The Crystal and Molecular Structure of Nickel(II)octaethylporphyrin

By Edgar F. Meyer, Jr

Department of Biochemistry and Biophysics, Texas A&M University, College Station, Texas 77843, U.S.A.

The structure of the nickel(II) complex of octaethylporphyrin, $C_{36}H_{44}N_4Ni$, has been determined by the heavy-atom method from diffractometer data and was refined by least-squares methods to an R value of 0·077 based on F^2. The cell is tetragonal and cell constants are $a=b=14·93\pm0·01$, $c=13·84\pm0·01$ Å. The space group is $I4_1/a$, $Z=4$. The nickel atom exhibits normal, square-planar coordination. The nickel–pyrrole nitrogen atom bond distance is 1·929 (3) Å, the shortest metal–nitrogen bond distance for a metalloporphyrin found so far. The individual pyrrole groups within the macrocycle are markedly noncoplanar; each lies at an angle of $\pm14·2°$ to the nitrogen–nickel plane.

Introduction

The distortion of the porphyrin macrocycle from the preferred planar configuration has been observed by various investigators. Effects of geometric changes upon a biological system are illustrated in the recent report of Perutz (1970) on the geometric changes of hemoglobin associated with oxygen binding. The tendency to a tent-shaped molecule of α-chlorohemin was reported by Koenig (1965). The possibility for non-planarity was discussed by Hamor, Caughey & Hoard (1965) who observed gentle ruffling of a nickel(II) deuteroporphyrin (NiDeut). The distortions caused by close proximity of central hydrogen atoms in diacid and metal-free porphyrins have been treated by Stone & Fleischer (1968) and by Silvers & Tulinsky (1967). The latter study observed a slight distortion of a peripheral phenyl group, attributed to packing forces.

With terminal ethyl groups, octaethylporphyrin (OEP), like the more frequently studied tetraphenylporphyrin (TPP), may have higher molecular symmetry than naturally derived porphyrins. However, alkyl or aryl groups at the four methene carbon atoms (*e.g.*, TPP) may offer more steric opposition to the ideally planar, macrocyclic conjugation of the porphyrin than the hydrogen atoms in this study. Also, by choosing terminal alkyl groups, the packing forces at the periphery of the porphyrin moiety should be limited to van der Waals interactions. A potential source of packing disorder (Hamor *et al.*, 1965) from peripheral methyl, ethyl, vinyl, *etc.*, groups is avoided by the choice of eight terminal ethyl groups on OEP. To study the geometric changes in the macrocycle resulting from the substitution of various metals and coordination states, a series of investigations of metal complexes of OEP was begun.

Experimental

Crystal data and data collection

Crystal data are as follows:

Nickel(II) octaethylporphyrin, (NiOEP), $C_{36}H_{44}N_4Ni$

(by difference synthesis, combustion analysis, and nuclear magnetic resonance).

$a=b=14·93\pm0·01$, $c=13·84\pm0·01$ Å; $D_c=1·19$ g.cm^{-3}, $D_o=1·16$ g.cm^{-3} [flotation in Ni(NO$_3$)$_2$], $Z=4$, $V=3085$ Å^3, $F(000)=1264$, $\mu=6·6$ cm^{-1} for Mo $K\alpha$ (0·71069 Å) radiation.

Crystals were supplied by Dr David Dolphin, Harvard University. They were dark red, tetragonal dipyramids (2nd order). Crystal thickness ranged from 0·246 to 0·294 mm. The space group, $I4_1/a$ (No. 88), was assigned on the basis of absent reflections, the appearance of the three-dimensional Patterson map, and the successful solution of the structure. The cell constants and intensities were determined on a Datex automated GE quarter-circle diffractometer using a Nb filter. Thirty-four reflections were used in the least-squares determination of the cell constants and orientation matrix of the crystal. Measurements were made at 20°C.

Intensities

3127 reflections were measured out to a sin θ/λ value of 0·595 or 25°θ; 1205 independent reflections with F^2 greater than $3\sigma(F^2)$ were used for the analysis. Equivalent reflections agreed to within 3·4%. No absorption correction was made. The appropriate Lorentz–polarization factor was applied to obtain F^2 values.

Determination and refinement of the structure

Positions for the nickel and nitrogen atoms were found from the three-dimensional Patterson map; nickel is at a special position (a), a location with $\bar{4}$ site symmetry. Approximate starting positions for the macrocyclic carbon atomic positions were obtained by superimposing a porphyrin skeleton on the nickel and nitrogen positions using the computer graphics program *DISPLAY* (Meyer, 1970). A three-dimensional Fourier synthesis, phased on the ring atoms, permitted the remaining carbon atoms to be located.

Full-matrix least-squares refinement, minimizing the function $\sum w(F_o^2-F_c^2)^2$, was carried out first with all

isotropic thermal parameters and finally with all heavy atoms anisotropic; hydrogen atoms were located from a difference synthesis and were refined isotropically. The refinement converged with $R = \sum |\Delta F^2_{\text{meas}}|/\sum |F^2_c| = 0.077$ and $R' = [\sum w(\Delta F^2_{\text{meas}})/\sum F^4_o]^{1/2} = 0.137$, where $\Delta F^2_{\text{meas}} = ||F^2_{\text{meas}}| - |F^2_{\text{calc}}||$.

Table 1. *Miller indices,* F^2_{obs}, F^2_{cal}

A correction for anomalous dispersion was made for the nickel atom, $\Delta F' = 0.4$ to 0.3; $\Delta F'' = 1.2$ to 1.1 (*International Tables for X-ray Crystallography*, 1962). Scattering factors from *International Tables*, Vol. IV (in the press), were used; nickel was assumed to be in the zero ionization state.

Hydrogen positions adjacent to terminal ethyl carbon atom C(8) had shifted into a distorted tetrahedron compared with the normal carbon–hydrogen geometry

of the other terminal ethyl carbon atom, C(7). There-fore, before the last refinement cycle, more reasonable positional parameters were chosen for the three hydrogen atoms, H(18), H(28), H(38). Additional refinement resulted in a slight decrease (0.005) in the R value to the final value of 0.077 and a renewal of the distorted carbon–hydrogen geometry. All other bond lengths and angles are normal. The highest point in the difference $(F_o - F_c)$ synthesis is 0.16 e.Å^{-3} and is found at the posi-

Table 2. *Fractional atomic coordinates and standard deviations*

U is in the from $\exp(-2\pi^2 \sum_{ij} a_i^* a_j^* h_i h_j U_{ij})$. 10^4. Hydrogen B values ($\times 10$) are in column U_{11}.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.0000	0.2500	0.1250	282 (8)	282 (8)	300 (5)	0	0	0
N	0.1290 (1)	0.2420 (1)	0.1246 (1)	319 (14)	325 (14)	327 (14)	12 (11)	14 (11)	−1 (11)
C(1)	0.1896 (2)	0.3092 (2)	0.1022 (2)	304 (17)	376 (18)	336 (17)	−28 (14)	46 (13)	−13 (14)
C(2)	0.1811 (2)	0.1677 (2)	0.1458 (2)	320 (17)	391 (18)	279 (17)	14 (14)	2 (13)	−29 (13)
C(3)	0.2803 (2)	0.2761 (2)	0.1074 (2)	338 (18)	431 (20)	358 (19)	−31 (15)	32 (14)	−66 (14)
C(4)	0.2757 (2)	0.1892 (2)	0.1371 (2)	310 (17)	451 (20)	343 (19)	15 (14)	5 (14)	−73 (15)
C(5)	0.3625 (2)	0.3287 (3)	0.0821 (3)	355 (21)	465 (25)	673 (28)	−36 (18)	52 (20)	−29 (21)
C(6)	0.3508 (2)	0.1239 (2)	0.1537 (3)	326 (19)	512 (23)	516 (24)	39 (18)	−59 (17)	−3 (19)
C(7)	0.3826 (4)	0.3268 (4)	−0.0240 (4)	840 (43)	712 (37)	821 (40)	−184 (34)	432 (35)	−49 (31)
C(8)	0.3752 (4)	0.0710 (4)	0.0640 (4)	800 (43)	706 (35)	809 (41)	347 (33)	−13 (32)	−174 (32)
C(9)	0.1471 (2)	0.0836 (2)	0.1621 (2)	363 (19)	372 (19)	376 (18)	77 (16)	−12 (15)	53 (15)
H(9)	0.186 (2)	0.038 (2)	0.180 (2)	16 (8)					
H(15)	0.404 (3)	0.309 (3)	0.114 (3)	26 (11)					
H(25)	0.360 (2)	0.388 (2)	0.106 (2)	12 (8)					
H(16)	0.332 (2)	0.085 (2)	0.209 (3)	17 (8)					
H(26)	0.398 (2)	0.161 (3)	0.178 (3)	18 (8)					
H(17)	0.332 (3)	0.351 (3)	−0.060 (4)	36 (13)					
H(27)	0.433 (3)	0.356 (3)	−0.041 (4)	46 (13)					
H(37)	0.390 (3)	0.266 (4)	−0.047 (4)	53 (14)					
H(18)	0.319 (6)	0.026 (5)	0.047 (6)	86 (25)					
H(28)	0.378 (5)	0.101 (5)	0.013 (6)	93 (26)					
H(38)	0.420 (6)	0.042 (6)	0.080 (6)	52 (28)					

Table 3. *Anisotropic and isotropic temperature factors*

Factors are of the form: $\exp[-\frac{1}{4}(\sum_{ij} h_i h_j a_i^* a_j^* B_{ij})]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	2.23 (7)	2.23 (7)	2.38 (4)	0.00 (0)	0.00 (0)	0.00 (0)
N	2.52 (11)	2.57 (12)	2.59 (11)	0.10 (9)	0.12 (9)	−0.01 (9)
C(1)	2.41 (14)	2.97 (14)	2.66 (14)	−0.22 (12)	0.36 (11)	−0.11 (11)
C(2)	2.53 (14)	3.09 (15)	2.21 (14)	0.12 (12)	0.02 (10)	−0.23 (11)
C(3)	2.67 (14)	3.41 (16)	2.83 (15)	−0.25 (12)	0.26 (11)	−0.53 (12)
C(4)	2.45 (14)	3.57 (16)	2.71 (15)	0.12 (12)	0.04 (11)	−0.59 (12)
C(5)	2.81 (17)	3.67 (20)	5.32 (23)	−0.29 (14)	0.41 (17)	−0.23 (17)
C(6)	2.58 (16)	4.05 (19)	4.08 (20)	0.31 (14)	−0.47 (14)	−0.02 (15)
C(7)	6.63 (34)	5.63 (30)	6.49 (32)	−1.45 (27)	3.41 (28)	−0.39 (25)
C(8)	6.32 (34)	5.58 (28)	6.39 (32)	2.75 (26)	−0.11 (26)	−1.38 (26)
C(9)	2.87 (15)	2.94 (15)	2.97 (14)	0.62 (13)	−0.10 (12)	0.42 (12)

Table 3 (*cont.*)

	B
H(9)	1.60 (0.8)
H(15)	2.64 (1.2)
H(25)	1.28 (0.8)
H(16)	1.73 (0.8)
H(26)	1.85 (0.8)
H(17)	3.65 (1.4)
H(27)	4.67 (1.4)
H(37)	5.31 (1.5)
H(18)	8.68 (2.5)
H(28)	9.22 (2.6)
H(38)	5.24 (2.8)

tion of the nickel atom. The ratios of final shifts to standard deviations were less than 0.1, except for the Z parameters of C(8) and H(38), which had values of 0.9 and 3.8. Due to the fact that the other hydrogen positions behaved normally, the reasons for the unusual behaviour of the atoms about C(8) are not clear. Further refinement did not seem to be justified.

The weights (w) were defined in terms of the statistical variances of the count as $\sigma(F_o^2) = [\sigma^2 (\text{count}) + (0.05 \, F_o^2)]^{1/2}$, $w = 1/\sigma^2(F_o^2)$. The final value of the standard deviation of an observation of unit weight is

$S = [\sum(\Delta F^2_{meas}/\sigma(F^2_0)^2/(m-n)]^{1/2} = 2\cdot07$, for $m = 1205$ reflections and $n = 138$ variables.

The observed and calculated squared structure factors are listed in Table 1. The final positional and thermal parameters from the last cycle of refinement are given in Table 2. The final thermal parameters are shown in Table 3. Table 4 lists the root-mean-square components of thermal displacement along the principal axes of the thermal ellipsoids. Bond lengths and angles are shown in Table 5. Fig. 1 illustrates the numbering sequence. Fig. 2 is a stereo view to illustrate the nonplanarity of the macrocycle.

Table 4. *Root-mean-square thermal displacement in* Å *along the principal axes of thermal-motion ellipsoids*

Ni	0·1682 (25)	0·1682 (25)	0·1734 (16)
N	0·1741 (42)	0·1809 (42)	0·1852 (41)
C(1)	0·1642 (51)	0·1863 (49)	0·2003 (48)
C(2)	0·1648 (53)	0·1786 (50)	0·2002 (49)
C(3)	0·1763 (52)	0·1826 (50)	0·2200 (48)
C(4)	0·1721 (53)	0·1790 (50)	0·2212 (48)
C(5)	0·1842 (56)	0·2162 (59)	0·2623 (57)
C(6)	0·1740 (57)	0·2260 (54)	0·2328 (56)
C(7)	0·1924 (68)	0·2634 (71)	0·3620 (87)
C(8)	0·1915 (72)	0·2823 (73)	0·3397 (79)
C(9)	0·1642 (58)	0·1959 (50)	0·2143 (51)

Table 5. *Bond distances and bond angles*

* Corrected for thermal motion.

Ni—N	1·929 (3) Å	Ni—N—C(1)	127·4°
N—C(1)	1·386 (4)	Ni—N—C(2)	127·5
N—C(2)	1·387 (4)	N—C(1)—C(9′)	124·0
C(1)—C(3)	1·444 (5)	N—C(2)—C(9)	124·0
C(1)—C(9)	1·372 (5)	N—C(1)—C(3)	110·7
C(2)—C(4)	1·453 (5)	N—C(2)—C(4)	110·6
C(2)—C(9′)	1·373 (5)	C(9)—C(2)—C(4)	125·1
C(3)—C(4)	1·362 (5)	C(9′)—C(1)—C(3)	124·9
C(3)—C(5)	1·498 (5)	C(1)—C(3)—C(4)	107·1
C(4)—C(6)	1·504 (5)	C(2)—C(4)—C(3)	106·6
C(5)—C(7)	1·499 (8)	C(6)—C(4)—C(3)	128·7
C(5)—C(7)	1·528*	C(5)—C(3)—C(4)	127·7
C(6)—C(8)	1·515 (7)	C(2)—C(4)—C(6)	124·6
C(6)—C(8)	1·545*	C(1)—C(3)—C(5)	125·2
C(9)—H(9)	0·93 (4)	C(3)—C(5)—C(7)	112·6
C(5)—H(15)	0·82 (5)	C(4)—C(6)—C(8)	113·0
C(5)—H(25)	0·95 (5)		
C(6)—H(16)	1·00 (4)		
C(6)—H(26)	0·95 (5)		
C(7)—H(17)	0·98 (6)		
C(7)—H(27)	0·90 (6)		
C(7)—H(37)	0·97 (6)		
C(8)—H(18)	1·11 (9)		
C(8)—H(28)	0·84 (9)		
C(8)—H(38)	0·83 (10)		

The following computer programs were used: *DATAPH* (Lorentz–polarization), *ESORTH* (sorting and averaging data), *JIMDAP* (version of Zalkin–Fourier summation program), *LINUS* [modification of the Busing, Martin & Levy (1962) *ORFLS* least-squares program], *ORFFE* (function and error, Busing *et al.*, 1964), *ORTEP* (thermal-ellipsoid plot) (Johnson, 1965), and *DISPLAY* (Meyer, 1970).

Discussion of the structure

The five atoms in the pyrrole group [N(1), C(1), C(2), C(3), C(4), Fig. 1] deviate by 0·01 Å or less from the best-fit plane passing through them (Table 6); thus, the planarity of the pyrrole group is maintained. With respect to this plane, the bridging methene atoms are −0·158, −0·178 Å from the plane. The two independent pyrrole carbon to methene carbon bond lengths are essentially equivalent, C(1)–C(9) = 1·372 Å; C(2)–C(9) = 1·373 Å.

Table 6. *Distance from the mean plane passing through* (a) *nickel and four pyrrole nitrogen atoms,* (b) *five atoms in pyrrole ring*

	(a)	(b)
Ni	0·000 Å	−0·026 Å
N	−0·006	−0·002
C(1)	−0·316	0·011
C(2)	0·288	−0·007
C(3)	−0·244	−0·015
C(4)	−0·167	0·013
C(5)	−0·594	−0·091
C(6)	0·398	−0·003
C(9)	0·514	−0·158

Likewise, the independent bond lengths, angles, and internal geometry of the pyrrole group show a close relationship, so that the *pseudo* mirror plane perpendicular to the pyrrole ring and passing through the nitrogen atom is maintained. The terminal ethyl carbon to carbon single (sp^3) bond lengths refine to 1·499 (8) and 1·515 (7) Å. The inordinate shortening of these bonds can be partially attributed to thermal motion. When the bond distance is averaged over the thermal motions, assuming the terminal atoms [C(7), C(8)] are riding on the methylene carbon atoms [C(5), C(6)], these distances are calculated (*ORFFE*) to be 1·528, 1·545 Å.

Another feature of this structure is the virtual planarity (± 0·006 Å) of the nickel and coordinated nitrogen atoms (Table 6). Thus, the square-planar coordination of the complex is maintained.

A distinguishing feature of this structure is the nonplanarity of the macrocycle. As Fig. 2 illustrates, the adjacent pyrrole rings and the pyrrole rings *vis-à-vis* make an angle of 14·2° to the N–Ni coordination system and, therefore, the planes are at an angle of 28·4° to each other. Methene carbon atoms are ± 0·51 Å from the mean N–Ni plane. This may be compared with a displacement of +0·06 to −0·07 Å from the mean plane of the porphine skeleton in NiDeut.

A folding of the macrocycle about lines joining opposite methene carbon atoms in NiOEP is reminiscent of the 13° inclination between the planes composed of pyrrole rings *A–B* and *C–D* in α-chlorohemin (Koenig, 1965), or the 9 to 19° angles between planes composed of pyrroline rings *A–B* and *C–D* in the corrin nuclei of vitamin B_{12} (Hodgkin, 1964), and its coenzyme (Lenhert, 1968). More flexibility is evident at the

methene carbon bridge .han within the pyrrole ring.

Stone & Fleischer (1968) exclude packing forces as a major factor. They attribute the nonplanarity of the porphyrin diacid to the steric repulsion of the central four hydrogen atoms and the electrostatic repulsions of the pyrrole nitrogen atoms, which have been assigned a formal charge of $+\frac{1}{2}$. In this study, the coordination of the nickel atom is definitely square planar. No unusually short intermolecular contact distances are observed. However, if the pyrrole groups were constrained to assume a planar configuration, hydrogen atoms H(15), H(25), H(16), H(26) of methylene carbon atoms C(5) and C(6), which are now in a staggered

configuration, would be brought into close proximity with similar atoms of adjacent molecules. Close contacts could be relieved only by rotations about the C–C σ bonds [e.g., C(3)–C(5)], which in turn would bring the terminal methyl hydrogen atoms [H(17)···, H(18)...] into an unfavorable position with respect to their neighboring H atoms of molecules above and below. Thus, one can argue that in the course of minimizing contacts with neighboring molecules, while packing as efficiently as possible (a density of 1·16 g.cm³ is not all that large), the porphyrin group is forced into a somewhat strained, nonplanar configuration. An attempt to estimate the forces and couples of
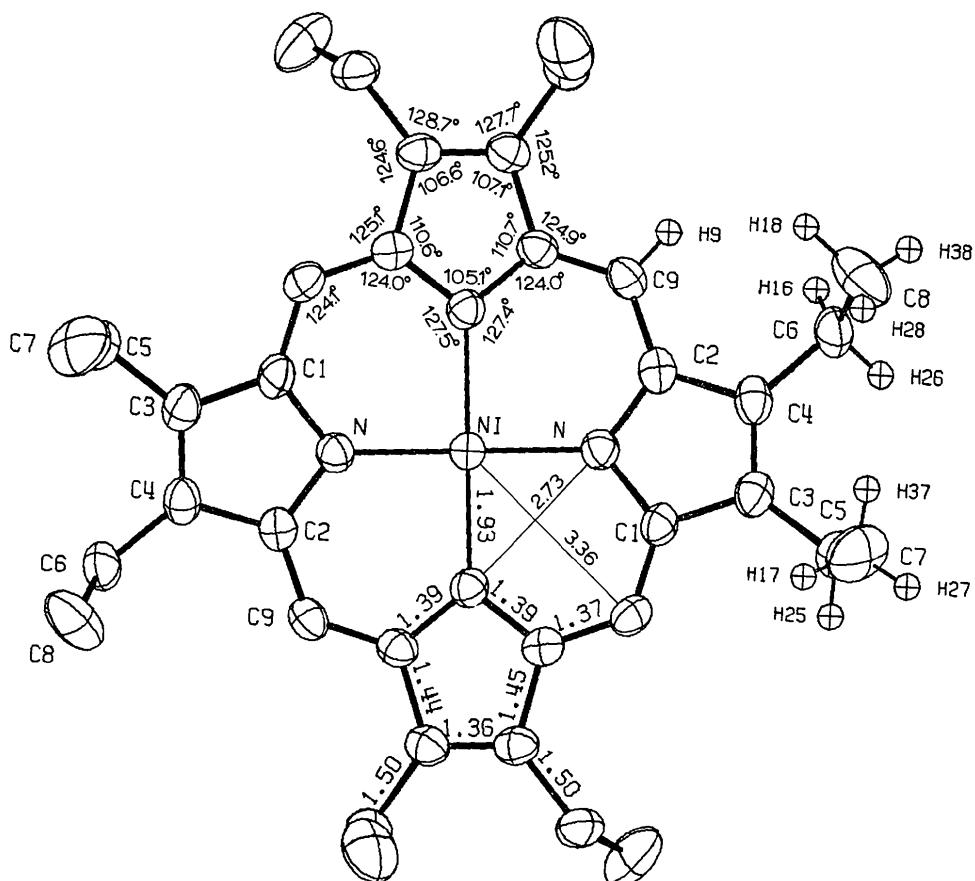
Fig. 1. Molecule of NiOEP showing thermal ellipsoids of vibration as viewed down the Z axis. Atom H(15) is hidden by atom C(7).
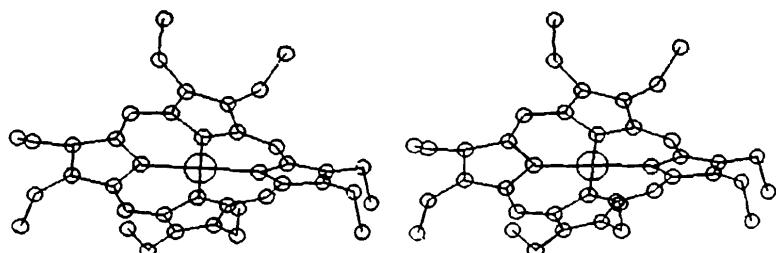
Fig. 2. Stereo view of NiOEP viewed 30° from the Z axis as rotated about the Y axis.

various atoms (Nyberg, 1970) was abandoned, due to difficulty in determining the appropriate value for the metal atom and due to the ill-determined hydrogen positions of H(18)–H(38).

That nonplanarity is not an attribute of the OEP molecule is demonstrated by the perfectly planar configuration of the macrocycle in the dichlorooctaethyl-porphinatotin(IV) structure now being refined in this laboratory by Dr David Cullen (Cullen & Meyer, 1971).

Collins & Hoard (1970) have recently discussed bond strains in the porphyrin skeleton. Several points in their excellent paper may be enlarged upon as a result of this study. First, the Ni–N bond distance (Table 7) of 1·929 (3) Å is slightly (0·031 Å) shorter than the value of 1·960 (4) Å reported by Hamor et al. (1965) for NiDeut and predicted by Collins & Hoard to be the minimum metal–nitrogen bond distance in a metalloporphyrin. The nickel–methene carbon, C(9), distance is 0·047 Å shorter than the distance reported for NiDeut. The nitrogen-to-α-carbon distances agree within one standard deviation, as do the α-carbon-to-β-carbon distances. The β-carbon-to-β-carbon distances vary by 2·4 standard deviations. Thus, the geometry of the pyrrole group is largely unchanged. However, the pyrrole rings appear to be shifted toward the nickel atom by about 0·03 Å. As Collins & Hoard point out, and as reviewed by Sacconi (1968), the normal Ni–N bond length for diamagnetic, square planar nickel(II) ion varies from 1·84 to 1·92 Å, depending on stereochemical constraints. Thus, the 1·929 Å bond here is not markedly different from the 1·92 Å bond reported by Braun & Lingafelter (1966) for the bis-(N-isopropylsalicylaldiminato)nickel(II) complex. Although the nickel–nitrogen bond length in NiOEP is longer by 0·017 to 0·061 Å than the compressed ring system in nickel(II) corrin (Dunitz & Meyer, 1971), it compares closely with the Ni–N bond lengths (1·87–1·90 Å) in the sterically more relieved nickel(II) A/D-seco-corrinoid (Currie & Dunitz, 1971) or the similar 1·83–1·89 Å distances in the nickel(II) C/D-seco-corrinoid complex (Dobler & Dunitz, 1971).

Table 7. *Comparison of bond distances between this structure and* NiDeut (*Hamor et al.*, 1965)

	NiOEP	NiDeut
Ni---N	1·929 (3) Å	1·960 (4) Å
Ni---C(9)	3·355 (4)	3·402 (4)
N---C(1), C(2)	1·386 (4)	1·383 (3)
C(1)-C(9)	1·373 (5)	1·375 (4)
C(1)-C(3)	1·444 (4)	1·447 (3)
C(2)-C(4)	1·453 (4)	1·447 (3)
C(3)-C(4)	1·362 (5)	1·350 (5)
N---N	2·728	2·772

Another measure of the macrocycle's degree of compression is the distance between adjacent pyrrole nitrogen atoms. The 2·728 Å distance here is 0·04 Å less than the average distance of 2·772 Å in NiDeut, but it is greater than the (2·65–2·62 Å) distance between nonbonded nitrogen atoms in the less planar nickel(II) corrinoid complexes (Currie & Dunitz, 1971). Thus, if the macrocycle is to relieve the strain built up by the inward shift of the pyrrole groups, bond angles and especially the planarity will clearly yield before bond lengths (*e.g.*, nitrogen to α-carbon or α-carbon to methene carbon) are greatly affected. The C(1')–C(9)–C(2) bond angle of 124·1° in NiOEP is quite similar to the 122·1–125·2° (average 123·9°) angles reported for NiDeut.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. (1962) *ORFLS, A Fortran Crystallographic Least-Squares Program*, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

BUSING, W. R., MARTIN, K. O. & LEVY H. (1964). *ORFFE, A Fortran Crystallographic Function and Error Program*. Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

COLLINS, D. M. & HOARD, J. L. (1970). *J. Amer. Chem. Soc.* **92**, 3761.

CULLEN, D. L. & MEYER, E. F. (1971). *Chem. Comm.* p. 616.

CURRIE, M. & DUNITZ, J. D. (1971). *Helv. Chim. Acta.* **54**, 98.

DOBLER, M. & DUNITZ, J. D. (1971). *Helv. Chim. Acta,* **54**, 90.

DUNITZ, J. D. & MEYER, E. F. JR (1971). *Helv. Chim. Acta,* **54**, 77.

HAMOR, T. A., CAUGHEY, W. S. & HOARD, J. L. (1965). *J. Amer. Chem. Soc.* **87**, 2305, 2309.

HODGKIN, D. C. (1964). *Vitamin B₁₂ and the Porphyrins. Fed. Proc.* **23**, 3, p. 592.

International Tables for X-ray Crystallography (1962). Vol. III, p. 215. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations.* Report ORNL-3794-Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KOENIG, D. F. (1965). *Acta Cryst.* **18**, 663.

LENHERT, P. G. (1968). *Proc. Roy. Soc.* A**303**, 45.

LINGAFELTER, E. C. & BRAUN, R. L. (1966). *J. Amer. Chem. Soc.* **88**, 2951.

MEYER, E. F. (1970). *J. Appl. Cryst.* **3**, 392.

NYBERG, S. C. (1970). *Trans. Amer. Cryst. Assn.* **6**, 95.

PERUTZ, M. F. (1970). *Nature, Lond.* **228**, 726, 734.

SACCONI, L. (1968). *Transition Metal Chemistry*, Ed. R. L. CARLIN. Vol. 4. p. 199. New York: Marcel Dekker,

SILVERS, S. J. & TULINSKY, A. (1967). *J. Amer. Chem. Soc.* **89**, 3331.

STONE, A. L. & FLEISCHER, E. B. (1968). *J. Amer. Chem. Soc.* **90**, 2735, 2742.