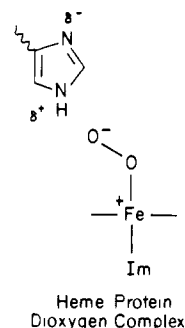


this imidazole and the $\text{Fe}^{\delta+}-\text{OO}^{\delta-}$ dipole of bound dioxygen. Thus, the proteins afford pocket environments similar to that provided by the "polar pocket porphyrin" described here.

We propose that both heme proteins and model compounds sometimes control the absolute affinities for both carbon monoxide and dioxygen using steric effects and differentiate carbon monoxide and dioxygen with "local polar effects" as previously discussed.^{5a,9,18,21}



It now appears that the affinities of CO and O₂ for heme compounds can be controlled independently and therefore materials could be designed to preferentially carry either CO or O₂.

Acknowledgment. We are grateful to the National Institutes of Health (Grant HL-13581) for support of this research.

Registry No. 1, 98677-60-2; 1P, 98652-49-4; 1⁺Cl⁻, 98652-50-7; 1-DCIm(CO), 98652-51-8; 1-DCIm, 98652-52-9; 1-CO, 98677-61-3; 1-Py(CO), 98677-62-4; DCIm-1-O₂, 98677-63-5; 1,5-dicyclohexylimidazole, 80964-44-9; 1-methylimidazole, 616-47-7; 3,5-pyridinedicarboxylic acid, 499-81-0; carbon monoxide, 630-08-0; pyridine, 110-86-1; 3,13-bis(3-aminopropyl)-8,18-bis(2-carbobenzyloxyethyl)-2,7,12,17-tetramethylporphyrin, 90552-83-3.

Supplementary Material Available: Eight figures comprising a titration of **1** with 1,5-dicyclohexylimidazole and seven plots of the rates of reaction of carbon monoxide or dioxygen with **1** (after carbon monoxide photolysis) as functions of concentrations of carbon monoxide, dicyclohexylimidazole, or dioxygen; slopes and intercepts of these plots are discussed in the text (9 pages). Ordering information is given on any current masthead page.

A Complex Containing a Ni-O Unit at the Center of a Porphyrin. The X-ray Crystal and Molecular Structure of the Nickel(II) Complex of Octaethylporphyrin *N*-Oxide Dianion

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Abstract: The structure of the nickel(II) complex of octaethylporphyrin *N*-oxide dianion has been determined by X-ray crystallography. The complex, C₃₆H₄₄N₄NiO, crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with two molecules per unit cell of dimensions $a = 10.610$ (2) Å, $b = 13.203$ (2) Å, $c = 13.199$ (1) Å, $\alpha = 115.49$ (1)°, $\beta = 102.33$ (1)°, $\gamma = 102.85$ (1)° at 140 K. The structure was refined to $R = 0.068$ for 518 parameters and 3639 reflections. The molecule contains a nickel ion bound to three of the four nitrogens and the oxygen in a somewhat distorted planar array (Ni-N: 1.922 (4), 1.929 (5), 1.900 (4) Å; Ni-O: 1.788 (4) Å). The distance from nickel to the remaining nitrogen of 2.489 (5) Å indicates there is no direct bond between these atoms. The N-O distance is 1.363 (6) Å. The oxygen atom lies 0.65 (1) Å above the porphyrin, and the pyrrole ring to which it is attached is tilted by 38.3 (4)° out of the porphyrin plane. The structure is disordered as a result of packing of pairs of major (82.6%) and minor (17.4%) forms. The basic structural features of the porphyrin core in the two forms are similar.

Experimental¹⁻⁴ as well as theoretical studies^{5,6} have suggested that the reactive forms of highly oxidized heme proteins involved in oxygen activation and heme destruction may contain structure

(1) Bonnett, R.; Ridge, R. J.; Appelman, E. H. *J. Chem. Soc., Chem. Commun.* **1978**, 310.

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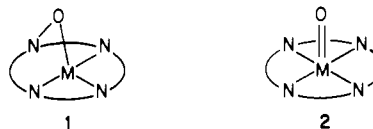
(3) Latos-Grazynski, L.; Cheng, R.-J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270.

(4) Olmstead, M. M.; Cheng, R. J.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 4143.

(5) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3771.

(6) Strich, A.; Veillard, A. *Nouv. J. Chim.* **1983**, *7*, 347.

1 (M = Fe) in which an oxygen atom is inserted into a N-Fe bond



as an alternate to the more conventional oxo structure **2**. Although a number of stable oxo metalloporphyrins that can serve as models for **2** (M = Fe) have been structurally characterized,⁷⁻¹⁰ no ex-

(7) Molinaro, F. S.; Ibers, J. A. *Inorg. Chem.* **1976**, *15*, 2278.

Table I. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA} \times 10^3$)

| atom | x | y | z | U |
|-------|------------|-----------|-----------|---------------------|
| Ni | 2952 (1) | 3691 (1) | 993 (1) | 29 (1) ^a |
| O(1) | 1624 (4) | 2633 (3) | 1048 (3) | 31 (2) ^a |
| O(2) | 1979 (24) | 1981 (21) | 132 (21) | 37 |
| N(1) | 1540 (5) | 1551 (4) | 176 (4) | 32 (2) ^a |
| N(2) | 1539 (4) | 3638 (3) | -234 (3) | 25 (2) ^a |
| N(3) | 4236 (4) | 5155 (3) | 1335 (4) | 37 (2) ^a |
| N(4) | 4239 (4) | 3456 (3) | 2070 (3) | 27 (2) ^a |
| N(5) | 980 (25) | 1802 (21) | 651 (21) | 37 |
| C(1) | 520 (5) | 931 (5) | -936 (5) | 26 (2) ^a |
| C(2) | -138 (5) | 1516 (5) | -1373 (4) | 26 (2) ^a |
| C(3) | 255 (5) | 2751 (4) | -1023 (4) | 34 (2) ^a |
| C(4) | 1598 (5) | 4562 (4) | -475 (4) | 27 (2) ^a |
| C(5) | 2785 (5) | 5569 (4) | -2 (4) | 34 (2) ^a |
| C(6) | 4019 (5) | 5830 (4) | 818 (4) | 36 (2) ^a |
| C(7) | 5551 (5) | 5748 (4) | 2167 (4) | 37 (2) ^a |
| C(8) | 6112 (5) | 5376 (4) | 2932 (4) | 34 (2) ^a |
| C(9) | 5496 (5) | 4311 (4) | 2897 (4) | 29 (2) ^a |
| C(10) | 4123 (5) | 2468 (4) | 2228 (4) | 37 (2) ^a |
| C(11) | 3267 (6) | 1292 (5) | 1451 (5) | 30 (3) ^a |
| C(12) | 2142 (6) | 821 (5) | 410 (5) | 28 (2) ^a |
| C(13) | 1412 (6) | -366 (5) | -612 (5) | 28 (3) ^a |
| C(14) | 444 (6) | -296 (4) | -1426 (5) | 27 (2) ^a |
| C(15) | 1756 (6) | -1463 (5) | -735 (5) | 31 (3) ^a |
| C(16) | 2929 (6) | -1627 (5) | -1236 (5) | 34 (3) ^a |
| C(17) | -535 (6) | -1303 (5) | -2662 (5) | 36 (3) ^a |
| C(18) | 125 (8) | -1652 (7) | -3600 (6) | 54 (4) ^a |
| C(19) | -519 (5) | 3180 (4) | -1688 (4) | 31 (2) ^a |
| C(20) | 305 (5) | 4290 (4) | -1359 (4) | 28 (2) ^a |
| C(21) | -1933 (5) | 2473 (5) | -2628 (5) | 39 (2) ^a |
| C(22) | -1893 (6) | 1696 (5) | -3876 (5) | 57 (3) ^a |
| C(23) | 14 (5) | 5114 (4) | -1802 (4) | 33 (2) ^a |
| C(24) | 570 (5) | 5050 (5) | -2790 (5) | 39 (3) ^a |
| C(25) | 5286 (5) | 6842 (4) | 1280 (4) | 37 (2) ^a |
| C(26) | 6227 (5) | 6794 (4) | 2111 (4) | 37 (2) ^a |
| C(27) | 5485 (6) | 7774 (4) | 897 (5) | 42 (3) ^a |
| C(28) | 5058 (7) | 8800 (5) | 1600 (5) | 56 (3) ^a |
| C(29) | 7713 (5) | 7631 (5) | 2859 (5) | 41 (3) ^a |
| C(30) | 7849 (7) | 8652 (6) | 4034 (6) | 64 (3) ^a |
| C(31) | 6141 (5) | 3907 (4) | 3656 (4) | 31 (2) ^a |
| C(32) | 5299 (5) | 2781 (4) | 3246 (4) | 33 (2) ^a |
| C(33) | 7457 (5) | 4639 (5) | 4718 (4) | 35 (2) ^a |
| C(34) | 7190 (6) | 5382 (5) | 5845 (5) | 46 (3) ^a |
| C(35) | 5515 (6) | 1978 (5) | 3744 (5) | 48 (3) ^a |
| C(36) | 4668 (7) | 1904 (7) | 4491 (7) | 74 (5) ^a |
| C(37) | -348 (31) | 1542 (26) | 92 (26) | 37 |
| C(38) | -1176 (32) | 1054 (30) | 693 (26) | 37 |
| C(39) | -132 (31) | 984 (26) | 1499 (26) | 37 |
| C(40) | 1228 (31) | 1531 (26) | 1537 (26) | 37 |
| C(41) | -704 (30) | 1986 (26) | -656 (25) | 37 |
| C(42) | 2578 (30) | 1653 (26) | 2225 (25) | 37 |
| C(43) | -2622 (31) | 694 (26) | 368 (26) | 37 |
| C(44) | -3377 (31) | 1318 (26) | 999 (25) | 37 |
| C(45) | -319 (30) | 634 (26) | 2420 (25) | 37 |
| C(46) | -300 (31) | 1272 (26) | 3635 (25) | 37 |

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ample of **1** has as yet been subject to thorough structural characterization. The only appropriate models for **1** which are available involve species with carbene^{2-4,11-14} or nitrene¹⁵ fragments in place of the isoelectronic oxo unit.

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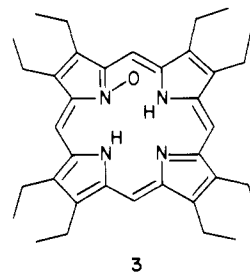
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(15) Callot, H. J.; Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4733.

Table II. Bond Lengths (\AA) for Nickel(II) Octaethylporphyrin *N*-Oxide

| Major (82.6%) Form | | | |
|------------------------|------------|-------------|------------|
| Ni-O(1) | 1.788 (4) | C(10)-C(11) | 1.376 (6) |
| Ni-N(2) | 1.922 (4) | C(10)-C(32) | 1.453 (7) |
| Ni-N(3) | 1.900 (4) | C(11)-C(12) | 1.391 (8) |
| Ni-N(4) | 1.929 (5) | C(12)-C(13) | 1.439 (6) |
| O(1)-N(1) | 1.363 (6) | C(13)-C(14) | 1.370 (9) |
| N(1)-C(1) | 1.375 (6) | C(13)-C(15) | 1.521 (10) |
| N(1)-C(12) | 1.370 (9) | C(14)-C(17) | 1.518 (6) |
| N(2)-C(3) | 1.395 (5) | C(15)-C(16) | 1.543 (10) |
| N(2)-C(4) | 1.380 (7) | C(17)-C(18) | 1.503 (11) |
| N(3)-C(6) | 1.363 (9) | C(19)-C(20) | 1.349 (7) |
| N(3)-C(7) | 1.373 (6) | C(19)-C(21) | 1.500 (6) |
| N(4)-C(9) | 1.375 (5) | C(20)-C(23) | 1.496 (9) |
| N(4)-C(10) | 1.391 (8) | C(21)-C(22) | 1.537 (8) |
| C(1)-C(2) | 1.366 (10) | C(23)-C(24) | 1.521 (9) |
| C(1)-C(14) | 1.437 (8) | C(25)-C(26) | 1.351 (9) |
| C(2)-C(3) | 1.419 (8) | C(25)-C(27) | 1.510 (10) |
| C(3)-C(19) | 1.447 (9) | C(26)-C(29) | 1.517 (6) |
| C(4)-C(5) | 1.395 (6) | C(27)-C(28) | 1.507 (9) |
| C(4)-C(20) | 1.452 (7) | C(29)-C(30) | 1.504 (8) |
| C(5)-C(6) | 1.370 (7) | C(31)-C(32) | 1.346 (7) |
| C(6)-C(25) | 1.454 (7) | C(31)-C(33) | 1.499 (6) |
| C(7)-C(8) | 1.385 (9) | C(32)-C(35) | 1.501 (10) |
| C(7)-C(26) | 1.448 (9) | | |
| C(8)-C(9) | 1.389 (8) | C(33)-C(34) | 1.518 (8) |
| C(9)-C(31) | 1.444 (9) | C(35)-C(36) | 1.486 (12) |
| Ni...N(1) | 2.489 (5) | | |
| Minor (17.4%) Fragment | | | |
| Ni-O(2) | 1.92 (2) | C(38)-C(39) | 1.41 (5) |
| O(2)-N(5) | 1.41 (4) | C(38)-C(43) | 1.41 (5) |
| N(5)-C(37) | 1.33 (4) | C(39)-C(40) | 1.44 (5) |
| N(5)-C(40) | 1.35 (5) | C(40)-C(42) | 1.45 (5) |
| C(3)-C(41) | 1.57 (4) | C(39)-C(45) | 1.51 (6) |
| C(10)-C(42) | 1.75 (6) | C(43)-C(44) | 1.41 (5) |
| C(37)-C(41) | 1.38 (6) | C(45)-C(46) | 1.45 (4) |
| C(37)-C(38) | 1.52 (6) | | |

In order to explore the chemical behavior of **1** and to provide stable structural models, we have undertaken a study of the interactions between metal ions and porphyrin *N*-oxides, **3**.^{1,16,17}



Recently we described the preparation and structural characterization in solution of the nickel(II) and copper(II) complexes of the dianion of octaethylporphyrin *N*-oxide.¹⁷ Here we report the results of an X-ray crystallographic study of the nickel(II) complex.

Results

The Molecular Structure. Table I gives the atomic positional parameters for the complex while Tables II and III contain interatomic distances and angles, respectively. Figure 1 shows a view of the entire molecule with the numbering scheme.

The structure is somewhat disordered (vide infra). The following discussion will focus on the major area form (82.6 (3)%) present. The minor form has similar structural features in all significant respects. In solution, where the ethyl groups are free

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

| Major (82.6%) Form | | | |
|------------------------|-----------|-------------------|-----------|
| O(1)-Ni-N(2) | 87.2 (2) | N(4)-C(9)-C(31) | 110.9 (5) |
| O(1)-Ni-N(3) | 162.1 (2) | N(4)-C(10)-C(11) | 128.7 (5) |
| O(1)-Ni-N(4) | 86.5 (2) | N(4)-C(10)-C(32) | 109.0 (4) |
| N(2)-Ni-N(3) | 94.2 (2) | C(8)-C(9)-C(31) | 124.5 (4) |
| N(2)-Ni-N(4) | 170.4 (1) | C(11)-C(10)-C(32) | 120.8 (6) |
| N(3)-Ni-N(4) | 94.0 (2) | C(10)-C(11)-C(12) | 128.9 (7) |
| Ni-O(1)-N(1) | 103.6 (4) | C(11)-C(12)-C(13) | 133.2 (6) |
| O(1)-N(1)-C(1) | 122.0 (5) | C(12)-C(13)-C(14) | 108.1 (6) |
| O(1)-N(1)-C(12) | 123.2 (5) | C(12)-C(13)-C(15) | 123.7 (5) |
| C(1)-N(1)-C(12) | 111.8 (4) | C(14)-C(13)-C(15) | 128.2 (4) |
| Ni-N(2)-C(3) | 130.6 (4) | C(1)-C(14)-C(13) | 108.5 (4) |
| Ni-N(2)-C(4) | 124.6 (2) | C(1)-C(14)-C(17) | 123.9 (6) |
| C(3)-N(2)-C(4) | 104.7 (4) | C(13)-C(14)-C(17) | 127.6 (6) |
| Ni-N(3)-C(6) | 126.6 (3) | C(13)-C(15)-C(16) | 114.2 (6) |
| Ni-N(3)-C(7) | 126.6 (4) | C(14)-C(17)-C(18) | 114.4 (5) |
| C(6)-N(3)-C(7) | 106.8 (4) | C(3)-C(19)-C(20) | 107.2 (4) |
| Ni-N(4)-C(9) | 124.5 (4) | C(3)-C(19)-C(21) | 125.6 (5) |
| Ni-N(4)-C(10) | 129.9 (3) | C(20)-C(19)-C(21) | 127.1 (6) |
| C(9)-N(4)-C(10) | 105.5 (4) | C(4)-C(20)-C(19) | 106.8 (5) |
| N(1)-C(1)-C(2) | 120.8 (5) | C(4)-C(20)-C(23) | 124.4 (4) |
| N(1)-C(1)-C(14) | 105.6 (6) | C(19)-C(20)-C(23) | 128.8 (4) |
| N(1)-C(12)-C(11) | 120.8 (5) | C(19)-C(21)-C(22) | 112.4 (5) |
| N(1)-C(12)-C(13) | 105.9 (5) | C(20)-C(23)-C(24) | 113.7 (5) |
| C(2)-C(3)-C(19) | 121.9 (4) | C(6)-C(25)-C(26) | 107.4 (6) |
| C(2)-C(1)-C(14) | 133.5 (4) | C(6)-C(25)-C(27) | 125.5 (5) |
| C(1)-C(2)-C(3) | 130.3 (4) | C(26)-C(25)-C(27) | 127.0 (4) |
| N(2)-C(3)-C(2) | 126.1 (5) | C(7)-C(26)-C(25) | 106.5 (4) |
| N(2)-C(3)-C(19) | 110.3 (5) | C(7)-C(26)-C(29) | 124.6 (6) |
| N(2)-C(4)-C(5) | 123.8 (5) | C(25)-C(26)-C(29) | 129.0 (6) |
| N(2)-C(4)-C(20) | 110.8 (4) | C(25)-C(27)-C(28) | 112.6 (6) |
| C(5)-C(4)-C(20) | 125.2 (5) | C(26)-C(29)-C(30) | 112.6 (5) |
| C(4)-C(5)-C(6) | 126.0 (6) | C(9)-C(31)-C(32) | 106.3 (4) |
| N(3)-C(6)-C(5) | 124.0 (5) | C(9)-C(31)-C(33) | 125.7 (5) |
| N(3)-C(6)-C(25) | 109.2 (5) | C(32)-C(31)-C(33) | 127.9 (6) |
| N(3)-C(7)-C(8) | 126.8 (6) | C(10)-C(32)-C(35) | 108.0 (5) |
| N(3)-C(7)-C(26) | 109.9 (5) | C(10)-C(32)-C(35) | 125.3 (4) |
| C(5)-C(6)-C(25) | 126.8 (6) | C(31)-C(32)-C(35) | 126.7 (4) |
| C(8)-C(7)-C(26) | 126.5 (4) | C(31)-C(33)-C(34) | 111.2 (5) |
| C(7)-C(8)-C(9) | 125.6 (4) | C(32)-C(35)-C(36) | 113.6 (6) |
| N(4)-C(9)-C(8) | 124.4 (5) | | |
| Minor (17.4%) Fragment | | | |
| O(2)-Ni-N(2) | 83.0 (9) | C(38)-C(39)-C(40) | 112.0 (3) |
| O(2)-Ni-N(3) | 155.9 (9) | C(39)-C(40)-C(42) | 131.0 (4) |
| O(2)-Ni-N(4) | 87.5 (9) | C(40)-C(42)-C(10) | 123.0 (4) |
| Ni-O(2)-N(5) | 105.0 (2) | C(39)-C(40)-N(5) | 104.0 (3) |
| O(2)-N(5)-C(37) | 121.0 (3) | C(38)-C(43)-C(44) | 127.0 (2) |
| O(2)-N(5)-C(40) | 121.0 (3) | C(37)-C(38)-C(43) | 125.0 (3) |
| C(37)-N(5)-C(40) | 115.0 (3) | C(39)-C(38)-C(43) | 134.0 (4) |
| N(2)-C(3)-C(41) | 123.0 (1) | C(39)-C(45)-C(46) | 135.0 (3) |
| C(19)-C(3)-C(41) | 111.0 (1) | C(40)-C(39)-C(45) | 121.0 (3) |
| C(3)-C(41)-C(37) | 129.0 (2) | C(38)-C(39)-C(45) | 126.0 (3) |
| C(41)-C(37)-C(38) | 131.0 (3) | N(5)-C(40)-C(42) | 125.0 (3) |
| N(5)-C(37)-C(38) | 108.0 (3) | N(5)-C(37)-C(41) | 119.0 (3) |
| C(37)-C(38)-C(39) | 101.0 (3) | | |

to rotate, the molecule has effective C_s symmetry with the mirror plane running through the N(1)-O-Ni-N(3) unit. In the solid, however, the orientations of the ethyl groups on the pyrrole rings containing N(2) and N(4) destroy this symmetry.

In accord with the diamagnetic nature of the molecule, the coordination about nickel is more nearly planar than tetrahedral. The four angles involving cis donors to nickel fall in the range 86.5–94.2°. However, the trans O-Ni-N(3) and N(2)-Ni-N(4) angles (162.1 (2)° and 170.4 (1)°, respectively) are somewhat less than the ideal 180°. The deviations from the least-squares plane of the NiN₃O unit show a slight distortion toward tetrahedral geometry with adjacent ligating atoms located on opposite sides of the mean plane: Ni, -0.074 (1) Å; O(1), 0.232 (4) Å; N(2), -0.175 (4) Å; N(3), 0.193 (4) Å; N(4), -0.176 (4) Å.

In the context of the two alternative structures, **1** and **2**, it is informative to compare the nickel(II) octaethylporphyrin *N*-oxide with oxo metal porphyrin structures. Some structural data on the latter are given in Table IV.^{7-10,18} The major difference

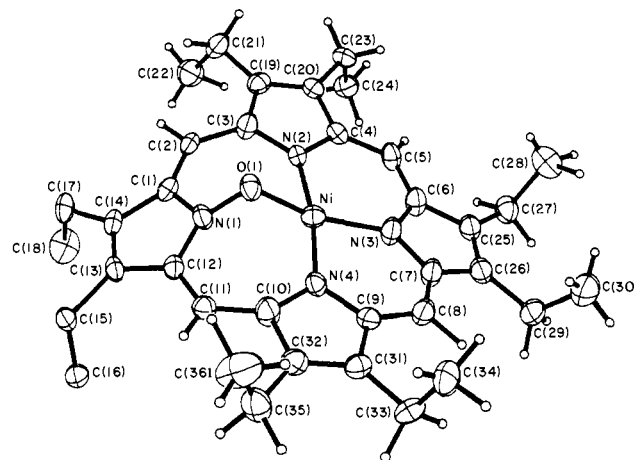


Figure 1. A view of the predominant form of the nickel(II) complex of octaethylporphyrin *N*-oxide. Anisotropic thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been given an arbitrarily smaller size. Hydrogen atoms on C(15)–C(18) were not located due to the disorder.

Table IV. Structural Parameters for Oxo Metal Porphyrins

| compound ^a | M-O, Å | M-N, Å | ref |
|---|-----------|-----------|-----|
| (OEP)V ^{IV} O | 1.620 (6) | 2.102 (6) | 7 |
| (TPP)Cr ^{IV} O | 1.572 (6) | 2.037 (7) | 10 |
| (TPP)Mo ^{IV} O | 1.656 (6) | 2.110 (6) | 9 |
| ((TPP)Mo ^V O) ₂ O | 1.707 | 2.094 | 8 |
| (base)PFe ^{IV} O ^b | ~1.6 | ~2.0 | 18 |

^aOEP is octaethylporphyrin dianion; TPP is tetraphenylporphyrin dianion. (Base)PFe^{IV}O includes [(*N*-methylimidazole)tetra-*m*-tolylporphyrin]Fe^{IV}O, tetramesitylporphyrin anion radical Fe^{IV}O, horseradish peroxidase compounds I and II. ^bFrom extended X-ray absorption fine structure studies.

between the two structural types is, of course, the location of the oxygen atom. In oxo metal porphyrins, the oxo ligand lies directly above the metal and above the center of the porphyrin, while in the nickel(II) complex of the porphyrin *N*-oxide, the oxygen atom lies to one side over a Ni...N vector. Additionally, there are significant differences in the metal–oxygen bond distances which reflect the presence of significant O→M π bonding in the oxo structure **2** and the lack of such multiple bonding in **1**. Although different metal ions with differing radii are involved, it is possible to make use of the M–N distances as an internal standard. Note that the Ni–O distance in nickel(II) octaethylporphyrin *N*-oxide is longer than any of the M–O distances in Table IV, while at the same time the Ni–N distances are all shorter than the M–N distances in the table. Thus although nickel(II) is smaller than the metal ions forming oxo structures, **2**, it has a longer M–O distance than do the oxo-type species.

While the molecule as a whole is not planar, the core, comprised of the three pyrrole rings containing N(2), N(3), and N(4) and the two connecting meso carbon atoms, is relatively flat. The plane and the deviations from it are shown in Figure 2. The pyrrole containing N(1) is tilted out and pushed down below it. The angle between the plane of the oxygenated pyrrole ring and the plane of the rest of the porphyrin is 38.3 (4)°.

It is instructive to compare the structure of the nickel complex with that of octaethylporphyrin *N*-oxide itself. The major difference resulting from the replacement of the two protons by the nickel involves the increased tilting of the oxygenated pyrrole ring in the nickel complex. The angle between the plane of that pyrrole and the plane of the other three pyrroles and meso carbons is only 6.1° in octaethylporphyrin *N*-oxide while it is 38.3° in the nickel(II) complex. As a result of that tilt the N–O bond lies closer to the oxygenated pyrrole plane in the complex (angle of 162.5°) than it does in the free porphyrin (angle of 149.8°). The N–O

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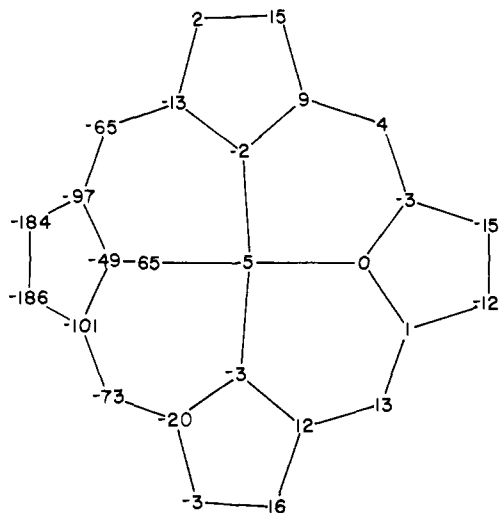


Figure 2. Diagram of the porphyrin core in an orientation corresponding to Figure 1. Each atom symbol has been replaced by a number representing the perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphyrin. This plane is based upon the location of the three unreacted pyrrole rings and the meso carbons connecting them.

distance in octaethylporphyrin *N*-oxide (1.398 (7) Å) is only slightly longer than it is in the nickel(II) complex (1.363 (6) Å).

In order to accommodate both an oxygen atom and nickel(II) ion within the center of the porphyrin, the molecule has had to suffer some strain. However, most of the bond lengths appear to fall within normal limits. The Ni–N bond lengths (1.900 (4), 1.922 (4), 1.929 (5) Å) are shorter than those in nickel(II) octaethylporphyrin (1.958 (2) Å in the triclinic form,¹⁹ 1.929 (3) Å in the tetragonal form²⁰), but shorter Ni–N distances have been observed in less constrained environments.^{21,22} The Ni–O distance (1.788 (4) Å) is comparable to the range of distances (1.80–1.84 Å) found in diamagnetic nickel(II) complexes of substituted salicylaldehydes.²² The N(1)–O distance of 1.363 (6) Å is within the range (1.28–1.44 Å) of N–O distances found in substituted pyridine *N*-oxides^{23,24} and is only slightly shorter than that in octaethylporphyrin *N*-oxide (1.398 (7) Å).¹⁷ However, there is noticeable strain in some of the bond angles. The trans O–Ni–N(3) and N(2)–Ni–N(4) angles (162.1 (2)° and 170.4 (1)°) are distorted from linearity. The nickel(II) ion is pushed toward the oxygen atom so that the O–Ni–N(2) and O–Ni–N(4) angles (87.2 (2)° and 86.5 (2)°) are compressed relative to the N(3)–Ni–N(2) and N(3)–Ni–N(4) angles (94.2 (2)° and 94.0 (2)°). The Ni–O–N angle (103.6 (4)°) is very sharply bent. For comparison, the corresponding angle in Ni(pyridine *N*-oxide)₆²⁺, where no strain should be present, is 119°. Finally the oxygenated pyrrole ring has been bent out of the porphyrin plane, a feature which is best appreciated by turning to Figure 2. However, although the N–O bond would ideally lie within the plane of the attached pyrrole ring, it is bent from that plane less (17.5°) in the nickel complex than it is in octaethylporphyrin *N*-oxide (30.2°).¹⁷

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(26) Inspection of the unit cell dimensions suggested the transformation to a monoclinic C lattice via the transformation (0,1,-1/0,1,1/0,0); however, the transformed coordinate system has two angles of 92 (1)° and 91 (1)° rather than 90° and cannot be satisfactorily indexed. Solution of the structure in *P*1 with *z* = 2 reveals a geometry in accord with the lack of any point symmetry.

Table V. Comparison of Distances and Angles in Nickel(II) Porphyrins with Oxene, Nitrene, or Carbene Units Inserted between One Ni–N Unit

| parameters | compounds | | |
|---------------------------|--------------------|---|--|
| | X = O ^a | X = NSO ₂ <i>p</i> -C ₆ H ₄ CH ₃ ^b | X = CHC(O)-OC ₂ H ₅ ^c |
| Bond Distances, Angstroms | | | |
| X–Ni | 1.788 (4) | 1.830 (4) | 1.905 (4) |
| N(2)–Ni | 1.922 (4) | 1.920 (3) | 1.911 (3) |
| N(3)–Ni | 1.900 (4) | 1.883 (4) | 1.910 (3) |
| N(4)–Ni | 1.929 (5) | 1.920 (4) | 1.928 (3) |
| N(1)···Ni | 2.489 (5) | 2.639 (4) | 2.409 (7) |
| N(1)–X | 1.363 (6) | 1.380 (5) | 1.409 (7) |
| Bond Angles, deg | | | |
| Ni–X–N(1) | 103.6 (4) | 109.7 (2) | 102.9 (2) |
| N(2)–Ni–N(4) | 170.4 (1) | 167.1 (2) | 167.1 (1) |
| N(3)–Ni–X | 162.1 (2) | 165.6 (2) | 160.4 (2) |

^a Octaethylporphyrin derivative. ^b Tetraphenylporphyrin derivative, data from ref 15. ^c Tetraphenylporphyrin derivative data from ref 11, renumbered to conform with numbering scheme used in Figure 1.

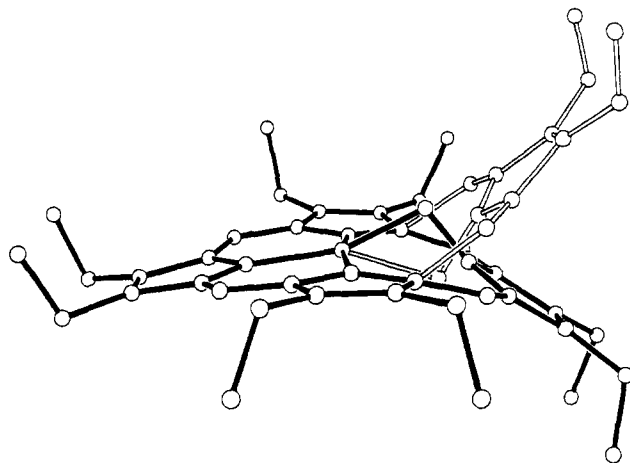


Figure 3. A diagram showing the disordered forms. The major form is shown with solid lines. The deviant part of the minor form is shown by open lines.

The structural changes in the basic porphyrin geometry are similar to those found for the related complexes which bear carbene or nitrene substituents in place of the oxygen atom. Table V contains some comparative data. Note the similarities in the N(2)–Ni–N(4) and X–Ni–N(3) angles and in the Ni–N distances. In all three cases the distortions of the core seem to have little effect on π -electron delocalization and on porphyrin core bond lengths. Using C_α and C_β to denote the α and β pyrrole carbons and C_m to denote the meso carbon atoms, the average values for bond lengths within the porphyrin core are the following: N– C_α , 1.378 Å; C_α – C_β , 1.447 Å; C_α – C_m , 1.394 Å; C_β – C_β , 1.354 Å. Not only are these similar to the values for the carbene and nitrene counterparts but also they are similar to those in the tetragonal and triclinic forms of nickel(II) octaethylporphyrin (N– C_α , 1.386, 1.376 Å; C_α – C_β , 1.449, 1.443 Å; C_α – C_m , 1.372, 1.371 Å; C_β – C_β , 1.362, 1.346 Å).¹⁹

Aspects of the Disorder. The molecular packing leads to disorder within the structure. In Figure 3 the predominant orientation (shown as solid lines) is compared with the minor orientation (shown as open lines). Both forms share a large common section involving the three pyrrole rings containing N(2), N(3), and N(4), the two connecting meso carbons, the six appended ethyl groups, and the nickel atom. The deviation of the minor form results from an effective inversion of the location of the oxygen atom, the pyrrole ring containing N(1), the attached ethyl groups, and meso carbons to the opposite side of the porphyrin. The minor form is present to the extent of 17.4 (3)%. The structurally significant features of the minor form are quite similar to those of the major form. However, the external shapes of the two forms are different.

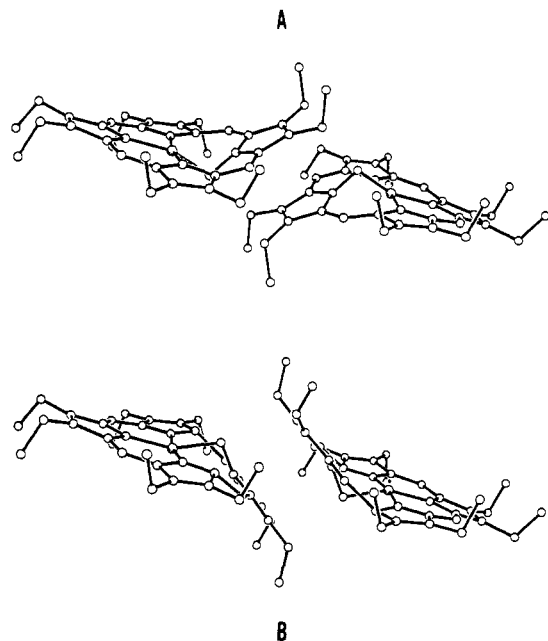


Figure 4. Diagram showing packing of the two forms about the center of symmetry at 0, 0, 0. In A the interaction of two of the major forms is shown, while B shows two of the minor forms.

In particular note that in the minor form six ethyl groups lie on one side of the porphyrin plane while two protrude on the opposite side. In the major form these groups are distributed so that four lie on either side. The difference in external shape of these forms is much greater than usually seen in disordered structures where disorder arises because the two orientations have rather similar external shapes.

In the present case the disorder results because *pairs* of the major form or *pairs* of the minor form can pack about a center of symmetry so that the external shapes of the two pairs are similar. The packing of these forms about the center of symmetry located at 0, 0, 0 is shown in Figure 4. The packing of the two major forms is shown in A at the top, while the corresponding packing of the two minor forms is shown in B at the bottom. While the interactions within the two pairs are clearly different, the external shape of each pair is relatively similar. Notice, however, that the major and minor forms cannot form a suitable pair: unreasonable interatomic contacts result.

Experimental Section

X-ray Data Collection. A sample of the nickel complex was prepared by insertion of nickel(II) into octaethylporphyrin *N*-oxide as described before.¹⁷ A suitable crystal of the complex was obtained only with great difficulty. A concentrated dichloromethane solution of the complex was placed in the bottom chamber of a glass tube (8 mm × 25 cm) which was constricted to 2 mm at 4 cm from the bottom of the tube. Acetonitrile was layered over this solution. After standing for 2 weeks at 5 °C, suitable crystals had grown at the constriction where the interface of the two solvents had been. Crystal data and the parameters for X-ray data collection are summarized in Table VI. The reported cell dimensions are based upon a least-squares fit of 24 centered reflections, including Friedel pairs, in the range 60° < 2θ < 89°. Neutral atom scattering factors and corrections for anomalous dispersion²⁷ were from common sources. A correction for absorption effects was made.²⁸ Solution of

Table VI. Summary of Crystallographic Data for Nickel(II) Octaethylporphyrin *N*-Oxide

| | |
|---|--|
| formula | C ₃₆ H ₄₄ N ₄ NiO |
| fw | 607.49 |
| crystal system | triclinic |
| space group | P1̄ (No. 2) |
| based on conditions | no conditions |
| crystal dimensions, mm | 0.075 × 0.17 × 0.30 |
| crystal color and habit | dark red plates |
| a, Å (140 K) | 10.610 (2) |
| b, Å | 13.203 (2) |
| c, Å | 13.199 (1) |
| α, deg | 115.49 (1) |
| β, deg | 102.33 (1) |
| γ, deg | 102.85 (1) |
| Z | 2 |
| V, Å ³ | 1523.5 (3) |
| d(140 K) _{calcd} , g/cm ³ | 1.32 |
| radiation | Cu Kα (λ = 1.54178 Å) |
| | graphite monochromator |
| linear absorption coefficient, cm ⁻¹ | 11.5 |
| temperature, K | 140 |
| instrument | Syntex P2 ₁ ; modified LT-1 low temp apparatus |
| scan speed, deg/min | 15 |
| scan width, deg | 1.3 |
| type of scan | ω |
| offset for background, deg | ±1.3 |
| 2θ range, deg | 0–130 |
| range of transmission factors | 1.08–1.16 |
| octants | h ± k ± l |
| variables | 518 |
| data/variable ratio | 7.7 |
| programs | SHELXTL, Version 4 |
| check reflections | 3 measd every 200 reflns |
| no. unique data | 5063 |
| no. data I > 2σ(I) | 3639 |
| R(F) | 0.068 |
| Rw(F) | 0.073 |
| largest Δ/σ | –0.025 for U ₂₂ of C(15) |

the structure followed from location of the nickel on a Patterson map. All atoms, including those of a disordered portion of the molecule and most of the hydrogen atoms, were located on difference Fourier maps. The hydrogen atoms of the two ethyl groups in the major form and all the hydrogen atoms of the minor form were not observed in difference maps and were not included in the refinement. The disordered part of the molecule was refined with a variable occupancy factor which converged with a value of 82.6 (3)% for the major form and 17.4 (3)% for the minor form. The carbon atoms, O(2), and N(5) of the minor form were refined with use of a fixed isotropic thermal parameter of 0.037 Å², which was the average value found from cycles in which the thermal parameters were not fixed. All non-hydrogen atoms of the major form were assigned anisotropic thermal parameters. The hydrogen atoms were refined with free positional parameters and with isotropic thermal parameters fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. The final discrepancy index and other indicators at convergence are given in Table VI.

Acknowledgment. We thank the National Institutes of Health (Grant GM 26266) for support.

Registry No. Nickel(II) octaethylporphyrin *N*-oxide, 95156-28-8.

Supplementary Material Available: Tables of refined hydrogen coordinates, bond distances and angles, anisotropic thermal parameter, and structure factors (27 pages). Ordering information is given on any current masthead page.

(27) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, (a) pp 99–101, (b) pp 149–150.

(28) The method obtains an empirical absorption tensor from an expression relating F_o and F_c . Hope, H.; Moezzi, B., unpublished results.