Crystal structure and molecular stereochemistry of α,γ-dimethyl-α,γ-dihydrooctaethylporphinatonickel(II)

3 AUTHORS, INCLUDING:

J. W. Buchler
Technical University Darmstadt
109 PUBLICATIONS **2,431** CITATIONS

SEE PROFILE

W. Robert Scheidt
University of Notre Dame
363 PUBLICATIONS **13,711** CITATIONS

SEE PROFILE

reported. We estimate $D(\text{Ni-L}) = 30$ kcal/mol in NiL_3 since Ni–P bonds in NiL_3 should be somewhat stronger than NiL_4 as a consequence of hybridization changes on Ni and decreased steric repulsions. Assuming $\Delta S_1 \sim 0$ (Table VII) and using the well-known relation $\Delta F = \Delta H - T\Delta S = RT \ln K$ and eq 8 we obtain eq 9. On this basis we estimate $D(\text{Ni–Ol})$ to be

$$D(\text{Ni–Ol}) \sim 30 + RT \ln K_1 \qquad (9)$$

about 25 kcal/mol for trans-$(\text{CH}_3)_3\text{CCH}{=}\text{CHC-}$ $(\text{CH}_3)_3$, 33 kcal/mol for C_2H_4, and 42 kcal/mol for trans-$(\text{NC})\text{CH}{=}\text{CH}(\text{CN})$. Our value for ethylene is somewhat higher than the activation energy of 31 kcal/mol measured by Cramer[48] for dissociation of ethylene from $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$.

Summary

The results of our studies on olefin complexes of nickel indicate that electron donation from filled metal d to empty olefin π^* orbitals is extremely important in determining the stability of the complexes. Steric effects of substituents are relatively unimportant compared to electronic effects, and resonance is more important than inductive interaction. Ring strain and chelation both assist olefin coordination. Reducing the ability of the metal to back bond in the series $\text{Ni}(0) \gtrsim \text{Pt}(0) > \text{Rh}(I) > \text{Pt}(II) > \text{Ag}^+$ reduces the importance of resonance and decreases the selectivity of the metal for differently substituted olefins, while at the same time reducing the $\text{C}{=}\text{C}$ bond length and increasing the stretching force constant. Our data suggest that the degree to which substituents are bent back away from the metal in transition metal olefin complexes is not simply related to the metal–olefin bond strength. Tetrafluoroethylene, which shows extreme bending back in other systems, shows a bond strength to $\text{Ni}(0)$ which is no greater than, and probably less than, that of ethylene itself.

(48) R. Cramer, *J. Amer. Chem. Soc.*, **94**, 5681 (1972).

Crystal Structure and Molecular Stereochemistry of α,γ-Dimethyl-α,γ-dihydrooctaethylporphinatonickel(II)

Patrick N. Dwyer,[1a] J. W. Buchler,[1b] and W. Robert Scheidt*[1a]

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and The Institut für Anorganische Chemie, Rheinisch-Westfälische Technische Hochschule, D-51 Aachen, Federal Republic of Germany. Received September 25, 1973

Abstract: Crystals of α,γ-dimethyl-α,γ-dihydrooctaethylporphinatonickel(II) utilize the space group $C2/c$; the unit cell has $a = 22.456$ (6), $b = 14.980$ (6), $c = 20.615$ (8) Å, and $\beta = 96.04$ (1)° and contains eight molecules. The calculated and experimental densities are 1.197 and 1.20 g/cm³, respectively. Intensity data were collected by θ–2θ scanning with Mo Kα radiation, and 2890 data were retained as observed and used for the solution and refinement of structure; the conventional and weighted R values are 0.071 and 0.082, respectively. The air-stable reduced porphyrin has a folded and ruffled core which leads to an average Ni–N distance of 1.908 Å for the square-planar NiN_4 coordination group. The core of the molecule has approximate C_{2v} geometry; the two methyl groups at C-α and C-γ are in the syn–axial configuration.

Structural data for dihydroporphyrins are limited,[2,3] although the molecular stereochemistry of a large variety of the closely related porphyrins and metalloporphyrins has been reported.[4,5] Dihydroporphyrin derivatives may be divided into three classes according to the position of the two additional hydrogen atoms on the porphine (1) nucleus.[6] The isophlorins have both hydrogen atoms substituted on the nitrogen atoms.[7,8]

The phlorins have one hydrogen substituted on a nitrogen atom and one on a meso-carbon atom.[7,8] The third class has both hydrogen atoms substituted on carbon atoms of the porphine nucleus. The three possible stable species[6,9] are chlorin (2), α,β-dihydroporphine (3), and α,γ-dihydroporphine (4) (porphodimethene). The chlorophyll pigments of plants[10] and photosynthetic algae utilize the chlorin moiety. Although 3 and its derivatives are unknown, derivatives of 4 have been suggested as intermediates in porphyrin syntheses.[11-14] These derivatives have not been isolated

(1) (a) University of Notre Dame. (b) Technische Hochschule Aachen.
(2) W. Hoppe, G. Will, J. Gassman, and H. Weichselgartner, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallachem.*, **128**, 18 (1969); J. Gassman, I. Strell, F. Brandl, W. Sturm, and W. Hoppe, *Tetrahedron Lett.*, 4609 (1971).
(3) M. S. Fischer, D. H. Templeton, A. Zalkin, and M. Calvin, *J. Amer. Chem. Soc.*, **94**, 3613 (1972).
(4) J. L. Hoard, *Science*, **174**, 1295 (1971).
(5) E. B. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970).
(6) D. Mauzerall, *J. Amer. Chem. Soc.*, **84**, 2437 (1962).
(7) R. B. Woodward, *Ind. Chim. Belge*, (11) 1293 (1962).

(8) H. H. Inhoffen, J. W. Buchler, and P. Jäger, *Fortschr. Chem. Org. Naturst.*, **26**, 284 (1968).
(9) J. W. Buchler, Habilitationsschrift, Technische Hochschule Aachen, 1971.
(10) L. P. Vernon and G. R. Seely, Ed., "The Chlorophylls," Academic Press, New York, N. Y., 1966.
(11) D. Mauzerall and S. Granick, *J. Biol. Chem.*, **232**, 1141 (1958).
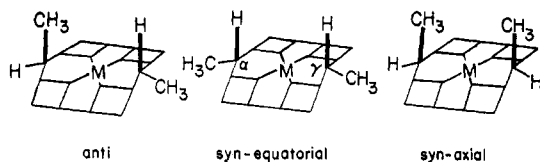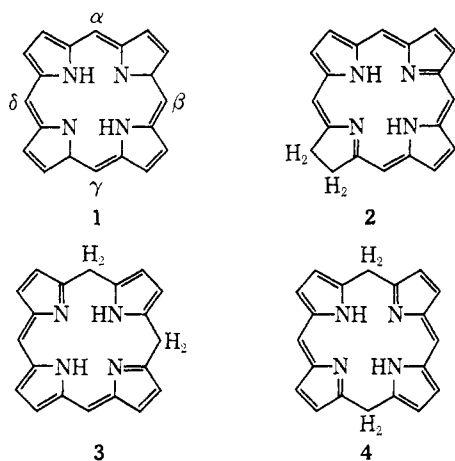(12) R. B. Woodward, *Angew. Chem.*, **72**, 651 (1960).

Figure 1. Schematic representation of the possible configurations for α,γ-dimethyl-α,γ-dihydroporphyrins.

as pure materials because they are rapidly dehydrogenated to porphyrins by oxygen.[15,16] The porphodimethenes, rather than the chlorins, are the primary products of the chemical[15,16] or photochemical[17,18] hydrogenation of metalloporphyrins; the chemical process is a "reductive protonation," i.e., electron addition and protonation of the resulting dianion.

Air-stable porphodimethenes were initially prepared as the nickel,[8,19] copper,[19] and zinc[14,19] complexes; all derivatives have alkyl substituents on the pyrrole carbon atoms and alkyl or aryl substituents on two (α, γ) or four meso-carbon atoms. The most general synthetic procedure for the preparation of the stable porphodimethenes is the reductive methylation of a metalloporphyrin[19]—a reaction analogous to reductive protonation. The preparation of α,γ-dimethyl-α,γ-dihydrooctaethylporphinatonickel(II) (6), to be written as Ni(OEPMe₂), by this procedure is illustrated below.
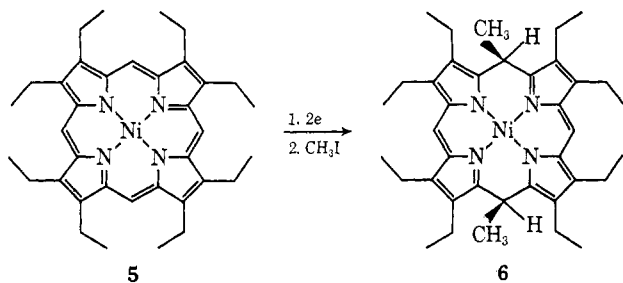
Ni(OEPMe₂) thus represents a model compound of the dihydroporphyrins having potential biochemical in-

(13) A. Treibs and H. Häberle, Justus Liebigs Ann. Chem., 718, 183 (1968).

(14) D. Dolphin, J. Heterocycl. Chem., 7, 275 (1970).

(15) J. W. Buchler, L. Puppe, and H. H. Schneehage, Justus Liebigs Ann. Chem., 749, 134 (1971).

(16) J. W. Buchler and H. H. Schneehage, Tetrahedron Lett., 3803 (1972).

(17) G. R. Seely and K. Talmadge, Photochem. Photobiol., 3, 195 (1964).

(18) A. N. Sidorov, Biofizika, 10, 226 (1965).

(19) J. W. Buchler and L. Puppe, Justus Liebigs Ann. Chem., 740, 142 (1970).

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

Atom	$10^4 X$	$10^4 Y$	$10^4 Z$
N_1	1214 (2)	966 (4)	3555 (3)
N_2	410 (2)	−322 (4)	3753 (3)
N_3	−401 (2)	931 (4)	3972 (3)
N_4	391 (2)	2219 (3)	3777 (3)
C_{a1}	1629 (3)	1622 (5)	3746 (4)
C_{a2}	1513 (3)	309 (5)	3286 (4)
C_{a3}	794 (3)	−871 (5)	3492 (3)
C_{a4}	93 (3)	−850 (5)	4147 (3)
C_{a5}	−653 (3)	275 (5)	4322 (3)
C_{a6}	−800 (3)	1583 (5)	3898 (4)
C_{a7}	−79 (3)	2776 (5)	3718 (4)
C_{a8}	881 (3)	2761 (5)	3948 (4)
C_{b1}	2202 (3)	1336 (6)	3584 (4)
C_{b2}	2123 (3)	523 (5)	3286 (4)
C_{b3}	730 (3)	−1763 (5)	3705 (4)
C_{b4}	290 (4)	−1741 (5)	4127 (4)
C_{b5}	−1222 (3)	567 (6)	4489 (4)
C_{b6}	−1329 (3)	1383 (6)	4205 (4)
C_{b7}	91 (4)	3670 (5)	3864 (4)
C_{b8}	704 (4)	3642 (6)	4018 (5)
C_{m1}	1467 (3)	2458 (5)	3954 (4)
C_{m2}	1214 (3)	−533 (5)	3026 (3)
C_{m3}	−397 (3)	−554 (5)	4422 (4)
C_{m4}	−699 (3)	2432 (5)	3528 (4)
C_{11}	2764 (4)	1910 (6)	3683 (6)
C_{21}	2589 (4)	−26 (7)	2917 (9)
C_{31}	1081 (4)	−2552 (5)	3489 (5)
C_{41}	50 (4)	−2530 (6)	4482 (4)
C_{51}	−1636 (4)	31 (6)	4873 (4)
C_{61}	−1892 (5)	1971 (7)	4171 (6)
C_{71}	−341 (4)	4464 (6)	3839 (6)
C_{81}	1122 (6)	4466 (9)	4341 (10)
C_1	900 (4)	−381 (5)	2341 (4)
C_2	−813 (3)	2269 (6)	2792 (4)
C_{12}	2823 (5)	2560 (8)	3113 (6)
C_{23}	2803 (7)	−584 (13)	3387 (9)
C_{32}	831 (6)	−2983 (7)	2869 (5)
C_{42}	−514 (5)	−2926 (7)	4131 (5)
C_{52}	−2041 (5)	−620 (9)	4462 (6)
C_{62}	−1828 (7)	2712 (13)	4670 (9)
C_{72}	−510 (6)	4829 (8)	3180 (7)
C_{82}	1272 (7)	4798 (10)	3796 (8)

Atom	$10^5 X$	$10^5 Y$	$10^5 Z$
Ni	3938 (4)	9488 (6)	37365 (5)

[a] Figures in parentheses are the estimated standard deviations in the last significant figure.

terest as intermediates in the formation of chlorophylls from porphyrins.

The saturated α- and γ-meso-carbon atoms of 6 are expected to give the ligand increased flexibility compared to porphyrins; examination of molecular models suggests a roof-like folding of the ligand about the line joining the α- and γ-carbons. Analysis of the ¹H nmr spectra of several α,γ-dimethyl-α,γ-dihydrooctaethylporphinatometal complexes, XₙM(OEPMe₂), indicates a synconfiguration for the porphodimethene[20] (cf. Figure 1 for schematic representations of the three possible configurations discussed elsewhere[20]). The expected steric crowding of the peripheral ethyl and methyl groups should favor the syn–axial configuration; however, this configuration cannot be unambiguously assigned from the ¹H nmr spectra. The determination of the molecular structure of Ni(OEPMe₂), reported herein, confirms that the molecule has the syn–axial configuration in the solid state.

(20) L. Puppe, Thesis, Technischen Hochschule Aachen, 1972; J. W. Buchler and L. Puppe, in preparation; J. W. Buchler, L. Puppe, K. Rohbock, and H. H. Schneehage, Ann. N. Y. Acad. Sci., 206, 116 (1973).

Table II. Anisotropic Thermal Parameters $(\text{Å}^2)^a$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B^b
Ni	4.17 (3)	4.02 (4)	5.78 (4)	−0.52 (4)	1.30 (3)	−0.30 (4)	4.47
N_1	3.9 (2)	4.3 (3)	6.2 (3)	0.0 (2)	0.6 (2)	0.0 (3)	4.7
N_2	4.9 (3)	4.5 (3)	5.5 (3)	−0.5 (3)	1.1 (2)	0.2 (3)	4.9
N_3	4.5 (3)	4.2 (3)	5.5 (3)	0.0 (2)	1.5 (2)	0.1 (3)	4.6
N_4	4.2 (2)	3.9 (3)	6.1 (3)	−0.3 (2)	1.1 (2)	−0.5 (3)	4.6
C_{a1}	3.9 (3)	4.7 (4)	7.7 (5)	−0.8 (3)	0.9 (3)	0.2 (3)	5.1
C_{a2}	4.0 (3)	4.9 (4)	6.7 (4)	0.0 (3)	0.8 (3)	0.3 (3)	5.0
C_{a3}	5.1 (3)	4.3 (3)	5.9 (4)	0.0 (3)	0.5 (3)	−0.3 (3)	5.1
C_{a4}	5.5 (4)	4.0 (3)	5.6 (4)	−0.7 (3)	0.6 (3)	0.3 (3)	4.9
C_{a5}	4.3 (3)	6.3 (4)	5.2 (4)	−1.3 (3)	1.3 (3)	−0.5 (3)	5.0
C_{a6}	4.6 (3)	5.7 (4)	5.9 (4)	−0.8 (3)	1.8 (3)	−1.3 (3)	5.1
C_{a7}	5.0 (4)	4.9 (4)	5.8 (4)	−0.2 (3)	1.4 (3)	−0.7 (3)	5.1
C_{a8}	6.1 (4)	3.7 (4)	7.5 (5)	−0.4 (3)	1.6 (3)	−0.9 (3)	5.4
C_{b1}	3.6 (3)	6.8 (5)	8.6 (5)	0.0 (3)	1.0 (3)	0.4 (4)	5.9
C_{b2}	4.4 (4)	4.8 (4)	9.1 (5)	−0.4 (3)	1.3 (3)	−0.2 (4)	5.7
C_{b3}	6.4 (4)	4.1 (4)	6.6 (4)	−0.1 (3)	0.7 (3)	0.1 (3)	5.5
C_{b4}	6.9 (4)	4.5 (4)	5.7 (4)	−0.9 (3)	0.9 (3)	0.7 (3)	5.5
C_{b5}	5.2 (4)	7.1 (5)	5.6 (4)	−1.1 (3)	1.7 (3)	−0.8 (3)	5.7
C_{b6}	5.0 (4)	6.7 (5)	6.3 (4)	−0.5 (3)	1.8 (3)	−0.5 (4)	5.7
C_{b7}	6.4 (4)	4.7 (4)	9.0 (5)	−0.4 (3)	1.8 (4)	−1.4 (4)	6.2
C_{b8}	5.8 (4)	5.2 (4)	11.0 (6)	−1.8 (4)	1.5 (4)	−1.8 (4)	6.5
C_{m1}	5.8 (4)	5.5 (4)	6.8 (5)	−1.4 (3)	0.7 (3)	−0.7 (4)	5.9
C_{m2}	4.5 (3)	3.9 (3)	5.8 (4)	0.3 (3)	1.2 (3)	0.3 (3)	4.6
C_{m3}	5.7 (4)	5.5 (4)	5.3 (4)	−1.4 (3)	0.8 (3)	−0.2 (3)	5.4
C_{m4}	4.4 (3)	4.7 (4)	6.2 (4)	0.2 (3)	1.6 (3)	−0.6 (3)	4.9
C_{11}	3.7 (4)	8.2 (6)	14.6 (8)	−0.9 (4)	1.0 (4)	−1.9 (5)	7.5
C_{21}	4.9 (5)	4.3 (5)	34.5 (18)	0.4 (4)	−3.2 (7)	−0.3 (7)	8.9
C_{31}	9.5 (6)	4.0 (4)	10.5 (6)	1.0 (4)	2.6 (5)	0.8 (4)	7.2
C_{41}	8.5 (6)	5.4 (5)	8.3 (5)	−0.1 (4)	2.1 (4)	1.3 (4)	7.1
C_{51}	6.1 (5)	9.6 (6)	8.4 (5)	−1.8 (4)	3.0 (4)	0.7 (5)	7.2
C_{61}	11.0 (7)	7.2 (6)	15.1 (9)	0.9 (5)	9.9 (7)	−0.2 (6)	7.8
C_{71}	6.4 (5)	4.6 (4)	18.3 (10)	0.0 (4)	0.8 (6)	−2.9 (5)	7.9
C_{81}	9.0 (8)	8.9 (8)	34.5 (20)	1.5 (6)	8.6 (10)	7.1 (10)	12.1
C_1	6.5 (4)	5.8 (4)	6.1 (4)	0.1 (4)	0.6 (3)	0.3 (3)	6.1
C_2	5.7 (4)	6.4 (5)	7.3 (5)	−0.1 (4)	0.8 (4)	−0.4 (4)	6.4
C_{12}	10.3 (7)	9.5 (7)	14.3 (9)	−4.1 (6)	3.9 (6)	1.6 (6)	9.8
C_{22}	11.6 (10)	21.8 (16)	22.5 (16)	−2.3 (10)	7.1 (10)	−6.4 (13)	16.2
C_{32}	14.0 (9)	8.4 (7)	9.9 (7)	1.8 (6)	1.5 (6)	−2.9 (5)	10.0
C_{42}	11.3 (8)	8.7 (7)	11.2 (8)	−5.5 (6)	−0.2 (6)	−0.5 (6)	9.2
C_{52}	8.9 (7)	14.8 (10)	11.8 (8)	−6.9 (7)	0.4 (6)	0.0 (7)	10.0
C_{62}	11.5 (10)	23.4 (17)	18.9 (14)	2.6 (11)	5.8 (9)	−1.8 (12)	16.1
C_{72}	12.6 (9)	9.8 (8)	14.6 (10)	3.8 (7)	−0.2 (7)	1.1 (7)	11.7
C_{82}	14.3 (11)	11.7 (10)	21.0 (14)	−1.7 (8)	−5.9 (10)	−1.2 (9)	14.5

^{a} The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij} in Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. ^{b} Isotropic thermal parameter in Å^2 calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/2}$.

Experimental Section

Crystals of Ni(OEPMe$_2$) were obtained by slow evaporation of saturated benzene solutions. Preliminary X-ray photographic study established a monoclinic eight-molecule unit cell with Cc or $C2/c$ as the possible space groups. Lattice constants, $a = 22.456$ (6), $b = 14.980$ (6), $c = 20.615$ (8) Å, and $\beta = 96.04$ (1)° (λ 0.71069 Å), came from a least-squares refinement that utilized the setting angles of 22 reflections, each collected at $\pm 2\theta$. These constants led to a calculated density at $20 \pm 1°$ of 1.197 g/cm^3, which compares well with the measured value (by flotation) of 1.20 g/cm^3.

Intensity data were measured on a Syntex P$\bar{1}$ diffractometer using the θ–2θ scanning technique with graphite-monochromated Mo Kα radiation. Data collection techniques were essentially the same as described previously.[21] Some crystal decomposition was noted in the course of data collection; two crystals were therefore used in order to limit the decrease in the intensity of standards to ~15%. The dimensions of the two crystals were 0.25 × 0.25 × 0.50 mm and 0.3 × 0.3 × 0.6 mm. All independent data having $\sin\theta/\lambda \leqslant 0.620 \text{ Å}^{-1}$ were measured.

The net intensities were reduced to a set of relative squared amplitudes as described previously.[21] A linear correction for crystal decomposition was applied. Standard deviations were calculated[21] and all data having $F_o < 3\sigma(F_o)$ were taken to be unobserved; 2890 independent data were coded as observed (47% of the theoretical number possible). Only the observed data were used for the determination and refinement of structure.

(21) W. R. Scheidt, *J. Amer. Chem. Soc.*, **96**, 84 (1974).

The initial choice of $C2/c$ as the space group was fully confirmed by all subsequent developments during the determination of structure. The structure was solved by the standard heavy-atom technique. Block-diagonal least-squares refinement[22] of the structure was followed by a difference Fourier synthesis which revealed electron density concentrations appropriately located for the hydrogen atoms bonded directly to the ring, the hydrogen atoms of the two methyl groups bonded directly to the ring, and most of the methylene carbon hydrogen atoms. These hydrogen atoms were then fixed in the theoretically calculated positions (C–C–H = 109.5°, C–H = 1.0 Å) and included in the subsequent refinements. No hydrogen atom contributions of the methyl hydrogen atoms of the eight ethyl groups were included in the refinement. The refinement was then carried to convergence using anisotropic thermal parameters for all heavy atoms. The final value of $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$ was 0.071, that of $R_2 = [\Sigma w \cdot (|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2}$ was 0.082. The estimated standard deviation of an observation of unit weight was 2.1. The final parameter shifts were less than 15% of the estimated standard deviations during the last cycle.[23] A final difference Fourier was

(22) The program, REFINE, written by J. J. Park at Cornell University, was used. The function minimized was $\Sigma w(F_o - sF_c)^2$ where w is the weight ($= 1/\sigma^2$) and s is the scale factor. Atomic form factors were from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with real and imaginary corrections for anomalous dispersion in the form factor of the nickel atom from D. T. Cromer, *ibid.*, **18**, 17 (1965).

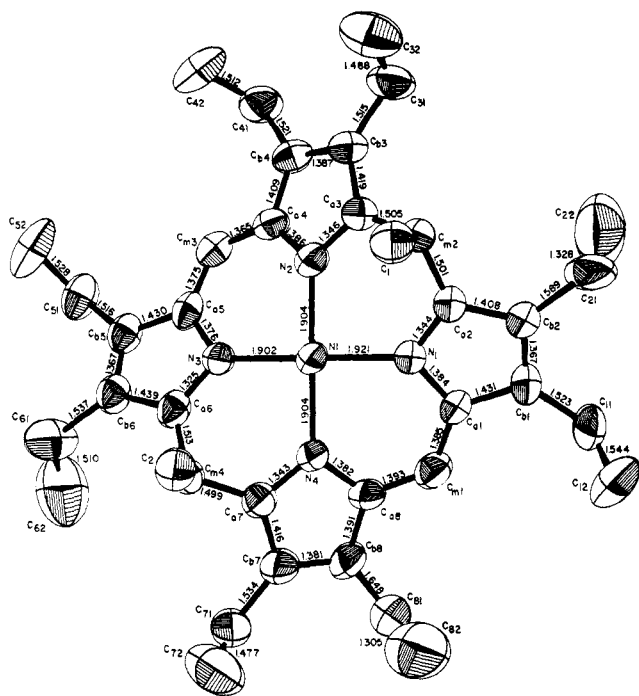(23) See paragraph at end of paper regarding supplementary material.

Figure 2. Computer-drawn model in perspective of Ni(OEPMe$_2$) as it exists in the crystal. Each atom is identified with the symbol used throughout the paper. Also displayed are the bond distances of the core and the peripheral ethyl groups.

judged to be significantly free of features with no peaks greater than 0.3 e Å^{-3}.

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

Discussion

The numbering system employed in Tables I–IV for

Table III. Bond Lengths[a] in the Coordination Group and the Macrocycle

Type	Length, Å	Type	Length, Å
Ni–N$_1$	1.921 (5)	C$_{a6}$–C$_{b6}$	1.439 (10)
Ni–N$_2$	1.904 (5)	C$_{a7}$–C$_{b7}$	1.416 (11)
Ni–N$_3$	1.902 (5)	C$_{a8}$–C$_{b8}$	1.391 (11)
Ni–N$_4$	1.904 (5)	C$_{b1}$–C$_{b2}$	1.367 (11)
N$_1$–C$_{a1}$	1.384 (9)	C$_{b3}$–C$_{b4}$	1.387 (11)
N$_1$–C$_{a2}$	1.344 (9)	C$_{b5}$–C$_{b6}$	1.367 (12)
N$_2$–C$_{a3}$	1.346 (9)	C$_{b7}$–C$_{b8}$	1.381 (12)
N$_2$–C$_{a4}$	1.386 (9)	C$_{m1}$–C$_{a8}$	1.393 (11)
N$_3$–C$_{a5}$	1.376 (9)	C$_{m1}$–C$_{a1}$	1.385 (10)
N$_3$–C$_{a6}$	1.325 (9)	C$_{m2}$–C$_{a2}$	1.501 (10)
N$_4$–C$_{a7}$	1.343 (9)	C$_{m2}$–C$_1$	1.527 (11)
N$_4$–C$_{a8}$	1.382 (9)	C$_{m2}$–C$_{a3}$	1.505 (10)
C$_{a1}$–C$_{b1}$	1.431 (10)	C$_{m3}$–C$_{a4}$	1.365 (10)
C$_{a2}$–C$_{b2}$	1.408 (10)	C$_{m3}$–C$_{a5}$	1.375 (11)
C$_{a3}$–C$_{b3}$	1.419 (10)	C$_{m4}$–C$_{a6}$	1.513 (10)
C$_{a4}$–C$_{b4}$	1.409 (10)	C$_{m4}$–C$_2$	1.531 (11)
C$_{a5}$–C$_{b5}$	1.430 (10)	C$_{m4}$–C$_{a7}$	1.499 (10)

[a] The estimated standard deviations are given in parentheses.

the carbon and nitrogen atoms in the asymmetric unit of structure is displayed in Figure 2. This is a computer-drawn[24] model in perspective of the Ni(OEPMe$_2$) molecule as it exists in the crystal. Bond parameters

(24) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table IV. Bond Angles[a] in the Coordination Group and the Macrocycle

Type	Angle, deg	Type	Angle, deg
N$_1$NiN$_2$	90.0 (2)	C$_{m3}$C$_{a4}$C$_{b4}$	126.2 (7)
N$_2$NiN$_3$	89.9 (2)	N$_3$C$_{a5}$C$_{b5}$	109.8 (6)
N$_3$NiN$_4$	89.7 (2)	N$_3$C$_{a5}$C$_{m3}$	122.3 (6)
N$_4$NiN$_1$	90.2 (2)	C$_{m3}$C$_{a5}$C$_{b5}$	127.6 (7)
N$_1$NiN$_3$	176.5 (4)	N$_3$C$_{a6}$C$_{b6}$	112.2 (7)
N$_2$NiN$_4$	176.5 (4)	N$_3$C$_{a6}$C$_{m4}$	122.8 (6)
C$_{a1}$N$_1$C$_{a2}$	106.6 (5)	C$_{m4}$C$_{a6}$C$_{b6}$	125.0 (7)
C$_{a1}$N$_1$Ni	125.9 (5)	N$_4$C$_{a7}$C$_{b7}$	112.1 (6)
C$_{a2}$N$_1$Ni	127.2 (5)	N$_4$C$_{a7}$C$_{m4}$	120.7 (6)
C$_{a3}$N$_2$C$_{a4}$	106.3 (6)	C$_{m4}$C$_{a7}$C$_{b7}$	127.1 (7)
C$_{a3}$N$_2$Ni	128.0 (5)	N$_4$C$_{a8}$C$_{b8}$	110.9 (6)
C$_{a4}$N$_2$Ni	124.8 (5)	N$_4$C$_{a8}$C$_{m1}$	122.5 (6)
C$_{a5}$N$_3$C$_{a6}$	106.0 (5)	C$_{m1}$C$_{a8}$C$_{b8}$	126.0 (7)
C$_{a5}$N$_3$Ni	126.5 (5)	C$_{a8}$C$_{m1}$C$_{a1}$	124.9 (7)
C$_{a6}$N$_3$Ni	127.1 (5)	C$_{a2}$C$_{m2}$C$_{a3}$	110.0 (6)
C$_{a7}$N$_4$C$_{a8}$	104.8 (5)	C$_{a2}$C$_{m2}$C$_1$	110.5 (6)
C$_{a7}$N$_4$Ni	128.6 (5)	C$_{a3}$C$_{m2}$C$_1$	112.4 (6)
C$_{a8}$N$_4$Ni	126.3 (5)	C$_{a4}$C$_{m3}$C$_{a5}$	125.1 (7)
N$_1$C$_{a1}$C$_{b1}$	108.5 (6)	C$_{a6}$C$_{m4}$C$_{a7}$	110.1 (6)
N$_1$C$_{a1}$C$_{m1}$	122.5 (6)	C$_{a6}$C$_{m4}$C$_2$	110.4 (6)
C$_{m1}$C$_{a1}$C$_{b1}$	128.1 (7)	C$_{a7}$C$_{m4}$C$_2$	111.4 (6)
N$_1$C$_{a2}$C$_{b2}$	111.4 (6)	C$_{a1}$C$_{b1}$C$_{b2}$	107.1 (6)
N$_1$C$_{a2}$C$_{m2}$	122.5 (6)	C$_{a2}$C$_{b2}$C$_{b1}$	106.4 (6)
C$_{m2}$C$_{a2}$C$_{b2}$	126.1 (6)	C$_{a3}$C$_{b3}$C$_{b4}$	106.0 (6)
N$_2$C$_{a3}$C$_{b3}$	111.1 (6)	C$_{a4}$C$_{b4}$C$_{b3}$	106.8 (6)
N$_2$C$_{a3}$C$_{m2}$	121.6 (6)	C$_{a5}$C$_{b5}$C$_{b6}$	106.9 (6)
C$_{m2}$C$_{a3}$C$_{b3}$	127.3 (6)	C$_{a6}$C$_{b6}$C$_{b5}$	105.0 (7)
N$_2$C$_{a4}$C$_{b4}$	109.8 (6)	C$_{a7}$C$_{b7}$C$_{b8}$	105.1 (7)
N$_2$C$_{a4}$C$_{m3}$	123.2 (6)	C$_{a8}$C$_{b8}$C$_{b7}$	107.0 (7)

[a] Figures in parentheses are the estimated standard deviations in the last significant figure.

(with estimated standard deviations)[25] are listed in Tables III and IV. Individual bond distances found in the macrocyclic skeleton are also displayed in Figure 2. Figure 3 is a stereoscopic view of the molecule, with the peripheral ethyl groups omitted for clarity. Although not required of the molecule in the crystal, the core of the molecule has approximate C_{2v} symmetry.

As expected, the porphodimethene skeleton is far from planar and displays a folding at the saturated C-α and C-γ carbon atoms (C$_{m2}$ and C$_{m4}$ of Figure 2). The folding of the ring along with the preservation of local flatness for each pyrrole ring (the mean deviation from exact planarity does not exceed 0.02 Å) is accompanied by a pronounced ruffling of the core. The displacement of the skeletal carbon atoms from the mean plane of the four nitrogen atoms, as given in Figure 4, shows that the ruffling can be described as a quasi-D_{2d} type of ruffling. The mean plane of the porphodimethene skeleton is displaced from the mean plane of the four nitrogen atoms by ~0.13 Å; consequently, the deviations from the mean plane of the core can be obtained by adding ~0.13 Å to each cited displacement in Figure 4. Although the qualitative pattern of displacements from the mean plane of the core is similar to that which characterizes the strongly ruffled porphyrin cores, the magnitudes of the displacements are notably larger. An examination of Figure 3 reveals that the overall effect of the folding and ruffling of the skeleton is to generate a saddle surface.

The nature of the ruffling and folding can be further

(25) These calculations followed W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
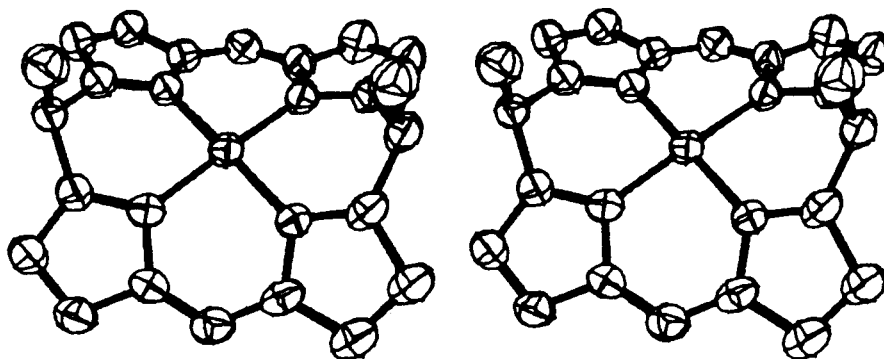
Figure 3. Stereoscopic view of Ni(OEPMe₂) with the peripheral ethyl groups omitted for clarity.

defined by citing the angles between the normals of selected planes in the molecule. The folding, specified by the angle between the normals of the mean planes of the two halves of the molecule defined by respectively C_{m1}, pyrrole rings 1 and 4, and C_{m3}, pyrrole rings 2 and 3, amounts to 52°. The ruffling can be partially specified by the angles between the normals to rings 1 and 4 and rings 2 and 3 (Figure 4) which are 24.7 and 22.0°, respectively.

We then consider the possible contributing factors of the large ruffling of the porphodimethene core. The reduction of the porphinato core at the C_{m2} and C_{m4} atoms (Figure 2) to give the porphodimethene effectively breaks the π-electron system of the parent porphine into two equal pyrromethene halves. This chemical change will also require alterations in the C–C bond lengths and in the angles subtended at these two carbon atoms, compared to the normal values for a porphyrin. The porphodimethene skeleton should have greater flexibility at these two carbon atoms compared to the porphine skeleton in which deformations from planarity are somewhat inimical to the delocalization of π bonding.

A folding of the core along the line connecting the tetrahedral C_{m2} and C_{m4} atoms (Figure 2) is required to minimize the nonbonded contacts between the methyl groups and the adjacent ethyl groups; examination of a scaled molecular model suggests that, for a planar molecule, the nonbonded distances between these groups are required to be unrealistically close. The observed methyl carbon–methylene carbon distances are $C_1 \cdots C_{21}$, 3.89 Å, and $C_2 \cdots C_{61}$, 3.96 Å; the remaining contacts are greater than 4.0 Å. The minimization of these nonbonded contacts does not, however, require as marked a folding of the core and the concomitant out-of-plane displacement of the C_{m2} and C_{m4} atoms as are observed. The folding in the core of the related complex OTi(OEPMe₂)[26] is much less pronounced; nonetheless, the contacts between the methyl groups and the adjacent methylene carbons are $\geqslant 3.90$ Å.

The preservation of planar pyrrole rings and nearly planar trigonal bond systems at the bridgehead C_a atoms requires a second folding of the core along the line connecting the trigonal C_{m1} and C_{m3} atoms (Figure 2) to give the quasi-D_{2d} ruffling. The absolute out-of-plane displacements of the trigonal C_m atoms (Figure 4) are smaller than those of the tetrahedral C_m atoms primarily because the C_a–C_m bond lengths are ~0.12 Å

(26) P. N. Dwyer, J. W. Buchler, and W. R. Scheidt, to be submitted.
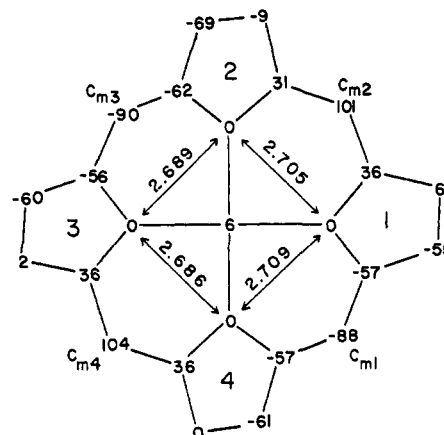
Figure 4. Formal diagram of the porphodimethene core having the same relative orientation as Figure 2. Each atom symbol has been replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the four nitrogens. Also displayed are the four N $\cdots$ N distances.

shorter for the bonds involving the trigonal C_m atoms. The modest departures from planarity of the trigonal bonds centered at the bridgehead carbon atoms C_{a1}, C_{a8}, C_{a4}, and C_{a5} also contribute to the smaller out-of-plane displacements at C_{m1} and C_{m3}. The average sum of the angles subtended at these four bridgehead carbon atoms, which connect the pyrromethene chromophores, is seen to deviate by 0.8° from the ideal 360.0° required for planarity; the average sum of the angles subtended at the bridgehead carbon atoms, C_{a2}, C_{a3}, C_{a6}, and C_{a7}, bonded to the saturated bridges is 360.0°. The nonplanarity of the bridgehead atoms C_{a1}, C_{a8}, C_{a4}, and C_{a5} presumably represents a favorable compromise in the geometry associated with the delocalized bonding; it reduces the angle between the normals to contiguous trigonal bond systems at the joined C_m and C_a atoms.[27] No such considerations apply for bridgehead atoms C_{a2}, C_{a3}, C_{a6}, and C_{a7} which join the reduced C_{m2} and C_{m4} bridges.

The Ni–N bond lengths in Ni(OEPMe₂), which average to 1.908 (6,5) Å,[28] are 0.03–0.06 Å shorter than the corresponding linkage in the nickel porphyrins. The very large magnitude of the quasi-D_{2d} ruffling of the core

(27) J. L. Hoard, Ann. N. Y. Acad. Sci., 206, 18 (1973).
(28) The first number in parentheses following each averaged length is the mean deviation in units of 0.001 Å and the second is the value of the estimated standard deviation for an individually determined length. This notation for reporting averaged values is used throughout the discussion.
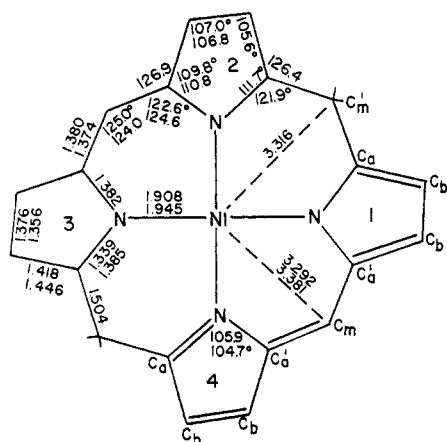
Figure 5. Formal diagram of the porphodimethene core carrying averaged values (C_{2v} symmetry) of the bond lengths, angles, and radii (- - -). The lower number of a pair of values is the averaged value of the corresponding parameter for selected nickel porphyrins.

is wholly conducive to stronger complexing of the nickel ion as can be understood from well-defined principles of metalloporphyrin structure.[27,29] It is well known to porphyrin chemists that the quasi-rigid porphinato core resists undue radial expansion or contraction in the equatorial plane of the core, i.e., the range of metal–porphyrin nitrogen ($M-N_p$) bond lengths is restricted relative to the normal range of values that characterize metal–monodentate nitrogen ligand bond lengths. Thus, $Ni-N_p$ bond lengths in the contracted nickel porphyrins are seen to be stretched by 0.05–0.10 Å and the $Sn-N_p$ bonds of the expanded core in Cl_2SnTPP[29] to be compressed by $\sim$0.05 Å.

Objectively significant variations in the $M-N_p$ lengths within a given class of metalloporphyrins are attributable to changes in the conformation of the porphinato core. Accordingly, if the planar configuration of the porphinato core leads to $M-N_p$ bonds which are stretched beyond the length preferred with monodentate ligands, an S_4 or D_{2d} ruffling will be conducive to a shortening of the $M-N_p$ bonds. Thus the $Ni-N_p$ distances in the essentially planar Ni(II) derivatives of 2,4-diacetyl-deuterioporphyrin IX dimethyl ester[30] and octaethyl-porphyrin[31a] are 1.96 Å, whereas, in the strongly ruffled (S_4) octaethylporphyrin[31b] derivative, the $Ni-N_p$ distance is significantly shortened to 1.929 Å. The accompanying alterations in the bond parameters of the core are confined to small adjustments in bond angles. Further, in crystals of essentially planar bis(piperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(III),[32] the $Co-N_p$ distance is 1.98 Å, but, in the strongly ruffled nitro-3,5-lutidinecobalt(III) derivative of tetraphenylporphyrin,[33] the ruffling leads to a $Co-N_p$ bond length of 1.954 Å, a value typical of Co(III) and monodentate ligands.

It is not clear whether the dominant factor in determining the observed degree of ruffling of the molecular conformation is that induced by the nickel ion to achieve

(29) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 6689 (1972).

(30) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Amer. Chem. Soc.*, **87**, 2305 (1965).

(31) (a) D. L. Cullen and E. F. Meyer, Jr., Abstracts, American Crystallographic Society Meeting, Jan 1973, A1; (b) E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **28**, 2162 (1972).

(32) W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8289 (1973).

(33) J. A. Kaduk and W. R. Scheidt, *Inorg. Chem.*, in press.

stronger complexing or that caused by the intermolecular packing relationships. The observation[19] that Ni(OEPMe₂) is less readily demetallated than Ni(OEP) by concentrated acid suggests that the influence of the nickel ion may be the dominant factor in the observed conformation. In either case, we may still emphasize that the small nickel ion is well-adapted to utilize the flexibility of the porphodimethene core to achieve shorter Ni–N bonds than in the porphyrin.

Figure 5 is a formal diagram of a porphodimethene skeleton carrying values, averaged in accordance with C_{2v} symmetry, for selected bond distances, angles, and radii of Ni(OEPMe₂). When appropriate, the averaged value of the corresponding parameter found in Ni(Deut)[30] and tetragonal Ni(OEP)[31b] is also entered as the lower number of a pair of values in Figure 5. Several of the C–N and C–C bond lengths of the porphodimethene core are seen to differ significantly from the corresponding parameter of the porphinato core. Qualitatively, the differences can be accounted for in terms of simple resonance descriptions of π-electron delocalization in the ligand; one of the two limiting Kekule formulas is indicated in Figure 5. Thus, the C_a-C_b bonds (Figure 5) in the porphodimethene would be expected to have lengths corresponding to a bond order of $\sim$1.5 and to be shorter than the geometrically equivalent bonds in the porphinato core which have bond lengths corresponding to a formal bond order of 1.25. Similarly, the C_b-C_b bonds in the porphodimethene core would be expected to have a bond order of $\sim$1.5 and to be longer than the corresponding C_b-C_b bonds of a porphyrin (bond order 1.75). The average C_a-C_b bond length of 1.418 (10,10) Å[28] and the average C_b-C_b bond of 1.376 (9,11) Å in the porphodimethene core tend toward the expected 1.39 Å. The deviation from 1.39 Å reflects the inadequacies of this simple model to completely define the π-electron delocalization.

This simple model also suggests two types of C–N bonds: the C_a-N bonds (Figure 5) would have a partial π contribution; the $C_a'-N$ bonds would not. The average values for the bond types, 1.339 (8,9) Å and 1.382 (3,9) Å, respectively, qualitatively follow the expected pattern. The shortening of the $C_a'-N$ bonds from the $\sim$1.42 Å expected for a single bond suggests some π delocalization for these bonds. The lengths of the C_a-C_m' and $C_a'-C_m$ bonds are close to the expected lengths.[34] The variation in bond angles in the porphodimethene core, compared to the porphinato core, are as much attributable to differences in the ruffling of the cores as to differences in π delocalization. It is interesting to note that similar variations in the bond distances are found for the pyrrole moieties of bis(pyrromethane) complexes of nickel[35] and palladium.[36]

Thus, apart from the altered bonding pattern, the observed ruffling is mainly introduced to meet the steric requirements of the Ni–N₄ coordination group and the bulky alkyl groups. The repulsive forces between the two meso alkyl groups (C_1 and C_2) and the four neigh-

(34) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18, S15s (1965).

(35) F. A. Cotton, B. G. DeBoer, and J. R. Pipal, *Inorg. Chem.*, **9**, 783 (1970).

(36) (a) F. C. March, D. A. Couch, K. Emerson, J. E. Fergusson, and W. T. Robinson, *J. Chem. Soc. A*, 440 (1971); (b) F. C. March, J. E. Fergusson, and W. T. Robinson, *J. Chem. Soc., Dalton Trans.*, 2069 (1972).

boring ethyl groups would very much increase if Ni(OEPMe₂) were dehydrogenated to α,γ-dimethyloctaethylporphinatonickel(II), Ni(ODM). Therefore, Ni(OEPMe₂) is air-stable. Ni(ODM) may be obtained, however, by metal insertion into the parent porphine.[19] In Ni(ODM), the methyl···methylene carbon contacts are expected to be substantially smaller than the $\geqslant 3.9$ Å contacts found for Ni(OEPMe₂). Indeed, if Ni(ODM) has the same highly ruffled core of Ni(OEP),[31b] the nonbonded contacts can be calculated to be an unreasonably tight 2.8 Å. Hence, Ni(ODM) must represent a metalloporphyrin with a severely distorted core.

Acknowledgments. This research was supported by

Spectroscopic Studies for Tetraphenylporphyrincobalt(II) Complexes of CO, NO, O₂, RNC, and (RO)₃P, and a Bonding Model for Complexes of CO, NO, and O₂ with Cobalt(II) and Iron(II) Porphyrins

B. B. Wayland,* J. V. Minkiewicz, and M. E. Abd-Elmageed

Contribution from the E. F. Smith Laboratory of Chemistry, and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174. Received August 25, 1973

Abstract: Epr and electronic spectra are reported for tetraphenylporphyrincobalt(II) [CoᴵᴵTPP] complexes of CO, NO, O₂, (CH₃O)₃P, and nitrogen donors. Epr spectra show that each CoᴵᴵTPP complex with a closed shell ligand has a $(d_{xz,yz}, d_{xy})^6(d_z^2)^1$ ground configuration. Ligand hyperfine coupling constants (^{13}C and ^{31}P) are reported for the CO, (CH₃O)₃P, and (Bu)₃P complexes and are used in examining the nature of the ligand σ-donor orbitals. The carbon monoxide donor orbital is found to be essentially a sp hybrid, while the phosphorus donor orbital character is very sensitive to substituents. Toluene glass electronic spectra for CoᴵᴵTPP complexes of CO, NO, and O₂, are reported. Two bands are observed in the Soret region of the CO and NO complexes. CoᴵᴵTPP complexes of CO, CH₃NC, and R₃P form dioxygen complexes with epr spectra consistent with the odd electron occupying a highly localized oxygen based π* level. A molecular orbital model is proposed for correlating the structure and bonding in adducts of diatomic molecules with low spin cobalt(II) and iron(II) complexes. This model is found to be compatible with all available data on CO, NO, and O₂ complexes of cobalt(II) and iron(II) porphyrins and is used as a basis for a myoglobin–O₂ model.

C obalt(II) porphyrins and related low spin cobalt(II) complexes have recently received considerable attention because of their unusual ability to form dioxygen complexes reversibly.[1-12] Nitrogen donor

adducts and their dioxygen complexes have been thoroughly studied, but little is yet known about the corresponding complexes with potential π-acceptor ligands such as CO, CH₃NC, and R₃P.

This paper in part reports on epr and electronic spectral studies for CoᴵᴵTPP complexes of CO, NO, O₂, CH₃NC, and (CH₃O)₃P. A molecular orbital bonding model is used in discussing and correlating the general electronic, magnetic, and molecular structures for complexes of diatomic molecules with CoᴵᴵTPP. This model is extended to the CO, NO, and O₂ complexes of iron(II) porphyrins including hemeproteins.

Experimental Section

Materials. Tetraphenylporphyrincobalt(II) [CoᴵᴵTPP] was prepared according to the procedure of Rothemund and Menotti.[13]

(1) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.,* **92,** 55 (1970).

(2) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.,* **92,** 61 (1970).

(3) F. A. Walker, *J. Amer. Chem. Soc.,* **92,** 4235 (1970).

(4) G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.,* **92,** 1551 (1970).

(5) J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.,* **91,** 2775 (1969).

(6) B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci. U. S.,* **67,** 637 (1970).

(7) B. B. Wayland and D. Mohajer, *J. Chem. Soc., Chem. Commun.,* 776 (1972).

(8) B. B. Wayland and D. Mohajer, *J. Amer. Chem. Soc.,* **93,** 5295 (1971).

(9) B. B. Wayland and D. Mohajer, *Inorg. Nucl. Chem. Lett.,* **9,** 633 (1973).

(10) J. C. W. Chien and L. C. Dickinson, *Proc. Nat. Acad. Sci. U. S.,* **67,** 2783 (1972).

(11) T. Yonetani, H. Yamamoto, F. Kayne, and G. Woodrow, *Biochem. Soc. Trans.,* **1,** 44 (1973).

(12) H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.,* **94,** 1559 (1972).

(13) P. Rothemund and A. R. Menotti, *J. Amer. Chem. Soc.,* **70,** 1808 (1948).