

II, are -14.4 (2) kcal/mol and -47.4 (7) cal/(mol K) for O_2 binding to FeTTPPP(1,2-Me₂Im) compared to -14.6 (5) kcal/mol and -42 (2) cal/(mol K) for FeTpivPP(1,2-Me₂Im).¹⁴ In comparison of the picket-fence porphyrin, then, the diminished O_2 affinity of the bis-pocket porphyrin is primarily entropic. This again emphasizes the contribution which solvation of the porphyrin complexes makes to the observed equilibrium. Comparisons to the capped porphyrin¹⁸ show the distortion induced by the cap affects the enthalpy of ligand binding primarily, as expected. Comparison to Mb shows enthalpies and entropies which are similar, but detailed comparison is difficult due to the reported variation among different species' Mb.²⁹ Due to the complexity of Hb's cooperative binding, meaningful comparisons to the ΔH° and ΔS° of oxygenation are difficult. The effect of steric hindrance in the axial base (i.e., 1,2-Me₂Im) within related systems is principally enthalpic for the picket-fence porphyrins but entropic for the capped porphyrin; the origin of this difference remains unknown.

Conclusion

We have described the synthesis and ligand binding of a bis-pocket iron porphyrin complex in which both faces of the mac-

rocycle are well protected by nonpolar pockets. The steric protection provides for reversible dioxygen binding by Fe(II) complexes of the bis-pocket porphyrin with remarkable kinetic stability. The greatly diminished O_2 affinity of this system is due to the nonpolar nature of the binding site, as confirmed from the effect of polar solvents and not to conformational steric strain, as confirmed by equilibria base binding studies. Clearly, *even in protected pocket porphyrin complexes*, the local polarity and choice of solvent can have significant impact on O_2 binding. In addition to yielding stable dioxygen complexes, this bis-pocket porphyrin also allows the oxidation of its ferric complex by a wide range of oxidants, including hydroperoxides, peracids, and iodosoarenes, to produce the same intermediate stable for days at room temperature without oxidative ring cleavage of the macrocycle.²⁶ Further studies are presently underway to characterize this highly oxidized species.

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Registry No. 5,10,15,20-Tetrakis(2,4,6-triphenylphenyl)porphyrin, 85390-97-2; pyrrole, 109-97-7; 2,4,6-triphenylbenzaldehyde, 85390-98-3; 2,4,6-triphenylbromobenzene, 10368-73-7; iron 5,10,15,20-tetrakis(2,4,6-triphenylphenyl)porphyrin, 85390-99-4; 1,2-dimethylimidazole-Fe^{II}TTPPP adduct, 85391-00-0; oxygen, 7782-44-7; 1,2-dimethylimidazole, 1739-84-0.

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Isolation, Purification, and Characterization of Intermediate (Iodosylbenzene)metalloporphyrin Complexes from the (Tetraphenylporphinato)manganese(III)-Iodosylbenzene Catalytic Hydrocarbon Functionalization System

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Abstract: A second type of high-valent complex has been isolated from the reaction of (tetraphenylporphinato)manganese(III) derivatives, $XMn^{III}TPP$, with iodosylbenzene. This new type of complex, isolated from the $XMn^{III}TPP$ -iodosylbenzene system when $X = Cl^-$ or Br^- , is a dimeric μ -oxo manganese(IV) porphyrin complex that contains one iodosylbenzene per manganese, $[XMn^{IV}TPP(OiPh)]_2O$, **1**. These complexes are distinct from those complexes isolated from the $XMn^{III}TPP$ -iodosylbenzene system when $X = N_3^-$ or OCN^- , $[XMn^{IV}TPP]_2O$, **2**. The iodosylbenzene complexes, **1**, have been characterized by visible, infrared, and ¹H NMR spectroscopy and magnetic measurements. Absorption bands at 810 and 575 cm^{-1} have been assigned to Mn-O-Mn and Mn-O-I bands, respectively, based on ¹⁸O-labeling experiments. A comparison of the NMR spectra of the complexes **1** with the well-characterized dimeric complexes **2** indicates the same dimeric structure in both types of complexes. The NMR results also indicate that the phenyl ring of the iodosyl moiety is located above the porphyrin core. The solid-state magnetic susceptibility at 28 °C gave $\mu_{eff} = 1.5 \mu_B$ /atom of manganese. Oxidations of triphenylphosphine to triphenylphosphine oxide by **1** and **2** indicate that the iodosylbenzene complexes **1** contain two additional two-electron oxidizing equivalents over that of **2**. This is consistent with a formulation in which iodine is present in the 3+ oxidation state. On the basis of the low magnetic moment, the absence of an observable EPR signal, and the absence of the diagnostic π -cation radical IR absorption band, the ground electronic state of **1** is determined to be two antiferromagnetically coupled d^3 Mn(IV) atoms in neutral porphyrins.

The ability of the cytochrome P-450 enzymes to selectively oxidize alkanes through the activation of molecular oxygen has focused attention on synthetic metalloporphyrins and their potential as oxidation catalysts.¹ Synthetic metalloporphyrins have been screened for their ability to catalytically oxidize organic

substrates with a variety of reduced oxygen sources.² Our group, as well as that of Groves, reported the use of (tetraphenyl-

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porphyrinato)manganese(III) derivatives, $\text{XMn}^{\text{III}}\text{TPP}$,³ and iodosylbenzene for the catalytic oxidation of alkanes.^{2f,g} This system produces high yields of hydroxylated product as well as stoichiometric yields of halogenated product. We reported the isolation and characterization of two dimeric μ -oxo manganese(IV) porphyrin complexes from the $\text{XMn}^{\text{III}}\text{TPP}$ -iodosylbenzene system, $[\text{XMn}^{\text{IV}}\text{TPP}]_2\text{O}$, **2**, for $\text{X} = \text{N}_3^-$ and OCN^- , as well as the X-ray crystallographic structural analysis of the azide complex **2-N₃**.⁴ In this paper we report the isolation and characterization of a new type of complex, $[\text{XMn}^{\text{IV}}\text{TPP}(\text{OIPh})]_2\text{O}$, **1**, isolated from the $\text{XMn}^{\text{III}}\text{TPP}$ -iodosylbenzene system when $\text{X} = \text{Cl}^-$ or Br^- . This second type of complex is also a dimeric μ -oxo manganese(IV) porphyrin complex but is distinct from the azide and cyanate complexes in that this second type of complex contains one iodosylbenzene per manganese. The presence of two trivalent iodines per dimer for **1** gives this complex a six-electron oxidizing capability, two oxidizing deriving from the μ -oxo moiety $[\text{Mn}^{\text{IV}}-\text{O}-\text{Mn}^{\text{IV}}]$ and four equivalents deriving from the iodosyl moieties $[\text{Mn}^{\text{IV}}-\text{O}-\text{I}^{\text{III}}]$.

Although high-valent manganese complexes have been postulated as intermediates in several systems that utilize manganese porphyrins as catalysts^{2f-m} and have been shown capable of oxidizing water both thermally⁵ and photochemically,⁶ the high reactivity of these complexes has prevented their isolation and characterization. The determination of the structural and physical properties of these complexes is critical to an understanding of their reactivity. The characterization of the high-valent complexes described here and in previous reports⁴⁻⁷ may therefore aid in understanding the role of oxidized manganese porphyrins in other oxidation systems in which they are involved. In the accompanying paper, we present the reaction chemistry and detailed mechanism of alkane functionalization by the iodosylbenzene complexes, **1**.

Experimental Section

Physical Measurements. Visible spectra were recorded on a Cary Model 118 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. Solid samples were recorded as KBr pellets at 3 or 6 wt % sample in KBr. Magnetic moments were measured in the solid state on a SQUID apparatus (SHE Corp. VTS 800 spectrometer) which had been calibrated at room temperature by using a Pt standard. X-band EPR spectra were recorded on a Varian Model E-109 spectrometer with the probe at one of several temperatures between 8 and 300 K. Fourier transform ¹H NMR were recorded on either the UC-B-200 or the UCB-180 instrument at 201.96 and 180.86 MHz, respectively. The samples were prepared by vacuum transfer of degassed CDCl_3 (100 atom %, Aldrich) into an NMR tube containing the sample. The tube was then sealed under a vacuum. The samples were stored at liquid N_2 temperature until placed in the spectrometer. The sample concentration was approximately 5 mg/mL. No peaks were found for any of the reported compounds outside of the range 0–10 ppm downfield from Me_4Si . The spectral region ± 150 ppm from Me_4Si was searched for peaks. Both spectra presented in Figure 3 were recorded on the UCB-200 using quadrature phase detection, a sweep width of ± 1500 Hz,

an 8K data set, and 64 acquisitions. The small residual CHCl_3 peak was used as reference, this being set at 7.27 ppm. The relaxation time data was obtained by graphical workup of the data acquired using an inversion recovery pulse sequence.⁸ Gas chromatographic analyses were performed on a Hewlett-Packard Model 5710A gas chromatograph equipped with FID detectors and coupled with a Hewlett-Packard Model 3390A reporting integrator. Nitrogen was used as the carrier gas. Analysis for triphenylphosphine oxide was accomplished by using a 12-m OV-101 fused silica capillary column (Hewlett-Packard) at 250 °C. Elemental analyses were performed by the Microanalytical laboratory operated by the Department of Chemistry, University of California, Berkeley.

Materials. Because the high-valent manganese porphyrin complexes reported in this paper decompose easily to manganese(III) species, relatively inert solvents were used. The solvents chlorobenzene, dichloromethane, hexane, and heptane were purified as described previously.⁴ Low temperatures and an inert atmosphere were required for most manipulations. Iodosylbenzene (iodosobenzene) was made by literature methods.⁹ A sample of 90 atom % ¹⁸O-labeled iodosylbenzene was prepared from iodobenzene dimethoxide, $\text{C}_6\text{H}_5\text{I}(\text{OCH}_3)_2$,¹⁰ and 90 atom % ¹⁸O-labeled water (Alfa). Triphenylphosphine was obtained from Mallinckrodt and was used without further purification. The complexes $[\text{N}_3\text{Mn}^{\text{IV}}\text{TPP}]_2\text{O}$, $[(\text{OCN})\text{Mn}^{\text{IV}}\text{TPP}]_2\text{O}$,⁴ and $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$ ⁷ were prepared as previously described. The complex $(\text{OAc})\text{Mn}^{\text{III}}\text{TPP}$ was made by the method of Alder et al.,¹¹ and the complexes $\text{XMn}^{\text{III}}\text{TPP}$, $\text{X} = \text{Cl}^-$ and Br^- , were prepared by ligand exchange with $(\text{OAc})\text{Mn}^{\text{III}}\text{TPP}$ by the procedure used by Ogoshi¹² on the corresponding iron complexes.

Syntheses. $[\text{ClMn}^{\text{IV}}\text{TPP}(\text{OIPh})]_2\text{O}$, **1-Cl**. To a green solution of 1.0 g (1.34 mmol) of $\text{ClMn}^{\text{III}}\text{TPP}$ in 25 mL of chlorobenzene at 25 °C was added 1.0 g (4.54 mmol) of iodosylbenzene. The mixture was vigorously stirred for 5 min, after which time the green color of $\text{ClMn}^{\text{III}}\text{TPP}$ was replaced by a red-brown color. The mixture was then filtered into a Schlenk flask which had been cooled to -40 °C. Hexane or heptane (ca. 50 mL) was slowly added to the stirred, chilled filtrate. The resulting reddish-brown precipitate was collected in air on a medium frit, washed with hexane or heptane, and dried in vacuo. An 88% yield of product was obtained on the basis of $\text{ClMn}^{\text{III}}\text{TPP}$. Additional product could be obtained from the filtered solution by cooling it to -30 °C. Further purification was achieved by dissolving the product in a minimum volume of chlorobenzene at 0 °C and then adding greater than one volume of hexane or heptane. Allowing the solution to stand at -30 °C for a day produced purple crystals that were collected, washed with hexane or heptane, and dried in vacuo. Since both the amorphous and crystalline forms of the complex decompose to $\text{XMn}^{\text{III}}\text{TPP}$ in the solid state at 25 °C with a half-life of days, the product was subsequently stored at -30 °C.

Anal. Calcd for $[\text{ClMn}^{\text{IV}}\text{TPP}(\text{OIPh})]_2\text{O}$ ($\text{C}_{100}\text{H}_{66}\text{N}_8\text{Cl}_2\text{I}_2\text{Mn}_2\text{O}_3$): C, 64.49; H, 3.58; N, 6.02; Cl, 3.81; I, 13.63. Found: C, 65.06; H, 3.82; N, 5.95; Cl, 3.93; I, 13.48.

$[\text{BrMn}^{\text{IV}}\text{TPP}(\text{OIPh})]_2\text{O}$, **1-Br**. This complex was prepared and purified by procedures analogous to those used for the chloro analogue to yield purple crystalline material in 87% yield based on $\text{BrMn}^{\text{III}}\text{TPP}$.

Anal. Calcd for $[\text{BrMn}^{\text{IV}}\text{TPP}(\text{OIPh})]_2\text{O}$ ($\text{C}_{100}\text{H}_{66}\text{N}_8\text{Br}_2\text{I}_2\text{Mn}_2\text{O}_3$): C, 61.68; H, 3.42; N, 5.76; Br, 8.21; I, 13.03. Found: C, 61.94; H, 3.67; N, 5.77; Br, 8.3; I, 12.9.

$[\text{ClMn}^{\text{IV}}\text{TPP}(\text{OIPh})]_2\text{O}$, ¹⁸O. Flame-dried glassware and solvents freshly dried by distillation from P_2O_5 were used. To a solution of 100 mg (0.142 mmol) of $\text{ClMn}^{\text{III}}\text{TPP}$ in 5 mL of dichloromethane was added 100 mg (0.454 mmol) of 90 atom % [¹⁸O]iodosylbenzene. The mixture was vigorously stirred for 2 min and then filtered into a Schlenk flask which had been cooled to -78 °C. Heptane was slowly added to the stirred filtrate until a precipitate had formed. The purple microcrystalline material was collected in air, washed with heptane, and dried. The electronic spectra of the labeled complex were identical with that of the unlabeled complex and showed <1% $\text{XMn}^{\text{III}}\text{TPP}$ decomposition products.

Triphenylphosphine Oxidations. All reactions were run anaerobically in Schlenk flasks with Kontes high-vacuum Teflon valves. In a typical reaction, 3 mL of dichloromethane was degassed through three freeze-thaw cycles and vacuum transferred into a Schlenk flask containing 20

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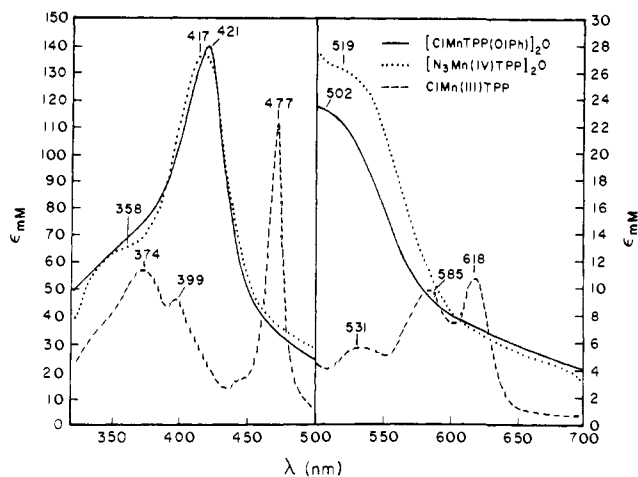


Figure 1. Electronic absorption spectra: **1-Cl**, (—); $[\text{N}_3\text{Mn}^{\text{IV}}\text{TPP}]_2\text{O}$, (···); $\text{ClMn}^{\text{III}}\text{TPP}$, (---). All spectra were recorded as ca. 1 mM chlorobenzene solutions.

mg (1.07×10^{-5} mol) of **1-Cl** and 60 mg (2.16×10^{-4} mol) of triphenylphosphine. The reaction was stirred at room temperature until the brown color of the oxidized porphyrin was replaced by the green color of $\text{XMn}^{\text{III}}\text{TPP}$, approximately 1 h. An internal standard was then added and the reaction solution analyzed by GLC.

Results and Discussion

The high-valent species obtained from the reaction of $\text{XMn}^{\text{III}}\text{TPP}$ with iodosylbenzene when $\text{X} = \text{Cl}^-$ or Br^- are distinctly different from the dimeric μ -oxo Mn(IV) porphyrin complexes, $[\text{XMn}^{\text{IV}}\text{TPP}]_2\text{O}$, formed when $\text{X} = \text{N}_3^-$ or OCN^- . The complete characterization of the azide complex, including the X-ray crystal structure, has been reported previously.⁴ When $\text{X} = \text{Cl}^-$ or Br^- , complexes containing iodosylbenzene are isolated. The elemental analyses of these complexes, after recrystallization from various solvents, indicates a stoichiometry of one iodosylbenzene per $\text{XMn}^{\text{IV}}\text{TPP}$ and establishes that the iodosylbenzene strongly interacts with the manganese porphyrin and is not merely physically occluded.

Electronic Spectra. The electronic absorption spectra of **1-Cl**, **2-N₃**, and $\text{ClMn}^{\text{III}}\text{TPP}$ are presented in Figure 1. The complex **1-Cl** displays the characteristic absorption bands of an oxidized manganese porphyrin complex; in this case a broad Soret band at 421 nm and a broad shoulder at 502 nm. This spectrum is similar to the spectra displayed by the Mn(IV) dimeric azide complex **2-N₃** and the monomeric complex $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$.⁷ The spectra of all these oxidized manganese porphyrin complexes are quite different from their $\text{XMn}^{\text{III}}\text{TPP}$ precursors as can be seen for **1-Cl** and $\text{ClMn}^{\text{III}}\text{TPP}$ in Figure 1. Thus it is clear that the complex **1-Cl** is in a higher oxidation state than Mn(III) and is not merely an iodosylbenzene adduct of $\text{ClMn}^{\text{III}}\text{TPP}$. The (iodosylbenzene)manganese porphyrin complexes decompose to the corresponding $\text{XMn}^{\text{III}}\text{TPP}$ species with a half-life of ca. 1 h in chlorobenzene at room temperature, 23 °C.

Infrared Spectra. An infrared spectral feature common to both the (iodosylbenzene)manganese porphyrin complexes, **1**, and the μ -oxo azide and cyanate dimer complexes, **2**, is an intense broad absorption band in the region of 810 cm^{-1} (Figure 2). This band was identified as the Mn–O–Mn absorption in the complex **2-OCN** by ¹⁸O labeling and by the existence of the Mn–O–Mn moiety as confirmed by X-ray crystallography of the azide complex, **2-N₃**.⁴ Similarly, on labeling the (iodosylbenzene)manganese porphyrin complex, **1-Cl**, using 90 atom % [¹⁸O]iodosylbenzene, the intensity of the 810- cm^{-1} band decreases (Figure 2). A new peak for the ¹⁸O-labeled compound is observed ca. 40 cm^{-1} lower in frequency at 770 cm^{-1} in qualitative agreement with theory ($\nu_{18} \approx 0.95\nu_{16}$).¹³

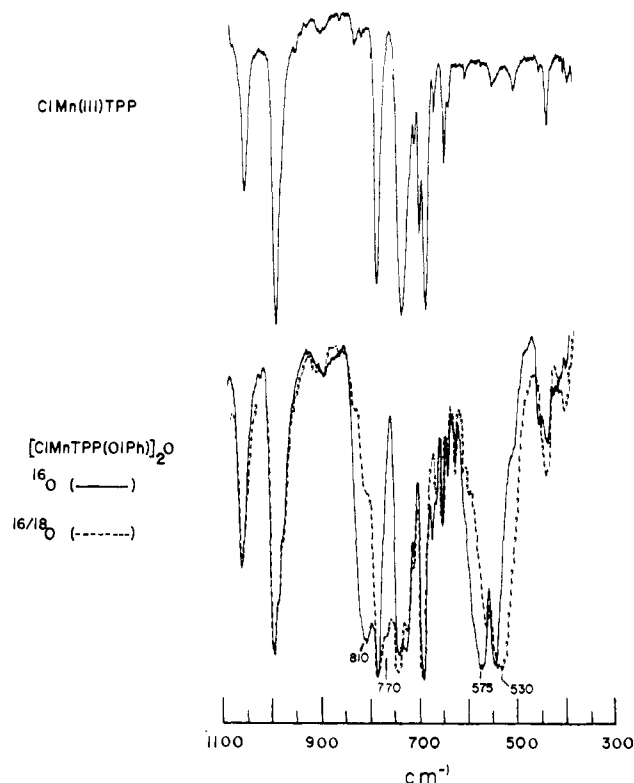


Figure 2. Infrared spectra of ¹⁶O and 90 atom % ¹⁸O-labeled **1-Cl** and $\text{ClMn}^{\text{III}}\text{TPP}$.

Table I. Infrared^a Absorption Bands (cm^{-1}) Characteristic of **1** and Iodosylbenzene

$[\text{XMn}^{\text{IV}}\text{TPP}(\text{OiPh})_2]\text{O}$		
X = Cl	X = Br	$\text{C}_6\text{H}_5\text{IO}$
1572 (m, b)	1572	1570
	1560 (sh)	1565 (sh)
1465	1468	1471
1276	1275	1279
1055 (w, sh)	1055 (w, sh)	1068
735	730	739 (b)
684	685	689
652	655	654
575 (b)	580 (b)	590
550 (b)	550 (b)	490 (b)

^a Spectra of samples recorded as KBr pellets.

Although the existence of the Mn–O–Mn moiety cannot be confirmed by X-ray crystallography in this case, assignment of this band in **1-Cl** to a Mn–O–Mn absorption, as in the complex **2-OCN**, indicates that **1-Cl** also has a μ -oxo dimeric structure. ¹H NMR provides further support for this structural assignment (vide infra).

Further examination of the infrared spectra of the (iodosylbenzene)manganese porphyrin complexes provides some indication as to the nature of the iodosylbenzene interaction in these complexes. The absorption bands of the iodosylbenzene complexes listed in Table I are not present in the spectra of **2-N₃** or **2-OCN** or in the spectra of the Mn(III) complexes. The absorption bands located at 575 and 550 cm^{-1} are exceptionally intense and represent the most characteristic difference between the spectra of **1** and **2** (Figure 2). The bands listed in Table I for the iodosylbenzene complexes are also present in the spectrum of iodosylbenzene, although they are slightly shifted. Most of these bands can be assigned to aromatic C–H stretches and the usual monosubstituted benzene ring absorptions.¹⁴ The band at 590 cm^{-1} in iodosylbenzene can be assigned to an I–O absorption on the basis of

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Table II. ^1H NMR Data for the Compounds 1-Cl, 1-Br, 2-N₃, and 2-OCN^a at +10 and -60 °C

	β	a	b	c	d	e	ortho	meta	para
1-Cl ^b	7.49 ^c	7.49	7.72	7.86	8.03	8.50	4.04	6.09	6.35
	7.85	7.54	7.75	7.88	8.02	8.35	4.07	6.03	6.36
	(27)	(27)	(118)	(109)	(91)	(18)	(12)	(62)	(109)
1-Br	7.51 ^c	7.51	7.74	7.85	8.04	8.49	4.14	6.07	6.36
	7.89	7.58	7.74	7.89	8.00	8.30	4.20	6.00	6.39
2-N ₃ ^b	7.39	7.53	7.67	7.82	8.02	8.61			
	7.87	7.69	7.69	7.87	8.02	8.46			
	(20)	(32)	(99)	(126)	(100)	(21)			
2-OCN	7.44 ^c	7.44	7.75 ^d	7.75	8.06	8.50			
PhI							7.72	7.12	7.35
PhI(OMe) ₂ ¹⁰							7.94	7.47	
PhI(OAc) ₂							8.10	7.55	

^a β is used to designate the porphyrin β pyrrole protons. The other labels are those used in Figure 3. Shifts are in ppm downfield from Me₄Si. Two sets of shifts are given for each compound; the first was measured at +10 °C and the second at -60 °C. ^b Measured T_1 relaxation times for the protons in this compound are given in parentheses, values are in ms. ^c β and a proton peaks overlap. ^d b and c proton peaks overlap.

¹⁸O-labeling experiments.¹⁰ This band occurs in the region where I-O single bonds are expected¹⁴ and is in accord with the polymeric structure composed of I-O-I chains postulated for iodosylbenzene.¹⁵ On the basis of these results, it is reasonable to assign the absorption at 575 cm⁻¹ in the complex 1-Cl to an I-O stretch. Confirmation of this assignment is obtained from the spectrum of the 90% ¹⁸O-labeled complex of 1-Cl (Figure 2). The absorption at 575 cm⁻¹ has decreased in intensity, and a new absorption at 530 cm⁻¹ is observed. Because the absorption attributable to the IO group in these complexes lies in the lower frequency region expected for an I-O single bond, it is clear that the iodosyl moiety in these complexes does not contain a discrete I=O unit. Bands attributable to I=O absorptions occur at a much higher frequency (700-800 cm⁻¹).^{14,16} We propose, therefore, that the iodosyl moiety is bound to the manganese in these complexes and assign the absorption band at 575 cm⁻¹ to a Mn-O-I stretch. This conclusion is supported by the NMR results (vide infra). The assignment of the band at 550 cm⁻¹ in the complex 1-Cl is uncertain. Since the band at 490 cm⁻¹ in the spectrum of iodosylbenzene is apparently also an IO absorption on the basis of labeling experiments,¹⁰ the 550-cm⁻¹ band in 1-Cl may also be an IO absorption. It is not clear whether this band is affected by ¹⁸O labeling (Figure 2). The C-I vibrational frequency has been assigned in iodobenzene at 447 cm⁻¹ and at 457 cm⁻¹ in the compound [C₆H₅I(NO₃)₂]₂O.¹⁴ The 550-cm⁻¹ absorption in 1-Cl thus seems too high in frequency to be assigned as a C-I stretch, although it cannot be ruled out on this basis.

Other infrared spectral features pertinent to the characterization of these complexes is the lack of an absorption in the region 1250-1300 cm⁻¹ where TPP π -cation radical absorptions are believed to occur.¹⁷

Magnetic Data. The magnetic susceptibility of the iodosylbenzene complex 1-Cl was determined in the solid state at 28 °C. A value for χ_g of 1.93×10^{-7} cgs units was obtained. Assuming a stoichiometry of one iodosylbenzene per ClMnTPP and using a diamagnetic correction of -826×10^{-6} cgs units for the combined porphyrin ring,¹⁸ iodobenzene, manganese, and chloride¹⁹ results in a value for $\chi_A(\text{corrected})$ of 1.01×10^{-3} cgs units. On the basis of the equation $\mu_{\text{eff}} = 2.83(\chi_A T)^{1/2}$, a value of $\mu_{\text{eff}} = 1.5 \mu_B/\text{atom}$ of manganese is obtained. Because of paramagnetic impurities present in the samples of 1-Cl, estimated to be about 3%, this value

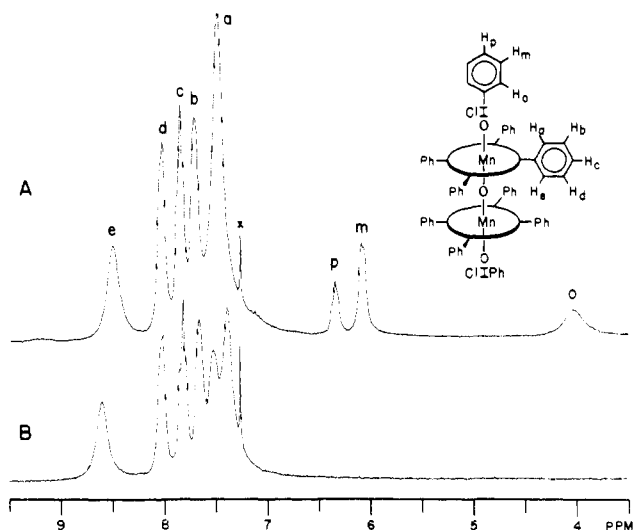


Figure 3. NMR spectra: A, 1-Cl; B, [N₃Mn^{IV}TPP]₂O, 2-N₃ (temperature +10 °C; shifts in ppm downfield from Me₄Si; X = CHCl₃, 7.27 ppm).

of $\mu_{\text{eff}} = 1.5 \mu_B/\text{Mn}$ can be considered as an upper limit for the magnetic moment. An EPR signal was not observed for the iodosylbenzene complexes at temperatures down to 8 K. The absence of an EPR signal and the low magnetic moment support an antiferromagnetically coupled dimeric structure.

¹H NMR Spectroscopic Data. Comparison of ¹H NMR spectra of the complexes 1-Cl and 1-Br with the NMR of the characterized complexes 2-N₃ and 2-OCN allows the structural features of 1 to be deduced. The ¹H NMR data for the compounds 1-Cl, 1-Br, 2-N₃, and 2-OCN are presented in Table II and Figure 3.

The complex 2-N₃ is known to have a dimeric structure with a distance of 3.72 Å between the porphyrin rings. In the NMR spectrum of this compound (Figure 3B), peaks corresponding to each of the six types of unique hydrogens are found. Assignment of these peaks was based on integration of peak areas, ring current calculations, relaxation time measurements, and the temperature dependence of the chemical shifts.

The distinct pattern of peaks observed in these spectra is due to the large chemical shift differences for protons a, b, c, d, and e induced by the ring current of the second porphyrin in the dimeric structure. The same type of pattern has previously been observed in [Ru(TPP)]₂.²⁰

Abraham has parameterized a ring current model for tetraphenylporphyrin by using the experimental NMR data for a series of Zn(TPP) complexes with axially coordinated nitrogen bases.²¹

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Using this model, one can calculate the expected shift of the phenyl group resonances (a-e) that is caused by the ring current of the second ring in the dimer complex. All that is required is a knowledge of the distance between the two rings of the dimer and positional data for the protons of interest. These data are readily obtained from the available structural information.⁴ Calculations using a staggered conformation and a distance between the rings of 3.7 Å yielded the following predictions: (1) the *p*-phenyl proton c should shift <0.01 ppm. (2) The shift of protons a and b should be upfield; the shift of protons d and e should be downfield. (3) The resulting separation of the *o*-phenyl protons a and e should be 1.5 ppm; the separation of the *m*-phenyl protons should be 0.3 ppm.²² For the complex **2-N₃**, the predictions hold reasonably well. The observed separations in **2-N₃** between a and e and between b and d are 1.1 and 0.29 ppm, respectively. The *p*-phenyl proton is not shifted very much from the value of 7.72 ppm observed for this proton in the monomeric complex Zn(TPP).²¹ Factors other than the ring current do affect the shifts as can be seen from the significant difference between the shifts observed for **2-OCN** and **2-N₃**.

Striking similarities and differences exist between the two spectra presented in Figure 3. The dimeric nature of **1-Cl** is fully supported by the correspondence of peaks in the 7-9 ppm region of the spectra. Given the similarity in this region of the spectra, the electronic state of the manganese in both types of complexes must be the same. **2-N₃** was shown to have a Mn(IV) ground electronic state; therefore the complexes **1-Cl** and **1-Br** must also have a Mn(IV) ground electronic state.⁴

Peaks for the iodobenzene protons are clearly present in the NMR of **1-Cl** and **1-Br**. The peak intensities are as required by a stoichiometry of one iodobenzene per porphyrin ring. Even at -60 °C, the phenyl group must be undergoing substantial motion since only two peaks are observed for the four ortho and meta protons. The large upfield shifts of these peaks indicates that the iodobenzene is directly above the central porphyrin core. Since the magnitude of the shift of the ortho hydrogen is much larger than the shifts of the meta and para hydrogens, the iodine atom of the iodobenzene must be oriented toward the manganese atom.²¹

One can use Abraham's ring current model to calculate the ring current shifts above the plane of the porphyrin plane in a dimer complex. A map of the calculated shifts can then be compared to the observed data in order to obtain the approximate distances of the phenyl group atoms from the manganese atom. The ring current shifts of the iodobenzene protons must be calculated relative to an appropriate unshifted reference compound. Notice that in the NMR spectrum, the phenyl proton peaks of organic iodine(III) compounds are shifted downfield from those in iodobenzene. The iodine(III) compounds are likely to be the more appropriate reference compounds. The data indicates that the iodine atom is 2.5-3.5 Å from the Mn atom and that the para-proton is 7.5-8.5 Å from the Mn atom.²³

The location of the Cl⁻ and Br⁻ atoms in these complexes is not clear. A change of the axial ligand from N₃⁻ to OCN⁻ in the complexes **2**, where X is directly bound to the manganese, resulted in a substantial change of the chemical shifts of the porphyrin phenyl group protons in the NMR spectrum. For the complexes **1**, the only significant difference in the NMR spectra of **1-Cl** and **1-Br** is in the positions of the ortho hydrogens of the iodobenzene which are at 4.04 and 4.14 ppm, respectively.

Triphenylphosphine Oxidations. The facile oxidation of triphenylphosphine to triphenylphosphine oxide by the high-valent manganese porphyrin complexes provides a useful diagnostic method for determining the number of oxidizing equivalents

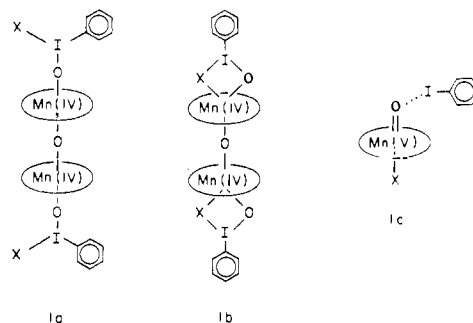
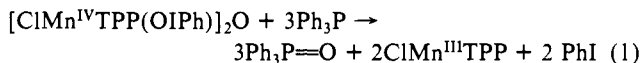


Figure 4. Possible structures for the (iodosylbenzene)manganese porphyrin complexes.

available in these complexes. The reaction of the complex **1-Cl** with triphenylphosphine produced 3 equiv of triphenylphosphine oxide, in contrast to **2-N₃**, which produced 1 equiv. The monomeric complex Mn^{IV}TPP(OCH₃)₂ yielded 0.63 equiv., and a control experiment with ClMn^{III}TPP showed no oxidation.

These results indicate that the iodobenzene complexes have two additional two-electron oxidizing equivalents over that of **2-N₃**. This is consistent with the dimeric formulation for these complexes containing manganese in the 4+ oxidation state and iodine in the 3+ oxidation state. The iodobenzene complexes thus contain two types of oxidizing units—the μ -oxo unit (Mn-O-Mn), common to both the complexes **1** and **2**, and the iodobenzene unit (Mn-O-I). The stoichiometry of the triphenylphosphine reaction is given by eq 1. The formation of 2 equiv of iodobenzene was confirmed by GLPC analysis.



Conclusions

On the basis of the results presented above, some possible structures for the (iodosylbenzene)manganese porphyrin complexes can be formulated. The IR, NMR, and magnetic data indicate that the iodobenzene complexes have a dimeric structure containing the μ -oxo (Mn-O-Mn) moiety. Therefore, all monomeric structures such as **1c** in Figure 4 can be eliminated on this basis. The infrared and NMR data confirm the presence of iodobenzene in these complexes and indicate that the iodobenzene moiety is bound to the manganese with the phenyl ring being located above the central porphyrin core. The triphenylphosphine oxidation results indicate that these complexes contain trivalent iodine. Two structures that are consistent with the data are **1a** and **1b** in Figure 4. Structure **1a** in which the ligand, X, is not bound to the metal is favored on the basis of the chemical shift independence of the porphyrin phenyl protons with change in ligand. This is in contrast to the complexes **2** in which the ligand X is bound to the metal and which display ligand-dependent behavior of the porphyrin phenyl group chemical shifts in the NMR spectrum. A formulation similar to **1a** in which the ligand X is present as the free ion rather than covalently bound to the iodine is also possible for these complexes. Conductivity experiments addressing this possibility were inconclusive due to decomposition of the iodobenzene complexes under the experimental conditions utilized. Other structures containing multiple bridges between the porphyrins rings are not consistent with IR and NMR results.

Several lines of evidence are in accord with a Mn(IV) neutral porphyrin ground electronic state for the iodobenzene complexes: (1) The electronic absorption spectra show that **1** is oxidized above Mn(III) and is similar to the complexes **2-N₃** and Mn^{IV}TPP(OCH₃)₂. (2) The absence of the diagnostic absorption band ca. 1280 cm⁻¹ in the IR for porphyrin π -cation radicals indicates that the oxidation is metal centered. (3) The similarities of the NMR spectra of **1** and **2**, the low magnetic moment, and the absence of an observable EPR signal are consistent with antiferromagnetic coupling of the manganese atoms in **1**. Other physical methods, including ¹²⁷I Mössbauer spectroscopy and

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(22) The calculations were performed on an IBM 4341 computer using programs written in APL by one of the authors (Bruce C. Schardt). The correct operation of the program was verified by the reproduction of the calculations presented by Abraham.²¹

(23) These calculations were performed by using rings staggered at 45°, a distance between the rings of 3.7 Å, and averaging the results for rotation of the iodobenzene about the perpendicular to the porphyrin plane.

manganese X-ray absorption spectroscopy, are presently being employed to further characterize these complexes.

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Chemical Society, is acknowledged.

Registry No. 1-Cl, 85185-72-4; 1-Br, 85185-73-5; 2-N₃, 79775-62-5; 2-OCN, 81602-67-7; [XMn^{IV}TPP(OiPh)]₂O, 85185-74-6; CIMn^{III}-TPP, 32195-55-4; BrMn^{III}TPP, 55290-32-9; iodosylbenzene, 536-80-1; [¹⁸O]iodosylbenzene, 80572-92-5.

Hydrocarbon Functionalization by the (Iodosylbenzene)manganese(IV) Porphyrin Complexes from the (Tetraphenylporphinato)manganese(III)-Iodosylbenzene Catalytic Hydrocarbon Oxidation System. Mechanism and Reaction Chemistry

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Abstract: The two types of complexes isolated from the reaction of (tetraphenylporphinato)manganese(III) derivatives, XMn^{III}TPP, with iodosylbenzene—[XMn^{IV}TPP(OiPh)]₂O, **1**, X = Cl⁻ or Br⁻, and [XMn^{IV}TPP]₂O, **2**, X = N₃⁻—are capable of oxidizing alkane substrates in good yields at room temperature. Several lines of evidence establish the intermediacy of free alkyl radicals in the reactions of **1** and **2** with alkanes. Oxygen exchange with water in both the iodosyl (Mn—O—I) and μ -oxo (Mn—O—Mn) moieties of **1** suggests the formation of oxo manganese porphyrin complexes from these moieties. Hydrogen abstraction from the alkane substrate by an oxo manganese porphyrin intermediate is postulated to be the mechanism for reaction of **1** and **2** with alkanes. Observation of a monomeric manganese(IV) porphyrin intermediate by EPR spectroscopy during the reactions of **1** with alkanes is consistent with the formation of a hydroxymanganese(IV) porphyrin complex resulting from substrate hydrogen abstraction by an oxo intermediate. The formation of RX product from oxidation of RH by **1** has been determined to result from ligand-transfer oxidation of free alkyl radicals by the porphyrin complexes in solution. Through competition reactions and time-dependent product formation studies, ligand-transfer oxidation by XMn^{III}TPP was found to be the major pathway for RX production. Observation of Mn^{II}TPP by EPR spectroscopy during the reactions of **1** with alkanes supports this conclusion. Formation of ROH product may result from ligand-transfer oxidation of free radicals or from the collapse of an intermediate caged radical pair. The mechanism of ROH product formation in the caged radical pair is postulated to be an outer-sphere electron-transfer process due to the expected slow rate of inner-sphere ligand transfer for the high-spin d³ hydroxymanganese(IV) porphyrin complex. Thus the ability of the substrate radical to undergo electron-transfer oxidation determines the ratio of radicals that undergo cage escape to give free radicals to radicals that undergo oxidation and subsequent formation of alcohol product in the caged species. Studies with tertiary substrates support these conclusions.

Manganese porphyrin complexes have been shown to be versatile synthetic oxidation catalysts for the oxidation of a wide variety of organic substances.¹ One of the most interesting oxidation processes mediated by manganese porphyrin complexes is that of alkane oxidation.^{1a-e} The activation of C—H bonds, particularly those of saturated hydrocarbons, presents one of the most challenging problems in the field of homogeneous catalysis. Because of the inertness of the strong covalent C—H bond (bond dissociation energies for saturated hydrocarbons range from 91 kcal for tertiary C—H bonds to 104 kcal for methane C—H bonds), very few systems are capable of reacting with alkanes.² In nature, the biological activation of alkane C—H bonds is accomplished by the heme-containing monooxygenases, exemplified by the cytochrome P-450 group of enzymes.³ The development of synthetic oxidation catalysts which are industrially useful as well as possible insight into the mechanistic features of selective hydrocarbon hydroxylation by the cytochrome P-450 enzymes, make these manganese porphyrin catalyzed oxidation processes a subject of great interest. In order to elucidate the mechanism of alkane activation catalyzed by manganese porphyrins, we have isolated and characterized two types of high-valent complexes from the XMn^{III}TPP-iodosylbenzene, X = Cl⁻, Br⁻, N₃⁻, and OCN⁻, catalytic alkane oxidation system.^{4,5} Both types of complexes are dimeric μ -oxo manganese(IV) species. The complexes isolated

from the XMn^{III}TPP-iodosylbenzene system for X = Cl⁻ or Br⁻, [XMn^{IV}TPP(OiPh)]₂O, are distinct from those complexes isolated when X = N₃⁻ or OCN⁻, [XMn^{IV}TPP]₂O, in that they contain two additional two-electron oxidizing equivalents in the form of

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- (5) Abbreviation: TPP = *meso*-tetraphenylporphinato dianion ligand.

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