signal is observed in the magnetic fields lower than 2900 G for the solution prior to irradiation, the ESR spectrum observed around 2650 G ($g = 2.46$) is ascribed to the photoproduct from $ClRh^{III}TPP$ at 77 K; the signal cannot be ascribed to any organic radical. Taking into account the $g_\perp$ values of 2.4–2.5[9,10] for rhodium(II) complexes with axial symmetry, we conclude that the signal is assigned to the perpendicular components of the monomeric $Rh^{II}TPP$. Owing to heavy background absorption due to $RhTPP(O_2)$ and solvent radicals produced by irradiation with the mercury lamp, we could not determine the $g_\parallel$ value of $Rh^{II}TPP$, which is expected to be nearly 2.0. The ESR signal vanishes when the irradiated solution is warmed to room temperature and recooled to 77 K. This is in accord with the fact that $Rh^{II}TPP$ readily dimerizes to form the diamagnetic dimer, $[Rh^{II}TPP]_2$.[2,7]

Figure 2B shows the ESR spectrum measured for the irradiated MTHF solution of $[Rh^{II}TPP]_2$ at 77 K. The irradiated solution shows the ESR signal at 2650 G, which is almost identical with that observed for the irradiated MTHF solution of $ClRh^{III}TPP$, indicating that the species giving rise to the spectrum is $Rh^{II}TPP$. No half-field signal is observed for the irradiated solution. The ESR signal disappears completely upon warming the irradiated solution to room temperature.

Rhodium(III) in $ClRh^{III}TPP$ is known to have a low-spin d^6 electronic configuration similar to cobalt(III) in $ClCo^{III}TPP$. We, therefore, preformed low-temperature photolysis of $ClCo^{III}TPP$ in MTHF at 77 K for comparison and found an ESR spectrum that is identical with that of authentic $Co^{II}TPP$.

Wavelength dependence on the photochemical reactions of $ClRh^{III}TPP$ and $[Rh^{II}TPP]_2$ was investigated by using cutoff filters. Optical and ESR measurements of the irradiated solutions revealed that $ClRh^{III}TPP$ and $[Rh^{II}TPP]_2$ form $Rh^{II}TPP$ with the irradiation light of $\lambda < 400$ nm and $\lambda < 310$ nm, respectively. No photochemical reaction was observed for the Q-band excitation of $ClRh^{III}TPP$ and $[Rh^{II}TPP]_2$ in MTHF solutions at 77 K.

Solvent radicals as well as $Rh^{II}TPP$ are the photoproducts from the irradiation of MTHF solutions of $ClRh^{III}TPP$ and $[Rh^{II}TPP]_2$. Since the irradiation of neat MTHF with the mercury lamp at 77 K gives rise to the formation of the solvent radicals, we consider that MTHF molecules absorbing UV light undergo C–H bond cleavage to produce a solvent radical (MTHF·) and an atomic hydrogen

$$\mathrm{MTHF} \xrightarrow{h\nu} \mathrm{MTHF}\cdot + \mathrm{H}\cdot$$

followed by

$$\mathrm{MTHF} + \mathrm{H}\cdot \rightarrow \mathrm{MTHF}\cdot + \mathrm{H_2}$$

The major amount of the solvent radicals in the irradiated MTHF solutions of $ClRh^{III}TPP$ and $[Rh^{II}TPP]_2$ are presumed to be formed according to the above reaction scheme.

The irradiation of $ClRh^{III}TPP$ in an MTHF solution was performed with a cutoff filter transmitting the light of $\lambda > 360$ nm. Although this filter prevented the formation of solvent radicals from neat MTHF, the irradiated MTHF solution of $ClRh^{III}TPP$ exhibited ESR signals due to solvent radicals and $Rh^{II}TPP$. The photochemical formation of $Rh^{II}TPP$ from $ClRh^{III}TPP$ is assumed to be represented as

$$\mathrm{ClRh^{III}TPP} \xrightarrow{h\nu\ (\lambda < 400\ \mathrm{nm})} \mathrm{Cl}\cdot + \mathrm{Rh^{II}TPP}$$

$$\mathrm{Cl}\cdot + \mathrm{MTHF} \rightarrow \mathrm{MTHF}\cdot + \mathrm{HCl}$$

The monomeric $Rh^{II}TPP$ is trapped stably in the MTHF matrix because of the high viscosity of the solvent at 77 K. The Cl–Co homolytic cleavage also takes place at 77 K for $ClCo^{III}TPP$

$$\mathrm{ClCo^{III}TPP} \xrightarrow{h\nu} \mathrm{Cl}\cdot + \mathrm{Co^{II}TPP}$$

followed by hydrogen abstraction of Cl· from an MTHF molecule. This homolytic cleavage may be justified from similar photoelimination of Cl· at 77 K frequently observed for benzyl chloride, $C_6H_5CH_2Cl$ and its derivatives in organic solvents:[11]

$$\mathrm{C_6H_5CH_2Cl} \xrightarrow{h\nu} \mathrm{Cl}\cdot + \mathrm{C_6H_5CH_2}\cdot$$

The photochemical formation of $Rh^{II}TPP$ from $[Rh^{II}TPP]_2$ is considered to involve the fission of the Rh–Rh bond at 77 K:

$$\mathrm{[Rh^{II}TPP]_2} \xrightarrow{h\nu\ (\lambda < 310\ \mathrm{nm})} 2\mathrm{Rh^{II}TPP}$$

Owing to the high viscosity of the solvent at 77 K, the resulting two $Rh^{II}TPP$ molecules, each of which has an unpaired electron, are expected to be located in close proximity; however, slight displacement of the two $Rh^{II}TPP$ molecules is presumably enough for each electron to be isolated electronically and magnetically. The solvent radicals observed in the irradiated solution are produced by photolysis of MTHF molecules, which absorb the light of $\lambda < 260$ nm. It should be noted that photodissociation of some organic dimers occurs readily in low-temperature matrices,[12-15] as in the present case.

Registry No. $Rh^{II}TPP$, 38856-19-8; $ClRh^{III}TPP$, 77944-60-6; $[Rh^{II}TPP]_2$, 88083-37-8.

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EPR Spectroscopy of Mixed-Valence μ-Oxo-Bridged Manganese(III)/Manganese(IV) Porphyrin Complexes

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Several manganese ions in close proximity have been proposed to be present at the oxygen-evolving site of photosystem II.[1] The four-electron oxidation of water at this site may involve the cycling of the oxidation states of manganese ions that are bridged by oxygen ligands. The study of the interactions between manganese ions in synthetic complexes as they change oxidation states may improve the understanding of the interactions between the manganese ions in photosystem II.

We have previously reported the characterization of the oxo-bridged dimeric manganese(IV) porphyrin complexes $[(OCN)Mn^{IV}TPP]_2O$ and $[(N_3)Mn^{IV}TPP]_2O$, including a crystal and molecular structure determination for the latter complex.[2,3] The two manganese(IV) ions in each of these complexes are strongly antiferromagnetically coupled, making the complexes EPR silent.[3] The isolated complex $[(N_3)Mn^{IV}TPP]_2O$ has been shown to oxidize cyclohexane at room

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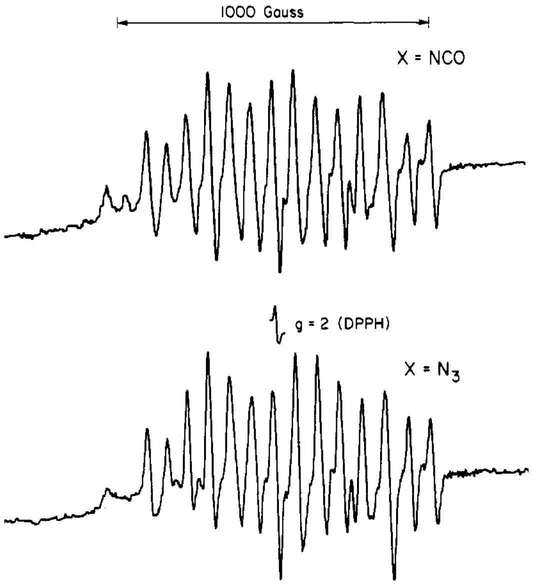


Figure 1. X-Band EPR spectra (9.21 GHz) of the complexes $[XMn^{IV}TPP]$–O–$[Mn^{III}TPP]$ that are formed by allowing ~1.5 mM solutions of the complexes $[XMn^{IV}TPP]_2O$ in 60:40 toluene/chloroform to partially decompose at room temperature. The total elapsed times at room temperature were 17 min for X = NCO and 10 min for X = N_3. The spectrometer parameters were modulation frequency 100 kHz, modulation amplitude 16 G peak to peak, scan time 8 min, time constant 0.128 s, spectrometer gain 1.6×10^4, microwave power 10 mW, and temperature 12 K.

temperature to give cyclohexyl azide and oxygenated products.[4] Thermal decomposition of these μ-oxo-bridged manganese(IV) porphyrin complexes yields deeply trapped mixed-valence dimeric complexes containing distinct manganese(III) and manganese(IV) centers. In this paper, the characteristic EPR spectra of these mixed-valence complexes are described and a mechanism for their formation is proposed.

Experimental Section

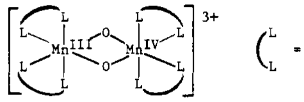
The thermally unstable complexes $[(N_3)Mn^{IV}TPP]_2O$ and $[(OCN)Mn^{IV}TPP]_2O$ were synthesized by literature methods[3] and stored at −30 °C. Solvent purifications have been described elsewhere.[5] Solutions of the complexes for EPR studies were prepared under nitrogen in a 5 °C cold room. Freshly made samples of the complexes $[XMn^{IV}TPP]_2O$ are EPR silent down to 8 K.[3,4] For this study, samples of the complexes (~2 mg) were dissolved in 0.4 mL of chloroform, diluted with 0.6 mL of toluene, and frozen in liquid nitrogen. These solutions were warmed to room temperature for timed intervals until partial decomposition occurred and then were refrozen for determination of the EPR spectra. The total elapsed times at room temperature for the spectra shown in Figure 1 were 10 min for X = N_3 and 17 min for X = OCN. For these samples, the visible spectra suggested that the manganese(IV) complexes were still the primary species in solution ($\lambda_{max} \sim 414$ nm).[3,5] The visible spectra at this point were distinct from the visible spectra of the known manganese(III) complexes $XMn^{III}TPP$ (X = N_3, OCN; $\lambda_{max} = 484$ and 474 nm, respectively).[5] Hence the EPR-active mixed-valence complexes probably were not the predominant porphyrin species in solution. We have not been able to isolate the mixed-valence species. When the complexes $[XMn^{IV}TPP]_2O$ were allowed to decompose for more than 1 h, new signals that probably corresponded to small amounts of manganese(II) porphyrin complexes[4] appeared in the EPR spectra near $g = 7$ and the intensity of the ~16-line pattern associated with the mixed-valence species decreased greatly.

The EPR spectra were recorded on a Varian E-109 spectrometer. The field was calibrated with 2,2-diphenyl-1-picrylhydrazyl radical (DPPH). Temperatures near 12 K were obtained by using an Air Products Helitran low-temperature accessory.

Results and Discussion

Frozen solutions containing freshly prepared samples of the complexes $[XMn^{IV}TPP]_2O$ (X = N_3, OCN), **1**, are EPR silent due to the strong antiferromagnetic coupling between the two manganese(IV) ions ($J \sim 250$ cm^{-1}).[3,6] When solutions of the complexes $[XMn^{IV}TPP]_2O$ are allowed partially to decompose at room temperature and are then frozen to form glasses, EPR signals with an apparent ~16-line hyperfine pattern centered at $g \sim 2$ are observed (Figure 1). Since monomeric manganese(III) porphyrin complexes do not exhibit EPR spectra and the observed ~16-line EPR spectra are distinct from the highly anisotropic EPR spectra of known monomeric manganese(IV)[5,7] and manganese(II)[7b,8] porphyrin complexes, we conclude that these signals are due to dimeric species. The EPR spectra in Figure 1 are consistent with the presence of mixed-valence oxo-bridged Mn(III)/Mn(IV) dimers, **2**, and are very similar to the EPR spectra of known bis(μ-oxo)-bridged Mn(III)/Mn(IV) complexes.[9,10] The pseudo-16-line EPR spectra are characteristic of binuclear complexes that contain an $S = {}^3/_2$ Mn(IV) ion and an $S = 2$ Mn(III) ion that are strongly antiferromagnetically coupled to give an effective $S = {}^1/_2$ ground state.[9] The unpaired spin is not delocalized equally over the two manganese centers to give a $Mn^{3.5+}$ averaged oxidation state since this would yield an 11-line pattern with intensity ratios 1:2:3:4:5:6:5:4:3:2:1 due to hyperfine coupling to two equivalent ^{55}Mn ($I = {}^5/_2$) nuclei. The apparent ~16-line hyperfine coupling pattern arises from the coupling of the unpaired electron spin with distinct Mn(III) and Mn(IV) ions. In the idealized case where the coupling of the electron spin to the Mn(III) nucleus is twice the coupling to the Mn(IV) nucleus,[9] a 16-line pattern with intensities 1:1:2:2:3:3:3:3:3:3:3:3:2:2:1:1 is predicted.

Spectra similar to those shown in Figure 1 have been reported previously for a series of bis(μ-oxo)-bridged mixed-valence complexes:[9,10]



= 2,2'-bipyridyl, 1,10-phenanthroline, or 2,2'-bipyridyl N,N'-dioxide

The EPR spectra of these complexes were also analyzed in terms of a deeply trapped mixed-valence Mn(III)/Mn(IV) system.[9,10] The inequivalence of the Mn(III) and Mn(IV) centers has been unequivocally established by X-ray crystallography for the bis(μ-oxo)-bridged bipyridyl complex.[11] Simulations of the EPR spectra for the bis(μ-oxo)-bridged complexes have been reported by Dismukes and co-workers.[9,10] Their simulations demonstrated that the hyperfine coupling to the manganese(III) nucleus was not exactly twice the hyperfine coupling to the manganese(IV) nucleus, thus explaining

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in part the nonidealized pseudo-16-line pattern. The presence of more than 16 lines in the EPR spectra of the mixed-valence porphyrin complexes can also be explained on this basis. Other factors that may contribute to the differences between the experimental spectra and the idealized intensity ratios and positions of the hyperfine lines based on the simple coupling scheme (i.e. $|A_{\mathrm{Mn(III)}}| = |2A_{\mathrm{Mn(IV)}}|$) include (1) anisotropic coupling of the electron spin to the manganese nuclei, (2) g-value anisotropy, (3) second-order hyperfine interactions since for manganese the hyperfine interactions are not small compared to the Zeeman interactions,[9] and (4) line widths that are approaching the splitting between adjacent hyperfine lines. The magnitude of the EPR line widths in the porphyrin complexes may in large part be due to unresolved ^{14}N superhyperfine splittings, as has been proposed for the bis(μ-oxo) complexes.[10]

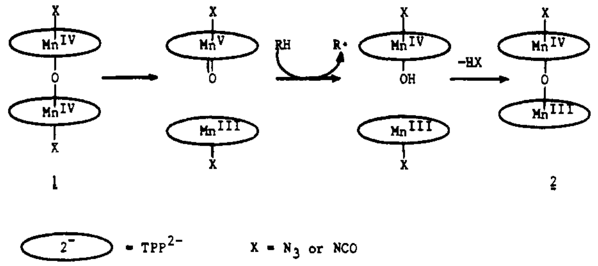
The average separation of the hyperfine lines in the porphyrin mixed-valence complexes, assuming a 16-line pattern, is 69.3 ± 0.7 G for both complexes. There are, however, small differences between the anisotropies of the hyperfine lines in the two complexes that may be due to electronic differences between the NCO and N_3 ligands. Electronic differences between the NCO and N_3 ligands have also been observed in the EPR spectra of the monomeric complexes $(N_3)_2Mn^{IV}TPP$ and $(OCN)_2Mn^{IV}TPP$.[5] The average hyperfine coupling to the manganese nuclei in the porphyrin complexes is significantly smaller than the average hyperfine coupling observed in the bis(μ-oxo)-bridged mixed-valence complexes, suggesting the presence of less manganese-centered spin density in the porphyrin complexes (the average separation of hyperfine lines in the bis(μ-oxo) complexes is ~81 G).[9,10] This is consistent with greater manganese–ligand covalency in the porphyrin complexes.

The proposed mono(μ-oxo) structure of **2** is reasonable on the basis of the known mono(μ-oxo) structure of the starting material,[3] the known 5-coordinate structures of $XMn^{III}TPP$ complexes,[12] and the known pseudooctahedral coordination about the manganese in the related monomeric complexes $X_2Mn^{IV}TPP$ (X = N_3, OCN, CH_3O).[5,13] The inequivalence of the two manganese ions in the mixed-valence porphyrin complexes is not surprising since only one manganese is likely to be coordinated by a sixth anionic ligand. Since the occupation of the antibonding d_{z^2} orbital in manganese(III) porphyrin complexes is known to induce long axial bond lengths[12] whereas manganese(IV) porphyrin complexes have short axial bond lengths,[3,5,13] large barriers to vibrationally allowed intramolecular electron transfer are expected for these complexes.

The similarity of the EPR spectra of the mixed-valence bis(μ-oxo)-bridged complexes, where the Mn–O–Mn angle is near 97°,[11] and the mono(μ-oxo)-bridged porphyrin complexes, where the Mn–O–Mn angle is expected to be near 180°, indicates that the EPR spectra of oxo-bridged mixed-valence Mn(III)/Mn(IV) dimers are not very sensitive to the number or the geometry of the bridging oxo groups. The magnitude of the antiferromagnetic coupling between the Mn(III) and Mn(IV) ions may be more sensitive to the number and geometry of the oxo bridges, but our inability to isolate the mixed-valence porphyrin dimers in a pure form has precluded the determination of *J* in these complexes by magnetic susceptibility measurements.

The EPR spectra of the mixed-valence complexes described here are similar to the EPR spectrum observed when spinach chloroplasts are flashed with one pulse of light and then frozen.[10] However, Dismukes and co-workers have recently suggested that some additional weak transitions observed outside the field range where the Mn(III)/Mn(IV) dimers show absorptions can be explained by the presence of a 3Mn(III)/Mn(IV) tetramer. This EPR-active tetranuclear cluster was proposed to be the water oxidation site of photosystem II.[10]

A potential mechanism for the formation of the mixed-valence porphyrin complexes, **2**, from the starting complexes, **1**, is as follows (eq 1): first, one (IV/IV) dimer disproportionates into Mn(III) and O=Mn$^{\mathrm{V}}$ fragments, and the O=Mn$^{\mathrm{V}}$ complex then abstracts a hydrogen atom from the solvent to form an alkyl radical and a hydroxo Mn$^{\mathrm{IV}}$ porphyrin. Evidence for this portion of this mechanism has been presented elsewhere.[4,14] The recombination of the hydroxo Mn(IV) complex and a Mn$^{\mathrm{III}}$ porphyrin with elimination of HX gives the mixed-valence complex.



(1)

The free radical that was formed can undergo inner-sphere attack on the coordinated pseudohalide of a second molecule of **1** to yield an alkyl pseudohalide product, RX, and a second molecule of **2**. The formation of alkyl radicals and the formation of alkyl azide products during the reaction of the complex $[(N_3)Mn^{IV}TPP]_2O$ with cyclohexane have been demonstrated previously.[4] The appearance of signals near *g* = 7 in the EPR spectra when the samples of **1** are decomposed for greater than 1 h is consistent with the formation of some $Mn^{II}TPP$ by attack of the alkyl radicals on the $XMn^{III}TPP$ species that build up late in the reaction. The formation of $Mn^{II}TPP$ has been demonstrated previously during the functionalization of hydrocarbons by other high-valent manganese porphyrin complexes.[4]

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Registry No. **1** (X = N_3), 79775-62-5; **1** (X = NCO), 81602-67-7; **2** (X = N_3), 90064-42-9; **2** (X = NCO), 90064-43-0; Mn, 7439-96-5.

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Preparation and Aquation Kinetics of (Acetonitrile)pentaaquochromium(III)

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Metal complexes of organic nitriles, of the general type $L_5M{-}NC{-}R^{3+}$, are known for many of the kinetically inert metal ions.[1,2] These complexes show kinetic stability toward