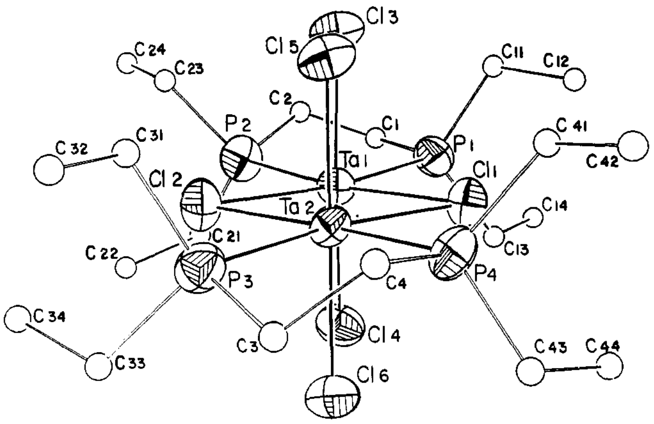

Figure 2. ORTEP view and atom-labeling scheme for Ta$_2$Cl$_6$(depe)$_2$ (**2**). Carbon atoms are drawn as spheres of arbitrary diameter.

the metal–metal distances indicate the presence of Ta–Ta double bonds, which would be expected between the two d^2 metal atoms.

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Registry No. **1**, 110796-21-9; **2**, 110796-20-8; Ta, 7440-25-7.

Supplementary Material Available: Complete tables of bond distances and angles and tables of anisotropic displacement parameters for both compounds (6 pages); tables of calculated and observed structure factors for both compounds (22 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry
and Lawrence Berkeley Laboratory, University of California,
Berkeley, California 94720, and Department of Chemistry,
University of the Pacific, Stockton, California 95211

Temperature-Dependent Valence Isomerization in a Manganese Tetraphenylporphyrin

Anthony C. Maliyackel, J. W. Otvos, Melvin Calvin,
and L. O. Spreer*

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The characterization of oxidized metalloporphyrins is of much current interest because they serve as model systems for many redox reactions of metalloporphyrin-containing enzymes. It is well-established that oxidation of a metalloporphyrin can be metal-centered or ligand-centered, the latter producing a π cation radical. Our interest in this subject, particularly in the characterization of high-valent manganese porphyrins, derives from our work on potential multipole-electron redox catalysts for an artificial photosynthesis assembly.[1] A prerequisite for a multiple-electron redox catalyst is the accessibility of a variety of oxidation states. Manganese porphyrins have been fully characterized with manganese in the +2, +3,[2] +4,[3,4] and +5[5] oxidation states. In addition, several groups have described manganese π-cation-radical porphyrins[6,7] where oxidation has occurred on the macrocycle.

The axial ligands on the metal are of prime importance in determining the electronic configuration of oxidized metalloporphyrins. Recently we described a case in which a Mn(III) tetraphenylporphyrin π cation radical, Mn^{III}TPP$^{\bullet+}$, is converted to a Mn^{IV}TPP species by addition of a strong π-donating ligand, CH$_3$O$^-$.[8] In the present paper we describe the preparation and properties of the compound MnTPP(CF$_3$SO$_3$)$_2$, which we believe undergoes a temperature-dependent valence isomerization from a manganese(III) π cation radical at higher temperature to a manganese(IV) porphyrin at reduced temperatures.

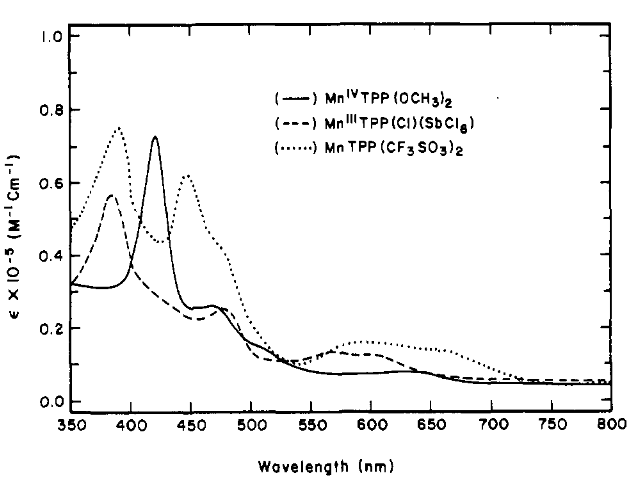

Figure 1. Electronic spectra of manganese tetraphenylporphyrin species: (—) Mn^{IV}TPP(OCH$_3$)$_2$; (- -) Mn^{III}TPP(Cl)(SbCl$_6$) (Mn^{III} π cation radical); (···) MnTPP(CF$_3$SO$_3$)$_2$.

Experimental Section

The chemicals used were all reagent grade. Dichloromethane and toluene were purified by distillation and stored over activated molecular sieves. Preparation of Mn^{III}TPP(Cl) is discussed elsewhere.[8]

Synthesis of MnTPP(CF$_3$SO$_3$)$_2$. To a solution of Mn^{III}TPP(Cl) (0.5 mM) in dichloromethane (50 mL) at –70 °C were added solutions of iodine (2.0 mM) in dichloromethane (15 mL) and silver trifluoromethane sulfonate (1.0 mM) in toluene (10 mL). After the mixture was stirred for 15 min, the precipitate of silver iodide and silver chloride was filtered off quickly. The filtrate was then added to an excess of hexane kept at –70 °C. The resulting precipitate was collected by filtration and air-dried. Anal. Calcd for MnTPP(CF$_3$SO$_3$)$_2$: Mn, 5.69; C, 57.20; N, 5.80; H, 2.90; S, 6.63. Found: Mn, 5.41; C, 54.30; N, 5.31; H, 2.97; S, 6.28. (The experimental values are low compared to the calculated ones, but the experimental N/Mn mole ratio is 4.0 and the experimental S/Mn mole ratio is 2.0. Contamination by a small amount of moisture would account for the discrepancies.) The compound was free from Ag, I, and Cl (<0.5%).

Visible absorption spectra were recorded on a Hewlett-Packard 845A spectrometer. Variable-temperature magnetic susceptibility measurements in the solid state were carried out on a SQUID apparatus (SHE Corp., VPS 800 susceptometer). The experimental details are discussed elsewhere.[8] The X-band EPR spectra were recorded on a Varian Model E-109 spectrometer equipped with a low-temperature Dewar (Air Products, Ltd.).

Results and Discussion

The compound MnTPP(CF$_3$SO$_3$)$_2$ (**1**) is produced by a one-electron oxidation from the starting Mn^{III}TPP(Cl) material. The oxidation could conceivably take place at the metal, producing a Mn^{IV}TPP^{2+} ion, or at the porphyrin ring, producing a Mn(III) π-cation-radical species. In fact, the electronic spectrum and solid-state magnetic susceptibility data, both near room temperature, support designation of **1** as a Mn(III) π cation radical. However, the magnetic moment of **1** shows a significant temperature dependence, and this, coupled with the features of the low-temperature (<80 K) EPR spectrum, strongly suggests that a temperature-dependent oxidation-state change takes place. At the lower temperatures the ground-state electronic configuration

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* To whom correspondence should be addressed at the University of the Pacific.

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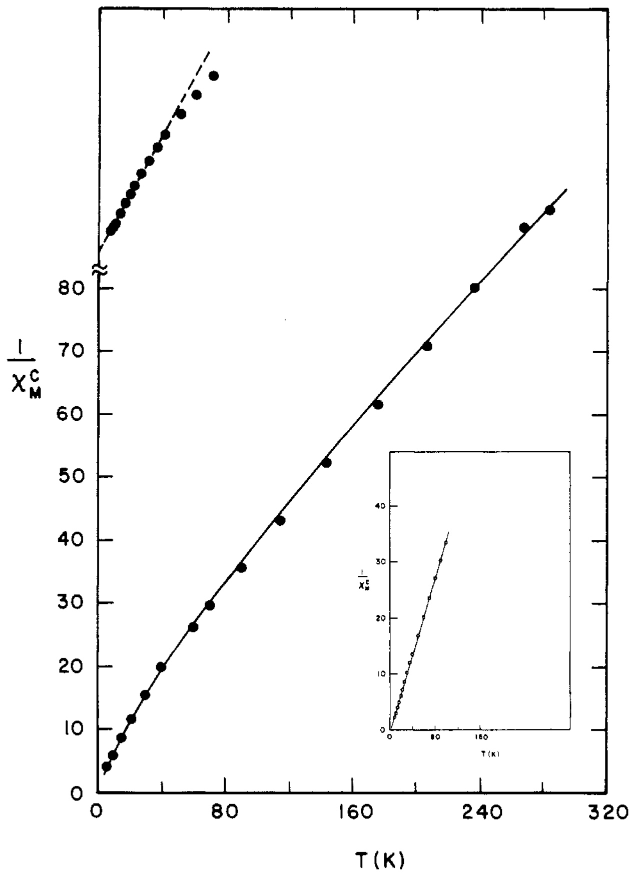

Figure 2. Solid-state magnetic data for MnTPP(CF_3SO_3)$_2$. The molar susceptibility has been corrected for diamagnetic contribution of the constituent atoms. The field strength is 5000 G; the Weiss constant is -1.19 K. The upper line shows all the low-temperature data. The insert shows data for MnTPP(Cl)($SbCl_6$)·4$C_2H_2Cl_4$ from ref 8.

of **1** becomes that of a manganese(IV) tetraphenylporphyrin.

The visible absorption spectrum of MnTPP(CF_3SO_3)$_2$ (**1**) in dichloromethane at -25 °C is shown in Figure 1. Also shown in the figure are the absorption spectra of MnTPP(Cl)($SbCl_6$),[8] which has been identified as a Mn(III) π-cation-radical species, and of MnTPP(OCH_3)$_2$, which has been well-characterized as a Mn^{IV}TPP compound.[9] There are important similarities in the spectra of **1** and the species characterized as a $Mn^{III}TPP^{\bullet+}$ species while a bona fide Mn(IV) porphyrin shows marked differences. Compound **1** is unstable even at -25 °C and reverts quickly to Mn^{III}TPP at room temperature. The shoulder at 476 nm in the spectrum of **1** in Figure 1 is probably due to decomposition.

The magnetic susceptibility of **1** was measured in the solid state at temperatures of 5–280 K. These measurements were done at field strengths ranging from 5000 to 40 000 G. A plot of the reciprocal of the molar susceptibility, after appropriate correction for the diamagnetism of all constituent atoms, against temperature is shown in Figure 2. The shapes of the plots are independent of field strength. The Curie–Weiss plot for **1** showed appreciable curvature with a linear region in the 5–50 K temperature range and another linear region above 100 K. The top portion of Figure 2 shows the low-temperature region with all data points included. In contrast the Curie–Weiss plot for MnTPP(Cl)($SbCl_6$) is remarkably linear and is shown as an insert in Figure 2. Magnetic moments for **1** were calculated from the linear portions of the plots and were 3.9 μ_B at low temperature and 4.9 μ_B for the high-temperature region.

Expected magnetic moments for different electronic configurations are shown in Table I. Mn(IV) is a d^3 ion and would have a spin-only moment of 3.87 μ_B (A). Three different spin states must be considered if **1** is a Mn(III), $S = 2$, π-cation-radical species, $S = {}^1/_2$: (B) the ferromagnetically coupled state with a resultant spin of ${}^5/_2$ and an expected moment of 5.91 μ_B; (C) the antiferromagnetically coupled state with resultant $S = {}^3/_2$ and a magnetic moment of 3.87 μ_B; and (D) the independent spin state composed of $S = 2$ and $S = {}^1/_2$ with a theoretical moment $(\mu_1{}^2 + \mu_2{}^2)^{1/2} = 5.19\ \mu_B$. The observed value of 4.9 μ_B at temperatures above 100 K effectively rules out the Mn(IV) configuration (A) and the antiferromagnetically coupled $Mn^{III}TPP^{\bullet+}$ configuration (C). The value is close to that for $Mn^{III}TPP^{\bullet+}$ with independent spins (D), and this is consistent with the visible spectrum of **1**, which supports a π-cation-radical species.

Table I. Calculated Magnetic Moments for Manganese Porphyrin Configurations

	confign	μ_{eff}(calcd), μ_B
A	Mn^{IV}TPP	3.87
B	$Mn^{III}TPP^{\bullet+}$ (ferromag coupling)	5.91
C	$Mn^{III}TPP^{\bullet+}$ (antiferromag coupling)	3.87
D	$Mn^{III}TPP^{\bullet+}$ (indep spins)	5.19

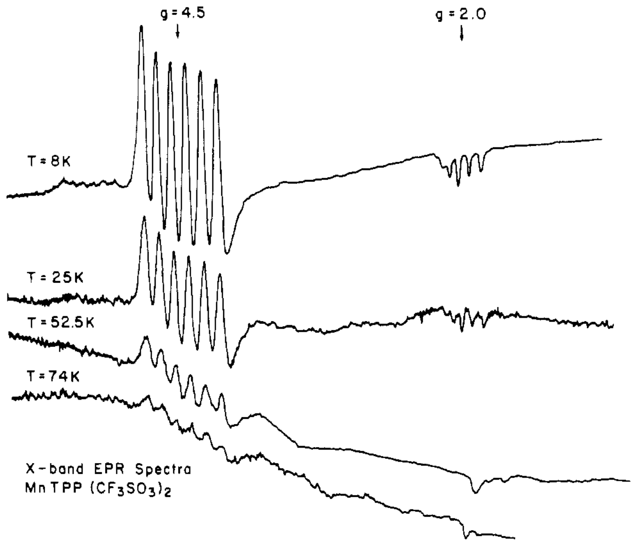

Figure 3. X-Band EPR spectra for MnTPP(CF_3SO_3)$_2$ in CH_2Cl_2 as a function of temperature. The instrument settings were kept constant.

However, the value of 3.9 μ_B at low temperature does not agree with moments expected for configurations B or D and is close to the expected moments for either a Mn(IV) porphyrin or an antiferromagnetically coupled Mn(III) π-cation-radical species.

The temperature-dependent EPR spectra of **1** provide a means of distinguishing between the Mn(IV) and Mn(III) π-cation-radical antiferromagnetically coupled states. The X-band EPR spectrum of **1** in CH_2Cl_2 at 8 K is given as the top spectrum in Figure 3. A pronounced sextet with a central g value of 4.5 is observed. The spectrum is anisotropic, having another sextet pattern in the $g = 2$ region. In addition, a very low intensity feature near $g = 5$ was observed in most sample preparations, which is probably due to a $\Delta M_s = 3$ transition. The hyperfine splitting arises from the $I = {}^5/_2$ ^{55}Mn nucleus, and the hyperfine splitting constants are 64 G in the $g = 4.5$ region and 60 G in the $g = 2$ region. This spectrum is entirely consistent with interpretation as a Mn^{IV}TPP configuration with Mn in the high-spin ${}^3/_2$ state and in an environment of lower than octahedral symmetry. Very similar spectra have been reported for well-characterized Mn^{IV}TPP[9,10] species with methoxide, azide, or cyanate as anionic ligands. In contrast Mn(III) porphyrins are in general EPR-silent. Goff[7] has reported that the Mn(III) π cation radical with Cl^- and ClO_4^- as ligands gave a broadened $g = 2$ signal at 70 K. The Mn^{III}TPP(Cl)($SbCl_6$) compound[8] showed no EPR spectrum from room temperature to 8 K.

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A consistent diminution of signal intensity of a given sample was observed as the temperature was raised from 8 to 100 K. The loss of signal intensity was not due to decomposition of the sample since return to lower temperature gave all of the original absorption. One possible explanation for the disappearance of signal with increasing temperature is an increasing rate of relaxation, which leads to broadening of the signal. However, our observations of the nonlinear Curie–Weiss behavior of the solid and changes in magnetic moment with temperature support an interpretation of an oxidation-state change at temperatures above 100 K. The electronic spectrum, solid-state magnetic moment, and absence of an EPR signal for **1** all support its characterization as a Mn(III) π cation radical at temperatures above 100 K, while at temperatures between 8 and 50 K the solid-state magnetic moment and EPR spectrum indicate a $Mn^{IV}TPP$ species. Thus **1** mimics the behavior of nickel tetraphenylporphyrin, where the room-temperature species is $Ni^{II}TPP^{\bullet +}$ while at 77 K it is characterized as $[Ni^{III}TPP]^+$.[11] The ground state of $MnTPP(CF_3SO_3)_2$ appears to be a Mn(IV) oxidation level. However, there must be a very closely related structural configuration that favors an oxidation-state change to a Mn(III) π-cation-radical state since this isomerization occurs in the solid state.

Summary

A survey of recent papers on oxidized Mn tetraphenylporphyrins demonstrates the importance of the axial ligands on the Mn in determinining the electronic properties of the compound. Species with one coordinating anion such as Cl^- and a poorly coordinating anion such as ClO_4^- or $SbCl_6^-$[7,8] are characterized as Mn(III) π cation radicals over all temperature ranges, but they can be converted to Mn(IV) porphyrins by addition of such ligands as CH_3O^- or N_3^-. The present paper describes $MnTPP(CF_3SO_3)_2$, a species with two poorly coordinating anions, which has a Mn(IV) ground state and a low-lying Mn(III) π-cation-radical configuration. There is another report of a $MnTPP(Cl)_2$ compound that also exhibits a temperature-dependent oxidation-state change.[12] However, in this compound with two coordinating anions the ground state appears to be a Mn(III) π cation radical and the predominant species at room temperature is a $Mn^{IV}TPP$ species.

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Contribution from the Department of Chemistry,
Haverford College, Haverford, Pennsylvania 19041

Correlation between Electron-Transfer Rate Constants and Intervalence-Transfer Energies

Daniel A. Geselowitz

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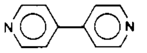
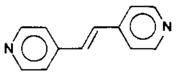
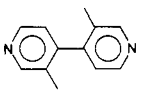
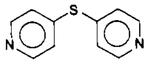
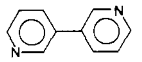
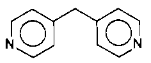
Long-range intramolecular electron-transfer reactions, especially those involving proteins, have become a topic of great excitement and intense research. Recent work has included the study of metal-to-metal electron transfer through covalently modified proteins such as cytochrome *c*,[1–6] azurin[7,8] and myoglobin,[9] protein dimers and tetramers,[10–15] and several oligopeptide systems,[16–18] over distances of as much as 25 Å. Several reviews of the topic have also appeared.[19–21] These studies not only hold the promise of revealing how such all-important biological redox processes as photosynthesis, respiration, and nitrogen fixation occur but may also hold the answers to some of the most fundamental questions about electron transfer.

Table I. Literature Data for Electron Transfer in Complexes of the Form $[(NH_3)_4(H_2O)Ru^{II}\text{–}L\text{–}Co^{III}(NH_3)_5]^{5+}$[a]

L	10^3k_{298}, s^{-1}	ΔH^*, kJ/mol	ΔS^*, J/(mol K)	ΔG^*_{298}, kJ/mol
	44[b]	84.1 ± 1.3	10.9	80.9
	18.7[b]	84.6 ± 1.3	5.0	83.1
	5.5[b]	84.6 ± 1.3	−4.6	86.0
	4.9[b]	83.7 ± 1.3	−8.0	86.1
	4.2[c]	*d*	*d*	86.5
	2.1[c]	77.0 ± 2	−37 ± 7	88.0

[a] In 0.4 M CF_3COOH. [b] Reference 25. [c] Reference 26. [d] Not reported.

Perhaps one of the most interesting questions addressed by these studies is, what is the effect of the donor–acceptor (reductant–oxidant) separation distance on the rate constant of electron transfer? Empirically, a fairly clear picture is emerging. The general trend, which is seen plainly in studies with oligopeptides as bridging ligands and is also apparent in the protein work, is that the first-order rate constant decreases with increasing separation. However, the fundamental question remains, what is the

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