Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Insertion of Manganese and Cobalt into Octaethylporphyrin *N*-Oxide. Formation of Layered Diporphyrin Structures Joined through M-O-N Links

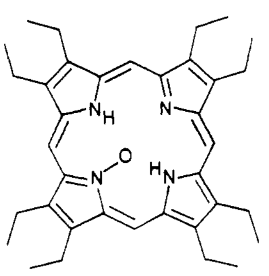
Ramesh D. Arasasingham, Alan L. Balch,* Marilyn M. Olmstead, and Mark W. Renner

Received May 28, 1987

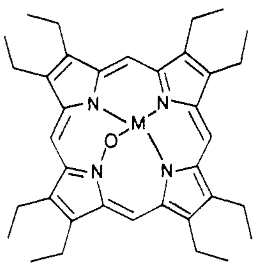
Treatment of octaethylporphyrin *N*-oxide (OEPH$_2$-*N*-O) with manganese(II) acetate or cobalt(II) acetate in ammoniacal methanol produces the cations [(OEP)M^{III}(OEPH$_2$-*N*-O)]$^+$ (OEP is octaethylporphyrin dianion), which have been isolated as the acetate, chloride, or hexafluorophosphate salts. [(OEP)Mn^{III}(OEPH$_2$-*N*-O)]CH$_3$COO·3CH$_2$Cl$_2$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a = 10.224 (2) Å, b = 12.329 (2) Å, c = 15.021 (2) Å, α = 77.18 (2)°, β = 86.88 (2)°, γ = 82.45 (2)°, and Z = 1 at 130 K. The structure was refined to R = 0.087 for 446 parameters and 4764 reflections. [(OEP)Co^{III}(NH$_3$)(OEPH$_2$-*N*-O)][CoCl$_4$]$_{0.5}$·1.5CH$_2$Cl$_2$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a = 18.566 (9) Å, b = 14.405 (9) Å, c = 28.688 (16) Å, β = 105.31 (2)°, and Z = 4, at 130 K. The structure was refined to R = 0.106 with 505 parameters and 4818 reflections. Both cations consist of a metal bound to a normal octaethylporphyrin with a monodentate O-bound OEPH$_2$-*N*-O as an axial ligand. The Mn(III) complex is five-coordinate (Mn–N = 1.977–2.125 Å, Mn–O = 2.070 Å with Mn 0.148 Å out of plane) while the Co(III) complex is six-coordinate with an axial ammonia ligand (Co–N$_{por}$ = 1.971–1.993 Å, Co–NH$_3$ = 1.961 Å, Co–O = 1.976 Å with Co 0.035 Å out of plane toward O). Spectroscopic data (UV/vis, ^{1}H NMR, and mass spectra) that confirm the structures are reported. The Mn(III) complex is high spin with μ = 4.70 μ_B at 296 K.

Introduction

Octaethylporphyrin *N*-oxide (**1**; OEPH$_2$-*N*-O) contains a crowded central core that is occupied by the two pyrrole protons and an oxygen atom that is bound to one pyrrole nitrogen (N–O distance 1.398 (7) Å) and placed 1.0 Å above the porphyrin plane.[1-3] Insertion of nickel(II) or copper(II) into **1** produces the complexes **2**,[3,4] in which the metal ions are bound to a nearly planar set of three nitrogen atoms and one oxygen atom. Complexes of type **2** are of current interest as models for the highly reactive and highly oxidized forms of heme enzymes and as potential intermediates in heme metabolism.[1-9] Because of the geometric constraints necessary to accommodate both a metal and an oxygen atom within the center of a porphyrin, there may be limitations on the size of metal ions that can assume structure **2**. In order to investigate the range of metal ions that can be inserted into **1**, we have extended our previous studies to the insertion of cobalt and manganese into **1**. Here we report the preparation and structural characterization of two related cations consisting of a porphyrin *N*-oxide bound to a normal metalloporphyrin (obtained by deoxygenation of **1**).



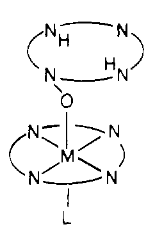
1



2

Results

Insertion Reactions. Treatment of **1** with cobalt acetate in methanol/ammonia at 25 °C using conditions similar to those reported for the formation of the copper complex **2b** produces the brown cation **4**, which has been isolated in 47% yield. This complex has also been prepared by adding **1** to CoOEP under aerobic conditions. The manganese complex **3** has been obtained under somewhat more vigorous metalation conditions (heating under reflux in methanol for 24 h) in 57% yield. Although divalent metal ions were used in the metalation procedure, the physical characteristics of the complexes indicated that Co(III) and Mn(III) compounds result. While we have not undertaken identification of the oxidizing agent, two likely sources are present. One is **1** itself, while the other is dioxygen, which is present at several stages during the preparation. However, it is certain that the normal porphyrin component of **3** and **4** comes from deoxygenation of **1**; the samples of **1** that we used contained less than 2% OEPH$_2$ as impurity by ^{1}H NMR spectroscopy. This deoxygenation process could serve to oxidize the divalent metal ions during the metalation process.



cation **3**, M = Mn, L = nothing
cation **4**, M = Co, L = NH$_3$

X-ray Crystal Structure of [(OEP)Mn(OEPH$_2$-*N*-O)](CH$_3$COO)·3CH$_2$Cl$_2$ (3). Table I gives the atomic positional parameters, while Tables II and III give selected interatomic distances and angles. The cation has a disordered structure. Figure 1 shows a view of the entire cation of **3**. It is composed of two porphyrin units packed about a center of symmetry. Figure 2 shows the porphyrin itself and our numbering system. The disorder involves the position of the manganese, oxygen, and two inner pyrrole protons. The manganese atoms are present in each porphyrin at 0.50 occupancy. The oxygen atom is also disordered and occupies sites O(1) and O(1)' with 0.50 occupancy. Finally, two hydrogen atoms (shown in Figure 1 but not shown in Figure 2) are bound to N(2) and N(4), and each has 0.50 occupancy. Combining these two units by placing one manganese in one

---

(1) Bonnett, R.; Ridge, R. J.; Appelman, E. H. *J. Chem. Soc., Chem. Commun.* **1978**, 310.
(2) Andrews, L. E.; Bonnett, R.; Ridge, R. J.; Appelman, E. H. *J. Chem. Soc., Perkin Trans. 1* **1983**, 103.
(3) Balch, A. L.; Chan, Y. W.; Olmstead, M. M.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2393.
(4) Balch, A. L.; Chan, Y. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 6510.
(5) Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J. C.; Mansuy, D. *J. Am. Chem. Soc.* **1981**, *103*, 2899.
(6) Latos-Grazynski, L.; Cheng, R. J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270.
(7) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3771.
(8) Olmstead, M. M.; Cheng, R. J.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 4143.
(9) Strich, A.; Veillard, A. *Nouv. J. Chim.* **1983**, *7*, 347.

0020-1669/87/1326-3562$01.50/0

Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[(OEP)Mn(OEPH_2\text{-}N\text{-}O)](CH_3COO)\cdot 3CH_2Cl_2$

	x	*y*	*z*	*U*
Mn	617 (1)	1194 (1)	−28 (1)	18 (1)^a
O(1)	−662 (5)	22 (4)	−19 (4)	17 (2)^a
N(1)	2050 (4)	−242 (4)	98 (3)	41 (2)^a
N(2)	540 (3)	992 (3)	1380 (2)	21 (1)^a
N(3)	−571 (3)	2616 (3)	−139 (2)	20 (1)^a
N(4)	1004 (3)	1545 (3)	−1425 (3)	23 (1)^a
C(1)	2500 (4)	−910 (4)	916 (3)	31 (2)^a
C(2)	2047 (4)	−775 (4)	1776 (3)	29 (2)^a
C(3)	1161 (4)	92 (4)	1997 (3)	27 (2)^a
C(4)	−273 (4)	1640 (4)	1864 (3)	23 (1)^a
C(5)	−1106 (4)	2579 (4)	1480 (3)	24 (1)^a
C(6)	−1251 (4)	3038 (4)	549 (3)	22 (1)^a
C(7)	−1006 (4)	3330 (4)	−931 (3)	23 (1)^a
C(8)	−543 (4)	3254 (4)	−1813 (3)	25 (1)^a
C(9)	403 (4)	2444 (4)	−2402 (3)	23 (1)^a
C(10)	1786 (4)	869 (4)	−1905 (3)	26 (2)^a
C(11)	2585 (4)	−113 (4)	−1528 (3)	29 (2)^a
C(12)	2751 (4)	−591 (4)	−611 (3)	29 (2)^a
C(13)	3685 (4)	−1535 (4)	−227 (3)	30 (2)*a*
C(14)	3539 (4)	−1729 (4)	695 (3)	29 (2)^a
C(15)	4708 (5)	−2123 (4)	−798 (4)	44 (2)^a
C(16)	5865 (6)	−1460 (6)	−1069 (5)	68 (3)^a
C(17)	4291 (5)	−2595 (4)	1417 (4)	42 (2)^a
C(18)	5364 (6)	−2137 (5)	1786 (4)	52 (2)^a
C(19)	754 (4)	214 (4)	2910 (3)	28 (2)^a
C(20)	−140 (4)	1164 (4)	2826 (3)	26 (2)^a
C(21)	1249 (5)	−558 (4)	3768 (3)	33 (2)^a
C(22)	2565 (5)	−274 (5)	4054 (4)	42 (2)^a
C(23)	−865 (5)	1632 (4)	3583 (3)	33 (2)^a
C(24)	−231 (6)	2539 (5)	3856 (4)	47 (2)^a
C(25)	−2139 (4)	4050 (4)	184 (3)	24 (1)^a
C(26)	−2000 (4)	4226 (4)	−739 (3)	25 (1)^a
C(27)	−2972 (4)	4751 (4)	741 (3)	29 (2)^a
C(28)	−2200 (5)	5534 (4)	1089 (4)	40 (2)^a
C(29)	−2653 (5)	5165 (4)	−1441 (3)	31 (2)^a
C(30)	−1786 (5)	6103 (4)	−1777 (4)	42 (2)^a
C(31)	873 (4)	2358 (4)	−2942 (3)	25 (1)^a
C(32)	1714 (4)	1391 (4)	−2871 (3)	26 (2)^a
C(33)	529 (5)	3248 (4)	−3790 (3)	34 (2)^a
C(34)	1207 (8)	4292 (5)	−3839 (4)	68 (3)^a
C(35)	2416 (5)	924 (4)	−3631 (3)	31 (2)^a
C(36)	3684 (6)	1415 (6)	−3962 (4)	61 (3)^a
C(37A)	5655 (12)	2910 (10)	4062 (8)	47 (3)
C(37B)	4901 (14)	3348 (12)	3813 (10)	62 (3)
Cl(1A)	6320 (2)	4009 (2)	3278 (2)	60 (1)
Cl(1B)	5970 (4)	4082 (4)	3105 (3)	49 (1)
Cl(2A)	4917 (3)	2074 (3)	3426 (2)	83 (1)
Cl(2B)	5305 (4)	1788 (3)	3601 (3)	40 (1)
Cl(3)	2481 (3)	−5402 (3)	−6043 (2)	51 (1)
Cl(4A)	3260 (7)	−3093 (5)	−6034 (5)	54 (1)
Cl(4B)	3651 (6)	−3476 (5)	−6202 (4)	57 (2)
O(2)	2812	−4462	−6444	69 (3)
O(3)	3946	−4594	−5380	89 (3)
C(38)	3311	−4168	−5844	54 (3)
C(39)	2859	−3056	−5817	45 (3)
C(40)	3177	−4691	−5428	181 (11)

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

Table II. Selected Bond Distances (Å)

$[(OEP)Mn^{III}(OEPH_2\text{-}N\text{-}O)]^+$		$[(OEP)Co(NH_3)(OEPH_2\text{-}N\text{-}O)]^+$	
Mn–O(1)	2.070 (6)	Co–O(1)	1.976 (7)
Mn–N(1)	2.125 (4)	Co–N(1)	1.971 (9)
Mn–N(2)	2.073 (4)	Co–N(2)	1.987 (9)
Mn–N(3)	1.977 (3)	Co–N(3)	1.993 (10)
Mn–N(4)	2.072 (4)	Co–N(4)	1.977 (9)
		Co–N(9)	1.961 (10)
N(1′)–O(1)	1.415 (6)	N(5)–O(1)	1.374 (12)

Table III. Selected Bond Angles (deg)

$[(OEP)Mn(OEPH_2\text{-}N\text{-}O)]^+$		$[(OEP)Co(NH_3)(OEPH_2\text{-}N\text{-}O)]^+$	
O(1)–Mn–N(1)	82.3 (2)	O(1)–Co–N(1)	82.8 (3)
O(1)–Mn–N(2)	93.7 (2)	O(1)–Co–N(2)	90.8 (3)
O(1)–Mn–N(3)	103.4 (2)	O(1)–Co–N(3)	96.4 (3)
O(1)–Mn–N(4)	96.7 (2)	O(1)–Co–N(4)	92.0 (3)
N(1)–Mn–N(2)	89.7 (1)	N(1)–Co–N(2)	90.8 (4)
N(1)–Mn–N(3)	174.3 (2)	N(1)–Co–N(3)	179.0 (4)
N(1)–Mn–N(4)	88.9 (1)	N(1)–Co–N(4)	90.1 (4)
N(2)–Mn–N(3)	89.7 (1)	N(2)–Co–N(3)	88.8 (4)
N(2)–Mn–N(4)	169.2 (2)	N(2)–Co–N(4)	177.2 (3)
N(3)–Mn–N(4)	90.7 (1)	N(3)–Co–N(4)	90.4 (4)
		N(9)–Co–N(1)	90.6 (4)
		N(9)–Co–N(2)	88.6 (4)
		N(9)–Co–N(3)	90.3 (4)
		N(9)–Co–N(4)	88.8 (4)
		N(9)–Co–O(1)	173.3 (4)
Mn–O(1)–N(1′)	126.3 (4)	Co–O(1)–N(5)	118.0 (5)

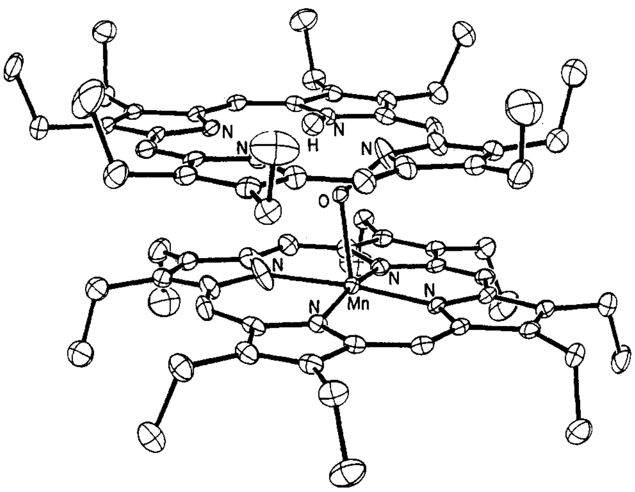


Figure 1. Complete view of $(OEP)Mn(OEPH_2\text{-}N\text{-}O)^+$ (cation of **3**).

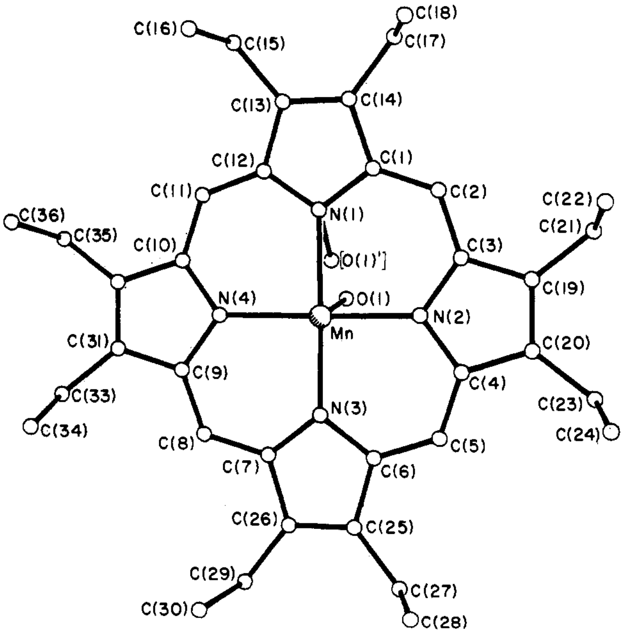


Figure 2. Drawing of the asymmetric unit in $(OEP)Mn(OEPH_2\text{-}N\text{-}O)^+$ (cation of **3**), showing the atomic numbering scheme. Due to the disorder, the Mn, O(1), and O(1)′ sites have each 0.50 occupancy. Two of these units are arranged about a center of symmetry to give the entire cation shown in Figure 1.

porphyrin and the two hydrogens in the other and using one oxygen position that forms an Mn–O bond to one ring and an N–O bond to the other gives the cation shown in Figure 1. Coexisting with this in the crystal are cations in which the manganese atom occupies the upper porphyrin, two hydrogen atoms occupy the lower porphyrin, and the oxygen atom occupies the alternate O site,

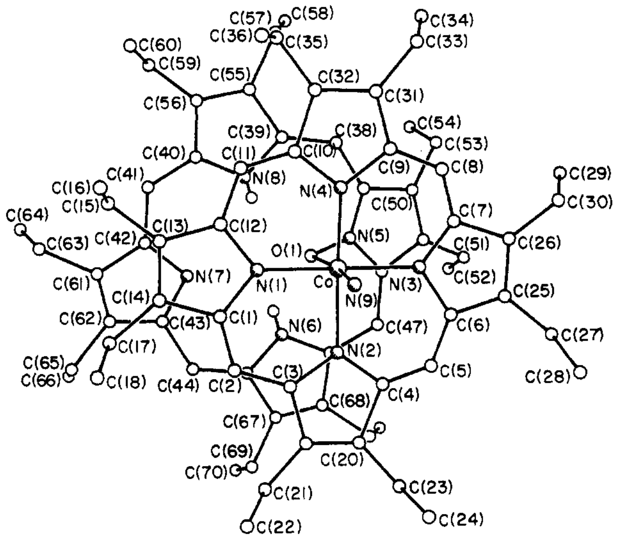


Figure 3. View of (OEP)Co(NH$_3$)(OEPH$_2$-*N*-O)$^+$ (cation of **4**), showing the atomic numbering scheme.

which is not shown in Figure 1.

The manganese atom is five-coordinate. Its coordination geometry can be compared to two other Mn^{III} complexes: high-spin five-coordinate (TPP)Mn^{III}Cl[10] (TPP is the anion of *meso*-tetraphenylporphyrin) and high-spin six-coordinate (TPP)-Mn^{III}(N$_3$)CH$_3$OH.[11] Three of the Mn–N distances in **3**, 1.977 (3), 2.073 (4), and 2.072 (4) Å, are similar to those in (TPP)-Mn^{III}Cl (range 1.992–2.022 Å)[10] and to those in high-spin six-coordinate (TPP)Mn(N$_3$)CH$_3$OH (range 2.020–2.046 Å).[11] The long Mn–N(1) distance, 2.125 (4) Å, is subject to special error because of the disorder and should not be taken as evidence of real abnormality. The Mn–O distance, 2.070 (6) Å, is shorter than the Mn–O distance in (TPP)Mn(N$_3$)CH$_3$OH, 2.329 Å.[11] The manganese ion sits 0.148 Å out of the plane of the four nitrogens. This is considerably less than the out-of-plane distance, 0.27 Å, found for (TPP)Mn^{III}Cl[10] and is remarkable in view of the close approach of the two porphyrin units in **3**. The N–O distance, 1.415 (6) Å, is similar to that in the porphyrin *N*-oxide **1**, 1.398 (7) Å.[3]

The porphyrin in **3** is relatively planar. The largest deviation from the least-squares plane of the porphyrin core is only 0.10 Å for C(31). In contrast, the porphyrin in (TPP)Mn^{III}Cl is markedly ruffled to give approximate S_4 symmetry with out-of-plane atomic deviations up to 0.47 Å.[10] In **3**, the pyrrole bearing the oxygen atom is only slightly tipped out of the plane of the porphyrin. The dihedral angle between these planes is 5.1°. This of course is subject to some error due to the disorder that packs this pyrrole ring and a normal Mn-bound pyrrole into the same site. The elongated thermal ellipsoid for N(1) results from this disorder. The separation between the two different nitrogen sites involved is not resolvable, but if it were resolved, the degree of tipping of the affected pyrrole would be greater. The observed degree of tipping is similar to that seen in the free *N*-oxide **1**, where the angle is 6.1°.[3] This produces some strain in the O–N–pyrrole ring angle since the oxygen atom lies 1.00 Å above the plane of the porphyrin *N*-oxide and 139.9° out of the plane of the associated pyrrole ring.

The presence of the center of symmetry requires the planes of the two porphyrins in **3** to be parallel. The separation between these two planes is 3.34 Å, which is close to the sum of the van der Waals radii of two aromatic rings (3.4 Å).

X-ray Crystal Structure of [(OEP)Co(NH$_3$)(OEPH$_2$-*N*-O)]-[CoCl$_4$]$_{0.5}$·3CH$_2$Cl$_2$ (4). Table IV gives the atomic positional parameters, while selected interatomic distances and angles are given in Tables II and III. Figure 3 shows the atomic numbering scheme used for the cation, which is shown in a projection that gives an idea of the extensive overlapping of the two porphyrin units. Figure 4 shows another view of the cation.

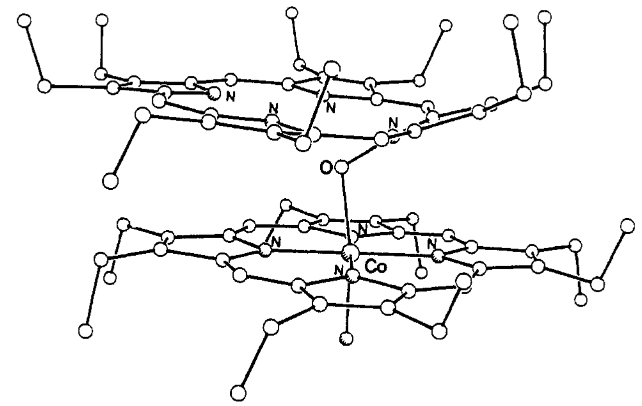


Figure 4. Perspective drawing of (OEP)Co(NH$_3$)(OEPH$_2$-*N*-O)$^+$ (cation of **4**).

The basic structure of **4** is similar to that of **3**. However, in **4** the cobalt ion is six-coordinate with an ammonia molecule and the *N*-oxide **1** as axial ligands. The Co–N distances range from 1.971 to 1.993 Å and are similar to those in (TPP)Co^{III}(pip)$_2$$^+$ (pip is piperidine), which has, like **4**, a planar porphyrin:[13] 1.974 (3), 1.983 (3) Å. In (TPP)Co^{III}(NO$_2$)(3,5-lutadine) with a ruffled porphyrin core the Co–N distances are shorter, 1.949 (2) and 1.958 (2) Å.[14] This has been attributed to packing effects.[14] The Co–N(9) (ammonia) distance in **4** is 1.961 (10) Å. This is shorter than the Co–N (piperidine) distance, 2.060 (3) Å in (TPP)-Co^{III}(pip)$_2$$^+$, as a result of the reduced steric interaction of the smaller axial ligand in **4**. The Co–O distance, 1.976 (7) Å, in **4** is shorter than the Mn–O distance, 2.070 (6) Å, in **3**. The cobalt ion is 0.035 Å out of the N$_4$ plane and set off toward the *N*-oxide ligand. The Co–N(NH$_3$) bond is nearly perpendicular to the CoN$_4$ plane. The cis N–Co–N angles range only from 88.8 to 90.8°. In contrast, the *N*-oxide ligand is slightly offset from the normal to the CoN$_4$ plane. The O(1)–Co–N(1) angle is compressed to 82.8 (3)° while the O(1)–Co–N(3) angle is opened to 96.4 (3)°; the other cis O(1)–Co–N angles are 90.8 (3) and 92.0 (3)°. The porphyrin bound to cobalt is planar, as can be seen from the data in Table IV.

The porphyrin *N*-oxide ligand is not so planar. The pyrrole ring bearing the oxygen atom is tipped out of the plane of the rest of the ring by 24.3°. Notice that this is greater than found either in the free *N*–oxide **1**[3] or in complex **3**. However, in both of these cases, disorder and packing forces present in the crystals probably result in an underestimation of the intrinsic degree of pyrrole tilting. As a result of this tilting, the N–O bond can be nearer to coplanarity with the pyrrole ring. The angle between the N–O bond and the associated pyrrole ring is 165.3°, significantly greater than that in **1**, 149.8°,[3] or in **3**, 139.9°. In unobstructed aromatic amine *N*-oxides like pyridine *N*-oxide the N–O bond lies within the plane of the aromatic moiety.[15] The N–O bond distance in **4**, 1.374 (12) Å, is comparable to the corresponding distances in **1**, 1.398 (7),[3] and in **3**, 1.415 (6) Å.

The porphyrin *N*-oxide ligand and the cobalt-bound porphyrin in **4** are nearly parallel, with a dihedral angle of only 2.2° between them. The average separation between these planes is 3.34 Å.

Spectroscopic Characterization. The electronic spectra of **3** and **4** are shown in traces A and B of Figure 5. The spectrum of **3** is compared to that of (OEP)Mn^{III}Cl shown in trace C while

---

(10) Tulinsky, A.; Chen, B. M. L. *J. Am. Chem. Soc.* **1977**, *99*, 3647.
(11) Day, V. W.; Stults, B. R.; Tasset, E. L.; Day, R. O.; Marianelli, R. S. *J. Am. Chem. Soc.* **1974**, *96*, 2650.
(12) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.
(13) Scheidt, W. R.; Cunningham, J. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8289.
(14) Kaduk, J. A.; Scheidt, W. R. *Inorg. Chem.* **1974**, *13*, 1875.
(15) Ulku, D.; Huddle, B. P.; Morrow, J. C. *Acta Crystallogr., Sect. B*: **1971**, *B27*, 432.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[(OEP)Co(NH_3)(OEPH_2\text{-}N\text{-}O)][CoCl_4]_{0.5}\cdot 1.5CH_2Cl_2$

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
Co(1)	2799 (1)	4391 (1)	3814 (1)	36 (1)^a	C(42)	1262 (7)	5060 (9)	1917 (5)	60 (4)
O(1)	2036 (4)	5286 (5)	3469 (3)	35 (3)^a	C(43)	2144 (8)	6100 (10)	2033 (5)	68 (4)
N(1)	2725 (5)	3943 (6)	3154 (3)	37 (2)	C(44)	2633 (8)	6798 (10)	2263 (5)	68 (4)
N(2)	3611 (5)	5262 (6)	3774 (3)	40 (2)	C(45)	2745 (7)	7105 (9)	2708 (4)	52 (3)
N(3)	2869 (5)	4866 (6)	4477 (3)	40 (2)	C(46)	2681 (7)	7265 (9)	3785 (5)	52 (3)
N(4)	2028 (5)	3488 (6)	3876 (3)	37 (2)	C(47)	2454 (7)	7178 (9)	3894 (5)	52 (3)
N(5)	1658 (5)	5790 (6)	3736 (3)	35 (2)	C(48)	1928 (6)	6560 (8)	3993 (4)	40 (3)
N(6)	2435 (5)	6805 (7)	3055 (4)	49 (3)	C(49)	1487 (7)	6706 (9)	4334 (5)	52 (3)
N(7)	1641 (5)	5640 (7)	2255 (4)	52 (3)	C(50)	956 (7)	6009 (8)	4257 (4)	48 (3)
N(8)	792 (5)	4687 (6)	2830 (3)	35 (2)	C(51)	1590 (7)	7495 (9)	4670 (5)	62 (4)
N(9)	3563 (5)	3455 (7)	4081 (4)	51 (3)	C(52)	1252 (8)	8388 (10)	4434 (6)	75 (4)
C(1)	3135 (6)	4269 (8)	2842 (4)	42 (3)	C(53)	320 (7)	5941 (10)	4481 (5)	62 (4)
C(2)	3661 (6)	4955 (8)	2954 (4)	44 (3)	C(54)	−378 (8)	6451 (10)	4172 (6)	72 (4)
C(3)	3893 (6)	5416 (8)	3377 (4)	44 (3)	C(55)	−137 (6)	3764 (8)	2925 (4)	46 (3)
C(4)	3987 (6)	5881 (7)	4125 (4)	40 (3)	C(56)	−113 (6)	3681 (8)	2455 (4)	43 (3)
C(5)	3852 (6)	6008 (8)	4565 (4)	45 (3)	C(57)	−682 (7)	3314 (9)	3163 (5)	56 (3)
C(6)	3329 (6)	5528 (8)	4737 (4)	42 (3)	C(58)	−1341 (9)	3922 (12)	3126 (6)	86 (5)
C(7)	2465 (6)	4547 (8)	4797 (4)	46 (3)	C(59)	−608 (8)	3090 (9)	2068 (5)	63 (4)
C(8)	1956 (7)	3834 (8)	4694 (4)	47 (3)	C(60)	−300 (8)	2139 (10)	2034 (6)	70 (4)
C(9)	1763 (7)	3344 (8)	4282 (4)	48 (3)	C(61)	1508 (9)	5119 (11)	1470 (6)	76 (4)
C(10)	1677 (6)	2831 (7)	3533 (4)	37 (3)	C(62)	2009 (9)	5727 (12)	1546 (6)	83 (5)
C(11)	1784 (6)	2753 (7)	3093 (4)	37 (3)	C(63)	1174 (11)	4512 (13)	1004 (17)	107 (6)
C(12)	2288 (6)	3254 (7)	2908 (4)	38 (3)	C(64)	488 (9)	4963 (12)	689 (6)	87 (5)
C(13)	2377 (6)	3144 (8)	2423 (4)	45 (3)	C(65)	2490 (12)	6055 (15)	1198 (8)	123 (7)
C(14)	2909 (6)	3790 (8)	2391 (4)	45 (3)	C(66)	2186 (11)	6897 (14)	973 (7)	112 (6)
C(15)	1994 (7)	2463 (8)	2063 (4)	51 (3)	C(67)	3239 (8)	7925 (11)	2973 (6)	72 (4)
C(16)	2312 (9)	1489 (11)	2127 (6)	82 (5)	C(68)	3192 (7)	8003 (9)	3397 (5)	60 (4)
C(17)	3249 (7)	3971 (9)	1963 (5)	60 (4)	C(69)	3746 (10)	8442 (13)	2681 (7)	98 (6)
C(18)	3961 (9)	3457 (12)	2003 (7)	87 (5)	C(70A)	3363 (15)	9336 (20)	2483 (10)	63 (7)
C(19)	4469 (6)	6127 (8)	3494 (4)	44 (3)	C(70B)	3197 (23)	8967 (29)	2177 (15)	115 (13)
C(20)	4536 (7)	6407 (8)	3941 (4)	47 (3)	C(71)	3568 (9)	8702 (11)	3763 (6)	84 (5)
C(21)	4882 (7)	6459 (9)	3144 (5)	53 (3)	C(72)	3076 (13)	9566 (15)	3729 (8)	133 (8)
C(22)	5532 (8)	5848 (11)	3120 (6)	76 (4)	Cl(1)	2673 (7)	2887 (9)	729 (4)	150 (6)^a
C(23)	5071 (7)	7094 (9)	4243 (5)	54 (3)	Cl(2)	2296 (8)	4379 (10)	38 (5)	160 (7)^a
C(24)	5765 (8)	6604 (10)	4566 (6)	72 (4)	C(73)	2908 (17)	3589 (21)	421 (11)	71 (8)
C(25)	3223 (6)	5671 (8)	5209 (4)	45 (3)	Co(2)	5511 (3)	459 (3)	4700 (2)	42 (2)^a
C(26)	2694 (7)	5064 (9)	5231 (5)	53 (3)	Cl(5)	5526 (6)	−307 (7)	4005 (4)	64 (4)^a
C(27)	3647 (7)	6327 (10)	5572 (5)	69 (4)	Cl(6)	6626 (7)	1172 (9)	4987 (5)	91 (6)^a
C(28)	4422 (9)	6011 (11)	5820 (6)	83 (5)	Cl(7)	4626 (7)	1609 (8)	4580 (4)	72 (5)^a
C(29)	1702 (10)	5403 (12)	5632 (6)	95 (5)	Cl(8)	4782 (4)	714 (4)	4867 (2)	80
C(30)	2388 (8)	4876 (11)	5686 (6)	77 (4)	Co(3)	4782 (4)	714 (4)	4867 (2)	80
C(31)	1237 (7)	2570 (8)	4180 (5)	51 (3)	Cl(9)	4624 (9)	474 (11)	5645 (6)	42 (4)
C(32)	1167 (6)	2274 (8)	3729 (4)	46 (3)	Cl(10)	3717 (12)	1401 (15)	4442 (8)	70 (6)
C(33)	862 (8)	2183 (10)	4547 (5)	69 (4)	Cl(11)	5870 (16)	1550 (20)	4914 (11)	97 (8)
C(34)	167 (9)	2627 (13)	4550 (7)	96 (5)	Cl(12)	4942 (11)	−627 (14)	4541 (7)	61 (5)
C(35)	730 (7)	1483 (8)	3465 (5)	54 (3)	Cl(3)	5914 (4)	7045 (4)	1825 (2)	117 (3)^a
C(36)	1200 (9)	598 (10)	3477 (6)	77 (4)	Cl(4A)	4740 (8)	5575 (13)	1704 (5)	188 (9)^a
C(37)	1053 (6)	5443 (7)	3868 (4)	37 (3)	Cl(4B)	4562	7305	1819	195 (16)^a
C(38)	570 (6)	4743 (7)	3633 (4)	37 (3)	C(74)	5163 (15)	6361 (19)	1486 (9)	136 (13)^a
C(39)	439 (6)	4407 (8)	3164 (4)	38 (3)	Cl(13)	3053	5754	128	128 (11)
C(40)	474 (7)	4256 (9)	2400 (4)	50 (3)	Cl(14)	3285	3901	640	105 (9)
C(41)	702 (7)	4419 (9)	1969 (5)	52 (3)	C(75)	3539	4610	211	28 (14)

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

the spectrum of **4** is compared to that of $(OEP)Co^{III}(py)Br$ shown in trace D. In the spectra of **3** and **4** it is not possible to resolve features characteristic of the *N*-oxide ligand **1**, which has a Soret peak at 395 nm and a broad absorption centered at 528 nm. The spectrum of **3** shows certain similarities to that of $(OEP)Mn^{III}Cl$, which displays a d-type hyperporphyrin spectrum.[16] There is a high-energy absorption at 362 nm compared to 356 nm in $(OEP)Mn^{III}Cl$, a very characteristic peak at 472 nm (vs. 470 nm in $(OEP)Mn^{III}Cl$) due to a ring to metal charge transfer,[17] and broad bands at 564 and 656 nm. The spectrum of **4**, like that of (OEP)Co(py)Br, is a normal porphyrin spectrum. However, the spectra of both **3** and **4** are broadened in comparison to the simpler model compounds. Such broadening is a common characteristic of cofacial porphyrin dimers[18-20] and is not unexpected in view of the proximity of the two porphyrin π-systems in **3** and **4**. This broadening is in part responsible for the inability to resolve separate absorbances for the two porphyrin components. The blue shift of the Soret peak in **3** relative to those in **1** and (OEP)Co(py)Br is also characteristic of cofacial diporphyrin units.[18-20] The position of the 362-nm band for **3** probably arises from a composite of a blue-shifted Soret band for the *N*-oxide axial ligand and the Soret band of manganese porphyrin.

The ^1H NMR spectrum of **4** is characteristic of a diamagnetic compound and provides firm evidence that the cation retains its structure in solution but that free rotation about the Co–O bond occurs. The spectrum shows three single-line resonances at 9.77, 9.15, and 7.85 ppm in a 2:4:2 intensity ratio. The most intense of these is assigned to the four meso protons of the cobalt-bound porphyrin. The other two arise from the two types of meso protons of the *N*-oxide ligand. The upfield shift of the one at 7.85 ppm

---

(16) Gouterman, M. *Porphyrins* **1979**, *3*, 1.

(17) Kobayashi, H.; Yanagawa, Y.; Osada, H.; Minami, S.; Shimizu, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1471.

(18) Kagan, N. E.; Mauzerall, D.; Merrifield, R. B. *J. Am. Chem. Soc.* **1977**, *99*, 5484.

(19) Chang, C. K. *Adv. Chem. Ser.* **1979**, *No. 173*, 162.

(20) Collman, J. P.; Chong, A. O.; Jameson, G. B.; Oakley, R. T.; Rose, E.; Schmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516.

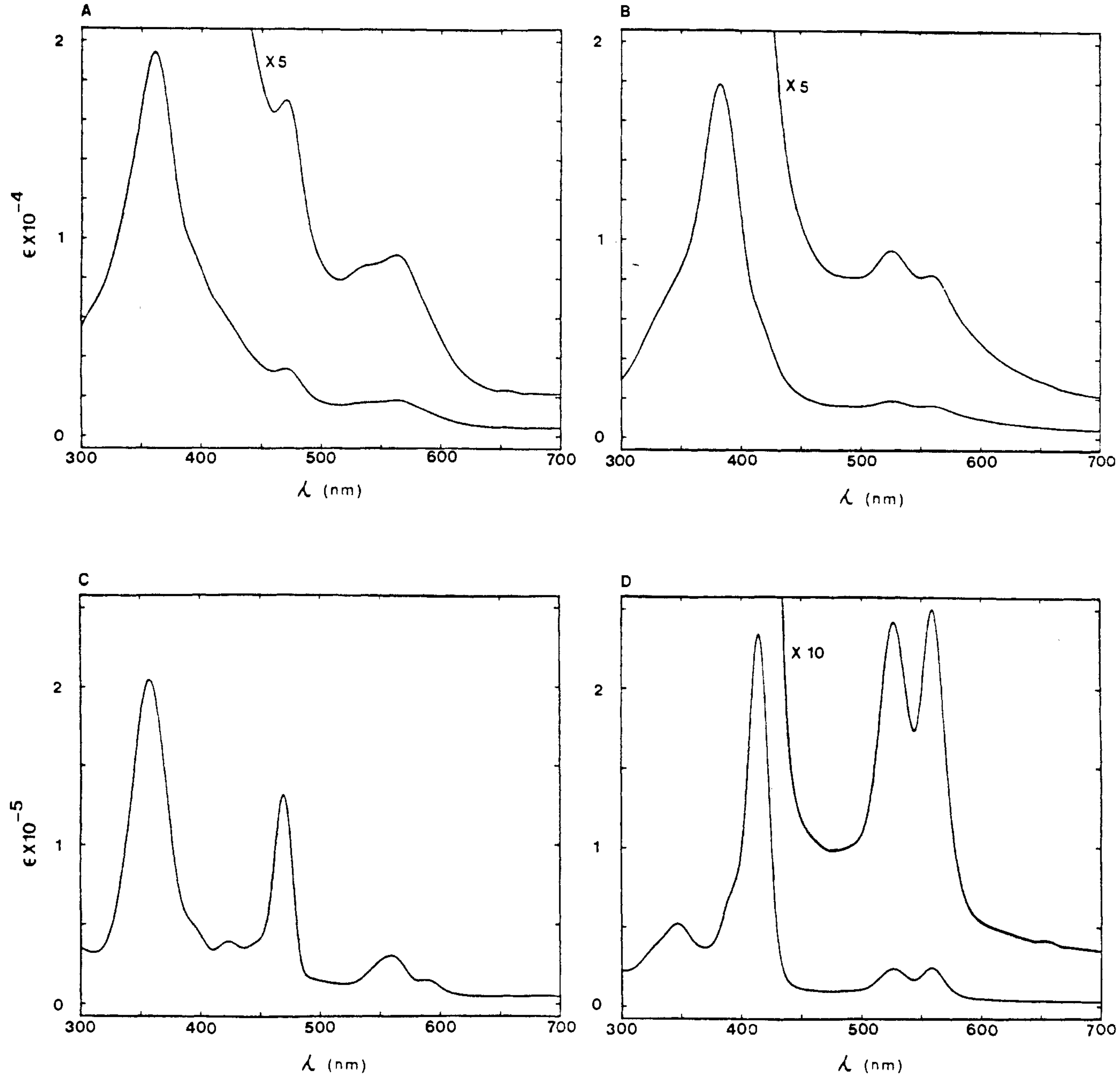


Figure 5. Electronic spectra: A, $(OEP)Mn^{III}(OEPH_2\text{-}N\text{-}O)^+$ (cation of **3**); B, $(OEP)Co^{III}(NH_3)(OEPH_2\text{-}N\text{-}O)^+$ (cation of **4**); C, $(OEP)Mn^{III}Cl$; D, $(OEP)Co^{III}(py)Br$.

relative to that of free **1**, which has meso resonances at 10.1 and 9.9 ppm,[3] arises from the ring current of the cobalt porphyrin and can be assigned to the meso protons nearest the *N*-oxide group (i.e., the hydrogens attached to C(38) and C(47) in Figure 3). A pair of upfield, single-line resonances at −9.02 and −9.21 ppm in a 2:3 intensity ratio are assigned to the NH protons of the *N*-oxide ligand and of the axial ammonia, respectively. When the NMR sample is shaken with D_2O, both of these resonances are diminished in intensity due to rapid and selective deuteriation. The rate of deuteriation of the ammonia protons is faster than for the *N*-oxide protons. The large upfield shifts of these resonances are caused by ring current effects. The complex methyl and methylene region is shown in Figure 6. Five methyl triplets are observed. The most intense is assigned to the methyl groups of the cobalt-bound porphyrin. The other four equally intense triplets arise from the four different methyl groups on the *N*-oxide ligand. These methyl groups are all coupled to pairs of methylene protons that appear in the 4.4–2.9 ppm region. All methylene groups are diastereotopic, since both porphyrin units lack a plane of symmetry. Thus for the cobalt-containing porphyrin there are two types of methylene protons although all eight methylene groups are equivalent. For the *N*-oxide ligand there are eight unique methylene protons arising from four different methylene groups. Selective decoupling experiments have allowed us to determine the interconnectings between resonances as shown by the connecting lines in Figure 6. Irradiation of the intense methyl triplet at 1.88 ppm produces the simplified pattern shown in the inset. This clearly reveals the AB doublet pattern for the methylene protons. Similar effects are seen for the other pairs of methyl and methylene groups.

Free rotation about the Co–O bond appears to persist down to −60 °C in chloroform. Restriction of rotation is expected to produce a more complex spectrum due to the low symmetry (idealized C_s at best) of the entire complex. However, the observed ^1H NMR spectrum shows no further broadening or splitting on cooling to −60 °C.

The manganese complex **3** is paramagnetic. Its magnetic moment measured in chloroform solution by the Evans technique[21] is 4.70 (10) μ_B. It follows the Curie law over the temperature

---

[21] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

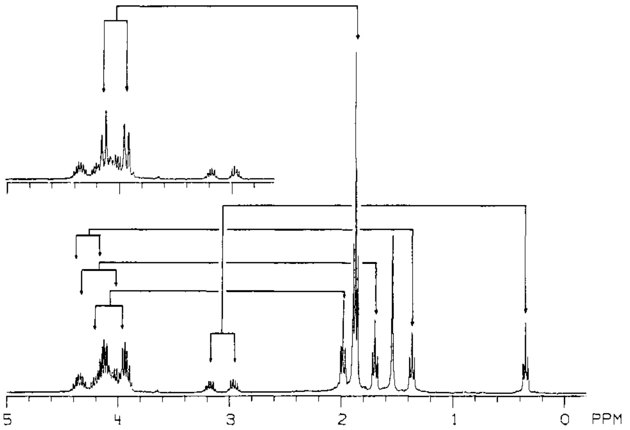


Figure 6. 360-MHz ^{1}H NMR spectrum of (OEP)Co^{III}(NH$_3$)(OEPH$_2$-*N*-O)PF$_6$ (4-PF$_6$) in chloroform-*d*, at 25 °C in the methylene and methyl region. The insert shows the offset of selective decoupling of the methyl resonance at 2.97 ppm. The results of other decoupling experiments are indicated by lines that connect the methyl resonances to the AB doublets, which result from decoupling.

296–213 K. This is consistent with an S =2 ground state, for which the anticipated spin-only value is 4.9 μ_B and is indicative of a high-spin Mn(III) complex. The ^{1}H NMR spectrum of **3** is very broad, as is characteristic of high-spin Mn(III) complexes.[22] An intense resonance at 3 ppm is assigned to the methyl protons, while broad resonances at 11, 17, and 22 ppm are probably due to methylene protons. For comparison, (OEP)Mn^{III}Cl has a methyl resonance at 3 ppm, a methylene resonance at 24 ppm, and a meso resonance at 53 ppm.[22]

The mass spectra of these compounds also provide confirmation of their composition. The normal electron-impact spectra show only peaks due to the metal–porphyrin fragment and the free porphyrin. However, the fast-atom-bombardment (FAB) spectra show clear evidence for the diporphyrin nature of **3** and **4**.[23,24] The FAB spectrum of **3** shows a parent weak at 1138 amu with a pattern of higher mass peaks totally consistent with the natural isotopic abundances expected. Other intense peaks occur at 588 and 535 amu, and these are assigned to MnOEP and OEPH$_2$, respectively. The FAB spectrum of **4** shows a higher mass peak at 1142 amu that can be assigned to the (**4** – NH$_3$) fragment, and the pattern of peaks is in total agreement with the expected natural isotopic abundances. Other intense peaks appear at 592, 552, and 535 amu and are assigned to CoOEP, OEP-*N*-O, and OEPH$_2$, respectively.

Discussion. There has been considerable attention given recently to the design and construction of molecules containing two porphyrin units. A variety of such compounds with organic functionalities connecting the porphyrin peripheries are now known, and these can be designed to accommodate a variety of spacings between the porphyrins.[25,26] Connections involving a central metal and its axial coordination are also possible. Among the best known of these are the μ-oxo dimers with an oxygen atom bridging two metalloporphyrins.[27] Other bridging groups (e.g., carbido and nitrido) can also serve to connect two porphyrins.[28,29] Direct metal–metal bonding also can produce diporphyrin molecules that necessarily must have close contacts between the porphyrin planes.[30,31] A group of phenolate-bridged porphyrins use a phenol as a meso peripheral substituent on one porphyrin to coordinate to the central metal ion of a second porphyrin.[32,33]

The M–O–N bridge found in **3** and **4** produces cations with unusually close contacts between the porphyrin planes. For comparison, in the μ-oxo dimer [(TPP)Mn^{IV}(N$_3$)]$_2$O the separation of the two porphyrin planes is 3.88 Å;[34] and in the metal–metal double-bonded dimer [(OEP)Ru]$_2$, which has a very short Ru–Ru distance of 2.408 (1) Å, the two porphyrins are 3.26 Å apart.[30] In [(TTOP)Fe]$_2$ [TTOP is the trianion of 5-(2-hydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin], the average perpendicular separation between porphyrin planes is 4.09 Å.[32] Factors contributing to the close proximity of porphyrins in **3** and **4** include the constraints of the M–O–N unit itself, the placement of Co and Mn relatively near the porphyrin plane, and the near planarity and lack of doming of the porphyrins themselves.

Oxygen atom transfer and subsequent dealkylation of *p*-cyano-*N*,*N*-dimethylaniline are catalyzed by cytochrome P450.[35] Iron(III) and manganese(III) porphyrins also catalyze oxygen atom transfer and dealkylation reactions in model systems.[36–38] Mechanistic studies have shown that complex formation between the metalloporphyrin and the amine *N*-oxide precedes the critical formation of the reactive oxometal species in these reactions. The cations of **3** and **4** can be taken as highly hindered models for the initial metalloporphyrin/amine *N*-oxide interaction. At this stage in **3** and **4** both the metal–oxygen and oxygen–nitrogen bonds appear to be normal single bonds. Additionally, the Co–O–N and Mn–O–N bond angles, 118.2 (6) and 126.3 (4)°, appear to be normal despite the congestion at the core of these cations. The Co–O–N angle in hexakis(pyridine *N*-oxide)cobalt(II), a cation with no apparent steric strain, is 119.5 (2)°.

Experimental Section

Preparation of Compounds. Octaethylporphyrin *N*-oxide was prepared by using maleic peracid as the oxidant according to the procedure of Bonnett and co-workers.[2] Dichloromethane was purified by washing with aqueous sodium bicarbonate, drying over anhydrous sodium sulfate, and distillation.

[(OEP)Co^{III}NH$_3$(OEPH$_2$-*N*-O)][CoCl$_4$]$_{0.5}$. Method 1. A methanol solution (2 mL) that had been successively saturated with ammonia and cobalt(II) chloride was added to a solution of 50 mg (0.09 mmol) of octaethylporphyrin *N*-oxide in 50 mL of dichloromethane. The mixture was stirred under an argon atmosphere for 1 h. The solvent was removed under reduced pressure and the solid material dissolved in 50 mL of dichloromethane. The resulting brown solution was washed three times with 20-mL portions of water and dried over anhydrous sodium sulfate. The solution was concentrated to 10 mL under vacuum and applied to a dry silica gel column (1 × 8 in). The column was eluted with dichloromethane to give a brown fraction of unreacted octaethylporphyrin *N*-oxide. Further elution with dichloromethane/5% methanol produced the dark brown [(OEP)Co^{III}NH$_3$(OEPH$_2$-*N*-O)][CoCl$_4$]$_{0.5}$ fraction, which was recovered after removing the solvent under reduced pressure. Recrystallization from dichloromethane/*n*-hexane produced 26 mg (0.02 mmol, 23%) of the desired substance. The electrical conductivity of the complex in dichloromethane solution (1 mM) is 22 Ω^{-1} m^2 mol^{-1}. When the complex is prepared as described above but ammonium hexafluorophosphate is used to precipitate the PF$_6^-$ salt of cation **4**, the infrared spectrum shows an absorbance at 840 cm^{-1} due to P–F stretching. The conductivity of **4**-PF$_6$ is 28 Ω^{-1} m^2 mol^{-1}. When it is prepared from cobalt acetate, a band appears at 1737 cm^{-1} due to acetate as the counterion.

Method 2. Cobalt(II) octaethylporphyrin (20 mg, 0.03 mmol) in

---

(22) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1975**, *97*, 5103.

(23) Barber, M.; Bordoli, R. S.; Elliot, G. J.; Sedgwick, R. D.; Tyler, A. N. *Anal. Chem.* **1982**, *54*, 645A.

(24) Kurlansik, L.; Williams, T. J.; Strong, J. M.; Anderson, L. W.; Campana, J. E. *Biomed. Mass Spectrom.* **1984**, *11*, 475.

(25) Dolphin, D.; Hiom, J.; Paine, J. B., III *Heterocycles* **1981**, *16*, 417.

(26) Baldwin, J. E.; Perlmutter, T. J. *Top. Curr. Chem.* **1984**, *121*, 181.

(27) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1.

(28) Mansuy, D.; Lecomte, J. P.; Chottard, J. C.; Bartoli, J. F. *Inorg. Chem.* **1981**, *20*, 3119.

(29) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623.

(30) Collman, J. P.; Barnes, C. E.; Sweptston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.

(31) Jones, N. L.; Carroll, P. J.; Wayland, B. B. *Organometallics* **1986**, *5*, 33.

(32) Goff, H. M.; Shimomura, E. T.; Lee, Y. J.; Scheidt, W. R. *Inorg. Chem.* **1984**, *23*, 315.

(33) Godziela, G. M.; Tilotta, D.; Goff, H. M. *Inorg. Chem.* **1986**, *25*, 2142.

(34) Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3964.

(35) Heimbrook, D. C.; Murray, R. I.; Egeberg, K. D.; Sligar, S. G.; Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1514.

(36) Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6123.

(37) Powell, M. F.; Pai, E. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3277.

(38) Dicken, C. M.; Lu, F.-L.; Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 5776.

(39) Bergendahl, T. J.; Wood, J. S. *Inorg. Chem.* **1975**, *14*, 338.

Table V. Crystal Data and Data Collection Parameters for **3** and **4**

	3	**4**
formula	$MnC_{77}H_{99}N_8O_3Cl_6$	$Co_{1.5}C_{73.5}H_{96}N_9OCl_5$
fw	1452	1387
color and habit	dark purple, brown parallelepipeds	dark brown prisms
space group	$P\bar{1}$	$P2_1/c$
a, Å	10.224 (2)	18.566 (9)
b, Å	12.329 (2)	14.405 (9)
c, Å	15.021 (3)	28.688 (16)
α, deg	77.18 (2)	
β, deg	86.88 (2)	105.31 (2)
γ, deg	82.45 (2)	
T, K	130	130
Z	1	4
cryst dimens, mm	0.62 × 0.35 × 0.18	0.87 × 0.50 × 0.37
d_{calcd}(130 K), g cm^{-3}	1.31	1.25
radiation; γ, Å	Mo Kα; 0.710 69	Mo Kα; 0.710 69
μ(Mo Kα), cm^{-1}	4.5	5.7
range of abs cor factors	1.09–1.16	1.20–1.36
scan method	ω	ω
2θ range, deg	0–50	0–45
hkl	$h,\pm k,\pm l$	$h,k,\pm l$
scan speed, deg min^{-1}	20	60 up to $\theta = 15.5°$; 15 at $\theta = 15–22.5°$
no. of reflns measd	6442	10 909
R(merge)	0.005	0.005
no. of unique data	6512	9542
no. of data considered obsd	4764 ($>2\sigma(I)$)	4818 ($>3\sigma(I)$)
no. of parameters refined	446	505
R	0.087	0.106
R_w	0.098	0.116
wt	$[\sigma^2(F)]^{-1}$	$[\sigma^2(F)]^{-1}$

dichloromethane (25 mL) and a solution of methanol saturated with ammonia and sodium acetate (2 mL) was treated with octaethylporphyrin *N*-oxide (19 mg, 0.04 mmol). The mixture was stirred under an argon atmosphere for 1 h. The solvent was removed under reduced pressure,and the residue was dissolved in dichloromethane, washed with water, and dried over anhydrous sodium sulfate. The filtered, concentrated solution was chromatographed on silica gel (1 × 8 in). After dichloromethane/1% methanol had eluted a small amount of octaethylporphyrin and octaethylporphyrin *N*-oxide, dichloromethane/5% methanol eluted the acetate salt of the main product (brown solution), which was recrystallized from dichloromethane/*n*-heptane (25 mg, 64%).

[(OEP)Mn^{III}(OEPH$_2$-*N*-O)][CH$_3$COO]. To a solution of octaethylporphyrin *N*-oxide (20 mg, 0.04 mmol) in dichloromethane (25 mL) was added 2 mL of a methanolic solution saturated with ammonia and manganese(II) acetate tetrahydrate. The mixture was refluxed under an argon atmosphere for 24 h. The solvent was removed under reduced pressure and the brown residue dissolved in 25 mL of dichloromethane. The solution was washed with water (20 mL × 3), dried over anhydrous sodium sulfate, and concentrated. Chromatogrpahy on silica gel (1 × 8 in.) gave octaethylporphyrin (eluted with dichloromethane), followed by octaethylporphyrin *N*-oxide (eluted with dichloromethane/2% methanol) and the brown [(OEP)Mn^{III}(OEPH$_2$-*N*-O)][CH$_3$COO] (eluted with dichloromethane/5% methanol). Recrystallization from dichloromethane/*n*-heptane gave 12.4 mg (23%) of the product. The infrared spectrum shows a band at 1734 cm^{-1} due to the acetate anion.

X-ray Crystallographic Studies. Suitable crystals of the cobalt and the manganese complexes were grown with great difficulty from a concentrated solution of the complex in dichloromethane. The solution was placed in the bottom of a glass tube (8 mm × 25 cm), and *n*-hexane was layered over this solution. After the mixture was allowed to stand for 6 weeks at 23 °C, suitable crystals appeared at the interface of the two solvents. All X-ray data were collected with a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device. Calculations were carried out on a Data General Eclipse computer with use of the SHELXTL, version 4, program system. Both structures were solved by the Patterson method. An absorption correction was applied.[40] Scattering factors for the neutral atoms and corrections for anomalous dispersion were from the usual source.[41] For both structures, hydrogen atoms were included in the refinements with use of a riding model in which idealized positions were recalculated with each least-squares cycle (C–H = 0.96 Å). Crystal data and data collection procedures for the two complexes are summarized in Table V.

Crystals of the cobalt species, **4**, diffract poorly at high diffraction angle, and in fact, the first data set collected had so many absent reflections that the structure could not be completely solved. A second data set was collected on a very large crystal with use of a fast scan speed (60° min^{-1}) out to 2θ of 30° and a 15° min^{-1} scan speed between 30 and 45° in 2θ. Of the 9542 unique data collected, 48% still had $I < 3\sigma(I)$. However, the remaining data were sufficient to locate all of the atoms of the cation, as well as three disordered molecules of dichloromethane and disordered $CoCl_4^{2-}$ moiety. One OEP ethyl group comprised of C(69) and C(70) is disordered and consists of a 50:50 mixture of two positions for C(70). A severe disorder problem with the anion involves two sites for a disordered $CoCl_4^{2-}$: Co(2), Cl(5), Cl(6), Cl(7), and Cl(8) at 0.33 occupancy share the region of the crystal lattice with Co(3), Cl(9), Cl(10), Cl(11), and Cl(12) at 0.17 occupancy. The tetrahedral geometry at Co and typical Co–Cl bond distances leave little doubt as to the identity of this anion. In addition, there are three disordered dichloromethane molecules with a total occupancy of 1.5 (0.50 for C(73), Cl(1), and Cl(2); 0.83 for C(74), Cl(3), and Cl(4); and 0.17 for C(75), Cl(13), and Cl(14)). The high final *R* value of 0.106 and the poor diffraction can be traced to the disorder present in this crystal. In the final difference map, the largest peak is 1.1 e Å^{-3}, 2 Å from a chlorine of the full dichloromethane. No spurious peaks are in the vicinity of the cation. In the final cycles of refinement, seven low-angle reflections, which appeared to be affected by extinction, were omitted. All atoms were assigned isotropic thermal parameters except cobalt, oxygen, and those chlorines with occupancies >0.33. The latter were refined with anisotropic thermal parameters.

The manganese complex, **3**, also suffers some disorder. First, the manganese atom and oxygen atom are disordered with respect to the center of symmetry and are therefore assigned 0.50 occupancies. That this is reasonable can be appreciated from a drawing of the cationic species and its space-filling requirements. It is also in keeping with the size of the thermal parameters for these atoms. In the final stages of refinement, the hydrogen atoms belonging to the pyrrole nitrogens of the *uncomplexed* ring were also located, and these were subsequently included in the refinement at 0.50 occupancy. The lattice also contains an acetate ion at half-occupancy (to balance charge); this site is shared with a molecule of dichloromethane. Although the acetate atomic positions could be deduced from a difference map, they could not be refined, and were included in the structure factor calculation with fixed positions as taken from the difference map. Another full molecule of dichloromethane is also present in the lattice; however, it also is disordered between two sites in a ratio of 0.67:0.33. In the final cycles of refinement, all the non-hydrogen atoms of the cation were assigned anisotropic thermal parameters.

Physical Measurements. ^{1}H NMR spectra were recorded at 360 MHz on a Nicolet NT360 Fourier-transform spectrometer. Electronic spectra were obtained by using a Hewlett-Packard 8456A spectrometer. FAB mass spectra were obtained on a VG Analytical ZAB-HS-2F double-focusing mass spectrometer using xenon as the fast atom beam and a mixture of dithiothreitol and dithioerythritol (3:1) as the liquid matrix.

Acknowledgment. This work was supported by the National Institutes of Health (Grant GM26226).

Registry No. 3(OAc)·3CH$_2$Cl$_2$, 109838-61-1; 4(CoCl$_4$)·1.5CH$_2$Cl$_2$, 109800-94-4; 4(PF$_6$), 109838-62-2; 4(OAc), 109786-99-4; OEPH$_2$-*N*-O, 67514-01-6; CoOEP, 17632-19-8.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths, bond angles, and hydrogen atom positions (11 pages); listings of structure factors for 3 and 4 (56 pages). Ordering information is given on any current masthead page.

---

(40) Program XABS by H. Hope and B. Moezzi. The method obtains an empirical absorption tensor from an expression relating F_o and F_c.

(41) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.