methanol to yield dark green micro-needles (35 mg, 16.2%) shown (n.m.r.) to be the 10,15′-*diformyl derivative* (Found: C, 72.4; H, 7.1; N, 9.15%), δ_H 1.04,

1.55, 1.64, 1.68, 1.75, and 1.83 (overlapping t, CH_3 of peripheral Et), 2.83vbr, 3.26br (q), and 3.71br (q) (CH_2 of peripheral Et), 3.69br (s, bridge CH_2), 8.87 (s, 20-H), 9.09 (s, 15-, 10′-, and 20′-H), 11.55 (s, 10-CHO), and 11.70 (s, 15′-CHO).

5,5′-Ethylenebis[octaethyl-10-hydroxymethylporphyrinatonickel(II)].—The foregoing 10,10′-diformyl derivative (70 mg) was stirred in damp tetrahydrofuran (40 ml) with sodium borohydride (100 mg). After 3 h the mixture had changed colour from green to red. Ether and water were added, and the organic layer was separated, washed with saturated aqueous ammonium chloride, dried, and evaporated to give a red solid. This was shown by t.l.c. to contain no starting material. It was chromatographed on alumina (activity III; 25% hexane–dichloromethane for elution). The major red product was separated and crystallised from acid-free dichloromethane–methanol as violet *prisms* (58 mg, 83%). A sample was purified further by t.l.c. on silica (acid-free chloroform for elution) and then further crystallisation from dichloromethane–methanol (Found: C, 71.75; H, 7.25; N, 8.8. $C_{76}H_{94}N_8Ni_2O_2$ requires C, 71.95; H, 7.45; N, 8.85%), *m/e* (no M^+ at *m/e* 1266) 634 (<5%), 618 (100), and 604 (80) (confirming the ready loss of CH_2OH under these conditions), $\lambda_{max.}$ 360, 430br 560, and 599 nm (ε 31 400, 231 000, 25 100, and 24 000), δ_H 0.95, 1.02, 1.43, 1.68, and 1.78 (overlapping t, CH_3 of peripheral Et), 1.42 (s, 2 × CH_2OH, removed after D_2O exchange), 2.8, 3.4vbr (m), and 3.74br (q) (CH_2 of peripheral Et), 3.52 (s, bridge CH_2), 6.07 (d, 2 × CH_2OH, collapsed to s after D_2O exchange), 8.97 (s, 15- and 15′-H), and 9.19 (s, 20- and 20′-H).

Reduction of meso-*Formyloctaethylporphyrinatonickel*(II).—The formyl compound (50 mg) was heated under reflux for 3 h with lithium aluminium hydride (10 mg) in dry tetrahydrofuran (20 ml). The product was treated with an excess of saturated aqueous ammonium chloride and ether, and the organic layer was separated and dried. Removal of the solvent left a red-brown solid, which was dissolved in 50% chloroform–hexane and chromatographed on alumina (elution with the same solvent). The fastest moving red band was followed by a green band (starting material). Elution with chloroform gave nickel *meso*-hydroxymethyl-OEP (1; R = CH_2·OH) as another red band. The first red band was separated and the eluate subjected to preparative t.l.c. on silica (10% chloroform–hexane for elution); two fractions were obtained. The less polar component, meso-*methyloctaethylporphyrinatonickel*(II) (1; R = Me) crystallised from chloroform–methanol as purple plates (7.5 mg, 15%) (Found: C, 73.65; H, 7.85; N, 9.45. $C_{37}H_{46}N_4Ni$ requires C, 73.4; H, 7.65; N, 9.25%), *m/e* 604 (100% *M*), and 589 (*ca.* 5 *M* − CH_3), $\lambda_{max.}$ 290, 340, 410, 536, and 572 nm (ε 20 860, 14 650, 182 300, 10 920, and 14 650), δ_H 1.69 and 1.73 (both t, 24 H of CH_3 of peripheral Et), 3.76 (q, 18 H of CH_2 of peripheral Et), 3.80 (s, *meso*-CH_3), and 9.32br (s, 3 *meso*-H). This compound was also prepared by the reaction of *meso*-methyl-OEP (4 mg) with nickel(II) acetate (4 mg) and sodium acetate (3 mg) in refluxing chloroform–acetic acid, and was purified by preparative t.l.c. on silica (25% chloroform–hexane for elution).

The more polar component (16 mg, 33%) was shown to be the dimer (2) by direct comparison.

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