ratios. For our system, preferential CO association or, more likely, a faster rate of migratory insertion of one stereoisomer over the other determines product ratios. At present, the origin of selectivity is not at all clear. This is particularly true when one considers that starting with $CpFeCO[P(OPh)_3](\eta^1\text{-}(E)\text{-}C(Me){=}C(R)Ph)$, the *E*-isomer products are formed exclusively when R = H, but the *Z*-isomer products are predominantly (in the case of esters) or exclusively (in the case of alkenylacyl) formed when R = Me.

From a synthetic viewpoint, the completely stereoselective nature (as judged from 400-MHz NMR spectra) of alkenylacyl formation and alkenyl ester formation (in all but two cases) is of paramount importance. Even in the two instances (line 1 and 4, Table IV) where mixtures of esters are obtained, pure alkenyl ester can be prepared by effecting the oxidative cleavage on the iron-alkenylacyl complex (lines 2, 3, and 5, Table IV). An obvious complication is the inversion of alkene stereochemistry for the complexes in eq 6. However, these complexes are very similar (after finding one case of isomerization, we deliberately synthesized similar analogues) in that each possesses a phenyl group at the β-alkenyl position which is geminal to a group other than hydrogen. In general, we anticipate that the CO insertion step will proceed with retention of alkene stereochemistry.

The stereoselective synthetic route to alkenylacyliron complexes presented here allows the use of relatively mild reaction conditions, thus circumventing the potential thermal decomposition inherent in a thermally induced migration reaction. The described procedures for the preparation of tetrasubstituted alkenyl esters are quite different from the methods generally used[19-24] (mainly Horner–Emmons reactions) to prepare these compounds. Most notable is the observed high selectivity for the formation of a single stereoisomer, whereas the earlier methods generally give mixtures (ca. 2/1 of the two stereoisomers). New methodology for di- and trisubstituted alkenyl esters is also developed.[37] Overall, the ester formation is essentially a two-step sequence. The first is the η^2-alkyne complex preparation and the nucleophile addition. The second step is the oxidative cleavage. We have found the yields to be good in each step. In addition, one is afforded extensive control over the type of alkene substituents. Two of the groups are dictated by the choice of alkyne and the third by the nucleophile employed. In general, the nucleophile can be a stabilized carbanion, a carbon based nucleophile for which the lithium salt can be prepared[9] or a heteroatom nucleophile.[12] For additional flexibility, alkenyliron complexes can also be prepared via an iron–vinylidene route[13] and from η^2-allene complexes.[11] Although the reactions need to be carried out by using standard inert atmosphere techniques, they are not particularly sensitive procedures. The iron starting material, $CpFeCO[P(OPh)_3]I$, is inexpensive and can be prepared relatively easily on a large scale. The sum total is a unique and flexible route to alkenylacyliron complexes and highly functionalized alkenes.

Acknowledgment. Acknowledgment is made to the National Science Foundation (CHE 8019513 and EPSOR) and the NIH (Biomedical Research Grant S07-RR07160) for support of this research. We thank Dr. Robert Bly for helpful discussions.

Supplementary Material Available: Complete listings of bond angles, bond distances, torsional angles, positional parameters of H-atoms, general temperature factors, and structure factor amplitudes for **1** and **6** (110 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of a Mn^{III} Porphyrin Cation Radical and Its Conversion to Mn^{IV} by Ligand Metathesis

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Abstract: The complex (5,10,15,20-tetraphenylporphinato)manganese chloro hexachloroantimonate, **1**, $MnTPP(Cl)(SbCl_6)$, was synthesized by the oxidation of MnTPP(Cl) with phenoxathiin hexachloroantimonte in dichloromethane. The assignment of **1** as a manganese(III) porphyrin π-cation radical species was based on its X-ray crystal structure, visible and infrared spectra, and magnetic properties. The crystal structure was determined as a tetrachloroethane solvate. The manganese in the compound is five-coordinated with the chloride anion axially bound to the Mn with 50% occupancy at sites above and below the porphyrin ring. The second anion, $SbCl_6^-$, is displaced from the Mn with a Mn–Cl–Sb angle of 132°. The porphyrin core carbon and nitrogen atoms as well as Mn are coplanar. Variable-temperature magnetic susceptibility measurements on the solid gave $\mu_{eff} = 4.9\ \mu_B$ which is close to that expected for a Mn^{III} cation (d^4) $S = 2$, π-cation radical $S = {}^1/_2$, with independent spin states. Magnetic susceptibility measurements on solutions of **1** gave a range of values for μ_{eff} between 5.7 and 6.7 μ_B. This suggests that the spin independent state of **1** in the solid changes into a ferromagnetically coupled state, resultant spin of five-halves, in the solution phase. The IR spectrum of **1**, with four solvent molecules ($C_2H_2Cl_4$) present, shows a peak at 1280 cm^{-1}. A band in this region has been suggested as diagnostic of metallotetraphenylporphyrin π-cation radical species. The 1280-cm^{-1} band observed for **1** disappeared when all the solvent molecules from **1** were removed under vacuum. The crystalline nature of the solid was lost by the removal of the solvent molecules; however, magnetic moment (4.7 μ_B) and the visible spectrum remained virtually unchanged. We believe that the 1280-cm^{-1} band in **1** is associated with the solvent molecules; neat $C_2H_2Cl_4$ also shows strong absorption in the 1280-cm^{-1} region. Treatment of **1** with basic methanol or oxidation of MnTPP(Cl) with phenoxathiin hexachloroantimonate in the presence of basic methanol gave another species whose visible and EPR spectra are identical with that reported for $Mn^{IV}TPP(OCH_3)_2$. These results suggest that the site of oxidation in MnTPP(Cl) is shifted from the ligand to the metal in the presence of the strong π-donating ligand, CH_3O^-.

The development of stable and efficient oxidation catalysts is difficult but essential to work aimed at producing an artificial photosynthesis assembly capable of converting solar energy to storable high energy chemical compounds. A useful oxidation catalyst in an assembly designed to split water would mediate the four-electron conversion of water to oxygen. An alternate goal would be the use of an oxidation catalyst to produce more useful

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intermediate oxidants.[1] In connection with our interest in artificial photosynthesis we have examined manganese porphyrin compounds as potential redox catalysts.

Our interest in manganese porphyrin compounds is longstanding[2-4] and originated in the knowledge that some type of manganese complex is involved in the oxidation cycle of natural chloroplasts. The porphyrin ligands are resistant to irreversible oxidation or reduction reactions, and this is a very desirable property since it increases the possibility for the central metal ion to participate in redox reactions. A primary requisite for a multiple electron redox catalyst is the accessibility of a variety of oxidation states, and manganese porphyrin species have been characterized with manganese in the +2,[5] +3,[5] and +4[6] levels, and species have been proposed for the +5[7] state. In addition, there have been recent reports of the use of manganese porphyrins as oxidation catalysts for a variety of organic substrates.[8] We report here results of work on a one-electron oxidation product of MnTPPCl: TPP = 5,10,15,20-tetraphenylporphyrin, which we believe is best classified as a manganese(III) porphyrin π-cation radical. Addition of a hard base ligand, such as methoxide ion, to a solution containing $\mathrm{Mn^{III}TPP^{+}\cdot}$ produces another species whose spectral properties are consistent with those of $\mathrm{Mn^{IV}TPP(OCH_3)_2}$.

Experimental Section

Visible spectra of the compounds were recorded on a Hewlett-Packard 8450A spectrometer.

Infrared spectra of solid samples were recorded as KBr pellets (4–6 wt. % sample) on a Perkin-Elmer 299B spectrometer.

Variable-temperature magnetic susceptibility measurements in solid state were carried out on a SQUID apparatus (SHE Corp. VPS 800 susceptometer). The SQUID apparatus had been calibrated by using $\mathrm{HgCo(SCN)_4}$ as a standard.

The magnetic moment in solution was determined by the Evans method[9] by using a 200-MHz Fourier transform ^{1}H NMR instrument (UCB-200). In this method, shifts in the proton resonance lines of inert molecules caused by the paramagnetic molecules (e.g., manganese porphyrin) are measured, and the magnetic moment of the paramagnetic substance was calculated by the standard procedure.[9] In a typical experiment, the manganese porphyrin was accurately weighed (1–2 mg) and dissolved in a known volume (0.3–0.5 mL) of dichloromethane-d_2 (99.6+ atom %) containing tetramethylsilane ($\mathrm{Me_4Si}$) as an internal standard. The solution was placed in the inner tube of a 5-mm double concentric tube (Wilmad Glass Co.). The solvent containing $\mathrm{Me_4Si}$ was then placed in the outer portion of the tube. The frequency shifts due to manganese porphyrin were then measured from the $\mathrm{Me_4Si}$ signal and that of the residual protons of the solvent. The shifts in both cases agreed within 0.2 Hz, and the average value was taken for the calculation of magnetic susceptibility. The possible thermal decomposition of the compound was minimized by carrying out the experiment within 5 min of the preparation of the solution; the amount of decomposition (as checked from the visible spectrum) was less than 5%.

X-band EPR spectra were recorded on a Varian Model E109 spectrometer equipped with a low-temperature dewar (Air Products, Ltd.).

Spectroelectrochemistry was performed in an optically transparent thin-layer electrode assembly[10] in dichloromethane with tetrabutylammonium perchlorate as supporting electrolyte with an IBM EC/225 Voltametric Analyzer potentiostat.

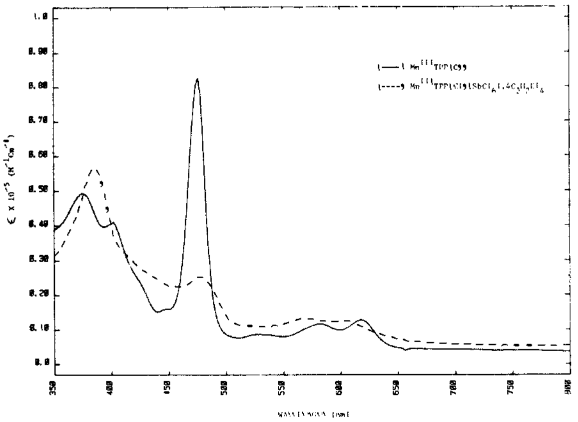

Figure 1. Quantitative optical absorption spectra of $\mathrm{Mn^{III}TPP(Cl)}$ (—) and **1** ($\mathrm{Mn^{III}TPP(Cl)(SbCl_6)\cdot 4C_2H_2Cl_4}$) (---) in dichloromethane.

Elemental analyses were performed by the Microanalytical Laboratory operated by the Department of Chemistry, University of California, Berkeley.

Materials. $\mathrm{Mn^{III}TPP(OAc)}$ was synthesized by literature methods.[11] The chloride form of this compound was made by the addition of an ice-cold aqueous solution of sodium chloride to a cold solution (5 °C) of MnTPP(OAc) in DMF. The green precipitate formed was filtered, washed several times with water, and air dried. The crude sample so obtained was dissolved in dichloromethane and loaded on an alumina column. The manganese porphyrin was then eluted with methanol–chloroform (1:9 v/v). The eluent was then evaporated to dryness, dissolved in methanol, and reprecipitated by the addition of an equal volume of 6 M HCl. The green precipitate was filtered, washed with water, and air dried. The sample was recrystallized by dissolving in benzene and precipitating by the addition of hexane. The precipitate was then filtered, washed with hexane, and dried in vacuum. Purity of this compound was checked by its elemental analysis and visible and IR absorption spectra.

Phenoxathiin hexachloroantimonate $[(\underline{\mathrm{C_6H_4SC_6H_4O}})\mathrm{SbCl_6}]$ was synthesized[12] by reacting stoichiometric amounts of phenoxathiin and antimony pentachloride in dichloromethane. The cation radical formed was filtered under a stream of nitrogen and dried under vacuum. Purity of the compound was checked by elemental analysis.

Dichloromethane was purified by refluxing over calcium hydride followed by distillation in a $\mathrm{N_2}$ atmosphere onto activated molecular sieves. Hexane, chloroform, and tetrachlorethane were HPLC grade, or the best commercially available grade, and were used without further purification.

Synthesis of $\mathrm{MnTPP(Cl)(SbCl_6)}$. MnTPP(Cl) (0.5 g, 0.71 mmol was dissolved in 50 mL of $\mathrm{CH_2Cl_2}$ at room temperature, and phenoxathiin hexachloroantimonate (0.55 g, 1.03 mmol) was added to it. The reaction was carried out in a nitrogen atmosphere. The solution was stirred for 30 min and filtered into 100 mL of cold (5 °C) hexane. The resulting precipitate was collected by filtration, rinsed with hexane, and air dried to yield amorphous powder of $\mathrm{MnTPP(Cl)(SbCl_6)}$.

Crystal Growth. Diffraction-quality single crystals of $\mathrm{MnTPP(Cl)(SbCl_6)\cdot 4C_2H_2Cl_4}$ (**1**) were grown by dissolving the amorphous powder of $\mathrm{MnTPP(Cl)(SbCl_6)}$ in a minimum quantity of 1,1,2,2-tetrachloroethane and adding an equal volume of hexane to it. The solution was then left undisturbed at -20 °C for 24 h. The resultant black crystals were filtered, rinsed carefully with hexane, and dried in air. The sample crystallized with four solvent molecules as determined from the carbon and chlorine analysis. Calculated for $\mathrm{MnTPP(Cl)(SbCl_6)\cdot 4C_2H_2Cl_4}$: C, 36.56; H, 2.11; N, 3.28; Cl, 47.68; Mn, 3.22; Sb, 7.15. Found: C, 36.57; H, 2.05; N, 3.25; Cl, 46.20; Mn, 3.22; Sb, 7.98. Purity of the compound was judged mainly from the ratios of C/N and Mn/N which were in good agreement with the calculated values. An attempt to grow crystals from dichloromethane was not successful.

Crystallographic Methods. A shiny black crystal of approximate dimensions 0.20 × 0.30 × 0.36 mm, mounted with epoxy on a glass fiber, was used for collection of the X-ray diffraction data. Intensities were collected on an Enraf-Nonius CAD-4 automatic diffractometer at room temperature. The data reduction was standard, with the exception that

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Table I. Calculated Magnetic Moments for Manganese Porphyrin Configurations

	configuration	μ_{eff}(calcd) (μ_B)
A	Mn^{III}TPP$^{\bullet+}$ (independent spins)	5.19
B	M^{IV}TPP	3.87
C	Mn^{III}TPP$^{\bullet+}$ (ferromagnetic coupling)	5.91
D	Mn^{III}TPP$^{\bullet+}$ (antiferromagnetic coupling)	3.87

no absorption corrections were made. The structure was solved by first locating the Sb atom, using Patterson and direct methods, and then locating other atoms by iterative difference Fourier maps. The program SHELX[13] was used for both the structure solution and the refinement. During the latter stages of the refinement the phenyl groups attached to the porphyrin ring were constrained to an ideal geometry in order to reduce the number of overall parameters. After it was clear that the chloride attached to the manganese was distributed between two sites, their occupancies and temperature factors were refined in alternate cycles due to the high correlation between these parameters. All atoms were refined anisotropically, except for the phenyl atoms which were assigned rigid body anisotropic thermal parameters (which can be converted to atomic isotropic temperature factors). No hydrogen positions were included in the model. The largest peaks in the final difference Fourier were the correct distance from appropriate atoms and were likely due to hydrogens.

Results and Discussion

Oxidation of Mn^{III}TPP(Cl) in dichloromethane by 1 equiv of the one-electron oxidant phenoxathiin hexachloroantiomonate, $C_6H_4SC_6H_4O(SbCl_6)$, followed by recrystallization of the crude material from $C_2H_2Cl_4$ leads to black crystals of MnTPPCl)-$(SbCl_6)\cdot 4C_2H_2Cl_4$ (**1**), which exhibits the visible spectrum shown in Figure 1. An identical spectrum is obtained when Mn^{III}TPPCl is electrochemically oxidized by one electron at a gold minigrid electrode in a thin-layer cell (oxidation at +1.1 V relative to an SCE reference electrode in dichloromethane containing 0.1 M tetrabutylammonium perchlorate). The spectrum shown in Figure 1 is that of the one-electron oxidation product of Mn^{III}TPP(Cl), and the peak in the spectrum at 476 nm is not due to residual Mn^{III}TPP(Cl), as excess phenoxathiin oxidant or prolonged electrochemical oxidation does not change the spectrum. Similar electronic spectra of oxidized MnTPP species have been reported by Harriman[14] and Goff.[15]

The assignment of **1** as a Mn^{III} π-cation radical compound is based on its crystal structure, the magnetic susceptibility of both the solid and its solution, its solution visible spectrum, and its spectral behavior upon ligand metathesis. The results are summarized briefly below and then followed by detailed comments.

Magnetic susceptibility measurements on the solid gave a magnetic moment $\mu_{eff} = 4.91\ \mu_B$. This is close to the calculated value of $\mu_{eff} = 5.19\ \mu_B$ for a MnIII species, which is d^4 ($S = 2$) together with an independent spin ($S = {}^1/_2$) on the oxidized porphyrin ring. Table I shows the magnetic moments for this configuration (A) as well as other possible ones for a one-electron oxidation product of Mn^{III}TPP.

Species B is ruled out on two counts. The μ_{eff} value of 3.8 is not consistent with the observed one of 4.91, and the visible solution spectrum shows no evidence of bands at 420 and 535 nm that are characteristic of a MnIV porphyrin.[7]

Species C and D in the solid are also ruled out, both by their mismatch of μ_{eff} with the observed value and by evidence from the X-ray crystal structure, which shows that the C and N atoms of the porphyrin ring as well as the Mn atom are all coplanar. Magnetic coupling of the two spin sites is only possible if the ring is puckered.

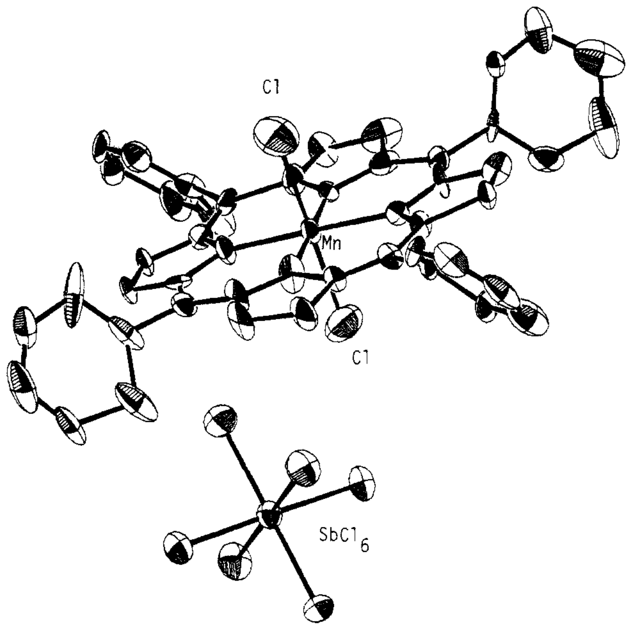

Figure 2. ORTEP diagram of **1**, Mn^{III}TPP(Cl)$(SbCl_6)\cdot 4C_2H_2Cl_4$. Each atom is represented by its vibrational ellipsoid (50%) having the shape and the relative size concomitant with its thermal motion in the crystal. Hydrogen atoms and solvent molecules are omitted for clarity. The chloride axially bound to Mn has 50% occupancy at sites above and below the plane of the porphyrin.

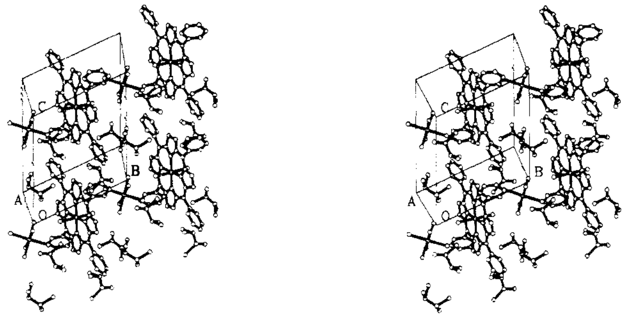

Figure 3. Stereo view of the crystal packing diagrams of **1**, Mn^{III}TPP-(Cl)$(SbCl_6)\cdot 4C_2H_2Cl_4$, as viewed perpendicular to the crystallographic BC plane. Molecules lying within 2 unit cells in the B and C directions and one cell in the A direction are included in the diagram.

In solution, **1** appears to change to state C as shown by the increase of its μ_{eff} to a value between 5.7 and 6.7. Then upon substitution of CH_3O^- ligands for Cl^- and $SbCl_6^-$, an electron is moved from the metal center to the porphyrin ligand with the production of a MnIV porphyrin species as shown by visible and EPR spectra.

Electronic Spectra. Numerous studies of electronic spectra of metalloporphyrin species have led to the compilation of a few "empirical rules" that help to distinguish between a π-radical and a porphyrin where the central metal ion has been oxidized.[16] In general, the broadening of a Soret band with less intensity relative to that of unoxidized metalloporphyrins was taken as indicative of π-cation species. The appearance of the visible spectrum of **1** with a broadened Soret of diminished intensity is consistent with the formulation of **1** as a π-radical species. For a MnIV porphyrin species a Soret band with maximum around the 420-nm region with a single band about 535 nm is expected.[7]

Structure. A drawing of MnTPP(Cl)$(SbCl_6)\cdot 4C_2H_2Cl_4$, showing the coplanarity of the porphyrin core atoms with the manganese atom, is shown in Figure 2. The four solvent molecules are not shown in Figure 2 but are included in the stereo view of the crystal packing in the unit cell as shown in Figure 3. Im-

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Table II. Crystallographic Data for $\mathrm{Mn^{III}TPP(Cl)(SbCl_6)\cdot 4C_2H_2Cl}$

space group	P_1
cell params	
$a = 12.1969\ (14)$	
$b = 12.4478\ (9)$	
$c = 12.9537\ (12)$	
$\alpha = 64.795\ (7)°$	
$\beta = 70.701\ (8)°$	
$\gamma = 87.398\ (7)°$	
vol.	1669 Å^3, $Z = 1$
radiatn = Mo Kα (λ = 0.71073 Å)	
data collectn	4352 data (2θ = 3–45°) 4048 data greater than $3.0\sigma F_o$
R (4163 data)	4.22%
R_w (4048 data)	4.57%
important distances	
Mn–N	2.00 (8) Å (av. of four distances)
Mn–Cl	2.32 (1) Å
Mn–Cl(SbCl$_6$)	4.72 Å

portant bond distances and the crystal parameters are given in Table II.

The structure (Figure 3) consists of parallel rows of MnTPP units with centers offset; an $SbCl_6$ anion is located equidistant between porphyrin cores. A chloride is axially bound to the Mn and has a 50% occupancy at sites above and below the porphyrin ligand. The $SbCl_6$ anion is not situated on this Mn–Cl axis but rather is displaced with a Mn–Cl–Sb angle of 132°; the closest approach of a Cl of the $SbCl_6$ anion to the Mn is 4.72 Å. Thus, the manganese is five coordinate and as such might be expected to be displaced out of the nitrogen plane toward the ligand in an analogous pattern to $\mathrm{Mn^{III}TPPX}$ compounds.[5] With the present case of disorder of the chloride sites, the manganese atom would exhibit an elongated vibrational ellipsoid, but our data do not show this result. The porphyrin core carbon atoms, as well as the nitrogen and manganese, are coplanar with only random small deviations from the mean plane (the largest displacement is 0.12 Å of a meso carbon, and the average absolute deviation is 0.05 Å).

Magnetic Susceptibility. The planarity vs. ruffling of metalloporphyrin cation radical species has been judged to be important in determining spin state.[19] The generalization is that loss of D_{4h} symmetry by ruffling of the porphyrin atoms destroys the orthogonality of the ligand a_u and the metal d magnetic orbitals, thereby providing an overlap pathway for ferromagnetic or antiferromagnetic coupling of unpaired metal d electrons and a *p*-cation radical unpaired electron. Conversely, a strictly planar metalloporphyrin cation radial species would be expected to have independent spin states of the paramagnetic metal and cation radical. Magnetic susceptibility measurements (SQUID method) on the X-ray diffraction crystalline material show normal paramagnetism over the temperature range of 5–100 K with no variation in susceptibility at field strengths ranging from 5 000–40 000 G. After application of diamagnetic corrections for all metalloporphyrin and solvent atoms, a plot of $^1/_{\chi_M}$ vs. temperature yielded a straight line with the temperature intercept of +0.38 K, indicating Curie–Weiss behavior. With use of the equation $\mu_{\mathrm{eff}} = 2.83(\chi_M(T-\theta))^{1/2}$ and the experimental Weiss constant of +0.38 K the magnetic moment was calculated to be 4.91 μ_B.

In the oxidation of $\mathrm{Mn^{III}TPP(Cl)}$ the electron could come from the metal-centered orbital to form an $\mathrm{Mn^{IV}TPP^{2+}}$ ion. MnIV is a d^3 ion and would have an expected spin-only moment of 3.87 μ_B. Three different spin states can be distinguished if **1** is a MnIII, $S = 2$, π-cation radical species, $S = {}^1/_2$: (A) the antiferromagnetic state with a resultant spin of three-halves and expected moment of 3.87 μ_B; (B) the ferromagnetic coupled state with a resultant spin of five-halves and spin-only magnetic moment of 5.91 μ_B; (C) and the independent spin $S = 2$, $S = {}^1/_2$ state ($\mu = (\mu_1{}^2 + \mu_2{}^2)^{1/2}$) with an expected moment of 5.19 μ_B. The observed value of 4.91 μ_B in the solid sample excludes a $\mathrm{Mn^{IV}TPP^{2+}}$ species as well as antiferromagnetic coupled $\mathrm{Mn^{III}}$ π-cation radical. The 4.91 μ_B value is closer to that expected for an independent spin system, and this choice is consistent with the structure determination, that is, the planarity of the molecule maintains strict orthogonality of porphyrin and metal magnetic orbitals. This provides no means of overlap leading to exchange and coupling.

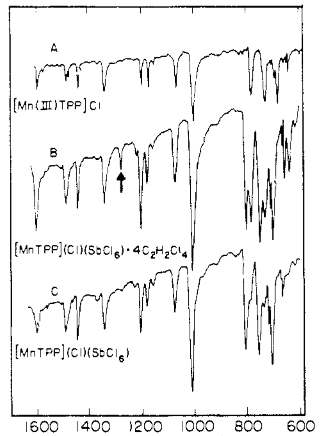

Figure 4. Infrared spectra (in KBr) of $\mathrm{Mn^{III}TPP(Cl)}$ (A); **1**, $\mathrm{Mn^{III}TPP(Cl)(SbCl_6)\cdot 4C_2H_2Cl_4}$ (B); and **2**, $\mathrm{Mn^{III}TPP(Cl)(SbCl_6)}$ (C). Spectra were recorded at room temperature. Compound **2** was obtained upon prolonged exposure of **1** under vacuum.

Repeated magnetic susceptibility measurements in dichloromethane-d_2 solution (^{1}H NMR shift method) gave a range of values 5.7–6.7 μ_B. Two approaches were used in determining these values. One was to dissolve weighed samples of **1** in dichloromethane, and the other was to titrate $\mathrm{Mn^{III}TPPCl}$ with phenoxathiin hexachloroantimonate (both in CD_2Cl_2). Both methods lead to higher μ_B values in solution than in the solid. This suggests that in solution the planarity of the metalloporphyrin metal and porphyrin core is lost and the ferromagnetically coupled spin system is favored. Our results differ from those of Goff et al.[15] who prepared $\mathrm{MnTPPCl(ClO_4)}$ by electrochemical oxidation. The electronic spectrum given by these workers agrees with Figure 1 in this work, but they report a solution mangetic moment of 4.9 μ_B, and they observe a $g = 2.0$ X-band EPR signal at 77 K. Species **1** is EPR silent to 8 K. Goff and co-workers also conclude that $\mathrm{MnTPPCl(ClO_4)}$ is a manganese(III) π-cation radical, and the only difference with **1** is in the ligands present.

We are currently examining a series of oxidized MnTPP(X)(X′) species to further explore possible spin state changes and changes in magnetic interactions as a function of coordinating anions.

IR Spectra. A recent paper by Goff, Reed, and co-workers concluded that a characteristic infrared band in the 1250–1300-cm^{-1} region can be used as a diagnostic tool for metallotetraphenylporphyrin π-cation radical species.[18] The appearance or absence of this band has been cited as evidence in a number of papers concerning oxidized metalloporphyrin compounds. The infrared spectra of MnTPPCl and **1** ($\mathrm{MnTPPClSbCl_6\cdot 4C_2H_2Cl_4}$) are given in Figure 4. A new band at 1280 cm^{-1} appears for **1**. There are also changes in the 600–800-cm^{-1} region. We noted that prolonged exposure of solid samples of **1** under vacuum leads to deterioration of the crystalline nature of the material, and elemental analyses confirmed that the solvate molecules were lost from the lattice. A material that analyzed as $\mathrm{MnTPP(Cl)(SbCl_6)}$ (**2**) yielded spectrum C in Figure 5. The "diagnostic" π-cation radical band at 1280 cm^{-1} disappeared, and there were accompanying changes in the 600–800-cm^{-1} region. With varying lengths of exposure under vacuum, materials could be obtained which gave analyses appropriate for removal of two or three solvent molecules. These materials, intermediate between **1** and **2**, exhibit consistent diminution of the 1280-cm^{-1} band as well as changes in the

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(17) (a) Sholz, W. F.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R.; Lang, G. *J. Am. Chem. Soc.* **1982**, *104*, 6791–6793. (b) Buisson, G.; Deronzier, A.; Duee, E.; Gans, P.; Marchon, J.-C.; Reynard, J.-R. *Ibid.* **1982**, *104*, 6793–6795.

(18) Shimomura, E. T.; Phillippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778–6780.

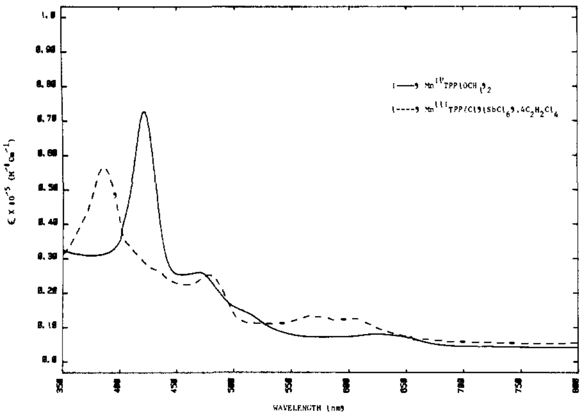

Figure 5. Optical absorption spectra of (a) **1** ($Mn^{III}TPP(Cl)(SbCl_6)\cdot 4C_2H_2Cl_4$) (---) and (b) **3** ($Mn^{IV}TPP(OCH_3)_2$) (—) in dichloromethane. Compound **3** was obtained either by addition of $NaOCH_3$ to **1** or by oxidation of $Mn^{III}TPPCl$ by phenoxathiin hexachloroantimonate in the presence of $NaOCH_3$.

600–800-cm^{-1} region. The solvent, $C_2H_2Cl_4$, shows broad intense absorptions at 600–800 and 1000–1300 cm^{-1}.

Our results seem to indicate that the band at 1280 cm^{-1} as well as others in the 600–800-cm^{-1} region are due to $C_2H_2Cl_4$ solvent molecules in the lattice. Samples of material **2** when dissolved in dichloromethane gave an electronic spectrum identical with that of **1**. Magnetic susceptibility measurements (SQUID) were also made on samples of **2**. These showed normal paramagnetism with a strictly linear Curie–Weiss plot over the temperature range 5–100 K with a Weiss constant of 0.16 K. There was no field dependence over a 5000–40000 G range. The experimental magnetic moment was 4.71 μ_B which compares to the 4.9 μ_B of samples of **1** which include four solvent molecules. This comparison would suggest that there were no major spin state changes in transforming the crystalline solid of **1** to the amorphous powder of solid **2**, even though the band at 1280 cm^{-1} disappears.

Many metallotetraphenylporphyrin oxidation studies are carried out in chlorocarbon solvents, and the possibility exists that incorrect interpretations of the appearance of infrared bands in the 1250–1300-cm^{-1} region have been made. However, we believe the best interpretation of our experimental results of electronic spectrum, X-ray structure, and magnetic susceptibility measurements is that **1** is indeed a MnIII π-cation radical species. In the absence of a definitive study of the origin of the 1250–1300-cm^{-1} band no conclusion regarding the validity of the use of the generalized diagnostic marker can be made.

Ligand Metathesis. Indirect evidence for assignment of **1** as a MnIII porphyrin cation radical is provided by ligand exchange reactions. Several species have been characterized as $Mn^{IV}TPPX_2$ compounds with X = N_3,[19] NCO,[20] and OCH_3.[20] The addition of an approximately tenfold excess of $NaOCH_3$ in methanol to a CH_2Cl_2 solution of **1** at 0 °C caused an immediate change in intensity in the brown solution. The visible spectrum of the new species, **3**, was dramatically different from that of **1** (Figure 5). In a different experiment an equivalent amount of the oxidant phenoxathiin hexachloroantimonate was added to a solution of $Mn^{III}TPP(Cl)$ in CH_2Cl_2 which also contained a fivefold excess of $NaOCH_3$ in methanol. In the absence of methoxide ion phenoxathiin hexachloroantimonate oxidizes $Mn^{III}TPP$ to the π-cation radical (Figure 5a); in the presence of methoxide ion spectrum 5b is produced. Spectrum 5b can be attributed to that of $Mn^{IV}TPP(OCH_3)_2$ as its absorption and EPR (see below) spectra are very similar to that reported for $Mn^{IV}TPP(OCH_3)_2$.[20] Thus $Mn^{IV}TPP(OCH_3)_2$ can be generated from either MnTPP(Cl) or the MnTPP cation radical.

Additional confirmation of the identity of **3** as a manganese(IV) species is provided by its X-band EPR. Species **1** is EPR silent from 200–10000 G at 8 K. If a solution of **1** in CH_2Cl_2 is warmed to about −50 °C and $NaOCH_3$ is added with the temperature then lowered to 8 K, the EPR spectrum exhibits a signal at $g = 5.4$ and a broad poorly resolved signal in the $g = 2$ region. This spectrum is similar to that observed for $Mn^{IV}TPP(OCH_3)_2$.[20] The electronic spectrum of the sample from the EPR measurements was identical with that shown in Figure 5b.

Taken together, these results indicate that coordination by methoxide, a strong π-donating ligand, has shifted the site of oxidation in the porphyrin ring in **1** to the manganese in **3**.

Redox Catalyst. In solution, after a time, **1** reverts to the original $Mn^{III}TPP$ species, as determined by the electronic spectrum. With purified, dried dichloromethane as the solvent this reduction occurs over a 10–15-min period. If the dichloromethane is not rigorously free of HCl or if small amounts of methanol, water, or similar solvents are added, the process occurs more rapidly. In none of these cases has the reducing agent or its oxidized products been identified. The reactivities of $Mn^{III}TPP^{+\cdot}$, $Mn^{IV}TPP$,[20] and other high-valent manganese porphyrin complexes,[6,8] as evidenced by their reactions with water, HCl, and other organic substrates, justify interest in them as potential redox catalysts in artificial photosynthesis assemblies. Spectral measurements indicate that oxidation of $Mn^{III}TPP$ to MnIII porphyrin π-cation radical followed by return to $Mn^{III}TPP$ can be repeated many times without significant degradation of starting materials. Our observation that the site of oxidation in $Mn^{III}TPP$ compounds can be controlled by the ligands coordinated to the manganese ion is also of potential importance. Conversion of MnIII porphyrin π-cation radical to a MnIV porphyrin by addition of a methoxide ion, a strong π-donating ligand, suggests that adjustment of redox reactivities and oxidation potentials may be possible by variation of coordinating ligands.

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