Reaction of Ethyl Diazoacetate with Cobalt Porphyrins.   Part 2 [1]

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The reactions of ethyl diazoacetate with various cobalt complexes of *meso*-tetraphenylporphyrin are shown to proceed similarly to those of cobalt complexes of octaethylporphyrin, although the products are less stable.   In the cobalt octaethylporphyrin series, two examples are provided of the nucleophilic fission of porphyrin nitrogen–carbon bonds with formation of alkylcobalt porphyrin derivatives.

THE condensation of ethyl diazoacetate with various cobalt complexes of octaethylporphyrin (OEP) was reported to give the adduct (1; $M = Co$, $R^1 = Et$, $R^2 = H$, $X = Cl$ or Br), and various reactions of this adduct were described.[1]   Thus, reduction with chromium(II) gave compound (2; $M = Co$, $R^1 = Et$, $R^2 = R^3 = H$, $X = Cl$), from which the metal could be removed with hydrochloric acid.   Treatment of the complex (1) with ethanolic hydrochloric acid gave first the product (2; $M = Co$, $R^1 = Et$, $R^2 = H$, $R^3 = X = Cl$) and then the bridged species (3; $R^1 = Et$, $R^2 = H$, $X = Cl$).   The ^1H n.m.r. spectrum of the adduct (1; $M = Co$, $R^1 = Et$, $R^2 = H$, $X = Cl$) in deuteriochloroform at -35 °C confirmed the assigned structure.[1] It indicated that substitution at β- or *meso*-positions had not occurred.   The methine proton of the diazoacetic ester residue corresponded to a singlet at $\delta -1.78$, but at room temperature this was not a separate signal.   Variable temperature studies (-35 to $+20$ °C) showed that the chemical shift of this signal increased with increasing temperature, and at room temperature it probably coincided with that of the peripheral methyl multiplet ($\delta 1.4-2.0$).   The increased sharpness of the peripheral β-methyl and methylene proton signals observed in decreasing the temperature from $+20$ to -35 °C suggests that increased mobility of the *CoN*-ethoxycarbonyl-methylene group at higher temperatures enhances the buckling of the porphyrin ring.   The ^1H n.m.r. spectrum of a solution of the complex (1; $M = Co$, $R^1 = Et$, $R^2 = H$, $X = Br$) in $[^2H_5]$pyridine showed a profound change and provided evidence for a novel rearrangement.   Signals corresponding to the protons of each of two pyridine rings were observed, and the methine proton corresponded to a signal at $\delta -2.71$. All the *meso*-protons were equivalent and resonated as a singlet at $\delta 10.30$.   The electronic spectrum of the polar product (conductivity measurements showed that it was a 1 : 1 electrolyte) revealed a strong Soret band at 423 nm (ε 101 610) and led us to formulate the product as (4; $R^1 = Et$, $R^2 = H$, $X = Br$), in which the pyridine has displaced the porphyrin ring nitrogen atom attached to carbon in (1).   On adding pyridine in 0.25 mol quantities to a solution of the complex (1; $M = Co$, $R^1 = Et$, $R^2 = H$, $X = Br$) in $[^2H]$chloroform and running ^1H n.m.r. spectra after each addition, it was found that the greatest change in the spectrum occurred after the addition of two equiv. of pyridine; thereafter the spectrum did not change even when a 10 molar excess of the base had been added.   A comparison of the ^{13}C n.m.r. spectra of the adducts (1; $M = Co$, $R^1 = Et$, $R^2 = H$, $X = Br$) and (4; $R^1 = Et$, $R^2 = H$, $X = Br$) reflects

the increased symmetry and free rotation about the cobalt–carbon bond in the latter.

The marked increase in the intensity of the Soret band when the complex (1; $M = Co$) (ε 60 000) is converted into (4) (ε 100 000) is in keeping with the increased


(1)

(2)

(3)

(4)

(5)
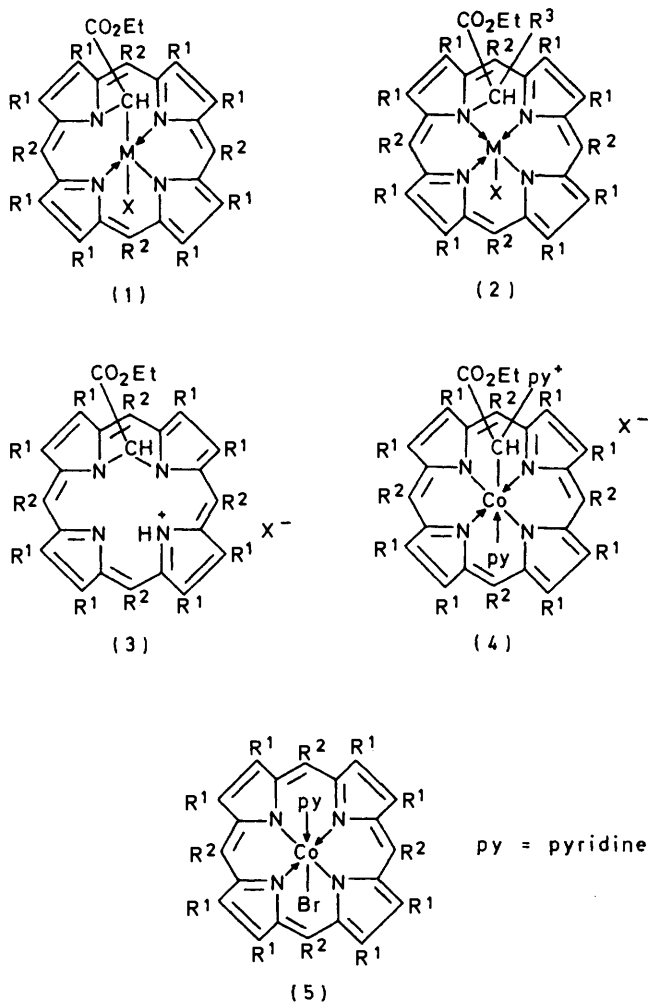
py = pyridine

planarity of the porphyrin chromophore.   The pyridinio-pyridine complex (4) was obtained as an amorphous solid, unstable in solution at *ca.* 60 °C, when it decomposed to the known bromopyridinecobalt(III) complex of OEP (5; $R^1 = Et$, $R^2 = H$) together with a second, unidentified porphyrin.

The nucleophilic displacement of the porphyrin by pyridine is a novel reaction of *N*-substituted porphyrins.

[1] Part I, A. W. Johnson, D. Ward, C. M. Elson, P. Batten, A. L. Hamilton, and G. Shelton, *J.C.S. Perkin I*, 1975, 2076.

However, another rearrangement involving nucleophilic fission of a porphyrin nitrogen–carbon bond, this time in compound (2; $M = Co$, $R^1 = Et$, $R^2 = R^3 = H$, $X = Cl$), was encountered during reduction with sodium borohydride in the absence of oxygen and light, resulting in rearrangement to the alkylcobalt derivative (6), isolated as dark purple needles (12%) after crystallisation in the dark. The ^1H n.m.r. spectrum contained a singlet at δ —4.41 corresponding to Co·CH$_2$ and a singlet at δ 10.24, showing equivalence of all four meso-protons. The mass spectrum showed the molecular ion at m/e 678 (21%) and a base peak at m/e 591 (loss of EtO$_2$C·CH$_2$). The rearrangement presumably involves an intermediate N-substituted cobalt(I) porphyrin (7), the nucleophilic metal then displacing the porphyrin ring nitrogen atom. Parallel rearrangements have been reported for cobalt [2] and rhodium [3] N-methyl derivatives of OEP. The mechanism is viewed as a reductive loss of the chloride ligand to yield the cobalt(I) complex, possibly with intermediate formation of the cobalt(I) radical anion.

(6)　　　(7)
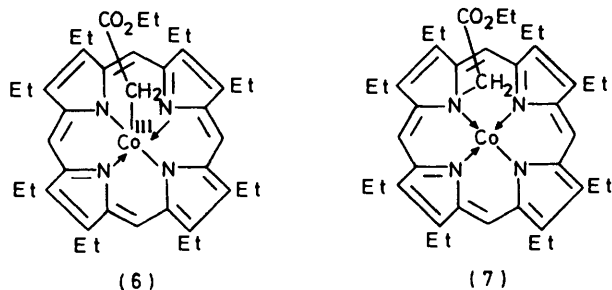
A reaction of the nickel complex (2; $M = Ni$, $R^1 = R^3 = H$, $R^2 = Ph$) in the meso-tetraphenylporphyrin (TPP) series, involving abstraction of a proton ($R^3 = H$) followed by rearrangement of the resulting carbanion led to an aziridine derivative, which rearranged on thermolysis to (1; $M = Ni$, $R^1 = H$, $R^2 = Ph$) and the isomeric homoporphyrins.[4,5] The reaction of ethyl diazoacetate with cobalt(II) TPP yields the complex (1; $M = Co$, $R^1 = H$, $R^2 = Ph$, $X = Cl$) which undergoes reactions similar to those of the OEP analogue. The products derived from TPP proved difficult to combust completely, and reliable carbon and nitrogen analyses were not obtained in most cases. The complexes were less stable than the corresponding compounds in the OEP series, presumably as a result of steric interactions involving the phenyl groups and the ethoxycarbonylmethylene fragment. Indeed, the interaction is apparent in the ^1H n.m.r. spectrum of compound (1; $M = Co$, $R^1 = H$, $R^2 = Ph$, $X = Cl$), where the nonequivalent methylene protons of the ester ethyl group correspond to a multiplet at δ 2.88. Irradiation at the frequency of the ester methyl triplet at δ —0.08 caused

the ester methylene multiplet to collapse to two doublets centred at δ 3.04 and 2.71 (J 10 Hz). This behaviour suggests a lack of free rotation about the $\rangle$CH–CO$_2$Et bond due to the steric effect of one of the meso-phenyl groups. The methine proton signal of the complex (1; $M = Co$, $R^1 = H$, $R^2 = Ph$) was not observed even at —35 °C (cf. ref. 1), suggesting that the fluxional character of the bridge was more pronounced in this case. The absorptions corresponding to the β- and meso-phenyl protons are appreciably spread, indicating buckling of the porphyrin ring. The X-ray crystal structure of compound (1; $M = Ni$, $R^1 = H$, $R^2 = Ph$), published recently,[4] gives clear evidence of deviations from planarity in the porphyrin ring. In the visible spectrum, the Soret band of the nickel(II) complex ($\lambda_{max.}$ 419 nm; ε 138 000) differs appreciably from that of the chlorocobalt(III) complex ($\lambda_{max.}$ 431 nm; ε 60 000), in which the degree of buckling of the porphyrin ring appears to be even greater. In the ^{13}C n.m.r. spectra the resonances for the methine carbons are at δ 22.57 (Ni complex) and 25.7 (CoCl complex). As in the OEP series, the cobalt(III) TPP bromide appeared to react much faster with ethyl diazoacetate that the cobalt(II) complex. Pyridine appeared to react with the complex (1; $M = Co$, $R^1 = H$, $R^2 = Ph$, $X = Cl$, Br) in a manner similar to that observed with the OEP analogue. However, the product (4; $R^1 = H$, $R^2 = Ph$, $X = Br$) was obtained only in solution, and attempts to isolate it in crystalline form led only to decomposition to (5; $R^1 = H$, $R^2 = Ph$). The ^1H n.m.r. spectrum of a solution of (4; $R^1 = H$, $R^2 = Ph$, $X = Br$) in [$^2H_5$]pyridine showed a signal for the methine proton (derived from ethyl diazoacetate) at δ —1.06, an ester methyl triplet at δ 0.32, and two singlets for the β-protons at δ 9.34 and 9.38. The electronic spectrum of a solution of (4; $R^1 = H$, $R^2 = Ph$, $X = Br$) in pyridine was similar to that of the OPE analogue, the Soret band being of comparable intensity ($\lambda_{max.}$ 437 nm; ε 100 560).

Reduction of the initial adduct (1; $M = Co$, $R^1 = H$, $R^2 = Ph$, $X = Cl$) with chromium(II) chloride gave cobalt(II) N-ethoxycarbonylmethyl-TPP as a crystalline penta-co-ordinate chloro-derivative (2; $R^1 = R^3 = H$, $R^2 = Ph$, $X = Cl$), which could be demetallated with ethanolic hydrochloric acid to yield N-ethoxycarbonylmethyl-TPP.[6] The cobalt complex showed a ^1H n.m.r. spectrum typical of a paramagnetic species, the sweep width of the spectrum being about three times greater than that of a diamagnetic cobalt complex.*

Treatment of the complex (1; $M = Co$, $R^1 = H$, $R^2 = Ph$, $X = Cl$) with ethanolic hydrogen chloride gave the metal-free bridged complex (3; $R^1 = H$, $R^2 = Ph$, $X = Cl$), which was formed in much lower yield (3%), in a slower reaction, than the OEP analogue, and was less stable and decomposed to (TPP) in hot solvents.

* Details of the ^1H n.m.r. spectrum of this and related complexes will be discussed in a forthcoming publication.

[2] H. Ogoshi, E. Watanabe, N. Kektzu, and Z. Yoshida, J.C.S. Chem. Comm., 1974, 943.

[3] H. Ogoshi, T. Omura, and Z. Yoshida, J. Amer. Chem. Soc., 1973, 95, 1666.

[4] H. J. Callot, T. Tschamber, B. Chevrier, and R. Weiss, Angew. Chem. Internat. Edn., 1975, 14, 567.

[5] H. J. Callot and T. Tschamber, J. Amer. Chem. Soc., 1975, 98, 6175.

[6] H. J. Callot and T. Tschamber, Bull. Soc. chim. France, 1973, 3192.

The electronic spectrum exhibited a very intense Soret band ($\lambda_{max.}$ 436 nm; ε 158 500), as did the OEP analogue. The ^{1}H n.m.r. spectrum showed a singlet at δ -1.07 corresponding to the methine proton (exchangeable with D_2O). This resonance is at much lower field than that of the corresponding proton in the OEP series (δ -5.78). The resonances of the ester methyl (δ -0.64) and methylene protons (δ 1.37) were roughly similar in both series.

EXPERIMENTAL

N.m.r. spectra were measured for solutions in [^{2}H]-chloroform and u.v.–visible spectra for solutions in dichloromethane (except where otherwise stated) with instruments listed in earlier papers in this series. Mass spectra were determined with an A.E.I. MS9 or MS30 instrument, by direct sample insertion into the ion source.

[*Ethoxycarbonyl(pyridinio)methyl*](*octaethylporphyrinato*)-*pyridinecobalt* (III) *Bromide* (4; R^1 = Et, R^2 = H, X = Br).—Bromo-(*Co*N-ethoxycarbonylmethyleneoctaethyl-porphyrinato)cobalt(III) (1; M = Co, R^1 = Et, R^2 = H, X = Br) (306.5 mg) was dissolved in acid-free dichloromethane (2 ml) and pyridine (1 ml) was added. The mixture was stirred at room temperature for 5 min. Light petroleum (30 ml) was added and the oily precipitate was separated by decantation and purified by repetition (2 ×) of the precipitation procedure at room temperature (the complex is heat-sensitive). The amorphous purple solid so obtained was separated and dried under high vacuum to yield the *product* (352 mg, 95%), *m/e* 591 (base peak; *M* $-$2py $-$ CHCO$_2$Et $-$ Br), $\lambda_{max.}$ 349, 423, 536, and 567 nm (ε, 27 980, 101 610, 13 680, and 10 490), $\nu_{max.}$ 1 601, 1 485, and 1 442 (complexed pyridine rings), 1 703 (C=O), and 1 184 and 1 155 (CO–O) cm^{-1}, δ_H 9.97 (s, 4 *meso*-H), 7.77 (distorted t, 2 α-H of pyridinium ring), 6.41 (m, 3 β- and γ-H of pyridinium ring), 5.84 (distorted t, 2 α-H of pyridine ring), 4.76 (distorted t, 3 β- and γ-H of pyridine ring), 4.06 (distorted q, 16 H of ethyl CH$_2$ groups), 1.94 (t, 12 H of 4 ethyl CH$_3$ groups), 1.90 (t, 12 H of 4 ethyl CH$_3$ groups), and -2.71 (s, methine H), δ_H (C$_5$D$_5$N) 10.30 (s, 4 *meso*-H), 4.07 (distorted q, 16 H of ethyl CH$_2$ groups), 1.92 (t, 24 H of ethyl CH$_3$ groups), 0.32 (t, 3 H of ester CH$_3$), and -2.19 (s, methine H), δ_C (natural abundance) 168.7 (s, C=O), 145.4 and 145.2 (both 4C, ring α-carbons), 141.6 and 141.4 (both s, 4C, ring β-carbons), 140.8 (d, 2C, pyridinium ring α-carbons), 134.9 (d, pyridinium ring γ-carbon), 120.7 (d, 2C, pyridinium ring β-carbons), 145.1 (d, 2C, pyridine ring α-carbons), 138.7 (d, pyridine ring γ-carbon), 124.1 (d, 2C, pyridinium ring β-carbons), 97.9 and 97.8 (both d, 2C, *meso*-carbons), 58.9 (t, ester CH$_2$), 19.9 (t, 8C, peripheral methylenes), 18.7 (q, 8C, peripheral methyls), and 12.9 (q, ester Me) (methine resonance not visible).

For comparison the complex (1; M = Co^{III}) showed δ_C 167.8br (s, C=O), 167.8br (2 α- or β-ring C), 156.4, 153.3, 151.7, 151.5, 151.0, 149.1, 147.4, 147.3, 146.0, 143.7, 142.2, 141.3, 129.4, and 127.8 (all s, ring α- and β-carbons), 105.9, 105.4, 99.6, and 95.4 (all d, *meso*-carbons), 59.0 (t, ester CH$_2$), 21.6—16.9 (m, 16C of peripheral CH$_2$ and CH$_3$), 12.2 (q, ester CH$_3$), and 22.6 (s, methine CH).

The foregoing bromide (32.1 mg) was heated under reflux in benzene (100 ml) for 4 h. The solvent was then evaporated off and the residue was chromatographed (preparative t.l.c.) on silica [60% acetone–chloroform as solvent, with pyridine (5 ml) present in the chromatography tank].

The least polar red band was separated and eluted with acetone. The product so obtained was crystallised from dichloromethane–light petroleum to yield small red plates (14 mg) of bromopyridinecobalt(III) OEP (5; R^1 = Et, R^2 = H), contaminated with a small quantity of an unknown red porphyrin. The ^{1}H n.m.r. spectrum and t.l.c. behaviour were identical with those of an authentic specimen.[1] The same product was obtained from (1; M = Co, R^1 = Et, R^2 = H, X = Br) when heated under reflux in chloroform for 1 h; δ 146.4, 140.0 (both 8C, ring α- and β-carbons), 146.1 (d, 2C, pyridine ring α-carbons), 136.8 (d, pyridine ring γ-carbon), 121.3 (d, 2C, pyridine ring β-carbons), 96.3 (d, 4 *meso*-carbons), 20.1 (t, 8C, peripheral CH$_2$), and 18.6 (q, 8C, peripheral CH$_3$).

(*Ethoxycarbonylmethyl*)(*octaethylporphyrinato*)*cobalt*(III).—To a solution of chloro-(N-ethoxycarbonylmethylocta-ethylporphyrinato)cobalt(III) (81.5 mg) in dry, deoxygenated tetrahydrofuran (30 ml) under nitrogen in the dark, was added sodium borohydride (6.1 mg), and the mixture was stirred at room temperature for 8 h. The solution was evaporated and the residue subjected to preparative t.l.c. on silica (8% acetone–light petroleum) with exclusion of light. The second most polar band was starting material (58.2 mg), which was crystallised from dichloromethane–light petroleum. Material from the least polar band was crystallised from dichloromethane–methanol and yielded red-purple needles of the alkylcobalt(III) derivative (9.4 mg, 12.1%) *m/e* 678 (21%) and 591 (100%) (*M* and *M* $-$ CH$_2$CO$_2$Et), $\lambda_{max.}$ 393, 414, 505, and 542 nm (ε 144 100, 76 040, 6 210, and 14 050), $\nu_{max.}$ 1 699 (C=O) and 1 265 and 1 240 cm^{-1} (CO–O), δ_H 10.24 (s, 4 *meso*-H), 4.07 and 4.035 (q, 16 H of peripheral ethyl CH$_2$ in ratio 1 : 1), 1.90 (t, 24 H of peripheral ethyl CH$_3$), 1.69 (q, ester CH$_2$), 0.17 (t, ester CH$_3$), and -4.44 (s, Co·CH$_2$).

Chloro-(*Co*N-*ethoxycarbonylmethylene*-*meso-tetraphenyl-porphyrinato*)*cobalt*(III) (1; M = Co, R^1 = H, R^2 = Ph, X = Cl).—Cobalt(II) tetraphenylporphyrin (287.5 mg) was treated with ethyl diazoacetate (0.24 ml) in chloroform (50 ml); the mixture was stirred for 20 min, and then quickly evaporated to small volume at room temperature *in vacuo*. Light petroleum (50 ml) was added and the solution again evaporated. The precipitate was separated, washed with light petroleum, and dissolved in dichloromethane (20 ml). The precipitation and dissolution were repeated three times each to give the *product* (208.5 mg, 61%) as an amorphous powder (Found: N, 7.05. C$_{48}$H$_{34}$-ClCoN$_4$O$_2$ requires N, 7.05%), *m/e* 671 (*M* $-$ Cl $-$ CHCO$_2$-Et), $\lambda_{max.}$ 419, 431, 513, 583, 600, and 632 nm (ε 56 750, 60 800, 9 200, 5 070, 4 250, and 3 900), $\lambda_{max.}$ (pyridine) 383, 437, 497, 554, and 593 nm (ε 1 200, 100 560, 5 480, 8 900, and 6 180), $\nu_{max.}$ 1 720 (C=O) and 1 216 and 1 194 cm^{-1} (CO–O), δ 9.47 (s), 8.83 (d), 6.94 (d), 5.59 (d), 4.94 (d), and 4.51 (d) (all single β- or phenyl protons), 8.47 (2 H, d, β- or phenyl protons), 7.80br (m, remaining β- and phenyl protons), 2.88 (m, non-equivalent ester CH$_2$), and -0.08 (t, ester CH$_3$), δ_C (natural abundance) 165.5 (s, C=O), 152.4, 150.3, 147.0, 146.0, 144.9, and 144.2 (all s, 6 ring α-carbons), 142.1, 141.8, 141.4, 140.9, 123.3, and 119.5 (s, 8 *meso*- and 1-phenyl carbons), 137.2, 135.8, 135.3, 134.5, 131.7, 129.5, 128.9, 127.7, and 127.7 (28 2-, 3-, and 4-phenyl and β-carbons), 57.6 (t, ester CH$_2$), 22.6 (d, methine C), and 12.3 (q, ester CH$_3$).

The analogous bromo-compound was prepared from tetraphenylporphyrinatocobalt(III) bromide (88 mg) and ethyl diazoacetate (0.065 ml) in chloroform (10 ml). After

stirring for 10 min the solution was evaporated to small volume and light petroleum (30 ml) was added to precipitate the product. The precipitation procedure was repeated twice to give the bromo-compound as a purple powder (69.7 mg, 71%), $\lambda_{max.}$ 285, 424, 433, 520, 579, 640, and 740 nm (ε 25 000, 61 300, 62 800, 10 380, 6 180, 4 500, and 1 580), $\nu_{max.}$ 1 719 (C=O) and 1 217 and 1 194 cm^{-1} (CO–O). The ^{1}H and ^{13}C n.m.r. spectra were similar to those of the chloro-derivative.

Chloro-(N-*ethoxycarbonylmethyl*-meso-*tetraphenylporphyrinato*)*cobalt*(II).—The foregoing chloro-(CoN-ethoxy-carbonylmethylene)cobalt(III) derivative (97.2 mg) was dissolved in ethanol (20 ml) in an atmosphere of nitrogen and chromium(II) chloride solution[1] (2 ml) was added. The solution was stirred for 20 min and poured into aqueous 5% sodium chloride (40 ml), and the product was extracted into dichloromethane (2 × 50 ml). The extract was purified by chromatography on a polyamide column and the green major band was eluted with 30% acetone–light petroleum. After removal of the solvent the *product* (33.1 mg, 34%) was crystallised from dichloromethane–light petroleum (Found: C, 71.9; H, 4.55; N, 7.15. $C_{48}H_{35}$-$ClCoN_4O_2$ requires C, 72.6; H, 4.45; N, 7.05%), m/e 793 (M, 1.7%), 757 (M — H — Cl, 1.9), and 671 (M — CH_2CO_2Et — Cl, 100), $\lambda_{max.}$ 441, 553, 599, and 632 nm (ε 147 500, 7 000, 12 500, and 6 800), $\nu_{max.}$ 1 742 (C=O) and 1 218 and 1 189 (CO–O) cm^{-1}, $\nu_{max.}$ (CsI prism; Nujol) 322 cm^{-1} (Co–Cl), δ_H 48.6, 42.7, 40.7, 22.2, 19.3, 13.5, 12.2, 9.47, 7.74, 6.79, 4.61, 3.74, 1.83, 1.46, 1.27, 0.88, 0.56, 0.27, —0.42, —0.59, —2.64 and —5.44 (all s, porphyrin ring H, phenyl H and N·CH$_2$), —8.52 (s, ester CH$_3$), and —10.9 (s, ester CH$_2$).

N-*Ethoxycarbonylmethyl*-meso-*tetraphenylporphyrin.*—The foregoing chlorocobalt(II) derivative (78.7 mg) was dissolved in chloroform (3 ml) and ethanol (8 ml) and concentrated hydrochloric acid (3.5 ml) was added. The solution was stirred for 30 min at room temperature, then poured into aqueous 5% sodium hydrogen carbonate (100 ml) and extracted with dichloromethane (3 × 50 ml). The extract was washed, dried, and evaporated and the residue crystallised from chloroform–ethanol to yield the product (59.0 mg, 85%) as a purple crystalline solid for which satisfactory analytical figures were not obtained; m/e 701 (M, 15.7%), and 614 (M — CH·CO$_2$Et, 100%), $\lambda_{max.}$ 427, 496, 520, 561, 598, and 655 nm (ε 229 000, 4 080, 9 120, 14 070, 5 050, and 4 950), $\nu_{max.}$ 3 300 (NH), 1 729 (C=O), and 1 219 and 1 190 cm^{-1} (CO–O), δ_H 8.84 (s, 2 β-H on ring c), 8.73 and 8.54

(d, AA′BB′ pattern for 4 β-H on rings B and D), 8.29 (m, 8 o-H of phenyl groups), 7.69 (m, 12 m- and p-H of phenyl groups and 2 β-H on ring A), 3.07 (q, ester CH$_2$), 0.43 (t, ester CH$_3$), and —3.70 (s, N·CH$_2$) (NH signal not observed at room temperature but was seen as a broad singlet at δ —2.23 at —40 °C), δ$_C$ (natural abundance) 166.6 (ester CO), 157.0, 152.9, 152.3, 142.5, 142.1, 139.4, 137.5, 135.4, 134.4, 133.1, 128.4, 127.9, 127.6, 127.2, 126.7, and 119.8 (porphyrin and phenyl ring carbons s), 59.7 (ester CH$_2$), 43.4 (N·CH$_2$), and 13.2 (ester CH$_3$).

cis-21,22-*Ethoxycarbonylmethylene*-meso-*tetraphenylporphyrin Hydrochloride from Chloro*-(CoN-*ethoxycarbonylmethylene*-meso-*tetraphenylporphyrinato*)*cobalt*(III).— The chlorocobalt(III) complex (1; M = Co, R^1 = H, R^2 = Ph, X = Cl) (389.7 mg) in chloroform (10 ml) and ethanol (40 ml) was stirred with concentrated hydrochloric acid (3 ml) at room temperature for 24 h. The mixture was poured into water and extracted with dichloromethane (2 × 50 ml). The resulting solution was shaken with aqueous 5% sodium chloride, then with water. Evaporation was followed by preparative t.l.c. (silica; 25% acetone–light petroleum). Three bands were separated. The least polar, orange band was separated and the product crystallised from dichloromethane–methanol as purple crystals (47.0 mg, 14%) of *meso*-tetraphenylporphyrinato-cobalt(II), identical with an authentic sample [t.l.c. (silica; 20% dichloromethane–light petroleum)]. The next, brown-yellow band was separated and the product precipitated as a black powder (131.8 mg) from dichloromethane–light petroleum, m/e 671 (100%, $C_{44}H_{28}CoN_4$), $\nu_{max.}$ 1 704 (C=O) and 1 218 cm^{-1} (CO–O). A closer t.l.c. examination showed four close-running bands. The most polar, green band was separated and the title hydrochloride was precipitated from dichloromethane–light petroleum as a green powder (8.9 mg, 3%), $\lambda_{max.}$ 419, 436, 518, 544, 586, and 624 nm (ε 141 360, 158 500, 8 400, 11 700, 11 900, and 6 350), $\nu_{max.}$ 1 741 (C=O) and 1 212 cm^{-1} (CO–O), δ$_H$ (CH$_2$Cl$_2$ reference), 9.17 (3 H, d), 8.93 (2 H, d), 8.91 (1 H, d), 8.54 (1 H, d), 8.52 (2 H, d), 8.25 (6 H, m), 7.18 (9 H, m), 6.50 (2 H, d), and 6.16 (2 H, d), (β- and phenyl protons), 1.57 (q, ester CH$_2$), —0.58 (t, ester CH$_3$), and —1.07 (s, CH, D$_2$O-exchangeable).