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Unusual Metalloporphyrin Derivative. Insertion of an Ethoxycarbonylcarbene Fragment into a Ni–N Bond of Nickel(II) *meso*-Tetraphenylporphine. Crystal and Molecular Structure of the Complex

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Abstract: The structure of the title compound has been determined from three-dimensional x-ray counter data. The crystals, grown from a chloroform–methanol solution, have the space group $P\bar{1}$ with $a = 13.677$ (6) Å, $b = 14.212$ (8) Å, $c = 11.958$ (5) Å, and $\alpha = 98.85$ (8)°, $\beta = 99.21$ (8)°, $\gamma = 113.73$ (7)°. This triclinic unit cell contains two molecules of the Ni(II) complex and two molecules of chloroform present as uncomplexed solvent of crystallization. Intensity data were collected by θ – 2θ scanning with Mo K α radiation, and 5493 independent data were retained as observed and used for the solution and refinement of structure; the conventional and weighted R values are 0.061 and 0.086, respectively. An ethoxycarbonylcarbene moiety is inserted into a Ni–N bond of the original nickel(II) *meso*-tetraphenylporphine. Thus, the nickel atom is tetracoordinated with nitrogen atoms of only three pyrrole bases and with the extra carbon atom of the carbene fragment. The Ni–C bond length of 1.905 (4) Å is close to that expected for a pure σ bond. The three Ni–N bond lengths are equivalent and equal to 1.916 ± 0.010 Å. The four nitrogen atoms of the pyrrole bases are approximately coplanar. The nickel and carbon atoms are displaced from this (4N) plane by 0.19 and 1.04 Å, respectively. The porphyrin macrocycle is distorted, leading to unusual distances between opposite pyrrole nitrogen atoms (3.81 and 4.49 Å). The pyrrole rings are quite planar but rotated with respect to the (4N) plane. Especially, owing to the insertion of the carbene moiety into the original Ni–N(4) bond, the N(4) pyrrole exhibits a very large angle of 46.4°.

Recent papers have described the reactions of ethyl diazoacetate with diverse metalloporphyrins. It appears from these studies that the nature of the adduct depends on the nature of the coordinating metal and even on the nature of the porphyrin. Thus, with copper(II) octaethylporphine, the reaction gives addition of the carbene fragment to the $\beta\beta$ double bonds to form chlorins together with a little *meso* substitution.¹ However, with cobalt(II) octaethylporphine reaction yields an unstable 1:1 adduct, a cobalt(III) salt where the carbene is inserted into one of the metal–nitrogen bonds.² On the other hand, zinc *meso*-tetraphenylporphine was shown to give mainly addition to the nitrogen atoms.^{3,4} Of prime interest, this last compound, if demetalated, reacts with nickel(II) salts to cause spectacular rearrangements,^{5,6} finally yielding novel nickel derivatives A and B.

One of them (A) is nickelhomoporphyrin. Its structure recently determined by x-ray analysis⁷ shows a severe ruffling of the porphyrato core mainly introduced by the carbene insertion between two pyrroles of the macrocyclic ligand. The other derivative (B) was presumed to be analogous to the above-mentioned Co(III) derivative, i.e., the

carbene is inserted into a Ni–N bond of nickel(II) *meso*-tetraphenylporphine.⁶

Details of an x-ray examination of such compounds are not yet available.⁸ Therefore, it is of interest to determine the structure of the air-stable derivative B and to specify the effects of the carbene moiety on the porphine skeleton and on the coordinated metal.

Experimental Section

The synthesis of this nickel(II) complex B and preliminary results on its structure have already been reported.⁶ Suitable crystals were grown by slow evaporation from a chloroform–methanol solution. Preliminary x-ray photographic study established a triclinic unit cell with $P\bar{1}$ or $P1$ as the possible space groups. Lattice constants, $a = 13.677$ (6), $b = 14.212$ (8), $c = 11.958$ (5) Å and $\alpha = 98.85$ (8), $\beta = 99.21$ (8), $\gamma = 113.73$ (7)°, came from a least-squares refinement⁹ that utilized the setting angles of 12 reflections measured on a Picker four-circle automatic diffractometer with Mo K α radiation (λ 0.70926 Å). The unit cell volume is 2038 Å³. A unit cell containing just two molecules of complex (C₄₈H₃₄N₄O₂Ni, $M = 757.5$) gives a calculated density of 1.234 g/cm⁻³. As measured by flotation in aqueous zinc chloride solu-

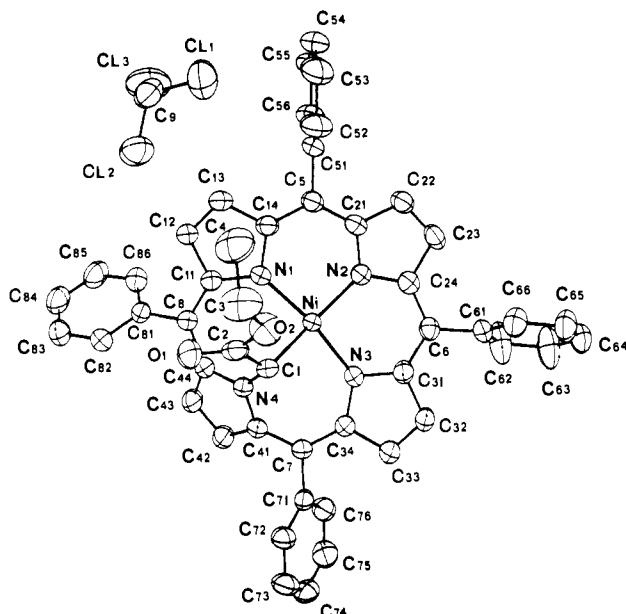


Figure 1. ORTEP drawing of the structure. Hydrogen atoms have been omitted for clarity.

tion, the density of the crystals is 1.41 g/cm^{-3} . The presence of two molecules of chloroform raises the calculated density to 1.428 g/cm^{-3} .

A crystal with approximate dimensions of $0.20 \times 0.30 \times 0.30 \text{ mm}$ was selected for data collection and mounted on the diffractometer. Data were collected by the θ - 2θ scan method using graphite-monochromated Mo $K\alpha$ radiation. Data collection techniques were essentially the same as described previously.⁷ The scan rate was 2° in 2θ per minute. The scan range was 1.8° . Backgrounds at either end of the scan were measured for 20 s. Three standard reflections well distributed in reciprocal space were used for periodic checking (every 75 reflections) on the alignment and possible deterioration of the crystal. The fluctuations of these standards were all within counting statistics, and thus no correction was made. Independent reflections were measured out to a $\sin \theta/\lambda$ of 0.70 \AA^{-1} or 30° in θ . All data having a net intensity smaller than $3\sigma I$ were taken to be unobserved, leaving 5493 independent observed data from about 12 000 independent observations. Standard deviations were calculated as described previously⁷ using an initial p value of 0.05. Corrections for Lorentz and polarization effects were applied. The small linear absorption coefficient of 0.52 mm^{-1} and the cited dimensions of the crystal indicated absorption effects could be neglected. Only the observed data were used for the determination and refinement of structure. This corresponds to a data/parameter ratio of 10.3 if hydrogen atoms are not included.

The initial choice of $P\bar{1}$ as the space group was fully confirmed by all subsequent developments during the determination of structure. The structure was solved by the heavy-atom method. The positions of the Ni atoms were readily obtained from a three-dimensional Patterson function. A structure factor calculation phased by these nickel atoms, followed by a three-dimensional Fourier synthesis, revealed all nonhydrogen atoms defining the porphine skeleton and the CHCl_3 solvate molecule. Values of the atomic scattering factors were taken from the usual sources.¹⁰ The effects of anomalous dispersion were included for nickel and chlorine atoms; the values of $\Delta f'$ and $\Delta f''$ used are those given in ref 11.

Least-squares refinement using full-matrix methods¹² was carried out. The function minimized was $\sum w(|F_d| - |F_o|)^2$, where $w = 1/\sigma^2(F_o)$. Initially, isotropic temperature factors were used, but in the final refinement all nonhydrogen atoms were refined assuming anisotropic thermal motion. Because of computer memory limitations, the parameters had to be refined in several blocks during the full-matrix least-squares refinement. The conventional unweighted $R = \sum |F_d| - |F_o| / \sum |F_d|$ and weighted $R_w = [\sum w(|F_d| - |F_o|)^2 / \sum w|F_o|^2]^{1/2}$ factors were 0.073 and 0.101. At this point a difference Fourier map was calculated clearly revealing the 35 independent hydrogen atoms. These were then fixed in the theoret-

Table I. Atomic Coordinates in the Unit Cell of the Crystal^a

Atom	x	y	z
Ni	0.00622 (3)	0.27289 (3)	0.04440 (3)
N(1)	-0.1362 (2)	0.1985 (2)	0.0705 (2)
C(11)	-0.2415 (3)	0.1772 (3)	0.0087 (3)
C(12)	-0.3220 (3)	0.1053 (3)	0.0566 (3)
C(13)	-0.2690 (3)	0.0854 (3)	0.1470 (3)
C(14)	-0.1531 (3)	0.1462 (3)	0.1596 (3)
N(2)	0.0829 (2)	0.2915 (2)	0.2003 (2)
C(21)	0.0389 (3)	0.3239 (3)	0.2766 (3)
C(22)	0.1252 (3)	0.2509 (3)	0.3740 (3)
C(23)	0.2202 (3)	0.3181 (3)	0.3566 (3)
C(24)	0.1939 (3)	0.3405 (3)	0.2450 (3)
N(3)	0.1356 (2)	0.3672 (2)	0.0045 (2)
C(31)	0.2415 (3)	0.4039 (3)	0.0720 (3)
C(32)	0.3199 (3)	0.4583 (3)	0.0100 (4)
C(33)	0.2640 (3)	0.4599 (4)	-0.0914 (4)
C(34)	0.1482 (3)	0.4054 (3)	-0.0961 (3)
N(4)	-0.1014 (2)	0.2842 (2)	-0.1500 (2)
C(41)	-0.0444 (3)	0.3676 (3)	-0.1942 (3)
C(42)	-0.1168 (3)	0.4134 (4)	-0.2284 (4)
C(43)	-0.2120 (3)	0.3615 (4)	-0.1958 (4)
C(44)	-0.2022 (3)	0.2822 (3)	-0.1419 (3)
C(5)	-0.0712 (4)	0.1617 (4)	0.2564 (4)
C(51)	-0.1046 (4)	0.0986 (4)	0.3442 (4)
C(52)	-0.1077 (5)	-0.0008 (5)	0.3299 (5)
C(53)	-0.1393 (6)	-0.0586 (6)	0.4143 (7)
C(54)	-0.1653 (5)	-0.0167 (8)	0.5088 (7)
C(55)	-0.1628 (6)	0.0789 (8)	0.5224 (6)
C(56)	-0.1317 (5)	0.1385 (6)	0.4407 (5)
C(6)	0.2708 (4)	0.3958 (4)	0.1857 (4)
C(61)	0.3911 (4)	0.4422 (4)	0.2460 (4)
C(62)	0.4516 (5)	0.5508 (5)	0.2897 (7)
C(63)	0.5642 (5)	0.5924 (6)	0.3398 (7)
C(64)	0.6141 (4)	0.5302 (6)	0.3526 (5)
C(65)	0.5551 (5)	0.4239 (6)	0.3109 (5)
C(66)	0.4438 (4)	0.3804 (5)	0.2575 (5)
C(7)	0.0689 (4)	-0.4092 (4)	-0.1840 (4)
C(71)	0.1082 (3)	0.4745 (4)	-0.2690 (4)
C(72)	0.0854 (4)	0.4259 (4)	-0.3856 (4)
C(73)	0.1204 (5)	0.4857 (5)	-0.4646 (5)
C(74)	0.1769 (4)	0.5934 (4)	-0.4295 (5)
C(75)	0.1982 (5)	0.6431 (4)	-0.3140 (5)
C(76)	0.1639 (4)	0.5837 (4)	-0.2337 (4)
C(8)	-0.2711 (4)	0.2227 (4)	-0.0789 (4)
C(81)	-0.3854 (4)	0.2133 (4)	-0.1053 (4)
C(82)	-0.4271 (4)	0.2490 (4)	-0.0178 (5)
C(83)	-0.5309 (4)	0.2448 (5)	-0.0440 (6)
C(84)	-0.5956 (4)	0.2023 (5)	-0.1565 (6)
C(85)	-0.5563 (4)	0.1663 (5)	-0.2434 (5)
C(86)	-0.4506 (4)	0.1726 (4)	-0.2188 (4)
C(1)	-0.0588 (4)	0.2142 (4)	-0.1184 (4)
C(2)	-0.1352 (4)	0.0987 (4)	-0.1576 (4)
O(1)	-0.2272 (3)	0.0583 (3)	-0.2200 (3)
O(2)	-0.0847 (3)	0.0447 (3)	-0.1149 (3)
C(3)	-0.1451 (6)	-0.0700 (4)	-0.1377 (6)
C(4)	-0.1918 (6)	-0.1006 (5)	-0.0402 (6)
Solvate			
C(9)	-0.5269 (5)	0.0997 (5)	0.3580 (5)
Cl(1)	-0.4062 (1)	0.0993 (2)	0.4305 (2)
Cl(2)	-0.5128 (1)	0.1271 (1)	0.2234 (1)
Cl(3)	-0.5548 (2)	0.1923 (2)	0.4415 (2)

^a Numbers in parentheses here and in succeeding tables are estimated standard deviations for the last significant figure.

cally calculated positions ($\text{C}-\text{C}-\text{H} = 109.5$ or 120.0° , $\text{C}-\text{H} = 1.0 \text{ \AA}$) and assumed to have isotropic thermal motion ($B_{\text{H}} = B_{\text{C}} + 1.0$). The R value was reduced to 0.064. The hydrogen atoms were added as fixed contributions in the subsequent refinement. A p value of 0.07 was used in the last cycles of refinement. The final value of R was 0.061, that of R_w was 0.086. The standard deviation of an observation of unit weight was 1.36.¹³ A final difference Fourier synthesis was essentially featureless with no peaks greater than 0.4 e/\AA^{-3} .

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively.

Table II. Anisotropic Thermal Parameters^a

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.0290 (2)	0.0359 (3)	0.0272 (2)	0.0107 (2)	0.0059 (2)	0.0115 (2)
N(1)	0.0368 (17)	0.0391 (18)	0.0295 (16)	0.0164 (15)	0.0076 (13)	0.0129 (13)
C(11)	0.0350 (20)	0.0429 (23)	0.0320 (19)	0.0154 (18)	0.0107 (16)	0.0098 (17)
C(12)	0.0378 (23)	0.0510 (26)	0.0371 (22)	0.0120 (20)	0.0096 (18)	0.0163 (19)
C(13)	0.0453 (23)	0.0482 (25)	0.0370 (21)	0.0154 (20)	0.0140 (19)	0.0175 (19)
C(14)	0.0419 (22)	0.0404 (24)	0.0338 (20)	0.0169 (19)	0.0126 (17)	0.0127 (18)
N(2)	0.0355 (17)	0.0396 (19)	0.0344 (17)	0.0134 (15)	0.0061 (14)	0.0120 (14)
C(21)	0.0433 (23)	0.0459 (25)	0.0291 (19)	0.0183 (20)	0.0076 (16)	0.0111 (18)
C(22)	0.0488 (25)	0.0585 (29)	0.0346 (21)	0.0286 (23)	0.0110 (19)	0.0161 (20)
C(23)	0.0466 (25)	0.0655 (31)	0.0320 (21)	0.0305 (24)	0.0012 (18)	0.0086 (20)
C(24)	0.0421 (22)	0.0390 (23)	0.0367 (21)	0.0226 (20)	0.0094 (17)	0.0078 (17)
N(3)	0.0322 (17)	0.0450 (20)	0.0347 (17)	0.0157 (15)	0.0053 (14)	0.0146 (15)
C(31)	0.0345 (21)	0.0397 (24)	0.0456 (23)	0.0139 (19)	0.0055 (18)	0.0149 (19)
C(32)	0.0299 (21)	0.0608 (29)	0.0559 (27)	0.0147 (21)	0.0074 (19)	0.0277 (23)
C(33)	0.0357(22)	0.0626 (31)	0.0490 (25)	0.0146 (21)	0.0085 (19)	0.0250 (23)
C(34)	0.0333 (20)	0.0441 (25)	0.0396 (21)	0.0153 (19)	0.0092 (16)	0.0160 (19)
N(4)	0.0321 (17)	0.0415 (19)	0.0371 (17)	0.0136 (15)	0.0083 (14)	0.0189 (15)
C(41)	0.0360 (21)	0.0483 (25)	0.0397 (22)	0.0145 (20)	0.0082 (17)	0.0240 (19)
C(42)	0.0390 (24)	0.0631 (31)	0.0586 (28)	0.0200 (23)	0.0095 (21)	0.0345 (24)
C(43)	0.0374 (23)	0.0614 (30)	0.0599 (28)	0.0225 (22)	0.0112 (20)	0.0309 (24)
C(44)	0.0333 (20)	0.0501 (25)	0.0389 (21)	0.0161 (19)	0.0061 (16)	0.0184 (19)
C(5)	0.0427 (27)	0.0485 (30)	0.0342 (25)	0.0254 (25)	0.0127 (21)	0.0154 (22)
C(51)	0.0405 (29)	0.0711 (41)	0.0385 (27)	0.0211 (28)	0.0097 (22)	0.0302 (27)
C(52)	0.0790 (44)	0.0638 (39)	0.0639 (40)	0.0268 (34)	0.0196 (33)	0.0388 (32)
C(53)	0.0853 (51)	0.0815 (56)	0.0895 (58)	0.0171 (44)	0.0037 (45)	0.0546 (48)
C(54)	0.0640 (44)	0.1334 (78)	0.0779 (51)	0.0318 (48)	0.0229 (37)	0.0772 (54)
C(55)	0.0818 (51)	0.1604 (85)	0.0523 (43)	0.0515 (56)	0.0275 (36)	0.0605 (52)
C(56)	0.0731 (42)	0.0983 (55)	0.0459 (33)	0.0417 (41)	0.0241 (30)	0.0340 (35)
C(6)	0.0368 (26)	0.0355 (26)	0.0423 (26)	0.0191 (22)	0.0070 (21)	0.0107 (21)
C(61)	0.0331 (26)	0.0515 (33)	0.0387 (27)	0.0148 (26)	0.0022 (21)	0.0147 (24)
C(62)	0.0571 (38)	0.0567 (41)	0.1190 (60)	0.0250 (33)	-0.0279 (38)	0.0006 (38)
C(63)	0.0524 (40)	0.0651 (48)	0.1147 (61)	0.0181 (38)	-0.0287 (38)	-0.0047 (42)
C(64)	0.0379 (32)	0.0860 (48)	0.0529 (35)	0.0214 (34)	-0.0014 (26)	0.0108 (32)
C(65)	0.0454 (35)	0.0898 (52)	0.0719 (39)	0.0377 (38)	0.0084 (30)	0.0176 (37)
C(66)	0.0443 (31)	0.0575 (39)	0.0678 (38)	0.0236 (30)	0.0111 (27)	0.0149 (31)
C(7)	0.0364 (26)	0.0425 (28)	0.0352 (25)	0.0120 (23)	0.0092 (20)	0.0167 (21)
C(71)	0.0309 (23)	0.0408 (28)	0.0420 (26)	0.0142 (22)	0.0082 (20)	0.0176 (21)
C(72)	0.0490 (31)	0.0456 (32)	0.0408 (28)	0.0153 (26)	0.0125 (23)	0.0172 (24)
C(73)	0.0672 (38)	0.0710 (42)	0.0414 (31)	0.0376 (34)	0.0194 (28)	0.0261 (30)
C(74)	0.0551 (32)	0.0570 (35)	0.0622 (37)	0.0277 (29)	0.0244 (28)	0.0380 (30)
C(75)	0.0577 (36)	0.0412 (34)	0.0682 (38)	0.0132 (30)	0.0122 (29)	0.0224 (30)
C(76)	0.0503 (32)	0.0467 (32)	0.0458 (31)	0.0140 (27)	0.0083 (25)	0.0122 (25)
C(8)	0.0354 (25)	0.0428 (28)	0.0330 (25)	0.0131 (23)	0.0087 (20)	0.0117 (21)
C(81)	0.0301 (24)	0.0439 (29)	0.0434 (27)	0.0118 (23)	0.0068 (21)	0.0178 (23)
C(82)	0.0411 (29)	0.0582 (37)	0.0490 (33)	0.0178 (27)	0.0082 (25)	0.0116 (27)
C(83)	0.0437 (33)	0.0761 (44)	0.0803 (47)	0.0287 (32)	0.0258 (33)	0.0243 (37)
C(84)	0.0386 (32)	0.0786 (45)	0.0888 (46)	0.0262 (32)	0.0154 (32)	0.0380 (38)
C(85)	0.0419 (31)	0.0672 (40)	0.0599 (37)	0.0178 (30)	0.0021 (28)	0.0254 (32)
C(86)	0.0420 (28)	0.0626 (36)	0.0416 (29)	0.0193 (27)	0.0071 (23)	0.0193 (26)
C(1)	0.0359 (26)	0.0412 (27)	0.0324 (23)	0.0157 (23)	0.0130 (20)	0.0145 (20)
C(2)	0.0522 (32)	0.0452 (32)	0.0341 (26)	0.0162 (27)	0.0199 (24)	0.0121 (24)
O(1)	0.0464 (22)	0.0560 (24)	0.0484 (21)	0.0093 (19)	0.0040 (18)	0.0018 (18)
O(2)	0.0767 (29)	0.0408 (23)	0.0712 (27)	0.0214 (22)	0.0098 (22)	0.0127 (20)
C(3)	0.1156 (58)	0.0330 (31)	0.0820 (49)	0.0250 (35)	0.0358 (44)	0.0096 (32)
C(4)	0.0927 (53)	0.0518 (41)	0.0892 (51)	0.0119 (38)	0.0289 (42)	0.0122 (37)
C(9)	0.0696 (38)	0.0760 (41)	0.0873 (43)	0.0120 (33)	0.0236 (33)	0.0212 (34)
Cl(1)	0.0868 (14)	0.1398 (19)	0.1431 (19)	0.0394 (13)	-0.0008 (12)	0.0489 (15)
Cl(2)	0.0979 (12)	0.1072 (13)	0.0811 (11)	0.0377 (10)	0.0405 (9)	0.0258 (10)
Cl(3)	0.1829 (23)	0.1516 (20)	0.1135 (16)	0.0927 (18)	0.0873 (16)	0.0489 (14)

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

Results and Discussion

The geometry of the complex and the numbering system used in Tables I–VI for the atoms in the asymmetric unit is displayed in Figure 1. This is a computerdrawn¹⁴ model in perspective as it exists in the crystal. Individual bond lengths and bond angles are listed in Table III; bond parameters for the peripheral phenyl groups and the chloroform solvate are given in Table IV.

In this compound, an ethoxycarbonylcarbene moiety appears as inserted into a Ni–N bond of the nickel(II) *meso*-tetraphenylporphine. Thus, the nickel atom is tetracoordinated with the extra carbon atom C(1) and with the nitro-

gen atoms N(1), N(2), and N(3) of only three pyrrole bases. The nitrogen N(4) is not bonded to the nickel as shows the large distance Ni . . . N(4) of 2.610 (3) Å. The three Ni–N bond lengths are not significantly different and their average value is 1.916 ± 0.010 Å. The Ni–C bond length of 1.905 (4) Å is close to the predicted single bond length of 1.92 Å, based on the accepted covalent radii¹⁵ of nickel (1.15 Å) and an sp³ carbon atom (0.77 Å). Furthermore this Ni–C distance is in good agreement with that of 1.94 (1) Å found for a simple alkyl derivative in a square-planar nickel complex.¹⁶

It is generally found that metalloporphyrins are essentially planar. Especially, in nickel(II) porphyrin complexes, the

Table III. Bond Lengths and Bond Angles in the Coordination Group and in the Porphinato Skeleton

Bond Lengths, Å			
Ni-N(1)	1.911 (3)	N(3)-C(31)	1.382 (5)
Ni-N(2)	1.910 (3)	C(31)-C(32)	1.435 (6)
Ni-N(3)	1.928 (3)	C(32)-C(33)	1.336 (6)
Ni-C(1)	1.905 (4)	C(33)-C(34)	1.444 (5)
		C(34)-N(3)	1.402 (5)
N(1)-C(11)	1.397 (5)		
C(11)-C(12)	1.435 (5)	N(4)-C(41)	1.369 (5)
C(12)-C(13)	1.336 (6)	C(41)-C(42)	1.430 (8)
C(13)-C(14)	1.435 (5)	C(42)-C(43)	1.367 (6)
C(14)-N(1)	1.388 (5)	C(43)-C(44)	1.422 (7)
		C(44)-N(4)	1.386 (6)
N(2)-C(21)	1.376 (5)		
C(21)-C(22)	1.429 (6)	C(1)-N(4)	1.409 (7)
C(22)-C(23)	1.339 (6)	C(1)-C(2)	1.494 (6)
C(23)-C(24)	1.442 (6)	C(2)-O(1)	1.207 (6)
C(24)-N(2)	1.360 (5)	C(2)-O(2)	1.327 (8)
		O(2)-C(3)	1.457 (6)
		C(3)-C(4)	1.458 (11)
Bond Angles, deg			
N(1)-Ni-N(2)	94.2 (1)	Ni-N(2)-C(21)	124.6 (2)
N(2)-Ni-N(3)	93.8 (1)	Ni-N(2)-C(24)	126.7 (2)
N(3)-Ni-C(1)	87.9 (1)	N(2)-C(21)-C(22)	109.3 (3)
C(1)-Ni-N(1)	87.8 (1)	C(21)-C(22)-C(23)	107.6 (4)
N(1)-Ni-N(3)	167.1 (1)	C(22)-C(23)-C(24)	106.8 (4)
N(2)-Ni-C(1)	160.4 (2)	C(23)-C(24)-N(2)	109.6 (3)
Ni-N(1)-C(11)	131.8 (2)	C(24)-N(2)-C(21)	106.4 (3)
Ni-N(1)-C(14)	122.9 (2)	N(2)-C(21)-C(5)	124.6 (4)
N(1)-C(11)-C(12)	109.1 (3)	C(5)-C(21)-C(22)	125.8 (4)
C(11)-C(12)-C(13)	108.2 (4)	N(2)-C(24)-C(6)	124.5 (4)
C(12)-C(13)-C(14)	107.2 (4)	C(6)-C(24)-C(23)	125.5 (4)
C(13)-C(14)-N(1)	110.0 (3)		
C(14)-N(1)-C(11)	105.0 (3)	Ni-N(3)-C(31)	123.7 (2)
N(1)-C(11)-C(8)	128.6 (4)	Ni-N(3)-C(34)	130.8 (2)
C(8)-C(11)-C(12)	121.9 (4)	N(3)-C(31)-C(32)	110.0 (3)
N(1)-C(14)-C(5)	125.0 (4)	C(31)-C(32)-C(33)	107.9 (4)
C(5)-C(14)-C(13)	124.3 (4)	C(32)-C(33)-C(34)	107.5 (4)
Ni-C(1)-N(4)	102.9 (2)	C(33)-C(34)-N(3)	109.2 (3)
Ni-C(1)-C(2)	117.8 (3)	C(34)-N(3)-C(31)	105.1 (3)
N(4)-C(1)-C(2)	116.6 (4)	N(3)-C(31)-C(6)	126.3 (4)
C(1)-N(4)-C(41)	122.5 (4)	C(6)-C(31)-C(32)	123.5 (4)
C(1)-N(4)-C(44)	127.6 (4)	N(3)-C(34)-C(7)	129.6 (4)
N(4)-C(41)-C(42)	107.1 (3)	C(7)-C(34)-C(33)	120.5 (4)
C(41)-C(42)-C(43)	107.5 (4)		
C(42)-C(43)-C(44)	108.7 (4)	C(1)-C(2)-O(1)	127.0 (5)
C(43)-C(44)-N(4)	106.3 (3)	C(1)-C(2)-O(2)	108.9 (4)
C(44)-N(4)-C(41)	109.8 (3)	O(1)-C(2)-O(2)	124.0 (5)
N(4)-C(41)-C(7)	123.8 (4)	C(2)-O(2)-C(3)	118.8 (5)
C(7)-C(41)-C(42)	127.9 (4)	O(2)-C(3)-C(4)	110.8 (6)
N(4)-C(44)-C(8)	125.0 (4)		
C(8)-C(44)-C(43)	128.0 (4)		

central nickel is tetracoordinated with the nitrogen atoms in a square-planar configuration.¹⁷⁻¹⁹ In the present complex, the four nitrogens are approximately coplanar. The deviations from the four nitrogen mean plane are +0.04 Å for N(1) and N(3), and -0.04 Å for N(2) and N(4). The nickel atom, however, lies out of this plane by 0.19 Å. The extra carbon C(1) is considerably removed from the (4N) plane; its displacement of 1.04 Å is in the same direction as that of the nickel atom but opposite that of nitrogen N(4).

The insertion of C(1) into the Ni-N(4) bond has profound consequences on the overall geometry of the macrocycle. Whereas in normal porphinato complexes the pyrrole rings are nearly coplanar with the (4N) plane, the porphyrin macrocycle is largely distorted in the present complex. Figure 2 indicates the porphine skeleton departures from a planar configuration. Although the individual pyrrole rings are quite planar, the angles between the (4N) plane and the pyrroles N(1) to N(4) are 13.3, 5.9, 3.6, and 46.4°. Of particular interest is the very large angle of 46.4°. Obviously, in the absence of unusually short intermolecular contacts

Table IV. Bond Lengths and Angles in the Phenyl Groups and the Chloroform Solvate

Bond lengths, Å		Bond angles, deg	
C(5)-C(14)	1.397 (6)	C(14)-C(5)-C(21)	124.1 (4)
C(5)-C(21)	1.391 (5)	C(14)-C(5)-C(51)	117.7 (4)
C(5)-C(51)	1.493 (8)	C(21)-C(5)-C(51)	118.1 (4)
C(51)-C(52)	1.380 (10)	C(5)-C(51)-C(52)	120.0 (5)
C(52)-C(53)	1.410 (11)	C(5)-C(51)-C(56)	120.9 (5)
C(53)-C(54)	1.361 (13)	C(51)-C(52)-C(53)	118.9 (6)
C(54)-C(55)	1.330 (17)	C(52)-C(53)-C(54)	120.6 (7)
C(55)-C(56)	1.397 (12)	C(53)-C(54)-C(55)	120.4 (8)
C(56)-C(51)	1.377 (9)	C(54)-C(55)-C(56)	120.5 (8)
		C(55)-C(56)-C(51)	120.4 (6)
		C(56)-C(51)-C(52)	119.0 (6)
C(6)-C(24)	1.403 (6)		
C(6)-C(31)	1.391 (6)	C(24)-C(6)-C(31)	123.3 (4)
C(6)-C(61)	1.504 (6)	C(24)-C(6)-C(61)	117.9 (4)
C(61)-C(62)	1.387 (8)	C(31)-C(6)-C(61)	118.6 (4)
C(62)-C(63)	1.394 (9)	C(6)-C(61)-C(62)	120.4 (5)
C(63)-C(64)	1.327 (13)	C(6)-C(61)-C(66)	121.4 (5)
C(64)-C(65)	1.357 (9)	C(61)-C(62)-C(63)	119.3 (6)
C(65)-C(66)	1.384 (8)	C(62)-C(63)-C(64)	121.6 (7)
C(66)-C(61)	1.352 (10)	C(63)-C(64)-C(65)	119.1 (7)
		C(64)-C(65)-C(66)	120.5 (6)
C(7)-C(34)	1.407 (6)	C(65)-C(66)-C(61)	121.1 (6)
C(7)-C(41)	1.396 (6)	C(66)-C(61)-C(62)	118.0 (6)
C(7)-C(71)	1.500 (7)		
C(71)-C(72)	1.382 (6)	C(34)-C(7)-C(41)	126.7 (4)
C(72)-C(73)	1.382 (8)	C(34)-C(7)-C(71)	118.3 (4)
C(73)-C(74)	1.364 (8)	C(41)-C(7)-C(71)	114.5 (4)
C(74)-C(75)	1.377 (8)	C(7)-C(71)-C(72)	119.9 (4)
C(75)-C(76)	1.389 (9)	C(7)-C(71)-C(76)	121.1 (4)
C(76)-C(71)	1.383 (7)	C(71)-C(72)-C(73)	120.2 (5)
		C(72)-C(73)-C(74)	120.8 (5)
C(8)-C(11)	1.402 (7)	C(73)-C(74)-C(75)	119.5 (6)
C(8)-C(44)	1.398 (6)	C(74)-C(75)-C(76)	120.1 (5)
C(8)-C(81)	1.490 (7)	C(75)-C(76)-C(71)	120.3 (5)
C(81)-C(82)	1.392 (8)	C(76)-C(71)-C(72)	118.8 (5)
C(82)-C(83)	1.378 (9)		
C(83)-C(84)	1.377 (8)	C(11)-C(8)-C(44)	126.5 (4)
C(84)-C(85)	1.367 (10)	C(11)-C(8)-C(81)	118.3 (4)
C(85)-C(86)	1.391 (9)	C(44)-C(8)-C(81)	115.0 (4)
C(86)-C(81)	1.389 (6)	C(8)-C(81)-C(82)	120.7 (4)
		C(8)-C(81)-C(86)	120.3 (4)
C(9)-Cl(1)	1.739 (7)	C(81)-C(82)-C(83)	120.4 (5)
C(9)-Cl(2)	1.735 (7)	C(82)-C(83)-C(84)	120.2 (6)
C(9)-Cl(3)	1.732 (8)	C(83)-C(84)-C(85)	120.1 (6)
		C(84)-C(85)-C(86)	120.2 (6)
		C(85)-C(86)-C(81)	120.1 (5)
		C(86)-C(81)-C(82)	118.8 (5)
		Cl(1)-C(9)-Cl(2)	109.2 (2)
		Cl(2)-C(9)-Cl(3)	110.9 (2)
		Cl(3)-C(9)-Cl(1)	110.0 (3)

(Table VI), the observed distortion is mainly introduced by the carbene moiety inserted into the original Ni-N(4) bond of tetraphenylporphinato nickel. Thereby the distortion is such that if one considers the four nitrogen plane, the pyrrole ring N(4) is inclined toward the metal atom while the pyrrole rings N(1), N(2), and N(3) remain almost in the (4N) plane. Mean planes were determined by the method of least-squares.²⁰ The distances of the respective atoms from these planes are summarized in Table V; also given are equations of the planes and the angles between them.

Accordingly, these distortions of the macrocycle lead to unusual distances between opposite pyrrole nitrogen atoms. The normal diameter of the "hole" in an undistorted metalloporphyrin complex has been estimated to 4.02 Å.²¹ The N(2) . . . N(4) distance of 4.495 (4) Å is unusually long; it is caused by the large deviation of the N(4) pyrrole from the four nitrogen mean plane. Also affected by the distortion is the N(1) . . . N(3) distance of 3.814 (4) Å. The geometry around the extra saturated carbon C(1) is also somewhat affected; especially the Ni-C(1)-N(4) bond

Table V. Least-Square Planes in the Form $AX + BY + CZ - D = 0^a$

Planes and Deviations (Å)			
Plane (4N): N(1), N(2), N(3), N(4)		Plane (N3): N(3), C(31)–C(34)	
N(1)	0.040 (3)	N(3)	0.016 (3)
N(2)	-0.046 (3)	C(31)	-0.022 (4)
N(3)	0.042 (3)	C(32)	0.012 (5)
N(4)	-0.038 (3)	C(33)	0.007 (5)
Ni	0.1914 (5) ^b	C(34)	-0.019 (4)
C(1)	1.046 (5) ^b		
Plane (N1): N(1), C(11)–C(14)		Plane (N4): N(4), C(41)–C(44)	
N1	0.018 (3)	N4	0.027 (3)
C(11)	-0.020 (4)	C(41)	-0.037 (4)
C(12)	0.004 (4)	C(42)	0.019 (4)
C(13)	0.016 (4)	C(43)	0.013 (4)
C(14)	-0.028 (4)	C(44)	-0.034 (4)
		Cl	0.130 (4) ^b
Plane (N2): N(2), C(21)–C(24)			
N(2)	-0.014 (3)		
C(21)	0.013 (4)		
C(22)	0.001 (5)		
C(23)	-0.017 (5)		
C(24)	0.023 (4)		

Plane	Equations			
	A	B	C	D
(4N)	0.517	-0.753	-0.405	-3.785
(N1)	0.445	-0.659	-0.605	-3.476
(N2)	0.548	-0.686	-0.476	-3.794
(N3)	0.464	-0.771	-0.434	-3.833
(N4)	-0.001	-0.430	-0.902	-0.248

Angles (deg) between the Planes			
(4N)–(N1)	13.3	(N1)–(N2)	9.5
(4N)–(N2)	5.9	(N2)–(N3)	7.2
(4N)–(N3)	3.6	(N3)–(N4)	43.6
(4N)–(N4)	46.4	(N4)–(N1)	33.9
		(N1)–(N3)	11.7
		(N2)–(N4)	43.5

^a X, Y, Z refer to the axial system $a, c^* || a, c^*$. ^b Atoms not included in the calculation.

angle is largely reduced to 102.9 (2)°. Interestingly, a similar constriction (99.9°) has been found for the Ni(II)-homoporphyrin complex⁷ where the ethoxycarbonylcarbene fragment is inserted between two pyrroles of the macrocycle.

Table VI. Interatomic Distances (Å)

Selected Intramolecular Contacts					
Ni...N(4)		2.610 (3)	N(1)...N(2)		2.799 (4)
Ni...C(5)		3.285 (5)	N(2)...N(3)		2.802 (4)
Ni...C(6)		3.324 (4)	N(3)...N(4)		3.108 (4)
Ni...C(7)		3.604 (5)	N(4)...N(1)		3.097 (4)
Ni...C(8)		3.576 (5)	N(1)...N(3)		3.814 (4)
C(1)...N(1)		2.647 (6)	N(2)...N(4)		4.495 (4)
C(1)...N(3)		2.661 (4)			
Intermolecular Distances less than 3.6 Å ^a					
N(1)...C(76)	2/010	3.584 (7)	C54...O(1)	1/001	3.592 (10)
C(14)...C(75)	2/010	3.593 (8)	C(73)...C(73)	2/011	3.566 (8)
N(2)...C(3)	2/000	3.581 (9)	O(1)...C(9)	2/100	3.174 (6)
C(21)...C(3)	2/000	3.540 (10)	O(1)...C(55)	2/001	3.360 (8)
C(53)...C(53)	2/001	3.584 (10)	O(1)...C(2)	2/100	3.458 (3)
Contacts around the Chloroform Solvate less than 3.8 Å ^a					
C(9)...O(1)	2/100	3.174 (6)	Cl(2)...C(82)	1/000	3.700 (6)
Cl(1)...C(55)	1/000	3.476 (10)	Cl(3)...C(66)	1/100	3.718 (7)
Cl(1)...C(56)	1/000	3.545 (8)	Cl(3)...C(65)	1/100	3.726 (8)
Cl(1)...Cl(1)	2/101	3.780 (3)	Cl(3)...C(63)	2/011	3.764 (9)
Cl(2)...O(1)	2/100	3.458 (3)			
Cl(2)...C(12)	1/000	3.607 (5)			

^a Second atoms not in the crystal chemical unit (i.e., not listed in Table I) are specified by the subscript l/uvw which denotes the manner in which the atomic parameters can be derived from the corresponding atom in the crystal unit. l refers to one of the following symmetry operations: (1) xyz ; (2) $\bar{x}\bar{y}\bar{z}$. The u, v, w digits code a lattice translation as $ua + vb + wc$.

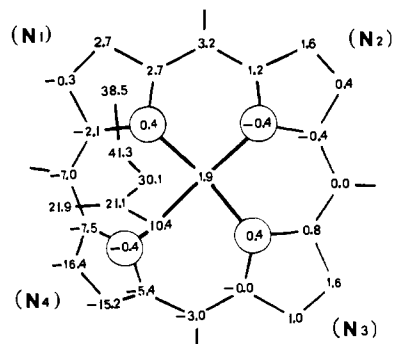


Figure 2. Formal diagram showing the departure of each atom from the (4N) mean plane. The numerical value (0.1 Å) of each such deviation replaces the atomic symbol in Figure 1. Phenyl groups are omitted.

The observed distortions of the porphyrinato core seem to have little or no effect on π -electron delocalization and on bond parameters. Using C_a and C_b to denote the respective α - and β -carbon atoms of a pyrrole ring and C_m for methine carbon, the averaged values for bond lengths in the porphyrin skeleton are $N-C_a = 1.382$ (6), $C_a-C_b = 1.434$ (8), $C_b-C_b = 1.344$ (6), and $C_a-C_m = 1.398$ (7) Å, wherein the number in parentheses is the greatest value of the estimated standard deviation for an individually determined length. All these distances are quite similar to those found in normal metalloporphyrin complexes.^{21,22} On the other hand, the phenyl groups are electronically isolated from the inner macrocycle: they are rotated with respect to the plane of the three neighboring carbons of the bridge positions between pyrroles; the rotational angles are 86.7, 74.7, 70.6, and 56.8° for the four phenyls Ph(5) to Ph(8), respectively.

Figure 3 shows as a stereoscopic view the contents of the unit cell. Table VI lists all intermolecular distances below 3.6 Å and all contacts around the chloroform molecule. The shortest packing separation, 3.17 Å, occurs between the C(9) chloroform carbon and the O(1) carbonyl oxygen of the ester group. Finally, chloroform is only present in the crystal as an uncomplexed solvent of crystallization and

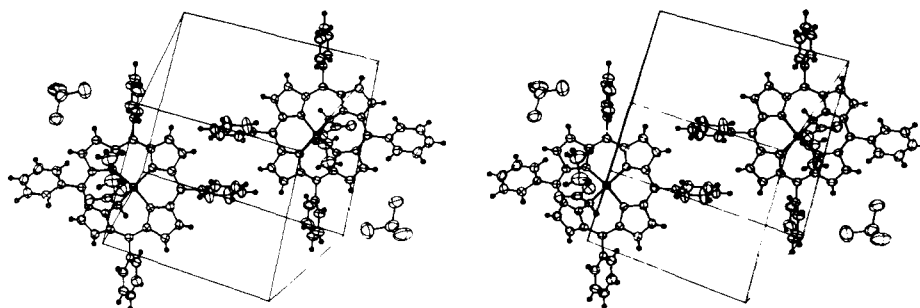


Figure 3. Molecular content of the unit cell (stereoscopic view). The thermal ellipsoids are drawn for 50% probability, except for those of the hydrogen atoms which are not drawn to scale.

contributes to increase cohesion between successive porphyrin complexed molecules.

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Supplementary Material Available. A listing of structure factor amplitudes (11 pp). Ordering information is given on any current masthead page.

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Conformational Energy Analysis of the Molecule, Luteinizing Hormone-Releasing Hormone. 1. Native Decapeptide

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Abstract: Low-energy conformations of luteinizing hormone-releasing hormone (<Glu-His-Trp-Ser-Tyr-Gly-Leu-Arg-Pro-Gly-NH₂) have been obtained using "empirical" energy calculations. The conformational space of the sections <Glu¹ to Gly⁶ and Gly⁶ to Gly¹⁰-NH₂ was searched as separate entities, and the minimum energy conformations of these two sections were then used as starting conformations for refinement of the complete molecule. The minimum energy structure is consistent with experimental assay data derived from a series of amino acid substitution analogues.

Since the characterization of the luteinizing hormone-releasing hormone (LH-RH) molecule, <Glu-His-Trp-Ser-Tyr-Gly-Leu-Arg-Pro-Gly-NH₂, as the factor responsible for stimulating the secretion of the pituitary hormone(s) which regulate ovulation,¹⁻³ many synthetic analogues have been assayed in an attempt to elucidate the structure-activity relationships and to search for inhibitors of LH-RH.⁴⁻⁹ A structure for LH-RH has been proposed,¹⁰ based on model building and using experimental analogue data. Two carbon-13 NMR studies^{11,12} have given some insight into selected aspects of the conformation of LH-RH, and a proton NMR study has added some understanding to the conformation.¹³ However, to date, the conformation(s) remain unknown for LH-RH, either in solution or in the solid state. In order to gain some further understanding of the stereochemistry of LH-RH, empirical energy calculations¹⁴⁻¹⁶

were carried out to search for the most stable conformation(s) of LH-RH.

LH-RH is not a small polypeptide from the standpoint of conformational studies (see Figure 1), and it is not feasible to attempt to examine *all* of its conformational space by generating all conformations and comparing their intramolecular energies. However, by using the observation that D-Ala substituted in place of glycine at the 6 position^{6,17} causes a conformational stabilization which greatly enhances the production of luteinizing hormone, while L-Ala at the 6 position reduces the LH-RH potency to ~4% of the natural LH-RH, it is possible to reduce the conformational space of Gly⁶ to a region defined by two possible sets of backbone dihedral angles around the Gly⁶ residue. Further, a carbon-13 NMR study¹¹ indicated that the proline peptide bond was completely trans in LH-RH. Using these two