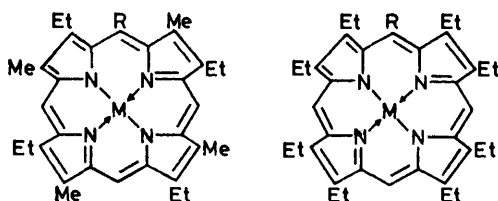


Wittig Condensation Products from Nickel *meso*-Formyl-octaethylporphyrin and -aetioporphyrin I and Some Cyclisation Reactions

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Various Wittig condensation products from the named *meso*-formylporphyrins are described, together with some transformations of the products. Vilsmeier formylation of the nickel *meso*-vinyl derivatives causes substitution mainly in the side-chain, and acid cyclisation of the *meso*-acrylaldehyde products results in the formation of a fused benzene ring and the structure of the product is fully defined by X-ray crystallography. In the absence of nickel, mild acid cyclisations of the *meso*-acrylaldehydes or esters yield purpurins.

In earlier papers,¹⁻³ we have described some reactions of the aldehyde group of nickel *meso*-formyl derivatives [(1a) and (2a) respectively] of aetioporphyrin I and octaethylporphyrin (OEP), and these included reductions to the carbinols (1b) and (2b) and the formation of

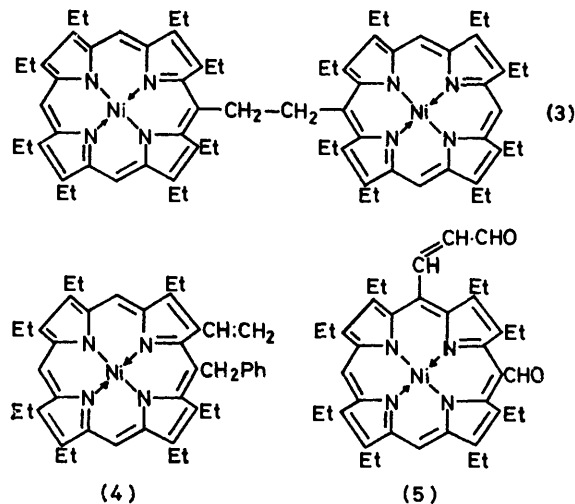


(1) M	R	(2) M	R
a; Ni	CHO	a; Ni	CHO
b; Ni	CH ₂ OH	b; Ni	CH ₂ OH
c; Ni	CN	c; Ni	CN
d; Ni	CH(OH)Ph	d; Ni	CH ₂
e; Ni	CH=CH·CO ₂ Me	e; Ni	⁺ CH ₂
f; Ni	CH=CH-CH=CH·CO ₂ Me	f; Ni	CH(OH)Me
g; Ni	CH=CH-CH=CH·CHO	g; Ni	CH(OH)Ph
h; Ni	CH=CH ₂	h; Ni	CH=CH ₂
i; Ni	CH=CHPh	i; Ni	CH=CH·CO ₂ Me
j; Ni	CH=CH·C ₆ H ₄ Me	j; Ni	CH=CHMe
k; Ni	CH=CH[CH ₂] ₄ Me	k; Ni	CH=CHPh
l; Ni	CH=CH·CHO	l; Ni	CH=CH·CHO
m; Ni	CH=CH·CH ₂ OH	m; Ni	CH=CH·CH ₂ OH
n; Ni	CH ₂ ·CH ₂ ·CH ₂ ·OH	n; H ₂	CH=CH·CHO
o; H ₂	CH=CH·CHO	o; H ₂	CH=CH·CO ₂ Me
		p; H ₂	CH=C $\begin{matrix} \diagup \text{CO}_2\text{Me} \\ \diagdown \text{CO}_2\text{H} \end{matrix}$
		q; H ₂	CH=C(CO ₂ H) ₂
		r; Ni	CH=CH·CH=CH ₂

several derivatives including the *meso*-cyanoporphyrins (1c) and (2c) by dehydration of the oximes. Wittig condensations,⁴ Knoevenagel condensations, Schiff base formation^{5,6} and other reactions^{7,8} have been described in the literature. Thus, the nickel *meso*-formylporphyrins (1a) and (2a) show most of the normal reactions of aromatic aldehydes. However, unlike other metal complexes of simple *meso*-substituted porphyrins, the nickel *meso*-formyl derivatives give bright green solutions and their electronic spectra show broadened and split Soret bands as well as an extra band at *ca.* 650

nm. These properties are probably a measure of distortion of the porphyrin ring.⁶ The ¹H n.m.r. spectra of the *meso*-formylporphyrins on the other hand are unexceptional and are in line with those of the planar porphyrins.

In our previous paper,² the reaction of the primary carbinol (2b) with sulphuric acid was described. The unexpected product was the dimer (3), presumably formed by dimerisation of the radical (2d), itself formed from the carbonium ion (2e), by electron transfer from the metal porphyrin. In an attempt to define the scope of this dimerisation, we prepared³ the methylcarbinol (2p) and the phenylcarbinol (2g) by appropriate Grignard (and now with phenyl-lithium) reactions. Reaction of the



methylcarbinol (2f) with sulphuric acid gave the *meso*-vinyl compound (2h) as expected; on the other hand, the phenylcarbinol gave (4), by a reaction involving formation of the carbonium ion, rearrangement, and loss of proton.

The present paper describes a study of reactions of various Wittig products from the nickel *meso*-formyl porphyrins. Previously, Callot⁴ had described the con-

⁵ J.-H. Fuhrhop and L. Witte, *Angew. Chem. Internat. Edn.*, 1975, **14**, 361.

⁶ J.-H. Fuhrhop, L. Witte, and W. S. Sheldrick, *Annalen*, 1976, 1537; see also A. Treibs, *Ann. New York Acad. Sci.*, 1973, **206**, 97.

⁷ H.-H. Inhoffen and W. Nolte, *Annalen*, 1969, **725**, 167.

⁸ P. S. Clezy, C. L. Lim, and J. S. Shannon, *Austral. J. Chem.*, 1974, **27**, 1103.

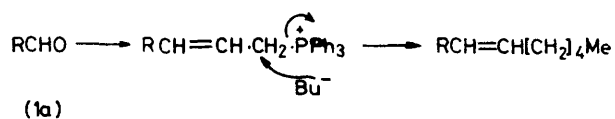
¹ A. W. Johnson and D. Oldfield, *J. Chem. Soc. (C)*, 1966, 794.

² D. P. Arnold, A. W. Johnson, and M. Winter, *J.C.S. Perkin I*, 1977, 1643.

³ D. P. Arnold, A. W. Johnson, and M. Mahendran, *J.C.S. Perkin I*, 1978, 366.

⁴ H. Callot, *Bull. Soc. chim. France*, 1973, 3413.

condensation of the stabilised Wittig reagent, methoxycarbonylmethylene(triphenyl)phosphorane with (2a) and showed that the product (2i) could be demetallated by the action of sulphuric acid. We have prepared analogous compounds (1e) and (2i) and have used the vinylogous Wittig reagent, methoxycarbonylallylidene-(triphenyl)phosphorane, in the aetioporphyryl series to give (1f) which was demetallated by acid treatment, and reduced to the corresponding aldehyde (1g) by treatment with a limited amount of aluminium hydride. Most of the Wittig reagents used however were prepared *in situ* using a mixture of the appropriate phosphonium salt and phenyl-lithium, and in this manner a range of *meso*-vinyl derivatives of nickel porphyrins have been prepared, comprising the *meso*-vinyl (1h) and (2h), -propenyl (2j), -styryl (1i) and (2k), and *p*-methylstyryl (1j) substituents. However, when (1a) was treated with the bisphosphonium salt, $(\text{Ph}_3\text{P}^+\text{CH}_2)_2 2\text{Br}^-$, prepared from ethylene dibromide and triphenylphosphine, in the presence of *n*-butyl-lithium in an attempt to prepare a bis-porphyrin, the product was, unexpectedly, the *meso*-heptenyl derivative (1k), presumably formed by the following mechanism:



Reaction of (1a) with allyl(triphenyl)phosphonium bromide in the presence of phenyl-lithium gave only the phenylcarbinol (1d).

Some reactions of the nickel *meso*-vinylporphyrins have been carried out. Thus, although reaction of nickel *meso*-styrylaetioporphyryl I (1i) with the Vilsmeier reagent caused further *meso*-substitution to yield a mixture of the 10- and 15-formyl derivatives, the nickel *meso*-vinyl porphyrins (1h) and (2h) under similar conditions gave the nickel *meso*-acrylaldehydes (1l) and (2l) in *ca.* 85% yield by reaction at the terminal position of the side-chain. Related reactions of porphyrin β -vinyl groups have been reported by Nichol.⁹ Like the nickel *meso*-formylporphyrins (1a) and (2a), the *meso*-acrylaldehydes were green and showed split Soret bands. In the formylation reaction two additional green products were isolated which were shown to have been formed by *meso*- as well as side-chain formylation. They were distinguished by the signals of the two remaining porphyrin *meso*-hydrogens. The more abundant and less polar isomer showed two separate signals and was therefore the 10-formyl derivative (5); the more polar isomer showed a single signal for the *meso*-hydrogens and this was the 15-formyl derivative. Reduction of the nickel *meso*-acrylaldehydes (1l) and (2l) with sodium borohydride gave the corresponding carbinols (1m) and (2m). A mixture of the aldehyde (1l), the carbinol (1m) as well as the saturated carbinol (1n) was obtained by borohydride

reduction of the *meso*-acrylic ester (1e), but the Vilsmeier route was preferable preparatively. With the *meso*-acrylic esters, aldehydes, and alcohols available, we have been able to extend our earlier studies on the effect of acids on porphyrins containing a variety of *meso*-substituents. When the metal-free *meso*-acrylaldehyde (2n) was heated under reflux in acetic acid under nitrogen it gave an isomeric compound, the n.m.r. and electronic spectra (λ_{max} 440, 505, 554, 592, 672, and 734 nm) of which suggested the purpurinaldehyde structure (6a). Under these cyclisation conditions, the nickel complex (2l) was unaffected. A similar cyclisation of the metal-free porphyrin containing a *meso*-acrylic methyl ester (2o) to the purpurin (6b) was also achieved. The formation of these purpurins recalls Woodward's classical chlorophyll synthesis,¹⁰ in which an unsymmetrical porphyrin was reduced in ring D to give the corresponding chlorin. That reaction was achieved using a porphyrin containing a *meso*-acrylic ester grouping which, first, was cyclised by heating in acetic acid to give the purpurin and then subjected to further manipulations (oxidation, hydrolysis) in order to produce the required C-17 hydrogen substituent. The cyclisation, doubtless aided by steric crowding and the electron-attracting powers of the ester group, remained a unique observation until recently when Fuhrhop⁶ reported that the porphyrin *meso*-unsaturated dicarboxylic acid monomethyl ester (2p) was cyclised by heating in toluene to give the purpurin (6b) whereas the diacid (2q) was cyclised by treatment with concentrated sulphuric acid to give the ketone (8).

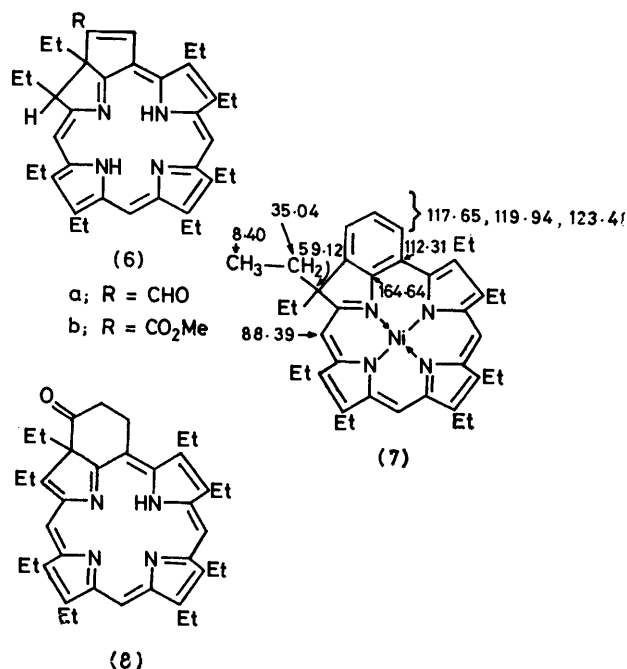
When the *meso*-acrylaldehydes (1l) and (2l) were treated with concentrated sulphuric acid for 3 min at room temperature, the metal-free porphyrin aldehydes (1o) and (2n) were obtained in *ca.* 40% yields along with a second green product in each case. Longer exposure to sulphuric acid caused decomposition of the metal-free *meso*-aldehydes and after 2 h at room temperature the products were mainly (*ca.* 40%) the green products, which each possessed a fused benzene ring and a *gem*-dialkyl group. The same green compounds were obtained in *ca.* 15% yield when the nickel complexes of the γ -porphyrinylallyl alcohol (2m) were treated with sulphuric acid in *NN*-dimethylformamide. The product was assigned structure (7) in the octaethylporphyrin series on the basis of its mass spectrum and n.m.r. spectra. The ¹H spectrum clearly demonstrated the presence of three *meso*-protons (δ 7.72, 8.45, and 8.82), the benzenoid protons (δ 7.70, 2 H and 8.8, 1 H), and the *gem*-diethyl group with signals at δ 0.04 (t) and 2.24 (q), recalling the ¹H n.m.r. spectra of the *gem*-dialkylporphyrin ketones of Inhoffen.^{7,11} The ¹³C spectrum assignments, fully supported by off-resonance decoupling, are shown on formula (7). The mass spectrum suggested the loss of an oxygen from the initial aldehyde (2l) and the electronic spectrum of (7) showed a strong chlorin-type band at 677 nm (ϵ 36 700) as well as a Soret band at 416 nm (ϵ 69 200). The cyclisation of the

⁹ A. W. Nichol, *J. Chem. Soc. (C)*, 1970, 903.

¹⁰ R. B. Woodward, *Angew. Chem.*, 1960, **72**, 651.

¹¹ H.-H. Inhoffen, J. W. Buchler, and P. Jäger, *Progr. Chem. Org. Nat. Prod.*, 1968, **26**, 284.

acylaldehyde side-chain to form a benzene ring formally involves a reduction step, the mechanism of which has



not been established, although it is known that nickel porphyrin complexes can act as electron donors under acidic conditions.²

Like the nickel *meso*-formylporphyrins, the *meso*-acrylaldehyde (2l) also underwent normal Wittig condensations and a sample of the *meso*-buta-1,3-dienyl derivative (2r) was prepared in good yield by this method.

Crystal Structure Determination of (7).—*Crystal data.* C₃₉H₄₆N₄Ni, *M* 629.5. Monoclinic, *a* = 14.132(1), *b* = 16.436(1), *c* = 15.720(1) Å, β = 115.487(5)°, *U* = 3 296.0 Å³, *D_c* = 1.268 g cm⁻³, *Z* = 4, space group *P*2₁/*c*, Mo-*K*_α radiation (graphite crystal monochromator), λ = 0.709 26 Å, μ = 6.24 cm⁻¹.

Crystals suitable for X-ray analysis were grown from dichloromethane-methanol solution. Measurements were made on a crystal of approximate dimensions 0.5 × 0.2 × 0.3 mm mounted about the *a*-axis. Oscillation, Weissenberg, and precession photographs showed the crystals to be monoclinic, with systematic absences *0k0* with *k* odd and *h0l* with *l* odd uniquely determining the space group to be *P*2₁/*c*. Accurate unit cell parameters, together with their estimated standard deviations (e.s.d.s) were derived by a least-squares analysis of the setting angles determined for 12 angularly well separated reflections, each with a 2θ value greater than 30°. All data were collected at 21 °C from a Hilger and Watts automatic four-circle diffractometer (Y290) using graphite monochromatised Mo-*K*_α radiation (λ = 0.709 26 Å). Intensities were measured *via* an ω-2θ scan regime within the range 2θ 0–50°; the intensities of 6 784 reflections were measured and 4 012 independent, statistically significant [*I* ≥ 30(*I*)] reflections formed the

basis for the structure determination and refinement. No significant variations in the intensities of 3 standard reflections were observed and the data were corrected for Lorentz and polarisation effects but not for absorption.

The structure solution and refinement proceeded using the SHEL-X system of G. M. Sheldrick, University of Cambridge. A three-dimensional Patterson synthesis together with a Fourier and difference synthesis yielded the positions of all non-hydrogen atoms. Least-squares refinement of atomic co-ordinates and individual isotropic temperature factors was performed in the full-matrix mode, the function minimised being Σ*w*Δ*F*² where *w* is the weight assigned to the |*F_o*| values and Δ*F* = ||*F_o*| – |*F_c*||. After five cycles using unit weights, refinement converged with *R*, defined as ΣΔ*F*/Σ|*F_o*|, 0.0623. A further difference synthesis then yielded the positions of all hydrogen atoms and these were included

TABLE 1

Final atomic parameters for (7). E.s.d. values (in parentheses) refer to the least significant digits

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni	0.224 4(0)	–0.113 6(0)	0.939 2(0)
N(1)	0.258 5(2)	–0.038 2(2)	0.861 8(2)
N(2)	0.364 0(2)	–0.158 6(2)	0.985 4(2)
N(3)	0.193 4(2)	–0.184 2(2)	1.022 0(2)
N(4)	0.079 3(2)	–0.075 7(2)	0.884 6(2)
C(1)	0.355 1(3)	–0.020 3(2)	0.865 1(2)
C(2)	0.445 2(3)	–0.064 4(2)	0.917 3(2)
C(3)	0.447 8(3)	–0.131 3(2)	0.968 7(2)
C(4)	0.536 7(3)	–0.185 5(2)	1.012 4(2)
C(5)	0.638 5(3)	–0.177 0(2)	1.005 4(3)
C(6)	0.638 9(4)	–0.221 8(3)	0.921 8(4)
C(7)	0.507 1(3)	–0.245 7(2)	1.054 0(2)
C(8)	0.567 5(3)	–0.318 7(2)	1.106 1(3)
C(9)	0.533 4(4)	–0.397 0(3)	1.049 1(3)
C(10)	0.400 7(3)	–0.227 5(2)	1.038 6(2)
C(11)	0.347 6(3)	–0.269 2(2)	1.081 2(2)
C(12)	0.254 4(3)	–0.244 3(2)	1.078 2(2)
C(13)	0.210 7(3)	–0.281 2(2)	1.142 2(2)
C(14)	0.289 1(3)	–0.278 4(2)	1.246 6(3)
C(15)	0.330 7(4)	–0.195 0(3)	1.283 3(3)
C(16)	0.177 1(3)	–0.370 5(2)	1.114 6(3)
C(17)	0.098 2(4)	–0.382 8(3)	1.013 7(3)
C(18)	0.116 7(3)	–0.228 3(2)	1.118 7(2)
C(19)	0.044 2(3)	–0.244 4(2)	1.154 3(3)
C(20)	–0.039 6(3)	–0.173 2(2)	1.116 1(3)
C(21)	–0.052 3(3)	–0.126 0(2)	1.039 3(2)
C(22)	0.019 0(3)	–0.129 3(2)	0.998 0(2)
C(23)	0.108 2(3)	–0.176 8(2)	1.044 7(2)
C(24)	0.000 9(3)	–0.091 1(2)	0.911 0(2)
C(25)	–0.099 6(3)	–0.068 0(2)	0.838 2(2)
C(26)	–0.206 5(3)	–0.082 8(2)	0.832 8(2)
C(27)	–0.252 8(3)	–0.011 3(3)	0.864 1(3)
C(28)	–0.080 4(3)	–0.035 4(2)	0.767 5(2)
C(29)	–0.158 6(3)	–0.006 0(3)	0.673 0(3)
C(30)	–0.174 7(4)	–0.067 8(4)	0.596 5(3)
C(31)	0.030 5(3)	–0.036 9(2)	0.797 7(2)
C(32)	0.082 1(3)	0.005 1(2)	0.755 7(2)
C(33)	0.189 0(3)	0.009 9(2)	0.788 9(2)
C(34)	0.244 1(3)	0.058 9(2)	0.749 1(2)
C(35)	0.193 5(3)	0.116 2(2)	0.667 0(2)
C(36)	0.157 2(4)	0.195 9(3)	0.690 0(3)
C(37)	0.347 7(3)	0.041 2(2)	0.797 7(2)
C(38)	0.436 8(3)	0.072 3(2)	0.779 7(2)
C(39)	0.452 8(3)	0.022 5(3)	0.704 9(3)

in the scattering model but were not refined, each hydrogen atom being given an isotropic temperature factor 1.5 times that of the atom to which it was bonded.

All non-hydrogen atoms were then refined aniso-

tropically (a total of 397 variables) in two blocks and a weighting scheme of the form $w = 1.6410/[\sigma^2(F_o) + 0.000306|F_o|^2]$ was applied. Refinement converged to R 0.0405 and R_w , defined as $(\sum w\Delta F^2/\sum w|F_o|^2)^{1/2}$, 0.0471. The maximum shift/error at convergence was 0.004 and a final difference synthesis was essentially featureless and showed no peaks larger than $|0.4|e \text{ \AA}^{-3}$.

Final C, N, and Ni atomic parameters and their e.s.d. values are listed in Table 1 and the H co-ordinates in

TABLE 2

Hydrogen atom co-ordinates in (7) obtained from a difference synthesis

Atom ^a	x/a	y/b	z/c
H(1)[C(2)]	0.5182	-0.0476	0.9208
H(2)[C(5)]	0.6547	-0.1210	1.0011
H(3)[C(5)]	0.6975	-0.2001	1.0633
H(4)[C(6)]	0.7176	-0.2240	0.9256
H(5)[C(6)]	0.5688	-0.2409	0.8595
H(6)[C(6)]	0.6107	-0.2840	0.9283
H(7)[C(8)]	0.5539	-0.3227	1.1668
H(8)[C(8)]	0.6497	-0.3077	1.1218
H(9)[C(9)]	0.5584	-0.3881	0.9989
H(10)[C(9)]	0.5720	-0.4535	1.0832
H(11)[C(9)]	0.4519	-0.3993	1.0289
H(12)[C(11)]	0.3840	-0.3154	1.1186
H(13)[C(14)]	0.2547	-0.3094	1.2815
H(14)[C(14)]	0.3494	-0.3235	1.2544
H(15)[C(15)]	0.3626	-0.1959	1.3444
H(16)[C(15)]	0.3625	-0.1654	1.2453
H(17)[C(15)]	0.2779	-0.1470	1.2781
H(18)[C(16)]	0.1472	-0.3960	1.1550
H(19)[C(16)]	0.2424	-0.4086	1.1351
H(20)[C(17)]	0.0380	-0.3378	0.9953
H(21)[C(17)]	0.0728	-0.4398	1.0030
H(22)[C(17)]	0.1183	-0.3653	0.9642
H(23)[C(19)]	0.0551	-0.2564	1.2158
H(24)[C(20)]	-0.0969	-0.1606	1.1405
H(25)[C(21)]	-0.1057	-0.0821	1.0195
H(26)[C(26)]	-0.2599	-0.0991	0.7662
H(27)[C(26)]	-0.1969	-0.1231	0.8729
H(28)[C(27)]	-0.2414	0.0341	0.8330
H(29)[C(27)]	-0.3161	-0.0247	0.8618
H(30)[C(27)]	-0.2004	0.0131	0.9358
H(31)[C(29)]	-0.1251	0.0475	0.6595
H(32)[C(29)]	-0.2210	0.0080	0.6791
H(33)[C(30)]	-0.1121	-0.0974	0.5916
H(34)[C(30)]	-0.2365	-0.0285	0.5443
H(35)[C(30)]	-0.2216	-0.0950	0.5434
H(36)[C(32)]	0.0417	0.0373	0.6962
H(37)[C(35)]	0.2449	0.1217	0.6328
H(38)[C(35)]	0.1348	0.0863	0.6154
H(39)[C(36)]	0.2212	0.2197	0.7318
H(40)[C(36)]	0.1427	0.2305	0.6361
H(41)[C(36)]	0.1092	0.1833	0.7077
H(42)[C(38)]	0.4235	0.1325	0.7598
H(43)[C(38)]	0.4997	0.0739	0.8416
H(44)[C(39)]	0.5111	0.0386	0.7025
H(45)[C(39)]	0.3819	0.0257	0.6429
H(46)[C(39)]	0.4655	-0.0365	0.7172

^a Hydrogen atoms are labelled with the carbon atom to which they are attached in parentheses.

Table 2. Atomic scattering curves for H, C, N, and Ni were taken from refs. 12 and 13, with that for Ni modified for the real and imaginary anomalous dispersion

¹² D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

¹³ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

¹⁴ D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

TABLE 3

Interatomic distances (Å) and angles (°) in (7)

Intramolecular distances			
Ni-N(1)	1.937(3)	C(13)-C(16)	1.546(5)
Ni-N(2)	1.932(3)	C(13)-C(18)	1.495(5)
Ni-N(3)	1.930(3)	C(14)-C(15)	1.505(6)
Ni-N(4)	1.953(3)	C(16)-C(17)	1.509(6)
N(1)-C(1)	1.376(5)	C(18)-C(19)	1.363(7)
N(1)-C(33)	1.392(4)	C(18)-C(23)	1.401(5)
N(2)-C(3)	1.393(5)	C(19)-C(20)	1.395(6)
N(2)-C(10)	1.371(4)	C(20)-C(21)	1.381(6)
N(3)-C(12)	1.357(4)	C(21)-C(22)	1.414(6)
N(3)-C(23)	1.400(5)	C(22)-C(23)	1.393(4)
N(4)-C(24)	1.364(5)	C(22)-C(24)	1.425(5)
N(4)-C(31)	1.392(4)	C(24)-C(25)	1.440(4)
C(1)-C(2)	1.385(4)	C(25)-C(26)	1.495(6)
C(1)-C(37)	1.435(5)	C(25)-C(28)	1.363(6)
C(2)-C(3)	1.355(5)	C(26)-C(27)	1.525(6)
C(3)-C(4)	1.450(4)	C(28)-C(29)	1.499(4)
C(4)-C(5)	1.495(6)	C(28)-C(31)	1.428(5)
C(4)-C(7)	1.348(5)	C(29)-C(30)	1.514(7)
C(5)-C(6)	1.510(8)	C(31)-C(32)	1.364(6)
C(7)-C(8)	1.496(5)	C(32)-C(33)	1.371(5)
C(7)-C(10)	1.447(5)	C(33)-C(34)	1.437(6)
C(8)-C(9)	1.523(6)	C(34)-C(35)	1.506(5)
C(10)-C(11)	1.384(6)	C(34)-C(37)	1.360(5)
C(11)-C(12)	1.361(6)	C(35)-C(36)	1.507(7)
C(12)-C(13)	1.515(6)	C(37)-C(38)	1.495(6)
C(13)-C(14)	1.535(4)	C(38)-C(39)	1.527(7)
Bond angles			
N(2)-Ni-N(1)	89.5(1)	C(16)-C(13)-C(18)	110.5(3)
N(4)-Ni-N(1)	91.0(1)	C(16)-C(13)-C(12)	110.9(3)
N(4)-Ni-N(2)	175.1(1)	C(16)-C(13)-C(14)	108.8(3)
N(3)-Ni-N(1)	176.7(1)	C(15)-C(14)-C(13)	114.8(3)
N(3)-Ni-N(2)	90.5(1)	C(17)-C(16)-C(13)	115.0(3)
N(3)-Ni-N(4)	89.3(1)	C(19)-C(18)-C(23)	121.6(3)
C(1)-N(1)-Ni	128.6(2)	C(13)-C(18)-C(23)	107.9(4)
C(33)-N(1)-Ni	127.1(2)	C(13)-C(18)-C(19)	130.5(3)
C(33)-N(1)-C(1)	104.3(3)	C(20)-C(19)-C(18)	118.7(4)
C(3)-N(2)-Ni	128.3(2)	C(19)-C(20)-C(21)	120.1(5)
C(10)-N(2)-Ni	127.0(3)	C(20)-C(21)-C(22)	122.0(3)
C(10)-N(2)-C(3)	104.6(3)	C(23)-C(22)-C(24)	120.0(4)
C(12)-N(3)-Ni	127.7(3)	C(21)-C(22)-C(24)	123.6(3)
C(12)-N(3)-C(23)	105.8(3)	C(21)-C(22)-C(23)	116.2(3)
C(23)-N(3)-Ni	126.1(2)	C(18)-C(23)-N(3)	112.5(3)
C(24)-N(4)-Ni	130.1(2)	C(22)-C(23)-N(3)	126.7(3)
C(31)-N(4)-Ni	124.1(3)	C(18)-C(23)-C(22)	120.7(4)
C(31)-N(4)-C(24)	105.0(3)	C(22)-C(24)-N(4)	122.7(3)
C(2)-C(1)-N(1)	123.7(3)	C(25)-C(24)-N(4)	111.2(3)
C(37)-C(1)-N(1)	111.5(3)	C(25)-C(24)-C(22)	126.0(4)
C(37)-C(1)-C(2)	124.2(4)	C(26)-C(25)-C(24)	129.0(3)
C(1)-C(2)-C(3)	124.1(4)	C(28)-C(25)-C(24)	106.1(3)
C(2)-C(3)-N(2)	124.5(3)	C(28)-C(25)-C(26)	124.6(3)
C(4)-C(3)-N(2)	110.3(3)	C(27)-C(26)-C(25)	114.8(3)
C(4)-C(3)-C(2)	125.3(4)	C(25)-C(26)-C(31)	107.3(3)
C(5)-C(4)-C(3)	125.0(3)	C(29)-C(28)-C(31)	124.8(4)
C(7)-C(4)-C(3)	107.1(3)	C(29)-C(28)-C(25)	127.9(4)
C(7)-C(4)-C(5)	127.8(3)	C(30)-C(29)-C(28)	111.4(4)
C(6)-C(5)-C(4)	112.5(3)	C(28)-C(31)-N(4)	110.1(3)
C(8)-C(7)-C(4)	129.1(4)	C(32)-C(31)-N(4)	124.4(3)
C(10)-C(7)-C(4)	106.6(3)	C(32)-C(31)-C(28)	124.7(3)
C(10)-C(7)-C(8)	124.3(4)	C(31)-C(32)-C(33)	125.2(3)
C(9)-C(8)-C(7)	113.3(3)	C(32)-C(33)-N(1)	123.5(3)
C(7)-C(10)-N(2)	111.4(3)	C(34)-C(33)-N(1)	110.8(3)
C(11)-C(10)-N(2)	124.3(3)	C(34)-C(33)-C(32)	125.6(3)
C(11)-C(10)-C(7)	123.9(3)	C(35)-C(34)-C(33)	125.2(3)
C(12)-C(11)-C(10)	123.6(3)	C(37)-C(34)-C(33)	106.8(3)
C(11)-C(12)-N(3)	125.1(4)	C(37)-C(34)-C(35)	127.9(4)
C(13)-C(12)-N(3)	113.4(3)	C(34)-C(35)-C(36)	115.0(4)
C(13)-C(12)-C(11)	121.4(3)	C(38)-C(37)-C(1)	125.5(3)
C(12)-C(13)-C(18)	100.1(3)	C(34)-C(37)-C(1)	106.6(3)
C(14)-C(13)-C(18)	113.7(3)	C(34)-C(37)-C(38)	127.7(3)
C(14)-C(13)-C(12)	112.7(3)	C(37)-C(38)-C(39)	112.2(3)

corrections.¹⁴ All computations were performed on the Atlas computer laboratory's ICL 1906A computer. Observed and calculated structure factors together with

the thermal parameters are available as Supplementary Publication No. 22369 (15 pp.).*

DISCUSSION

Interatomic distances, angles, and e.s.d.s are given in Table 3, and the molecular geometry and atom numbering are shown in Figure 1. The four Ni–N bond distances show considerable variation, from 1.930(3) to 1.953(3) Å. The N(1)–Ni–N(3) and N(2)–Ni–N(4) angles are significantly different from 180° [175.1(1), 176.7(1)°], and indicate a small distortion away from the normal square-planar nickel co-ordination generally observed in nickel(II) porphyrin complexes.^{15–18} A mean plane through the four nitrogen atoms confirms the lack of planarity within the co-ordination group (Table 4), and

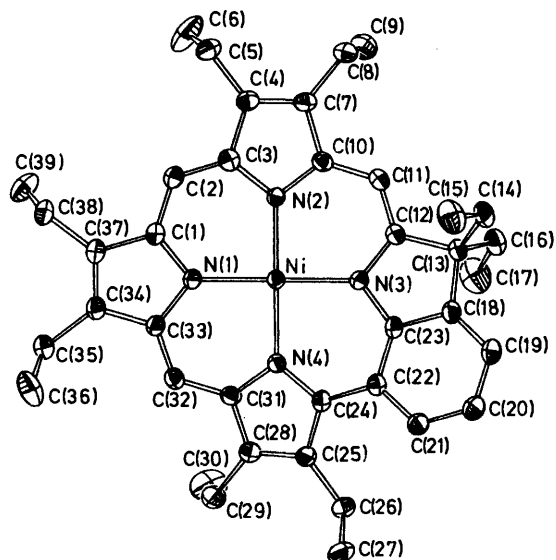


FIGURE 1 ORTEP drawing showing the atom numbering and molecular geometry of (7) with 35% thermal ellipsoids

the deviations of the nitrogen atoms from the mean plane suggest a departure from square planarity about the nickel atom. Each of the four five-membered rings is essentially planar, as too is the benzene ring (Table 5), with the two five-membered rings nearest to the benzene ring showing the larger deviations from planarity. The bond distances and angles of rings B, c, and D in (7) and the associated porphyrin skeleton are similar to those usually found in metalloporphyrin complexes,^{18,19} whereas in the remaining five-membered ring, the bond lengths and angles reflect the loss of conjugation.

It is of interest to compare the present structure with those of the two forms of octaethylporphyrinatonicel(II) (NiOPE). The tetragonal form of NiOEP¹⁷ is largely distorted from planarity and has an Ni–N distance of 1.929(3) Å which is very short for a metalloporphyrin.

* For details of the Supplementary Publications Scheme see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1977, Index issue.

¹⁵ E. B. Fleischer, *J. Amer. Chem. Soc.*, 1963, **85**, 146.

¹⁶ T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1965, **87**, 2305.

The triclinic form of NiOEP¹⁸ is essentially planar (the angle between planes of adjacent pyrrole rings is 2.1°

TABLE 4

Distances (Å) from the mean planes passing through (a) the four pyrrole nitrogen atoms N(1), N(2), N(3), N(4); (b) the five carbon atoms C(13), C(14), C(15), C(16), C(17)

	(a)		(b)
N(1)	–0.068	C(13)	–0.002
N(2)	0.069	C(14)	–0.010
N(3)	–0.069	C(15)	0.006
N(4)	0.068	C(16)	0.010
Ni	–0.014	C(17)	–0.004

TABLE 5

(i) Distances (Å) of atoms from the mean planes passing through the five-membered rings and benzene ring, and (ii) angles between the normals to these mean planes and the mean plane (6) through the co-ordination atoms [N(1), N(2), N(3), N(4)].

(i) Deviations from mean planes

(a) Plane 1: N(1), C(1), C(37), C(34), C(33)

N(1)	–0.011
C(1)	0.014
C(37)	–0.012
C(34)	0.006
C(33)	0.003

(b) Plane 2: N(2), C(3), C(4), C(7), C(10)

N(2)	0.006
C(3)	0.001
C(4)	–0.008
C(7)	0.011
C(10)	–0.010

(c) Plane 3: N(3), C(12), C(13), C(18), C(23)

N(3)	–0.007
C(12)	–0.014
C(13)	0.028
C(18)	–0.034
C(23)	0.028

(d) Plane 4: N(4), C(24), C(25), C(28), C(31)

N(4)	0.027
C(24)	–0.018
C(25)	0.001
C(28)	0.016
C(31)	–0.026

(e) Plane 5: C(18), C(19), C(20), C(21), C(22), C(23)

C(18)	0.013
C(19)	0.029
C(20)	–0.031
C(21)	–0.008
C(22)	0.049
C(23)	–0.052

(ii) Dihedral angles

Planes	Angle (°)	Planes	Angle (°)
1,6	10.8	1,4	18.0
2,6	11.4	1,5	27.4
3,6	15.8	2,3	19.8
4,6	20.6	2,4	31.8
5,6	17.8	2,5	24.0
1,2	17.6	3,4	28.1
1,3	26.3	3,5	5.2
		4,5	25.6

compared with an angle of 32.8° in the tetragonal form) and has an Ni–N distance of 1.958(2) Å. In both forms

¹⁷ E. F. Meyer, *Acta Cryst.*, 1972, **B28**, 2162.

¹⁸ D. L. Cullen and E. F. Meyer, *J. Amer. Chem. Soc.*, 1974, **96**, 2095.

¹⁹ J. L. Hoard, *Ann. N.Y. Acad. Sci.*, 1973, **206**, 18.

the nickel atom has square-planar co-ordination. As observed in the tetragonal form of NiOEP, and in contrast to the essentially planar metalloporphyrin structures usually observed, the present structure determination of (7) shows the macrocyclic ligand to be severely non-planar. This is evident from the side-view of the molecule shown in Figure 2. The angles between normals to mean planes through the five-membered rings and benzene ring and the mean N_4 co-ordination plane are given in Table 5.

Three of the Ni-N bond lengths in (7) [1.930(3), 1.932(3), and 1.937(3) Å] are comparable to the relatively short Ni-N (porphyrin) distance of 1.929(3) Å found in tetragonal NiOEP, and it can be postulated that the deformation of the macrocycle of (7) from planarity is necessary to decrease the Ni-N bond lengths. The normal radius of the cavity in an undistorted metalloporphyrin has been estimated to be 2.01 Å,²⁰ whereas the usual Ni-N bond length found in diamagnetic nickel(II) square-planar complexes is *ca.* 1.85 Å.²¹ Hence, the porphyrinato-core must contract from the ideal situation to accommodate a low-spin nickel(II) atom. It has been postulated^{19,20} that 1.96 Å is the smallest radius the porphyrin cavity may have in a planar structure and this is supported by experimental results; in triclinic NiOEP,¹⁸ the Ni-N distance is 1.958(2) Å, in nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester¹⁶ the Ni-N distance is 1.960(8) Å, in nickel(II) aetioporphyrin I¹⁵ the Ni-N distance is 1.957(13) Å, and all three compounds are essentially planar. In the cases where Ni-N distances significantly less than 1.96 Å are observed, in tetragonal NiOPE and in the present study of (9), as well as in three nickel(II) complexes of porphyrin-derived macrocyclic ligands [in 5,15-dimethyl-5,15-dihydro-octaethylporphyrinatonicel(II)²² with average Ni-N = 1.908(6) Å, and in two homoporphyrin nickel(II) complexes with average Ni-N = 1.879(4) Å²³ and with Ni-N = 1.886(4) Å (average of three distances, fourth Ni-N distance = 1.961(3) Å)²⁴], the macrocyclic ligands adopt severely nonplanar structures.

However, nonplanar porphyrin structures are also encountered in compounds in which there is no requirement to decrease the M-N distance (where M represents the centre of the porphyrin cavity) from the ideal 2.01 Å; for example in the tetragonal form of the free base 5,10,15,20-tetraphenylporphyrin (H_2TPP)²⁵ and in the square-planar copper(II) complex CuTPP²⁶ [the copper(II) atom is able to occupy the porphyrin cavity with Cu-N distances very close to the optimum 2.01 Å for undistorted accommodation, as seen in the average Cu-N distance of 2.000(5) Å in the essentially planar structure of copper(II) 5,10,15,20-tetra-n-propylporphyrin²⁷]. Hence it appears that packing forces also play an im-

portant role in determining the planar/nonplanar structures of the macrocyclic ligands. In tetragonal NiOEP,¹⁷ the nonplanarity is attributed to both intermolecular close contacts which would cause considerable strain in a reasonably dense planar structure and to the relief of strain caused by the small size of the nickel(II) atom. Similarly, in the present study, the nonplanarity of the ligand in (7) is probably a result of packing forces as well as strain caused by contraction of the co-ordination group due to the relatively small nickel(II) atom. Selected intramolecular contacts, together with all significant intermolecular contact distances involving non-hydrogen atoms are given in Table 6, and each intermolecular

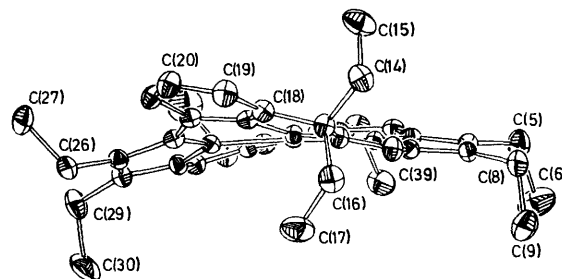


FIGURE 2 ORTEP drawing of (7) showing distortions of the porphyrin ligand from planarity and the conformations of the terminal ethyl groups (thermal ellipsoids are drawn for 35% probability)

contact is seen to involve a methylene or methyl carbon atom of a terminal ethyl group.

TABLE 6

(i) Selected intramolecular contacts (Å)			
N(1) ... N(3)	3.864	Ni ... C(2)	3.381
N(2) ... N(4)	3.882	Ni ... C(11)	3.348
N(1) ... N(2)	2.723	Ni ... C(22)	3.414
N(1) ... N(4)	2.775	Ni ... C(32)	3.344
N(2) ... N(3)	2.741		
N(3) ... N(4)	2.729		
(ii) Intermolecular contacts (Å) within the limits of the contact radii: Ni, 2.1 Å; C, N, 1.9 Å ^a			
C(36) ... C(26) ^I	3.749		
C(9) ... C(39) ^{II}	3.734		
C(14) ... Ni ^{II}	3.942		
C(14) ... N(1) ^{II}	3.636		
C(14) ... N(2) ^{II}	3.587		
C(14) ... C(1) ^{II}	3.714		
C(14) ... C(2) ^{II}	3.694		
C(14) ... C(3) ^{II}	3.561		
C(16) ... C(32) ^{II}	3.766		
C(16) ... C(33) ^{II}	3.520		
C(16) ... C(34) ^{II}	3.638		

^a Roman numeral superscripts refer to the following co-ordinate transformations:

$$\text{I} \quad -x, \frac{1}{2} + y, 1\frac{1}{2} - z \quad \text{II} \quad x, 1\frac{1}{2} - y, \frac{1}{2} + z$$

As seen from Figure 2, the carbon atoms of the *gem*-diethyl group attached to C(13) are essentially planar

²⁰ D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3761.

²¹ L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199.

²² P. N. Dwyer, J. W. Buchler, and W. R. Scheidt, *J. Amer. Chem. Soc.*, 1974, **96**, 2789.

²³ B. Chevrier and R. Weiss, *Inorg. Chem.*, 1976, **15**, 770.

²⁴ B. Chevrier and R. Weiss, *J. Amer. Chem. Soc.*, 1975, **97**, 1416.

²⁵ M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1964, **86**, 1938.

²⁶ E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, 1964, **86**, 2342.

²⁷ I. Moustakali and A. Tulinsky, *J. Amer. Chem. Soc.*, 1973, **95**, 6811.

(Table 4), the angle between the normals to this mean plane [C(13), C(14), C(15), C(16), C(17)] and to the mean co-ordination plane [N(1), N(2), N(3), N(4)] being 72.7°.

EXPERIMENTAL

N.m.r. spectra were measured for solutions in [²H]-chloroform and u.v.-visible spectra for solutions in chloroform (except where otherwise stated) with instruments listed in the earlier paper.² Mass spectra were determined with an A.E.I. MS30 instrument by direct insertion into the ion source.

Nickel meso- α -Hydroxybenzyl-aetioporphyrin I (1d).—Allyl triphenylphosphonium chloride (55 mg) was treated with phenyl-lithium (0.042 ml of 3M in ether) under nitrogen in tetrahydrofuran (25 ml; dried over LiAlH₄). After 20 min, solid nickel *meso*-formyl-aetioporphyrin I (47.5 mg) was added and the mixture stirred at room temperature for 18 h. Water (10 ml) and benzene (30 ml) were added and the organic layer separated, dried, and chromatographed on alumina using 20% chloroform–light petroleum for elution. The main band was separated, the solvent removed, and the residue crystallised from dichloromethane–methanol to give the *product* as red-violet crystals (11 mg, 20%), m.p. 193–195 °C (Found: C, 73.2; H, 6.1; N, 9.0. C₃₉H₄₂N₄NiO requires C, 73.0; H, 6.5; N, 8.75%), *m/e* 640 (M⁺), λ 346, 408, 536, and 578 nm (ϵ 15 300, 162 880, 9 130, and 15 055 respectively); δ_{H} 1.67 (m, CH₃ of peripheral Et), 3.27, 3.32, and 3.35 (all s, 1 : 1 : 2, peripheral Me), 3.45 (s, OH, exchangeable with D₂O), (q, CH₂ of peripheral Et), 6.50 (m, phenyl H's), 7.69br (s, benzyl H), and 9.41 (s, 3 *meso*-H).

meso-(β -Methoxycarbonylvinyl)OEP (2o).—The nickel complex (2i) was prepared following Callot⁴ from nickel *meso*-formylOEP (2a) and methoxycarbonylmethylene-(triphenyl)phosphorane. The product (2i) (100 mg) was stirred in concentrated sulphuric acid (5 ml) at room temperature for 2 h and then poured into ice–water and neutralised with sodium hydrogen carbonate. The porphyrin-free base was extracted into chloroform, the extract dried, and the solvent evaporated. The residue was chromatographed on alumina, using 20% hexane–chloroform for elution. The major red fraction was collected, evaporated, and the *product* crystallised from dichloromethane–methanol as red needles, m.p. 208–210 °C (78 mg, 85%) (Found: N, 9.05. C₄₀H₅₀N₄O₂ requires N, 9.05%). Carbon values for this compound were consistently low; λ_{max} 408, 509, 542, 579, and 631 nm (ϵ 145 000, 11 300, 6 200, 5 700, and 2 400 respectively); δ_{H} –3.1br (NH), 1.66, 1.82, and 1.87 (overlapping t, CH₃ of peripheral Et), 3.93 (s, ester CH₃), 4.0 (q, CH₂ of peripheral Et), 6.18 (d, *J* = 15 Hz, α -H of acrylic ester), 9.89 and 10.05 (both s, 1 : 2, *meso*-H), and 10.38 (d, *J* = 15 Hz, β -H of acrylic ester); ν_{max} 1 640 (C=C) and 1 721 cm⁻¹ (C=O).

meso-(β -Methoxycarbonylvinyl)aetioporphyrin I (1d) and the Nickel Complex (1e).—A solution of nickel *meso*-formyl-aetioporphyrin I¹ (300 mg) and methoxycarbonylmethylene-(triphenyl)phosphorane (800 mg) in xylene (24 ml) was heated under reflux for 18 h. The product was cooled and then chromatographed on silica using benzene for elution. A small fraction of nickel aetioporphyrin I was eluted first and was followed by the main band which was collected. After removal of solvent *in vacuo*, the residue was crystallised from dichloromethane–methanol when the *product* (1d) was obtained as small brown needles, m.p. 235–

236 °C (225 mg, 68%) (Found: C, 69.5; H, 6.55; N, 9.0. C₃₈H₄₀N₄NiO₂ requires C, 69.8; H, 6.5; N, 9.05%), λ_{max} 404, 530, and 566 nm (ϵ 121 338, 9 415, and 13 390); ν_{max} (KBr) 1 730 cm⁻¹; δ_{H} 1.68 (m, CH₃ of peripheral Et), 3.28, 3.30, and 3.35 (all s, 1 : 1 : 2, peripheral Me), 3.80 (q, CH₂ of peripheral Et), 3.83 (s, ester CH₃), 5.26 (d, β -H of acrylic ester, *J* = 15.5 Hz), 9.48 (s, 3 *meso*-H), and 10.20 (d, α -H of acrylic ester, *J* = 15.5 Hz).

A solution of the nickel complex (50 mg) was dissolved in concentrated sulphuric acid (3 ml) and kept for 1 h at room temperature. The solution was then poured into cold chloroform and neutralised with saturated aqueous sodium hydrogen carbonate. The chloroform layer was separated and the aqueous layer extracted with more chloroform. The combined chloroform extracts were washed and dried and the solvent removed. The residue was purified by chromatography on silica plates using 70% light petroleum–chloroform for elution. Crystallisation of the product from dichloromethane–methanol gave the *product* (1e) as small brown needles (24 mg, 99%), m.p. 253–255 °C (Found: C, 76.75; H, 7.3; N, 9.95. C₃₈H₄₂N₄O₂ requires C, 76.85; H, 7.5; N, 9.95%), ν_{max} (KBr) 1 730 cm⁻¹; λ 406, 506, 540, 576, and 630 nm (ϵ 121 480, 9 860, 5 100, 4 750, and 1 580); δ_{H} –3.1br (s, NH), 1.70 (m, CH₃ of peripheral Et), 3.45, 3.48, and 3.50 (all s, 1 : 1 : 2 peripheral CH₃), 3.89 (q, CH₂ of peripheral Et), 3.93 (s, ester CH₃), 6.18 (d, β H of acrylic ester, *J* = 15 Hz), 9.80 (s, 1 *meso*-H), 9.98 (s, 2 *meso*-H), and 10.34 (d, α -H of acrylic ester, *J* = 15 Hz).

meso-(4-Methoxycarbonylbuta-1,3-dienyl)aetioporphyrin I and its Nickel Complex (1f).—A solution of nickel *meso*-formyl-aetioporphyrin I (150 mg) and the phosphorane (384 mg) derived from triphenylphosphine and methyl γ -bromocrotonate in xylene (12 ml) was heated under reflux for 15 h. The product was cooled and chromatographed on silica using benzene for elution. A minor fraction of nickel aetioporphyrin I was eluted first and the main fraction was then collected. After removal of the solvent *in vacuo*, the residue was crystallised from dichloromethane–methanol when the *product* (1f) was obtained as small brown crystals, m.p. 214 °C (82.5 mg, 50%) (Found: C, 70.25; H, 6.8; N, 8.6. C₃₈H₄₂N₄NiO₂ requires C, 70.7; H, 6.55; N, 8.65%), λ_{max} 404, 533, and 563 nm (ϵ 69 120, 6 530, and 9 220), *m/e* 644 (M⁺); ν_{max} (KBr) 1 720 cm⁻¹; δ_{H} 1.66 (m, CH₃ of peripheral Et), 3.20, 3.27, and 3.29 (all s, 1 : 1 : 2, peripheral CH₃), 3.68 (q, CH₂ of peripheral Et), 3.70 (s, ester CH₃), 5.51 (dd, β -H of *meso*-butadienyl chain, *J* _{α H- β H} 14.5 Hz), 5.68 (d, δ -H of *meso*-butadienyl chain, *J* _{γ H- δ H} 16 Hz), 7.80 (dd, γ -H of *meso*-butadienyl chain, *J* _{β H- γ H} 11 Hz), 9.10 (d, α -H of *meso*-butadienyl chain, *J* _{α H- β H} 14.5 Hz), and 9.40 (s, 3 *meso*-H).

The above nickel complex (45 mg) was dissolved in concentrated sulphuric acid (3 ml) and kept at room temperature for 1 h. The acid solution was then poured slowly onto ice and chloroform and cautiously neutralised with saturated aqueous sodium hydrogen carbonate. The chloroform layer was separated, washed, dried, and the solvent removed under reduced pressure. The residue was chromatographed on silica plates using 30% chloroform–light petroleum for elution. After removal of the solvent from the main fraction, the residue was crystallised from dichloromethane–methanol when it formed small brown needles (38 mg, 93%) (Found: C, 77.2; H, 7.4; N, 9.55. C₃₈H₄₄N₄O₂ requires C, 77.5; H, 7.55; N, 9.5%), *m/e* 590 (M⁺); ν_{max} (KBr) 1 720 cm⁻¹; δ_{H} –3.2br (s, NH), 1.72 (m, CH₃ of peripheral Et), 3.52, 3.55, and 3.58 (all s, 1 : 1 : 2, peri-

peral CH₃), 3.82 (s, ester CH₃), 3.92 (q, CH₂ of peripheral Et), 5.93 (d, δ-H of *meso*-butadienyl chain, $J_{\gamma\text{H}-\delta\text{H}} = 16$ Hz), 6.49 (dd, β-H of *meso*-butadienyl chain, $J_{\alpha\text{H}-\beta\text{H}} 14$ Hz), 8.03 (dd, γ-H of *meso*-butadienyl chain, $J_{\beta\text{H}-\gamma\text{H}} 11$ Hz), 9.51 (d, α-H of *meso*-butadienyl chain, $J_{\alpha\text{H}-\beta\text{H}} 14$ Hz), and 9.83 and 9.90 (both s, 1 : 2, 3 *meso*-H).

Nickel meso-(4-Formylbuta-1,3-dienyl)etioporphyrin I (1g).—The nickel complex (1f) (50 mg) in dry tetrahydrofuran (12 ml) was treated with aluminium hydride in tetrahydrofuran (1 ml) [prepared from LiAlH₄ (12 mg) and AlCl₃ (10.3 mg) in tetrahydrofuran (2.4 ml)] in an atmosphere of nitrogen and the mixture stirred for 30 min. The product was treated with ether (10 ml) containing water (0.5 ml) and the organic layer was separated, dried, and the solvent removed. The product was chromatographed on alumina using 30% light petroleum–chloroform for elution. The main fraction was separated, the solvent removed, and the residue crystallised to give the product as dark reddish green needles, m.p. 210–211 °C (14 mg, 27%) (Found: C, 71.8; H, 6.5; N, 9.05. C₃₇H₄₀N₄SiO requires C, 72.2; H, 6.55; N, 9.1%). m/e 614 (M^+); ν_{max} (KBr) 1 675 cm⁻¹; λ_{max} 400, 430, 566, and 594 nm (ϵ 46 530, 35 790, 7 340, and 6 800 respectively).

Nickel meso-Vinylaeioporphyrin I (1h).—Methyltriphenylphosphonium iodide (510 mg) was treated with phenyl-lithium (0.4 ml of 3*M*-etheral solution) in dry tetrahydrofuran (50 ml) in an atmosphere of nitrogen. After stirring for 10 min, solid *meso*-formylaeioporphyrin I (200 mg) was added and the stirring continued for 18 h. Water (20 ml) was added followed by benzene (20 ml) and the organic layer was separated, washed, dried, and the solvent removed under reduced pressure. The residue was chromatographed on alumina using 20% chloroform–light petroleum for elution. The main fraction was separated, the solvent removed, and the residue crystallised from dichloromethane–methanol when the *product* (140 mg, 70%) was obtained as long dark red needles (Found: C, 72.6; H, 6.8; N, 10.0. C₃₄H₃₈N₄Ni requires C, 72.75; H, 6.8; N, 10.0%), m/e 560 (M^+); λ_{max} 404, 530, and 566 nm (ϵ 160 110, 10 510, and 16 340 respectively), δ_{H} 1.67 (m, CH₃ of peripheral Et), 3.23, 3.27, and 3.30 (all s, 1 : 1 : 2, peripheral CH₃), 3.78 (q, CH₂ of peripheral Et), 4.5 (dd, *trans*-β-H of vinyl), 5.78 (dd, *cis*-β-H of vinyl), 9.02 (dd, α-H of vinyl; $J_{\text{trans}} 19$ Hz, $J_{\text{cis}} 10.5$ Hz, $J_{\text{gem}} 2$ Hz), and 9.47 (s, 3 *meso*-H).

Nickel meso-PropenylOEP (2j).—Ethyltriphenylphosphonium iodide (240 mg) was dissolved in dry tetrahydrofuran (30 ml) and phenyl-lithium (0.19 ml of a 3*M*-solution in ether) was added under nitrogen. After the mixture had been stirred for 10 min, solid nickel *meso*-formylOEP (2a) (120 mg) was added and the stirring continued overnight in an atmosphere of nitrogen; the mixture was then worked up in the usual manner. After removal of the organic solvent the residue was chromatographed on alumina using 30% hexane–chloroform for elution. The main red fraction was separated, the solvent removed, and the residue crystallised from dichloromethane–methanol to give the product as dark red needles, m.p. 275–277 °C (54 mg, 44%) identical in all respects with the product prepared earlier³ from (2a) and triethyl phosphite.

Nickel meso-StyrylOEP (2k).—Benzyl(triphenyl)phosphonium chloride (230 mg) was dissolved in dry tetrahydrofuran (30 ml) under nitrogen and phenyl-lithium (0.2 ml of a 3*M* solution in ether) was added and the mixture stirred for 10 min. Solid nickel *meso*-formylOEP (120 mg) was then added to the orange ylide solution and after being

stirred overnight in an atmosphere of nitrogen, the mixture was worked up in the usual manner. The residue from the organic extract after removal of solvent was chromatographed on alumina and eluted with 30% hexane–chloroform. The major red fraction was separated, solvent removed, and the residue crystallised from dichloromethane–methanol to yield the *product* as shining red prisms, m.p. 250–252 °C (66 mg, 49%) (Found: C, 76.5; H, 7.5; N, 8.25. C₄₄H₅₀N₄Ni requires C, 76.2; H, 7.25; N, 8.1%); λ_{max} 335, 407, 532, and 568 nm (ϵ 16 700, 154 000, 11 800, and 16 740); δ_{H} 1.62–1.73 (overlapping t, CH₃ of peripheral Et), 3.77 (q, CH₂ of peripheral Et), 5.66 (d, $J = 16.5$ Hz, styryl β-H), 7.15–7.55 (m, 5 H, phenyl H), 9.35 (d, $J = 16.5$ Hz, styryl α-H), and 9.36 and 9.38 (both s, 1 : 2, *meso*-H).

Nickel meso-Styrylaeioporphyrin I (1i).—This compound was prepared similarly from nickel *meso*-formylaeioporphyrin I (1a) (80 mg) and benzyltriphenylphosphonium chloride (55 mg). The residue from the organic extract after removal of solvent was chromatographed on silica plates using 90% light petroleum–chloroform for elution. The solvent was removed and the residue crystallised from dichloromethane–methanol when the *product* was obtained as red needles, m.p. 213–215 °C (53 mg, 59%) (Found: C, 75.15; H, 6.55; N, 8.7. C₄₀H₄₂N₄Ni requires C, 75.35; H, 6.65; N, 8.8%), m/e 636 (M^+); λ_{max} 405, 528, and 566 nm (ϵ 123 290, 8 450, and 12 780); ν_{max} 1 600 and 1 500 cm⁻¹; δ_{H} 1.68 (m, CH₃ of peripheral Et), 3.25, 3.31, and 3.36 (all s, 1 : 1 : 2, peripheral CH₃), 3.8 (q, CH₂ of peripheral Et), 5.68 (d, $J = 15$ Hz, styryl β-H), 7.42 (m, phenyl H), 9.38 (d, $J = 15$ Hz, styryl α-H), and 9.48 (s, 3 *meso* H).

Nickel meso-*p*-Methylstyrylaeioporphyrin I (1j).—This compound was prepared as above from (1a) (100 mg) and *p*-methylbenzyl(triphenyl)phosphonium chloride (326 mg), the product was purified by chromatography on alumina using 70% light petroleum–chloroform for elution. After removal of solvent from the main fraction, the residue was crystallised from dichloromethane–methanol when it formed small red needles, m.p. 259–260 °C (81 mg, 70%) (Found: C, 75.65; H, 6.45; N, 8.6. C₄₁H₄₄N₄Ni requires C, 75.6; H, 6.8; N, 8.6%), λ_{max} 404, 530, and 564 nm (ϵ 128 310, 9 570, and 13 645 respectively); δ_{H} 1.67 (m, CH₃ of peripheral Et), 2.38 (s, *p*-tolyl CH₃), 3.25, 3.32, and 3.36 (all s, 1 : 1 : 2, peripheral CH₃), 3.79 (q, CH₂ of peripheral Et), 5.65 (d, $J = 15.5$ Hz, styryl β-H), 7.40 (m, phenyl H), 9.38 (d, $J = 15.5$ Hz, styryl α-H), and 9.52 (s, 3 *meso*-H).

Nickel 5-(β-Formylvinyl)OEP (2l) and 10-(5) and 15-Formyl Derivatives.—Phosphorus oxychloride (2.5 ml) was added dropwise with stirring to dry *NN*-dimethylformamide (1.8 ml) at 0 °C and the mixture kept at room temperature for 30 min, when a solution of nickel *meso*-vinylOEP (2 h) (180 mg) in dry dichloroethane (40 ml) was added during 5 min; the colour of the solution changed rapidly from red to green. The mixture was stirred for 10 min and then saturated aqueous sodium acetate (40 ml) was added to it and the stirring continued for a further 15 min. The organic layer was separated, washed with water, dried, and evaporated. The residue was chromatographed on alumina using 40% hexane–chloroform and the major green fraction was collected, the solvent removed, and the residue crystallised from dichloromethane–methanol to give dark green needles, m.p. 240–243 °C (150 mg, 80%) (Found: C, 72.55; H, 7.1; N, 9.0. C₃₉H₄₆N₄NiO requires C, 72.55; H, 7.2; N, 8.7%), λ_{max} 337, 409, 434, 540sh, 571, and 602sh nm (ϵ 16 540, 62 200,

63 300, 6 390, 9 660, and 7 560 respectively); δ_{H} 1.60—1.62 (overlapping t, CH_3 of peripheral Et), 3.50—3.69 (overlapping q, CH_2 of peripheral Et), 5.43 (dd, β -H of acrylaldehyde), 9.30 (s, 3 *meso*-H), 9.63 (d, α -H of acrylaldehyde, $J = 16$ Hz), and 9.78 (d, formyl H, $J = 8$ Hz); ν_{max} 1 670 cm^{-1} (C=O).

Following the major green band on the chromatogram there were two other green bands which were separated and purified further by preparative t.l.c. on silica-gel plates using 30% hexane-chloroform for elution. The less polar component was separated and crystallised from dichloromethane-methanol as shining dark green needles (10 mg, 5%), m.p. 217—219 °C (Found: C, 71.55; H, 7.2; N, 8.3. $\text{C}_{40}\text{H}_{46}\text{N}_4\text{NiO}_2$ requires C, 71.35; H, 6.9; N, 8.3%), λ_{max} 338br, 441, and 660br nm (ϵ 15 490, 65 730, and 9 750 respectively); δ_{H} 1.44—1.58 (overlapping t, CH_3 of peripheral Et), 3.48—3.51 (overlapping q, CH_2 of peripheral Et), 5.48 (dd, β -H of acrylaldehyde), 8.95 and 9.00 (both s, 2 *meso*-H), 9.45 (d, α -H of acrylaldehyde, $J = 16$ Hz), 9.78 (d, formyl-H, $J = 8$ Hz), and 11.60 (s, 15-formyl H). The more polar component was purified similarly and was also obtained as dark green needles (3 mg, 15%) which had δ_{H} 1.52, 1.60 (t, CH_3 of peripheral Et), 3.52—3.56 (overlapping q, CH_2 of peripheral Et), 5.51 (dd, β -H of acrylaldehyde), 8.96 (s, 2 *meso*-H), 9.42 (d, α -H of acrylaldehyde, $J = 16$ Hz), 9.74 (d, formyl H, $J = 8$ Hz), and 11.61 (s, 10-formyl H).

meso-(β -Formylvinyl)OEP (2n).—The foregoing nickel complex (47 mg) was stirred for 3 min in concentrated sulphuric acid (3 ml), poured onto ice, neutralised with sodium hydrogen carbonate, and extracted with chloroform. The extract was chromatographed on alumina using more chloroform for elution when the cyclised product (7) was obtained as an initial green band followed by the demetallated product as a brown band. The latter was separated and the product isolated and crystallised from dichloromethane-methanol to give greenish brown needles (16 mg, 37%), m.p. 227—230 °C (Found: C, 78.8; H, 8.4; N, 9.75. $\text{C}_{39}\text{H}_{48}\text{N}_4\text{O}$ requires C, 79.55; H, 8.2; N, 9.5%); λ_{max} 383infr, 410, 510, 543, 581, and 632 nm (ϵ 61 500, 104 500, 10 500, 5 850, 6 800, and 3 950 respectively); δ_{H} -2.87br (NH), 1.61—1.81 (overlapping t, CH_3 of peripheral Et), 3.85, 3.93, and 3.95 (overlapping q, CH_2 of peripheral Et), 6.39 (dd, α -H of acrylaldehyde), 9.87 and 10.00 (both s, 1 : 2, *meso*-H), 10.22 (d, CHO), and 10.27 (d, β -H of acrylaldehyde); ν_{max} 1 687v, strong, sharp band cm^{-1} (C=O).

Nickel *meso*-(β -Formylvinyl)aetioporphyrin I (1l).—By a similar method, nickel *meso*-vinylaetioporphyrin I (180 mg) was converted into the *meso*- β -formylvinyl derivative. The product was purified by chromatography on alumina using 20% light petroleum-chloroform for elution. After removal of solvent from the main fraction, the residue was crystallised from dichloromethane-methanol when it formed dark green needles, m.p. 225—226 °C (150 mg, 79%) (Found: C, 71.15; H, 6.95; N, 9.75. $\text{C}_{35}\text{H}_{38}\text{N}_4\text{NiO}$ requires C, 71.45; H, 6.35; N, 9.5%), m/e 588 (M^+); λ_{max} 408, 436, 536, 560, and 592 nm (ϵ 77 560, 87 040, 6 240, 8 660, and 5 970); ν_{max} (KBr) 1 680 cm^{-1} ; δ_{H} 1.68 (m, CH_3 of peripheral Et), 3.23, 3.28, and 3.32 (all s, 1 : 1 : 2, peripheral CH_3), 3.74 (q, CH_2 of peripheral Et), 5.58 (dd, $J_{\alpha\text{H}-\beta\text{H}} = 15.5$ Hz, β -H of acrylaldehyde), 9.40 (s, 3 *meso*-H), 9.68 (d, $J = 15$ Hz, α -H of acrylaldehyde), and 9.92 (d, formyl H; $J_{\beta\text{H}-\gamma\text{H}} 7$ Hz).

Nickel *meso*-(3-Hydroxypropenyl)OEP (2m).—Nickel *meso*-(β -formylvinyl)OEP (21) (103 mg) was reduced with

sodium borohydride (5 mg) in tetrahydrofuran (25 ml) containing water (0.5 ml) at room temperature. After 10 min the colour of the solution changed from green to red and after 1 h water (5 ml) was added followed by benzene (30 ml). The organic layer was separated, washed, dried, and the solvent removed. The residue was chromatographed on silica plates using 20% light petroleum-chloroform for elution. The main fraction was separated, the solvent removed, and the residue crystallised from dichloromethane-methanol to yield the product as dark red needles, m.p. 234—235 °C (80 mg, 77%) (Found: C, 69.0; H, 6.55; N, 9.15. $\text{C}_{39}\text{H}_{48}\text{N}_4\text{NiO}$ requires C, 69.2; H, 6.65; N, 9.2%); m/e 646 (M^+); λ_{max} 404, 530, and 567 nm (ϵ 139 500, 9 420, and 14 500 respectively); δ_{H} 1.52 (s, OH, exchangeable with D_2O), 1.70 and 1.78 (both t, CH_3 of peripheral Et), 3.45 (s, OH, exchangeable with D_2O), 3.82 (q, CH_2 of peripheral Et), 4.45 (d, propenyl CH_2), 4.98 (d, $J = 15$ Hz, β -H of propenyl), 9.18 (d, $J = 15$ Hz, α -H of propenyl), and 9.42 (s, 3-*meso*-H).

Nickel *meso*-(3-Hydroxypropenyl)aetioporphyrin I (1m).—Nickel *meso*-(β -formylvinyl)aetioporphyrin I (1l) (90 mg) was reduced similarly and gave the *carbinol* as red needles, m.p. 230—231 °C (68 mg, 75%) (Found: C, 70.9; H, 6.5; N, 9.55. $\text{C}_{35}\text{H}_{40}\text{N}_4\text{NiO}$ requires C, 71.05; H, 6.8; N, 9.45%); m/e 592 (M^+); λ_{max} 404, 530, and 566 nm (ϵ 141 540, 9 640, and 14 970 respectively); δ_{H} 1.48 (s, OH), 1.66 (m, CH_3 of peripheral Et), 3.23, 3.32, and 3.35 (all s, 1 : 1 : 2, peripheral CH_3), 3.78 (q, CH_2 of peripheral Et), 4.46 (d, propenyl CH_2 , collapses to s in presence of D_2O), 4.98 (d, β -H of propenyl; $J_{\alpha\text{H}-\beta\text{H}} 15$ Hz), 8.98 (d, α -H of propenyl; $J_{\alpha\text{H}-\beta\text{H}} 15$ Hz), and 9.49 (s, 3 *meso*-H).

Nickel *meso*-(3-Hydroxypropyl)aetioporphyrin I (1n).—Nickel *meso*-(β -methoxycarbonylvinyly)aetioporphyrin I (1e) (75 mg) was treated with lithium aluminium hydride in dry tetrahydrofuran (20 ml) and heated under reflux for 3 h. Ether and aqueous ammonium chloride were added and the organic layer separated and dried. After removal of solvent the residue was chromatographed on silica plates when three fractions were obtained. Each was separated, solvent removed, and the products crystallised from chloroform-methanol. The fastest-running product was identified as nickel *meso*-(β -formylvinyl)aetioporphyrin I (1l) (5 mg) by direct comparison with an authentic specimen (above). The second product was similarly identified as nickel *meso*-(3-hydroxypropyl)aetioporphyrin I (1m) (9 mg) and the final product (1n) (26 mg, 36%) was nickel *meso*-(3-hydroxypropenyl)aetioporphyrin I, m.p. 239—240 °C (Found: C, 70.4; H, 7.25; N, 9.5. $\text{C}_{35}\text{H}_{42}\text{N}_4\text{NiO}$ requires C, 70.85; H, 7.15; N, 9.45%), m/e 594 (M^+); λ_{max} 338, 410, 538, and 574 nm (ϵ 11 410, 136 990, 8 370, and 10 080 respectively); δ_{H} 1.22 (m, propyl β - CH_2), 1.72 (CH_3 of peripheral Et), 2.29 (t, propyl γ - CH_2), 3.28, 3.30, and 3.34 (all s, 1 : 1 : 2 peripheral CH_3), 3.82 (q, CH_2 of peripheral Et), 4.62 (t, propyl α - CH_2), and 9.40 (3 *meso*-H).

Nickel *meso*-Buta-1,3-dienylOEP (2r).—Methyl-(triphenyl)phosphonium iodide (200 mg) was stirred in dry tetrahydrofuran (20 ml) under nitrogen and an ethereal solution of phenyl-lithium (0.2 ml of 3M) was added. After the mixture had been stirred for 10 min, solid nickel *meso*- β -formylvinylOEP (2o above) (100 mg) was added with stirring when the initial green colour rapidly changed to red. The stirring was continued for a further 2 h, when the mixture was worked up as usual and the product after removal of solvent subjected to chromatography on alumina using 30% hexane-chloroform for elution. The major red fraction was

separated, the solvent removed, and the residue crystallised from dichloromethane-methanol when it was obtained as long red needles, m.p. 208–210 °C (75 mg, 75%) (Found: C, 74.7; H, 7.45; N, 8.95. $C_{40}H_{48}N_4Ni$ requires C, 74.7; H, 7.5; N, 8.7%), λ_{max} 338, 408, 534, and 568 nm (ϵ 15 100, 130 600, 10 390, and 14 970 respectively); δ_H 1.61–1.71 (overlapping t, CH_3 of peripheral Et), 3.75 (q, CH_2 of peripheral Et), 4.86–5.48 [m, 2'-H + 2(4'-H)], 6.75 (dt, 3'-H), 8.8 (d, 1'-H), and 9.33 and 9.35 (both s, 1:2, 3 *meso*-H).

Formation of the Nickel Complex (7). (i) *From Nickel meso- β -FormylvinylOEP.*—Nickel β -formylvinylOEP (2l) (100 mg) was stirred for 2 h in concentrated sulphuric acid (10 ml). The mixture was poured into ice-water (200 ml), neutralised with saturated aqueous sodium hydrogen carbonate, and extracted with chloroform to give a green solution. After the chloroform extract had been washed with water, it was dried and evaporated and the residue was chromatographed on alumina using 30% hexane-chloroform for elution. The major green band was collected and the product purified further by preparative t.l.c. on silica using chloroform for elution. After removal of solvent the residue was crystallised from dichloromethane-methanol, and the product was obtained as shining dark blue rods (40 mg, 41%), m.p. 224–225 °C (Found: C, 74.35; H, 7.55; N, 9.15. $C_{39}H_{46}N_4Ni$ requires C, 74.4; H, 7.35; N, 8.9%); λ_{max} 364, 416, 500, 566, 625, and 677 nm (ϵ 8 860, 69 250, 5 020, 4 190, 9 780, and 36 730 respectively); ν_{max} 1 645 cm^{-1} ; δ_H 0.04 (t, CH_3 of *gem*-Et₂ groups), 1.42, 1.45, 1.48, and 1.49 (overlapping t, CH_3 of peripheral Et), 2.28 (q, CH_2 of *gem*-Et₂ groups), 3.23, 3.31, 3.33, and 3.52 (overlapping d br q, CH_2 of peripheral Et), 7.70br (d, 2 H of benzene ring), 7.72, 8.45, and 8.82 (s, 3 *meso*-H), and 8.9br (t, 1 H of benzene ring); *m/e* 628 (100%), 599 (95), 584 (16), and 569 (20); δ_C 8.40 (q, CH_3 of *gem*-Et₂), 16.07–21.45 (peripheral Et), 35.04 (t, CH_2 of *gem*-Et₂), 59.12 (s, C bearing *gem* Et₂), 88.39, 98.04, and 106.88 (all d, 3 *meso*-C), 112.31 (s, quaternary *meso*-C), 117.65, 119.94, and 123.48 (all d, C of benzene ring), 133.18 (1), 135.03 (2), 135.71 (1), 137.84 (1), 139.25 (1), 140.03 (2), 141.53 (1), 141.92 (1), 142.50 (1), 143.14 (1), 144.35 (2), 147.94 (1), and 164.64 (1) (all s, ring Cs).

(ii) *From Nickel meso-(3-Hydroxypropenyl)OEP.*—The nickel complex (2m) (45 mg) in *NN*-dimethylformamide (7 ml) containing sulphuric acid (3 drops of concentrated) was heated under reflux for 3 h. After 10 min the colour of the solution changed from red to green. The reaction mixture was poured into ice-water (100 ml) and the product extracted into chloroform. The extract was separated, dried, and the solvent removed. The residue was chromatographed on alumina using 70% light petroleum-chloroform for elution. The major green fraction was collected, the solvent removed, and the residue crystallised from dichloromethane-methanol to give the complex (7) as small greenish blue prisms (13 mg, 28%) identical in all respects with the product of the previous experiment.

Cyclisation of meso- β -FormylvinylOEP to (6a).—The aldehyde (2n) (16 mg) was heated with acetic acid (4 ml) under reflux in a nitrogen atmosphere for 20 h. The acetic acid was distilled off and the resulting oil extracted with chloroform and the extract washed with aqueous sodium hydrogen carbonate and water and then dried and concentrated. The product was then chromatographed on a column of alumina, using chloroform for elution, which gave a minor green band followed by a major greenish brown

band. This was separated, the solvent removed, and the residue crystallised from dichloromethane-methanol when it formed brown micropisms (4 mg, 25%), m.p. 223–226 °C, which was identified as the purpurin (6a) on spectral evidence, λ_{max} 440, 505, 554, 592, 672, and 734 nm (intensity ratios 9.9, 1.1, 1, 1.65, 1.15, and 4.15 respectively); δ_H 0.2 (t, one CH_3 of peripheral Et), 1.62br (overlapping t, CH_3 of peripheral Et), 2.35br (q, 2 CH_2 of peripheral Et), 3.65br (overlapping q, CH_2 of peripheral Et), 4.15 (m, H-2), 8.83 (s, H of isocyclic ring), 9.09, 9.28, and 9.32 (all s, 3 *meso*-H), and 10.16 (s, CHO), *m/e* 588 (95%) and 559 (100) ($C_{39}H_{48}N_4O$ requires *M*, 588).

Cyclisation of meso- β -MethoxycarbonylvinylOEP to (6b).—(i) The porphyrin *meso*-acrylic ester (2o) (74 mg) was heated under reflux in glacial acetic acid (20 ml) in an atmosphere of nitrogen for 24 h. The solvent was distilled off and the residue dissolved in dichloromethane; the extract was washed several times with water, dried, and evaporated. The residue was chromatographed on alumina using 40% hexane-chloroform for elution and the major reddish brown band was separated. In solution, the product appeared red in bulk, but green in thin sections. After removal of solvent, the residue was crystallised from dichloromethane-methanol when it formed brown microneedles, m.p. 243–245 °C (40 mg, 54%) (Found: N, 8.95. Calc. for $C_{40}H_{50}N_4O_2$: N, 9.05%), λ_{max} 415infl, 430, 503, 573, 652, and 704infl nm (ϵ 87 500, 142 800, 5 700, 6 960, 14 300, 6 600, and 41 000 respectively); δ_H -1.10br (NH), -0.44 (t, one CH_3 of 1,2 Et groups), 1.65–1.79 (overlapping t, CH_3 of remaining Et), 2.5, 3.1 (m, CH_2 of 1,2 Et groups), 3.7–3.8 (overlapping q, CH_2 of peripheral Et), 3.98 (s, ester CH_3), *ca.* 4.0 (m, 2-H), 8.66 (s, H of isocyclic ring), and 9.35, 9.40, and 9.42 (all s, 3 *meso*-H).

(ii) The porphyrin *meso*-acrylic ester was heated under reflux for 3 days in dry toluene but there was no evidence of cyclisation and the starting product was recovered unchanged.

Nickel meso-(Hept-1-enyl)aetioporphyrim I (1k).—A suspension of 1,2-bis(triphenylphosphonium)ethane dibromide (91 mg) in anhydrous tetrahydrofuran (50 ml) was treated with *n*-butyl-lithium (0.48 ml of a 0.35M-hexane solution) in a nitrogen atmosphere. After 10 min, solid nickel meso-formylaetioporphyrim I¹ (100 mg) was added with vigorous stirring, which was continued for another 30 min, after which the mixture was heated under reflux for 30 min. It was cooled, benzene (100 ml) was added, and the product poured into water. The benzene layer was separated, washed, dried, and the solvent removed. The residue was chromatographed on alumina using 50% chloroform-light petroleum (b.p. 60–80°) for elution. The first red fraction was collected and purified further by preparative t.l.c. on silica using 25% chloroform-light petroleum for elution. The major purple-red band was separated and the product crystallised from dichloromethane-methanol to give purple plates (41 mg, 39%), m.p. 166–167° (Found: C, 74.3; H, 7.8; N, 9.15%; *m/e* 630. $C_{39}H_{46}N_4Ni$ requires C, 74.25; H, 7.65; N, 8.9%; M^+ 630), λ_{max} 406, 529, and 564 nm (ϵ 160 895, 9 925, and 14 890); δ_H 0.85 (t, *meso*-7'- CH_3), 1.3 (m, *meso*-4', 5', and 6'- CH_2), 1.7 (CH_3 of β -Et), 2.4 (m, *meso*-3'- CH_2), 3.28 (s, 1 β - CH_3), 3.33 (s, 1 β - CH_3), 3.35 (s, 2 β - CH_3), 3.8 (unsym. q, 4 CH_2 of β -Et), 4.8 (dt, *meso*-2'-CH; $J_{1'2'} = 16$ Hz), and 8.6 (d, *meso*-1' H). A second band was eluted from the column with chloroform-light petroleum (1:1). The product was further separated by preparative t.l.c. on silica using chloroform-light petroleum (1:3) when

a green fraction proved to be uncharged aldehyde (1a) and a red fraction (6 mg, 6%) after crystallisation from chloroform-methanol proved to be the corresponding carbinol (1b) on the basis of comparison of u.v., i.r., and n.m.r. spectra.

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