

The Crystal and Molecular Structure of 2,3,7,8,12,13,17,18-Octaethylporphinatomonopyridinezinc(II)

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The structure of 2,3,7,8,12,13,17,18-octaethylporphinatomonopyridinezinc(II), $C_{41}H_{49}N_5Zn$, has been determined from three-dimensional counter data. 6315 independent reflections were measured. The compound crystallizes in the triclinic space group $P\bar{1}$ with a unit cell of $a=10.486$ (2), $b=17.192$ (4), $c=10.048$ (2) Å, $\alpha=93.99$ (2), $\beta=93.81$ (2), $\gamma=83.84$ (2)°. There are two molecules in the unit cell. The structure was solved by heavy-atom methods and refined by least-squares techniques to a final conventional R index of 0.040 (based on F) for the 4059 reflections having $I \geq 3\sigma_I$. The metalloporphyrin is a square-pyramidal complex with a pyridine group as the axial ligand. The average zinc-pyrrole nitrogen atom bond length is 2.067 (6) Å, while the zinc-pyridine nitrogen atom bond distance is 2.200 (3) Å. The zinc ion is 0.31 Å out of the plane of the four pyrrole nitrogen atoms. The macrocycle shows small deviations from planarity. Interplanar angles between adjacent rings range from 4 to 9°. Interesting comparisons may be made with other zinc metalloporphyrins and with other octaethylporphyrin complexes.

Introduction

The structures of a wide variety of metalloporphyrins have now been studied by X-ray diffraction techniques. Most commonly, two synthetic macrocycles have been used. The most popular is $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin (H_2TPP), which is substituted at the methine carbon atoms. In recent years 2,3,7,8,12,13,17,18-octaethylporphyrin (H_2OEP) has been increasingly used. This latter macrocycle is substituted at the β -pyrrole carbon atoms, as are all naturally occurring porphyrins. It is less likely to suffer from steric effects than tetraphenylporphyrin.

The free bases of both macrocycles have been studied (Silvers & Tulinsky, 1967; Hamor, Hamor & Hoard, 1964; Lauher & Ibers, 1973). In addition the structures of bis(imidazole)iron(III)TPP chloride (Collins, Countryman & Hoard, 1972) and bis(imidazole)iron(III)OEP perchlorate (Takenaka, Sasada, Watanabe, Ogoshi & Yoshida, 1972) have been studied. In these the central hole has almost the optimum size. On the other hand the porphinato core in the structures of $Cl_2Sn^{IV}OEP$ (Cullen & Meyer, 1973) and $Cl_2Sn^{IV}TPP$ (Collins, Scheidt & Hoard, 1972) is expanded. In all of the complexes mentioned the metal ion has octahedral coordination and lies in the plane of the porphyrin. Several differences in certain bond lengths and angles for analogous complexes have been observed.

We report here the structure of 2,3,7,8,12,13,17,18-octaethylporphinatomonopyridinezinc(II) (PyrZnOEP). Since the structure of an analogous *meso*-substituted complex, $\alpha,\beta,\gamma,\delta$ -tetra-(4-pyridyl)porphinatomonopyridinezinc(II), PyrZnTPyP, has already been reported (Collins & Hoard, 1970), the present study allows comparisons to be extended to the case of five-coordinate square-pyramidal geometry in which

the metal ion lies out of the plane of the macrocycle. It is also of interest to see how this complex fits the trends in the bond parameters which have been noted as a function of the radius of the central hole (Hoard, 1973). There is a 0.15 Å range in this radius among the various octaethylporphyrin complexes which have been studied, a wider range than in the tetraphenylporphyrin complexes, so trends should be more evident.

Experimental

Samples of 2,3,7,8,12,13,17,18-octaethylporphinatomonopyridinezinc(II) were supplied by Dr David Dolphin. Crystals of the monopyridine adduct were obtained from a 1:1 pyridine-dioxane solution. The crystals grew as reddish rods elongated along **a** and bounded by {001} and {010}. The crystal used for intensity measurements was mounted in a glass capillary (Meyer, 1973). The approximate dimensions of the crystal were 0.43 × 0.12 × 0.24 mm in the directions of **a**, **b** and **c** respectively.

Cell data are summarized in Table 1. Cell dimensions were determined by least-squares calculations, minimizing the differences between observed and calculated 2θ values (measured at both + and -2θ) for 24 reflections. The ambient temperature was 22°C. Cell-constant data and subsequent intensity data were measured on a Datex-Syntex automated diffractometer using Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). The radiation was monochromatized by pyrolytic graphite. The density was measured by flotation in an aqueous thallos formate solution. The choice of the centrosymmetric space group, $P\bar{1}$, was confirmed by the successful solution of the structure.

Data were collected by the θ - 2θ scan method, monitoring the intensity scale by remeasuring a group

Table 1. *Crystal data*

In this and subsequent tables e.s.d.'s for the least significant figure are in parentheses.

$(C_{36}H_{44}N_4)Zn(C_5H_5N)$	F.W. 677.2
$a = 10.486$ (2) Å	$Z = 2$
$b = 17.192$ (4)	$D_c = 1.25$ g cm ⁻³
$c = 10.048$ (2)	$D_m = 1.25$ (1)
$\alpha = 93.99$ (2)°	$\mu(\text{Mo } K\alpha) = 7.43$ cm ⁻¹
$\beta = 93.81$ (2)	Systematic absences: None
$\gamma = 83.84$ (2)	Space group $P\bar{1}$
$V = 1793.4$ Å ³	

of five standard reflections periodically. The fluctuations in the intensities of these standard reflections showed no systematic trend and were not considered significant, hence no corrections were made. The scan rate was 2° min⁻¹ for reflections with $2\theta \leq 40^\circ$; for reflections with $2\theta > 40^\circ$ the scan rate was 1° min⁻¹ if the peak height at the calculated position was more than 4 counts s⁻¹, and 2° min⁻¹ if it was less than this threshold. The average background was about 4 counts s⁻¹, and hence reflections at or below this threshold were not likely to be statistically observed. As these reflections were not to be used in the analysis, they were collected relatively quickly. The scan range was 2°. Backgrounds at either end of the scan range were collected for half the scan time. Independent reflections (6315) were measured out to a $\sin \theta/\lambda$ of 0.595 or 25° θ . Of these, 4059 had a net intensity greater than $3\sigma_I$ and were used in the analysis. The standard deviation σ_I was defined in terms of the statistical variances of the counts as $\sigma_I^2 = \sigma_I^2(\text{count}) + K^2(S + B1 + B2)^2$ where S , $B1$, and $B2$ are the observed counts for the scan and two backgrounds respectively. $\sigma_I^2(\text{count})$ is the variance determined solely from counting statistics. A value of 0.03 was used for K .

The intensities were corrected for coincidence using the method of Sletten, Sletten & Jensen (1969) ($\tau = 3.49 \times 10^{-7}$ counts⁻¹). The data were corrected for absorption by means of a Gaussian integration method. The transmission coefficients varied from 0.84 to 0.92. Structure factors were calculated in the usual way, assuming an ideally imperfect monochromator for the polarization factor.

Determination and refinement of the structure

Because there are two molecules in the unit cell of space group $P\bar{1}$, all atoms lie in general positions. The position of the zinc atom was found from an unsharpened Patterson synthesis. The rest of the 47 nonhydrogen atoms were found from a series of Fourier and difference maps. The 49 hydrogen atoms were located from a difference synthesis later in the refinement procedure.

Least-squares refinement using block-diagonal and finally full-matrix methods was carried out. The function minimized was $\sum w(F_o - F_c)^2$, where $w = 1/\sigma_F^2$. Initially isotropic temperature factors were used, but in the final refinement all nonhydrogen atoms were

varied assuming anisotropic thermal motion. The hydrogen atoms, which were also refined, were assumed to have isotropic thermal motion. Because of computer-memory limitations the parameters had to be refined in three blocks during the full-matrix least-squares refinement. In block I the metal ion and all the atoms in the porphyrin skeleton were refined. In block II the zinc ion and the atoms in six of the ethyl groups were refined, while in block III the metal ion, the four pyrrole nitrogen atoms, the atoms in the remaining two ethyl groups and the atoms in the pyridine molecule were refined. The refinement converged with $R = \sum ||F_o| - |F_c|| / \sum F_o = 0.040$ and $R_w = [\sum w ||F_o| - |F_c||^2 / \sum w F_o^2]^{1/2} = 0.039$.

A correction for anomalous dispersion was made for the zinc ion ($\Delta f' = 0.222$, $\Delta f'' = 1.431$) (Cromer & Liberman, 1970). Scattering factors were from *International Tables for X-ray Crystallography* (1974). The zinc ion was assumed to be in the zero ionization state.

In the last cycle of refinement all shifts were less than one standard deviation with virtually all of the nonhydrogen atom parameters having a shift/error ratio less than 0.3. The final value of the standard deviation of an observation of unit weight, defined as $[\sum w ||F_o| - |F_c||^2 / (N_o - N_p)]^{1/2}$ was 1.19 for $N_o = 4059$ reflections, $N_p = 620$ parameters. In the final difference synthesis no peak greater than 0.30 e Å⁻³ was found. The highest peak and one of only slightly lower electron density (0.28 e Å⁻³) did not conform to any feature of the molecule. The closest nonhydrogen atom to both peaks was C(26), located 2.0–2.5 Å away. The next several highest peaks on the difference map were located close to atomic positions. None of these was considered of any significance.

Most of the programs used have been summarized elsewhere (Cullen & Meyer, 1974a). Other programs included *DATAPH* (Gaussian numerical integration absorption corrections), *FOURIER* (another version of the Zalkin Fourier program written by Robinson & Dellaca), *XANADU*, a molecular geometry program by Roberts & Sheldrick, and *LIST* by Snyder for listing the structure factors. Use was made of the interactive color TV raster display in this laboratory (Willoughby, Morimoto, Sparks & Meyer, 1974) as well as the PDP 11/40 Vector General graphics system which is a part of the *CRYSNET* network (Meyer *et al.*, 1974; Morimoto & Meyer, 1975).

The final positional and thermal parameters for nonhydrogen atoms are given in Table 2 and for hydrogen atoms in Table 3, while the r.m.s. components of thermal displacement along the principal axes of the thermal ellipsoids are given in Table 4.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31698 (29 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The structure 2,3,7,8,12,13,17,18-octaethylporphyrin-atomopyridinezinc(II), PyrZnOEP, is shown in Fig. 1. This figure also shows the numbering system used. A stereo view of the molecule is shown in Fig. 2. Bond lengths and angles are listed in Table 5. The complex is a five-coordinate square-pyramidal metalloporphyrin with a pyridine molecule as the axial ligand. The zinc ion lies 0.31 Å out of the plane of the four pyrrole nitrogen atoms towards the pyridine molecule.

Averaged bond lengths and angles for PyrZnOEP are shown in Fig. 3. Also shown in this figure is the nomenclature for the different types of atoms in the

porphyrin macrocycle to be used in the subsequent discussion. Agreement between chemically equivalent bond lengths and angles is very good, allowing comparisons with other zinc porphyrin complexes and other octaethylporphyrin compounds.

The average zinc-pyrrole nitrogen atom bond length is 2.067(6) Å. Collins & Hoard (1970) have postulated that the optimum radius of the hole in a metalloporphyrin is 2.01 Å and that an overlarge, weakly complexing ion such as zinc(II) will not lie in the plane of the porphyrin, thus causing the observed five-coordinate structure. The macrocycle blocks the addition of another axial ligand.

Thermodynamic studies bear out the observation

Table 2. Fractional coordinates ($\times 10^4$) and thermal-motion parameters ($\times 10^4$) derived from the least-squares refinement

The Debye-Waller factor is defined as: $T = \exp[-2\pi^2 \sum_i \sum_j a_i^* a_j^* h_i h_j U_{ij}]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Zn	544 (1)	-2367 (1)	497 (1)	381 (2)	387 (2)	433 (2)	-57 (1)	12 (1)	76 (1)
N(1)	1940 (2)	-2368 (1)	-864 (2)	356 (15)	409 (16)	459 (16)	-79 (13)	33 (13)	68 (12)
N(2)	-545 (2)	-1498 (1)	-511 (2)	414 (16)	400 (14)	397 (16)	-38 (14)	31 (13)	104 (12)
N(3)	-606 (2)	-2102 (1)	2085 (2)	496 (18)	429 (16)	343 (15)	-87 (14)	32 (13)	81 (12)
N(4)	1913 (2)	-2937 (1)	1778 (2)	449 (17)	409 (16)	411 (16)	-53 (13)	-10 (13)	77 (12)
N(5)	-336 (2)	-3416 (1)	-330 (2)	477 (17)	437 (16)	543 (17)	-118 (14)	-84 (14)	87 (13)
C(1)	3152 (3)	-2747 (1)	-787 (3)	361 (19)	324 (17)	547 (21)	-75 (15)	55 (16)	-14 (15)
C(2)	3824 (3)	-2610 (1)	-1945 (3)	432 (20)	372 (19)	544 (21)	-97 (16)	62 (17)	-58 (16)
C(3)	3005 (3)	-2139 (1)	-2714 (3)	436 (20)	350 (17)	508 (20)	-64 (16)	103 (16)	-34 (15)
C(4)	1822 (3)	-1990 (1)	-2027 (2)	420 (19)	374 (17)	423 (19)	-116 (16)	13 (15)	25 (14)
C(5)	746 (3)	-1498 (1)	-2436 (3)	452 (21)	468 (20)	367 (19)	-99 (17)	22 (16)	101 (16)
C(6)	-338 (3)	-1258 (1)	-1736 (3)	397 (19)	375 (17)	416 (19)	-71 (15)	-26 (15)	58 (14)
C(7)	-1394 (3)	-696 (1)	-2172 (3)	416 (19)	352 (17)	422 (18)	-71 (15)	-50 (15)	56 (14)
C(8)	-2228 (3)	-604 (1)	-1195 (3)	407 (20)	344 (17)	473 (19)	-74 (15)	-38 (16)	44 (14)
C(9)	-1691 (3)	-1110 (1)	-157 (3)	376 (19)	350 (17)	474 (20)	-56 (15)	0 (16)	58 (14)
C(10)	-2251 (3)	-1198 (1)	1026 (3)	361 (20)	372 (19)	568 (22)	-29 (17)	84 (17)	22 (16)
C(11)	-1765 (3)	-1655 (1)	2084 (3)	403 (20)	390 (19)	462 (20)	-58 (16)	71 (16)	-19 (15)
C(12)	-2380 (3)	-1712 (1)	3311 (3)	568 (23)	370 (19)	450 (20)	-131 (17)	95 (17)	-25 (15)
C(13)	-1561 (3)	-2187 (1)	4075 (3)	582 (24)	406 (19)	398 (19)	-166 (17)	81 (17)	-1 (15)
C(14)	-443 (3)	-2417 (1)	3303 (3)	505 (22)	380 (19)	439 (20)	-116 (17)	7 (17)	39 (15)
C(15)	641 (3)	-2886 (1)	3738 (3)	642 (25)	486 (22)	335 (20)	-153 (18)	-11 (17)	75 (16)
C(16)	1746 (3)	-3116 (1)	3053 (3)	526 (23)	386 (19)	450 (20)	-118 (17)	-80 (17)	51 (15)
C(17)	2884 (3)	-3584 (1)	3577 (3)	558 (23)	367 (19)	510 (21)	-98 (17)	-157 (18)	49 (16)
C(18)	3730 (3)	-3667 (1)	2611 (3)	495 (23)	359 (19)	562 (22)	-100 (17)	-111 (18)	34 (16)
C(19)	3118 (3)	-3256 (1)	1473 (3)	382 (20)	349 (17)	588 (22)	-64 (16)	-39 (17)	59 (16)
C(20)	3670 (3)	-3174 (1)	286 (3)	343 (20)	387 (20)	657 (25)	-24 (17)	-5 (18)	33 (17)
C(21)	5193 (3)	-2888 (2)	-2171 (4)	468 (23)	518 (25)	643 (27)	-76 (19)	146 (20)	-25 (20)
C(22)	6132 (4)	-2359 (2)	-1499 (5)	433 (26)	731 (32)	850 (37)	-125 (24)	60 (24)	-19 (27)
C(23)	3243 (4)	-1783 (2)	-3977 (3)	545 (25)	600 (25)	457 (22)	-98 (21)	189 (20)	-34 (19)
C(24)	3583 (5)	-946 (2)	-3766 (5)	838 (36)	592 (28)	611 (29)	-191 (26)	131 (27)	159 (23)
C(25)	-1477 (4)	-282 (2)	-3446 (3)	576 (26)	526 (23)	474 (22)	-59 (20)	-32 (20)	144 (19)
C(26)	-765 (6)	438 (3)	-3331 (5)	1138 (49)	694 (33)	692 (34)	-311 (33)	21 (33)	275 (28)
C(27)	-3433 (3)	-60 (2)	-1116 (4)	471 (23)	482 (22)	569 (25)	9 (17)	10 (19)	110 (19)
C(28)	-3243 (5)	704 (2)	-322 (5)	802 (38)	545 (28)	878 (38)	95 (27)	1 (31)	-103 (25)
C(29)	-3702 (3)	-1344 (2)	3606 (4)	579 (25)	517 (23)	525 (24)	-74 (19)	175 (20)	-36 (19)
C(30)	-4742 (5)	-1823 (3)	3015 (5)	556 (30)	791 (35)	724 (33)	-91 (26)	86 (25)	32 (27)
C(31)	-1757 (5)	-2463 (2)	5413 (3)	695 (30)	607 (26)	444 (23)	-141 (24)	91 (23)	57 (19)
C(32)	-2157 (5)	-3286 (2)	5339 (4)	948 (40)	638 (29)	586 (29)	-224 (28)	167 (29)	138 (24)
C(33)	3027 (4)	-3903 (2)	4933 (4)	769 (32)	552 (26)	539 (25)	-63 (24)	-232 (24)	122 (20)
C(34)	2341 (6)	-4628 (3)	5031 (5)	1210 (53)	725 (33)	658 (35)	-278 (35)	-171 (36)	264 (28)
C(35)	5047 (4)	-4102 (2)	2624 (4)	515 (25)	515 (23)	757 (30)	-15 (19)	-177 (22)	89 (21)
C(36)	5067 (6)	-4939 (3)	2080 (6)	824 (41)	608 (30)	1046 (47)	119 (29)	-91 (36)	-71 (31)
C(37)	-1316 (4)	-3669 (2)	226 (4)	538 (25)	625 (26)	785 (30)	-196 (21)	32 (23)	4 (23)
C(38)	-1831 (4)	-4351 (2)	-233 (5)	660 (31)	738 (32)	1099 (42)	-373 (26)	-8 (29)	42 (30)
C(39)	-1357 (5)	-4782 (2)	-1297 (5)	844 (36)	560 (29)	837 (35)	-246 (26)	-280 (29)	42 (25)
C(40)	-371 (5)	-4524 (2)	-1881 (4)	1035 (41)	697 (30)	695 (32)	-277 (30)	-87 (29)	-127 (25)
C(41)	111 (4)	-3841 (2)	-1384 (4)	757 (32)	669 (28)	621 (27)	-241 (25)	-12 (24)	5 (22)

that while the addition of one molecule of pyridine to zinc porphyrins is favorable, the addition of a second molecule is highly unlikely (Cole, Curthoys, Magnuson & Phillips, 1972; Miller & Dorough, 1952). It is interesting to note that while a pyridine adduct was obtained for the zinc octaethylporphyrin complex, the same mixture of solvents (1:1 pyridine-dioxane) yielded crystals of a four-coordinate nickel octaethylporphyrin complex (Cullen & Meyer, 1974a) containing no pyridine ligands. This is in full agreement with the conclusions of Cole *et al.* (1972) that zinc(II)

Table 3. Fractional coordinates and thermal-motion parameters derived from the least-squares refinement of hydrogen atoms

Isotropic temperature factors are defined by:

$$T = \exp[-B(\sin^2 \theta)/\lambda^2].$$

	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^3$)	B
H(1)	80 (2)	-131 (1)	-325 (2)	2.6 (6)
H(2)	-298 (2)	-91 (1)	118 (2)	3.0 (7)
H(3)	66 (2)	-303 (1)	460 (2)	3.1 (6)
H(4)	445 (2)	-342 (1)	23 (2)	3.5 (7)
H(5)	538 (3)	-340 (1)	-187 (3)	5.2 (9)
H(6)	532 (3)	-291 (1)	-313 (3)	4.0 (8)
H(7)	601 (3)	-232 (2)	-59 (3)	6.3 (11)
H(8)	594 (3)	-186 (2)	-194 (3)	6.3 (10)
H(9)	699 (3)	-252 (1)	-167 (3)	4.5 (8)
H(10)	253 (3)	-185 (2)	-461 (3)	5.9 (10)
H(11)	390 (3)	-204 (1)	-440 (3)	4.3 (8)
H(12)	295 (4)	-59 (2)	-337 (4)	7.2 (13)
H(13)	437 (4)	-89 (2)	-320 (4)	7.5 (13)
H(14)	370 (3)	-76 (2)	-456 (3)	5.9 (10)
H(15)	-117 (3)	-62 (1)	-418 (3)	4.1 (8)
H(16)	-240 (3)	-17 (1)	-372 (3)	5.6 (9)
H(17)	17 (4)	33 (2)	-306 (4)	7.8 (14)
H(18)	-114 (4)	80 (2)	-268 (4)	7.5 (14)
H(19)	-83 (3)	69 (1)	-415 (3)	5.5 (9)
H(20)	-369 (3)	4 (1)	-199 (3)	5.0 (9)
H(21)	-403 (3)	-30 (1)	-75 (3)	4.9 (9)
H(22)	-292 (3)	56 (2)	63 (3)	6.4 (10)
H(23)	-263 (4)	99 (2)	-80 (4)	8.6 (14)
H(24)	-400 (3)	98 (2)	-22 (3)	6.0 (11)
H(25)	-385 (3)	-81 (2)	327 (3)	6.3 (10)
H(26)	-374 (3)	-125 (1)	452 (3)	4.8 (9)
H(27)	-465 (3)	-231 (2)	341 (3)	6.4 (11)
H(28)	-472 (3)	-193 (2)	208 (3)	6.2 (10)
H(29)	-556 (3)	-160 (2)	315 (3)	5.9 (11)
H(30)	-230 (3)	-212 (2)	585 (3)	6.6 (12)
H(31)	-105 (3)	-245 (1)	595 (3)	4.1 (9)
H(32)	-153 (3)	-366 (2)	485 (3)	5.5 (10)
H(33)	-298 (4)	-335 (2)	479 (4)	8.6 (14)
H(34)	-220 (3)	-347 (1)	616 (3)	4.1 (8)
H(35)	390 (3)	-406 (1)	517 (3)	5.4 (9)
H(36)	274 (3)	-353 (2)	563 (3)	5.5 (10)
H(37)	271 (4)	-503 (2)	437 (4)	7.7 (14)
H(38)	144 (3)	-453 (2)	479 (3)	6.8 (12)
H(39)	245 (3)	-481 (2)	589 (3)	6.7 (11)
H(40)	571 (3)	-381 (1)	229 (3)	5.7 (10)
H(41)	535 (3)	-409 (1)	353 (3)	5.8 (10)
H(42)	454 (4)	-521 (2)	256 (4)	8.6 (16)
H(43)	471 (4)	-494 (2)	118 (4)	8.8 (15)
H(44)	592 (3)	-520 (2)	201 (3)	6.0 (10)
H(45)	-159 (3)	-339 (2)	107 (3)	6.5 (11)
H(46)	-243 (4)	-449 (2)	30 (4)	8.5 (13)
H(47)	-172 (4)	-522 (2)	-167 (4)	8.8 (12)
H(48)	8 (4)	-478 (2)	-266 (4)	8.2 (13)
H(49)	76 (2)	-366 (1)	-171 (2)	4.6 (7)

Table 4. *R.m.s. amplitudes of vibration (in Å) along principal axes of thermal ellipsoids*

	Axis 1	Axis 2	Axis 3
Zn	0.186 (1)	0.195 (1)	0.216 (1)
N(1)	0.179 (6)	0.202 (4)	0.219 (4)
N(2)	0.177 (5)	0.204 (4)	0.218 (4)
N(3)	0.174 (5)	0.209 (4)	0.226 (4)
N(4)	0.188 (5)	0.207 (5)	0.220 (4)
N(5)	0.193 (5)	0.205 (5)	0.256 (4)
C(1)	0.171 (6)	0.192 (5)	0.237 (5)
C(2)	0.179 (6)	0.207 (5)	0.244 (5)
C(3)	0.183 (5)	0.197 (6)	0.238 (4)
C(4)	0.176 (6)	0.206 (5)	0.217 (5)
C(5)	0.177 (7)	0.207 (5)	0.230 (4)
C(6)	0.187 (6)	0.189 (5)	0.218 (5)
C(7)	0.183 (6)	0.187 (5)	0.225 (5)
C(8)	0.180 (6)	0.195 (5)	0.228 (5)
C(9)	0.183 (6)	0.194 (5)	0.221 (5)
C(10)	0.185 (6)	0.194 (6)	0.241 (5)
C(11)	0.192 (5)	0.195 (6)	0.225 (5)
C(12)	0.181 (6)	0.205 (6)	0.250 (4)
C(13)	0.183 (7)	0.196 (5)	0.253 (4)
C(14)	0.184 (6)	0.209 (5)	0.231 (5)
C(15)	0.178 (6)	0.209 (6)	0.262 (5)
C(16)	0.185 (6)	0.198 (6)	0.250 (5)
C(17)	0.183 (6)	0.194 (6)	0.272 (5)
C(18)	0.180 (6)	0.204 (6)	0.262 (5)
C(19)	0.182 (6)	0.193 (5)	0.248 (5)
C(20)	0.184 (6)	0.198 (6)	0.258 (5)
C(21)	0.201 (7)	0.224 (6)	0.267 (5)
C(22)	0.203 (7)	0.266 (6)	0.298 (6)
C(23)	0.180 (7)	0.235 (6)	0.265 (5)
C(24)	0.198 (10)	0.268 (6)	0.297 (6)
C(25)	0.193 (7)	0.236 (6)	0.253 (5)
C(26)	0.197 (11)	0.288 (7)	0.351 (6)
C(27)	0.199 (6)	0.228 (6)	0.247 (5)
C(28)	0.213 (7)	0.282 (7)	0.323 (7)
C(29)	0.198 (7)	0.226 (6)	0.265 (5)
C(30)	0.232 (7)	0.270 (6)	0.282 (6)
C(31)	0.203 (7)	0.240 (6)	0.271 (5)
C(32)	0.200 (10)	0.266 (6)	0.317 (6)
C(33)	0.187 (8)	0.239 (6)	0.311 (6)
C(34)	0.213 (9)	0.271 (8)	0.370 (7)
C(35)	0.195 (7)	0.233 (6)	0.300 (6)
C(36)	0.226 (7)	0.284 (8)	0.352 (8)
C(37)	0.205 (8)	0.266 (5)	0.283 (6)
C(38)	0.190 (10)	0.311 (5)	0.334 (7)
C(39)	0.200 (9)	0.255 (7)	0.346 (6)
C(40)	0.210 (8)	0.296 (6)	0.334 (6)
C(41)	0.224 (8)	0.255 (6)	0.296 (5)

is better able to accommodate the forced square-pyramidal geometry than nickel(II). Their calculations have shown that the addition of a second molecule of pyridine to nickel porphyrins is also unlikely, at least for complexes of tetraphenylporphyrin in organic non-polar solvents. Recently the structure of a six-coordinate complex of nickel with the water-soluble tetra-(4-*N*-methylpyridyl)porphyrin has been reported (Kirner, Garofalo & Scheidt, 1975). The axial ligands in that compound are imidazole groups.

Collins & Hoard (1970) have studied a complex similar to PyrZnOEP, $\alpha,\beta,\gamma,\delta$ -tetra-(4-pyridyl)porphyrinatomonopyridinezinc(II), PyrZnTPyP, which is also a five-coordinate square-pyramidal complex. This complex differs from PyrZnOEP in that it is substituted at

the methine carbon atoms rather than the β -pyrrole carbon atoms. Recently the radical perchloratotetraphenylporphinatozinc(II), ClO_4ZnTPP , has been studied (Spaulding, Eller, Bertrand & Felton, 1974). The three complexes all have very similar geometries. Averaged bond lengths and angles for three compounds are listed in Table 6. Some non-bonded distances of interest are also shown.

A fourth zinc(II) metalloporphyrin, tetraphenylporphinatmonoquoquozinc(II), has been reported (Glick, Cohen & Hoard, 1967). However the structure is plagued with disorder so that the bond parameters

Table 5. Bond lengths and angles in PyrZnOEP

Some non-bonded distances of interest are also given. An asterisk denotes a value corrected for thermal motion.

Zn—N(1)	2.068 (3) Å	N(1)—Zn—N(2)	88.9 (1)°
Zn—N(2)	2.062 (3)	N(1)—Zn—N(3)	164.1 (1)
Zn—N(3)	2.061 (3)	N(1)—Zn—N(4)	88.7 (1)
Zn—N(4)	2.075 (3)	N(1)—Zn—N(5)	98.5 (1)
Zn—N(5)	2.200 (3)	N(2)—Zn—N(3)	88.6 (1)
N(1)—C(1)	1.364 (4)	N(2)—Zn—N(4)	161.8 (1)
N(1)—C(4)	1.368 (4)	N(2)—Zn—N(5)	101.4 (1)
N(2)—C(6)	1.364 (4)	N(3)—Zn—N(4)	88.8 (1)
N(2)—C(9)	1.366 (4)	N(3)—Zn—N(5)	97.5 (1)
N(3)—C(11)	1.366 (4)	N(4)—Zn—N(5)	96.8 (1)

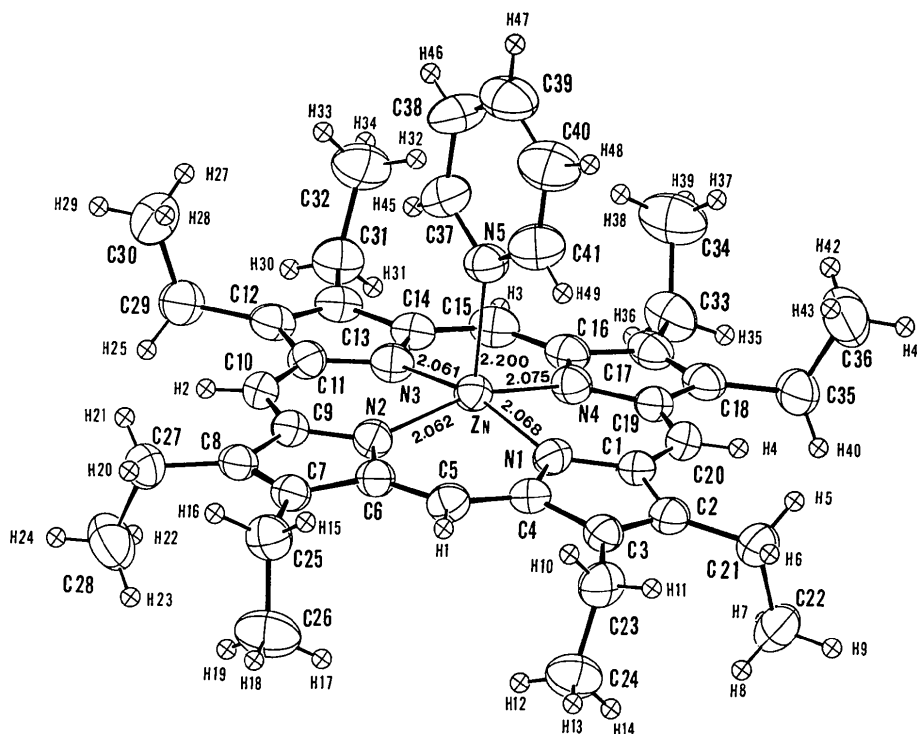


Fig. 1. ORTEP (Johnson, 1965) drawing of the structure of 2,3,7,8,12,13,17,18-octaethylporphinatmonopyridinezinc(II). Numbering scheme and Zn—N bond distances are shown. The thermal ellipsoids are drawn for 50% probability, except for those of the hydrogen atoms which are not drawn to scale. H(26) and H(41) are hidden behind C(29) and C(35) respectively.

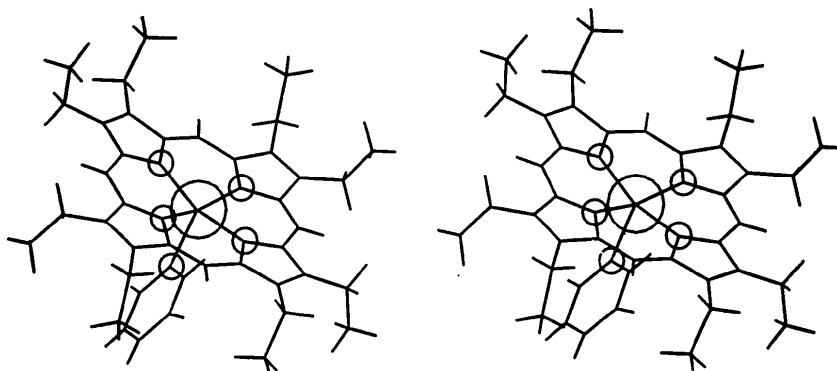


Fig. 2. Stereo view of a single molecule of PyrZnOEP. Large circle denotes the zinc atom, smaller circles denote nitrogen atoms.

Table 5 (cont.)

N(3)—C(14)	1.366 (4)	Zn—N(1)—C(1)	127.0 (2)
N(4)—C(16)	1.365 (4)	Zn—N(1)—C(4)	126.5 (2)
N(4)—C(19)	1.367 (4)	C(1)—N(1)—C(4)	106.5 (3)
C(1)—C(2)	1.446 (5)	Zn—N(2)—C(6)	126.6 (2)
C(1)—C(20)	1.394 (4)	Zn—N(2)—C(9)	126.9 (2)
C(2)—C(3)	1.357 (4)	C(6)—N(2)—C(9)	106.1 (2)
C(2)—C(21)	1.491 (5)	Zn—N(3)—C(11)	127.1 (2)
C(3)—C(4)	1.450 (5)	Zn—N(3)—C(14)	126.6 (2)
C(3)—C(23)	1.494 (5)	C(11)—N(3)—C(14)	105.8 (3)
C(4)—C(5)	1.392 (5)	Zn—N(4)—C(16)	126.3 (2)
C(5)—C(6)	1.387 (5)	Zn—N(4)—C(19)	126.5 (2)
C(6)—C(7)	1.455 (4)	C(16)—N(4)—C(19)	107.0 (3)
C(7)—C(8)	1.348 (5)	N(1)—C(1)—C(2)	110.1 (3)
C(7)—C(25)	1.500 (5)	N(1)—C(1)—C(20)	124.4 (3)
C(8)—C(9)	1.452 (4)	C(2)—C(1)—C(20)	125.5 (3)
C(8)—C(27)	1.491 (5)	C(1)—C(2)—C(3)	106.9 (3)
C(9)—C(10)	1.385 (5)	C(1)—C(2)—C(21)	125.5 (3)
C(10)—C(11)	1.402 (5)	C(3)—C(2)—C(21)	127.4 (3)
C(11)—C(12)	1.443 (5)	C(2)—C(3)—C(4)	106.5 (3)
C(12)—C(13)	1.358 (5)	C(2)—C(3)—C(23)	128.9 (3)
C(12)—C(29)	1.500 (5)	C(4)—C(3)—C(23)	124.5 (3)
C(13)—C(14)	1.453 (5)	N(1)—C(4)—C(3)	110.0 (3)
C(13)—C(31)	1.491 (5)	N(1)—C(4)—C(5)	124.4 (3)
C(14)—C(15)	1.386 (5)	C(3)—C(4)—C(5)	125.5 (3)
C(15)—C(16)	1.394 (5)	C(4)—C(5)—C(6)	127.7 (3)
C(16)—C(17)	1.456 (5)	N(2)—C(6)—C(5)	124.5 (3)
C(17)—C(18)	1.349 (5)	N(2)—C(6)—C(7)	110.1 (3)
C(17)—C(33)	1.497 (6)	C(5)—C(6)—C(7)	125.3 (3)
C(18)—C(19)	1.462 (5)	C(6)—C(7)—C(8)	106.8 (3)
C(18)—C(35)	1.498 (5)	C(6)—C(7)—C(25)	125.3 (3)
C(19)—C(20)	1.383 (5)	C(8)—C(7)—C(25)	127.8 (3)
C(21)—C(22)	1.509 (7)	C(7)—C(8)—C(9)	106.5 (3)
	1.520 (7)*	C(7)—C(8)—C(27)	128.2 (3)
C(23)—C(24)	1.517 (7)	C(9)—C(8)—C(27)	125.1 (3)
	1.530 (7)*	N(2)—C(9)—C(8)	110.4 (3)
C(25)—C(26)	1.507 (8)	N(2)—C(9)—C(10)	124.2 (3)
	1.534 (8)*	C(8)—C(9)—C(10)	125.4 (3)
C(27)—C(28)	1.513 (6)	C(9)—C(10)—C(11)	128.3 (3)
	1.539 (7)*	N(3)—C(11)—C(10)	123.2 (3)
C(29)—C(30)	1.504 (7)	N(3)—C(11)—C(12)	110.8 (3)
	1.517 (7)*	C(10)—C(11)—C(12)	125.9 (3)
C(31)—C(32)	1.514 (7)	C(11)—C(12)—C(13)	106.6 (3)
	1.527 (7)*	C(11)—C(12)—C(29)	125.0 (3)
C(33)—C(34)	1.516 (8)*	C(13)—C(12)—C(29)	128.3 (3)
	1.538 (8)*	C(12)—C(13)—C(14)	106.4 (3)
C(35)—C(36)	1.502 (7)	C(12)—C(13)—C(31)	128.3 (4)
	1.525 (7)*	C(14)—C(13)—C(31)	125.3 (3)
N(1)—N(2)	2.893 (4)	N(3)—C(14)—C(13)	110.4 (3)
N(1)—N(4)	2.896 (4)	N(3)—C(14)—C(15)	124.6 (3)
N(2)—N(3)	2.881 (4)	C(13)—C(14)—C(15)	125.0 (3)
N(3)—N(4)	2.893 (4)	C(14)—C(15)—C(16)	127.6 (3)
C(5)—C(15)	6.813 (5)	N(4)—C(16)—C(15)	124.6 (3)
C(10)—C(20)	6.810 (5)	N(4)—C(16)—C(17)	109.9 (3)
N(1)—N(3)	4.090 (4)	C(15)—C(16)—C(17)	125.5 (3)
N(2)—N(4)	4.085 (4)	C(16)—C(17)—C(18)	106.7 (3)
N(5)—C(37)	1.328 (5)	C(16)—C(17)—C(33)	124.7 (3)
N(5)—C(41)	1.327 (7)	C(18)—C(18)—C(33)	128.6 (3)
C(37)—C(38)	1.381 (7)	C(17)—C(18)—C(19)	107.0 (3)
C(38)—C(39)	1.349 (7)	C(17)—C(18)—C(35)	128.8 (3)
C(39)—C(40)	1.351 (8)	C(19)—C(18)—C(35)	124.1 (3)
C(40)—C(41)	1.378 (7)	N(4)—C(19)—C(18)	109.3 (3)
N(4)—C(19)—C(20)	124.6 (3)°	C(18)—C(35)—C(36)	113.8 (4)°
C(18)—C(19)—C(20)	126.0 (3)	Zn—N(5)—C(37)	121.6 (2)
C(1)—C(20)—C(19)	127.9 (3)	Zn—N(5)—C(41)	121.7 (3)
C(2)—C(21)—C(22)	113.7 (3)	C(37)—N(5)—C(41)	116.6 (3)
C(3)—C(23)—C(24)	113.6 (3)	C(5)—C(37)—C(38)	122.3 (4)
C(7)—C(25)—C(26)	112.9 (3)	C(37)—C(38)—C(39)	120.3 (5)
C(8)—C(27)—C(28)	113.2 (4)	C(38)—C(39)—C(40)	117.8 (5)
C(12)—C(29)—C(30)	112.7 (3)	C(39)—C(40)—C(41)	119.6 (5)
C(13)—C(31)—C(32)	112.9 (3)	N(5)—C(41)—C(40)	123.2 (5)
C(17)—C(33)—C(34)	113.9 (4)		

Table 6. Averaged bond lengths (Å) and angles (°) for zinc porphyrins

In this table (and in Table 9) some non-bonded distances of interest are also given; figures in parentheses are r.m.s. standard deviations of least significant figures when there is more than one contribution to the average; otherwise the estimated standard deviation is given. References are given in the text.

	(Pyr)ZnOEP	(Pyr)ZnTPyP	(ClO ₄)ZnTPP
Zn—N	2.067 (6)	2.073 (8)	2.076 (9)
Zn—N _p ^(a)	2.200 (3)	2.143 (4)	—
C _a —N	1.366 (1)	1.369 (5)	1.35 (1)
C _a —C _b	1.452 (6)	1.447 (4)	1.43 (1)
C _a —C _m	1.390 (6)	1.406 (5)	1.40 (1)
C _b —C _b	1.353 (5)	1.355 (8)	1.35 (2)
C _i —C _m	3.406 (1)	3.447 (6)	3.422 (6)
C _i —C _a	3.061 (3)	3.066 (6)	—
C _i —N	2.043 (2)	2.047 (12)	2.046 (10)
N—N	2.891 (7)	2.894 (11)	2.894 (6)
C _p —N _p ^(a)	1.328 (1)	1.335 (5) ^(b)	—
C _p —C _p ^(a)	1.364 (17)	1.379 (7) ^(b)	—
N—Zn—N(adj.)	88.8 (1)	88.6 (4)	88.4 (4)
N—Zn—N(opp.)	163.0 (16)	161.7 (16)	165.5 (4)
N—Zn—N _p ^(a)	98.6 (16)	99.1 (8)	—
Zn—N—C _a	126.7 (3)	126.3 (3)	125.5 (7)
C _a —N—C _a	106.4 (5)	106.6 (2)	107.6 (5)
N—C _a —C _m	124.3 (5)	125.7 (3)	126.1 (8)
N—C _a —C _b	110.1 (4)	109.8 (2)	109.4 (10)
C _b —C _a —C _m	125.5 (3)	125.7 (3)	124.4 (12)
C _a —C _m —C _a	127.9 (3)	125.2 (9)	124.7 (4)
C _a —C _b —C _b	106.7 (2)	106.9 (1)	106.9 (13)
Zn—N _p —C _p ^(a)	121.6 (1)	120.9 (3)	—
C _p —N _p —C _p ^(a)	116.6 (3)	118.0 (4) ^(b)	—
C _p —C _p —C _p ^(a)	119.2 (13)	118.8 (4) ^(b)	—
N _p —C _p —C _p ^(a)	122.3 (1)	123.0 (3) ^(b)	—

(a) Subscript refers to atoms of coordinated pyridine ring. Pyrrole nitrogen atoms have no subscript.

(b) Atoms of coordinated pyridine only used in average.

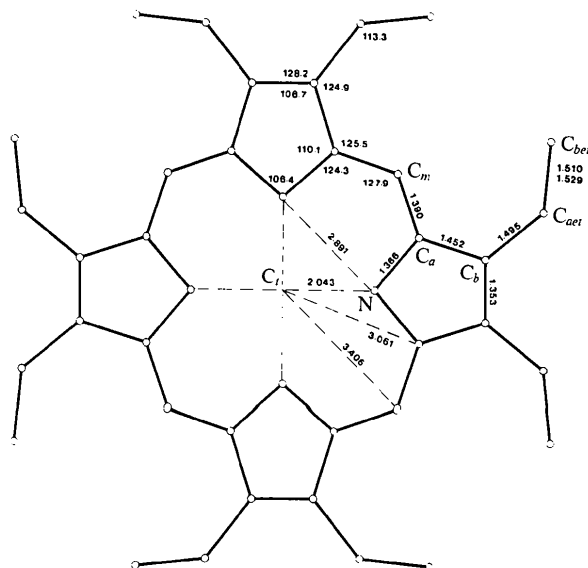


Fig. 3. Schematic drawing of the macrocycle in PyrZnOEP showing average bond lengths (Å) and angles (°). The two values for the C_{aet}—C_{bet} bonds are the uncorrected distance (upper value) and the distance corrected for thermal motion (lower value). Also shown is the notation for different types of carbon atoms. C_i refers to the center of the macrocycle.

are not very accurate, and for this reason it is not included in Table 6. However within the limits of accuracy, the bond parameters appear to agree with those in the other zinc metalloporphyrins [*i.e.* Zn–N(pyrrole) = 2.05, Zn–O = 2.20 Å].

Within standard deviations, the zinc–pyrrole nitrogen atom distances for all three complexes in Table 6 are the same. Only a few examples of five-coordinate square-pyramidal zinc complexes have been reported. However a tabulation of several of these has been made (Marongiu, Cannas & Carta, 1973). Where comparisons are possible, the Zn–N(pyrrole) distances agree with those tabulated. Baenziger & Schultz (1971) have compiled several Zn–N distances for other coordination geometries, mainly tetrahedral coordination. The range is 2.01–2.10 Å for tetrahedral zinc(II) complexes with most of the values grouped from 2.04–2.07 Å.

The zinc–pyridine nitrogen atom distance, on the other hand, does appear to be abnormally long in both

PyrZnOEP and PyrZnTPyP. In the aforementioned tabulation of five-coordinate zinc complexes (Marongiu, Cannas & Carta, 1973) the apical bond length for ligands other than porphyrins is approximately the same as or slightly longer than the equatorial bond lengths. The Zn–N bond length in PyrZnOEP [2.200 (3) Å] is significantly longer than that in PyrZnTPyP [2.143 (4) Å]. This difference can probably be attributed to the different orientations of the pyridine molecule in the two complexes.

To discuss this difference it is necessary to define a dihedral angle, ϕ , as was originally done by Collins, Countryman & Hoard (1972) in describing the structure of bis(imidazole)tetraphenylporphyrinatoiron(III) chloride, (Im)₂FeTPPCL. The axial bond is taken to be a dimensionally exact twofold axis. The angle ϕ is defined as the angle between the plane of the axial ligand (originally imidazole, pyridine in the present study) and the plane passing through the twofold axis and one of the pyrrole nitrogen atoms. When $\phi = 0^\circ$

Table 7. Orientation of planar axial ligands in metalloporphyrins and hemeproteins

	M–N _{ax}	$\Delta^{(b)}$	Minimum H _{ax} –N(pyrrole)	$\phi^{(c)}$	Reference
PyrZnOEP ^(a)	2.200 Å	0.31 Å	2.64 Å	4°	(e)
PyrZnTPyP	2.143	0.33	2.87 ^(d)	23	(f)
(Im) ₂ NiTMePyP	2.160	0.0	2.73	23	(g)
(3-MePyr) ₂ CoOEP	2.386	0.0	2.63	11	(h)
(1-MeIm)CoTPP	2.157	0.14	2.62	0	(i)
(1-MeIm)CoOEP	2.15	0.13	2.8	10	(j)
(1,2-Me ₂ Im)CoTPP	2.216	0.15	2.57 ^(d)	20	(k)
(3,5-Me ₂ Pyr)CoTPP	2.161	0.14	2.72	41	(l)
(3,5-Me ₂ Pyr)(NO ₂)CoTPP	2.036	0.0	2.55	9	(m)
(Im) ₂ CoTPP ⁺	1.945, 1.909	0.0	2.59 ^(d) , 2.63 ⁽ⁿ⁾	43, 42	(n)
(Im) ₂ CoOEP ⁺	1.99	0.0	2.45	11	(o)
(2-MeIm)FeTPP	2.16	0.42	2.60	7	(p)
(1-MeIm)Fe(CO)TPivalPP	2.05	–0.03	2.55	19	(q)
(Im) ₂ FeTPP ⁺	1.957, 1.991	0.01	2.79, 2.56	39, 18	(r)
(Im) ₂ FeOEP ⁺	2.01	0.0	2.50	7	(s)
(1-MeIm) ₂ Fe(Proto-IX)	1.966, 1.988	0.01	2.51, 2.54	16.3	(t)
(1-MeIm)(NO)FeTPP	2.18	–0.07	2.67	26	(u)
(Pyr)(Cl)MnTPP	2.444	–0.12	2.74	37	(v)
(Pyr)(CO)RuTPP	2.193	–0.08	2.51	26	(w)
(Pyr) ₂ RuOEP	2.089, 2.100	0.00	2.69 ^(x) , 2.52	44, 30	(x)
Cytochrome b ₅				30–40	(y)
Horse Deoxyhemoglobin				18, 17	(z)
Horse Met-hemoglobin				20, 30	(aa)
Lamprey Hemoglobin				45–48	(bb)
Myoglobin				25–30	(cc)

(a) Abbreviations: Pyr, pyridine; Im, imidazole; Me, methyl (usually preceded by a number indicating its point of substitution on the ring); OEP, octaethylporphyrin dianion; TPyP, tetra-(4-pyridyl)porphyrin dianion; TMePyP, tetra-(4-N-methylpyridyl)porphyrin dianion; TPP, tetraphenylporphyrin dianion; TPivalPP, *meso*-tetra-($\alpha,\alpha,\alpha,\alpha$ -*o*-pivalamidophenyl)porphyrin dianion; Proto-IX, protoporphyrin IX trianion (one propionic acid side group is ionized). (b) Δ is the deviation of the metal ion from the plane of the four pyrrole nitrogen atoms. A negative Δ indicates the metal ion is out of the plane on the opposite side from the axial ligand of interest. (c) See text for definition of ϕ . (d) Closest contact is with an alpha carbon atom of the porphyrin. (e) This work. (f) Collins & Hoard (1970). (g) Kirner, Garofalo & Scheidt (1975). (h) Little & Ibers (1974b). (i) Scheidt (1974). (j) Little & Ibers (1974a). (k) Dwyer, Madura & Scheidt (1974). (l) Scheidt & Ramanuja (1975). (m) Kaduk & Scheidt (1974). (n) Lauher & Ibers (1974). Note values are given for the two crystallographically independent molecules. For the second molecule, closest contact is with a methine carbon atom. (o) C. N. Morimoto, private communication. (p) Hoard & Scheidt (1973). (q) J. L. Hoard, private communication. (r) Collins, Countryman & Hoard (1972). There are two independent imidazole ligands. (s) Takenaka, Sasada, Watanabe, Ogoshi & Yoshida (1972). (t) Little, Dynock & Ibers (1975). There are two independent imidazole ligands. The iron atom is formally Fe^{III} with the charge balanced by an ionized propionic acid group. (u) Piculo, Rupprecht & Scheidt (1974). (v) Kirner & Scheidt (1975). (w) Little & Ibers (1973). (x) Hopf, O'Brien, Scheidt & Whitten (1975). There are two independent molecules. For the first molecule closest contact is with a methine carbon atom. (y) Mathews, Argos & Levine (1971). (z) Bolton & Perutz (1970). (aa) Perutz (1965). (bb) Hendrickson, Love & Karle (1973). (cc) Watson & Kendrew (1969).

there will be maximum steric interactions between the pyrrole nitrogen atoms and the hydrogen atoms on the axial ligand. The plane of the axial ligand can be projected on a metal-pyrrole nitrogen atom vector. When $\varphi = 45^\circ$ the steric interactions are minimized and the plane of the axial ligand can be projected on a vector from the center of the macrocycle to a methine carbon atom.

If N(1) is the atom chosen as the pyrrole nitrogen atom to define the second plane, φ is 4.4° for PyrZnOEP. By comparison this angle is 23.1° for PyrZnTPyP. For the two independent imidazole molecules in (Im)₂FeTPPCL, the φ angles are 18 and 39° and the iron-imidazole nitrogen atom bond length is 0.034 Å longer for the group with the lower angle. This presumably is because of H(Im)-N(pyrrole) interactions.

Such interactions probably explain the longer axial bond length in PyrZnOEP. The closest intramolecular contacts between pyridine hydrogen atoms and the pyrrole nitrogen atoms are 2.71 and 2.65 Å for H(49)-N(1) and H(45)-N(3), respectively. The closest such contact in PyrZnTPyP is 2.87 Å with a C_a atom. The sum of the van der Waals radii for nitrogen and hydrogen atoms is 2.90 Å.

An orientation with a low φ angle would appear to be energetically unfavorable, especially in the absence of any steric constraints. In Table 7 are listed the φ values for several porphyrin complexes which have planar axial ligands. Also tabulated are the M-N axial bond lengths, the deviation of the metal ion from the plane of the four pyrrole nitrogen atoms (where applicable) and the closest intramolecular contacts between a hydrogen atom of the axial ligand and an atom in the macrocycle.

No chemical explanation for the low φ angle in PyrZnOEP is readily apparent. However it will be noted that for many of the compounds in Table 7, the H_{ax}-N (or C) contacts are considerably shorter than those found in PyrZnOEP.

One oddity is to be observed in Table 7. With one exception the φ angle for the seven metalloporphyrins in this table which have substitution at the β -pyrrole carbon atoms (*i.e.* octaethylporphyrin and protoporphyrin-IX complexes) is small ($<15^\circ$) whereas with three exceptions φ is relatively large ($>15^\circ$) for the thirteen *meso*-substituted metalloporphyrins. The one exception for the octaethylporphyrin complexes is (Pyr)₂RuOEP (Hopf, O'Brien, Scheidt & Whitten, 1975) in which the intramolecular contacts are tight even with a large φ angle. Where comparisons are possible the M-N axial bond is generally longer in the octaethylporphyrin complexes than in the corresponding *meso*-substituted porphyrins. In the case of LCoOEP and LCoTPP (L = 1-methylimidazole) the φ angle is small for both complexes and the Co-N distances are approximately the same (Little & Ibers, 1974a; Scheidt, 1974). Whether this difference in orientation is truly significant or merely coincidence remains to

be seen. External factors, such as packing effects, need to be considered.

At any rate it appears that for heme proteins, φ is usually large. Use was made of the program *SEARCH* (Meyer, 1974) to examine the environment of the iron atom in five heme proteins whose coordinates are stored in the Protein Data Bank (Berman, Koetzle & Meyer, 1976) at Brookhaven National Laboratory. For comparison the estimated φ values for these heme proteins are listed in Table 7. They range from 18 – 45° .

Table 8 lists the deviations from several least-squares planes of interest and the angles between these planes. As noted earlier the zinc ion lies 0.31 Å out of the plane of the four pyrrole nitrogen atoms (the 4N plane). This displacement is similar to that found in both PyrZnTPyP (0.33 Å) and ClO₄ZnTPP (0.25 Å).

Crystallographic symmetry requires the plane of the pyridine ring in PyrZnTPyP to lie exactly normal to the plane of the macrocycle. However no such restrictions are present in PyrZnOEP and the plane of the pyridine group forms an angle of 85.1° with the plane of the macrocycle or an angle of 84.9° with the 4N plane.

The macrocycles for all three five-coordinate zinc complexes in Table 6 show definite deviations from planarity. Interplanar angles between adjacent pyrrole groups in PyrZnOEP range from 4.3 to 9.1° . By comparison the range is 14.4 to 16.9° in ClO₄ZnTPP, while the pyrrole interplanar angle in PyrZnTPyP is 7.5° .

It is only for PyrZnOEP that the deviation from planarity can be described as 'tenting', where the pyrrole rings are pointing toward the metal ion in a rough approximation of C_{4v} symmetry. This can be noted by observing that for three of the pyrrole rings, the β -pyrrole carbon atoms lie 0.16 – 0.27 Å out of the 4N plane in the opposite direction from the metal ion. The fourth pyrrole group [N(3), C(11)–C(14)] shows very little tenting and is almost coplanar with the 4N plane. C(12) and C(13) lie only -0.001 and 0.005 Å respectively out of the 4N plane. A similar geometry has been found in five-coordinate octaethylporphyrin complexes of even larger metal ions, such as octaethylporphinatomonochlorothallium(III) (Cullen & Meyer, 1974b). This also has one pyrrole group almost coplanar with the 4N plane and the other three showing significant 'tenting'. Whether this trend is real or a consequence of molecular packing is uncertain.

There are a few differences in the averaged bond lengths and angles when the three zinc porphyrin complexes are compared (Table 6), although the standard deviations for bond parameters in ClO₄ZnTPP are high enough to make comparisons with this compound somewhat difficult. The C_a-C_m distance is slightly shorter in PyrZnOEP than in the other two complexes, while the C_r-C_m distance is 0.04 Å shorter, a significant amount. The N-C_a-C_m angle is smaller and the C_a-C_m-C_a angle is larger in PyrZnOEP. These differences appear to be an effect of

the different substitution on the porphyrins, as they have been observed by several authors (Cullen & Meyer, 1973; Lauher & Ibers, 1973; Coddling & Tulinsky, 1972). It is to be noted that all the bond parameters that change involve the methine carbon atom. One might also expect to see differences in the bond lengths and angles involving the β -pyrrole carbon atoms. While this has been observed in a comparison of the free bases (Lauher & Ibers, 1973) of octaethylporphyrin and tetraphenylporphyrin, no significant

Table 8. *Least-squares planes*

(a) Deviations (Å) from planes

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6	Plane 7
Zn	-0.395	-0.307	-0.023	-0.184	-0.288	-0.165	
N(1)	-0.150	-0.020	-0.002	-0.114	0.010	0.111	
N(2)	-0.060	0.020	0.328	0.001	0.049	0.327	
N(3)	-0.068	-0.020	-0.523	0.088	-0.013	0.131	
N(4)	-0.077	0.020	0.275	0.283	0.028	-0.006	
C(1)	-0.047	0.103	0.003	0.318	0.132	0.141	
C(2)	0.094	0.270	-0.003	0.464	0.310	0.335	
C(3)	0.087	0.257	0.001	0.357	0.304	0.432	
C(4)	-0.069	0.072	0.003	0.136	0.113	0.288	
C(5)	-0.056	0.070	0.074	0.040	0.115	0.396	
C(6)	-0.029	0.069	0.247	-0.002	0.109	0.437	
C(7)	0.083	0.168	0.417	-0.006	0.212	0.651	
C(8)	0.120	0.178	0.600	0.001	0.214	0.667	
C(9)	0.026	0.081	0.540	-0.001	0.109	0.460	
C(10)	0.019	0.050	0.671	-0.011	0.067	0.398	
C(11)	-0.023	0.003	0.667	0.032	0.011	0.246	
C(12)	-0.002	-0.001	0.836	0.047	-0.004	0.215	
C(13)	-0.001	0.005	0.824	0.147	-0.005	0.111	
C(14)	-0.021	0.015	0.650	0.194	0.011	0.081	
C(15)	0.011	0.062	0.622	0.335	0.054	0.018	
C(16)	0.014	0.093	0.478	0.405	0.090	0.006	
C(17)	0.105	0.198	0.511	0.609	0.190	-0.004	
C(18)	0.090	0.210	0.349	0.629	0.210	0.001	
C(19)	-0.022	0.101	0.203	0.426	0.110	0.003	
C(20)	-0.026	0.121	0.061	0.424	0.140	0.053	
N(5)	-2.593	-2.505	-2.201	-2.371	-2.487	-2.362	0.009
C(37)	-3.256	-3.191	-2.735	-3.061	-3.180	-3.042	-0.007
C(38)	-4.630	-4.565	-4.095	-4.423	-4.554	-4.422	0.001
C(39)	-5.355	-5.267	-4.940	-5.110	-5.251	-5.135	0.002
C(40)	-4.692	-4.581	-4.409	-4.421	-4.558	-4.453	-0.001
C(41)	-3.321	-3.210	-3.045	-3.063	-3.187	-3.077	-0.005

(b) Angles (°) between least-squares planes

	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6	Plane 7
Plane 1	1.2	6.3	4.5	1.5	4.5	85.1
Plane 2		7.4	4.0	0.5	4.7	84.9
Plane 3			9.1	7.7	8.1	85.5
Plane 4				4.3	8.7	80.9
Plane 5					4.4	85.2
Plane 6						89.6

(c) Equations of planes (x, y, z in triclinic fractional coordinates)

Plane 1: Macrocycle; N(1)–N(4), C(1)–C(20)
 $5.04x + 14.08y + 3.36z = -2.50$

Plane 2: N(1)–N(4)
 $5.21x + 14.04y + 3.23z = 2.57$

Plane 3: Pyrrole 1; N(1), C(1)–C(4)
 $4.16x + 14.03y + 4.12z = -2.87$

Plane 4: Pyrrole 2; N(2), C(6)–C(9)
 $5.62x + 13.32y + 3.57z = -2.49$

Plane 5: Pyrrole 3; N(3), C(11)–C(14)
 $5.22x + 14.09y + 3.16z = -2.60$

Plane 6: Pyrrole 4; N(4), C(16)–C(19)
 $4.71x + 14.80y + 2.80z = -2.94$

Plane 7: Pyridine; N(5), C(37)–C(41)
 $5.84x - 8.62y + 6.08z = 2.54$

difference is observed in these zinc metalloporphyrins.

The average C_r-N distance, 2.043 (2) Å, in PyrZnOEP is somewhat larger than the optimum value of 2.01 Å postulated by Collins & Hoard (1970). The averaged bond parameters for this complex are included in Table 9, along with those for the tetragonal and triclinic forms of nickel octaethylporphyrin, in which the core is contracted (Meyer, 1972; Cullen & Meyer, 1974a); octaethylporphinatobis-(3-methylpyridine)-cobalt(II) (Little & Ibers, 1974b) which has a radius of nearly optimum size; and octaethylporphinatodichlorotin(IV) (Cullen & Meyer, 1973) in which the core is markedly expanded. The radius changes by 0.15 Å through this series.

Definite trends may be observed for those metalloporphyrins which are approximately planar. The tetragonal form of nickel octaethylporphyrin is an apparent anomaly, but as has been pointed out by Hoard (1973), strain in this complex is relieved by severe ruffling of the macrocycle rather than by changes

in the bond parameters, allowing most of these to return to more optimum values.

As might be expected, most of the larger changes occur in bond lengths and angles involving the methine carbon atoms. The C_a-C_m and C_r-C_m lengths and the $C_a-C_m-C_a$ angles all increase with increasing radius. The $C_b-C_a-C_m$ and $N-C_a-C_b$ angles decrease, while within standard deviations, the $N-C_a-C_m$ angle is constant. Most of the other bond parameters remain relatively constant with the notable exception of the C_a-N-C_a angle which increases by 5° as the radius increases from 1.96 to 2.08 Å.

PyrZnOEP fits all the trends well with the exception of the C_a-N distance for which it has the shortest length among those metalloporphyrins in Table 9. However this difference is small and may not be significant.

Although not included in Table 9, the data for bis(imidazole)octaethylporphinatoiron(III) perchlorate (Takenaka, Sasada, Watanabe, Ogoshi & Yoshida,

Table 9. Averaged bond lengths (Å) and angles ($^\circ$) for various octaethylporphyrin complexes

	Tetragonal NiOEP	Triclinic NiOEP	(3-MePyr) ₂ CoOEP	PyrZnOEP	Cl ₂ SnOEP
M—N	1.929 (3)	1.958 (2)	1.992 (1)	2.043 (2) ^(a)	2.082 (2)
C _a —N	1.386 (2)	1.376 (6)	1.374 (3)	1.366 (1)	1.379 (5)
C _a —C _m	1.372 (2)	1.371 (4)	1.381 (2)	1.390 (6)	1.386 (10)
C _a —C _b	1.449 (5)	1.443 (3)	1.449 (2)	1.452 (6)	1.437 (12)
C _b —C _b	1.362 (5)	1.346 (2)	1.355 (3)	1.352 (6)	1.368 (5)
C _b —C _{aet}	1.501 (3)	1.495 (7)	1.501 (4)	1.495 (4)	1.498 (13)
C _{aet} —C _{bet}	1.509 (10)	1.505 (15)	1.509 (5)	1.510 (6)	1.491 (7)
C _{aet} —C _{bet} ^(b)	1.536 (10)	1.522 (15)	—	1.529 (18)	1.523 (12)
M—C _m	3.355 (4)	3.381 (1)	3.400 (4)	3.406 (1) ^(a)	3.424 (10)
M—C _a	2.983 (1)	3.006 (4)	3.032 (3)	3.061 (3) ^(a)	3.099 (4)
N—N	2.728 (4)	2.768 (5)	2.817 (4)	2.891 (7)	2.994 (2)
C _a —N—C _a	105.1 (3)	103.9 (4)	105.0 (1)	106.4 (5)	108.2 (2)
N—C _a —C _m	124.0 (2)	124.4 (3)	124.5 (3)	124.3 (2)	124.4 (4)
N—C _a —C _b	110.6 (2)	111.6 (3)	111.0 (2)	110.1 (4)	108.3 (7)
C _b —C _a —C _m	125.0 (2)	124.1 (4)	124.4 (3)	125.5 (3)	127.3 (4)
C _a —C _m —C _a	124.1 (2)	125.1 (1)	125.8 (5)	127.9 (3)	129.5 (4)
C _a —C _b —C _b	106.8 (3)	106.5 (4)	106.5 (3)	106.7 (2)	107.6 (3)
C _a —C _b —C _{aet}	124.9 (4)	125.5 (2)	125.4 (5)	124.9 (5)	124.4 (11)
C _b —C _b —C _{aet}	128.1 (7)	128.0 (4)	128.0 (4)	128.2 (5)	128.1 (10)
C _b —C _{aet} —C _{bet}	112.8 (4)	113.5 (2)	113.7 (5)	113.3 (5)	113.3 (7)

(a) For PyrZnOEP, in which the metal ion is located out of the porphyrin plane, M refers to the center of the macrocycle.

(b) Distance corrected for thermal motion.

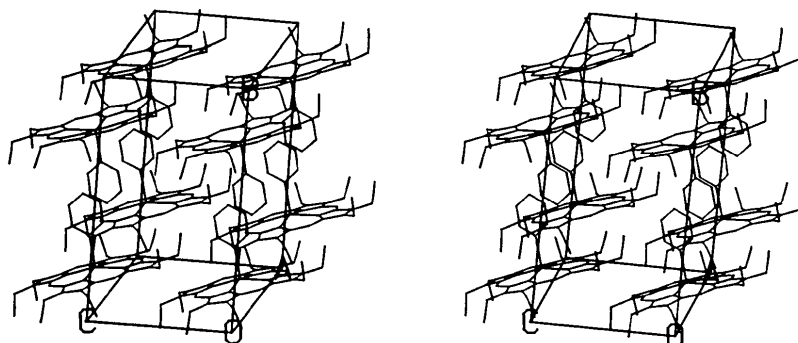


Fig. 4. Stereo view of the packing in the unit cell of PyrZnOEP.

1972), which exhibits an average M–N distance of 1.99 Å, fit the trends observed, as far as the rather large standard deviations will allow comparison.

The terminal C–C bond lengths as originally calculated are unusually short. This is probably due to thermal shortening. When these bond distances were corrected for thermal motion assuming a 'riding' model, more reasonable values were obtained. Both values are given in Table 5. The C–H bond lengths range from 0.89 to 1.03 Å. The range of C_a – C_m –H angles is 114–118°, while the C–C–H angles in the ethyl groups range from 107–114°.

Fig. 4 shows the molecular packing in the unit cell. There are four intermolecular contacts within 3.5 Å; N(1)–C(28)', 3.41; N(3)–C(26)', 3.46; C(4)–C(28)', 3.49; and C(9)–C(22)'', 3.45 Å. The first three involve contacts with the molecule related by the symmetry operation $x' = -x$, $y' = -y$, $z' = -z$, while the last involves a contact with the molecule related by the operation $x'' = -1 + x$, $y'' = y$, $z'' = z$. None of these contacts is considered important.

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