valence will be associated with the three-coordinate Te atoms and a smaller share with the two-coordinate atoms and we have arbitrarily assigned total valences of 3.0 and 2.25, respectively, to these atoms. If each atom contributes equally 0.2 valence unit (vu) to the interionic bonding, 2.80 and 2.05 vu, respectively, are left for the intraionic bonding. As can be seen from Table III, this leads to the intraionic bonds having valences of either 0.93 or 1.12 vu, and the alternation of bond strengths is seen to be a direct consequence of the three-coordination around Te(1).

The bond lengths (R) can be calculated from the bond valences (S) using the expression[16]

$$S = (R/R_0)^{-N}$$

where R_0 and N are fitted parameters for each pair of bonds. The parameters for Se–Se (R_0 = 2.38 Å, N = 5) and Te–Se (R_0 = 2.57 Å, N = 5) were chosen to fit the observed bond lengths; the values for Te–Te (R_0 = 2.76 Å, N = 5) were chosen so that any Te–Se bond had a length midway between the Se–Se and Te–Te bonds of the same strength. As a further check these parameters also predict that all the bonds in the isostructural series Se_4^{2+} (2.28 Å), $Se_2Te_2^{2+}$ (2.476 Å), and Te_4^{2+} (2.664 Å) have the expected strength of 1.25 vu.[18] The predicted bond valences and bond lengths for the three ions with x = 2, 3, and 4 are compared with the observed lengths in Table III.

Registry No. $Te_2Se_8(AsF_6)_2\cdot SO_2$, 58249-22-2; $Te_{3.7}Se_{6.3}(AsF_6)_2$, 58249-23-3; Se–Te, 12067-42-4; $Se_8(AsF_6)_2$, 52374-78-4; Te, 13494-80-9; AsF_5, 7784-36-3.

Supplementary Material Available: Listings of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. J. Gillespie and J. Passmore, *Acc. Chem. Res.*, **4**, 413 (1971).
(2) C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, **10**, 2781 (1971).
(3) R. K. McMullan, D. J. Prince, and J. D. Corbett, *Inorg. Chem.*, **10**, 1749 (1971).
(4) R. J. Gillespie, J. Passmore, P. K. Ummat, and O. C. Vaidya, *Inorg. Chem.*, **10**, 1327 (1971).
(5) I. D. Brown, D. B. Crump, and R. J. Gillespie, *Inorg. Chem.*, **10**, 2319 (1971).
(6) T. W. Crouch, D. A. Lokken, and J. D. Corbett, *Inorg. Chem.*, **11**, 347 (1972).
(7) R. J. Gillespie and P. K. Ummat, *Can. J. Chem.*, **48**, 1239 (1970).
(8) P. A. W. Dean, R. J. Gillespie, and P. K. Ummat, *Inorg. Synth.*, **15**, 213 (1974).
(9) "International Tables for X-ray Crystallography", Vol. I, Kynoch Press, Birmingham, U.K., 1965.
(10) J. M. Stewart, F. A. Kundell, and J. C. Baldwin, "X-Ray 71 System of Crystallographic Programs", Technical Report, University of Maryland, 1971.
(11) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, U. K., 1975.
(12) In *Pbcn* it is not possible to distinguish between II and III, and while in *Pbc*2$_1$ and *P*2$_1$*cn* it is possible in principle to distinguish between them, in this event the difference proved undetectable.
(13) Supplementary material.
(14) G. Nickless, "Inorganic Sulphur Chemistry", Elsevier, Amsterdam, 1968.
(15) See references given by A. F. Wells, "Structural Inorganic Chemistry", 3d ed, Clarendon Press, Oxford, 1962, p 413.
(16) B. Post, R. S. Schwatz, and I. Faukuchen, *Acta Crystallogr.*, **5**, 372 (1952).
(17) I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A*, **29**, 266 (1973), and references therein.
(18) W. H. Baur, *Am. Mineral.*, **57**, 709 (1972).
(19) P. Boldrini, I. D. Brown, R. J. Gillespie, and E. M. Maharajh, submitted for publication in *Inorg. Chem.*

Contribution from the Institut de Chimie,
Laboratoire de Cristallochimie associé au CNRS, Université Louis Pasteur, BP 296/R8, Strasbourg, France

A Highly Distorted Homoporphyrin Complex. Crystal and Molecular Structure of (10*H*-10-Hydroxyl-21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21-homoporphinato)nickel(II)

BERNARD CHEVRIER and RAYMOND WEISS*

Received July 15, 1975 AIC504988

The (10*H*-10-hydroxyl-21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21-homoporphinato)nickel(II) crystallizes in the space group $P2_1/c$; the unit cell has the dimensions a = 11.895 (5) Å, b = 29.229 (8) Å, c = 12.963 (5) Å, and β = 121.81 (6)° and contains four molecules. Intensity data were collected by θ–2θ scanning with Mo Kα radiation, and 4461 data were retained as observed and used for the solution and refinement of structure. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to conventional and weighted R values of 0.065 and 0.082, respectively. The nickel atom exhibits square-planar coordination; the four Ni–N bond lengths are equal to 1.879 ± 0.010 Å. The homoporphyrin skeleton is far from planar and highly distorted. The individual pyrrole groups within the macrocycle are markedly noncoplanar; each makes an angle of 39–45° with the four-nitrogen plane. There are also very large angles (88.0 and 81.5°) between the opposite pyrrole planes. The overall effect of the distortions of the skeleton is to generate a saddle-shaped surface.

Introduction

Homoporphyrins are synthetic porphyrin derivatives by insertion of an *extra* carbon atom between two pyrroles of the macrocycle. The first recently described metal complex with such an expanded macrocyclic ligand is the (21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21*H*-21-homoporphinato)nickel(II).[1] A severe distortion of the homoporphinato core was observed limiting the π delocalization within the macrocycle. According to spectroscopic studies (visible spectra, NMR),[2] the (10*H*-10-hydroxyl-21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21-homoporphinato)nickel(II) appeared to be much more distorted than the former complex. For this reason, we have undertaken its structure determination.

Experimental Section

A sample of the title compound was kindly supplied by Dr. H. J. Callot. Crystals suitable for x-ray study were grown by slow evaporation of nitromethane–dichloromethane solutions. Preliminary precession photographs indicated the crystal symmetry to be monoclinic and the systematic absences were consistent with the unique space group $P2_1/c$. Precise lattice constants were obtained by least-squares

Table I. Coordinates and Thermal Parameters of the Atoms in the Crystal[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.03720 (5)	0.17074 (1)	0.08531 (5)	0.0224 (2)	0.0317 (4)	0.0252 (3)	0.0009 (2)	0.0099 (2)	−0.0023 (3)
N1	0.2064 (3)	0.1911 (1)	0.1262 (3)	0.030 (2)	0.044 (2)	0.033 (2)	0.001 (1)	0.017 (1)	−0.001 (1)
C11	0.3058 (5)	0.1713 (2)	0.1224 (5)	0.033 (2)	0.047 (3)	0.029 (2)	−0.002 (3)	0.014 (2)	−0.005 (3)
C12	0.4008 (6)	0.2048 (2)	0.1374 (6)	0.037 (3)	0.067 (5)	0.053 (4)	−0.014 (3)	0.028 (3)	−0.017 (3)
C13	0.3555 (6)	0.2457 (2)	0.1482 (5)	0.048 (3)	0.064 (5)	0.041 (3)	−0.021 (3)	0.027 (3)	−0.015 (3)
C14	0.2377 (5)	0.2374 (2)	0.1472 (5)	0.034 (3)	0.049 (4)	0.025 (3)	−0.008 (2)	0.012 (2)	−0.007 (2)
N2	0.0103 (3)	0.1366 (1)	−0.0485 (3)	0.027 (1)	0.029 (2)	0.031 (2)	0.001 (1)	0.011 (1)	0.002 (1)
C21	−0.1045 (5)	0.1399 (2)	−0.1623 (5)	0.032 (3)	0.031 (3)	0.027 (3)	−0.005 (2)	0.011 (2)	−0.003 (2)
C22	−0.0884 (6)	0.1131 (2)	−0.2446 (5)	0.045 (3)	0.049 (4)	0.035 (3)	−0.005 (3)	0.017 (3)	−0.009 (3)
C23	0.0303 (6)	0.0919 (2)	−0.1806 (6)	0.044 (3)	0.048 (4)	0.052 (3)	0.002 (3)	0.025 (3)	−0.017 (3)
C24	0.0915 (5)	0.1073 (2)	−0.0581 (3)	0.033 (3)	0.028 (3)	0.044 (3)	−0.001 (2)	0.022 (2)	−0.004 (2)
N3	−0.1410 (3)	0.1609 (1)	0.0333 (3)	0.029 (2)	0.031 (2)	0.030 (2)	0.002 (1)	0.012 (1)	0.001 (1)
C31	−0.1945 (5)	0.1650 (2)	0.1007 (5)	0.033 (2)	0.037 (3)	0.036 (3)	−0.002 (2)	0.019 (2)	0.003 (2)
C32	−0.3311 (5)	0.1753 (2)	0.0265 (5)	0.031 (3)	0.054 (4)	0.045 (3)	0.004 (2)	0.020 (2)	0.004 (3)
C33	−0.3583 (5)	0.1776 (2)	−0.0892 (5)	0.028 (2)	0.051 (4)	0.043 (3)	0.010 (2)	0.013 (2)	0.001 (2)
C34	−0.2410 (5)	0.1679 (2)	−0.0868 (4)	0.027 (2)	0.034 (3)	0.031 (2)	0.002 (2)	0.012 (2)	0.002 (2)
N4	0.0505 (3)	0.2076 (1)	0.2098 (3)	0.032 (2)	0.043 (2)	0.031 (2)	−0.000 (1)	0.014 (1)	0.000 (1)
C41	0.1037 (5)	0.2515 (2)	0.2349 (5)	0.035 (3)	0.039 (3)	0.032 (3)	0.000 (2)	0.014 (2)	−0.001 (2)
C42	0.0672 (6)	0.2731 (2)	0.3112 (5)	0.046 (3)	0.044 (4)	0.036 (3)	0.002 (3)	0.017 (2)	−0.010 (3)
C43	−0.0062 (6)	0.2426 (2)	0.3321 (5)	0.045 (3)	0.052 (4)	0.039 (3)	0.005 (3)	0.023 (3)	−0.004 (3)
C44	−0.0166 (5)	0.2029 (2)	0.2657 (5)	0.034 (3)	0.042 (3)	0.032 (3)	0.006 (2)	0.013 (2)	0.001 (2)
C5	0.1839 (4)	0.2670 (1)	0.1954 (4)	0.037 (2)	0.039 (3)	0.024 (2)	0.002 (2)	0.008 (2)	−0.003 (2)
C51	0.2244 (5)	0.3161 (2)	0.2130 (5)	0.044 (3)	0.045 (3)	0.048 (3)	−0.010 (2)	0.026 (2)	−0.011 (2)
C52	0.3129 (5)	0.3325 (2)	0.3272 (6)	0.037 (3)	0.048 (4)	0.053 (4)	−0.006 (3)	0.018 (3)	−0.013 (3)
C53	0.3522 (7)	0.3786 (2)	0.3421 (8)	0.050 (4)	0.058 (5)	0.076 (6)	−0.014 (3)	0.029 (4)	−0.026 (4)
C54	0.2989 (9)	0.4067 (3)	0.2437 (9)	0.098 (6)	0.049 (6)	0.091 (7)	−0.021 (4)	0.063 (6)	−0.015 (5)
C55	0.209 (1)	0.3906 (3)	0.1310 (8)	0.168 (9)	0.061 (6)	0.058 (6)	−0.032 (5)	0.049 (6)	−0.001 (4)
C56	0.171 (1)	0.3456 (3)	0.1151 (7)	0.137 (8)	0.062 (5)	0.043 (5)	−0.023 (5)	0.034 (5)	0.001 (4)
C6	−0.1077 (4)	0.1627 (1)	0.2372 (4)	0.041 (2)	0.043 (3)	0.037 (2)	−0.004 (2)	0.023 (2)	−0.003 (2)
C61	−0.0425 (5)	0.1159 (2)	0.2749 (4)	0.048 (3)	0.053 (3)	0.029 (2)	0.000 (2)	0.013 (2)	0.008 (2)
C62	0.0846 (7)	0.1076 (2)	0.3025 (6)	0.056 (4)	0.061 (5)	0.053 (4)	0.006 (3)	0.021 (3)	0.004 (3)
C63	0.1380 (9)	0.0631 (3)	0.3266 (8)	0.073 (6)	0.071 (6)	0.071 (5)	0.014 (5)	0.027 (4)	0.002 (4)
C64	0.062 (1)	0.0279 (3)	0.322 (1)	0.079 (6)	0.065 (7)	0.109 (8)	0.007 (5)	0.015 (5)	0.009 (6)
C65	−0.062 (1)	0.0351 (4)	0.296 (1)	0.081 (7)	0.076 (9)	0.17 (1)	−0.012 (6)	0.041 (7)	0.018 (7)
C66	−0.1153 (9)	0.0791 (3)	0.272 (1)	0.067 (6)	0.074 (7)	0.124 (8)	0.000 (5)	0.044 (5)	0.026 (6)
C7	−0.2223 (4)	0.1583 (1)	−0.1826 (4)	0.028 (2)	0.027 (3)	0.027 (2)	−0.002 (1)	0.006 (1)	−0.002 (1)
C71	−0.3351 (4)	0.1644 (1)	−0.3100 (4)	0.038 (2)	0.048 (3)	0.029 (2)	0.004 (2)	0.010 (2)	−0.004 (2)
C72	−0.4523 (6)	0.1398 (2)	−0.3526 (6)	0.040 (3)	0.088 (6)	0.045 (4)	−0.011 (3)	0.008 (3)	−0.008 (4)
C73	−0.5565 (7)	0.1464 (4)	−0.4716 (8)	0.041 (4)	0.120 (9)	0.051 (4)	−0.001 (4)	−0.002 (4)	−0.015 (5)
C74	−0.5491 (8)	0.1767 (3)	−0.5449 (7)	0.066 (5)	0.114 (8)	0.035 (4)	0.019 (5)	0.000 (3)	−0.002 (4)
C75	−0.433 (1)	0.2012 (3)	−0.5034 (7)	0.102 (7)	0.089 (7)	0.042 (4)	−0.014 (5)	−0.005 (4)	0.020 (4)
C76	−0.3264 (8)	0.1940 (3)	−0.3855 (6)	0.070 (5)	0.079 (6)	0.033 (3)	−0.026 (4)	−0.003 (3)	0.014 (3)
C8	0.2241 (4)	0.0928 (1)	0.0398 (4)	0.036 (2)	0.037 (3)	0.048 (3)	0.009 (2)	0.028 (2)	0.004 (2)
C81	0.2488 (5)	0.0432 (1)	0.0410 (5)	0.042 (3)	0.041 (3)	0.060 (3)	0.005 (2)	0.033 (2)	0.005 (2)
C82	0.3454 (9)	0.0255 (2)	0.026 (1)	0.106 (6)	0.051 (5)	0.162 (9)	0.024 (4)	0.111 (7)	0.024 (5)
C83	0.369 (1)	−0.0207 (3)	0.033 (1)	0.117 (7)	0.048 (5)	0.17 (1)	0.034 (5)	0.110 (7)	0.026 (5)
C84	0.2962 (8)	−0.0509 (2)	0.0550 (9)	0.071 (5)	0.037 (5)	0.118 (7)	0.010 (4)	0.049 (5)	0.013 (4)
C85	0.1982 (9)	−0.0340 (2)	0.0671 (9)	0.075 (6)	0.046 (5)	0.116 (7)	−0.002 (4)	0.052 (5)	0.013 (4)
C86	0.1766 (7)	0.0125 (2)	0.0644 (8)	0.051 (4)	0.048 (5)	0.088 (5)	0.000 (3)	0.043 (4)	0.000 (4)
O3	−0.1843 (3)	0.1718 (1)	0.2908 (3)	0.054 (2)	0.076 (3)	0.061 (2)	−0.017 (2)	0.042 (2)	−0.016 (2)
C1	0.3187 (4)	0.1221 (2)	0.1151 (4)	0.028 (2)	0.055 (3)	0.039 (2)	0.008 (2)	0.018 (2)	0.006 (2)
C2	0.4562 (5)	0.1054 (2)	0.2034 (5)	0.032 (3)	0.085 (5)	0.051 (5)	0.016 (3)	0.015 (2)	0.004 (3)
O1	0.5511 (4)	0.1152 (2)	0.1977 (5)	0.039 (2)	0.126 (4)	0.128 (4)	0.016 (2)	0.042 (2)	0.023 (3)
O2	0.4605 (4)	0.0815 (1)	0.2907 (4)	0.052 (2)	0.109 (4)	0.069 (3)	0.025 (2)	0.020 (2)	0.034 (3)
C3	0.589 (1)	0.0634 (5)	0.383 (1)	0.086 (6)	0.19 (1)	0.129 (9)	0.069 (8)	0.006 (6)	0.085 (9)
C4	0.588 (1)	0.0224 (1)	0.394 (2)	0.19 (1)	0.17 (1)	0.37 (2)	0.07 (1)	−0.06 (1)	0.09 (1)

[a] Figures in parentheses here and in succeeding tables are estimated standard deviations. The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2\Sigma_i\Sigma_j a_i^* a_j^* h_i h_j U_{ij}]$.

refinement of the diffraction geometry based on the angular settings of 12 reflections. All measurements were made on a Picker four-circle diffractometer at 18 ± 2 °C using graphite-monochromated Mo Kα radiation (λ 0.70926 Å). The lattice constants, a = 11.895 (5) Å, b = 29.229 (8) Å, c = 12.963 (5) Å, and β = 121.81 (6)°, were thus obtained. These constants led to a calculated density of 1.341 g cm^{-3} for a cell content of four molecules ($C_{48}H_{34}N_4O_3Ni$; mol wt 773.5); an experimental density of 1.33 g cm^{-3} was determined by flotation in aqueous zinc chloride solution.

Intensity data were measured on a Picker diffractometer using the θ–2θ scanning technique. The approximate dimensions of the crystal used were 0.35 × 0.35 × 0.40 mm. All independent reflections for which $(\sin\theta)/\lambda \leq 0.81$ Å^{-1} were scanned at the rate of 1.0°/min in θ; background counts of 10-s duration were taken at the extremes of each scan. The intensities of three standard reflections were monitored every 70 reflections throughout the data collection and showed no falloff as a function of x-ray exposure by the crystal. With a linear absorption coefficient of 0.42 mm^{-1} no absorption corrections were deemed necessary. The intensity data were reduced to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factors. Standard deviations were calculated as previously described[1] using a p value of 0.05. All data having a net intensity smaller than $3\sigma(I)$ were taken to be unobserved, and then 4461 independent data from about 15000 observations were retained as objectively observed and used for determination and refinement of structure. This corresponds to a data:parameter ratio of 8.8 if hydrogen atoms are omitted.

The structure was solved by the heavy-atom technique. The coordinates of the nickel atoms were obtained by inspection of the three-dimensional Patterson synthesis. Using the calculated contributions of nickel to determine the phases, a Fourier synthesis gave positions for all nonhydrogen atoms. In all structure factor calculations the atomic scattering factors used were those tabulated by Cromer and Waber.[3] The effect of anomalous dispersion was included for

Table II. Molecular Bond Lengths and Angles

Bond Lengths, Å

Ni-N1	1.888 (4)	N4-C41	1.391 (7)	C6-O3	1.432 (9)	C8-C1	1.341 (6)
Ni-N2	1.876 (4)	C41-C42	1.422 (12)	C6-C31	1.508 (7)	C8-C24	1.472 (6)
Ni-N3	1.877 (4)	C42-C43	1.373 (11)	C6-C44	1.508 (8)	C8-C81	1.476 (7)
Ni-N4	1.877 (4)	C43-C44	1.409 (10)	C6-C61	1.520 (7)	C81-C82	1.367 (15)
N1-C11	1.340 (8)	C44-N4	1.337 (10)	C61-C62	1.379 (11)	C82-C83	1.372 (12)
C11-C12	1.430 (10)	C5-C41	1.375 (10)	C62-C63	1.409 (12)	C83-C84	1.370 (17)
C12-C13	1.347 (12)	C5-C14	1.403 (10)	C63-C64	1.348 (16)	C84-C85	1.350 (17)
C13-C14	1.415 (11)	C5-C51	1.492 (7)	C64-C65	1.347 (19)	C85-C86	1.378 (12)
C14-N1	1.392 (7)	C51-C52	1.375 (8)	C65-C66	1.394 (16)	C86-C81	1.383 (12)
N2-C21	1.388 (5)	C52-C53	1.405 (11)	C66-C61	1.370 (13)	C1-C8	1.341 (6)
C21-C22	1.414 (11)	C53-C54	1.361 (13)	C7-C21	1.391 (8)	C1-C11	1.454 (9)
C22-C23	1.354 (9)	C54-C55	1.363 (12)	C7-C34	1.401 (9)	C1-C2	1.500 (7)
C23-C24	1.427 (9)	C55-C56	1.367 (14)	C7-C71	1.491 (5)	C2-O1	1.203 (10)
C24-N2	1.347 (8)	C56-C51	1.382 (10)	C71-C72	1.397 (9)	C2-O2	1.309 (10)
N3-C31	1.331 (9)			C72-C73	1.392 (9)	O2-C3	1.456 (10)
C31-C32	1.416 (7)			C73-C74	1.335 (16)	C3-C4	1.208 (24)
C32-C33	1.358 (10)			C74-C75	1.387 (15)		
C33-C34	1.408 (10)			C75-C76	1.395 (9)		
C34-N3	1.388 (5)			C76-C71	1.350 (11)		

Bond Angles, Deg

N1-Ni-N2	93.6 (1)	Ni-N3-C31	126.2 (3)	C14-C5-C41	122.1 (6)	C21-C7-C34	121.6 (5)
N2-Ni-N3	88.6 (1)	Ni-N3-C34	121.2 (3)	C14-C5-C51	118.2 (5)	C21-C7-C71	118.9 (5)
N3-Ni-N4	87.9 (1)	N3-C31-C32	110.2 (3)	C41-C5-C51	119.4 (5)	C34-C7-C71	119.1 (5)
N4-Ni-N1	89.0 (1)	C31-C32-C33	106.3 (6)	C5-C51-C52	120.2 (5)	C7-C71-C72	120.2 (5)
N1-Ni-N3	169.8 (2)	C32-C33-C34	107.9 (6)	C5-C51-C56	120.4 (7)	C7-C71-C76	120.7 (6)
N2-Ni-N4	175.0 (2)	C33-C34-N3	107.9 (5)	C51-C52-C53	119.6 (7)	C71-C72-C73	119.0 (7)
Ni-N1-C11	133.1 (3)	C34-N3-C31	107.4 (5)	C52-C53-C54	119.5 (8)	C72-C73-C74	121.8 (9)
Ni-N1-C14	119.8 (3)	N3-C31-C6	119.8 (5)	C53-C54-C55	120.6 (1.0)	C73-C74-C75	119.4 (9)
N1-C11-C12	110.3 (5)	C6-C31-C32	129.6 (6)	C54-C55-C56	120.2 (1.1)	C74-C75-C76	119.4 (9)
C11-C12-C13	106.8 (6)	N3-C34-C7	121.5 (4)	C55-C56-C51	120.5 (9)	C75-C76-C71	121.1 (8)
C12-C13-C14	107.2 (6)	C7-C34-C33	129.7 (6)	C56-C51-C52	119.3 (8)	C76-C71-C72	119.0 (7)
C13-C14-N1	109.1 (5)	Ni-N4-C41	123.4 (3)	C31-C6-C44	102.1 (5)	C1-C8-C81	122.3 (5)
C14-N1-C11	106.1 (5)	Ni-N4-C44	127.0 (3)	C31-C6-C61	109.6 (5)	C1-C8-C24	123.3 (5)
N1-C11-C1	123.6 (5)	N4-C41-C42	107.7 (5)	C31-C6-O3	110.0 (4)	C24-C8-C81	114.0 (5)
C1-C11-C12	125.7 (6)	C41-C42-C43	107.8 (6)	C44-C6-C61	116.3 (5)	C8-C81-C82	123.3 (7)
N1-C14-C5	123.2 (5)	C42-C43-C44	106.0 (6)	C44-C6-O3	107.1 (4)	C8-C81-C86	119.8 (6)
C5-C14-C13	124.9 (6)	C43-C44-N4	111.1 (5)	C6-C61-C62	123.0 (6)	C81-C82-C83	121.5 (9)
Ni-N2-C21	122.6 (3)	C44-N4-C41	107.2 (5)	C6-C61-C66	119.3 (7)	C82-C83-C84	121.1 (1.0)
Ni-N2-C24	130.0 (3)	N4-C41-C5	122.4 (5)	C61-C6-O3	111.0 (4)	C83-C84-C85	117.9 (1.0)
N2-C21-C22	108.4 (5)	C5-C41-C42	129.6 (6)	C61-C62-C63	121.5 (8)	C84-C85-C86	121.2 (9)
C21-C22-C23	107.7 (6)	N4-C44-C6	120.2 (5)	C62-C63-C64	118.8 (9)	C85-C86-C81	121.2 (8)
C22-C23-C24	106.9 (6)	C6-C44-C43	127.7 (6)	C63-C64-C65	120.8 (1.1)	C86-C81-C82	116.8 (8)
C23-C24-N2	109.5 (5)			C64-C65-C66	120.5 (1.2)	C2-C1-C8	120.4 (5)
C24-N2-C21	107.2 (5)			C65-C66-C61	120.7 (1.0)	C2-C1-C11	112.4 (5)
N2-C21-C7	123.7 (5)			C66-C61-C62	117.4 (8)	C8-C1-C11	127.1 (5)
C7-C21-C22	126.5 (6)					C1-C2-O1	123.8 (6)
N2-C24-C8	126.7 (5)					C1-C2-O2	111.2 (5)
C8-C24-C23	123.7 (6)					O1-C2-O2	124.7 (6)
						C2-O2-C3	116.5 (8)
						O2-C3-C4	112.7 (1.2)

the nickel atom using the $\Delta f'$ and $\Delta f''$ values given in ref 4.

The structure was refined by full-matrix least-squares techniques.[5] The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights w were taken as $1/\sigma^2(F_o)$. Refinement of the positional parameters of each nonhydrogen atom and the isotropic temperature factors assigned to each led to a conventional index $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.113. Subsequent refinement in which each atom was allowed anisotropic vibrations reduced the value of R to 0.081; the weighted index $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was then 0.117. At this point a difference Fourier map was calculated which revealed most of the hydrogen atoms. The coordinates of the hydrogen atoms were idealized and the contributions of these atoms were held fixed in further cycles of refinement. A p value of 0.07 was used in the last cycles of refinement. The refinement then converged with $R = 0.065$ and $R_w = 0.082$. The final value of the standard deviation of an observation of unit weight was 1.35.

A list of observed and calculated structure factors is available.[6] Coordinates with estimated standard deviations for all atoms are given in Table I. Also listed are individual thermal parameters from the final cycle of anisotropic least-squares refinement. Large thermal parameters, increasing with the distance of the central nickel atom, characterize atoms in the substituent side chains. Especially a very large thermal motion occurs to the C4 methyl carbon of the ester group. It may be attributed to the molecular packing; indeed the C4 carbon provides no contacts with neighboring molecules, and thus some disorder probably also affects this atom.

Description and Discussion

Molecular bond lengths and angles are listed in Table II. Figure 1 shows a perspective view of the homoporphyrin complex with the essential atomic numbering scheme used.

The coordination of the nickel atom is essentially square planar, involving the four nitrogen atoms N1, N2, N3, and N4 of the pyrrole bases of the macrocyclic ligand. The homoporphyrin skeleton is far from planar and highly distorted. The pyrrole rings are quite planar but are rotated with respect to the four-nitrogen mean plane; thus, the N1–N4 pyrrole planes make dihedral angles of 45.1, 43.7, 44.5, and 39.0°, respectively, with the four-nitrogen plane. It is also interesting to note the very large angles occurring between opposite pyrrole planes: N1–N3, 88.0°; N2–N4, 81.5°.

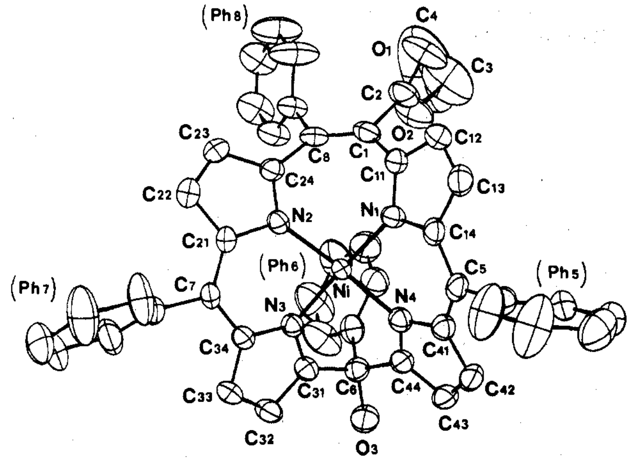

Figure 1. Perspective drawing of the nickel homoporphyrin molecule. Numbering scheme is shown, but carbon atoms of the phenyl groups Ph5–Ph8 are not labeled for clarity.

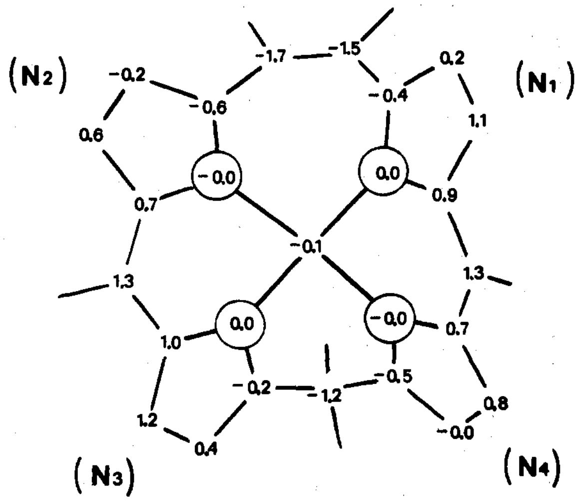

Figure 2. Formal diagram of the homoporphinato core having the same relative orientation as in Figure 1. Each atom symbol has been replaced by its perpendicular displacements, in units of Å, from the mean plane of the four nitrogens.

Table III. Some Compared Values for Homoporphyrins[a]

	A	B
	Bond Lengths, Å	
Ni–N1	1.889 (4)	1.888 (4)
Ni–N2	1.961 (3)	1.876 (4)
Ni–N3	1.885 (4)	1.877 (4)
Ni–N4	1.883 (4)	1.877 (4)
	Angles between Planes, Deg	
4N–N1	43.6	45.1
4N–N2	33.4	43.7
4N–N3	24.0	44.5
4N–N4	31.9	39.0
N1–N2	73.4	71.0
N2–N3	29.6	32.7
N3–N4	38.3	80.3
N4–N1	39.3	33.1
N1–N3	65.6	88.0
N2–N4	62.7	81.5

[a] A is the (21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21*H*-21-homoporphinato)nickel,[1] and B is the present compound.

Table IV. Least-Squares Planes[a]

Planes and Deviations (Å)

		Plane 4N: N1, N2, N3, N4			
N1	0.050 (4)	N3	0.046 (3)	Ni	−0.112 (1)[b]
N2	−0.044 (3)	N4	−0.053 (4)		
		Plane N1: N1, C11–C14			
N1	0.008 (3)	C12	−0.010 (7)	C14	−0.024 (5)
C11	−0.007 (5)	C13	0.027 (6)		
		Plane N2: N2, C21–C24			
N2	0.006 (4)	C22	0.022 (7)	C24	−0.005 (6)
C21	−0.019 (6)	C23	−0.009 (7)		
		Plane N3: N3, C31–C34			
N3	−0.003 (3)	C32	0.004 (7)	C34	0.008 (6)
C31	0.002 (6)	C33	−0.009 (6)		
		Plane N4: N4, C41–C44			
N4	−0.004 (4)	C42	0.003 (7)	C44	0.012 (6)
C41	0.004 (6)	C43	−0.011 (7)		
		Plane P: C1, C2, C8, C11, C24, C81			
C1	−0.026 (6)	C8	−0.033 (6)	C24	−0.010 (6)
C2	0.052 (6)	C11	−0.018 (6)	C81	0.058 (7)
		Plane Ph5: C51–C56			
C51	0.007 (7)	C54	0.005 (12)	C56	−0.006 (13)
C52	−0.012 (8)	C55	−0.009 (14)	C5	0.013 (6)[b]
C53	0.008 (10)				
		Plane Ph6: C61–C66			
C61	0.001 (5)	C64	0.002 (11)	C66	−0.003 (11)
C62	−0.001 (7)	C65	−0.000 (13)	C6	0.127 (5)[b]
C63	−0.000 (9)				
		Plane Ph7: C71–C76			
C71	−0.002 (5)	C74	−0.009 (11)	C76	0.012 (9)
C72	−0.004 (8)	C75	−0.006 (11)	C7	−0.036 (5)[b]
C73	0.016 (11)				
		Plane Ph8: C81–C86			
C81	0.002 (5)	C84	−0.009 (10)	C86	−0.014 (9)
C82	0.004 (11)	C85	0.022 (10)	C8	−0.051 (5)[b]
C83	−0.003 (12)				
		Plane Es: C1, C2, O1, O2			
C1	−0.004 (5)	O1	−0.006 (6)	O2	−0.005 (5)
C2	0.022 (7)				

Equations

Plane	*A*	*B*	*C*	*D*
4N	−0.025	0.800	−0.598	3.551
N1	0.020	0.141	−0.989	−0.558
N2	0.605	0.768	−0.204	3.447
N3	−0.185	−0.976	−0.108	−4.279
N4	−0.476	0.351	−0.806	0.673
Ph5	0.963	−0.229	−0.136	−1.274
Ph6	0.198	−0.127	−0.971	−3.847
Ph7	0.609	−0.725	−0.320	−3.526
Ph8	−0.162	−0.078	−0.983	−0.980
P	0.744	0.130	−0.654	1.882
Es	0.148	−0.825	−0.544	−3.189

Angles (deg) between Planes

4N–N1	45.1	4N–N3	44.5
4N–N2	43.7	4N–N4	39.0
N1–N2	71.0	N4–N1	33.1
N2–N3	32.7	N1–N3	88.0
N3–N4	80.3	N2–N4	81.5
4N–P	61.5	P–Es	68.9
4N–Es	70.9		

[a] All planes are in the form $AX + BY + CZ - D = 0$. [b] Atoms not included in the calculation.

Equations of the planes referred to the axial system a, b, c^* were calculated according to the method of Schomaker et al.[7] (Table IV). The displacements of the homoporphyrin skeletal atoms from the four-nitrogen plane are illustrated in Figure 2. The overall effect of the distortions of the skeleton is to generate a saddle-shaped surface (see Figure 3).

Such distortions of the macrocyclic ligand were observed in the first described nickel(II)–homoporphyrin complex.[1] Compared values are summarized in Table III. In this last

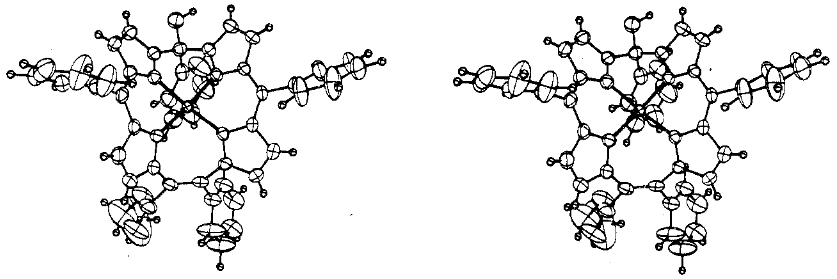

Figure 3. Stereoscopic view of the structure. The thermal ellipsoids are drawn for 50% probability, except those of the hydrogen atoms which are drawn artificially small.

Table V. Intermolecular Contacts Less Than 3.6 Å[a]

C14···C43	$3/00\bar{1}$	3.599 (7)	C42···N2	3/000	3.467 (9)
N2···C42	$3/00\bar{1}$	3.467 (9)	C52···C33	3/100	3.477 (9)
C21···C42	$3/00\bar{1}$	3.390 (10)	C53···C33	3/100	3.481 (11)
N3···C84	2/000	3.582 (9)	C53···C32	3/100	3.591 (9)
C32···C53	$3/\bar{1}0\bar{1}$	3.591 (9)	C74···O2	$1/\bar{1}0\bar{1}$	3.544 (12)
C33···C52	$3/\bar{1}0\bar{1}$	3.477 (9)	C84···C34	2/000	3.548 (11)
C33···C53	$3/\bar{1}0\bar{1}$	3.481 (11)	C84···N3	2/000	3.582 (9)
C34···C84	2/000	3.548 (11)	O3···O1	$1/\bar{1}00$	3.177 (6)
C43···C14	3/000	3.599 (7)	O1···O3	1/100	3.177 (6)
C42···C21	3/000	3.390 (10)	O2···C74	1/101	3.544 (12)

[a] Second atoms not in the crystal chemical unit (i.e., not listed in Table I) are specified by *I*/*uvw* which denotes the manner in which the atomic parameters can be derived from the corresponding atom in the crystal unit. *I* refers to one of the following symmetry operations: 1, x, y, z; 2, $\bar{x}, \bar{y}, \bar{z}$; 3, $x, \bar{y} + {}^1/_2, z + {}^1/_2$; 4, $\bar{x}, y + {}^1/_2, \bar{z} + {}^1/_2$. The u, v, and w digits code a lattice translation as $ua + vb + wc$.

compound, three Ni–N bond lengths were found equal to 1.886 ± 0,010 Å while the fourth was markedly different as equal to 1.961 (3) Å. In the present compound, all the four Ni–N bond lengths are equivalent to 1.879 ± 0.010 Å. Accordingly it appears that a greatest distortion of the macrocyclic ligand is conducive to stronger complexing by the nickel ion. The contraction of the Ni–N bond length is then so that it tends to the value of about 1.85 Å usually found in square-planar complexes.[8] On the other hand, the normal Ni–N bond lengths are 1.96 Å in the planar nickel porphyrins. As postulated by Hoard,[9] 1.96 Å is the smallest value in a porphyrin to still retain a planar macrocycle. All structural data on metalloporphyrins have confirmed this assumption; thus, the most distorted derivative recently described is the (α,γ-dimethyl-α,γ-dihydroporphinato)nickel(II)[10] with an average Ni–N bond length of 1.908 (6) Å and angles between pyrroles in the range 22–25°.

An essential characteristic of porphyrins is the existence of an aromatic conjugated system. However, in the present homoporphyrin ligand, π delocalization is broken down at the C1–C8 bridging bond and at the C6 saturated carbon in the opposite site of the homoporphinato core. First, accordingly with the coplanarity of the six carbon atoms C1, C2, C8, C11, C24, and C84 (Table IV), the C1–C8 bond length of 1.341 (6) Å is consistent with a localized double bond. Second, the geometry around the C6 carbon atom agrees with an sp^3 hybridization, but the bond angle C31–C6–C44 is reduced to 102.1 (5)°.

The homoporphinato core is thus divided in two electronic distinguishable parts: one includes N1 and N4 pyrrole groups; the other includes N2 and N3 pyrrole groups. Using Ca and Cb to design the respective α- and β-carbon atoms of a pyrrole ring, the averaged values for bond lengths are Ca–Cb = 1.417 (12) Å and Cb–Cb = 1.358 (12) Å, wherein the number in parentheses is the greatest value of the estimated standard deviation for an individually determined length. The deviation of these bond lengths from the expected 1.39-Å value (bond order 1.5) reflects the inadequacy of this simple model to define completely the π-electron delocalization. Furthermore, this model also suggests two types of N–C bonds: the N–Ca bonds would have a partial π contribution (Ca: C11, C24, C31, C44), but the N–Ca' bonds would not (Ca': C14, C21, C34, C41). Qualitatively, the mean values for these bond types, 1.338 (10) and 1.389 (7) Å, follow the expected pattern; nevertheless the shortening of the N–Ca' bonds from the theoretical 1.42 Å for single bonds also denotes some π delocalization. It is interesting to note that similar variations in bond lengths were found for the first described homoporphyrin system.[1]

Finally the phenyl groups are tilted with respect to the plane of the three neighboring carbons of the bridge positions between pyrroles; the tilted angles of the four phenyls Ph5–Ph8 are 74.3, 71.7, 62.6, and 60.7°, respectively.

A computer-drawn model[11] in perspective is shown in Figure 3. Intermolecular distances are listed in Table V. The closest of these range upward from 3.390 (10) Å for C···C, 3.467 (9) Å for C···N, and 3.177 (6) Å for O···O distances. The shortest distance occurs between the O3 hydroxyl oxygen and the O1 carbonyl oxygen of the ester group.

Registry No. (10*H*-10-Hydroxyl-21-ethoxycarbonyl-5,10,15,-20-tetraphenyl-21-homoporphinato)nickel(II), 57808-62-5.

Supplementary Material Available: Listing of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

References and Notes

(1) B. Chevrier and R. Weiss, *J. Am. Chem. Soc.*, **97**, 1416 (1975).
(2) H. J. Callot, Th. Tschamber, and E. Schaeffer, *Tetrahedron Lett.*, 2919 (1975).
(3) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(4) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, 1962, p 215.
(5) C. T. Prewitt, "A Fortran IV Full-Matrix Crystallographic Least-Squares Program", SFLS 5, 1966.
(6) Supplementary material.
(7) V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959).
(8) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).
(9) J. L. Hoard, *Ann. N.Y. Acad. Sci.*, **206**, 18 (1973).
(10) P. N. Dwyer, J. W. Buchler, and W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 2789 (1974).
(11) C. K. Johnson, ORTEP, Report 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.