Crystal and Molecular Structure of Di(pyridine)magnesium(II) Octaethylporphyrinate

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The title compound crystallises in the triclinic space group $P\bar{1}$ with unit-cell dimensions $a = 10.607(3)$, $b = 10.423(4)$, $c = 9.957(4)$ Å, $\alpha = 114.69(4)$, $\beta = 90.56(3)$, and $\gamma = 99.27(3)°$. The structure was solved and refined by standard methods to R 0.036 for 2115 significant intensities measured by diffractometer. The unit cell contains one centrosymmetric molecule in which the magnesium atom is six-co-ordinated by the four nitrogen atoms from the porphyrinate ligand [Mg–N 2.064(2) and 2.072(2) Å] and two pyridine nitrogen atoms with a unique distance of 2.389(2) Å. This contrasts with most other Mg(tetrapyrrole) complexes which are either four- or five-co-ordinate species. The macrocycle shows small but significant deviations from planarity and has bond lengths and angles comparable with those of other metalloporphyrins.

THE nature of the co-ordination sphere of the magnesium(II) ion in the chlorophylls is of particular importance because it is one of the factors likely to be responsible for the shift in absorption to lower energies (*e.g.* 665 →680 or 700 nm) on going from solution to chloroplast.[1] It is thus one of the factors to be considered in distinguishing antennae chlorophyll and photoreaction-centre chlorophyll from monomeric chlorophyll in solution.

X-Ray analyses of several magnesium(II) macrocyclic tetrapyrrole complexes have been reported. Apart from an early study[2] on magnesium(II) phthalocyaninate, which appears to have been an anhydrous square-planar complex, the compounds available for study have all been shown to be five-co-ordinated complexes with a square-pyramidal type of structure. The 'extra' ligand has in each case been water, and the magnesium(II) ion has been displaced towards it, *i.e.* out of the plane of

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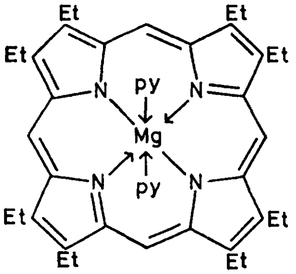
[1] For a review see J. J. Katz, W. Oettmeier, and N. R. Norris, *Phil. Trans.*, 1976, **B273**, 227.

[2] R. P. Linstead and J. M. Robertson, *J. Chem. Soc.*, 1936, 1736.

the nitrogen atoms of the macrocyclic ligand. The out-of-plane displacement varies from compound to compound, *e.g.* 0.27 in aquomagnesium(II) tetraphenylporphyrinate,[3] 0.39 in both ethyl chlorophyllide *a*[4] and ethyl chlorophyllide *b*,[5] 0.34 in methyl chlorophyllide *a* dihydrate[6] and 0.40 Å in methyl pyrochlorophyllide *a* monohydrate monoetherate.[7] This geometry is adopted even in the aquodi(pyridine)-complex of magnesium(II) phthalocyaninate[8] which has adequate potential ligands available: here the two pyridine molecules are merely hydrogen bonded to the water ligand, and the magnesium(II) ion is 0.496 Å out-of-plane. This structure is remarkable considering the six-co-ordination observed for Mg^{II} in simple salts (*e.g.* $MgSO_4 \cdot 6H_2O$).[9]

We report here the structure of di(pyridine)magnesium(II) octaethylporphyrinate (1), which appears to be



(1)

the first magnesium(II) complex of a macrocyclic tetrapyrrole whose six-co-ordinated structure has been demonstrated in this way.

EXPERIMENTAL

The magnesium(II) complex (1) was prepared in the usual way[10] and recrystallised from chloroform–pyridine. Preliminary unit-cell parameters and the crystal system were determined from oscillation and Weissenberg photographs. Accurate cell parameters were determned from least-squares refinement of setting angles for 15 reflections automatically centred on a computer-controlled diffractometer.

Crystal Data.—$C_{46}H_{54}MgN_6$, $M = 715$, triclinic, $a = 10.607(3)$, $b = 10.423(4)$, $c = 9.567(4)$ Å, $\alpha = 114.69(4)$, $\beta = 90.56(3)$, $\gamma = 99.27(3)°$, $U = 983$ Å^3, $D_m = 1.20$ g cm^{-3}, $Z = 1$, $D_c = 1.21$ g cm^{-3}, $F(000) = 384$. λ(Mo-K_α) = 0.710 69 Å; μ(Mo-K_α) = 0.76 cm^{-1}. Space group $P\bar{1}$.

The intensities of 2 712 unique reflections ($1.5 < \theta < 30°$) were measured from a crystal, with dimensions $0.30 \times 0.25 \times 0.15$ mm, mounted on a Nonius CAD4 diffractometer, using monochromated Mo-K_α radiation and an ω–2θ scan technique. Two reference reflections measured after every fifty reflections showed only minor fluctuations in the primary beam. The intensities were corrected for the usual Lp^{-1} factors but no absorption corrections were made. 2 115 unique reflections having $I_o > 1.5\sigma$ (I_o) were used in the structure analysis and refinement. The structure was determined assuming the space group to be $P\bar{1}$, a choice finally confirmed by successful refinement. The unit cell contains only one molecule of $(py)_2Mg(oep)$ (py = pyridine, oep = octaethylporphyrin) which is thus required to possess a centre of symmetry. The Patterson map was too complicated to interpret but a difference electron-density map phased on the Mg atom at 0,0,0 showed two peaks at *ca.* 2.0 Å from the origin which, with their centrosymmetric relatives formed a square around the metal, and 7 other peaks of which 4 completed one pyrrole ring. A second difference map phased on these atoms revealed the pyridine ring and 5 more carbon atoms. This model (21 atoms) was subjected to 3 cycles of isotropic least-squares refinement to give R 0.40 and a further difference map now revealed the positions of the remaining 6 non-hydrogen atoms in the asymmetric unit.

The structure was refined by blocked full-matrix least-squares methods to R 0.11 (all atoms isotropic) and R 0.08 (all atoms anisotropic). The hydrogen atoms were located on a difference map and included in the refinement with isotropic temperature factors. The final value of R was 0.036 4 and R' 0.034 1, with all parameter shifts/$\sigma \leqslant 0.03$. The weighting scheme $w = 1/\sigma^2 (F_o)$ was used and this gave reasonably flat analysis of variance with F_o, $\sin\theta$, reflection indices, and parity groups. Fractional atom co-ordinates with their estimated standard deviations are given in Tables 1 and 2. Anisotropic thermal parameters and lists

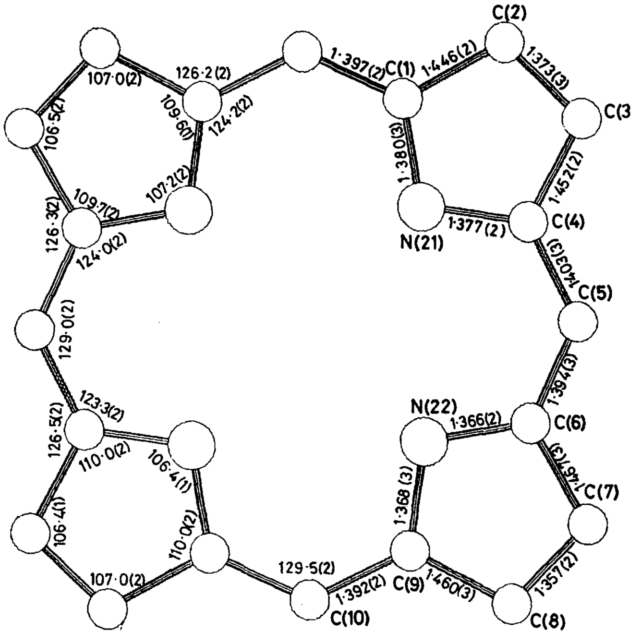


FIGURE 1 Illustration of important bond lengths (Å) and angles (°) in the porphyrin skeleton

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of F_o and F_c are listed in Supplementary Publication No. SUP 22115 (15 pp, 1 microfiche).* Important interatomic distances and angles are given in Table 3 and in Figure 1. Various least-squares planes are presented in Table 4. All calculations were performed on the Queen Mary College ICL 1904S and University of London CDC 7600 computers using the programs SHELX 76[11] for structure solution and refinement, XANADU[12] for least-

TABLE 1

Fractional co-ordinates (× 10^5) of the non-hydrogen atoms

Atom	x	y	z
Mg	0	0	0
N(21)	5 131(14)	20 527(16)	16 599(17)
N(22)	16 273(14)	−5 409(16)	6 452(17)
C(1)	−1 034(18)	31 900(19)	19 054(21)
C(2)	6 131(18)	44 899(20)	30 663(21)
C(3)	16 728(18)	41 280(20)	32 553(21)
C(4)	16 030(18)	26 014(19)	26 265(21)
C(5)	25 169(19)	17 789(21)	26 608(22)
C(6)	25 341(17)	3 350(20)	17 780(21)
C(7)	34 925(18)	−4 812(21)	19 170(21)
C(8)	31 245(17)	−18 445(21)	8 604(22)
C(9)	19 528(18)	−18 743(20)	580(21)
C(10)	12 425(19)	−30 680(22)	−11 088(22)
C(21)	2 762(23)	59 589(22)	35 694(26)
C(22)	7 222(32)	66 646(32)	25 542(39)
C(31)	27 135(22)	51 006(24)	47 113(25)
C(32)	38 388(29)	57 472(38)	41 389(39)
C(71)	46 676(21)	1 212(28)	29 918(29)
C(72)	58 065(26)	7 404(39)	23 980(43)
C(81)	37 762(22)	−31 092(24)	5 613(27)
C(82)	45 742(28)	−34 699(33)	−7 553(33)
N(25)	11 542(15)	8 129(17)	−16 312(18)
C(26)	10 349(23)	458(27)	−30 947(26)
C(27)	16 538(26)	5 032(32)	−40 731(31)
C(28)	24 426(26)	18 151(30)	−35 182(33)
C(29)	25 873(24)	26 169(29)	−20 267(31)
C(30)	19 314(21)	20 279(25)	−11 183(29)

TABLE 2

Fractional co-ordinates (× 10^4) and isotropic temperature factors (× 10^3) of the hydrogen atoms

Atom	x	y	z	U_{iso}
H(5)	3 225(18)	2 289(19)	3 337(20)	34(5)
H(10)	1 557(16)	−3 947(20)	−1 437(19)	31(5)
H(21a)	662(20)	6 587(23)	4 611(26)	54(6)
H(21b)	−649(21)	5 888(21)	3 649(22)	50(6)
H(22a)	442(27)	6 026(32)	1 448(37)	107(11)
H(22b)	1 626(30)	6 796(31)	2 465(32)	102(11)
H(22c)	434(25)	7 520(30)	2 850(28)	83(9)
H(31a)	2 357(20)	5 899(25)	5 483(25)	58(7)
H(31b)	3 001(19)	4 630(21)	5 289(22)	47(6)
H(32a)	4 489(26)	6 373(20)	4 983(32)	88(9)
H(32b)	4 187(29)	4 994(36)	3 316(37)	110(12)
H(32c)	3 533(32)	6 231(36)	3 506(40)	131(14)
H(71a)	4 481(20)	858(25)	3 972(26)	58(7)
H(71b)	4 844(20)	−609(25)	3 275(24)	58(7)
H(72a)	6 004(26)	−9(33)	1 456(34)	92(10)
H(72b)	5 584(30)	1 586(36)	2 228(35)	123(12)
H(72c)	6 546(31)	1 172(31)	3 184(34)	112(11)
H(81a)	3 095(19)	−4 012(22)	356(21)	43(6)
H(81b)	4 298(21)	−2 908(22)	1 482(25)	55(6)
H(82a)	4 992(22)	−4 349(25)	−928(24)	64(7)
H(82b)	4 073(24)	−3 699(26)	−1 663(29)	72(8)
H(82c)	5 230(25)	−2 622(30)	−607(28)	76(9)
H(26)	453(20)	−873(25)	−3 448(24)	59(7)
H(27)	1 497(25)	−202(29)	−5 137(31)	91(9)
H(28)	2 912(24)	2 149(27)	−4 144(28)	77(8)
H(29)	3 148(23)	3 598(27)	−1 542(26)	73(8)
H(30)	2 020(21)	2 691(24)	−9(27)	65(7)

* Hydrogen atoms are numbered according to the parent carbon atom, distinguished by a, b, or c if more than one is present.

TABLE 3

Selected interatomic distances (Å) and angles (°)

(*a*) Distances			
Mg–N(21)	2.064(2)	N(21) · · · N(25)	3.108
Mg–N(22)	2.075(2)	N(21′) · · · N(25)	3.205
Mg–N(25)	2.389(2)	N(22) · · · N(25)	3.203
N(21) · · · N(22)	2.915	N(22′) · · · N(25)	3.125
N(21) · · · N(22′)	2.938		
C(2)–C(21)	1.504(3)	C(21)–C(22)	1.518(5)
C(3)–C(31)	1.501(3)	C(31)–C(32	1.510(4)
C(7)–C(71)	1.501(3)	C(71)–C(72)	1.519(5)
C(8)–C(81)	1.508(3)	C(81)–C(82)	1.513(4)
Mean C(sp^2)–C(sp^3)	1.503	Mean C(sp^3)–C(sp^3)	1.515
N(25)–C(26)	1.330(3)	C(28)–C(29)	1.358(4)
C(26)–C(27)	1.381(5)	C(29)–C(30)	1.379(4)
C(27)–C(28)	1.366(4)	C(30)–N(25)	1.337(3)
(*b*) Angles			
N(21)–Mg–N(22)	89.6(1)	C(3)–C(31)–C(32)	113.8(2)
N(21)–Mg–N(25)	88.2(1)	C(7)–C(71)–C(72)	112.9(3)
N(22)–Mg–N(25)	91.4(1)	C(8)–C(81)–C(82)	114.2(3)
		C(26)–N(25)–C(30)	116.3(2)
C(1)–C(2)–C(21)	125.1(2)	N(25)–C(26)–C(27)	123.8(2)
C(3)–C(2)–C(31)	127.8(2)	N(25)–C(30)–C(29)	123.2(2)
C(2)–C(3)–C(31)	127.5(2)	C(26)–C(27)–C(28)	118.7(2)
C(4)–C(3)–C(31)	126.0(2)	C(28)–C(29)–C(30)	119.4(2)
C(6)–C(7)–C(71)	125.6(2)	C(27)–C(28)–C(29)	118.7(3)
C(8)–C(7)–C(71)	127.9(2)		
C(7)–C(8)–C(81)	127.4(2)	Mg–N(25)–C(26)	122.3(1)
C(9)–C(8)–C(81)	125.6(2)	Mg–N(25)–C(30)	121.4(2)
C(2)–C(21)–C(22)	112.2(2)		

TABLE 4

Least-squares planes in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates. Deviations (Å × 10^3) of relevant atoms are given in square brackets

Plane (1): N(21), N(22), Mg

$$-5.104\,5x - 5.444\,1y + 8.3103z = 0$$

[C(1) −101, C(2) −209, C(3) −172, C(4) −52, C(5) −42, C(6) 2, C(7) 72, C(8) 124, C(9) 72, C(10) 115]

Plane (2): N(21), N(22), C(1)—(10)

$$-5.227\,8x - 5.095\,2y + 8.362\,6z = 0.002\,6$$

[N(21) 71, N(22) 38, C(1) 19, C(2) −47, C(3) −32, C(4) 30, C(5) 0, C(6) −11, C(7) 20, C(8) 23, C(9) −20, C(10) −16, Mg −3, H(5) −31, H(10) −7]

Plane (3): N(21), C(1)—(4)

$$-5.229\,3x - 4.703\,8y + 8.486\,6z = 0.171\,5$$

[N(21) 3, C(1) −1, C(2) −2, C(3) 4, C(4) −4, Mg −172]

Plane (4): N(22), C(6)—(9)

$$-5.474\,4x - 4.955\,0y + 8.238\,1z = -0.090\,9$$

[N(22), 0, C(6) 2, C(7) −3, C(8) 3, C(9) −2, Mg 91]

Plane (5): N(25), C(26)—(30)

$$9.1254x - 6.633\,8y + 2.709\,5z = 0.073\,0$$

[N(25) −1, C(26) 3, C(17) −1, C(28) −1, C(29) 3, C(30) −2, H(26) −15, H(27) 35, H(28) 38, H(29) −5, H(30) −18, Mg −73]

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[11] G. M. Sheldrick, University of Cambridge.

[12] P. Roberts and G. M. Sheldrick, University of Cambridge.

squares plane calculations, and PLUTO[13] for drawing molecular diagrams. Neutral atom scattering factors were taken from ref. 14 for hydrogen and ref. 15 for other atoms.

DISCUSSION

The crystal structure consists of discrete, centrosymmetric molecules separated by the usual van der Waals contacts. A representation of the molecular packing is shown in Figure 2.

The structure of a single molecule is shown in Figure 3 which also indicates the labelling of atoms. The magnesium is six-co-ordinated by four porphyrinato and two pyridine nitrogen atoms forming an octahedron with considerable tetragonal distortion, the Mg-N(py) distance [2.389(2) Å] being much longer than the average Mg-N(pyrrole) distance [2.068(3) Å]. The corresponding distortion in the analogous Ru derivative[16] is much smaller with a Ru-N(py) distance of 2.100 Å and Ru-N-(pyrrole) distances of 2.046 and 2.048 Å. The Mg-N(py) distance in the present compound is also significantly longer than those in other six-co-ordinated Mg^{II} compounds, *e.g.* $MgBr_2 \cdot C_6H_5N$ [2.17(5), 2.22(8) Å][17] and $Mg(C_5H_4NCO_2)_2 \cdot 2H_2O$ (2.19 and 2.25 Å),[18] and this suggests that in $(py)_2Mg(oep)$ the pyridine ligands are weakly bound. The N(py) · · · N(pyrrole) contacts range from 3.108 to 3.205 Å and are approximately equal to normally accepted van der Waals distances. The present complex contrasts greatly with the structures so far reported for other magnesium(II) complexes of porphyrins and related compounds, most of which possess five-co-ordinate, square-pyramidal configurations with Mg-N(pyrrole) distances ranging from 2.004 to 2.167 Å. The only other complex in which magnesium(II) ion lies at the centre of an N_4 macrocycle is the square-planar magnesium(II) phthalocyaninate,[2] for which molecular dimensions are unavailable.

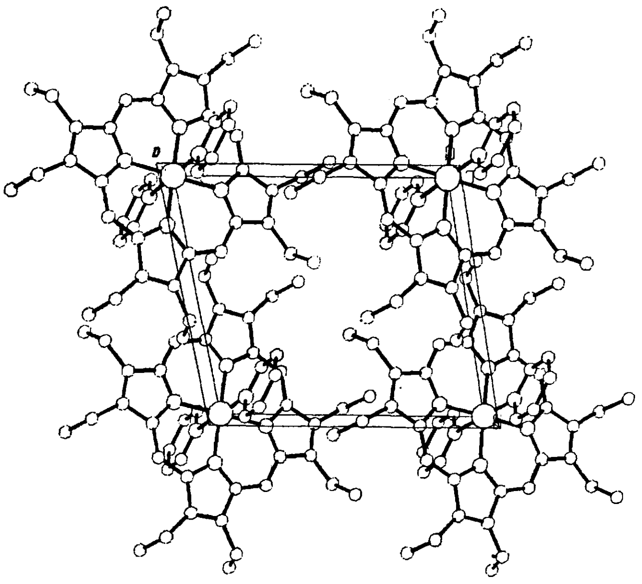


FIGURE 2 Packing of the molecules in the unit cell

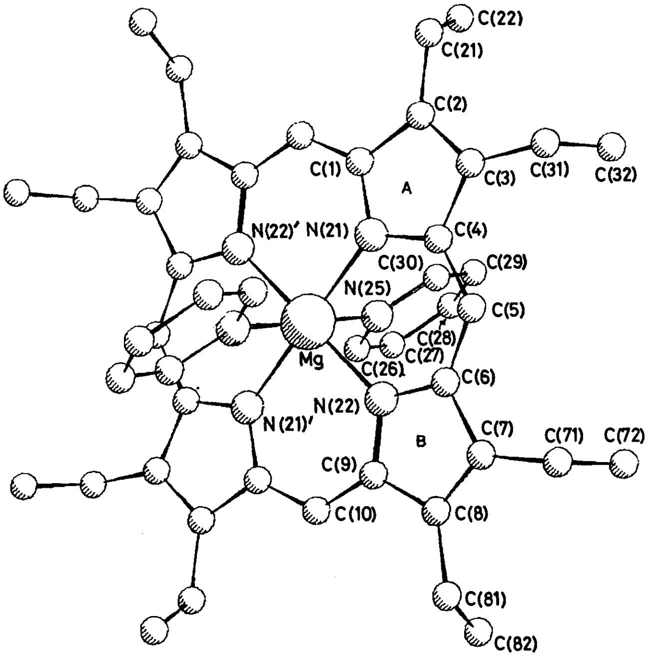
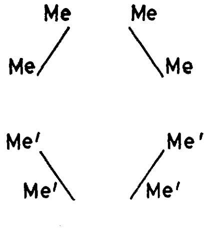


FIGURE 3 The structure of a single molecule together with the labelling of atoms

The bond lengths and angles within pyrrole ring A are strikingly similar to the corresponding values in the crystallographically independent ring B. This agrees with the situation in $(py)_2Ru(oep)$[16] but contrasts with that in metal-free porphyrin and some of its derivatives where significant differences are observed.[19-22] As expected, rings A and B are planar within 0.004 Å; they are inclined at 5.1 and 3.2° respectively to the MgN_4



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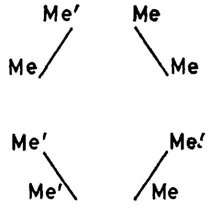

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plane and mutually at 3.1°. The porphyrin moiety as a whole is non-planar; the deviations of atoms from the least-squares plane of the macrocycle are small ($\leqslant$0.071 Å) but significant.

The bond lengths involving the *meso*-carbons, C(5) and C(10) range from 1.392(2) to 1.403(3) Å, and the mean 1.396(1) Å is comparable with those in other porphyrins. The methyl groups of the ethyl substituents are bent out of the plane. For each pyrrole ring the methyl groups are bent in the same sense as one another as shown schematically in (2). A similar arrangement exists in octaethylporphyrin,[22] but in $(py)_2(oep)Ru$ [16] the substituents are bent out of the plane in a different way, shown schematically in (3). [The oblique lines in (2) and (3) represent ββ′ bonds of the pyrrole rings. Primes indicate that the methyl group lies above the plane of the paper, unprimed groups are below.]

The dimensions of the ethyl groups, and of the pyridine ring, are normal. The C–H distances in the structure lie in the range 0.92(3)—1.04(5) Å, mean 0.99(1) Å.

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