# Reaction of Ethyl Diazoacetate with Cobalt Porphyrins. Part 3.[1] Structure and Reactions of the 2 :1 Adducts

By **Peter Batten, Alan L. Hamilton, Alan W. Johnson, Mailvaganam Mahendran**, and **David Ward**, School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ

**Trevor J. King**, Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD

Isomers of the neutral 2 :1 adducts. containing either co-ordinated nitrate or acetate. from condensation of ethyl diazoacetate with cobalt octaethylporphyrin are described : the structure of the main nitrato isomer has been established by X-ray crystallography. The nitrogen–carbon–cobalt bridges of the neutral adducts can be broken by reduction. to give trans-21.22-bis(ethoxycarbonylmethyl)octaethylporphyrin. or by acids. to give salts of 21.22-bis(ethoxycarbonylmethylene)-23-(ethoxycarbonylmethyl)octaethylporphyrin. both isolated as perchlorates.

WE have recently [2] described the reaction of equimolar amounts of ethyl diazoacetate with cobalt(II) and cobalt(III) complexes of octaethylporphyrin (OEP) in chloroform and shown that the reaction formally involves the insertion of ethoxycarbonylcarbene between the metal and a porphyrin ring nitrogen atom giving a polar product formulated as the chloride (1). Smaller amounts of an acid transformation product (2; R = Cl) could be isolated from the reaction mixture, as well as two isomeric neutral cobalt-containing compounds formed by condensation of the cobalt porphyrin with 2 mol. equiv. of ethyl diazoacetate. After longer periods of reaction and with greater quantities of ethyl diazoacetate or (preferably) by reaction of the chloride (1) with more ethyl diazoacetate, these neutral 1 : 2 adducts were formed as the major products. We have since shown [1] that similar reactions occur with cobalt complexes of

meso-tetraphenylporphyrin (TPP), leading both to 1 : 1 and 1 : 2 complexes. The 1 : 1 complex derived from nickel(II) TPP has recently been prepared by another method,[3] and its X-ray crystal structure has been described.

In this paper we describe the preparation and structure of the neutral 1 : 2 complexes derived from cobalt porphyrins and ethyl diazoacetate. At an early stage of the investigation we subjected a crystal of one of the neutral 1 : 2 complexes derived from cobalt(II) OEP and ethyl diazoacetate to X-ray crystallographic examination (details below); on the basis of these results it was clear that the carbene units had been inserted between the metal and the nitrogen atoms of rings A and B, giving a structure represented as the projection formula (3) (cf. ref. 4). The distance between the carbene-substituted nitrogen and the cobalt atom was 2.7 Å, which precluded

[1] Part 2, A. W. Johnson and D. Ward, *J.C.S. Perkin I*, 1977, in the press.

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

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

[4] A. W. Johnson, *Chem. Soc. Rev.*, 1975, **4**, 1.

the existence of a nitrogen–cobalt co-ordinate bond as had been postulated.[5] Of special interest was the existence, co-ordinated to the metal, of a nitrate grouping, the origin of which was probably residual nitrite which had been used in the preparation of the ethyl diazoacetate. In any event, addition of nitrate to the reaction mixture of the chloride (1) and ethyl diazoacetate gave and improved yield of the mixed neutral crystalline 1 : 2 adducts, of which the product (3), isomer C, was a major component. Two crystalline, less polar, minor components, isomers A and B, were also isolated from the crude product after repeated chromatography on silica; they were eluted in advance of isomer C.



(1)



(2)



(3)



(4)
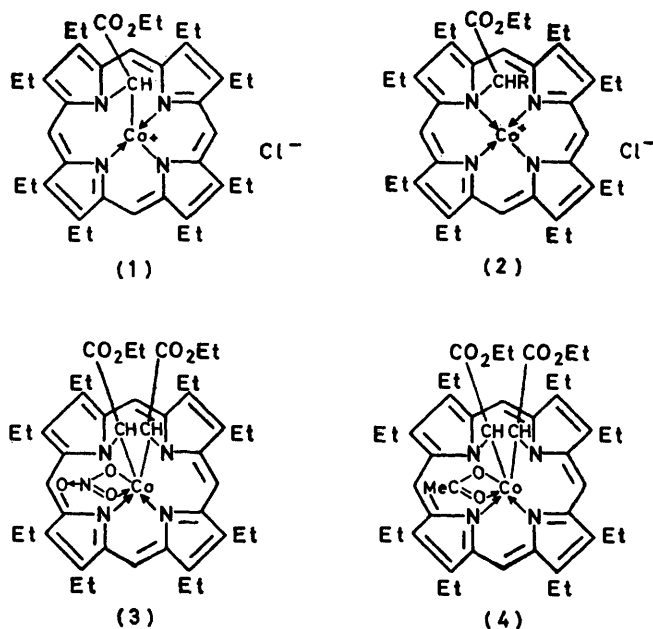
The $X$-ray crystal structure (3) was supported by analysis ($C_{44}H_{56}CoN_5O_7$; $M$ 825.9) and by the results of field desorption mass spectrometry: the molecular ion (19.2%) was observed together with the base peak obtained by loss of nitrate and two ethoxycarbonylmethylene units. In the conventional mass spectrum a small peak was also observed ($m/e$ 850) for loss of nitrate, but with addition of an extra carbene unit. The i.r. spectrum contained a band at 1 511 cm$^{-1}$, possibly associated with the nitrate group, and the $^1H$ n.m.r. spectrum contained singlets at $\delta$ —1.61 and —7.68 associated with the two bridging methine groups which from $X$-ray crystallography are known to occupy different environments with respect to the porphyrin ring. Likewise, the ester methyl signals at $\delta$ —0.01 and —1.29 are both shifted upfield because of shielding by the porphyrin ring, which is seen to be buckled because of the wide spread of the β-ethyl signals. The meso-proton signals appeared as four singlets ($\delta$ 9.97—9.57).

Similar considerations apply to the two minor neutral products isolated. They were shown to be isomeric with

(3) by mass spectrometry; in the $^1H$ n.m.r. spectra singlets at $\delta$ —1.59 and —7.85, and $\delta$ 0.36 and —7.91 corresponded to the bridging methine protons. The meso-proton signals were grouped in the ranges $\delta$ 9.95—9.54 and 10.08 —9.45. A $^{13}C$ n.m.r. spectrum (natural abundance) for one of these isomers was consistent with the foregoing main structural features (see Experimental section). Although the presence of nitrato groupings was inferred from high resolution mass spectrometry, a band at 1 511 cm$^{-1}$ was not detected in either of the i.r. spectra. Isomerism in this series could result from the relative positions of the protons and ester groups on the methine bridging carbon atoms as well as the positions of the carbene bridges relative to the porphyrin ring. It is possible that some of the theoretically possible isomers cannot exist for steric reasons.

The nitrato ligand of (3) appears to be fairly labile: when the complex is crystallised from acetone containing sodium acetate it is converted into a related complex (4) in which acetato has replaced the nitrato group. This assignment is based on analysis and spectral results. Thus the i.r. band at 1 511 cm$^{-1}$ in the spectrum of (3) is replaced by a band at 1 540 cm$^{-1}$, i.e. at slightly lower wavenumber than for the carbonyls of co-ordinated acetate in other metal porphyrins (1 560—1 570 cm$^{-1}$),[6] distinct from the methyl ester carbonyl bands at 1 703 cm$^{-1}$. The two methine protons correspond to n.m.r. singlets at $\delta$ —1.38 and —8.11, and the acetato methyl signal appears as a singlet at $\delta$ —0.38. Most other features of the $^1H$ n.m.r. spectrum remained unchanged after the substitution. When a solution of the chloride (1) in acetone was treated with 1 mol. equiv. of ethyl diazoacetate in the presence of sodium acetate and the product was crystallised from acetone containing sodium nitrate, or when the crude product was chromatographed repeatedly on silica plates, there was obtained the nitrato complex (3), together with smaller amounts of the isomeric products. However, when the crude product was crystallised from acetone containing sodium acetate, the neutral acetate complex (4) was obtained.

Several transformations of the chloride (1) have been described.[2] Thus, reduction with chromium(II) chloride gave (2; R = H), from which the metal could be removed with hydrochloric acid. Treatment of (1) with ethanolic hydrochloric acid gave first the product (2; R = Cl) and then the metal-free bridged species (5). Similar reactions have been studied with the neutral adduct (3). Reduction with chromium(II) chloride followed by crystallisation of the product in the presence of sodium perchlorate yielded the perchlorate of trans-21,22-bis(ethoxycarbonylmethyl)octaethylporphyrin (6). This compound had also been prepared [2] by reaction of octaethylporphyrin with ethyl bromoacetate followed by crystallisation as above. Treatment of (3) with methanolic 10% hydrogen chloride caused formation of a metal-free salt which was converted into the perchlorate. From analysis and spectral properties this salt has been formulated as the
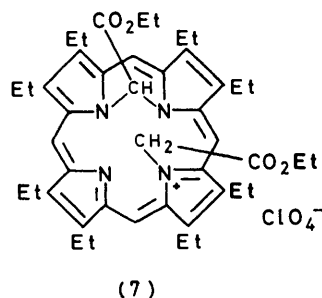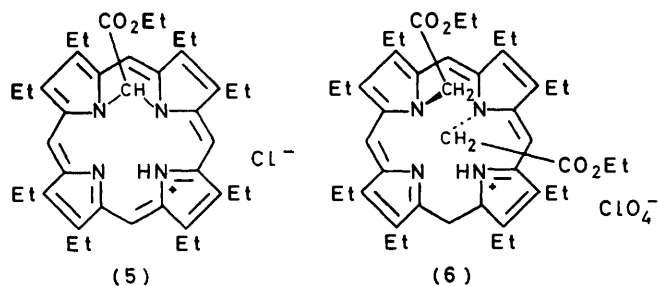
[5] P. Batten, A. L. Hamilton, A. W. Johnson, G. Shelton, and D. Ward, J.C.S. Chem. Comm., 1974, 550.

[6] R. J. Abraham, G. H. Barnett, and K. M. Smith, J.C.S. Perkin I, 1973, 2142.

*N*-ethoxycarbonylmethyl derivative (7) of the bridged species (5).

The product (7) showed a strong Soret band at 407 nm (ε 145 800) and i.r. bands corresponding to the two ester carbonyl groups. In the $^1H$ n.m.r. spectrum the signals for the four *meso*-protons appeared as three singlets at δ 10.59 (1 H), 10.51 (2 H), and 10.27 (1 H), the shielded ester methyl signals at 0.43 and —0.75 (both t), the methine bridge proton signal at —4.91 and the *N*-methylene signals at —3.79 and —5.27 (both d).

Evidence has also been obtained for the existence of corresponding neutral 1 : 2 adducts derived from cobalt(II) *meso*-tetraphenylporphyrin and ethyl diazoacetate, but, as with the 1 : 1 adduct,[1] the products are much less

The structure was solved by the heavy atom method, the light atoms being found routinely from difference maps. Refinement proceded normally and in the final stages, using anisotropic temperature factors, the variables were blocked in five groups (the four pyrrole moieties and one *meso* atom each making a block, the fifth block holding the remaining atoms). For the final two cycles a weighting scheme of the form $w = 1/ \{1 + [F_o - P(2)/P(1)]^2\}$ with $P(1) = 17.0$ and $P(2) = 14.0$
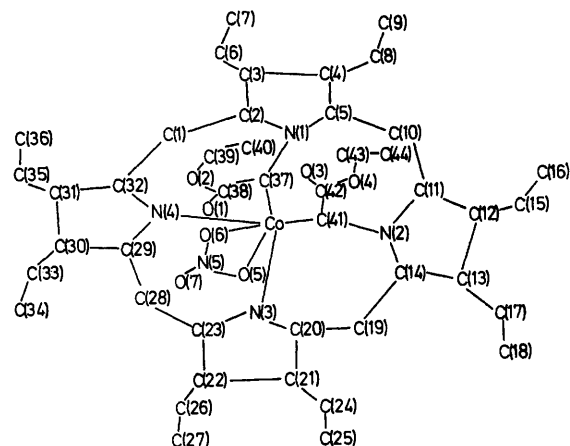


FIGURE 1  The molecule (3), showing the crystallographic numbering

was employed. At convergence $R$ was 8.1%. Because of the large number of parameters being refined and the relatively large thermal vibrations of the alkyl substituents no attempt was made to include hydrogen atoms in the calculations. Figure 1 is a line drawing of the molecule showing the crystallographic numbering,



(5)          (6)



(7)

stable than in the octaethylporphyrin series and as yet they have not been fully characterised.

*Crystal Structure Determination.—Crystal data.* $C_{44}H_{56}CoN_5O_7$, $M$ 825.87. Monoclinic, $a = 13.377(3)$, $b = 14.343(4)$, $c = 24.331(6)$ Å, $\beta = 105.05(5)°$, $D_c = 1.22$ g cm$^{-3}$, $U = 4\,508$ Å$^3$, $D_m = 1.23$, $Z = 4$, $F(000) = 1\,700$. Space group $P2_1/c$ from systematic absences. Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å (graphite monochromator), $\mu_a = 4.52$ cm$^{-1}$.

Measurements were made on a crystal of approximate dimensions $0.1 \times 0.2 \times 0.1$ mm mounted about the needle axis ($b$). Oscillation and Weissenberg photographs established the space group and the approximate cell dimensions. The parameters were refined by the least-squares method based on the setting angles of twelve reflections. Intensity measurements were made by ω –2θ scans for the range θ 0—25°. Three standard reflections were monitored every 100 reflections and did not change appreciably; 3 860 reflections with a net count >3σ were considered observed and were used in the refinement. Lorentz and polarisation but no absorption corrections were made.

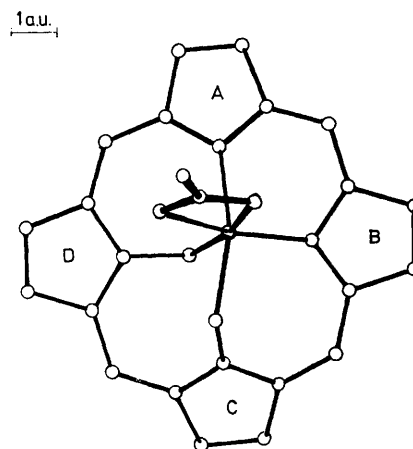FIGURE 2  Perspective drawing of the molecule (3) (several atoms removed for clarity)

Figures 2 and 3 are perspective drawings of the molecule with many atoms removed for clarity. Table 1 contains the positional parameters of the atoms. Table 2 the bond lengths, and Table 3 the bond angles. Observed and calculated structure factors, thermal parameters, and torsion angles are available as Supplemen-

tary Publication No. SUP 22045 (38 pp.).* All computations were carried out by using the Oxford CRYSTALS programs.[7]

EXPERIMENTAL

N.m.r. spectra were measured for solutions in [²H]chloroform and u.v.–visible spectra for solutions in chloroform

TABLE 1

Fractional co-ordinates of atoms ($\times 10^4$); standard deviations in parentheses

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| N(1) | 895(5) | 1 129(5) | 1 460(3) |
| C(1) | 530(6) | −579(6) | 1 407(4) |
| C(2) | 372(6) | 333(6) | 1 219(3) |
| C(3) | −385(6) | 650(7) | 709(3) |
| C(4) | −239(7) | 1 578(7) | 645(4) |
| C(5) | 613(6) | 1 887(6) | 1 109(4) |
| C(6) | −1 122(7) | −6(8) | 314(4) |
| C(7) | −2 036(9) | −228(11) | 537(5) |
| C(8) | −659(7) | 2 171(8) | 109(5) |
| C(9) | −1 536(9) | 2 686(11) | 219(5) |
| N(2) | 2 834(5) | 2 534(5) | 1 744(3) |
| C(10) | 1 031(7) | 2 792(7) | 1 182(4) |
| C(11) | 1 972(7) | 3 092(6) | 1 545(4) |
| C(12) | 2 168(7) | 3 962(6) | 1 856(4) |
| C(13) | 3 084(7) | 3 863(6) | 2 266(4) |
| C(14) | 3 549(7) | 2 939(6) | 2 227(4) |
| C(15) | 1 414(8) | 4 762(7) | 1 765(5) |
| C(16) | 1 236(11) | 5 236(9) | 1 173(7) |
| C(17) | 3 576(8) | 4 555(7) | 2 723(4) |
| C(18) | 3 134(12) | 4 456(11) | 3 255(6) |
| N(3) | 3 805(5) | 744(5) | 2 553(3) |
| C(19) | 4 214(6) | 2 470(7) | 2 656(4) |
| C(20) | 4 348(7) | 1 519(7) | 2 794(4) |
| C(21) | 5 127(6) | 1 213(7) | 3 304(4) |
| C(22) | 5 030(7) | 293(7) | 3 353(4) |
| C(23) | 4 166(6) | 3(6) | 2 897(3) |
| C(24) | 5 871(8) | 1 868(8) | 3 710(5) |
| C(25) | 6 727(11) | 2 179(11) | 3 468(7) |
| C(26) | 5 669(8) | −341(8) | 3 806(4) |
| C(27) | 5 203(11) | −437(11) | 4 326(5) |
| N(4) | 2 259(5) | −590(5) | 2 082(3) |
| C(28) | 3 740(7) | −911(6) | 2 860(4) |
| C(29) | 2 793(7) | −1 166(6) | 2 494(4) |
| C(30) | 2 184(7) | −2 001(6) | 2 510(4) |
| C(31) | 1 278(6) | −1 888(6) | 2 097(4) |
| C(32) | 1 328(6) | −981(6) | 1 836(4) |
| C(33) | 2 491(9) | −2 805(8) | 2 920(5) |
| C(34) | 2 211(13) | −2 634(12) | 3 480(6) |
| C(35) | 321(7) | −2 489(6) | 1 963(4) |
| C(36) | −510(8) | −2 080(8) | 2 233(6) |
| C(37) | 1 646(6) | 1 161(7) | 2 010(3) |
| C(38) | 1 207(7) | 742(6) | 2 480(4) |
| O(1) | 358(5) | 480(5) | 2 441(3) |
| O(2) | 1 938(5) | 813(5) | 2 971(2) |
| C(39) | 1 631(9) | 448(10) | 3 465(4) |
| C(40) | 2 437(13) | 828(20) | 3 968(6) |
| C(41) | 3 065(6) | 1 710(6) | 1 460(3) |
| C(42) | 4 068(7) | 1 797(7) | 1 312(4) |
| O(3) | 4 841(5) | 2 191(6) | 1 566(3) |
| O(4) | 4 027(5) | 1 308(5) | 829(3) |
| C(43) | 4 990(9) | 1 219(11) | 660(6) |
| C(44) | 4 916(16) | 1 717(19) | 151(9) |
| Co(1) | 2 842(1) | 521(1) | 1 840(1) |
| N(5) | 3 200(6) | −401(5) | 1 066(3) |
| O(5) | 2 336(4) | 2(4) | 1 038(2) |
| O(6) | 3 869(4) | −271(4) | 1 533(3) |
| O(7) | 3 352(6) | −885(6) | 686(3) |

[trans-21,22-Bis(ethoxycarbonylmethyl)octaethylporphyrinato (2−)-C^{N(21)},C^{N(22)},N^{13},N^{24}]nitratocobalt(iii).—(i) Bromo[21-ethoxycarbonylmethyloctaethylporphyrinato(2−)-C^{N(21)},N^{22},N^{23},N^{24}]cobalt(iii) (1; Br for Cl) (116.1 mg) was
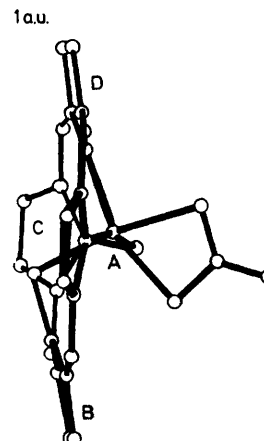


FIGURE 3 The molecule (3) viewed in the plane of ring B (several atoms removed for clarity)

dissolved in acetone (50 ml) and sodium nitrate (2 g) added. A solution of ethyl diazoacetate (0.5 ml) in acetone (75 ml) was added dropwise with stirring over 2 h. The solution was stirred for a further 2 h, then the excess of sodium nitrate

TABLE 2

Bond lengths (Å); standard deviations in parentheses

| | | | |
|---|---|---|---|
| N(1)–C(2) | 1.39(1) | C(23)–C(28) | 1.42(1) |
| C(1)–C(2) | 1.38(1) | N(4)–C(29) | 1.35(1) |
| C(3)–C(4) | 1.36(1) | C(28)–C(29) | 1.40(1) |
| C(4)–C(8) | 1.54(1) | C(30)–C(33) | 1.51(1) |
| C(8)–C(9) | 1.47(2) | C(33)–C(34) | 1.53(2) |
| N(2)–C(41) | 1.44(1) | C(37)–Co(1) | 1.98(1) |
| C(12)–C(13) | 1.37(1) | O(2)–C(39) | 1.47(1) |
| C(13)–C(17) | 1.51(1) | C(41)–Co(1) | 2.00(1) |
| C(17)–C(18) | 1.57(2) | O(4)–C(43) | 1.46(1) |
| N(3)–Co(1) | 1.90(1) | N(5)–O(6) | 1.26(1) |
| C(21)–C(22) | 1.33(1) | O(6)–Co(1) | 2.07(1) |
| C(22)–C(26) | 1.51(1) | N(1)–C(37) | 1.45(1) |
| C(26)–C(27) | 1.56(2) | C(2)–C(3) | 1.46(1) |
| N(5)–Co(1) | 1.93(1) | C(4)–C(5) | 1.45(1) |
| C(30)–C(31) | 1.45(1) | C(6)–C(7) | 1.55(1) |
| C(31)–C(36) | 1.51(1) | N(2)–C(14) | 1.38(1) |
| C(37)–C(38) | 1.54(1) | C(11)–C(12) | 1.45(1) |
| C(38)–O(2) | 1.34(1) | C(13)–C(14) | 1.43(1) |
| C(41)–C(42) | 1.48(1) | C(15)–C(16) | 1.55(2) |
| C(42)–O(4) | 1.36(1) | N(3)–C(23) | 1.36(1) |
| N(5)–O(5) | 1.28(1) | C(20)–C(21) | 1.47(1) |
| O(5)–Co(1) | 2.03(1) | C(22)–C(24) | 1.44(1) |
| N(1)–C(5) | 1.37(1) | C(24)–C(25) | 1.49(2) |
| C(1)–C(32) | 1.41(1) | N(4)–C(32) | 1.36(1) |
| C(3)–C(6) | 1.51(1) | C(29)–C(30) | 1.45(1) |
| C(5)–C(10) | 1.41(1) | C(31)–C(32) | 1.46(1) |
| N(2)–C(11) | 1.38(1) | C(35)–C(36) | 1.55(1) |
| C(10)–C(11) | 1.40(1) | C(38)–O(1) | 1.18(1) |
| C(12)–C(15) | 1.51(1) | C(39)–C(40) | 1.51(2) |
| C(14)–C(19) | 1.42(1) | C(42)–O(3) | 1.20(1) |
| N(3)–C(20) | 1.37(1) | C(43)–C(44) | 1.41(2) |
| C(19)–C(20) | 1.41(1) | N(5)–O(7) | 1.28(1) |
| C(21)–C(24) | 1.53(1) | | |

(except where otherwise stated) with instruments listed in earlier papers.[1,2] Mass spectra were determined with an A.E.I. MS9 or MS30 instrument by direct insertion into the ion source.

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1976, Index issue.

was separated and washed with acetone; the filtrates were combined and evaporated. The residue was dissolved in dichloromethane (3 ml) and then chromatographed [preparative t.l.c. on silica (0.75 mm); eluant 10% ethyl acetate–light

[7] J. R. Carruthers, personal communication.

petroleum, six developments]. Three brown bands were obtained, each containing a non-polar compound.

(a) Material from the least polar band was separated; dissolution in acetone followed by filtration gave a brown solution. Chromatography on silica as before gave *isomer A*, which crystallised from dichloromethane–light petroleum as purple crystals (8.03 mg, 6.35%) (Found: N, 7.95

### TABLE 3

Bond angles (°); standard deviations in parentheses

| | | | |
|---|---|---|---|
| C(2)–N(1)–C(5) | 111.3(6) | C(2)–N(1)–C(37) | 124.6(7) |
| C(5)–N(1)–C(37) | 124.1(7) | C(2)–C(1)–C(32) | 130.8(8) |
| N(1)–C(2)–C(1) | 128.5(7) | N(1)–C(2)–C(3) | 105.4(7) |
| C(1)–C(2)–C(3) | 126.1(8) | C(2)–C(3)–C(4) | 108.4(8) |
| C(2)–C(3)–C(6) | 122.8(9) | C(4)–C(3)–C(6) | 128.6(8) |
| C(3)–C(4)–C(5) | 108.5(7) | C(3)–C(4)–C(8) | 127.5(9) |
| C(5)–C(4)–C(8) | 122.1(9) | N(1)–C(5)–C(4) | 106.0(7) |
| N(1)–C(5)–C(10) | 128.0(7) | C(4)–C(5)–C(10) | 126.0(8) |
| C(3)–C(6)–C(7) | 111.4(8) | C(4)–C(8)–C(9) | 104.9(11) |
| C(11)–N(2)–C(14) | 108.7(7) | C(11)–N(2)–C(41) | 124.6(7) |
| C(14)–N(2)–C(41) | 126.5(7) | C(5)–C(10)–C(11) | 128.6(8) |
| N(2)–C(11)–C(10) | 125.0(8) | N(2)–C(11)–C(12) | 107.0(7) |
| C(10)–C(11)–C(12) | 127.1(8) | C(11)–C(12)–C(13) | 107.3(8) |
| C(11)–C(12)–C(15) | 123.8(9) | C(13)–C(12)–C(15) | 128.6(9) |
| C(12)–C(13)–C(14) | 108.1(8) | C(12)–C(13)–C(17) | 127.2(9) |
| C(14)–C(13)–C(17) | 124.5(9) | N(2)–C(14)–C(13) | 107.5(8) |
| N(2)–C(14)–C(19) | 125.8(8) | C(13)–C(14)–C(19) | 125.9(8) |
| C(12)–C(15)–C(16) | 113.9(9) | C(13)–C(17)–C(18) | 111.4(9) |
| C(20)–N(3)–C(23) | 107.8(7) | C(20)–N(3)–Co(1) | 133.2(6) |
| C(23)–N(3)–Co(1) | 118.6(6) | C(14)–C(19)–C(20) | 131.1(8) |
| N(3)–C(20)–C(19) | 131.5(8) | N(3)–C(20)–C(21) | 107.5(8) |
| C(19)–C(20)–C(21) | 120.8(8) | C(20)–C(21)–C(22) | 107.9(8) |
| C(20)–C(21)–C(24) | 124.3(9) | C(22)–C(21)–C(24) | 127.7(8) |
| C(21)–C(22)–C(23) | 107.1(8) | C(21)–C(22)–C(26) | 127.7(8) |
| C(23)–C(22)–C(26) | 125.2(9) | N(3)–C(23)–C(22) | 109.5(8) |
| N(3)–C(23)–C(28) | 127.5(7) | C(22)–C(23)–C(28) | 122.9(8) |
| C(21)–C(24)–C(25) | 111.6(10) | C(22)–C(26)–C(27) | 112.2(9) |
| C(29)–N(4)–C(32) | 108.9(7) | C(29)–N(4)–Co(1) | 123.6(5) |
| C(32)–N(4)–Co(1) | 127.1(6) | C(23)–C(28)–C(29) | 124.4(8) |
| N(4)–C(29)–C(28) | 122.0(8) | N(4)–C(29)–C(30) | 109.4(7) |
| C(28)–C(29)–C(30) | 128.4(8) | C(29)–C(30)–C(31) | 106.2(8) |
| C(29)–C(30)–C(33) | 126.0(8) | C(31)–C(30)–C(33) | 127.8(9) |
| C(30)–C(31)–C(32) | 107.1(7) | C(30)–C(31)–C(35) | 129.2(8) |
| C(32)–C(31)–C(35) | 123.3(8) | C(1)–C(32)–N(4) | 126.3(8) |
| C(1)–C(32)–C(31) | 125.2(8) | N(4)–C(32)–C(31) | 108.5(7) |
| C(30)–C(33)–C(34) | 112.3(10) | C(31)–C(35)–C(36) | 110.8(8) |
| N(1)–C(37)–C(38) | 111.5(7) | N(1)–C(37)–Co(1) | 101.3(5) |
| C(38)–C(37)–Co(1) | 117.4(6) | C(37)–C(38)–O(1) | 127.8(8) |
| C(37)–C(38)–O(2) | 107.6(7) | O(1)–C(38)–O(2) | 124.2(8) |
| C(38)–O(2)–C(39) | 114.3(7) | O(2)–C(39)–C(40) | 104.1(11) |
| N(2)–C(41)–C(42) | 111.6(7) | N(2)–C(41)–Co(1) | 113.6(5) |
| C(42)–C(41)–Co(1) | 116.0(6) | C(41)–C(42)–O(3) | 129.0(9) |
| C(41)–C(42)–O(4) | 109.3(8) | O(3)–C(42)–O(4) | 121.7(8) |
| C(42)–O(4)–C(43) | 116.7(8) | O(4)–C(43)–C(44) | 109.7(13) |
| N(3)–Co(1)–N(4) | 95.2(3) | N(3)–Co(1)–C(41) | 97.1(3) |
| N(3)–Co(1)–C(41) | 97.6(4) | N(3)–Co(1)–O(6) | 93.8(3) |
| N(3)–Co(1)–O(5) | 156.3(4) | N(4)–Co(1)–C(37) | 84.6(3) |
| N(4)–Co(1)–C(41) | 164.9(4) | N(4)–Co(1)–O(6) | 90.9(3) |
| N(4)–Co(1)–O(5) | 86.0(3) | C(37)–Co(1)–C(41) | 85.8(3) |
| C(37)–Co(1)–O(6) | 168.6(4) | C(37)–Co(1)–O(5) | 106.6(3) |
| C(41)–Co(1)–O(6) | 96.3(3) | C(41)–Co(1)–O(5) | 85.5(3) |
| O(6)–Co(1)–O(5) | 62.5(3) | O(6)–N(5)–O(7) | 123.3(8) |
| O(5)–N(5)–O(7) | 123.1(7) | O(6)–N(5)–O(5) | 113.6(7) |
| N(5)–O(5)–Co(1) | 92.5(4) | N(5)–O(6)–Co(1) | 91.4(4) |

$C_{44}H_{56}CoN_5O_7$ requires N, 8.5%), *m/e* 850 (2%, $M - NO_3 +$ CH·CO₂Et), 764 (15, $M - NO_3$), 677 (7, $M - NO_3 - $ CH·CO₂Et), and 591 ($M - NO_3 - 2$ CH·CO₂Et), $\lambda_{max.}$ 401, 512, and 541 nm (ε 64 100, 10 500, and 11 350), $\nu_{max.}$ 1 707 (C=O), and 1 189 and 1 171 cm⁻¹ (C–CO–O), $\delta_H$ [signals relative to chloroform (δ 7.27)] 10.08, 9.96, 9.88, and 9.45 (s, 4 *meso*-H), 3.87 (m, 12 H of 6 peripheral CH₂), 3.56 and 3.37 (q, 4 H of 2 peripheral CH₂), 2.42 (m, 2 H of 1 ester CH₂), 1.82 (m, 21 H of 7 peripheral CH₃), 1.39 (t, 3 H of one peripheral CH₃), 0.36 (s, methine H of 1 bridge ester), 0.19 (m, 2 H of one ester

CH₂), −0.15 (t, 3 H of one ester CH₃), −1.26 (t, 3 H of one ester CH₃), and −7.91 (s, one ester methine H) (neither methine H is exchangeable with D₂O), $\delta_C$ (natural abundance) 172.0 and 166.3 (s, 2 C of ester carbonyls), 154.6, 153.3, 152.8, 148.8, 148.0, 147.7, 147.07, 145.6, 143.5, 142.4, 139.7, 138.3, 138.1, 135.9, 130.6, and 123.5 (s, 16 α- and β-ring C), 129.5 (d, methine ester C), 102.5, 102.2, 102.0, and 102.4 (d, 4 *meso*-C), 57.3 and 55.4 (t, 2 ester CH₂), 36.3 (d, methine ester C), 29.7 (t, peripheral CH₂ and CH₃), 14.0 (q, 1 peripheral CH₃), and 12.6 and 11.1 (q, 2 ester CH₃).

(b) Material from the band of medium polarity was separated and chromatographed as in (a) giving purple crystals of *isomer B* (from dichloromethane–light petroleum) (6.83 mg, 5.4%), *m/e* 850 (2%), 825 (1, *M*), 763 (34, $M - NO_3$) (10), 677 (5), and 591 (100), field desorption *m/e* 825.5 (100%, *M*), (Found: C, 64.45; H, 7.4; N, 8.3. $C_{44}H_{56}CoN_5O_7$ requires C, 64.0; H, 6.85; N, 8.5%), $\lambda_{max.}$ 403 and 541 nm (ε 64 000 and 11 430), $\lambda_{infl.}$ 510 nm (ε 10 310), $\nu_{max.}$ 1 701 and 1 708 (2 C=O), and 1 189 and 1 170 cm⁻¹ (C–CO–O), $\delta_H$ (CHCl₃ δ 7.27) 9.95, 9.91, 9.88, and 9.54 (s, 4 *meso*-H), 3.92 (m, 12 H of 6 peripheral CH₂), 3.74 and 3.53 (q, 4 H of other peripheral CH₂), 2.44 (m, 2 H of ester CH₂), 1.83 (m, 18 H of 6 peripheral CH₃), 1.59 and 1.35 (t, 6 H of peripheral CH₃), 0.35 (m, 2 H of ester CH₂), −0.09 (t, 3 H of ester CH₃), −1.31 (t, 3 H of ester CH₃), −1.59 (s, methine H of ester), and −7.85 (s, methine H of ester) (neither ester methine proton was exchangeable with D₂O).

(c) Material from the most polar brown band was separated and chromatographed as before; crystallisation gave purple crystals of *isomer C* (3) (31.39 mg, 24.8%) (Found: C, 64.4; H, 7.0; N, 8.45%), *m/e* 850 (3%), 825 (4), 763 (18), and 591 (100), field desorption *m/e* 825.3 (19.23%) and 763.5 (100), $\lambda_{max.}$ 400, 518, and 541 nm (ε, 63 100, 10 300, and 11 000), $\nu_{max.}$ 1 511 (NO₃), 1 703 (C=O), and 1 186 and 1 173 cm⁻¹ (C–CO–O), $\delta_H$ (CHCl₃ δ 7.27) 9.97, 9.96, 9.93, and 9.57 (all s, 4 *meso*-H), 3.80 (m, 16 H of 8 peripheral CH₂), 2.50 (m, 2 H of ester CH₂), 1.88 (m, 18 H of 6 peripheral CH₃), 1.63 and 1.41 (t, 6 H of 2 peripheral CH₃), 0.36 (m, 2 H of ester CH₂), −0.01 (t, 3 H of ester CH₃), −1.29 (t, 3 H of ester CH₃), −1.61 (s, methine H of bridge ester), and −7.68 (s, methine H of bridge ester) (neither methine proton was exchangeable with D₂O).

(ii) The above experiment was repeated with bromo[21-ethoxycarbonylmethylporphyrinato(2−)-C²¹,N²²,N²³,N²⁴]-cobalt(III) (100 mg) in acetone (25 ml) in the presence of sodium acetate (2 g). Ethyl diazoacetate (0.5 ml) in acetone (5 ml) was added and the mixture treated as before. After removal of the dichloromethane, the residue was repeatedly (6 ×) chromatographed on silica plates (30% ethyl acetate–light petroleum as eluant). The major band (isomer C) was separated and purified by further chromatography on silica and crystallisation from either dichloromethane–light petroleum or acetone containing aqueous sodium nitrate to give purple crystals (30—35 mg), identical with the previous product.

*Acetato*[trans-21,22-*bis(ethoxycarbonylmethyl)octaethylporphyrinato*(2−)-C^N(21),C^N(22),N²³,N²⁴]*cobalt*(III).—(i) A repetition of the previous experiment gave a product which, after extraction and chromatography on silica, yielded a major fraction. This was removed and crystallised from acetone containing aqueous sodium acetate to give black thin irregular plates of the *acetato-complex* (24 mg), m.p. 160° (decomp.) (Found: C, 67.15; H, 7.5; N, 6.7. $C_{46}H_{59}CoN_4O_6$ requires C, 67.15; H, 7.2; N, 6.8%), $\lambda_{max.}$ 296, 396, 468, 512, 549, 570, 710, and 785 nm (ε 29 100, 78 680, 11 900, 6 990,

6 700, 6 100, 9 000, and 16 000), $\nu_{max.}$ 1 700, 1 540, 1 190, and 1 180sh cm$^{-1}$, $\delta_H$ 10.00, 9.93, 9.87, and 9.49 (all s, 4 meso-H), 3.87 (m, 16 H of peripheral CH$_2$), 2.87 (m, 2 H of ester CH$_2$), 1.86 (m, 21 H of peripheral CH$_3$), 1.36 (t, 3 H of peripheral CH$_3$), 0.47 (m, 2 H of ester CH$_2$), 0.14 (t, 3 H of ester CH$_3$), −0.38 (s, 3 H of acetato CH$_3$), −1.29 (t, 3 H of ester CH$_3$), −1.38 (s, methine H of bridge ester), and−8.11 (methine H of bridge ester).

(ii) Isomer C of the nitrato complex (10 mg) was dissolved in acetone (5 ml) and aqueous sodium acetate was added until a slight turbidity appeared. The mixture was kept for 2 h at room temperature, then the crystals which had separated were filtered off and dissolved in a little dichloromethane. The solution was chromatographed on silica (25% ethyl acetate–light petroleum as eluant). The major product was removed and crystallised from acetone containing aqueous sodium acetate to give deep purple crystals (7 mg) of the acetato-complex, identical with the product from experiment (i).

trans-21,22-Bis(ethoxycarbonylmethyl)octaethylporphin Perchlorate (6).—(i) Isomer C of the nitrato-complex (3) (35 mg) was dissolved in ethanol (15 ml); the solution was saturated with nitrogen and sealed under nitrogen (septum cap). Chromium(II) chloride solution [8] (2 ml) was added with a syringe and the solution stirred for 12 min. It was then exposed to air and poured into aqueous 5% sodium chloride (25 ml). The aqueous solution was extracted with dichloromethane and the extract washed, dried, and evaporated. The residue was chromatographed on alumina. Elution with chloroform removed starting material. Further elution with 5% methanol–chloroform gave the product as a greenish-red solution. Evaporation, and crystallisation of the residue from acetone containing aqueous sodium perchlorate gave deep violet needles of the perchlorate (6) (26.6 mg) (76%), identical (spectra) with the product from the following experiment.

(ii) A solution of octaethylporphyrin (500 mg) in ethyl bromoacetate (500 ml) was heated on a steam-bath for 28 h. Solvent was removed under reduced pressure and a solution of the residue in chloroform was chromatographed on alumina. Octaethylporphyrin was eluted with chloroform, and the product then eluted with 5% methanol–chloroform.

The greenish-red solution was evaporated giving a violet crystalline residue; this was dissolved in methanol and aqueous sodium perchlorate was added. Next day the perchlorate (100 mg, 7%) was obtained as deep violet needles, m.p. 204—205° (Found: C, 65.55; H, 7.15; N, 6.9. C$_{44}$H$_{59}$ClN$_4$O$_8$ requires C, 65.5; H, 7.3; N, 6.95%), $\lambda_{max.}$ 406, 545, 579, and 625 nm ($\varepsilon$ 187 300, 10 400, 14 200, and 6 160), $\nu_{max.}$ 1 760 and 1 740sh (ester C=O) and 1 045s cm$^{-1}$ (perchlorate), $\delta_H$ 10.22 (1 H, s), 10.03 (1 H, s), and 10.46 (2 H, s) (meso-H), 4.20—3.70 (16 H, m, peripheral CH$_2$), 2.72 (4 H, q, ester CH$_2$), 1.88—1.34 (30 H, m, peripheral CH$_3$ and ester CH$_3$), −4.14 (1 H, s, N$^+$H), and −5.00 and −6.66 (4 H, both d, J 17 Hz, N·CH$_2$).

21-Ethoxycarbonylmethyl-22,23-ethoxycarbonylmethylene-octaethylporphyrin Perchlorate (7).—A suspension of isomer C of the nitrato complex (33.4 mg) in methanolic 10% hydrogen chloride (10 ml) was shaken for 2 h at room temperature. The resulting solution was poured into saturated aqueous sodium carbonate and the product extracted into dichloromethane. The extract was washed, dried, and evaporated to give a residue which was chromatographed on alumina. Starting material was removed by elution with chloroform, after which elution with 5% methanol–chloroform gave a green-red solution of the product. The solvent was again removed and the residue crystallised from acetone containing aqueous sodium perchlorate to give dark purple crystals (17.4 mg), m.p. 168—170° (Found: N, 6.55. C$_{44}$H$_{57}$ClN$_4$O$_8$ requires N, 6.95%), $\lambda_{max.}$ 407, 501sh, 541, 579, 606sh, and 631 nm ($\varepsilon$ 145 800, 2 720, 9 600, 13 400, 4 500, and 5 070), $\nu_{max.}$ 1 750 and 1 740sh cm$^{-1}$ (ester C=O), $\delta_H$ (CHCl$_3$) $\delta$ 7.27, 10.59 (1 H, s), 10.51 (2 H, s), and 10.27 (1 H, s, 4 meso-H), 4.35 (8 H, m) and 3.91 (8 H, m), (peripheral CH$_2$), 2.99 (2 H, q, ester CH$_2$), 1.95 (21 H, m, peripheral CH$_3$), 1.39 (5 H, m, peripheral CH$_3$ and ester CH$_2$), 0.43 (3 H, t, ester CH$_3$), −0.75 (3 H, t, ester CH$_3$), −3.79 and 5.27 (both 1 H, d, N·CH$_2$), and −4.91 (1 H, s, bridge methine).

[8] J. R. Hanson, Synthesis, 1974, 1.