from the nucleophile to **3** followed by loss of NO and attack by a second molecule of **3**. While this matter is yet to be fully investigated, the probable role of single electron transfer in these reactions is strongly implicated by the effect of replacing a CO ligand in **3** by a more electron-releasing one. Thus, preliminary experiments show[21] that (cyclohexadienyl)Mn(CO)(NO)PBu_3^+ is much less susceptible to reduction to yield **2** (L = PBu_3) instead of **4** when treated with carbon donor nucleophiles. The replacement of a CO by PBu_3 has a dramatic effect on the diene product yields with the analogous seven-membered ring complexes.[21] Thus, it now appears likely to us that suitable procedures will soon be elaborated that permit the addition of carbon donors to **3** in good yields. Full details of these carbon additions as well as procedures for removal of the diene from the products (**4**) will be published separately.

In conclusion, we have shown that the manganese mediated conversion of coordinated arenes to coordinated cyclohexadienes can be a facile and high-yield procedure that may prove quite useful in synthesis. We have also discovered the first class of compounds for which hydride addition to a coordinated cyclic π-hydrocarbon occurs stereospecifically endo to the metal.

Acknowledgment. This work was supported by a grant from the National Science Foundation (No. CHE-8023964).

Structure of Octaethylporphyrin *N*-Oxide and the Characterization of Its Nickel(II) and Copper(II) Complexes

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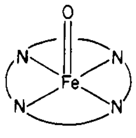
Received September 10, 1984

Abstract: The structure of octaethylporphyrin *N*-oxide has been determined by X-ray crystallography. It crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with one molecule per unit cell of dimensions $a = 7.612$ (3) Å, $b = 9.740$ (4) Å, $c = 10.566$ (4) Å, $\alpha = 91.61$ (3)°, $\beta = 98.49$ (3)°, $\gamma = 108.43$ (3)° at 140 K. The structure was refined to $R = 0.068$ for 1588 reflections and 207 parameters. The molecules pack in a disordered fashion so that a center of symmetry is present. The oxygen atom, which is disordered over four positions, is out of the porphyrin plane by 0.97 Å and bound to one nitrogen with an N–O distance of 1.398 (7) Å. ^1H NMR spectra indicate that at room temperature in solution the oxygen atom rapidly inverts through the center of the porphyrin while remaining attached to one nitrogen atom. A nickel(II) complex of the porphyrin *N*-oxide has been prepared, isolated, and characterized by ^1H NMR, mass, infrared, and UV–visible spectroscopy to have a structure incorporating an Ni–O–N unit. A copper(II) complex has been isolated and characterized by infrared, UV–visible, and electron spin resonance spectroscopy.

The alternative structures **1** and **2** have been proposed for highly



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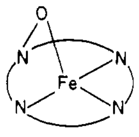

2

oxidized forms of heme proteins (particularly cytochrome P450 and the peroxidases) and as intermediates in heme catabolism.[1-3] Theoretical calculations have predicted that **2** may be significantly more stable than **1**.[4,5] Our approach to studying **2** began by examining the complexation of metal ions by porphyrin *N*-oxides. However, little information is available regarding these substances. Bonnett, Appelman, and co-workers have described the preparation of octaethylporphyrin *N*-oxide (**3**) by the attack of electrophilic oxygen on octaethylporphyrin.[6,7] In their characterization of this *N*-oxide, however, they point out "we have not succeeded in obtaining positive physical evidence for the existence of the N–O bond". A copper(II) complex was briefly described.[7] Here we present the results of an X-ray diffraction study of octaethylporphyrin *N*-oxide, an examination of its structure in solution, and the preparation and detailed characterization of its nickel(II) and copper(II) complexes. Nickel(II), particularly, was chosen

Table I. Atom Coordinates (×10^4) and Thermal Parameters (Å^2 × 10^3) for Octaethylporphyrin *N*-Oxide

atom	*x*	*y*	*z*	*U*
O(1)	306 (7)	−309 (6)	6271 (5)	24 (2)
O(2)	873 (35)	1294 (29)	4577 (24)	11 (9)
N(1)	−46 (4)	875 (3)	6830 (3)	21 (1)[a]
N(2)	2872 (4)	1276 (3)	5121 (3)	22 (1)[a]
C(1)	1375 (5)	2005 (4)	7503 (3)	20 (1)[a]
C(2)	3172 (5)	2578 (4)	7185 (3)	23 (1)[a]
C(3)	3895 (5)	2248 (4)	6124 (3)	21 (1)[a]
C(4)	3982 (4)	1220 (4)	4225 (3)	18 (1)[a]
C(5)	3381 (5)	331 (4)	3079 (3)	21 (1)[a]
C(6)	−1611 (5)	660 (4)	7388 (3)	19 (1)[a]
C(7)	−1139 (5)	1690 (4)	8512 (3)	19 (1)[a]
C(8)	693 (4)	2528 (4)	8570 (3)	17 (1)[a]
C(9)	5776 (4)	2860 (4)	2848 (3)	19 (1)[a]
C(10)	5835 (5)	2217 (4)	4696 (3)	20 (1)[a]
C(11)	−2446 (5)	1769 (4)	9421 (3)	24 (1)[a]
C(12)	−2407 (6)	793 (4)	10499 (4)	39 (2)[a]
C(13)	1834 (5)	3753 (4)	9540 (3)	25 (1)[a]
C(14)	3238 (5)	3363 (4)	10514 (4)	29 (2)[a]
C(15)	7320 (5)	4059 (4)	6666 (3)	22 (1)[a]
C(16)	7325 (5)	5549 (4)	6272 (4)	26 (1)[a]
C(17)	7486 (5)	2468 (4)	4011 (3)	23 (1)[a]
C(18)	7479 (5)	3505 (4)	2948 (4)	28 (1)[a]
H(1)	1654 (54)	703 (42)	5043 (37)	30

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Table II. Interatomic Distances (Å) for Octaethylporphyrin *N*-Oxide

O(1)–N(1)	1.398 (7)	N(1)–C(6)	1.376 (5)
O(2)–N(2)	1.552 (27)	N(2)–C(4)	1.369 (5)
N(1)–C(1)	1.365 (4)	C(1)–C(8)	1.452 (5)
N(2)–C(3)	1.364 (4)	C(3)–C(9)	1.444 (5)
C(1)–C(2)	1.399 (5)	C(4)–C(10)	1.442 (4)
C(2)–C(3)	1.391 (5)	C(6)–C(7)	1.458 (5)
C(4)–C(5)	1.397 (5)	C(7)–C(8)	1.367 (4)
C(5)–C(6^{i})	1.395 (4)	C(8)–C(13)	1.497 (4)
C(6)–C(5^{i})	1.395 (4)	C(9)–C(15)	1.505 (4)
C(7)–C(11)	1.498 (6)	C(11)–C(12)	1.507 (6)
C(9)–C(10)	1.367 (5)	C(15)–C(16)	1.520 (5)
C(10)–C(17)	1.499 (5)		
C(13)–C(14)	1.516 (5)	N(2)···O(1)	2.564 (7)
C(17)–C(18)	1.532 (5)	N(2^{i})···O(1)	2.517 (7)
		N(1)···O(2)	2.59 (3)
H(1)···O(1)	1.88 (1)	N(1^{i})···O(2)	2.40 (3)
H(1^{i})···O(1)	1.82 (1)		

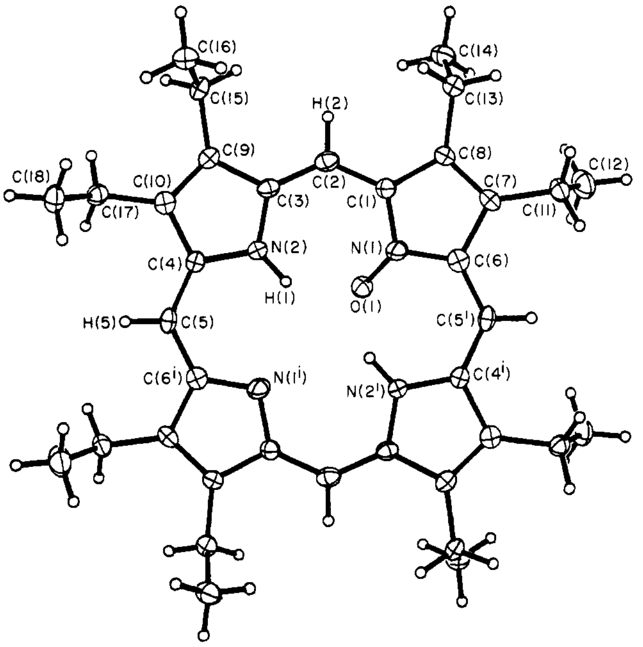


Figure 1. Drawing of octaethylporphyrin *N*-oxide viewed normal to the N_4 plane. Only one of the four possible positions for the oxygen atom is shown.

for this work because it was likely to give a diamagnetic product which would be easily characterized by ^{1}H NMR spectroscopy. Moreover, the virtual nonexistence of nickel oxo complexes and the general instability of nickel in oxidation states higher than (II) favored the formation of a material with structure **2**.

Results and Discussion

X-ray Crystal Structure of Octaethylporphyrin *N*-Oxide. Table I gives the atomic positional parameters while Tables II and III present interatomic distances and angles, respectively. Figure 1 shows a view of the entire molecule with the numbering scheme. Figure 2 shows another view of the structure without the hydrogen atoms. This latter view emphasizes the planar nature of the porphyrin core and shows the out-of-plane displacements of the oxygen atom and the ethyl groups.

The structure suffers from disorder in the location of the oxygen atom. There is only one oxygen atom per molecule. However, the macrocycles are packed so that the net structure is centrosymmetric. The oxygen atom occupies four sites which are shown in Figure 3. Our model indicates that there is 42% occupancy of the site which places the oxygen on N(1). The whole molecule resulting from this arrangement is that shown in Figures 1 and 2. The crystallographic center of symmetry requires, however, 42% occupancy of a site which places the oxygen atom on N(1^{i}) and on the opposite side of the porphyrin. In addition, there is a second, less populated orientation of the porphyrin which results in 8% occupancy of a site with the oxygen, O(2) bound to N(2) and a corresponding 8% occupancy of a site involving oxygen

Table III. Bond Angles (deg) for Octaethylporphyrin *N*-Oxide

O(1)–N(1)–C(1)	121.3 (4)	O(1)–N(1)–C(6)	120.0 (3)
C(1)–N(1)–C(6)	108.7 (3)	O(2)–N(2)–C(3)	118.4 (10)
O(2)–N(2)–C(4)	115.5 (10)	C(3)–N(2)–C(4)	109.8 (3)
N(1)–C(1)–C(2)	125.0 (3)	N(1)–C(1)–C(8)	108.8 (3)
C(2)–C(1)–C(8)	126.2 (3)	C(1)–C(2)–C(3)	130.3 (3)
N(2)–C(3)–C(2)	124.2 (3)	N(2)–C(3)–C(9)	107.6 (3)
C(2)–C(3)–C(9)	128.2 (3)	N(2)–C(4)–C(5)	124.8 (3)
N(2)–C(4)–C(10)	107.5 (3)	C(5)–C(4)–C(10)	127.7 (3)
C(4)–C(5)–C(6^{i})	128.9 (3)	N(1)–C(6)–C(7)	108.5 (3)
N(1)–C(6)–C(5^{i})	125.5 (3)	C(7)–C(6)–C(5^{i})	125.9 (3)
C(6)–C(7)–C(8)	106.9 (3)	C(6)–C(7)–C(11)	125.3 (3)
C(8)–C(7)–C(11)	127.8 (3)	C(1)–C(8)–C(7)	107.1 (3)
C(1)–C(8)–C(13)	125.1 (3)	C(7)–C(8)–C(13)	127.8 (3)
C(3)–C(9)–C(10)	107.6 (3)	C(3)–C(9)–C(15)	124.8 (3)
C(10)–C(9)–C(15)	127.5 (3)	C(4)–C(10)–C(9)	107.5 (3)
C(4)–C(10)–C(17)	124.7 (3)	C(9)–C(10)–C(17)	127.8 (3)
C(7)–C(11)–C(12)	112.9 (4)	C(8)–C(13)–C(14)	113.7 (3)
C(9)–C(15)–C(16)	111.8 (3)	C(10)–C(17)–C(18)	112.8 (3)
N(2)–H(1)···O(1)	130 (2)	N(2^{i})–H(1^{i})···O(1)	132 (2)

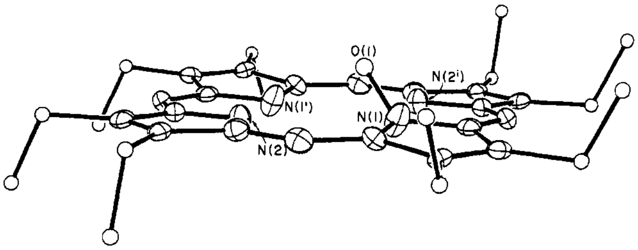


Figure 2. Side view of octaethylporphyrin *N*-oxide showing only one of the four locations of the oxygen atom. Ethyl hydrogen atoms have been omitted.

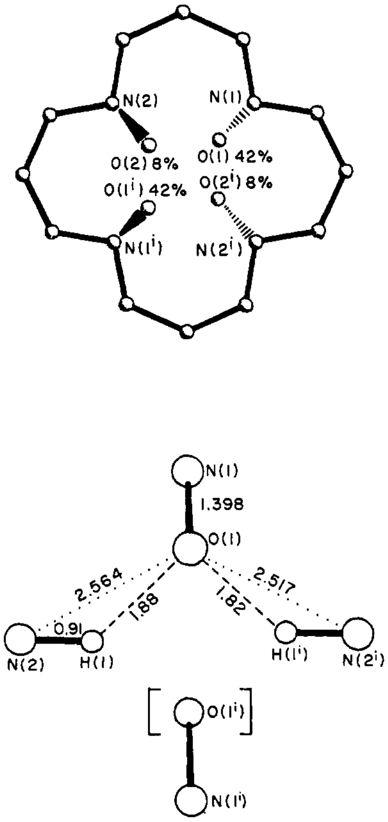


Figure 3. Top: Drawing of the porphyrin showing the positional disorder of the oxygen atom; pyrrole rings are omitted. Bottom: Diagram showing aspects of the core geometry in the most populated form of octaethylporphyrin *N*-oxide. The O(1) site is 42% occupied, the O(1^{i}) site is also 42% occupied.

Table IV. Least-Squares Planes within Porphyrin *N*-Oxide

Porphyrin Core I			
Equation of Plane: $0.2687x - 0.8508y - 0.4516z = 2.3858$			
Atomic Out-of-Plane Distances (Å)			
N(1)	0.122 (4)	C(6)	0.024 (5)
N(2)[a]	−0.015 (4)	C(7)	−0.141 (5)
C(1)	−0.013 (5)	C(8)	−0.180 (5)
C(2)[a]	−0.020 (5)	C(9)[a]	0.011 (5)
C(3)[a]	0.002 (5)	C(10)[a]	0.023 (5)
C(4)[a]	−0.009 (5)	O(1)	0.972 (6)
C(5)[a]	−0.018 (5)	O(2)	−0.986 (24)
		H(1)	0.02 (1)
Porphyrin Core II			
Equation of Plane: $0.2692x - 0.8436y + 0.4647z = 2.4549$			
Atomic Out-of-Plane Distances (Å)			
N(1)[a]	0.153 (4)	C(6)[a]	0.066 (5)
N(2)[a]	−0.130(4)	C(7)[a]	−0.078 (5)
C(1)[a]	0.031 (5)	C(8)[a]	−0.116 (5)
C(2)[a]	0.018 (5)	C(9)[a]	0.025 (5)
C(3)[a]	0.022 (5)	C(10)[a]	0.017 (5)
C(4)[a]	−0.023 (5)	O(1)	0.987 (6)
C(5)[a]	−0.052 (5)	O(2)	−0.986 (24)
Pyrrole Ring N(1):			
Equation of Plane: $0.2830x - 0.7804y + 0.5575z = 3.3213$			
Atomic Out-of-Plane Distances (Å)			
N(1)[a]	0.009 (4)	C(7)[a]	0.009 (5)
C(1)[a]	0.003 (5)	C(18)[a]	−0.004 (5)
C(6)[a]	−0.011 (5)	O(1)	0.712 (6)
Pyrrole Ring N(2):			
Equation of Plane: $-0.2545x + 0.85524y - 0.4516z = -2.3394$			
Atomic Out-of-Plane Distances (Å)			
N(2)[a]	0.000 (4)	C(9)[a]	0.007 (5)
C(3)[a]	−0.004 (5)	C(10)[a]	−0.007 (5)
C(4)[a]	0.004 (5)	O(2)	0.95 (2)

[a] Defining atoms for plane (includes primed counterparts in porphyrin planes).

bound to N(2$^{\mathrm{i}}$). This disorder was not unexpected. The location of the oxygen atom at the porphyrin core has little effect on the external shape of the molecule. Since the external shape is involved in the intramolecular forces that determine the placement of molecules within the crystal, this disorder is entirely reasonable. Unfortunately, however, it masks fine details of the structure.

The molecule, except for the methyl groups and the oxygen atom, is nearly planar. Table IV gives the equation of the least-squares plane constructed using C(2), C(5), the pyrrole ring containing N(2) and their primed counterparts. The out-of-plane distances of all core atoms are also listed in Table IV.

The N–O distance in the dominant orientation (1.398 (7) Å) falls within the range of distances (1.28–1.44 Å) found for variously substituted pyridine *N*-oxides.[8,9] The oxygen atom is 0.97 (1) Å above the plane given in Table IV. The pyrrole ring containing N(1), while planar, is tipped by 6.1° out of the porphyrin plane described above. Nevertheless, the oxygen atom does not lie within the plane of this pyrrole ring. The angle between the N–O vector and the pyrrole ring to which it is attached is 149.8°. This contrasts to the situation in pyridine *N*-oxide where the oxygen atom lies in the plane of the aromatic ring.[8,9] The size and orientation of the thermal elipsoid of N(1) suggest that it may be pulled out of the pyrrole plane toward the oxygen atom, but the disorder in the structure partly masks this distortion.

The two hydrogen atoms bound within the central cavity of the porphyrin were located. In the predominant orientation they are bound to N(2) and N(2$^{\mathrm{i}}$) and lie within the plane of the porphyrin. Figure 3 shows some of the details of the geometry of this portion of the molecule. The distances suggest significant hydrogen bonding between these protons and the oxygen atom. These data indicate that the porphyrin *N*-oxide has the structure **3** rather than the alternative, hydroxylamine structure **4**.

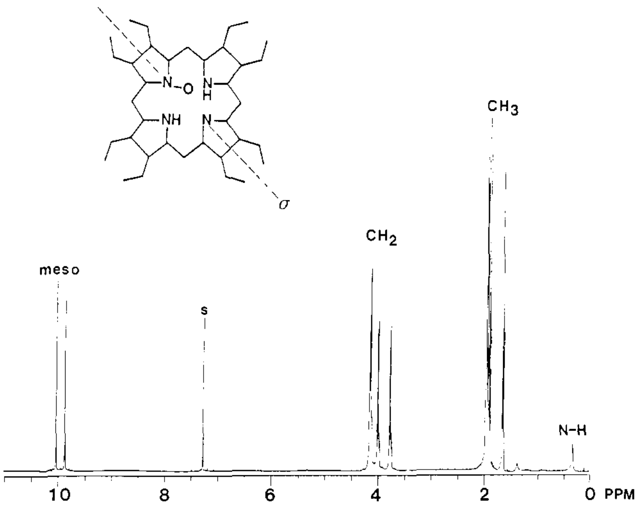
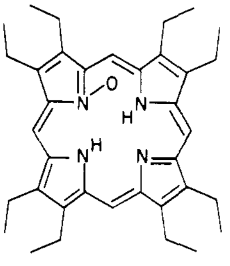


Figure 4. 500-MHz ^{1}H NMR spectrum of octaethylporphyrin *N*-oxide in chloroform solution.



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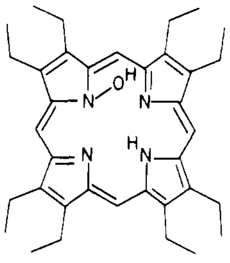

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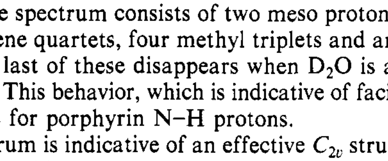
The ethyl groups on the porphyrin periphery all appear normal. The methyl and methylene hydrogens are staggered. The arrangement of four adjacent ethyl groups pointing toward one side of the porphyrin plane while the other four ethyl groups lie on the opposite side has been seen in other structural studies including the parent, octaethylporphyrin.[10]

Solution Structural Dynamics Inferred from the ^{1}H NMR Spectrum of Octaethylporphyrin *N*-Oxide. The 500-MHz ^{1}H NMR spectrum of the porphyrin *N*-oxide is shown in Figure 4. At 23 °C the spectrum consists of two meso proton resonances, four methylene quartets, four methyl triplets and an N–H resonance. The last of these disappears when D_2O is added to the NMR tube. This behavior, which is indicative of facile exchange, is diagnostic for porphyrin N–H protons.

The spectrum is indicative of an effective C_{2v} structure for the porphyrin *N*-oxide. We propose that the higher symmetry apparent at 23 °C in solution results from free rotation of the ethyl groups and a fluctional process, porphyrin inversion. The latter involves rapid movement of the oxygen atom through the center of the porphyrin as shown in eq 1. Variable-temperature studies should be capable of detecting this process. The diagnostic feature involves the behavior of the diastereotopic methylene protons. In the noninverting structure, there should be eight magnetically inequivalent methylene protons, since the asymmetry about the core N_4 plane renders the two protons of each methylene group nonequivalent. The temperature dependence in the methylene resonances is shown in Figure 6. The two upfield methylene



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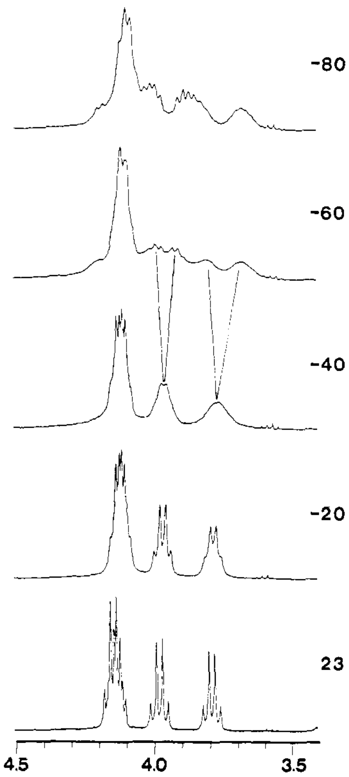

Figure 5. Variable-temperature 360-MHz ^{1}H NMR spectra of octaethylporphyrin in dichloromethane solution in the region of the methylene protons.

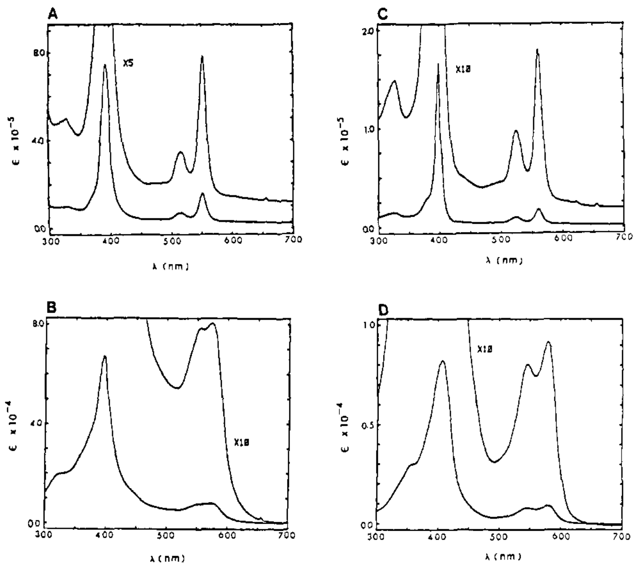

Figure 6. Electronic spectra A, nickel(II) octaethylporphyrin; B, nickel octaethylporphyrin *N*-oxide; C, copper(II) porphyrin; D, copper(II) porphyrin *N*-oxide.

resonances clearly show broadening and eventual splitting upon cooling. These changes are reversed upon warming. We take these observations to be indicative of slowing of the porphyrin inversion. Unfortunately, the other methylene resonances are not resolved clearly enough for us to confirm that all groups behave similarly. However, comparison with the spectrum of the nickel(II) complex (vide infra) is clear evidence for a nonstatic structure in solution. The cause of the rapid porphyrin inversion can be traced to the strain and crowding present at the center of the porphyrin. Conjugated heterocyclic *N*-oxides like this would prefer to have the oxygen atom within the plane of the pyrrole ring. This would allow N(1) to retain its expected sp^2 hybridization. The crowded core, which must accommodate the two protons as well, does not allow for this.

The temperature dependence of the ^{1}H NMR spectrum cannot be explained on the basis of simple interconversion between **3** and **4**. A process which renders the protons in each methylene group equivalent must make each face of the porphyrin equivalent. This can be accomplished only by allowing the oxygen atom to pass from one face to the other via porphyrin inversion. While proton transfer from nitrogen to oxygen may facilitate porphyrin inversion by opening up the porphyrin core to allow the oxygen to pass through, proton rearrangement alone cannot account for the spectra changes to show in Figure 5.

The porphyrin *N*-oxide has been heated to 90 °C in toluene solution without observing any change in its NMR spectrum. Consequently, at least on the NMR time scale the oxygen atom remains firmly bound to one nitrogen and is not free to move between different nitrogen atoms.

Characterization of the Nickel(II) and Copper(II) Complexes. Nickel(II) and copper(II) are readily inserted into octaethylporphyrin *N*-oxide to give the red crystalline complexes. They have moderate solubility in chloroform, dichloromethane, and toluene, and good thermal and air stability. Their compositions are confirmed by elemental analysis. For the nickel complex field desorption mass spectroscopy shows only a cluster of peaks due to the *N*-oxide complex and a less intense cluster due to nickel(II) octaethylporphyrin.

The electronic spectra of the porphyrin *N*-oxide complexes are presented and compared with those of their porphyrin counterparts in Figure 6. There are clear differences between related pairs of spectra. In particular, the porphyrin *N*-oxide complexes show broader absorption features with correspondingly lower absorbances than do their porphyrin counterparts. Nevertheless, the porphrin *N*-oxide complexes do have spectral characteristics which are porphyrin-like in nature with a prominent Soret peak at ca. 400 nm and weaker α and β bands in the visible region. These characteristics suggest that the basic conjugative pattern of porphyrins is retained in the *N*-oxide.

The infrared spectra of the porphyrin *N*-oxide complexes, which are given in the Experimental Section are distinct from their porphyrin counterparts. However, it has not been possible to unambiguously identify features diagnostic of the presence of a N–O–M unit. Similarly, a characteristic N–O absorption has not been found in the infrared spectrum of octaethylporphyrin *N*-oxide.[7]

The ^{1}H NMR spectrum of nickel(II) octaethylporphyrin *N*-oxide is indicative of a diamagnetic complex with C_s symmetry. The spectrum consists of two equally intense *meso*-proton resonances at 9.78 and 9.58 ppm, a complex methylene region and four methyl triplets. The methylene and methyl regions are shown at the top of Figure 7. The complex methylene region is simplified in the two-dimensional map shown in Figure 7. The cross peaks show that each methyl group 1, 2, and 4 is coupled to two of the methylene protons. For methyl group 3 the coupling to methylene protons is present but the resolution of the two methylene protons is low. Cross peaks also show pairwise coupling among the eight methylene resonances. This is clearest for the two highest and two lowest field pairs of peaks but it also holds for the more closely spaced peaks at 3.8 ppm when the spectrum is magnified. These observations are entirely in accord with the C_s structure shown for this complex with freely rotating ethyl groups. The oxygen atom is located on one side of the porphyrin plane in an N–O–Ni unit. Since the spectrum is unchanged on warming to 90 °C, there is no evidence for porphyrin inversion up to that temperature on the NMR time scale. Given the probable dimensions of the N_4ONi unit, it is an unlikely process.

The preparation of nickel(II) octaethylporphyrin *N*-oxide completes the series of nickel compounds which have O, NR,[11] or CR_2[12,13] units as well as a nickel atom sitting within a porphyrin. The existence of these materials and their considerable thermal

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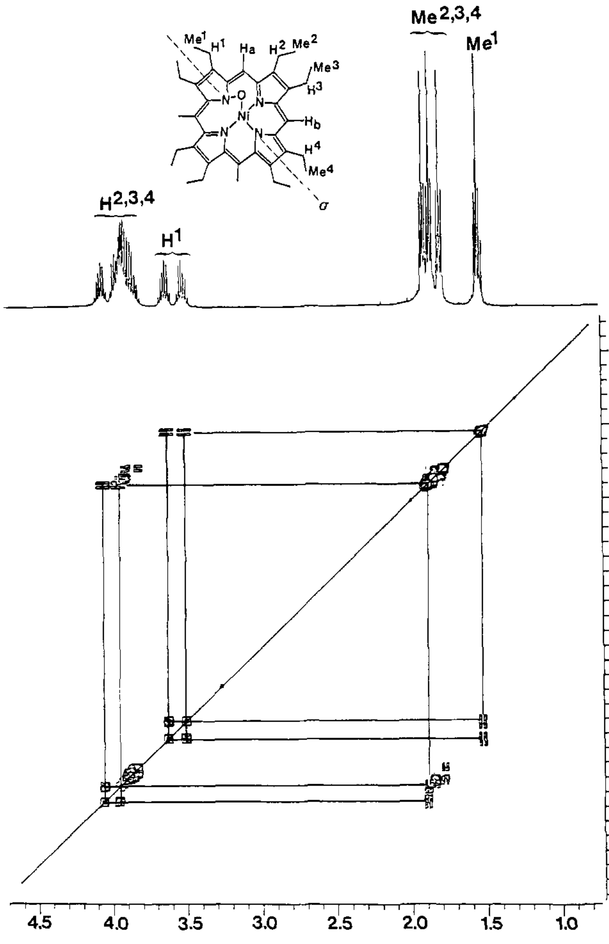
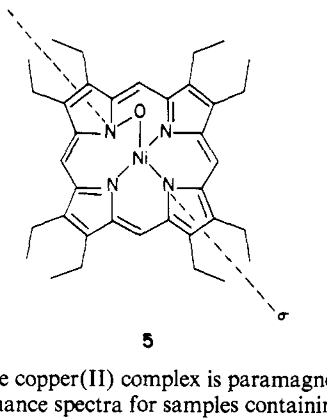


Figure 7. 500-MHz ^{1}H NMR spectrum of nickel(II) octaethylporphyrin N-oxide (3.8 mg, 1 mL $CDCl_3$). Top: normal methylene and methyl region. Bottom: contour plot of the correlation spectrum (COSY). Cross peaks indicating coupled spin in two of the four ABX_3 (ethyl) groups are shown with solid lines. The 2-D correlation map is composed of a 128 × 1024 data point spectrum of 16 transients, each incremented by 500 μs. A 5-s delay was allowed between each pulse sequence. The data were acquired with quadrature phase detection, zero filled twice in the t_1 dimension and symmetrized.

stability indicates the remarkable flexibility of the porphyrin core for expansion. The diamagnetism of the nickel complex suggests that it resides in a four-coordinate, nearly planar (rather than tetrahedral) environment. By analogy with the known structures of ((tosylamino)tetraphenylporphinato)nickel(II)[11] and ((ethoxycarbonyl)carbenetetraphenylporphinato)nickel(II),[12] the nickel coordination sphere in the porphyrin N-oxide complex is believed to be bonded to the three normal pyrrole nitrogen atoms and the oxygen atom as shown in **5**.



5

As expected, the copper(II) complex is paramagnetic. Relevant electron spin resonance spectra for samples containing 99.8% ^{63}Cu (spin $^{3}/_{2}$) are shown in Figure 8. The top trace shows the spectrum obtained from solution while the lower shows the anisotropic spectrum obtained from a sample doped into octaethylporphyrin N-oxide. The spectra are typical for planar copper(II) complexes. Relative to copper(II) octaethylporphyrin, the hyperfine couplings for copper and nitrogen are reduced in magnitude. The relevant parameters are: copper(II) octaethylporphyrin N-oxide; g_{iso}, 2.082; $A_{iso}(^{63}Cu)$, 77.0 G; $A_{iso}(^{14}N)$, 13.7 G; $g_{\parallel}$, 2.196; $A_{\parallel}(^{63}Cu)$, 166 G; $A_{\parallel}(N)$, 11.5 G. Copper(II) octaethylporphyrin: g_{iso}, 2.098; $A_{iso}(^{63}Cu)$, 90.5 G; $A_{iso}(^{14}N)$, 16.3 G; $g_{\parallel}$, 2.192; $A_{\parallel}(^{63}Cu)$, 195 G; $A_{\parallel}(^{14}N)$, 14.2 G.

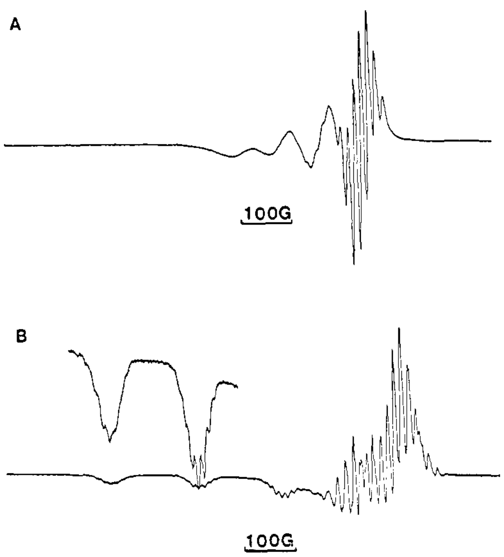


Figure 8. Electron spin resonance spectra of copper(II) octaethylporphyrin N-oxide: A, Isotropic spectrum obtained from toluene solution at 23 °C; B, Anisotropic spectrum obtained from a 1% sample doped in octaethylporphyrin N-oxide at 23 °C.

The pattern of nitrogen hyperfine coupling in the porphyrin N-oxide complex is significant since in both solutions and in the polycrystalline sample only seven lines are seen due to hyperfine interaction with nitrogen. Consequently, it appears that the unpaired spin is interacting with three, nearly equivalent nitrogen nuclei rather than with four nitrogens which is the usual case for porphyrins and phthalocyanines where a nine-line pattern is observed.[14,15] We take this to be a further indication that this complex has a structure analogous to **5** with a weaker interaction, if any, between the copper and the one pyrrole nitrogen which is bound to oxygen.

Further studies of the reactivity of these complexes as oxidizing agents as well as the interaction of other metal ions with the porphyrin N-oxide are in progress.

Experimental Section

Preparation of Compounds. Octaethylporphyrin N-oxide was prepared by using maleic peracid as oxidant according to the procedure of Bonnett and co-workers.[7] Dichloromethane was purified by washing with aqueous sodium bicarbonate, drying over anhydrous sodium sulfate and distillation.

Nickel(II) Octaethylporphyrin N-Oxide. Two milliliters of a methanol solution which had been successively saturated with ammonia and nickel(II) acetate hydrate was added to a solution of 50 mg of octaethylporphyrin N-oxide which was dissolved in 60 mL of dichloromethane. The mixture was heated under reflux under an argon atmosphere for 24 h. The solution was cooled and the solvent was removed at reduced pressure. The solid residue was dissolved in 50 mL of dichloromethane. The red solution was washed two times with 20-mL portions of 2 N aqueous ammonia and 20 mL of water. The solution was concentrated to 10 mL under vacuum and applied to a dry silica gel column (2 × 8 in.). The column was eluted with 50% hexane/dichloromethane to give a pink fraction which contained 12 mg of nickel(II) octaethylporphyrin. Further elution with dichloromethane, utilizing pressure to speed the elution and thereby lessen decomposition, produced a red fraction which

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Table V. Summary of Crystallographic Data for Octaethylporphyrin *N*-Oxide

formula	$C_{36}N_4H_{46}O$
fw	550.80
crystal system	triclinic
space group	$P\bar{1}$
based on conditions	no conditions
crystal dimensions, mm	0.26 × 0.15 × 0.08
crystal color and habit	dark red–purple petals
a, Å (140 K)	7.612 (3)
b, Å	9.740 (4)
c, Å	10.566 (4)
α, deg	91.61 (3)
β, deg	98.49 (3)
γ, deg	108.43 (3)
Z	1
V, Å^3	732.7 (5)
d (140 K)$_{\text{calcd}}$ g/cm^3	1.25
radiation	Mo Kα (λ = 0.71069 Å); graphite monochromator
linear absorption coeff, cm^{-1}	0.71
temp, K	140
instrument	Syntex P2$_1$; modified LT-1 low temp apparatus
scan speed, deg/min	4
scan width, deg	1.5
type of scan	ω
offset for backgrounds, deg	±1.0
2θ range, deg	0–45
range of transmission factors	0.98–1.00
octants	$h \pm k \pm l$
variables	207
data/variable ratio	7.7
programs	SHELXTL, Version 4
check reflections	2 measd every 200 reflctns
no. of unique data	1917
no. of data $I \geq \sigma(I)$	1588
$R(F)$	0.068
$R_w(F)$, $w = [\sigma^2(F) + 0.00075F^2]^{-1}$	0.062
largest Δ/σ	−0.025 for U_{22} of C(15)

was recovered after vacuum evaporation of the solvent. Recrystallization of this solid from dichloromethane/methanol produced 40 mg (76%) of the desired substance. Anal. Calcd for $C_{36}H_{44}N_4NiO$: C, 71.18; H, 7.30; N, 9.22. Found: C, 70.87; H, 7.31; N, 9.31. Field disportion mass spectrum: m/e, exptl intensity (calcd intensity) 606, 100 (100); 607, 44.7 (42.5); 608, 48.8 (54.6); 609, 19.1 (20.7); 610, 8.3 (4.2); 611, 2.0 (0.6); 612, 1.3 (1.8) as well as a cluster of peaks at and above 580 (relative observed intensity 44) due to nickel(II) octaethylporphyrin. Infrared spectrum (Nujol mull): 1315 w, 1366 w, 1292 w, 1261 w, 1175 w, 1150 w, 1140 w, 1106 w, 1050 m, 1015 m, 950 w, 830 w, 825 m, 815 w, 740 m, 730 m, 715 s, cm^{-1}.

Copper(II) Octaethylporphyrin *N*-Oxide. This complex was prepared by the route described for its nickel(II) analogue with the following modifications. The initial metalation was achieved within 3 h at room temperature. The column chromatography was performed on neutral alumina using dichloromethane followed by 5% methanol in dichloromethane as eluents. The yield was 70%. Anal. Calcd for $C_{36}H_{44}N_4CuO$: C, 70.62; H, 7.24; N, 9.15. Found: C, 70.42; H, 7.13; N, 9.26. A sample of this complex which was enriched in ^{63}Cu was prepared from ^{63}CuO (99.8% Oak Ridge) which was converted into its acetate and then incorporated into the porphyrin. Infrared spectrum (Nujol mull): 1317 w, 1267 w, 1180 m, 1146 m, 1053 m, 1020 m, 952 w, 890 w, 870 w, 840 w, 830 w, 820 w, 730 m, 715 s.

Physical Measurements. Infrared spectra were recorded from Nujol mulls using a Perkin-Elmer 180 spectrometer. ^{1}H NMR spectra were recorded at 360 or 500 MHz using Nicolet NT 360 or NT 500 Fourier transform spectrometers operating in the quatrature mode. Electronic spectra were obtained by using a Hewlett-Packard 8456 A spectrometer. Electron spin resonance spectra were collected on a Varian E4 spectrometer.

X-ray Crystallography. A suitable crystal of octaethylporphrin *N*-oxide was grown from a saturated 1:1 toluene–hexane solution. The solution and some additional solid were placed in a vertically aligned glass tube (5 mm × 30 cm). The bottom of the tube was warmed to ca. 60 °C. After a 2-week period crystals had grown near the top of the tube.

A summary of crystal data and data collection parameters is provided in Table V. The structure was solved in space group $P\bar{1}$ using direct methods.[16] Since the porphyrin is required to possess a center of symmetry, at least a 50–50 disorder of the single oxygen atom was expected. Due to the pseudo-4-fold symmetry of the porphyrin ring, the extreme of 25–25–25–25 disorder was a distinct possibility. However, from examination of difference maps it was clear that an intermediate situation existed. Thus, the site for O(1), bonded to N(1), has a higher occupancy than the alternative site filled by O(2), which is bonded to N(2).[17] In order to describe the disorder due to the presence of only one oxygen atom in two sets of two equivalent sites, refinement was carried out by using occupancy factors of $k/2$ for O(1) and $(1 - k)/2$ for O(2). In the final cycles of refinement all non-hydrogen atoms were assigned anisotropic thermal parameters except for these two oxygen atoms. Hydrogen atoms were refined at calculated positions using a riding model. A common isotropic thermal parameter for the methyl hydrogens was treated as a variable. It converged to a value of U = 0.042 (3) Å^2. Similarly, a common thermal parameter for the methylene hydrogen atoms converged to a value of U = 0.027 (3) Å^2. Thermal parameters for the meso hydrogen atoms were fixed at 1.2 times the isotropic thermal parameter of the bonded carbon atom at the time they were first included in the refinement. Only the higher occupancy hydrogen of the two possible hydrogens bonded to nitrogen was located on a difference map. It was refined with occupancy k using a fixed isotropic thermal parameter of 0.03 Å^2. The final value for k was 0.840 (7), indicating that the oxygen atom has a 42% occupancy of the O(1) site and a 8% occupancy of the O(2) site. Although the derived bond distance and angles associated with O(2) are of low accuracy, the reasonable overall geometry obtained confirms the model chosen to describe the oxygen and H(−N) positions. The final difference map contained no significant features.

Acknowledgment. We thank the National Institutes of Health (Grant GM 26266) for support and Professor A. L. Burlingame, Director, Mass Spectrometry Resource, UCSF for the field desorption mass spectra.

Registry No. Octaethylporphyrin *N*-oxide, 67514-01-6; nickel(II) octaethylporphyrin *N*-oxide, 95156-28-8; copper(II) octaethylporphyrin *N*-oxide, 95156-29-9; nickel(II) acetate, 373-02-4; copper(II) acetate, 142-71-2.

Supplementary Material Available: Tables of calculated hydrogen coordinates, anisotropic thermal parameters, and structure factors (12 pages). Ordering information is given on any current masthead page.

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(16) Refinement in the space group $P1$ was also attempted. A difficulty with refinement in $P1$ arises because the parameter/data ratio is low. Using the model described for $P\bar{1}$ (but removing all inversion symmetry), there are 396 parameters and 1588 reflections. Although a lower R value was obtained (R = 0.048), convergence was poor. For example, after the equivalent of five full-matrix cycles, the mean shift/esd was still greater than 10%. In addition, when hydrogens were allowed to refine freely, a number of their thermal parameters became either too large or too small. Most importantly, the O(1)/O(2) disorder persisted with an identical ratio, and the average geometry was essentially the same. We therefore report our results in $P\bar{1}$.

(17) Initially O(1) was assigned 0.50 occupancy. Refinement of all non-hydrogen atoms using isotropic thermal parameters converged with R = 0.116. A difference map computed at this stage showed "O(2)" at 0.92 eÅ^{-3}. Further refinement including hydrogens converged with R = 0.077. The hydrogen atoms were well-behaved and C–H distances ranged from 0.89 (4) to 1.07 (5) Å. The thermal parameters (U_{iso}) of the methylene hydrogens ranged from 0.018 to 0.046 Å^2 with an average of 0.030 Å^2; for methyl hydrogens the range was 0.023–0.069 Å^2 with an average of 0.044 Å^2. The largest peak on a difference map at this stage was "O(2)" at 0.92 eÅ^{-3}. Its position, 1.55 Å from N(2) and 1.28 Å from O(1), was a strong indication that it was not a hydrogen atom, but rather a disordered position for the oxide oxygen. However, refinement was attempted with it as a hydrogen, with the result that its thermal parameter was much too small (U_{iso} = 0.0024 Å^2). When refined as a disordered oxygen with occupancy $(1 - k)/2$, a normal thermal parameter resulted. It could not, however, be refined with anisotropic thermal parameters, or a nonpositive definite situation occurred. After O(2) was included, H(1) appeared as the largest peak on a difference map, with peak height corresponding to 0.49 eÅ from N(2). An atom of this size is not a good measure of occupancy and would not be expected to be well-behaved if both occupancy and thermal parameters were free. Therefore, it was refined by using free positional parameters but having its occupancy tied to two times that if O(1) and a fixed thermal parameter of 0.03 Å^2. Since there was nothing remarkable about the remaining hydrogen atoms, they were refined by using a riding model, as described. As a final check of the disorder model, the occupancies and thermal parameters of O(1), O(2), and H(1) were allowed to refine independently. The values obtained verify the model used O(1), k = 0.416 (8), U = 0.023 Å; O(2), k = 0.069 (9), U = 0.005 (12) Å^2; H(1), k = 0.90 (5), U = 0.106 (22) Å^2.