which exists at neutral or even acidic pH, in principle is capable of binding to a thymine N3 (or uracil N3) position,[50] even in a dinucleotide containing also guanine.[51]

A crucial question is the likelihood of a T-N^3,G-N^1 cross-link from a steric point of view. In 5, the C1b' and C9a' positions, which in DNA would correspond to the separations of the two C1' positions in the glycosidic bonds, are separated by 9.50 Å. This value is to be compared with C1'⋯C1' separations of 6.05–6.79 Å in cis-[Pt(NH₃)₂{d(pGpG)}] molecules[3] and ca. 8 Å in partially unwound DNA containing an intercalator between two bases,[52] for example. From model building it would seem that a 9.50-Å separation between the C1' positions of two adjacent bases in one strand represents the upper limit for backbone unwinding and that, for this reason, a 1,3-linkage with an intervening base probably would be accomplished more easily than a 1,2-linkage. 1,3-Cross-links within a DNA strand have been observed before, albeit between other bases.[53]

Like in other Pt(II) compounds containing N3-bound uracil or thymine ligands,[9] the 1-MeU ligand in 5 has a protective effect

on all three ligands. Treatment with excess CN⁻ quickly and selectively displaces the N7-bound (dien)Pt^II entity while leaving the N1-bound entity unaffected. We have not been able to get crystals suitable for X-ray analysis yet, but we expect the complex formed, cis-(NH₃)₂Pt(1-MeU-N^3)(9-MeG-N^1), to display a similarly large dihedral angle between the two nucleobases as has been found with 5.

Conclusions. Two complexes 4 and 5 have been isolated and characterized by X-ray methods that involve a guanine binding pattern of Pt(II) entities (N7,N1 bridging), previously observed in solution both for cis-(NH₃)₂Pt^II (on reaction with 9-EtGH, guanosine, and 5'-GMP) and for (NH₃)₃Pt^II. 5 is special in that it represents a novel model for a cross-link of cis-(NH₃)₂Pt^II with two nucleobase donor atoms present in double-helical DNA in the interior only. Provided it were to be formed, it would cause a major perturbation of DNA structure due to the large dihedral angle of 101.8° between the base planes, irrespective of a possible intra- or interstrand fashion. Compared to it, the kinking of DNA, as induced by G-N^7,G-N^7 cross-linking at the periphery, is considerably smaller.

Supplementary Material Available: Tables of atomic and thermal parameters, anion geometry parameters, close contact parameters, equations of planes, and deviations of atoms from planes and figures showing IR and Raman spectra (14 pages); tables of observed and calculated structure factors (50 pages). Ordering information is given on any current masthead page.

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Reaction of Hydroxide Ion with Manganese(III) Tetramesitylporphyrin and the Oxidation States of Manganese Tetramesitylporphyrins[†]

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The autoreduction reaction of the non-μ-oxo-dimer-forming chloromanganese(III) tetramesitylporphyrin, (TMP)Mn^III(Cl), with methanolic tetra-n-butylammonium hydroxide (YO⁻ species = OH⁻ or CH₃O⁻) in acetonitrile and dimethyl sulfoxide under anaerobic conditions has been examined by UV/visible and ²H NMR spectroscopies, where the spectral changes accompanying the reaction could be associated with changes in the oxidation and ligation states of the manganese porphyrin. Two intermediates, (TMP)Mn^II and [(TMP)Mn^II(OY)]⁻, may be directly observed to form during the reaction by a mechanism thought to involve homolytic bond cleavage, which in a slower reaction convert to a product whose structure is suggested to be that of a [(TMP)-Mn^III(OY)₂]⁻ species. Exposure to air at any time during the reaction leads to the formation of the manganese(III) peroxo complex, [(TMP)Mn^III(O₂)]⁻. The [(TMP)Mn^II(OY)]⁻ species may be prepared independently from the reaction of (TMP)Mn^II with YO⁻, and ²H NMR spectral studies on the titration of a toluene solution of (TMP-d₈)Mn^II with YO⁻ indicate only one YO⁻ ligation. The pyrrole β-deuterium chemical shift for the [(TMP-d₈)Mn^II(OY)]⁻ complex in toluene at 25 °C is 37 ppm. The various oxidation states of the manganese tetramesitylporphyrins were examined in order to identify the intermediates and products of the reaction. Thin-layer spectroelectrochemical oxidation of the chloromanganese(III) tetramesitylporphyrin in methylene chloride shows the first 1e oxidation to be porphyrin centered, providing the manganese(III) porphyrin π cation radical, (•⁺TMP)Mn^III(Cl). Exchange of the chloro ligand for the hydroxy ligand shows that the first 1e oxidation of the hydroxymanganese(III) tetramesitylporphyrin at low temperature is metal centered, providing the (TMP)Mn^IV(O) species. Further 1e oxidation of the latter produces a species identified as the oxidized porphyrin radical cation, (•⁺TMP)Mn^IV(O). Spectroscopic data for the (TMP)-Mn^IV(OY)₂ and [(•⁺TMP)Mn^III(Cl)](SbCl₆⁻) species (UV/vis and ²H NMR) and the (•⁻TMP)Mn^II and (²⁻TMP)Mn^II species (UV/vis) are reported.

Introduction

Manganese constitutes an essential metal in several biological systems that are involved in electron-transfer reactions. By variations in its oxidation and ligation states it mediates such diverse biological functions as the oxidation of water to molecular oxygen in green plant photosynthesis,[1] disproportionation of hydrogen peroxide in several microorganisms (catalase activity),[2]

and decomposition of O₂•⁻ in bacterial superoxide dismutase.[3] Among these functions the oxidation of water to yield oxygen is

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[†] Abbreviations used: TMP, dianion of tetramesitylporphyrin; TPP, dianion of tetraphenylporphyrin.

probably the least understood. In order to provide chemical models for the redox behavior of manganese ions in biological processes, we have undertaken a study of the reactions of complexes of a manganese(III) porphyrin. The porphyrin macrocycle serves as a convenient and sensitive reporter chelating agent that allows the various oxidation, ligation, and spin states of manganese to be spectroscopically detected and identified.

Herein, we describe UV/vis and ^{2}H NMR spectral studies on the various oxidation states of the non-μ-oxo-dimer-forming manganese tetramesitylporphyrins and the course for reaction of HO⁻ with the manganese(III) species [(TMP)Mn^{III}]⁺. An understanding of the mechanism of oxidation of HO⁻ by [(TMP)-Mn^{III}]⁺ may be of some relevance to the conversion of water to O$_2$ in photosystem II of green plant photosynthesis.

Experimental Section

Materials. TMPH$_2$ was prepared by a previously reported procedure, and manganese was inserted by the standard route.[5] TMPH$_2$-d_8 was prepared by the same procedure from pyrrole-d_4 (Cambridge Isotopes). Acetonitrile (Burdick and Jackson) and methanol (Aldrich) were used as received from the supplier. Dimethyl sulfoxide and methylene chloride (Aldrich) were purified by established procedures.[6] All solvents were deoxygenated by three freeze–pump–thaw cycles and stored over 4-Å molecular sieves in a Vacuum Atmospheres glovebox under purified nitrogen. Tetra-n-butylammonium hydroxide [(n-Bu)$_4$N⁺OH⁻, Aldrich, 1 M solution in methanol] was used as received. Samples of (TMP)Mn^{II} were prepared by reduction of (TMP)Mn^{III}(Cl) with amalgamated zinc in toluene in a Vacuum Atmospheres glovebox. The solutions were stirred for 5 h to ensure complete reduction, filtered, and evaporated to dryness. (TMP)Mn^{III}(OH), [(•⁺TMP)Mn^{III}(Cl)](SbCl$_6$⁻), and (TMP)Mn^{IV}(OCH$_3$)$_2$ were prepared by established procedures.[7,12,13]

Reaction of (TMP)Mn^{III}(Cl) (1) with (n-Bu)$_4$N⁺OH⁻. Solutions of **1** in acetonitrile or DMSO were prepared under a nitrogen atmosphere and placed either in a UV/visible cuvette or NMR tube, capped with a rubber septum and sealed with Parafilm. In a typical experiment (n-Bu)$_4$N⁺OH⁻ (in methanol) was added (via gastight syringe) to a solution of **1** (1.5 × 10⁻⁵ M for visible studies and 3 × 10⁻³ M for NMR studies). The progress of the reaction was followed by visible and NMR spectroscopy.

Instrumentation. Absorption spectra and changes in absorbance with time were recorded on a Cary 14 spectrophotometer interfaced to a Zenith computer equipped with OLIS (On-Line Instrument System Inc.) data acquisition and processing software. The stopped-flow spectrophotometer contained a rapid-scan Harrick monochromator and OLIS computer interface. ^{2}H NMR spectra were recorded on a General Electric GN 500 Fourier transform spectrometer operating in the quadrature mode (^{2}H frequency at 77 MHz). The spectra were collected over a 20-kHz bandwidth with 8-K data points and a 37-μs 90° pulse. For a typical spectrum, between 5000 and 10 000 transients were accumulated and the signal-to-noise ratio was improved by apodization of the free induction decay. ESR spectra were recorded at X-band (3.2 kG). Microwave power of 1 mW and field modulation amplitude of 6.3 G at a frequency of 100 kHz were employed. The various oxidation states of manganese were electrochemically generated via controlled-potential electrolysis using a Bioanalytical Systems (BAS) CV-27 potentiostat with a three-electrode system in a 1-mm quartz cuvette containing a transparent platinum-minigrid working electrode.

Results

The reactions of (TMP)Mn^{III}(Cl) with hydroxide/methoxide (YO⁻) have been examined in acetonitrile and dimethyl sulfoxide,

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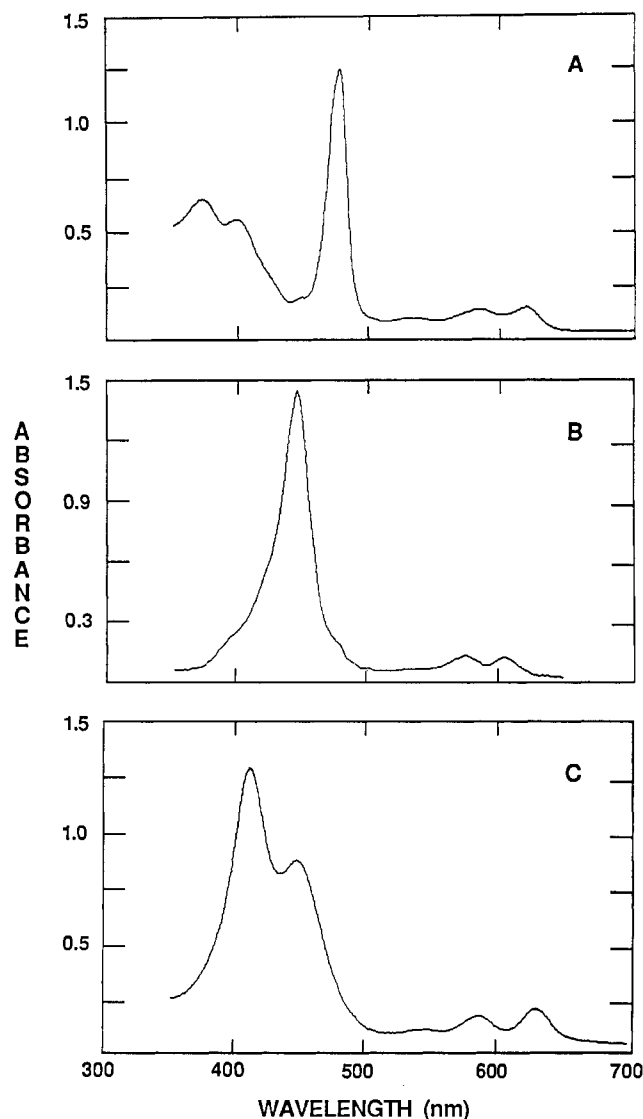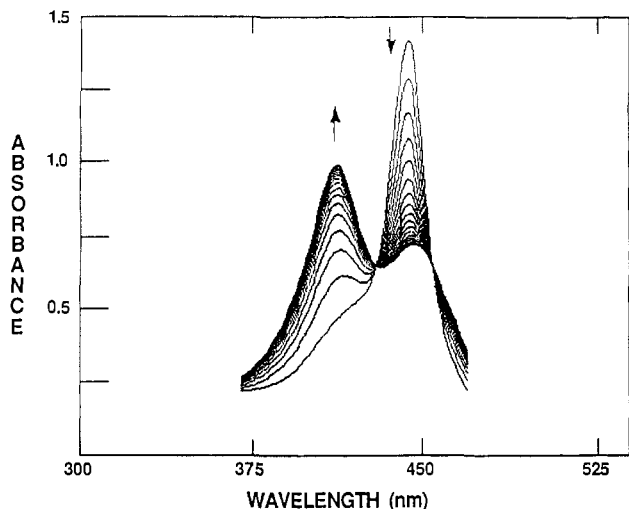

Figure 1. Electronic absorption spectra of an acetonitrile solution of (A) (TMP)Mn^{III}(Cl) (1.5 × 10⁻⁵ M), (B) product formed 3 ms after mixing (A) with (n-Bu)$_4$N⁺OH⁻/MeOH (1.7 × 10⁻³ M), and (C) **3** (after complete conversion).

by addition of aliquots of 1 M solutions of (n-Bu)$_4$N⁺OH⁻ in methanol. The reactions were monitored by optical and NMR spectroscopy, where the spectral changes accompanying the reaction could be associated with changes in the oxidation and ligation states of the manganese porphyrin.

Reactions of (TMP)Mn^{III}(Cl) with YO⁻. In CH$_3$CN and DMSO, (TMP)Mn^{III}(Cl) is known to dissociate to [(TMP)Mn^{III}]⁺ (cation of **1**) and Cl⁻.[8] Trace A of Figure 1 shows the visible spectrum of a 1.5 × 10⁻⁵ M solution of [(TMP)Mn^{III}]⁺ in CH$_3$CN. Addition of 1.7 × 10⁻³ M YO⁻ to this solution under anaerobic conditions gave the transient species **2** [λ_{max} = 445 nm (ϵ = 9.1 × 10⁴)] (trace B) within 3 ms after mixing. In experiments employing varying YO⁻ concentrations the minimum rate constant for **1** → **2** was estimated to be 10⁶ M⁻¹ s⁻¹.[4] The reactions were carried out under the pseudo-first-order conditions of [YO⁻] ≫ [[(TMP)Mn^{III}]⁺], and the second-order rate constant was approximated as 10⁶ M⁻¹ s⁻¹ by dividing the pseudo-first-order rate constant by [YO⁻]. With [YO⁻] = 1.7 × 10⁻³ M, **2** converts to **3** [λ_{max} = 412 (ϵ = 8.1 × 10⁴), 448 nm (6.3 × 10⁴)] (trace C) in a pseudo-first-order process with an observed rate of 6 × 10⁻³ s⁻¹. Figure 2 shows an expansion of the spectral changes observed in this experiment between 370 and 470 nm. At the concentration of YO⁻ employed there is seen clean isosbestic points (430, 456 nm), which demonstrates the absence of any long-lived intermediates. Thus, in the presence of sufficient YO⁻ one only observes the conversion of **2** → **3**. However, intermediates could be ob-

Figure 2. Visible spectral changes observed upon addition of a methanolic solution of $(n\text{-Bu})_4N^+OH^-$ (1.7×10^{-3} M) to an acetonitrile solution of $(TMP)Mn^{III}(Cl)$ (1.5×10^{-5} M). Spectral scans were taken at 30-s intervals.

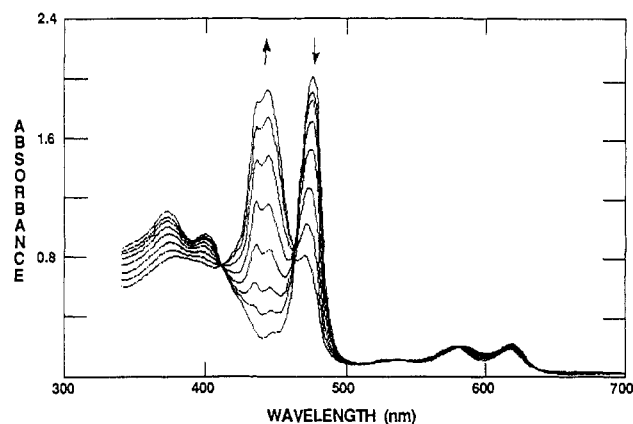**Figure 3.** Visible spectral changes observed for the titration of an acetonitrile solution of $(TMP)Mn^{III}(Cl)$ (3 mL, 1.5×10^{-5} M) with aliquots of $(n\text{-Bu})_4N^+OH^-$ in methanol (2 μL, 1×10^{-2} M). The exact end point is not shown because of competing formation of **3**.

served in the reaction when **1** was titrated with YO⁻. Figure 3 shows the spectral changes upon addition of aliquots of methanolic YO⁻ (2 μL, 1×10^{-2} M) to a 1.5×10^{-5} M (3 mL) CH₃CN solution of **1**. Examination of Figure 3 shows a decrease in the Soret absorbance for **1** ($\lambda_{max} = 477$ nm) with concomitant increase in absorbances at both 437 and 445 nm. On the basis of its Soret position, the absorbance at 437 nm can be assigned to $(TMP)Mn^{II}$. The Soret absorbance at 445 nm can be ascribed to $[(TMP)\text{-}Mn^{II}(OY)]^-$ (**2**). This species was prepared independently through the reaction of $(TMP)Mn^{II}$ with hydroxide in methanol (vide infra) and found to have a λ_{max} at 445 nm. Identical spectral changes were obtained when $NaOMe/MeOH$ replaced $(n\text{-Bu})_4N^+\text{-}OH^-/MeOH$ in the reaction with $[(TMP)Mn^{III}]^+$.

The study was further extended by examining the reaction of YO⁻ with $[(TMP\text{-}d_8)Mn^{III}]^+$ by ²H NMR spectroscopy, where the pyrrole β-protons of $(TMP)Mn^{III}(Cl)$ were replaced by deuterons. ²H NMR spectroscopy on the pyrrole β-deuterons was employed to facilitate the detection of the signals, which are paramagnetically broadened by the manganese ion. The ²H NMR spectrum of $[(TMP\text{-}d_8)Mn^{III}]^+$ (**1**) in CH_3CN/C_6H_6[9] at 25 °C showed a pyrrole β-deuterium resonance at ca. -21 ppm (line width 51 Hz). Titration with YO⁻ resulted in a downfield shift of the pyrrole β-deuterium signal until 2 equiv of YO⁻ had been added (to -10 ppm). Upon further addition of YO⁻, the β-pyrrole signal showed an *upfield shift* until it reached ca. -17 ppm. Further addition of YO⁻ showed no change, except a decrease in the intensity of the signal due to dilution.

Additionally, the ESR spectra of the reaction were examined to detect intermediates or free radicals. Unfortunately the rapid
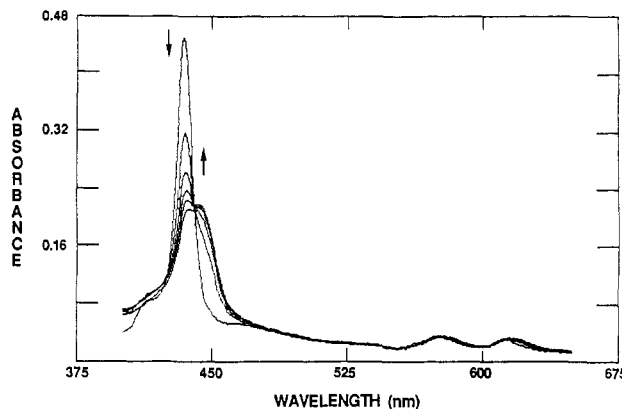

Figure 4. Visible spectral changes observed for the titration of an acetonitrile solution of $(TMP)Mn^{II}$ (3 mL, 1.5×10^{-5} M) with aliquots of $(n\text{-Bu})_4N^+OH^-$ in methanol (2 μL, 1×10^{-2} M). The exact end point is not shown because of competing formation of **3**.

conversion of **2** → **3** precludes elucidation of the ESR spectrum of **2**. However, the ESR spectrum of the reaction product (**3**) in frozen CH_3CN/C_6H_6[9] at 80 K showed no signals. Also several attempts to detect ESR signals attributable to any radical species formed during the reaction were unsuccessful. The possibility that a hydroperoxide species, formed by self-reaction of HO•, is involved in the conversion of **2** → **3** was examined by studying the reaction of $(TMP)Mn^{II}$ with hydrogen peroxide in the presence of 1×10^{-3} M YO⁻. There was found to be no change in the rate of **2** → **3** to a concentration of 2×10^{-2} M in hydrogen peroxide.

As observed in a previous study,[4] introduction of air at any time to CH₃CN or DMSO solutions that initially contained $[(TMP)Mn^{III}]^+$ plus YO⁻ resulted in the very slow ($k_{obs} = 10^{-4}$ to 10^{-5} s⁻¹, depending on time of exposure) but clean formation of a visible spectrum identical with that of $(TMP)Mn^{III}(O_2)^-$ [386, 425 sh, 445 ($\epsilon = 1.1 \times 10^5$), 574, 617 nm].

Characterization of $(TMP)Mn^{II}(OY)^-$. The Soret absorbance for $[(TMP)Mn^{II}(OY)]^-$ (**2**) formed in the reaction of YO⁻ with $[(TMP)Mn^{III}]^+$ in CH₃CN is equivalent to that produced by the titration of an acetonitrile solution of $(TMP)Mn^{II}$ with methanolic $(n\text{-Bu})_4N^+OH^-$. $(TMP)Mn^{II}$ (presumably coordinated by one CH_3CN[10]) shows a characteristic Soret absorbance at 437 nm. On addition of aliquots of a YO⁻ solution (1×10^{-2} M, 2 μL) to a CH₃CN solution of $(TMP)Mn^{II}$ (3 mL, 1.5×10^{-5} M), there is observed the growth of a new Soret absorbance at 445 nm, which is attributable to $[(TMP)Mn^{II}(OY)]^-$ (Figure 4). Interestingly, addition of an excess of YO⁻ (10 μL, 1 M) showed the formation of **3** ($\lambda_{max} = 412, 448$ nm).

Further evidence for the axial ligation of YO⁻ by the $(TMP)Mn^{II}$ moiety comes from ²H NMR studies accompanying the titration of a toluene solution of $(TMP\text{-}d_8)Mn^{II}$ with a methanolic solution of $(n\text{-Bu})_4N^+OH^-$. In toluene at 25 °C, $(TMP\text{-}d_8)Mn^{II}$ shows a pyrrole β-resonance at ca. 35 ppm (line width 71 Hz) that is consistent with observations on the $(TPP\text{-}d_8)Mn^{II}$ complex.[11] Addition of 1 equiv of YO⁻ to $(TMP\text{-}d_8)Mn^{II}$ produced a downfield shift in the pyrrole β-resonance to ca. 37 ppm (line width 129 Hz). The chemical shift value remains unchanged upon further YO⁻ addition (2-5 equiv). This observation may be interpreted to indicate that $(TMP\text{-}d_8)Mn^{II}$ ligates only one YO⁻. An alternative, but a very unlikely possibility, is that a second YO⁻ ligates but causes no NMR spectral change.

Spectral Characterization of High-Valent Manganese Tetramesitylporphyrins. In order to identify the product(s) **3**, it is necessary to examine the various oxidation states of the manganese tetramesitylporphyrins. The oxidation of manganese(III) porphyrins is well established to be either metal or ligand centered, the latter being a π cation radical.[12–17] We find that the first

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Table I. UV/Visible and NMR Spectral Parameters for the Various Oxidation, Ligation, and Spin States of Manganese Porphyrins

compd	oxidn state	spin state	λ_{max}, nm	δ(pyrrole), ppm (temp, °C)	ref
(TMP)Mn	II	$^5/_2$	437^d	35 (25)^{c,i}	k
(TPP)Mn	II	$^5/_2$	437^e	34 (25)^{e,i}	11, 49
[(TMP)Mn(OH)]⁻	II	$^5/_2$	445^b	37 (25)^{c,i}	k
(TMP)Mn(Cl)	III	2	477^b	−21 (25)^{f,i}	k
(TPP)Mn(Cl)	III	2	480^g	−30 (35)^{g,i}	45
[(TMP)Mn(O₂)]⁻	III	2	445^b	33 (25)^{b,i}	4, 47
[(TPP)Mn(O₂)]⁻	III	2	445	32 (25)^{e,i}	39
[(TPP)Mn(Im)₂]⁻	III	1	408, 451^e	−18 (26)^{e,i}	35
[(•⁺TMP)Mn(Cl)](SbCl₆)^a	III	2, $^1/_2$	392, 490^c	−40 (25)^{d,i}	k
(TMP)Mn(OCH₃)₂	IV	$^3/_2$	422^b	−16 (25)^{c,i}	k
(TMP)Mn(O)	IV	$^3/_2$	422^d	−32 (−40)^{d,i}	7
(TPP)Mn(N)	V		424^h	9 (20)^{g,i}	48

^{a} Porphyrin π cation radical. ^{b} Acetonitrile. ^{c} Toluene. ^{d} Methylene chloride. ^{e} Dimethyl sulfoxide. ^{f} Acetonitrile/benzene. ^{g} Chloroform. ^{h} Chlorobenzene. ^{i} ²H nucleus. ^{j} ¹H nucleus. ^{k} This work.

oxidation state of (TMP)Mn^III(X) (where X⁻ is a weakly basic anion as Cl⁻) in CH₂Cl₂ is a manganese(III) porphyrin π cation radical (•⁺TMP)Mn^III(Cl) [(+1.11 V vs SCE; λ = 389 (ε = 2.8 × 10³), 412, 483, 488 (2.1 × 10³), 578, 608 nm)]. The species [(•⁺TMP)Mn^III(Cl)](SbCl₆⁻) was chemically prepared by oxidation of (TMP)Mn^III(Cl) in CH₂Cl₂ by the one-electron-oxidant phenoxathiin hexachloroantimonate after the procedure of Spreer and co-workers[13] and found to possess a spectrum identical with that of (•⁺TMP)Mn^III(Cl) prepared by controlled-potential oxidation. The ²H NMR spectrum of [(•⁺TMP-d_8)Mn^III(Cl)]-(SbCl₆⁻) in CH₂Cl₂ at 25 °C showed a pyrrole β-deuterium signal at ca. −40 ppm (line width 110 Hz) in agreement with previous reports on the ¹H NMR spectrum of [(•⁺TPP)Mn^III(Cl)](ClO₄⁻).[17]

Exchange of Cl⁻ ligand for HO⁻ [to provide (TMP)Mn^III(OH)] changes the first oxidation potential to +1.04 V (SCE) and the product of the oxidation from porphyrin centered to metal centered. The resulting (TMP)Mn^IV(O) complex[51] exhibits a Soret absorbance at 424 nm (ε = 9.6 × 10⁴) at −78 °C, which is consistent with previous reports on manganese(IV) porphyrins [trace B (---) of Figure 5].[7,12,13,18−21] Further 1e oxidation of (TMP)Mn^IV(O) (+1.24 V vs SCE) at −78 °C in CH₂Cl₂ yields a spectrum with a broad Soret at 410 nm (ε = 6.8 × 10⁴) [trace C (—) of Figure 5]. Also, a shoulder at 395 nm increases in absorbance during the controlled-potential oxidation. The spectrum is atypical of manganese(V) species[22] and is reminiscent of the iron(IV) porphyrin π cation radicals.[23,24] Further, the presence of a low-energy absorption at 578 nm characterizes a porphyrin radical. On the basis of its visible spectrum, we assign a porphyrin π-cation-radical structure to the product of the second 1e oxidation of (TMP)Mn^IV(O).

The chemical or electrochemical oxidation of an acetonitrile solution of (TMP)Mn^III(Cl) made basic by addition of a methanolic solution of NaOMe (to 10⁻² M) yields the six-coordinate (TMP)Mn^IV(OCH₃)₂, which has a visible spectrum (λ_max = 422 nm) in agreement with reports on the analogous (TPP)Mn^IV(O-CH₃)₂ complex.[12,13] The ²H NMR spectrum of the six-coordinate ($S = ^3/_2$) (TMP-d_8)Mn^IV(OCH₃)₂ complex in toluene showed a pyrrole β-resonance at ca. −16 ppm (line width 66 Hz) at 25 °C. The related (TMP)Mn^IV(OY)₂ complex was prepared by the controlled-potential oxidation of a CH₃CN solution of (TMP)-Mn^III(Cl) (5 × 10⁻⁴ M) containing 0.1 M (n-Bu)₄N⁺ClO₄⁻ at
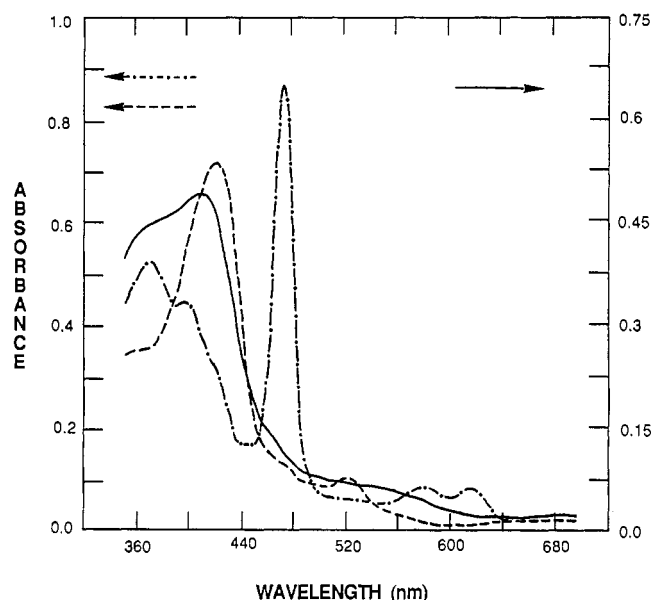

Figure 5. Visible spectra of (A) (TMP)Mn^III(OH) (·−·), (B) the product (TMP)Mn^IV(O) of the 1e oxidation of (TMP)Mn^III(OH) (---), and (C) the product (•⁺TMP)Mn^IV(O) of the 2e oxidation of (TMP)Mn^III(OH) (—). All reactions were carried out in methylene chloride with 0.1 M tetra-n-butylammonium perchlorate as supporting electrolyte at −78 °C.

+1.16 V, followed by the addition of a 20-μL methanolic solution 1 M in (n-Bu)₄N⁺OH⁻. The visible spectrum, consistent with the assigned structure, shows a characteristic λ_max at 422 nm.

Spectral Characterization of Low-Valent Manganese Tetramesitylporphyrins. It is known that manganese(III) porphyrins undergo three 1e reductions.[24,25] Thin-layer spectroelectrochemical controlled-potential reduction of (TMP)Mn^III(Cl) provides the UV/vis spectral characterization of the lower valent states of manganese tetramesitylporphyrin. Both electrochemical and chemical studies on (TMP)Mn^III(Cl) in acetonitrile confirm that the first reduction yields (TMP)Mn^II. The 2e reduction of (TMP)Mn^III(Cl) (5 × 10⁻⁴ M) in CH₃CN containing 0.1 M (n-Bu)₄N⁺ClO₄⁻ (−1.52 V vs SCE) provides a visible spectrum [408 (ε = 4.3 × 10⁴), 448 (4.3 × 10⁴), 584, 628 nm] ascribed to the anion-radical complex (•⁻TMP)Mn^II. Further 1e reduction (−1.98 V vs SCE) yielded the visible spectrum [428 (ε = 3.4 × 10⁴), 484 (3.7 × 10⁴), 569 nm] for the dianion (²⁻TMP)Mn^II complex.

Table I summarizes some of the optical and NMR spectral parameters for the various oxidation and ligation states of manganese tetramesitylporphyrins obtained in the present study. Also included in Table I are representative optical and NMR spectral parameters for manganese tetraphenylporphyrins obtained from the literature.
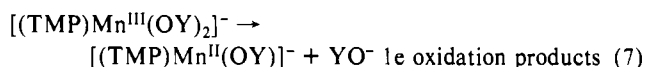
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(22) (TMP)Mn^VO(X) (X = monoanion) and (TPP)Mn^VN complexes exhibit characteristic Soret absorbances between 422 and 424 nm.⁴⁷,⁴⁸,⁵⁰
(23) Calderwood, T. S.; Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 8272.
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Discussion

The observations on the behavior of the manganese(III) tetramesitylporphyrin in CH_3CN or DMSO in the presence of HO^- and MeO^- (YO^- species) are consistent with an autoreduction reaction. The possible reactions involving both the irreversible reduction of $[(TMP)Mn^{III}]^+$ to $(TMP)Mn^{II}$ and the labile ligation equilibria of $[(TMP)Mn^{III}]^+$ and $(TMP)Mn^{II}$ are summarized in eqs 1–7 (where L = solvent). Two intermediates, (TMP)-

$$(TMP)Mn^{III}(Cl) + L \rightleftharpoons [(TMP)Mn^{III}(L)]^+ + Cl^- \quad (1)$$

$$[(TMP)Mn^{III}(L)]^+ + L \rightleftharpoons [(TMP)Mn^{III}(L)_2]^+ \quad (2)$$

$$[(TMP)Mn^{III}(L)_2]^+ + YO^- \rightleftharpoons (TMP)Mn^{III}(L)(OY) + L \quad (3)$$

$$(TMP)Mn^{III}(L)(OY) + YO^- \rightleftharpoons$$
$$[(TMP)Mn^{III}(OY)_2]^- + L \quad (4)$$

$$(TMP)Mn^{III}(L)(OY) \rightarrow$$
$$(TMP)Mn^{II}(L) + YO^- \text{ 1e oxidation products} \quad (5)$$

$$(TMP)Mn^{II}(L) + YO^- \rightleftharpoons [(TMP)Mn^{II}(OY)]^- + L \quad (6)$$

$$[(TMP)Mn^{III}(OY)_2]^- \rightarrow$$
$$[(TMP)Mn^{II}(OY)]^- + YO^- \text{ 1e oxidation products} \quad (7)$$
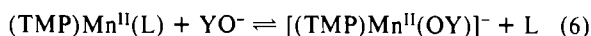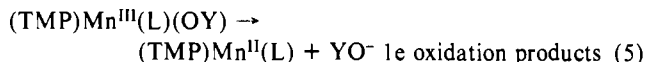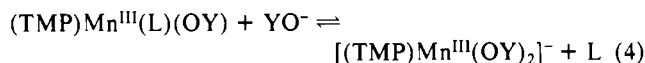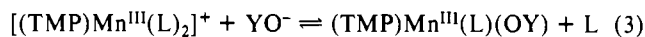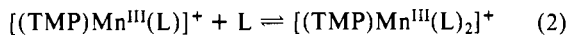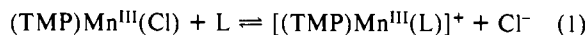
$Mn^{II}(L)$ and $[(TMP)Mn^{II}(OY)]^-$, have been directly observed during the reaction. The $[(TMP)Mn^{II}(OY)]^-$ complex was independently prepared from the reaction of YO^- with $(TMP)Mn^{II}$. ^2H NMR spectral observations during the titration of $(TMP-d_8)Mn^{II}$ with YO^- indicate only one YO^- ligates to provide the five-coordinate $[(TMP-d_8)Mn^{II}(OY)]^-$. The X-ray structure of the related pentacoordinated $[(TPP)Mn^{II}(Cl)]^-$ shows the central manganese(II) ion to be raised 0.64 Å out-of-plane of the porphyrin ring.[39] Such out-of-plane displacement prevents any strong bonding interactions at the sixth coordination site. The same considerations may apply to the pentacoordinated $[(TMP)-Mn^{II}(OY)]^-$ such that the formation of a six-coordinate $[(TMP)Mn^{II}(OY)_2]^{2-}$ complex is considered unlikely.

The autoreduction of $[(TMP)Mn^{III}]^+$ to yield the mananese(II) complexes (**1** → **2**) (eqs 5 and 7) requires a base-catalyzed electron transfer from YO^- to manganese(III). Possible paths include an outer-sphere electron transfer from free YO^- to manganese(III), an inner-sphere electron transfer from coordinated YO^- to manganese(III) by homolytic Mn–O bond cleavage, or, alternatively, nucleophilic attack on coordinated hydroxide by YO^-.

An outer-sphere electron-transfer oxidation of free hydroxide to hydroxyl radical (eq 8) is unlikely due to the redox potentials for the reactants. Electrochemical studies by Sawyer and co-

$$(TMP)Mn^{III}(L)(OH) + OH^- \rightarrow$$
$$[(TMP)Mn^{II}(OH)]^- + L + {}^\bullet OH \quad (8)$$
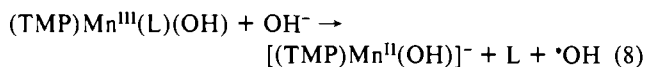
workers have demonstrated that the potential for the $HO^\bullet/HO^-$ redox couple is +0.7 V (vs SCE) as compared to –0.1 V for the $(TPP)Mn^{III}(ClO_4)/(TPP)Mn^{II}$ couple.[27,28] Further, these investigators have also shown that the potential for the oxidation of HO^- is considerably reduced if the HO^- moiety is complexed to a transition metal. The potential for the oxidation of HO^- (in CH_3CN) in the presence of $(TPP)Mn^{III}(ClO_4)$ has been determined to be –0.59 V (SCE).[28] Thus the reduction of the manganese(III) porphyrin by YO^- must involve an electron transfer from manganese(III)-bound YO^-.

Mechanisms involving simple homolytic cleavage of the Mn–O bond (eq 9) or nucleophilic attack on coordinated hydroxide by free YO^- (eq 10) would yield ${}^\bullet OY$ or $O^{\bullet-}$ radicals. The very facile

$$(TMP)Mn^{III}(L)(OY) \rightarrow (TMP)Mn^{II}(L) + {}^\bullet OY \quad (9)$$

$$(TMP)Mn^{III}(L)(OH) + YO^- \rightarrow$$
$$(TMP)Mn^{II}(L) + O^{\bullet-} + YOH \quad (10)$$

reaction of $[(TMP)Mn^{III}]^+$ with YO^- to provide $[(TMP)Mn^{II}-(OY)]^-$ (**2**) is followed by a slower conversion of **2** → **3**. The hydroxyl radicals that are formed in eq 9 could self-react to provide hydrogen peroxide. However, this is unlikely due to expected competing reactions of $HO^\bullet$ and $O^{\bullet-}$ with the solvent.[29,30] In any event, we have shown that the addition of hydrogen peroxide does not expedite the conversion of **2** → **3**.

Independent synthesis and UV/vis spectral characterization of $(TMP)Mn^{IV}(OY)_2$, $[({}^{\bullet+}TMP)Mn^{III}(Cl)](SbCl_6^-)$, $({}^{\bullet-}TMP)-Mn^{II}$, and $(^{2-}TMP)Mn^{II}$ (under Results) show that **3** does not consist of combination or separate manganese(IV) porphyrin, manganese(III) porphyrin π-cation-radical, manganese(II) porphyrin anion-radical, or manganese(II) dianion species.

On the basis of information obtained from chemical and spectroscopic studies, we suggest that **3** is a mixture of low-spin ($S = 1$) manganese(III) $[(TMP)Mn^{III}(OH)_2]^-$, $[(TMP)Mn^{III}-(OH)(OCH_3)]^-$, and $[(TMP)Mn^{III}(OCH_3)_2]^-$ complexes rather than $(TMP)Mn^{IV}(OY)_2$ (as previously proposed[4]) or $({}^{\bullet-}TMP)-Mn^{II}$. This conclusion is supported in part by the absence of ESR signals for the spent reaction solution taken at 80 K. Monomeric manganese(IV) and manganese(II) states are known to show distinct ESR signals,[31-33] whereas the even-spin d^4 manganese(III) in the ($S = 2$) high-spin state (as in $(TMP)Mn^{III}(OY)$) or ($S = 1$) low-spin state (as in $(TMP)Mn^{III}(OY)_2^-$) is not expected to be ESR active at liquid-nitrogen temperatures.[8] A high-spin manganese(III) formulation for **3** may be dismissed on the basis of its Soret absorbance ($\lambda_{max} = 412, 448$ nm). High-spin manganese(III) porphyrins are characterized by Soret absorbances in the 470–480-nm region.

The mechanism for the oxidation of $[(TMP)Mn^{II}(OY)]^-$ to $[(TMP)Mn^{III}(OY)_2]^-$ is unclear at this stage. However, it has recently been suggested that strong electron donating ligands such as methoxide, isopropoxide, or *sec*-butoxide can act as electron donors in the oxidation of $(P)Co^{II}$ to $[(P)Co^{III}(OCH_3)_2]^-$ (where P = protoporphyrin IX dimethyl ester) under strictly anaerobic conditions.[34] The same considerations may apply to the oxidation of $[(TMP)Mn^{II}(OY)]^-$. However, the possibility of trace adventitious dioxygen acting as an oxidant cannot be completely ruled out.

In general, low-spin manganese(III) complexes such as $[(TMP)Mn^{III}(OH)_2]^-$, $[(TMP)Mn^{III}(OH)(OCH_3)]^-$, or $[(TMP)Mn^{III}(OCH_3)_2]^-$ are not common. A very strong ligand field is required to induce the d^4 manganese(III) ions in the high-spin $S = 2$ state to the low-spin $S = 1$ state. Recently, diimidazolate and dicyanide complexes of manganese(III) tetraphenylporphyrins have been identified as low-spin derivatives through NMR and solid-state measurements.[35,36]
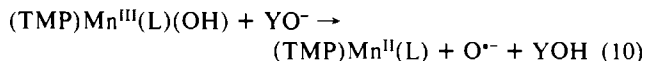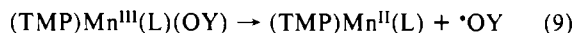
^2H NMR spectral studies on the reaction of YO^- with $[(TMP-d_8)Mn^{III}]^+$ in CH_3CN/C_6H_6 are also consistent with these observations. Titration of $[(TMP-d_8)Mn^{III}]^+$ with YO^- shows a continuing downfield shift of the pyrrole β-deuterium signal until 2 equiv of YO^- has been added. The downfield shift may be interpreted to indicate an average resonance of the pyrrole deuterons for the two oxidation states $[(TMP-d_8)Mn^{III}]^+$ and $[(TMP-d_8)Mn^{II}(OY)]^-$. The observation of an averaged chemical shift for the two species indicates rapid electron exchange, where the same manganese species exists in both oxidation states. Similar observations have been described by La Mar and co-workers for the autoreduction reactions of $(TPP)Fe^{III}(Cl)$ by CN^-.[37,38] The

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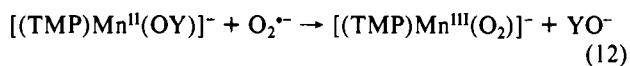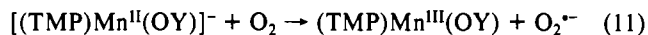
rate of electron exchange between $[(\text{TMP-}d_8)\text{Mn}^{III}]^+$ and $[(\text{TMP-}d_8)\text{Mn}^{II}(\text{OY})]^-$ is very fast on the NMR time scale, and from the pulse intervals the rate constant for the exchange may be estimated to be greater than 2×10^3 s^{-1}. Upon addition of YO⁻ in excess of 2 equiv, the pyrrole β-deuterium signal moved upfield (from −10 to −17 ppm). The upfield movement may be interpreted to indicate the onset of an averaged chemical shift between $[(\text{TMP-}d_8)\text{Mn}^{II}(\text{OY})]^-$ and $[(\text{TMP-}d_8)\text{Mn}^{III}(\text{OY})_2]^-$. Goff and co-workers have shown that the ¹H NMR spectra of low-spin manganese(III) tetraphenylporphyrin complexes are characterized by a sharp pyrrole β-resonance in the −14 to −18 ppm region (line width 25 Hz) at 26 °C.[35] Under our experimental conditions, we do not observe exclusive formation of $[(\text{TMP-}d_8)\text{Mn}^{III}(\text{OY})_2]^-$. The broad pyrrole β-deuteron resonance (ca. 60 Hz) indicates some competitive autoreduction and oxidation processes between $([\text{TMP-}d_8)\text{Mn}^{II}(\text{OY})]^-$ and $[(\text{TMP-}d_8)\text{Mn}^{III}(\text{OY})_2]^-$. Unfortunately, attempts to examine the reaction at low temperature have been unsuccessful due to the relatively high freezing points of the solvents that could be employed.

Clearly the solvent also plays an important role in the reactions of eqs 5 and 7 and in the conversion of **2 → 3**. Thus, the reactions occur in the ligating solvents CH₃CN and DMSO but not in CH₂Cl₂ or benzene. This may be explained by the stabilizing dipolar interactions of the solvent with the negatively charged $[(\text{TMP})\text{Mn}^{II}(\text{OY})]^-$ and $[(\text{TMP})\text{Mn}^{III}(\text{OY})_2]^-$ complexes and by the solvation of the hydroxy ligands. Further, the role of solvent coordination at the second axial site of $(\text{TMP})\text{Mn}^{III}(\text{OY})$ may well be important in promoting the oxidation of the bound hydroxide or methoxide.

Reaction of $[(\text{TMP})\text{Mn}^{II}(\text{OY})]^-$ with Oxygen. As reported previously,[4] addition of air to a reaction solution initially containing HO⁻ and $[(\text{TMP})\text{Mn}^{III}]^+$ produces the visible spectrum previously shown by Valentine and co-workers[39] to be characteristic of the peroxomanganese(III) species $[(\text{TPP})\text{Mn}^{III}(\text{O}_2)]^-$. Valentine prepared the latter by reaction of $(\text{TPP})\text{Mn}^{III}(\text{Cl})$ with 2 equiv of superoxide anion, O₂·⁻. The first equivalent was found to reduce $(\text{TPP})\text{Mn}^{III}(\text{Cl})$ to $(\text{TPP})\text{Mn}^{II}$, while the second equivalent reacts further to produce $(\text{TPP})\text{Mn}^{III}(\text{O}_2)^-$. A possible mechanism for the formation of $(\text{TMP})\text{Mn}^{III}(\text{O}_2)^-$ in our system is described by eqs 11 and 12. Reactions 11 and 12 offer an alternative means

$$[(\text{TMP})\text{Mn}^{II}(\text{OY})]^- + \text{O}_2 \rightarrow (\text{TMP})\text{Mn}^{III}(\text{OY}) + \text{O}_2\cdot^- \quad (11)$$

$$[(\text{TMP})\text{Mn}^{II}(\text{OY})]^- + \text{O}_2\cdot^- \rightarrow [(\text{TMP})\text{Mn}^{III}(\text{O}_2)]^- + \text{YO}^- \quad (12)$$

for preparing $[(\text{TMP})\text{Mn}^{III}(\text{O}_2)]^-$ under basic conditions in the absence of K⁺O₂⁻·. We suggest the reaction with O₂ to be slow due to the product **3** consisting predominantly of $[(\text{TMP})\text{Mn}^{III}(\text{OY})_2]^-$. Thus, the $[(\text{TMP})\text{Mn}^{III}(\text{OY})_2]^-$ must either dissociate YO⁻ and undergo reduction to $[(\text{TMP})\text{Mn}^{II}(\text{OY})]^-$ or directly undergo reduction to $[(\text{TMP})\text{Mn}^{II}(\text{OY})]^-$ before reacting with O₂. In contrast toluene solutions of $(\text{TPP})\text{Mn}^{II}$ or $(\text{TPP})\text{Mn}^{II}(\text{py})$ react very rapidly with O₂ to give a $(\text{TPP})\text{Mn}(\text{O}_2)$ adduct.[40,41]

Electronic Structure of Manganese Tetramesitylporphyrins. The ²H NMR spectral data for the various oxidation states of manganese tetramesitylporphyrins allow interpretations of electronic structure. The observed hyperfine shifts for the manganese porphyrin pyrrole deuterons are the sum of the contact and dipolar contributions. The contact contribution to the pyrrole deuteron shifts reflect the mode of spin delocalization of the manganese and may be used to provide some insight into the electronic structure of the manganese ions.[42] In particular, the direction

of the contact shifts provide information on unpaired spin density in the d orbitals.[43] The d-electron configuration for the high-spin $(S = {}^5/_2)$ manganese(II) ion in the C_{4v} symmetry is $d_{xy}{}^1$, $d_{xz}{}^1$, $d_{yz}{}^1$, $d_{z^2}{}^1$, $d_{x^2-y^2}{}^1$. Thus, the large downfield contact shift for the pyrrole deuteron signals for $(\text{TMP})\text{Mn}^{II}$ and $[(\text{TMP})\text{Mn}^{II}(\text{OY})]^-$ may be associated with the unpaired spin in the σ-type $d_{x^2-y^2}$ orbital. Moreover, the downfield bias in the pyrrole deuteron contact shift reflects a metal → porphyrin π-electron delocalization.[43] The electronic spectra of $(\text{TMP})\text{Mn}^{II}$ and $[(\text{TMP})\text{Mn}^{II}(\text{OY})]^-$ display pseudonormal porphyrin spectra,[44] where the Soret peak of $[(\text{TMP})\text{Mn}^{II}(\text{OY})]^-$ is red shifted relative to that of $(\text{TMP})\text{Mn}^{II}$.

In contrast, the contact shift of the high-spin $(S = 2)$ $(\text{TMP})\text{Mn}^{III}(\text{Cl})$ complex shows an upfield bias reflecting primarily a porphyrin → metal π bonding.[45] Consistent with this observation the electronic spectrum of $(\text{TMP})\text{Mn}^{III}(\text{Cl})$ displays a d-type hyperporphyrin spectrum[44] with a characteristic peak at 477 nm due to the ring-to-metal charge transfer.[8] The difference between the pyrrole deuteron contact shifts of the manganese(III) porphyrin and the manganese(II) porphyrins is attributed to the absence of the unpaired spin in the σ-type $d_{x^2-y^2}$ orbital of manganese(III) (d-orbital occupancy for the high-spin manganese(III) ion in C_{4v} symmetry is $d_{xy}{}^1$, $d_{xz}{}^1$, $d_{yz}{}^1$, $d_{z^2}{}^1$, $d_{x^2-y^2}{}^0$).

Similarly, the highly oxidized six-coordinate $(S = {}^3/_2)$ $(\text{TMP})\text{Mn}^{IV}(\text{OCH}_3)_2$ complex and the $[(\cdot^+\text{TMP})\text{Mn}^{III}(\text{Cl})]$-$(\text{SbCl}_6{}^-)$ complex (containing an oxidized porphyrin radical) exhibit negative hyperfine shifts, the major difference being the greater hyperfine shift observed for the $[(\cdot^+\text{TMP})\text{Mn}^{III}(\text{Cl})]$-$(\text{SbCl}_6{}^-)$ complex. The upfield bias of the pyrrole contact shifts reflect primarily a porphyrin → metal π bonding. The d-orbital configuration for the manganese(IV) ion in the D_{4h} symmetry is $d_{xy}{}^1$, $d_{xz}{}^1$, $d_{yz}{}^1$, $d_{z^2}{}^0$, $d_{x^2-y^2}{}^0$, which places the unpaired electron spins in the e-type orbitals of π symmetry, so that π spin delocalization with the porphyrin molecular orbitals $[3e(\pi)]$ occurs. The electronic spectrum of $(\text{TMP})\text{Mn}^{IV}(\text{OCH}_3)_2$ displays a d-type hyperporphyrin spectrum, with prominent absorptions at 422 and 447 nm. In contrast, the electronic spectrum of $[(\cdot^+\text{TMP})$-$\text{Mn}^{III}(\text{Cl})](\text{SbCl}_6{}^-)$ shows a reduction of the high-energy absorptions and the presence of low-energy absorptions at 578 and 608 nm.

The electrochemical and spectroscopic observations on highly oxidized manganese porphyrins underscores the importance of the axial ligands in determining the electronic structure of the oxidized manganese. Thus, hydroxy, methoxy, or oxo ligands favor a metal-centered-oxidized manganese(IV) structure, while halide ions form the manganese(III) porphyrin π-cation-radical structure. The interaction between the axial ligand orbitals and the manganese π-electron orbitals must contribute significantly to these differences. Substantial π interaction between the manganese and axial ligand orbitals would localize the unpaired spin density within the metal–axial ligand orbitals, thereby favoring a metal-centered oxidation.

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