Inorg. Chem. **1987**, *26*, 4155–4160

Contribution from the Department of Chemistry,
Emory University, Atlanta, Georgia 30322

Molecular Stereochemistry of Aquamanganese(III) Porphyrins. Demonstrable Effect of π-Arene–Porphyrin Interaction on the Metal Coordination Environment in a Metalloporphyrin

Michael M. Williamson and Craig L. Hill*

Received February 2, 1987

Monoaqua five-coordinate cationic complexes of $S = 2$, Mn^{III} tetraphenylporphyrins form in nonpolar organic solvents such as benzene in the presence of 1.0 equiv of water, while the diaqua six-coordinate cationic complexes form in the same media in the presence of 2.0 equiv of water. Both coordination forms can be isolated as crystalline solids in good yield from the benzene/heptane solvent system. Purple-red prisms of one five-coordinate cationic complex, $[(H_2O)Mn^{III}TPP]^+(SbF_6)^-\cdot 2C_6H_6$ (**1**), crystallize in the monoclinic space group $P2_1/n$ with $a = 11.355$ (3) Å, $b = 17.925$ (11) Å, $c = 24.145$ (12) Å, $\beta = 97.97$ (3)°, $V = 4866.9$ (3.6) Å^3, and $Z = 4$. Complex **1** is the first structurally characterized metalloporphyrin cation complex containing one proximal π-interacting arene that is not another porphyrin ring, a benzene molecule in this case, and one neutral conventionally ligated molecule, water. Lustrous black solvate-free prisms of one six-coordinate cationic complex, $[(H_2O)_2Mn^{III}TPP]^+(ClO_4)^-$ (**2**), also crystallize in monoclinic space group $P2_1/n$ with $a = 10.522$ (4) Å, $b = 8.193$ (4) Å, $c = 21.361$ (10) Å, $\beta = 95.53$ (3)°, $V = 1832.9$ (1.4) Å^3, and $Z = 2$. Although the EPR, ^1H NMR, and UV–visible spectra of **1** and **2** confirm the presence of $S = 2$, Mn^{III} ions in both complexes, these methods do not provide much information regarding π-arene–metalloporphyrin interactions. An analysis of the structural features of **1**, **2**, and the conventional five-coordinate monoaqua Mn^{III} porphyrin recently reported helps define further the role of π-arene–metalloporphyrin interactions with respect to metalloporphyrin stereochemistry in the solid state. The interacting benzene molecule not only modulates the porphyrin ruffling but also increases the length of the bond between the manganese and the axially ligated water molecule, $d_{Mn-O(ax)}$, by 0.04 Å.

Introduction

In the last 5 years effective homogeneous systems, based on manganese porphyrins, for oxidation of both hydrocarbons[1-12] and water[13] have been reported. Much attention has focused on these metalloporphyrin systems, for saturated hydrocarbons and water are among the most oxidatively resistant organic and inorganic materials, respectively, and methods for the facile homogeneous oxidation of these materials are as important as they are scarce. While a variety of high-valent metalloporphyrin complexes related to the homogeneous catalytic hydrocarbon functionalization processes have now been adequately characterized,[14-19] few manganese porphyrin complexes of relevance to homogeneous water oxidation have been adequately characterized.[20] The first aqua complex of a Mn^{III} porphyrin, a five-coordinate, $S = 2$, Mn^{III} cation, was recently characterized in solution and in the solid state.[21] In this paper we report the isolation and characterization of two complexes that represent new coordination forms involving water and Mn^{III}porphyrins, aqua(tetraphenylporphinato)manganese(III) hexafluoroantimonate-2-benzene (**1**) and diaqua(tetraphenylporphinato)manganese(III) perchlorate (**2**).

A voluminous quantity of data derived from biological and abiological systems testify to the demonstrable and often profound effects that axial ligands have on the electronic, structural, and chemical properties of metalloporphyrins.[22,23] Much smaller, but

---

(1) (a) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374. (b) Hill, C. L.; Smegal, J. A. *Nouv. J. Chim.* **1982**, *6*, 287. (c) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515. (d) Smegal, J. A.; Hill, C. L. *Ibid.* **1983**, *105*, 2920. (e) Hill, C. L.; Smegal, J. A.; Henly, T. J. *J. Org. Chem.* **1983**, *48*, 3277.

(2) Hill, C. L. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: Greenwich, CT, in press.

(3) References 4–12 address the manganese porphyrin catalyzed hydrocarbon oxidation processes that have appeared in the literature in the last 4 years.

(4) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Groves, J. T.; Watanabe, Y.; McMurry, T. J. *Ibid.* **1983**, *105*, 4489.

(5) (a) Powell, M. F.; Pai, E. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3277. (b) Lindsey Smith, J. R.; Nee, M. W.; Noar, J. B.; Bruice, T. C. *J. Chem. Soc., Dalton Trans.* **1984**, 255. (c) Yuan, L.-C.; Bruice, T. C. *J. Chem. Soc., Chem. Commun.* **1985**, 868. (d) Yuan, L.-C.; Bruice, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1643.

(6) (a) Collman, J. P.; Kodadek, T.; Taybuck, S. A.; Meunier, B. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7039. (b) Collman, J. P.; Brauman, J. I.; Meunier, B.; Raybuck, S. A.; Kodadek, T. *Ibid.* **1984**, *81*, 3245. (c) Meunier, B.; Guilmet, E.; De Carvalho, M.-E.; Poilblanc, *J. Am. Chem. Soc.* **1984**, *106*, 6668. (d) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *Ibid.* **1985**, *107*, 2000.

(7) Lindsay Smith, J. R.; Mortimer, D. N. *J. Chem. Soc., Chem. Commun.* **1985**, 64.

(8) (a) Mansuy, D.; Fontecave, M.; Bartoli, J.-F. *J. Chem. Soc., Chem. Commun.* **1983**, 253. (b) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *Ibid.* **1984**, 1161. (c) Mansuy, D.; Battioni, P.; Renaud, J.-P. *Ibid.* **1984**, 1255. (d) Renaud, J.-P.; Battioni, P.; Bartoli, J.-F.; Mansuy, D. *Ibid.* **1985**, 888. (e) Battioni, P.; Renaud, J.-P.; Bartoli, J.-F.; Mansuy, D. *Ibid.* **1986**, 341.

(9) (a) Meunier, B.; Guilmet, E.; De Carvalho, M.-E.; Poilblanc, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668 and references cited therein. (b) De Poorter, B.; Ricci, M.; Meunier, B. *Tetrahedron Lett.* **1985**, *26*, 4459 and references cited therein.

(10) (a) Razenberg, J. A. S. J.; van der Made, A. W.; Smeets, J. W. H.; Nolte, R. J. M. *J. Mol. Catal.* **1985**, *31*, 271. (b) Razenberg, J. A. S. J.; Nolte, R. J. M.; Drenth, W. *J. Chem. Soc., Chem. Commun.* **1986**, 277. (c) Nolte, R. J. M.; Razenberg, J. A. S. J.; Schuurman, R. *J. Am. Chem. Soc.* **1986**, *108*, 2751.

(11) (a) Suslick, K.; Cook, B.; Fox, M. *J. Chem. Soc., Chem. Commun.* **1985**, 580. (b) Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 7281. (c) Suslick, K. S.; Cook, B. R. *J. Chem. Soc., Chem. Commun.* **1987**, 200. (d) Suslick, K. S.; Acholla, F. V.; Cook, B. R. *Ibid.* **1987**, *109*, 2818.

(12) Tabushi, I.; Morimitsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 6871 and references cited therein.

(13) (a) Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1543. (b) Porter, G. *Proc. R. Soc. London, A* **1978**, *362*, 281. (c) Tabushi, I.; Kojo, S. *Tetrahedron Lett.* **1975**, 305.

(14) (a) Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1982**, *21*, 4301. (b) Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Ibid.* **1983**, *22*, 3776.

(15) (a) Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3964. (b) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *Ibid.* **1983**, *105*, 3510.

(16) Spreer, L.; Maliyackel, A. C.; Holbrook, S.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1986**, *108*, 1949.

(17) Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 7318.

(18) (a) Buchler, J. W.; Dreher, C.; Lay, K.-L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1155. (b) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Lee, Y. J. A.; Scheidt, W. R. *Inorg. Chem.* **1983**, *22*, 888.

(19) (a) Bortolini, O.; Meunier, B. *J. Chem. Soc., Chem. Commun.* **1983**, 139. (b) Bortolini, O.; Ricci, M.; Meunier, B.; Friant, P.; Ascone, I.; Goulon, J. *Nouv. J. Chim.* **1986**, *10*, 39.

(20) (a) Carnieri, N.; Harriman, A.; Porter, G. *J. Chem. Soc., Dalton Trans.* **1982**, 931. (b) Carnieri, N.; Harriman, A.; Porter, G.; Kalyanasundaram, K. *Ibid.* **1982**, 1231. (c) Carnieri, N.; Harriman, A. *Inorg. Chim. Acta* **1982**, *62*, 103. (d) Ellul, H.; Harriman, A.; Richoux, M.-C. *J. Chem. Soc., Dalton Trans.* **1985**, 503.

(21) Williamson, M. M.; Hill, C. L. *Inorg. Chem.* **1986**, *25*, 4668.

(22) (a) *The Porphyrins*; Dolphin, D., Ed.; Wiley: New York, 1978, 1979; particularly several chapters in Vols. III–V. (b) *Porphyrins and Metalloporphyrins*; Smith, K. S., Ed.; Elsevier: Amsterdam, 1975; several chapters.

0020-1669/87/1326-4155$01.50/0

nevertheless observable, effects on these metalloporphyrin properties can be exerted by π-interactions between various aromatic groups and the porphyrin ring. Such effects have been documented in solution[24,25] and in the solid state.[26-28] These small but potentially significant π-arene interactions are hard to quantify in solution; thus, their ability to modulate some of the electronic and reactivity features of metalloporphyrins remains relatively undefined. Many of the solvents of optimal use for catalytic, magnetic resonance, and other studies of metalloporphyrins disrupt weak electron donor–acceptor and other subtle π-arene–porphyrin interactions. A comparison here of the structural features of both compounds **1** and **2** and complexes reported earlier allows more information to be gleaned regarding the effect of π-arene interactions on metalloporphyrin stereochemistry in the solid state.

Experimental Section

Methods and Materials. All solvents were of Burdick and Jackson glass-distilled grade and were used without purification. The water was deionized and then purified further by factional distillation from $KMnO_4$. The metalloporphyrins $Mn^{III}TPP(OAc)$ and $Mn^{III}TPP(Cl)$ were prepared as described previously.[1] The compounds $Mn^{III}TPP(SbF_6)$ and "$Mn^{III}TPP(ClO_4)$" were prepared by metathesis of $Mn^{III}TPP(Cl)$ with $AgSbF_6$ (Alfa) and $AgClO_4$ (Alfa), respectively, in hot toluene and recrystallized twice from hot toluene/heptane. In the course of the work presented in this paper and in a previous paper,[21] it became apparent that obtaining totally hydrate-free $Mn^{III}TPP(ClO_4)$ is not an easy task, as this complex picks up even traces of water from organic solvents.[29] This fact places some doubt on the quantitative formulation of the "$Mn^{III}TPP(ClO_4)$" used in various literature studies. *Caution! Although "$Mn^{III}TPP(ClO_4)$" and complex **2**, described below, have not given any indication of shock or thermal sensitivity with respect to detonation in our laboratory, they are potentially hazardous materials and should be handled with care.* The KBr pellet infrared spectra of complexes **1** and **2** proved difficult to obtain without partial H_2O–Br^- axial ligand exchange, a problem noted before for both the solvate-free five-coordinate monoaqua complex $[(H_2O)Mn^{III}TPP]^+(OTf)^-$[21] and other $S = 2$, Mn^{III} porphyrin cations containing weakly bound axial ligands with oxygen donor atoms.[31,32] The electronic absorption spectra were recorded on an HP 8451A ultraviolet–visible multidiode array spectrophotometer, and the ^1H NMR spectra were obtained by using a Nicolet 360NB 360-MHz spectrometer. The crystallographic methods are described below. Elemental analyses were performed by Atlantic Microlabs.

Aqua(tetraphenylporphinato)manganese(III) Hexafluoroantimonate–2-Benzene, $[(H_2O)Mn^{III}TPP]^+(SbF_6)^-\cdot 2C_6H_6$ (1). Deep purple-red prisms of **1** were grown by allowing heptane to diffuse slowly into a saturated benzene solution of $Mn^{III}TPP(SbF_6)$ containing exactly 1 equiv of H_2O. Crystals of **1** were isolated in 60% yield. The solvated crystals do not show sensitivity with respect to efflorescent desolvation. The electronic spectrum (λ = 325–700 nm) in toluene was identical with that reported previously for the $[(H_2O)Mn^{III}TPP]^+(OTf)^-$ complex in the same solvent.[21] The crystallography is described below. Elemental analyses (C, H, and N) were satisfactory.

Table I. Crystallographic Data for Aqua(tetraphenylporphinato)manganese(III) Hexafluoroantimonate–2-Benzene, $[(H_2O)Mn^{III}TPP]^+SbF_6^-\cdot 2C_6H_6$ (**1**), and Diaqua(tetraphenylporphinato)manganese(III) Perchlorate, $[(H_2O)_2Mn^{III}TPP]^+ClO_4^-$ (**2**)

	A. Crystal Data	
compd	**1**	**2**
formula	$C_{56}H_{42}F_6MnN_4OSb$	$C_{44}H_{36}ClMnN_4O_6$
fw	1077.6	807.18
space group[a]	monoclinic $P2_1/n$ (alternate setting of No 14)	
a, Å	11.355 (3)	10.522 (4)
b, Å	17.925 (11)	8.193 (4)
c, Å	24.145 (12)	21.361 (10)
β, deg	97.97 (3)	95.53 (3)
V, Å^3	4866.9 (3.6)	1832.9 (1.4)
Z	4	2
D_{calcd}, g cm^{-3}	1.46	1.46
D_{obsd}, g cm^{-3}	1.44 (2)	1.44 (2)
cryst dimens, mm	0.35 × 0.46 × 0.80	0.68 × 0.70 × 1.36
cryst color	deep purple-red	lustrous black
cryst habit	prismatic	
μ_{calcd}, cm^{-1}	8.72	4.74
	B. Data Collection	
diffractometer	Syntex (Nicolet) $P2_1$	
radiation (monochromatic)	Mo Kα (λ = 0.71069 Å)	
R(merge), R(sigma)	0.0055, 0.0489	0.0061, 0.0231
tot. no. of reflcns	7132	4849
no. of indep reflcns	4977 [$F_o > 2\sigma(F_o)$]	3641 [$F_o > 2.5\sigma(F_o)$]
scan method	ω (Wyckoff)	
2θ range, deg	3–45	3–50
scan speed, deg min^{-1}	4.88–14.65	4.88–19.53
bkgd/scan time	1	1
reflcns measd	$+h,+k,\pm l$	
temp, °C	25	20
	C. Refinement	
abs cor	semiempirical (ψ scan)	
max, min transmission	0.263, 0.234	0.352, 0.312
max resid electron dens, e Å^{-3}	0.63 (2.01 Å from Sb)	0.54 (1.08 Å from Cl)
R[b]	0.0645	0.0520
R_w[c]	0.0637	0.0545
GOF[d]	1.383	2.495

[a] Systematic absences for hkl: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]$. [d] 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 $w^{-1} = \sigma^2(F) + |0.0002|F^2$ for both **1** and **2**.

Diaqua(tetraphenylporphinato)manganese(III) Perchlorate, $[(H_2O)_2Mn^{III}TPP]^+(ClO_4)^-$ (2). A complex with this exact formulation was prepared by Kennedy and Murray and characterized by magnetic susceptibility and elemental analysis.[30] Exactly 2 equiv of water was added dropwise to a solution of 10 mg of $Mn^{III}TPP(ClO_4)$ in 15 mL of stirred benzene at 80 °C. The resulting solution was allowed to cool to room temperature before it was layered carefully with heptane. The flask containing the mixture was then fitted with a stopper and left overnight. After 24 h, lustrous black crystals of **2** had formed along the walls of the vessel. The isolated yield of crystalline **2** was essentially quantitative. The electronic spectrum of **2** in toluene is very similar to those of **1** and other $S = 2$ $Mn^{III}TPP$ complexes previous characterized in our laboratory that contain axial ligands with oxygen donor atoms.[21,31,32] The X-ray crystallography is described below. Elemental analyses (C, H, and N) were satisfactory.

X-ray Crystallography: Collection and Reduction of Intensity Data for 1 and 2. Nearly all the pertinent crystal, data collection, and refinement parameters for the structural determinations of both **1** and **2** are given in Table I. The data collection and refinement procedures used were similar for the two structures. A deep purple prism of **1** with dimensions 0.35 × 0.46 × 0.80 mm was affixed to the end of a glass fiber with epoxy cement. Three reference reflections exhibited intensity changes no greater than 4% over the data collection time period. Crystal lattice parameters were determined by least-squares refinement of 25 centered

---

(23) The roles of axial ligation on the physical and chemical properties of heme-dependent enzymes (particularly cytochrome P-450 at present) continue to be a focus of much attention. Cf.: *Cytochrome P-450*; Ortiz de Montellano, P., Ed.; Plenum: New York, 1986.

(24) For example, see: Goff, H.; Shimomura, E. *J. Am. Chem. Soc.* **1980**, *102*, 31.

(25) See also: (a) Gouterman, M.; Stevenson, P. E. *J. Chem. Phys.* **1962**, *37*, 2266. (b) Mauzerall, D. *Biochemistry* **1965**, *4*, 1801. (c) Siderov, A. N. *Theor. Exp. Chem. (Engl. Transl.)* **1973**, *9*, 435. (d) Barry, C. D.; Hill, H. A. O.; Mann, B. E.; Sadler, P. J.; Williams, R. J. P. *J. Am. Chem. Soc.* **1973**, *95*, 4545.

(26) Bis(toluene) solvates of M(TPP) systems: (a) Kirner, J. F.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 1093. (b) Scheidt, W. R.; Kastner, M. E.; Hatano, K. *Inorg. Chem.* **1978**, *17*, 706. (c) Scheidt, W. R.; Reed, C. A. *Ibid.* **1978**, *17*, 710.

(27) Structurally characterized five-coordinate metalloporphyrins with an anionic axial ligand and a π-arene–porphyrin ring interaction: (a) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948. (b) Shelly, K.; Bartczak, T.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 4325.

(28) π-Arene–porphyrin interactions with substantial ground-state electron donor–acceptor character: Pace, L. J.; Ulman, A.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 199 and references cited therein.

(29) Kennedy and Murray have documented the sensitivity of solid samples of related high-spin Mn^{III} porphyrin complexes with respect to picking up water from the atmosphere.[30]

(30) Kennedy, B. J.; Murray, K. S. *Inorg. Chem.* **1985**, *24*, 1557.

(31) Hill, C. L.; Williamson, M. M. *Inorg. Chem.* **1985**, *24*, 2836.

(32) Hill, C. L.; Williamson, M. M. *Inorg. Chem.* **1985**, *24*, 3024.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times$ 10^3) for **1**

atom	x	y	z	U_{eq}[a]
Mn	6882 (1)	2226 (1)	544 (1)	43 (1)
O	6059 (4)	1181 (3)	289 (2)	69 (2)
N(1)	5932 (4)	2841 (3)	−48 (2)	46 (2)
N(2)	5751 (4)	2490 (3)	1073 (2)	44 (2)
N(3)	7918 (4)	1716 (3)	1163 (2)	46 (2)
N(4)	8163 (4)	2140 (3)	58 (2)	46 (2)
C(1)	6177 (5)	2965 (3)	−589 (2)	52 (2)
C(2)	5276 (6)	3428 (4)	−871 (3)	65 (3)
C(3)	4501 (6)	3591 (4)	−527 (3)	64 (3)
C(4)	4896 (5)	3232 (3)	−6 (2)	48 (2)
C(5)	4336 (5)	3274 (3)	458 (2)	49 (2)
C(6)	4729 (5)	2923 (3)	961 (3)	50 (2)
C(7)	4151 (5)	2946 (3)	1452 (3)	55 (2)
C(8)	4769 (5)	2534 (3)	1850 (3)	53 (2)
C(9)	5768 (5)	2240 (3)	1622 (2)	46 (2)
C(10)	6650 (5)	1799 (3)	1910 (2)	48 (2)
C(11)	7654 (5)	1568 (3)	1698 (2)	49 (2)
C(12)	8619 (6)	1172 (4)	2005 (3)	63 (3)
C(13)	9448 (6)	1084 (4)	1668 (3)	65 (3)
C(14)	9029 (5)	1415 (3)	1146 (2)	48 (2)
C(15)	9662 (5)	1443 (3)	692 (2)	48 (2)
C(16)	9249 (5)	1774 (3)	183 (2)	48 (2)
C(17)	9840 (5)	1752 (4)	−293 (2)	59 (2)
C(18)	9131 (5)	2088 (4)	−709 (3)	64 (3)
C(19)	8098 (5)	2339 (3)	−502 (2)	50 (2)
C(20)	7176 (5)	2714 (3)	−810 (2)	49 (2)
C(21)	7207 (5)	2862 (4)	−1412 (2)	57 (2)
C(22)	6343 (7)	2579 (5)	−1808 (3)	82 (2)
C(23)	6361 (8)	2739 (5)	−2382 (3)	100 (4)
C(24)	7232 (8)	3164 (5)	−2531 (3)	96 (4)
C(25)	8091 (7)	3451 (5)	−2146 (3)	86 (4)
C(26)	8072 (6)	3313 (4)	−1584 (3)	71 (3)
C(27)	3209 (5)	3717 (4)	425 (2)	58 (2)
C(28)	2129 (5)	3380 (4)	235 (3)	78 (3)
C(29)	1092 (7)	3784 (7)	233 (4)	114 (5)
C(30)	1131 (9)	4501 (7)	411 (4)	133 (5)
C(31)	2191 (11)	4850 (6)	575 (4)	126 (5)
C(32)	3235 (8)	4437 (5)	589 (3)	96 (4)
C(33)	6505 (5)	1564 (3)	2496 (2)	51 (2)
C(34)	6165 (5)	847 (4)	2604 (3)	65 (3)
C(35)	6064 (7)	636 (4)	3144 (3)	81 (3)
C(36)	6293 (6)	1134 (5)	3578 (3)	79 (3)
C(37)	6607 (7)	1838 (5)	3468 (3)	84 (3)
C(38)	6723 (6)	2056 (4)	2932 (3)	73 (3)
C(39)	10846 (5)	1062 (4)	745 (2)	54 (2)
C(40)	10922 (7)	305 (5)	666 (4)	122 (5)
C(41)	12020 (8)	−31 (5)	693 (5)	149 (6)
C(42)	13028 (6)	367 (5)	816 (4)	102 (4)
C(43)	12962 (6)	1099 (4)	903 (3)	73 (3)
C(44)	11878 (5)	1445 (4)	863 (3)	62 (2)
Sb	8272 (1)	4089 (1)	3907 (1)	82 (1)
F(1)	7674 (10)	3411 (4)	4328 (4)	272 (6)
F(2)	8775 (8)	3343 (6)	3512 (4)	269 (6)
F(3)	8898 (10)	4801 (6)	3543 (4)	330 (7)
F(4)	7663 (14)	4821 (5)	4266 (4)	344 (8)
F(5)	7061 (10)	4097 (7)	3378 (5)	350 (8)
F(6)	9555 (9)	4089 (7)	4383 (5)	376 (8)
C(1a)	7127 (8)	4270 (4)	916 (4)	104 (4)
C(2a)	6709 (8)	4295 (5)	1418 (4)	108 (4)
C(3a)	7302 (10)	3945 (6)	1862 (4)	112 (5)
C(4a)	8310 (11)	3555 (6)	1820 (5)	116 (5)
C(5a)	8713 (8)	3534 (5)	1303 (5)	123 (5)
C(6a)	8105 (7)	3878 (4)	862 (4)	108 (4)
C(1b)	3503 (13)	4758 (7)	2103 (5)	198 (8)
C(2b)	2365 (13)	4620 (7)	2125 (5)	186 (7)
C(3b)	2015 (17)	4271 (8)	2520 (5)	242 (10)
C(4b)	2816 (20)	4033 (11)	2950 (8)	392 (15)
C(5b)	3988 (17)	4149 (7)	2932 (6)	282 (11)
C(6b)	4378 (12)	4524 (6)	2538 (5)	166 (6)

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

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times$ 10^3) for **2**

atom	x	y	z	U_{eq}[a]
Mn	0	0	0	34 (1)
O(1)	1799 (2)	−1542 (2)	43 (1)	56 (1)
N(1)	969 (2)	1862 (2)	−330 (1)	37 (1)
N(2)	461 (2)	798 (2)	881 (1)	37 (1)
C(1)	1128 (2)	2196 (3)	−953 (1)	38 (1)
C(2)	1820 (2)	3681 (3)	−991 (1)	46 (1)
C(3)	2089 (2)	4245 (3)	−408 (1)	46 (1)
C(4)	1583 (2)	3102 (3)	10 (1)	39 (1)
C(5)	1728 (2)	3234 (3)	662 (1)	38 (1)
C(6)	1203 (2)	2133 (3)	1061 (1)	39 (1)
C(7)	1336 (2)	2243 (3)	1735 (1)	47 (1)
C(8)	657 (2)	1024 (3)	1954 (1)	48 (1)
C(9)	100 (2)	108 (3)	1429 (1)	39 (1)
C(10)	−654 (2)	−1273 (3)	1467 (1)	40 (1)
C(11)	−1020 (2)	−1779 (3)	2101 (1)	47 (1)
C(12)	−142 (3)	−2486 (4)	2545 (1)	64 (1)
C(13)	−527 (4)	−2927 (4)	3129 (1)	83 (1)
C(14)	−1740 (4)	−2651 (4)	3268 (1)	91 (2)
C(15)	−2617 (4)	−1978 (4)	2831 (2)	80 (1)
C(16)	−2264 (3)	−1543 (3)	2241 (1)	61 (1)
C(17)	2510 (2)	4620 (3)	943 (1)	40 (1)
C(18)	3806 (2)	4706 (3)	872 (1)	56 (1)
C(19)	4523 (3)	6014 (4)	1122 (2)	67 (1)
C(20)	3978 (3)	7222 (3)	1435 (1)	59 (1)
C(21)	2693 (3)	7156 (3)	1509 (1)	55 (1)
C(22)	1967 (2)	5850 (3)	1266 (1)	48 (1)
Cl	5000	0	0	110 (1)
O(2)	4088 (4)	280 (6)	454 (3)	122 (2)
O(3)	4047 (6)	487 (8)	−478 (3)	158 (3)
O(4)	4473 (6)	−1840 (8)	−107 (3)	155 (3)

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

reflections. Intensity data were collected on a Syntex P2_1 four-circle diffractometer with Mo Kα radiation (λ = 0.710 69 Å). The monoaqua complex, **1**, crystallizes in the monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$) with the crystal parameters given in Table I. The data were corrected for absorption by using the ψ-scan method.[33] The structure was solved by conventional heavy-atom/Patterson methods.[34] Blocked-cascade least-squares refinement of 4977 unique reflections, $F_o > 2\sigma(F_o)$ and $3° < 2\theta < 45°$, resulted in the final residuals given in Table I. The weighting scheme utilized weights of the form $w = [\sigma^2(F_o) + |g|(F_o)^2]^{-1}$ (where $g = 0.0002$). Scattering factors were those for neutral atoms.[35] Neither the metalloporphyrin cation with the proximal π-benzene nor the SbF_6^- counterion was disordered. Final positional and thermal parameters for **1** are given in Table II.

A lustrous black prism of **2** with dimensions 0.68 × 0.70 × 1.36 mm was attached to a glass capillary with epoxy cement. The fiber was mounted on a goniometer head that was then placed on the same diffractometer. After the crystal was optically centered, accurate cell parameters was obtained by least-squares refinement of 25 reflections. The ω Wyckoff scan method was used with a variable scan rate of 4.88–19.53°/min. Intensity measurements of three standards every 197 reflections showed no evidence of crystal deterioration. Intensities (2θ = 3–50°) were measured for 4849 reflections, of which 3641 unique reflections were observed, $F_o > 2.5\sigma(F_o)$. The structure was again solved in the uniquely determined monoclinic space group $P2_1/n$. The position of the Mn atom was placed at the origin 0, 0, 0. A Patterson vector for Cl was present at the special position $^1/_2$, 0, 0. All non-hydrogen atoms were located in subsequent difference Fourier syntheses. Only the hydrogen atoms bonded to carbon were placed in calculated positions and allowed to remain "linked" to their parent carbon atoms throughout the refinement (C–H = 0.96 Å; $U_{iso}(H) = 1.2U_{eq}(C)$). The final electron density map was featureless with the largest positive peak being 0.54 e Å^{-3} (1.08 Å from Cl). Blocked-cascade-matrix least-squares refinement of 273 variables gave final residuals given in Table I. The data were corrected for the Lorentz effect, polarization, and absorption.[33] The same weighting scheme utilized for **1** was utilized for **2**, and the scattering factors used were, again, those for neutral atoms.[35] The perchlorate counterion is disordered, yielding six regions of high electron density for the oxygen atoms with the chlorine occupying a special position. Each

---

(33) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968** *A24*, 351.

(34) Calculations were performed on a Data General ECLIPSE S/140 computer using SHELXTL (version 4.1) software supplied by Nicolet XRD Corp.

(35) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

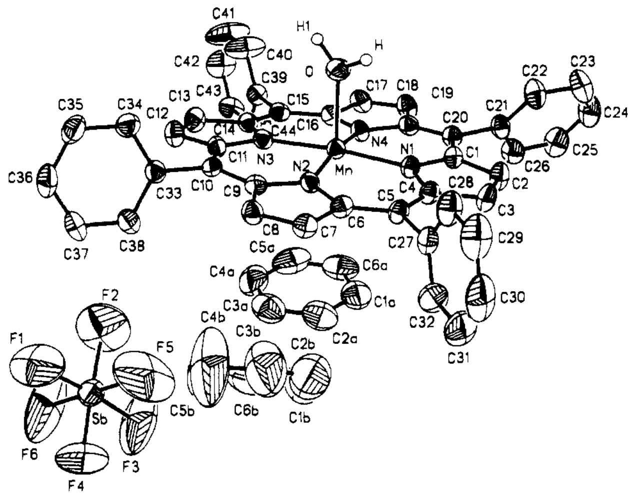

Figure 1. ORTEP and atom-numbering diagram for **1** showing interacting and noninteracting benzene rings as well as the SbF_6^- counterion. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30% probability level.

region of electron density was assigned a two-thirds occupancy. A similar type of disorder involving species with localized T_d symmetry residing at crystallographic inversion centers and a reasonable procedure for addressing this type of disorder have been given by Evans and Pope.[36] Final positional and thermal parameters for **2** are given in Table III.

Results and Discussion

In the course of investigating the relationships between the chemical reactivity and the structural and electronic features of manganese porphyrins containing aqua, hydroxo, and oxo ligands, we were able to isolate two more coordination forms of $S = 2$, aqua Mn^{III} porphyrin complexes. Addition of 1 equiv of water to the complex $Mn^{III}TPP(SbF_6)$ in benzene produces a chromophore indistinguishable from that of the recently reported monoaqua(tetraphenylporphinato)manganese(III) cation in toluene.[21] Slow diffusion of heptane into this benzene solution produces purple-red prisms of aqua(tetraphenylporphinato)manganese(III) hexafluoroantimonate-2-benzene, $[(H_2O)Mn^{III}TPP]^+(SbF_6^-)\cdot C_6H_6$ (**1**). Although monoaqua Mn^{III} porphyrin cations are readily generated in a variety of solutions and can be isolated in the solid state in this form, the corresponding six-coordinate diaqua complexes start forming in solution when the mole ratio of water to $[Mn^{III}TPP]^+$ exceeds 1.0 in nonpolar solvents such as benzene. When 2 mol of water/mol of $[Mn^{III}TPP]^+$ is present in benzene solution and the counterion is perchlorate, the crystalline complex diaqua(tetraphenylporphinato)manganese(III) perchlorate, $[(H_2O)_2Mn^{III}TPP]^+(ClO_4)^-$ (**2**), can be isolated in high yield.

Characterization of the isolated complexes **1** and **2** by several physical methods produced little information. Both complexes are EPR silent. The UV-visible spectra in these particular complexes yield little information about π-interactions between the metalloporphyrin and the benzene. The ^1H NMR spectra for the complexes in deuteriated noncoordinating solvents show rapid exchange of water on the time scale of the experiment at 25 °C obscuring kinetic effects of π-benzene-metalloporphyrin interactions on axial ligand binding. The EPR, UV-visible, and ^1H NMR data unequivocally confirm that both complexes possess $S = 2$, Mn^{III} ions. The unusually high exchange rates of the axial water ligands as well as the bond distances and angles discussed below are also in accord with the presence of high-spin tetragonally elongated Mn^{III} ions in both complexes both in the solid state and in solution. In the absence of information concerning π-benzene-metalloporphyrin interactions from application of the above techniques, we were compelled to resort to X-ray crystallography to definitively characterize these two complexes.

Selected bond distances and angles for **1** are summarized in Table IV. This complex contains a neutral axial ligand, H_2O, and a proximal π-bound small arene, benzene, that appears to be stereochemically noninnocent. The combination ORTEP and atom-numbering diagram (Figure 1) shows that although one benzene molecule of crystallization and the counterion are not within van der Waals distance of any atom of the metalloporphyrin, the second benzene molecule of crystallization is located directly under the porphyrin ring at a sufficiently close distance to facilitate a weak π-interaction between the two aromatic moieties.[26-28,37] Although a large number of electron donor-acceptor complexes between arenes and porphyrins are known[28,37] and several electron donor-acceptor complexes between arenes and metalloporphyrins have been characterized crystallographically,[26-28] **1** represents the first example of a metalloporphyrin cation complex containing two proximal groups: one, a π-interacting arene that is not another porphyrin ring, and one, a

Table IV. Selected Bond Lengths (Å) and Angles (deg) in **1**

Mn–O	2.145 (5)	Mn–N(1)	1.999 (4)
Mn–N(2)	1.990 (5)	Mn–N(3)	1.991 (4)
Mn–N(4)	1.998 (5)	N(1)–C(1)	1.391 (7)
N(1)–C(4)	1.385 (7)	N(2)–C(6)	1.392 (7)
N(2)–C(9)	1.397 (7)	N(3)–C(11)	1.391 (7)
N(3)–C(14)	1.378 (7)	N(4)–C(16)	1.392 (7)
N(4)–C(19)	1.390 (7)	C(1)–C(2)	1.416 (8)
C(1)–C(20)	1.385 (8)	C(2)–C(3)	1.323 (10)
C(3)–C(4)	1.428 (8)	C(4)–C(5)	1.365 (8)
C(5)–C(6)	1.384 (8)	C(5)–C(27)	1.499 (8)
C(6)–C(7)	1.435 (9)	C(7)–C(8)	1.331 (8)
C(8)–C(9)	1.429 (8)	C(9)–C(10)	1.385 (8)
C(10)–C(11)	1.377 (9)	C(10)–C(33)	1.506 (8)
C(11)–C(12)	1.425 (8)	C(12)–C(13)	1.337 (10)
C(13)–C(14)	1.414 (8)	C(14)–C(15)	1.392 (9)
C(15)–C(16)	1.387 (8)	C(15)–C(39)	1.497 (8)
C(16)–C(17)	1.410 (8)	C(17)–C(18)	1.340 (8)
C(18)–C(19)	1.412 (9)	C(19)–C(20)	1.380 (8)
O–Mn–N(1)	96.1 (2)	O–Mn–N(2)	95.6 (2)
N(1)–Mn–N(2)	89.7 (2)	O–Mn–N(3)	90.2 (2)
N(1)–Mn–N(3)	173.7 (2)	N(2)–Mn–N(3)	89.7 (3)
O–Mn–N(4)	95.0 (2)	N(1)–Mn–N(4)	89.2 (2)
N(2)–Mn–N(4)	167.4 (2)	N(3)–Mn–N(4)	90.2 (2)
Mn–N(1)–C(1)	127.0 (4)	Mn–N(1)–C(4)	127.4 (4)
C(1)–N(1)–C(4)	105.6 (4)	Mn–N(2)–C(6)	127.1 (4)
Mn–N(2)–C(9)	127.4 (3)	C(6)–N(2)–C(9)	105.4 (4)
Mn–N(3)–C(11)	127.1 (4)	Mn–N(3)–C(14)	127.3 (4)
C(11)–N(3)–C(14)	105.6 (4)	Mn–N(4)–C(16)	127.1 (4)
Mn–N(4)–C(19)	127.3 (4)	C(16)–N(4)–C(19)	105.0 (4)
N(1)–C(1)–C(2)	108.6 (5)	N(1)–C(1)–C(20)	126.1 (5)
C(2)–C(1)–C(20)	125.2 (5)	C(1)–C(2)–C(3)	109.1 (6)
C(2)–C(3)–C(4)	107.4 (6)	N(1)–C(4)–C(3)	109.3 (5)
N(1)–C(4)–C(5)	125.7 (5)	C(3)–C(4)–C(5)	125.0 (5)
C(4)–C(5)–C(6)	124.4 (5)	C(4)–C(5)–C(27)	118.5 (5)
C(6)–C(5)–C(27)	117.1 (5)	N(2)–C(6)–C(5)	125.7 (5)
N(2)–C(6)–C(7)	108.6 (5)	C(5)–C(6)–C(7)	125.8 (5)
C(6)–C(7)–C(8)	109.0 (5)	C(7)–C(8)–C(9)	107.1 (5)
N(2)–C(9)–C(8)	109.8 (5)	N(2)–C(9)–C(10)	125.0 (5)
C(8)–C(8)–C(10)	125.1 (5)	C(9)–C(10)–C(11)	124.2 (5)
C(9)–C(10)–C(33)	117.7 (5)	C(11)–C(10)–C(33)	118.1 (5)
N(3)–C(11)–C(10)	125.8 (5)	N(3)–C(11)–C(12)	109.3 (5)
C(10)–C(11)–C(12)	124.9 (5)	C(11)–C(12)–C(13)	107.2 (6)
C(12)–C(13)–C(14)	108.4 (6)	N(3)–C(14)–C(13)	109.5 (5)
N(3)–C(14)–C(15)	125.7 (5)	C(13)–C(14)–C(15)	124.8 (5)
C(14)–C(15)–C(16)	124.4 (5)	C(14)–C(15)–C(39)	118.2 (5)
C(16)–C(15)–C(39)	117.3 (5)	N(4)–C(16)–C(15)	125.0 (5)
N(4)–C(16)–C(17)	110.1 (5)	C(15)–C(16)–C(17)	124.8 (5)
C(16)–C(17)–C(18)	107.1 (5)	C(17)–C(18)–C(19)	108.7 (6)
N(4)–C(19)–C(18)	109.1 (5)	N(4)–C(19)–C(20)	125.7 (5)
C(18)–C(19)–C(20)	125.2 (5)	C(1)–C(20)–C(19)	123.5 (5)
C(1)–C(20)–C(21)	117.2 (5)	C(19)–C(20)–C(21)	119.3 (5)
C(20)–C(21)–C(22)	120.1 (6)	C(20)–C(21)–C(26)	121.2 (5)
C(5)–C(27)–C(28)	119.7 (6)	C(5)–C(27)–C(32)	120.5 (6)
C(10)–C(33)–C(34)	120.5 (5)	C(10)–C(33)–C(38)	120.7 (5)
C(15)–C(39)–C(40)	120.8 (5)	C(15)–C(39)–C(44)	121.9 (6)

---

(36) Evans, H. T.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 501.

(37) (a) Herbstein, F. H. In *Perspectives in Structural Chemistry*; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York; pp 166–395 and references cited therein. (b) Treibs, A. *Justus Liebigs Ann. Chem.* **1929**, *476*, 1 and references cited therein.

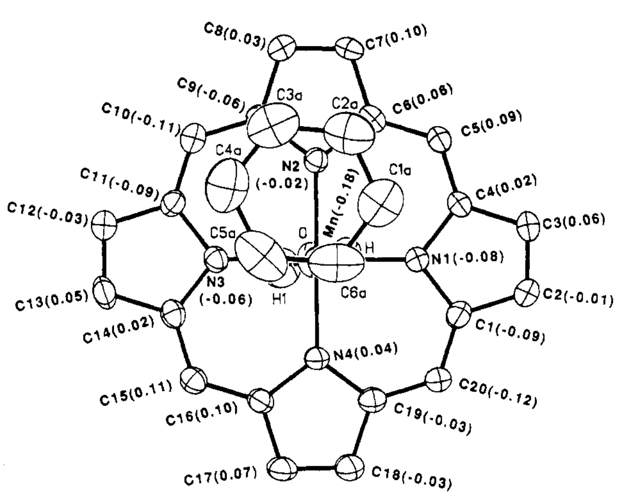

Figure 2. View of **1** down the axis defined by the manganese atom and the water oxygen, illustrating the orientation of the benzene molecule involved in π-interaction with the metalloporphyrin. Displacements, in angstrom units, of all the non-hydrogen atoms from the mean 24-atom porphyrin plane are given in parentheses after the atom number; positive displacement values are toward the side of the metalloporphyrin ring with the π-benzene moiety (toward the viewer), and negative values are toward the side with the aqua ligand.

neutral molecule (water) conventionally ligated to the metal. More pertinently, since both **1** and the monoaqua five-coordinate Mn porphyrin cation without a proximal π-arene have been crystallographically characterized, the effect of this π-interaction on the coordination stereochemistry of the metal in the solid state can be assessed (vide infra). The dihedral or tilt angle defined by the mean 6-atom benzene and 24-atom metalloporphyrin planes is 6.6°. The average distance between the 6 benzene carbon atoms and the mean metalloporphyrin plane is 3.28 Å. The π-interacting benzene in **1** is situated with two of the carbons straddling one of the porphyrin nitrogen atoms, and the benzene carbon atom in **1** closest to the Mn atom, C(6a), is also closest to the mean 24-atom metalloporphyrin plane (3.118 Å). Both these features are similar to those seen in several other structures containing π-arene–metalloporphyrin interactions.[27,28] In **1**, benzene carbon atom C(6a) lies almost directly under the Mn atom. These orientational features of the benzene with respect to the metalloporphyrin ring and, more interestingly, the conformational perturbations of the metalloporphyrin ring induced by the presence of the π-benzene are seen clearly in Figure 2. This figure views the molecule down the axis defined by the manganese and water oxygen atoms and illustrates the displacements of the metalloporphyrin atoms from the mean 24-atom metalloporphyrin plane.

Although the interplanar separation between the benzene and metalloporphyrin in **1** is close enough, on the basis of many other physical studies,[37] to permit some degree of electronic communication between these aromatic groups, the distance between the Mn d_{z^2} orbital and an appropriate π orbital of the benzene (at carbon C(6a)) precludes a substantial *specific orbital interaction* involving these particular atoms. The Mn–C(6a) carbon distance is 3.32 Å, while the sum of the covalent radius for octahedral Mn^{III} (ca. 1.4 Å)[38] and the half-thickness of the benzene molecule (1.7 Å)[40] is ca. 3.1 Å. The lack of evidence for a strong specific orbital interaction between the π-benzene and the Mn does not preclude the ability of the benzene moiety to affect the Mn stereochemistry. The latter, as defined by the classical coordination polyhedron constituted by the four porphyrin nitrogens and the oxygen of the axial water molecule in the case of **1**, is distorted by the presence of the benzene molecule (vide infra), on the basis of the structural paradigms derived from X-ray crystallographic examinations of many other first-row transition-metal porphyrin complexes. We find it most reasonable that such distortions result principally from the consequences of benzene–porphyrin π-interactions and orbital overlap, and not from benzene–Mn orbital overlap.

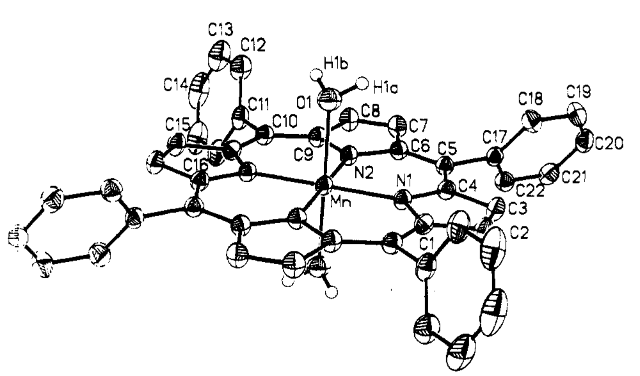

Figure 3. ORTEP and atom-numbering diagram for the cation of **2**, $[(H_2O)_2Mn^{III}TPP]^+$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30% probability level.

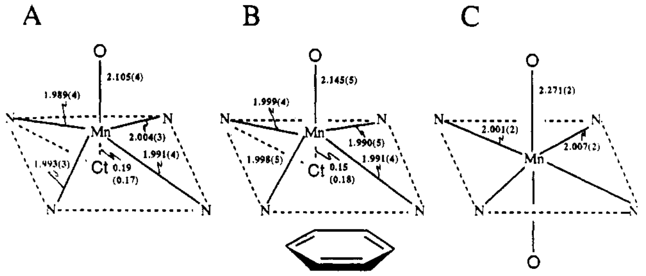

Figure 4. Comparison of coordination environments for Mn in three (tetraphenylporphinato)manganese(III) cationic complexes with aqua axial ligands. A is the monoaqua complex without a proximal interacting aromatic group, B is the monoaqua complex with a proximal benzene (**1**), and C is the diaqua complex (**2**). The d_{Mn-Ct} values for A and B are reported in two ways: the values before the parentheses are defined relative to the mean N_4 plane; those in the parentheses are defined relative to the mean 24-atom porphyrin plane.

The specific effect of the π-benzene interaction with respect to the conformation of the porphyrin ring can be assessed to some extent from Figure 2. The saddle-shaped conformation of the porphyrin ring, minimizing at meso carbon atoms C(10) and C(20) (maximal displacement toward the aqua ligand) and maximizing roughly at meso carbon atoms C(5) and C(15), is evident from the figure. It is not clear that there is a marked influence of the π-benzene on the overall shape of the 24-atom porphyrin periphery. However, the S_4 ruffling character of the four porphyrin nitrogens, expected here on the basis of the conformation of the other porphyrin atoms and from precedent derived from many high-spin Mn^{III} porphyrins[21,31,32,41,42] and related metalloporphyrin complexes in general,[43] clearly appears to be broken by the location of N(2), the nitrogen directly under the π-benzene moiety. This porphyrin nitrogen appears to be experiencing the presence of the benzene molecule that is causing it to move a few hundreds of an angstrom unit toward the side of the porphyrin containing the water

---

(38) There appear to be no adequate values for the covalent radius of high-spin Mn^{III}. From the covalent radius given by Cotton and Richardson for Mn^0 based on $Mn_2(CO)_8$, of 1.39 Å,[39] and the covalent radius for Mn^{II} based on several structures analyzed by Pauling,[40] of ~1.5 Å, we estimate an approximate covalent radius of 1.4 Å for the tetragonally distorted Mn^{III} with configuration of $(d_{xz}\pi,d_{yz}\pi)^2(d_{xy})^1(d_{z^2})^1$.

(39) Cotton, F. A.; Richardson, D. C. *Inorg. Chem.* **1966**, *5*, 1851.

(40) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(41) Structurally characterized five-coordinate Mn(III) complexes: (a) Scheidt, W. R.; Lee, Y. J.; Luangdilok, W.; Haller, K. J.; Anzai, K.; Hatano, K. *Inorg. Chem.* **1983**, *22*, 1516. (b) Tulinsky, A.; Chen, B. M. L. *J. Am. Chem. Soc.* **1977**, *99*, 3647. (c) Day, V. W.; Stults, B. R.; Tasset, E. L.; Marianelli, R. S.; Boucher, L. J. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 505.

(42) Structurally characterized six-coordinate Mn(III) complexes: (a) Kirner, J. F.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 2081. (b) Day, V. W.; Stults, B. R.; Tasset, E. L.; Day, R. O.; Marianelli, R. S. *J. Am. Chem. Soc.* **1974**, *96*, 2650.

(43) (a) Scheidt, W. R. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. III, Part A, Chapter 10. (b) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339.

Table V. Selected Bond Lengths (Å) and Angles (deg) in **2**

Mn–O(1)	2.271 (2)	Mn–N(1)	2.001 (2)
Mn–N(2)	2.007 (2)	N(1)–C(4)	1.372 (3)
N(1)–C(1)	1.384 (3)	N(2)–C(9)	1.386 (3)
N(2)–C(6)	1.377 (3)	C(1)–C(10a)	1.387 (3)
C(1)–C(2)	1.424 (3)	C(3)–C(4)	1.432 (3)
C(2)–C(3)	1.332 (3)	C(5)–C(6)	1.391 (3)
C(4)–C(5)	1.392 (3)	C(6)–C(7)	1.436 (3)
C(5)–C(17)	1.494 (3)	C(7)–C(8)	1.339 (4)
C(8)–C(9)	1.427 (3)	C(9)–C(10)	1.389 (3)
C(10)–C(11)	1.502 (3)		
O(1)–Mn–N(1)	89.3 (1)	O(1)–Mn–N(2)	91.0 (1)
N(1)–Mn–N(2)	89.8 (1)	O(1)–Mn–O(1a)	180.0
N(1)–Mn–O(1a)	90.7 (1)	N(2)–Mn–O(1a)	89.0 (1)
N(2)–Mn–N(1a)	90.2 (1)	N(1)–Mn–N(1a)	180.0
O(1a)–Mn–N(1a)	89.3 (1)	N(1)–Mn–N(2a)	90.2 (1)
N(2)–Mn–N(2a)	180.0	O(1a)–Mn–N(2a)	91.0 (1)
N(1a)–Mn–N(2a)	89.8 (1)	Mn–N(1)–C(1)	127.0 (1)
Mn–N(1)–C(4)	127.4 (1)	C(1)–N(1)–C(4)	105.5 (2)
Mn–N(2)–C(6)	126.9 (1)	Mn–N(2)–C(9)	126.8 (1)
C(6)–N(2)–C(9)	106.4 (2)	N(1)–C(1)–C(2)	109.5 (2)
N(1)–C(1)–C(10a)	125.9 (2)	C(2)–C(1)–C(10a)	124.6 (2)
C(1)–C(2)–C(3)	107.9 (2)	C(2)–C(3)–C(4)	107.3 (2)
N(1)–C(4)–C(3)	109.8 (2)	N(1)–C(4)–C(5)	126.0 (2)
C(3)–C(4)–C(5)	124.2 (2)	C(4)–C(5)–C(6)	123.5 (2)
C(4)–C(5)–C(17)	117.7 (2)	C(6)–C(5)–C(17)	118.8 (2)
N(2)–C(6)–C(5)	126.3 (2)	N(2)–C(6)–C(7)	109.1 (2)
C(5)–C(6)–C(7)	124.6 (2)	C(6)–C(7)–C(8)	107.4 (2)
C(7)–C(8)–C(9)	108.1 (2)	N(2)–C(9)–C(8)	108.9 (2)
N(2)–C(9)–C(10)	125.9 (2)	C(8)–C(9)–C(10)	125.2 (2)
C(9)–C(10)–C(11)	118.4 (2)	C(9)–C(10)–C(1a)	124.2 (2)
C(11)–C(10)–C(1a)	117.4 (2)	C(10)–C(11)–C(12)	121.3 (2)
C(10)–C(11)–C(16)	119.2 (2)	C(5)–C(17)–C(18)	120.2 (2)
C(5)–C(17)–C(22)	121.3 (2)		

molecule. We prefer to rationalize that this apparent displacement of N(2) from the expected position (by possibly as much as +0.05 Å) results from the consequences of both π-arene–metalloporphyrin electronic interactions and crystal packing forces. The latter are also likely manifesting themselves partially and unavoidably through the sterically sizable benzene ring. The manganese–porphyrin nitrogen distances in **1**, $d_{\mathrm{Mn-N(Por)}}$, of 1.990 (5)–1.999 (4) Å are similar to those in all other $S = 2$, $\mathrm{Mn^{III}}$ porphyrins that have been structurally characterized to date and reflect in large part an unoccupied $d_{x^2-y^2}$ orbital.[21,31,32,41-43] The data set was of sufficient quality that the hydrogen atoms on the water molecule could be located (Figure 1).

An ORTEP and atom-numbering diagram for **2** is given in Figure 3, and selected bond distances and angles for the compound are summarized in Table V. Again, the $d_{\mathrm{Mn-N(Por)}}$ values of 2.001 (2) and 2.007 (2) Å are typical of those seen in high-spin $\mathrm{Mn^{III}}$ porphyrins, and the hydrogen atoms of the crystallographically unique water molecule were located.

Figure 4 summarizes some of the salient structural features of the coordination environment of the Mn atom in the three high-spin aqua $\mathrm{Mn^{III}}$ porphyrin complexes characterized to date, the five-coordinate monoaqua cation (A in Figure 4), the monoaqua cation with the π-interacting benzene (B) (**1**), and the six-coordinate diaqua cation (C) (**2**). In order to make meaningful comparisons of the Mn coordination environments in these three structures, it is imperative that no interactions with any of the donor atoms in the primary coordination spheres of the Mn atoms, the four porphyrin nitrogens and the water oxygen atom(s), be evident. This is the case for all three structures. There are no close nonbonded contacts nor hydrogen bonds to any of these atoms in any of the structures. The manganese–porphyrin nitrogen distances do not vary greatly in the three structures. The Mn–porphyrin center (Ct) distances, $d_{\mathrm{Mn-Ct}}$, are 0.19 and 0.15 Å for $[(\mathrm{H_2O})\mathrm{MnTPP}]^+$ and the $[(\mathrm{H_2O})\mathrm{MnTPP}(\mathrm{C_6H_6})]^+$ cations, respectively, for Ct defined as the center of the $\mathrm{N_4}$ plane, and 0.17 and 0.18 Å for these complexes, respectively, for Ct defined as the center of the 24-atom plane. Finally, the Mn–axial-oxygen distances, $d_{\mathrm{Mn-O(ax)}}$, change systematically from A to B and from B to C and define to some extent the stereochemical impact of the proximal π-benzene. The presence of this aromatic molecule results in a lengthening of $d_{\mathrm{Mn-O(ax)}}$ by 0.04 Å. This lengthening of the bond between the metal and the axial oxygen has not only a thermodynamic aspect, the weakening of the bond, but likely also a kinetic aspect. π-Arene–metalloporphyrin interactions such as that in **1** may result in kinetic labilization of the axial ligand. The magnitude of such axial ligand labilization effects, however, might be difficult to substantiate experimentally. In any event, the complexes in Figure 4 collectively provide evidence that proximal π-interacting aromatic moieties can be sterically noninnocent and can influence, at least indirectly, metalloporphyrin stereochemistry.

In summary, NMR and other solution studies of metalloporphyrins as a function of solvent have suggested that arene–metalloporphyrin π-interactions can exert some influence on the ligand fields in metalloporphyrins, as discussed above,[24] but a search for π-interactions involving the highly labile aquamanganeseporphyrins **1** and **2** produced no substantive information concerning such interactions in the liquid phase for these complexes. Examination of the X-ray structures of three isoelectronic aquamanganese porphyrin complexes, however, yields some crystallographic evidence for perturbation of the stereochemistry of these Mn porphyrins by such interactions in the solid state.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8402994) for support.

Registry No. **1**, 111004-86-5; **2**, 95647-05-5; $\mathrm{Mn^{III}TPP(SbF_6)}$, 111004-87-6; $\mathrm{Mn^{III}TPP(ClO_4)}$, 79408-54-1.

Supplementary Material Available: For both structures, tables of anisotropic temperature factors, hydrogen coordinates and temperature factors, bond lengths, bond angles, nonbonded distances, and torsion angles and a complete ORTEP and atom-numbering diagram for **2** (19 pages); tables of observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.