Prior to this work only the nickel complex of **1** had been prepared.[4] Generation of this complex from the free ligand gave a 3:1 ratio of *R,S,R,S* to *R,R,S,S* stereoisomers. The stability of these diastereomers had not been investigated. Formation of the copper complex apparently occurs with lower selectivity, ca. 5.5:4.5. Because of the difficulty of completely separating the two diastereomeric copper complexes, studies to determine the stability of the individual isomers toward isomerization have not yet been made. However, preliminary studies on the mixture suggest that both an acid-catalyzed and a thermally promoted isomerization can occur to shift the ratio toward the *R,R,S,S* stereoisomer. Curiously, prolonged exposure to aqueous acid appears to give exclusively the *R,R,S,S* stereoisomer but with substantial decomposition of the sample. Further studies of the trimethylcyclam complexes of copper, nickel, and zinc are under way.

Acknowledgment. Portions of this work were supported by NSF Grant CHE-76-21758 and NIH Grant 1 R01 CA33526-01.

Supplementary Material Available: Table I, giving analytical data for metal complexes (1 page). Ordering information is given on any current masthead page.

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Isolation and Characterization of a Five-Coordinate Manganese(III) Porphyrin Cation. Crystal and Molecular Structure of Aquo(tetraphenylporphinato)manganese(III) Triflate

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Received June 9, 1986

Five-coordinate cationic manganese(III) porphyrin complexes exist in nonpolar organic media in the presence of a limiting amount of water. Slow diffusion of heptane into a benzene solution of (tetraphenylporphinato)manganese(III) triflate containing 1 equiv of water produces crystals of aquo(tetraphenylporphinato)manganese(III) triflate, $[(H_2O)Mn^{III}TPP]^+OTf^-$ (**1**), the first unequivocal and isolated example of a five-coordinate cationic manganese(III) porphyrin complex. Solvate-free crystals of **1** crystallize in space group $P\bar{1}$. The unit cell has $a = 11.1735$ (47) Å, $b = 13.0503$ (80) Å, $c = 13.8998$ (121) Å, $\alpha = 81.102$ (60)°, $\beta = 79.476$ (53)°, $\gamma = 75.312$ (41)°, $V = 1915.07$ (2.17) Å^3, and $Z = 2$. The structure was solved by conventional heavy-atom methods and converged to a final $R = 0.0746$. Complex **1** has a d_{Mn-O} of 2.105 (4) Å, and the Mn atom resides 0.17 and 0.19 Å above the mean 24-atom plane and the mean N_4 plane, respectively. The molecular stereochemistry and the electronic spectra for **1** clearly establish the Mn to be in the high spin, $S = 2$, state. Complex **1** reacts only with a large excess of iodosylbenzene to form one or more high-valent Mn porphyrin species. The five-coordinate cationic form of Mn^{III} porphyrins is accessible under the literature conditions for both the homogeneous catalytic oxygenation of hydrocarbons and the homogeneous oxidation of water by Mn porphyrins.

The ability of manganese porphyrin complexes to oxidize alkanes and other organic compounds of low reactivity,[1,2] as well as water,[3,4] one of the most oxidatively resistant inorganic substances, has generated substantial efforts recently to characterize these complexes. Much progress has been made with respect to the isolation, purification, and rigorous characterization of Mn(III),[5-8] Mn(IV),[9-11] and Mn(V)[12,13] porphyrins of relevance to catalytic organic oxygenation processes. In contrast, little progress has been made with respect to the isolation and rigorous characterization of Mn porphyrins of relevance to water oxidation and oxygen evolution.[14] In our attempts to isolate tractable and

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0020-1669/86/1325-4668$01.50/0

crystalline Mn complexes containing oxo, hydroxo, or aquo ligands, we have isolated a monoaquo complex of $[Mn^{III}TPP]^+$, aquo(tetraphenylporphinato)manganese(III) triflate (**1**), that constitutes the first well-characterized example of a five-coordinate Mn^{III} porphyrin cation. This coordination form of Mn^{III} clearly can exist in solution under conditions for the homogeneous oxidation of water as well as the catalytic oxygenation of organic substrates by Mn porphyrins. We report here the structural characterization and other properties of **1**.

Experimental Section

Materials and Methods. All solvents were glass-distilled grade from Burdick and Jackson and were used without further purification. Deionized water was further purified by distillation from $KMnO_4$ before use. All reagents were of analytical or reagent grade. The complexes $Mn^{III}TPP(OAc)$ and $Mn^{III}TPP(Cl)$ were prepared by published procedures,[1,8] and $Mn^{III}TPP(OTf)$ was prepared by metathesis of $Mn^{III}TPP(Cl)$ with AgOTf (Alfa) in hot toluene and recrystallized twice from hot toluene/heptane. The $NMn^{V}TPP$[12] and the reactive $[N_3Mn^{IV}TPP]_2O$[10] complexes were prepared by literature methods. Electronic absorption spectra were obtained by using a Hewlett-Packard 8451A multidiode array spectrophotometer. The crystallography is described below.

Synthesis of Aquo(tetraphenylporphinato)manganese(III) Triflate (1). Slow diffusion of heptane into a benzene solution of $Mn^{III}TPP(OTf)$ containing 1 and only 1 equiv of water produces deep purple rods of **1**. The complex is best handled in nonchlorinated solvents as even trace amounts of halide rapidly produce the previously characterized five-coordinate, $S = 2$, $Mn^{III}TPP(Cl)$ complex.[5,6] This halogenation process is slower with **1**, however, then with the previously characterized six-coordinate, $S = 2$, Mn^{III} porphyrin cations.[8] KBr-pellet infrared spectra were difficult to obtain on **1** for the same reason; a ready reaction of **1** in the solid state with KBr produces the bromide complex. The KBr-pellet infrared spectrum of **1** can be obtained, however, if the KBr and **1** are individually prepulverized and then 2–3% of **1** is added to the KBr and the mixture shaken for only a few seconds. One exemplary purple rod of the complex was submitted to analysis by X-ray crystallography (see below). The crystalline form of **1**, unlike the crystalline forms of most other metalloporphyrins,[8-10] does not contain solvent molecules of crystallization.

Anal. Calcd for $C_{45}H_{30}F_3MnN_4O_4S$: C, 64.75; H, 3.62; N, 6.71. Found: C, 64.61; H, 3.66; N, 6.68.

X-ray Crystallography. Collection and Reduction of Intensity Data. A purple rod of **1** with dimensions $0.08 \times 0.26 \times 0.86$ mm was attached to the end of a glass fiber with epoxy cement. Intensity data were collected on a Syntex (Nicolet) $P2_1$ four-circle diffractometer at 20 °C by using the ω-scanning technique and monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The value of mean $|E|^2 - 1 \approx 1$ suggested a centric space group, that is $P\bar{1}$ (No. 2), with $a = 11.1735$ (47) Å, $b = 13.0503$ (80) Å, $c = 13.8998$ (121) Å, $\alpha = 81.102$ (60)°, $\beta = 79.476$ (53)°, $\gamma = 75.312$ (41)°, $V = 1915.07$ (2.17) Å^3, and $Z = 2$. The structure was solved by conventional heavy-atom/Patterson methods.[15] Blocked-cascade least-squares refinement of 5355 unique reflections ($F_o > 2.5\sigma(F_o)$), $3° < 2\theta < 50°$, resulted in a final residual, $R_F = 0.0746$ ($R_w = 0.0829$). All non-hydrogen atoms were made anisotropic. The hydrogen atoms of the water molecule were located from difference Fourier syntheses, and their coordinates were fixed during the final stages of refinement. All other hydrogen atoms were placed in calculated positions and allowed to "ride" on their parent carbon (C–H = 0.96 Å; $U_{iso}(H) = 1.2U_{ij}(C)$). Scattering factors were those used for neutral atoms.[16] Other crystal data collection and refinement parameters and the positional and isotropic thermal parameters are summarized in Tables I and II, respectively.

Results and Discussion

The electronic absorption spectrum of **1** is distinctly the d-type hyperporphyrin spectrum of an $S = 2$ manganese tetraphenylporphyrin complex.[17] The spectrum displays the same features as the long known five-coordinate, $S = 2$, $Mn^{III}TPP(X)$ complexes (X = monoanion ligand)[6] and six-coordinate, $S = 2$, $Mn^{III}TPP(X)(L)$ complexes,[7] as well as the recently characterized six-coordinate, $S = 2$, $[Mn^{III}TPP(L)_2]^+X^-$ cationic complexes.[8] The ratio of the two prominent high-energy bands, bands IV and V as originally named by Boucher[5] (also known as the split Soret bands in d-type hyperporphyrin spectra), and also the absorption maxima values for these bands argue in addition that the axial ligand donor atom of **1** in solution is oxygen. It has been well documented that the ratios of bands IV and V as well as the λ_{max} values for these bands are highly variable and particularly sensitive to the electronic features of the axial ligand(s).[5] The very close correspondence of the spectra of the $S = 2$ $[Mn^{III}TPP(L)_2]^+ClO_4^-$ (L = *N,N*-dimethylformamide or 2,6-lutidine *N*-oxide) cationic complexes, containing only oxygen atoms as axial ligand donor atoms in the solid state and in solution,[8] and **1** strongly suggests that oxygen is the axial donor atom in **1** in solution, as it is in the solid state (vide infra).

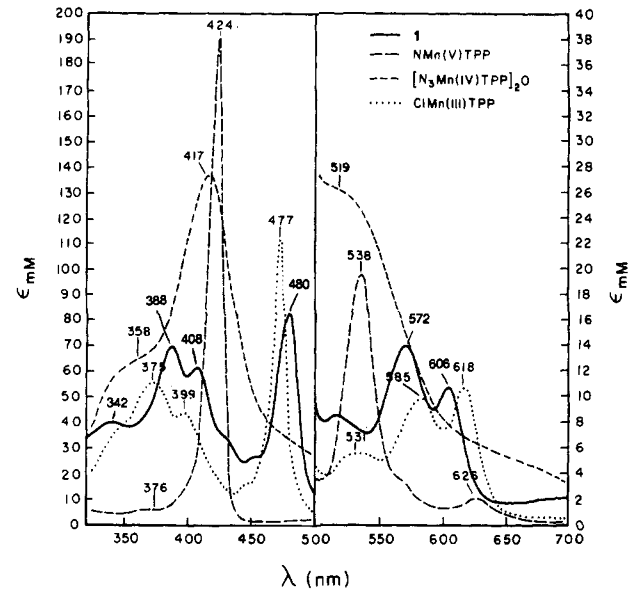

Figure 1. Electronic absorption spectra for **1** and representative manganese(III), -(IV), and -(V) tetraphenylporphyrin complexes. All spectra were recorded as ca. 1 mM solutions in toluene at 25 °C. The spectrum for $NMn^{V}TPP$ for λ 325–500 nm is half-scale.

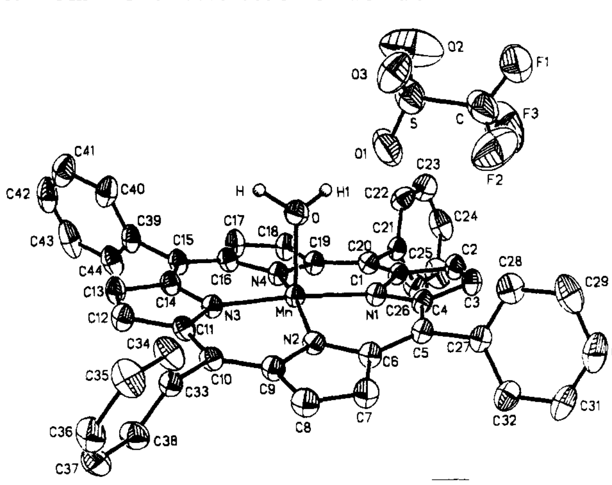

Figure 2. ORTEP and atom-numbering diagram for **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are the 30% probability level.

In contrast to the similarity of the electronic absorption spectra of **1** and the $S = 2$ $Mn^{III}TPP$ complexes, the spectra of **1** is quite distinct from the spectra of $S = {}^5/_2$ $Mn^{II}TPP$ complexes, $S = 1$ $Mn^{III}TPP(X)_2$ anionic complexes,[18] monomeric[9] and dimeric[10] $Mn^{IV}TPP$ complexes, and $Mn^{V}TPP$ complexes.[12,13] The absorption spectrum of **1** is compared with the spectra of representative tetraphenylporphinato complexes of Mn^{IV} and Mn^{V} and $S = 2$ Mn^{III} in Figure 1.

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Table I. Crystal and Data Collection Parameters for $[(H_2O)MnTPP]^+OTF^-$ (**1**)

	A. Crystal Data		
formula	$C_{45}H_{30}F_3MnN_4O_4S$	V, Å^3	1915.07 (2.17)
fw	834.76	Z	2
space group	triclinic $P\bar{1}$ (No. 2)	D_{calcd}, g cm^{-3}	1.45
		D_{obsd}, g cm^{-3}	1.47 (2)
a, Å	11.1735 (47)	cryst dimens, mm	0.08 × 0.26 × 0.86
b, Å	13.0503 (80)		
c, Å	13.8998 (121)	color	deep purple-red
α, deg	81.102 (60)	μ_{calcd}, cm^{-1}	4.45
β, deg	79.476 (53)		
γ, deg	75.312 (41)		
	B. Data Collection		
diffractometer	Syntex (Nicolet) $P2_1$		
radiation (monochromatic)	Mo Kα (λ = 0.71069 Å)		
R(merge), $R(\sigma)$	0.0075, 0.0430		
no. of total reflecns	7245/5355 ($F_o > 2.5\sigma(F_o)$)		
scan method	ω (Wyckoff)		
2θ range, deg	3–50		
scan speed, deg min^{-1}	3.91–14.65		
bkgd/scan time	1		
reflecns measd	$+h,\pm k,\pm l$		
temp, °C	20		
	C. Refinement		
abs cor	none	R^a	0.0746
max residual electron density, e Å^{-3}	1.28 (1.00 Å from S)	$R_w{}^b$	0.0829
		GOF^c	1.686

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]$. [c] GOF (goodness of fit) = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o is the number of observations, n_v is the number of parameters, and $w^{-1} = (\sigma^2(F) + |0.00147|F^2)$.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

atom	x	y	z	U^a
Mn	1201 (1)	4444 (1)	2906 (1)	39 (1)
O	587 (3)	4768 (3)	1523 (2)	61 (1)
N(1)	1609 (3)	5859 (3)	2796 (3)	42 (1)
N(2)	−438 (3)	5017 (3)	3725 (3)	44 (1)
N(3)	850 (3)	2997 (3)	3167 (3)	43 (1)
N(4)	2994 (3)	3791 (3)	2450 (3)	44 (1)
C(1)	2732 (4)	6121 (3)	2366 (3)	42 (2)
C(2)	2556 (4)	7243 (4)	2202 (4)	52 (2)
C(3)	1352 (4)	7679 (4)	2517 (3)	51 (2)
C(4)	762 (4)	6823 (3)	2918 (3)	43 (2)
C(5)	−441 (4)	6936 (3)	3451 (3)	45 (2)
C(6)	−946 (4)	6069 (3)	3896 (3)	47 (2)
C(7)	−2111 (4)	6134 (4)	4522 (4)	58 (2)
C(8)	−2344 (4)	5154 (4)	4704 (4)	60 (2)
C(9)	−1325 (4)	4459 (3)	4187 (3)	48 (2)
C(10)	−1291 (4)	3411 (4)	4084 (3)	47 (2)
C(11)	−277 (4)	2733 (4)	3593 (3)	47 (2)
C(12)	−208 (4)	1655 (4)	3458 (4)	55 (2)
C(13)	923 (4)	1255 (4)	2981 (4)	54 (2)
C(14)	1602 (4)	2085 (3)	2783 (3)	48 (2)
C(15)	2845 (4)	1951 (3)	2338 (3)	47 (2)
C(16)	3498 (4)	2749 (3)	2222 (3)	48 (2)
C(17)	4804 (4)	2626 (4)	1843 (4)	58 (2)
C(18)	5095 (4)	3567 (4)	1831 (4)	55 (2)
C(19)	3973 (4)	4314 (3)	2169 (3)	46 (2)
C(20)	3864 (4)	5401 (3)	2132 (3)	46 (2)
C(21)	5029 (4)	5809 (3)	1773 (3)	47 (2)
C(22)	5468 (5)	5969 (4)	789 (4)	67 (2)
C(23)	6578 (5)	6286 (4)	458 (4)	78 (2)
C(24)	7239 (5)	6458 (4)	1113 (5)	78 (3)
C(25)	6801 (5)	6333 (5)	2104 (5)	85 (3)
C(26)	5696 (5)	6008 (4)	2441 (4)	65 (2)
C(27)	−1231 (4)	8037 (3)	3548 (3)	47 (2)
C(28)	−1626 (4)	8678 (4)	2730 (4)	65 (2)
C(29)	−2361 (5)	9722 (4)	2813 (5)	86 (3)
C(30)	−2693 (5)	10084 (5)	3719 (5)	84 (3)
C(31)	−2321 (5)	9458 (4)	4525 (5)	78 (3)
C(32)	−1573 (5)	8442 (4)	4449 (4)	66 (2)
C(33)	−2434 (4)	2977 (4)	4514 (3)	48 (2)
C(34)	−3472 (4)	3287 (4)	4054 (4)	68 (2)
C(35)	−4522 (5)	2895 (5)	4456 (5)	76 (2)
C(36)	−4547 (5)	2208 (4)	5316 (4)	72 (2)
C(37)	−3490 (5)	1907 (5)	5770 (4)	72 (2)
C(38)	−2430 (5)	2274 (4)	5361 (4)	67 (2)
C(39)	3461 (4)	935 (4)	1926 (4)	57 (2)
C(40)	3043 (5)	694 (4)	1134 (4)	73 (2)
C(41)	3609 (6)	−262 (5)	727 (5)	95 (3)
C(42)	4586 (6)	−948 (5)	1114 (6)	94 (3)
C(43)	5006 (6)	−729 (5)	1887 (6)	97 (3)
C(44)	4443 (5)	224 (4)	2303 (4)	69 (2)
S	−1005 (2)	3058 (2)	559 (2)	103 (1)
O(1)	−1345 (9)	3613 (4)	−280 (5)	213 (5)
O(2)	−1923 (6)	3063 (8)	1518 (5)	218 (5)
O(3)	169 (5)	3124 (4)	779 (4)	116 (3)
C	−816 (11)	1747 (7)	420 (7)	135 (5)
F(1)	−392 (6)	1034 (4)	1119 (4)	154 (3)
F(2)	134 (11)	1508 (6)	−374 (5)	267 (6)
F(3)	−1735 (8)	1482 (5)	203 (6)	236 (5)

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

The X-ray crystal structure confirms that the Mn^{III} atom in **1** is in an $S = 2$ spin state and it shows some interesting features (Figure 2 and Table III). The manganese–nitrogen distances, $d_{Mn-N(Por)}$, ranging from 1.989 (4) to 2.004 (3) Å, are similar to those seen in other Mn^{III}, Mn^{IV}, and Mn^V porphyrin complexes[9–12] and indicative, in general, of first-row transition-metal metalloporphyrin complexes with a vacant $d_{x^2-y^2}$ orbital.[19] Despite the complete lack of crystallographically characterized Mn^{III} complexes with aquo or hydroxo axial ligands, a sufficient number of high-quality crystal structures of iron and manganese metalloporphyrins now exist that the axial bond distance in **1**, $d_{Mn-O(ax)}$, can be evaluated meaningfully. The $d_{Mn-O(ax)}$ is 2.105 (4) Å. Upon first examination this looks like a fairly conventional bond distance for a first-row transition metal to a neutral axial oxygen atom and is perhaps short for such a distance in a complex with a $(d_{z^2})^1$ transition-metal atom.[20] It is apparent, however, that adding a sixth ligand to five-coordinate high-spin d^4 metalloporphyrins increases the bond distance to the axial anionic ligand by at least 0.1 Å. For example the Mn^{III}–Cl distance increases 0.104 Å on going from $ClMn^{III}TPP$[6b] to $ClMn^{III}TPP(py)$[7a] while the Mn^{III}–N_3 distance increases 0.131 Å on going from $N_3Mn^{III}TPP$[6c] to $N_3Mn^{III}TPP(CH_3OH)$.[7d] Adding 0.11 Å in bond length to the $d_{Mn-O(ax)}$ of **1** gives a bond length of approximately 2.21 Å. This compares with 2.264 (4) and 2.217 (4) Å for the $d_{Mn-O(ax)}$ in $[L_2Mn^{III}TPP]^+ClO_4^-$ (L = DMF and 2,6-lutidine *N*-oxide, respectively)[8] and 2.329 Å in the $N_3Mn^{III}TPP(CH_3OH)$ complex.[7d] All these literature complexes are unequivocally $S = 2$ species. The slightly longer $d_{Mn-O(ax)}$ for the latter complex may attributable in part to the effect of the methyl group vs. hydrogen atom in the aquo complexes. Aquo complexes often have bond distances slightly shorter than the corresponding methanol or ethanol complexes. A useful case in point is the comparison of the $d_{Fe-O(ax)}$ of 2.095 (2) Å in $(H_2O)_2Fe^{III}TPP$[21] vs. 2.138 (24) Å in $[(EtOH)_2Fe^{III}OEP]^+X^-$.[22] Both these complexes are more than likely high-spin ferric, $S = {}^5/_2$, species.[22]

The mean out-of-plane displacements of the manganese atom in **1** from the mean N_4 plane and from the mean 24-atom plane are 0.19 and 0.17 Å toward the axial water molecule, respectively. These values for d_{M-Ct} are also unlike those of any $S = 2$ Mn^{III} porphyrin complex in the literature, but they fall into the range one predicts for a $S = 2$ five-coordinate Mn^{III} porphyrin cation. The conventional five-coordinate $S = 2$ Mn^{III} neutral porphyrins,

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Table III

(a) Selected Bond Lengths (Å)

Mn–O	2.105 (4)	Mn–N(1)	1.989 (4)
Mn–N(2)	2.004 (3)	Mn–N(3)	1.991 (4)
Mn–N(4)	1.995 (3)	N(1)–C(1)	1.390 (5)
N(1)–C(4)	1.382 (5)	N(2)–C(6)	1.385 (6)
N(2)–C(9)	1.384 (6)	N(3)–C(11)	1.392 (6)
N(3)–C(14)	1.390 (5)	N(4)–C(16)	1.395 (6)
N(4)–C(19)	1.399 (6)	C(1)–C(2)	1.415 (6)
C(1)–C(20)	1.389 (5)	C(2)–C(3)	1.341 (6)
C(3)–C(4)	1.428 (7)	C(4)–C(5)	1.395 (6)
C(5)–C(6)	1.400 (6)	C(5)–C(27)	1.495 (6)
C(6)–C(7)	1.419 (6)	C(7)–C(8)	1.347 (7)
C(8)–C(9)	1.419 (6)	C(9)–C(10)	1.387 (7)
C(10)–C(11)	1.389 (6)	C(10)–C(33)	1.514 (7)
C(11)–C(12)	1.429 (7)	C(12)–C(13)	1.332 (6)
C(13)–C(14)	1.439 (7)	C(14)–C(15)	1.393 (6)
C(15)–C(16)	1.391 (7)	C(15)–C(39)	1.479 (6)
C(16)–C(17)	1.435 (6)	C(17)–C(18)	1.344 (7)
C(18)–C(19)	1.432 (5)	C(19)–C(20)	1.387 (6)
C(20)–C(21)	1.502 (6)	S–O(1)	1.337 (7)
S–O(2)	1.526 (6)	S–O(3)	1.427 (6)
S–C	1.707 (10)	C–F(1)	1.304 (11)
C–F(2)	1.398 (13)	C–F(3)	1.261 (16)

(b) Selected Bond Angles (deg)

O–Mn–N(1)	92.9 (2)	O–Mn–N(2)	98.0 (1)
N(1)–Mn–N(2)	89.2 (1)	O–Mn–N(3)	93.6 (2)
N(1)–Mn–N(3)	173.5 (2)	N(2)–Mn–N(3)	89.6 (1)
O–Mn–N(4)	97.7 (1)	N(1)–Mn–N(4)	89.9 (1)
N(2)–Mn–N(4)	164.3 (2)	N(3)–Mn–N(4)	89.5 (1)
Mn–N(1)–C(1)	126.9 (3)	Mn–N(1)–C(4)	126.3 (3)
C(1)–N(1)–C(4)	105.2 (3)	Mn–N(2)–C(6)	126.8 (3)
Mn–N(2)–C(9)	127.2 (3)	C(6)–N(2)–C(9)	105.9 (3)
Mn–N(3)–C(11)	127.3 (3)	Mn–N(3)–C(14)	125.9 (3)
C(11)–N(3)–C(14)	105.7 (4)	Mn–N(4)–C(16)	126.9 (3)
Mn–N(4)–C(19)	127.1 (3)	C(16)–N(4)–C(19)	105.5 (3)
N(1)–C(1)–C(2)	109.6 (3)	N(1)–C(1)–C(20)	125.8 (4)
C(2)–C(1)–C(20)	124.6 (4)	C(1)–C(2)–C(3)	108.1 (4)
C(2)–C(3)–C(4)	107.2 (4)	N(1)–C(4)–C(3)	109.8 (3)
N(1)–C(4)–C(5)	124.6 (4)	C(3)–C(4)–C(5)	125.3 (4)
C(4)–C(5)–C(6)	123.2 (4)	C(4)–C(5)–C(27)	118.3 (4)
C(6)–C(5)–C(27)	118.4 (3)	N(2)–C(6)–C(5)	125.2 (4)
N(2)–C(6)–C(7)	109.0 (4)	C(5)–C(6)–C(7)	125.6 (4)
C(6)–C(7)–C(8)	108.1 (4)	C(7)–C(8)–C(9)	107.2 (4)
N(2)–C(9)–C(8)	109.6 (4)	N(2)–C(9)–C(10)	125.5 (4)
C(8)–C(9)–C(10)	124.7 (4)	C(9)–C(10)–C(11)	124.1 (4)
C(9)–C(10)–C(33)	118.5 (4)	C(11)–C(10)–C(33)	117.4 (4)
N(3)–C(11)–C(10)	124.9 (4)	N(3)–C(11)–C(12)	109.1 (3)
C(10)–C(11)–C(12)	126.0 (4)	C(11)–C(12)–C(13)	108.5 (4)
C(12)–C(13)–C(14)	107.5 (4)	N(3)–C(14)–C(13)	109.2 (4)
N(3)–C(14)–C(15)	126.4 (4)	C(13)–C(14)–C(15)	124.3 (4)
C(14)–C(15)–C(16)	122.7 (4)	C(14)–C(15)–C(39)	117.9 (4)
C(16)–C(15)–C(39)	119.3 (4)	N(4)–C(16)–C(15)	125.7 (4)
N(4)–C(16)–C(17)	109.3 (4)	C(15)–C(16)–C(17)	125.0 (4)
C(16)–C(17)–C(18)	107.9 (4)	C(17)–C(18)–C(19)	107.9 (4)
N(4)–C(19)–C(18)	109.3 (4)	N(4)–C(19)–C(20)	125.8 (3)
C(18)–C(19)–C(20)	124.6 (4)	C(1)–C(20)–C(19)	123.2 (4)
C(1)–C(20)–C(21)	119.3 (4)	C(19)–C(20)–C(21)	117.4 (3)
O(1)–S–O(2)	121.8 (5)	O(1)–S–O(3)	116.2 (5)
O(2)–S–O(3)	108.1 (4)	O(1)–S–C	106.1 (5)
O(2)–S–C	96.8 (5)	O(3)–S–C	104.5 (5)
S–C–F(1)	117.9 (8)	S–C–F(2)	107.5 (7)
F(1)–C–F(2)	101.5 (8)	S–C–F(3)	116.9 (7)
F(1)–C–F(3)	106.8 (9)	F(2)–C–F(3)	104.5 (10)

$XMn^{III}(Por)$ (X = anionic axial ligand), have values for d_{Mn-Ct} of 0.23 Å in the $N_3Mn^{III}TPP$ structure of Day and co-workers,[6c] 0.25 Å for the $NCMn^{III}TPP$ complex of Scheidt and co-workers,[6a] and 0.27 Å for the $ClMn^{III}TPP$ complex of Tulinsky and Chen.[6b] One would expect larger out-of-plane displacements toward the axial ligand in the latter complexes, for the bond to the axial ligand in these complexes is partially electrostatic in nature and doubtless stronger than the Mn–O(ax) bond in **1**.

The data set was of sufficient quality that the hydrogen atoms of the water molecule were located. There is a small amount of S_4 ruffling of the porphyrin core. The maximum deviation above the mean 24-atom plane is for C8 (0.41 Å) while the maximum deviation below this plane is for C3 (0.47 Å). On the basis of numerous metalloporphyrin X-ray crystal structure determinations, this ruffling of the porphyrin plane is most likely attributable in the case of **1** to crystal-packing forces as well as metal ion size effects.[8,19]

In summary, the electronic and structural data for **1** are most in accord with a tetragonally elongated square-pyramidal $S = 2$ (high-spin d^4) Mn^{III} with a ground electronic configuration of $(d_{xy})^1,(d_{xz})^1,(d_{yz})^1,(d_{z^2})^1$.

A key point in this work is the obvious potential relevance of the five-coordinate $S = 2$ Mn^{III} cationic porphyrins to the catalytic alkane functionalization and organic substrate oxygenation processes facilitated by Mn^{III} porphyrins that we[1] and others[2] have extensively investigated since 1980. Treatment of $XMn^{III}TPP$ (X = halide or pseudohalide) complexes with iodosylbenzene, one of many possible oxygen donors[2] capable of oxidizing Mn^{III} porphyrins to high-valent species, can produce a substantial number of isolable and/or spectroscopically detectable Mn^{IV} or Mn^{V} porphyrin complexes depending upon the rection conditions.[1,9,10] Likewise, **1** is oxidized by iodosylbenzene in dry highly purified toluene to one or more high-valent species. Interestingly however, a large excess of iodosylbenzene is required to form the high-valent species from **1** whereas a stoichiometric amount or a slight excess of iodosylbenzene is adequate for complete oxidation of the corresponding halide or pseudohalide complexes. This is consistent with the more limited ability of water and triflate relative to that of halides or pseudohalides to stabilize an oxomanganese(V) compound, the likely intermediate of highest reactivity in these oxygenation systems.[1,2] It is difficult to evaluate quantitatively the reactivity of the high-valent species produced from iodosylbenzene oxidation of **1** vs. the reactivity of the high-valent species produced from iodosylbenzene oxidation of the halide or pseudohalide complexes. In the former case, iodosylbenzene oxidation appears to generate byproducts that in turn produce other Mn^{III} and Mn^{V} complexes, further complicating the thermal decomposition and hydrocarbon oxidation chemistry. Since many of the oxygen donors in organic substrate oxygenation studies are aqueous reagents or contain water as an impurity and since the solvents in these studies are often slightly wet, the actual species $[(H_2O)Mn^{III}TPP]^+$ itself may be kinetically significant in some of these studies. It is also clear that $[(H_2O)Mn^{III}TPP]^+$ exists under conditions where Mn porphyrins have been shown to facilitate the stoichiometric homogeneous oxidation of water.[3,4] Having access to isolated characterized complexes such as **1** should aid in the mechanistic investigation of water oxidation in these and other manganese-containing systems that model some aspect of the Mn-based site for water oxidation/oxygen evolution in photosystem II.[23,24]

Acknowledgment. The research was supported by the National Science Foundation (Grant CHE-8402994).

Registry No. **1**, 105121-84-4; $Mn^{III}TPP(OTf)$, 105121-85-5; $Mn^{III}TPP(Cl)$, 32195-55-4; iodosylbenzene, 536-80-1.

Supplementary Material Available: Tables of calculated hydrogen parameters, bond lengths and bond angles, torsion angles and nonbonded distances, and thermal ellipsoids for the non-hydrogen atoms (11 pages); a listing of structure factors (32 pages). Ordering information is given on any current masthead page.

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