The Crystal Structure of the Compound *meso,meso'*-Ethylenebis[octaethylporphyrinatonickel(II)] *

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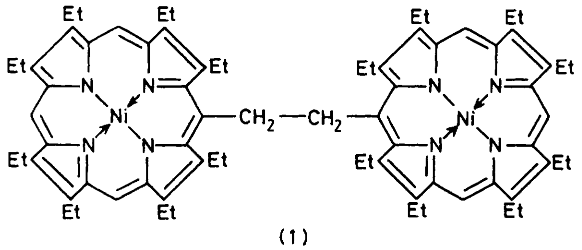
Crystals of the title compound as its chloroform solvate are triclinic, space group $P\bar{1}$, with $a = 11.056(2)$, $b = 11.595(2)$, $c = 15.112(3)$ Å, $\alpha = 75.48(2)$, $\beta = 78.81(3)$, $\gamma = 80.58(2)°$, and $Z = 1$. The structure has been refined to $R = 0.101$ for 2 252 reflections. The molecule has crystallographic $\bar{1}$ symmetry with parallel porphyrin rings. One methyl group from each ring lies almost directly under the edge of the other ring.

There is considerable interest in the preparation of bis-porphyrins, especially from the point of view of ring interaction, and several of these have been prepared in our laboratory.[1,2] The present work was undertaken to establish the relationship between the planes of the two porphyrin rings in a particular bis-porphyrin. When the title compound was first prepared it was found that there was a large upfield shift (*ca.* 0—9 p.p.m.) in the ^{1}H n.m.r. spectrum of one 6 H triplet, 2(β-CH_2-CH_3), presumably as a result of interaction with the other porphyrin ring. However, it was not at that time possible to find a crystal suitable for an *X*-ray structure determination. Recently another batch of crystals proved of better quality and we now report the structure of the title bis-porphyrin (1).



(1)

Results and Discussion

The molecular structure and atom-numbering scheme are shown in Figure 1. The molecule lies across a crystallographic inversion centre and thus the mean planes of the two porphyrin rings are parallel and the C(5)–C(21)–C(21')–C(5') torsion angle is 180°. The perpendicular distance between the two rings is 4.6 Å. The angle between the porphyrin ring planes and the plane defined by C(5),C(21),C(5'),C(21') is 59° and not the 90° which would maximise the perpendicular distance between the rings, presumably because at 90° there would be unacceptably short contacts between the C(24) and C(26') methylene groups. There is therefore a sideways shift of one ring relative to the other so as to bring C(26) over the gap between C(21') and C(24'). There is considerable distortion from planarity of the porphyrin rings as can be seen from Figure 2. In particular, C(5) is considerably out of the mean plane and so is C(21). This again is presumably to minimise the non-bonded contacts between the two rings. The rest of the atoms in the rings are disposed so as to accommodate this ' pulling ' of the C(5)–C(21) bond away from the plane of the ring. There is thus a broad shallow lip in each ring with their convex sides towards each other. The opposite end of each porphyrin ring at C(15) is also raised though to a lesser extent and the overall result is a shallow ' saddle ' shape for each ring.

The methyl group protons showing the large upfield shift in the ^{1}H n.m.r. spectrum are presumably those of the methyl group C(27) which lies almost directly under the edge of the other ring and would therefore be most affected by the field from the porphyrin ring current.

Experimental

A sample of (1) recrystallised from chloroform-methanol was supplied by Professor A. W. Johnson.

Crystal Data.—$C_{74}H_{90}N_8Ni_2 \cdot CHCl_3$, $M = 1\,328$, Triclinic, $a = 11.056(2)$, $b = 11.595(2)$, $c = 15.112(3)$ Å, $\alpha = 75.48(2)$, $\beta = 78.81(3)$, $\gamma = 80.58(2)°$, $U = 1\,826.2$ Å^3, $Z = 1$, $D_c = 1.21$ g cm^{-3}, $F(000) = 704$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 6.7$ cm^{-1}, space group $P\bar{1}$ from successful structure refinement.

Structure Solution and Refinement.—The crystal used was a dark red plate of dimensions *ca.* 0.3 × 0.3 × 0.1 mm which was sealed in a capillary to minimise solvent loss. All data were collected on an Enraf-Nonius CAD4 diffractometer. Preliminary cell dimensions were found using the SEARCH and INDEX routines. Accurate cell parameters were derived from the setting angles for 25 reflections with $\theta \simeq 15°$. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 20°$ were measured by a $\theta/2\theta$ scan with $\Delta\theta = (1.0 + 0.35 \tan\theta)°$ and monochromated Mo-K_α radiation. The scan rate for each reflection was determined by a rapid prescan at 20° min^{-1} in θ, at which point all reflections with $\sigma(I)/I > 2$ were coded as unobserved. The remainder were rescanned to give $\sigma(I)/I = 0.05$, subject to a maximum scan time of 60 s. Two standard reflections monitored every hour showed no significant variation. After correction for Lorentz and polarisation effects (Lp) but not for absorption, equivalent data were averaged and 2 252 reflections with $|F^2| > \sigma(F^2)$ were used in the structure analysis. The values of $\sigma(F^2)$ were calculated as $[\sigma^2(I) + (0.08I)^2]^{\frac{1}{2}}/\mathrm{Lp}$.

All non-hydrogen atoms of the complex were located by

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* *Supplementary data available* (No. SUP 23630, 14 pp.): bond distances and angles, anisotropic temperature factors, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

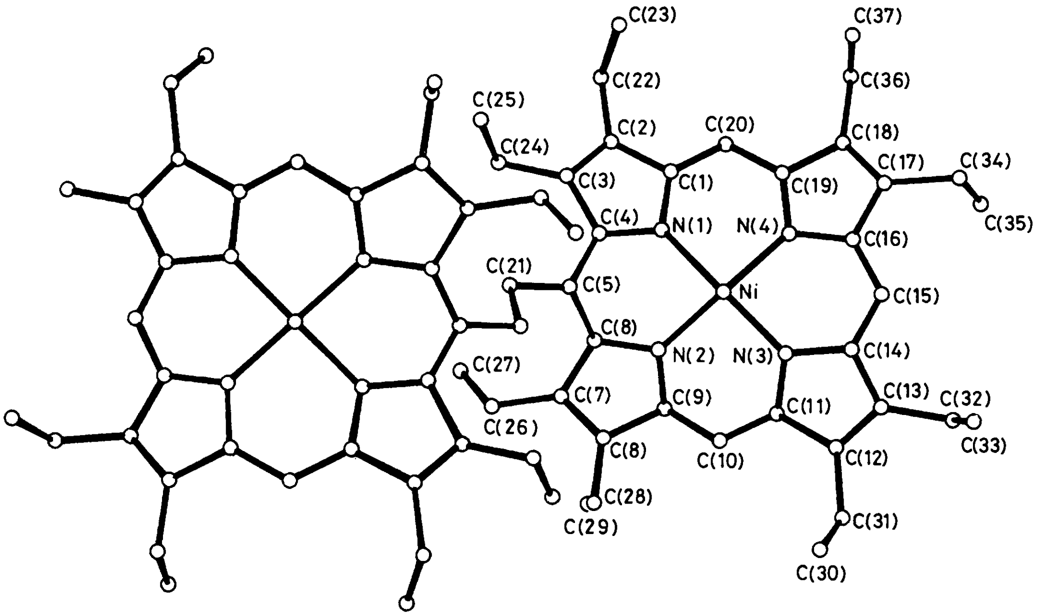

Figure 1. Molecular structure and atom-numbering scheme; only one of the two sites for C(29) is shown. The bond lengths to Ni are Ni–N(1) 1.918(8), Ni–N(2) 1.901(7), Ni–N(3) 1.927(7), and Ni–N(4) 1.911(8) Å

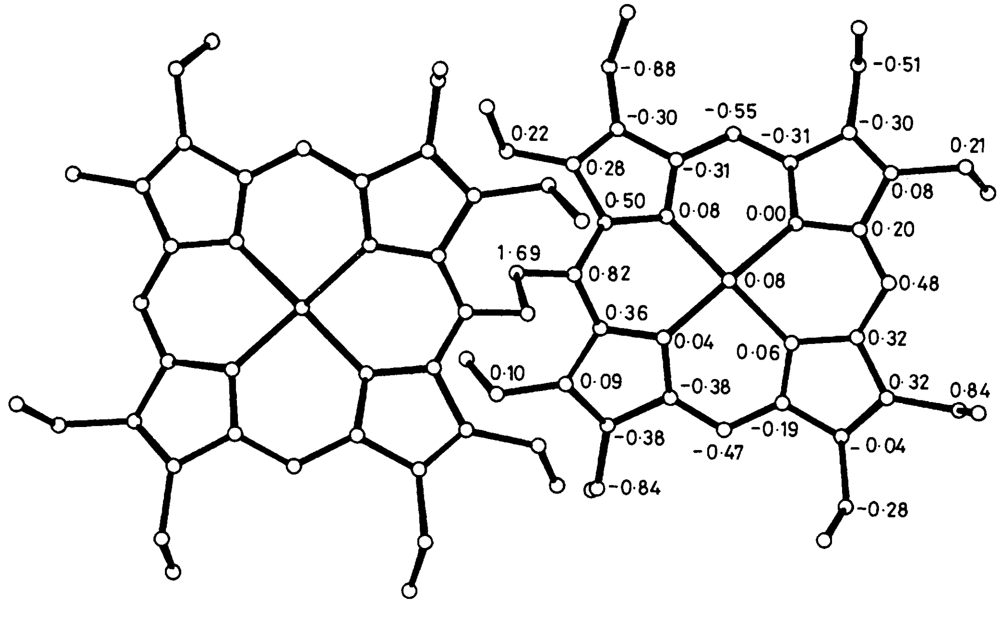

Figure 2. Deviations (Å) of atoms from the mean plane of the porphyrin ring. Atoms N(1)—N(4) and C(1)—C(20) were used to derive the plane

routine heavy-atom methods and were consistent with space group $P\bar{1}$. These atoms were refined by full-matrix least-squares methods with anisotropic temperature factors. A difference map revealed some rather diffuse peaks consistent with a molecule of chloroform in a general position and these atoms were included at half occupancy. Continued refinement converged at $R = 0.101$, $R' = 0.138$, where the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map had peaks of up to 1 e Å^{-3} near the solvent atoms but was elsewhere featureless. No attempt was made to include hydrogen atoms in the structure.

The structure solution and refinement were carried out on a PDP11/34 computer using the Enraf-Nonius structure determination package. Scattering factors for neutral atoms were taken from ref. 3. Final atomic co-ordinates are listed in the Table.

Table. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	−3 808(2)	1 125(1)	2 110(1)
N(1)	−3 743(10)	1 161(9)	826(7)
N(2)	−2 572(10)	−230(9)	2 186(7)
N(3)	−3 858(10)	1 089(9)	3 398(7)
N(4)	−5 104(10)	2 439(9)	2 063(7)
C(1)	−4 654(13)	1 683(12)	321(9)
C(2)	−4 320(16)	1 404(14)	−585(10)
C(3)	−3 142(13)	843(13)	−674(10)
C(4)	−2 766(13)	672(12)	237(8)
C(5)	−1 726(12)	−49(11)	516(8)
C(6)	−1 778(12)	−632(11)	1 443(9)
C(7)	−1 049(13)	−1 776(11)	1 808(9)
C(8)	−1 399(14)	−2 036(13)	2 746(11)
C(9)	−2 325(13)	−1 046(12)	2 992(10)
C(10)	−2 670(14)	−866(13)	3 866(9)
C(11)	−3 338(13)	191(12)	4 035(8)
C(12)	−3 547(14)	543(14)	4 921(9)
C(13)	−4 136(13)	1 631(12)	4 807(9)
C(14)	−4 397(13)	1 965(12)	3 880(9)
C(15)	−5 154(13)	2 973(13)	3 519(10)
C(16)	−5 557(13)	3 135(11)	2 680(9)
C(17)	−6 524(14)	4 018(12)	2 355(10)
C(18)	−6 740(13)	3 849(12)	1 591(9)
C(19)	−5 842(14)	2 885(11)	1 389(9)
C(20)	−5 679(13)	2 471(12)	576(10)
C(21)	−553(12)	−188(11)	−168(9)
C(22)	−5 268(16)	1 723(16)	−1 309(11)
C(23)	−5 164(20)	3 078(18)	−1 891(14)
C(24)	−2 592(17)	258(16)	−1 443(10)
C(25)	−1 953(20)	1 213(19)	−2 263(13)
C(26)	−219(13)	−2 617(12)	1 273(10)
C(27)	−994(16)	−3 248(13)	800(11)
C(28)	−970(15)	−3 115(13)	3 468(10)
C(29) *	−1 881(31)	−4 045(24)	3 730(24)
C(30)	−1 640(19)	−187(21)	5 687(14)
C(31)	−3 081(16)	−297(15)	5 817(10)
C(32)	−4 535(17)	2 403(15)	5 525(10)
C(33)	−3 674(19)	3 350(15)	5 381(12)
C(34)	−7 242(16)	4 930(15)	2 952(11)
C(35)	−8 257(22)	4 243(19)	3 722(16)
C(36)	−7 638(15)	4 592(14)	943(11)
C(37)	−7 086(19)	5 634(20)	300(13)
C(38) *	8 728(24)	2 389(24)	2 744(26)
Cl(1) *	8 922(10)	2 478(11)	3 625(6)
Cl(2) *	7 829(14)	3 777(12)	2 130(10)
Cl(3) *	10 023(20)	2 233(16)	1 888(9)
C(29A) *	−68(43)	−2 774(37)	3 900(28)

* Atom with an occupancy of 0.5.

References

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