

formation constant of the precursor.

In sum, symmetry barriers to electron transfer from octahedral d systems become operative when the electron arises from a high-energy (e_g) rather than a low-energy (t_{2g}) orbital, whereas, as a result of changes in coordination geometry and in the symmetry character of the donor orbitals, the reverse appears to be the case for f systems.

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Registry No. U(III), 22578-81-0; Co(en) $_3^{3+}$, 14878-41-2; Co(NH $_3$) $_6^{3+}$, 14695-95-5; imidazole(NH $_3$) $_5$ Co $^{3+}$, 38716-02-8; pyrazole(NH $_3$) $_5$ Co $^{3+}$, 59389-55-8; pyridine(NH $_3$) $_5$ Co $^{3+}$, 31011-67-3; dimethylformamide(NH $_3$) $_5$ Co $^{3+}$, 31125-61-8; *N,N*-dimethylnicotinamide(NH $_3$) $_5$ Co $^{3+}$, 31011-70-8; triethylacetato(NH $_3$) $_5$ Co $^{2+}$, 51965-36-7; trimethylacetato(NH $_3$) $_5$ Co $^{2+}$, 33887-25-1; cyclopentanecarboxylato(NH $_3$) $_5$ Co $^{2+}$, 51965-54-9; acetato(NH $_3$) $_5$ Co $^{2+}$, 16632-78-3; formato(NH $_3$) $_5$ Co $^{2+}$, 19173-64-9; lactato(NH $_3$) $_5$ Co $^{2+}$, 34464-03-4.

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Redox Chemistry of the Polyimine Complexes of Manganese(II), -(III), and -(IV) in Acetonitrile

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Electrochemical and spectroscopic studies have been made of the manganese(II), -(III), and -(IV) complexes formed by 2,2'-bipyridine, 1,10-phenanthroline, 2,2',2''-terpyridine, 4,4'-dimethyl-2,2'-bipyridine, 4,4'-diphenyl-2,2'-bipyridine, and 4,7-diphenyl-1,10-phenanthroline in acetonitrile solution. For both classes of complexes (bipyridine and phenanthroline) an irreversible oxidation of Mn(II) to Mn(III) occurs. The product species rapidly decomposes to form a dimeric manganese(III,IV) complex. Ultraviolet, visible, near-infrared, and electron paramagnetic resonance spectroscopies have been used to monitor species that are produced during electrolysis. The tridentate 2,2',2''-terpyridine ligand appears to prevent quantitative conversion of bis(2,2',2''-terpyridine)manganese(II) to a binuclear manganese(III,IV) complex. The tetrakis(1,10-phenanthroline)-di- μ -oxo-dimanganese(IV,IV) perchlorate complex has been prepared, and its reactivity with OH $^-$, Cl $^-$, and catechol has been studied.

Although manganese is an essential cofactor for photosynthetic oxygen evolution (photosystem II), its exact role and environment in the thylakoid membrane is unknown.^{1,2} Several groups believe that the manganese system serves as a "charge collector" in photosystem II. After the accumulation of four equivalents of oxidizing power (via a four-photon sequential process), it rapidly oxidizes two water molecules³⁻⁶



Joliet and co-workers⁷⁻¹⁰ have observed cooperation of photochemically produced intermediates of limited stability.

The proposed role of manganese in the buildup of oxidizing power has been based on the availability of higher oxidation states and variable coordination numbers.¹¹⁻¹³ Recent NMR relaxation experiments indicate that during the cyclic process photooxidation of Mn(II) to Mn(III) occurs, that the resting, dark-adapted system involves a mixed-oxidation-state manganese complex, and that the four-photon photoevent appears to involve four manganese ions.^{14,15}

Other studies indicate that there are two types of manganese binding sites.¹⁶⁻¹⁹ One form is bound to the interior of the

Table I. Oxidation-Reduction Potentials for Tris(ligand)manganese(II) Perchlorate, $MnL_3(ClO_4)_2$, and Tetrakis(ligand)di- μ -oxodimanganese(IV,IV) and -(III,IV) Perchlorate, $Mn_2O_2L_4(ClO_4)_4$ and $Mn_2O_2L_4(ClO_4)_3$, in Acetonitrile, 0.1 M TPAP

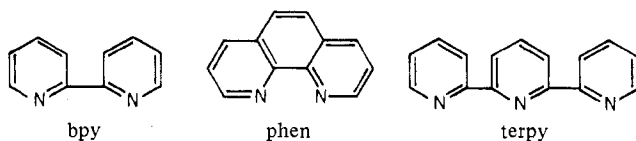
Ligand	$E_{1/2}$, V vs. SCE $Mn(II) \rightleftharpoons Mn(III)$	$E_{1/2}$, V vs. SCE $Mn_2O_2^{4+} \rightleftharpoons Mn_2O_2^{3+}$	$E_{P_{3C}}$, ^a V vs. SCE $Mn_2O_2^{3+} \rightleftharpoons Mn_2O_2^{2+} \rightarrow X$
2,2'-Bipyridine	+1.36	+1.33	+0.38
2,2',2''-Terpyridine	+1.28		
4,4'-Dimethyl-2,2'-bipyridine	+1.22	+1.20	+0.25
4,4'-Diphenyl-2,2'-bipyridine	+1.24	+1.21	+0.28
1,10-Phenanthroline	+1.28	+1.34	+0.47
4,7-Diphenyl-1,10-phenanthroline	+1.22	+1.26	+0.35

^a Scan rate, 0.1 V s⁻¹.

thylakoid membrane where O₂ is generated.²⁰⁻²³ In this site the manganese complex is more stable than Mn(II)-EDTA.^{24,25}

A useful model for the manganese cofactor in photosystem II should selectively oxidize water to molecular oxygen. However, the absence of the thylakoid membrane may preclude selective oxidation with model systems. A variety of nitrogen and nitrogen-oxygen donor complexes of manganese have been suggested as models for manganese in photosystem II, including porphyrin complexes^{12,26-28} and Schiff base complexes.^{29,30} For a variety of divalent manganese complexes, addition of molecular oxygen leads to irreversible metal oxidation at room temperature.²⁷⁻⁴⁰ Reversible O₂ binding by MnTPP, accompanied by electron transfer at low temperatures has been reported.⁴¹⁻⁴³ Recently, Russian investigators have described a tetravalent manganese system which oxidizes water in 6-15 M sulfuric acid.^{44,45}

Polyimines (such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2',2''-terpyridine (terpy)) commonly are



used for spectrophotometric and gravimetric determinations of trace metals⁴⁶ and are known to form stable Mn(II), -(III), and -(IV) complexes.⁴⁷ bpy and phen have been used in combination with thiocyanate ion for the gravimetric determination of Mn(II).^{48,49}

In a recent communication we reported the oxidation-reduction reactions and solution magnetic measurements for di- μ -oxo-dimanganese(III,IV) and -(IV,IV) phen and bpy complexes in acetonitrile.⁵⁰ These species have been suggested as models for the manganese cofactor in photosystem-II.^{29,30,51,52} The present paper presents further characterization of these and related complexes and includes the synthetic procedures as well as the results of electrochemical, EPR, and UV-visible-IR studies of the complexes and their reactions.

Experimental Section

The polyimine ligands, 2,2'-bipyridine (bpy) (G. F. Smith), 1,10-phenanthroline (phen) (Aldrich), terpyridine (terpy) (Sigma Chemical Co.), 4,7-diphenyl-1,10-phenanthroline (Ph₂phen) (Aldrich), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy) (Aldrich), and 4,4'-diphenyl-2,2'-bipyridine (Ph₂bpy) (Aldrich), were used as received. Manganese(II) complexes were formed by adding an aqueous solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith) to a slight excess of ligand in ethanol. Crystals of the yellow tris complex as formed by bpy, Ph₂phen, Me₂bpy, and Ph₂bpy, and of the yellow (terpy)₂ complex were filtered, washed with cold ethanol, and dried in vacuo at 80 °C for 24 h. The white tetrakis(1,10-phenanthroline)manganese(II) complex formed by this procedure was recrystallized from ethanol to form the yellow (phen)₃ complex.^{53,54} Di- μ -oxo-dimanganese(III,IV) and di- μ -oxo-dimanganese(IV,IV) complexes, $Mn_2O_2L_4^{3+}$ and $Mn_2O_2L_4^{4+}$, were originally synthesized by literature methods.⁵⁵⁻⁵⁷ Because exhaustive electrolysis of Mn(II) complexes at +1.50 V led to identical products with those produced by the synthetic methods (see Results), much of the solution data were obtained on electrogenerated species.

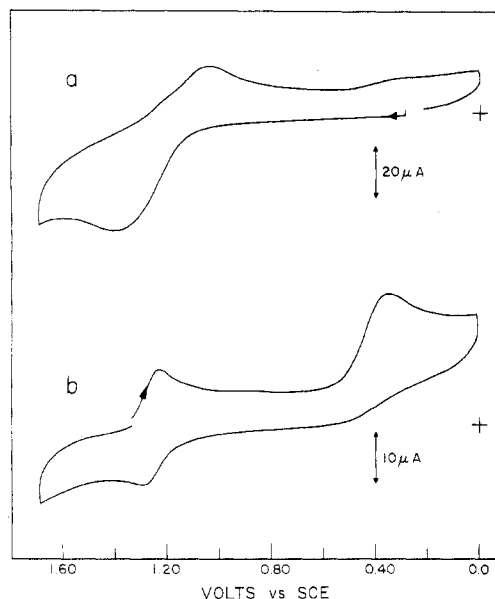


Figure 1. Cyclic voltammetry of (a) 1.00 mM tris(4,7-diphenyl-1,10-phenanthroline)manganese(II) perchlorate in acetonitrile, 0.1 M TPAP, and (b) after electrolysis at +1.50 V; scan rate 0.10 V s⁻¹; Pt working electrode area 0.23 cm².

Acetonitrile ("spectroquality", MCB) was used without further purification. Tetra-*n*-propylammonium perchlorate (TPAP) was recrystallized from absolute ethanol and dried in vacuo at room temperature. Deaeration was accomplished by passing solvent-saturated, high-purity argon through the solution for 10 min before electrochemical analysis and passing argon over the solution during the analysis.

Electrochemical and spectroscopic measurements were performed by use of conventional instrumentation that has been described elsewhere.⁵⁸ All measurements were made at 23 ± 1 °C, and potentials are reported vs. the saturated calomel electrode (SCE).

Results

Electrochemistry. The cyclic voltammogram of tris(4,7-diphenyl-1,10-phenanthroline)manganese(II) perchlorate in acetonitrile, which is shown in Figure 1a, is typical of the manganese(II) complexes that have been studied. The quasireversible oxidation of manganese(II) is followed by a chemical reaction. Half-wave potentials for the Mn(II) complexes are summarized in Table I and have been taken as the median of the cathodic and anodic peak potentials. The latter have been isolated from the redox reactions associated with the species from follow-up chemical reactions by use of rapid scan rates (up to 1 V s⁻¹). For all of the complexes, except bis(2,2',2''-terpyridine)manganese(II) perchlorate, controlled-potential electrolysis at +1.60 V for a period of 2-6 h abstracts 2.0 ± 0.1 electrons per manganese and yields a solution with electrochemical characteristics similar to those previously observed⁵⁰ for tetrakis(1,10-phenanthroline)di- μ -oxo-dimanganese(IV,IV) perchlorate, $Mn_2O_2(phen)_4(ClO_4)_4$. This is illustrated by Figure 1b for the 4,7-diphenyl-1,10-phenanthroline complex. Controlled potential reduction of the

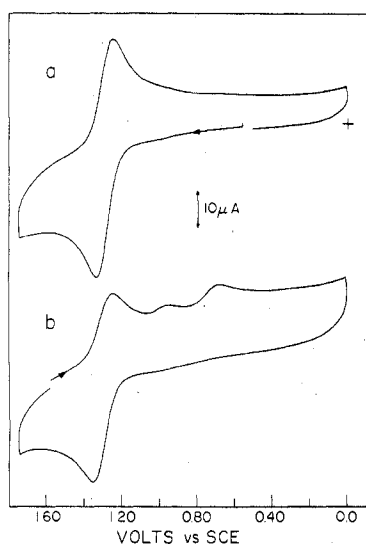


Figure 2. Cyclic voltammetry of (a) 1.00 mM tris(2,2',2''-terpyridine)manganese(II) perchlorate in acetonitrile, 0.1 M TPAP, and (b) after electrolysis at +1.75 V; scan rate 0.20 V s⁻¹; Pt working electrode area 0.23 cm².

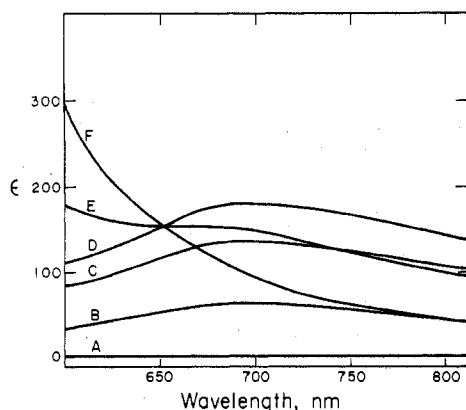


Figure 3. Near-infrared absorption spectra as a function of the extent of electrolysis at +1.60 V vs. SCE of Mn(phen)₃(ClO₄)₂ in acetonitrile, 0.1 M TPAP: A, before electrolysis; B-E, after solution electrolyzed 20, 40, 60, and 80%, respectively; F, after complete electrolysis.

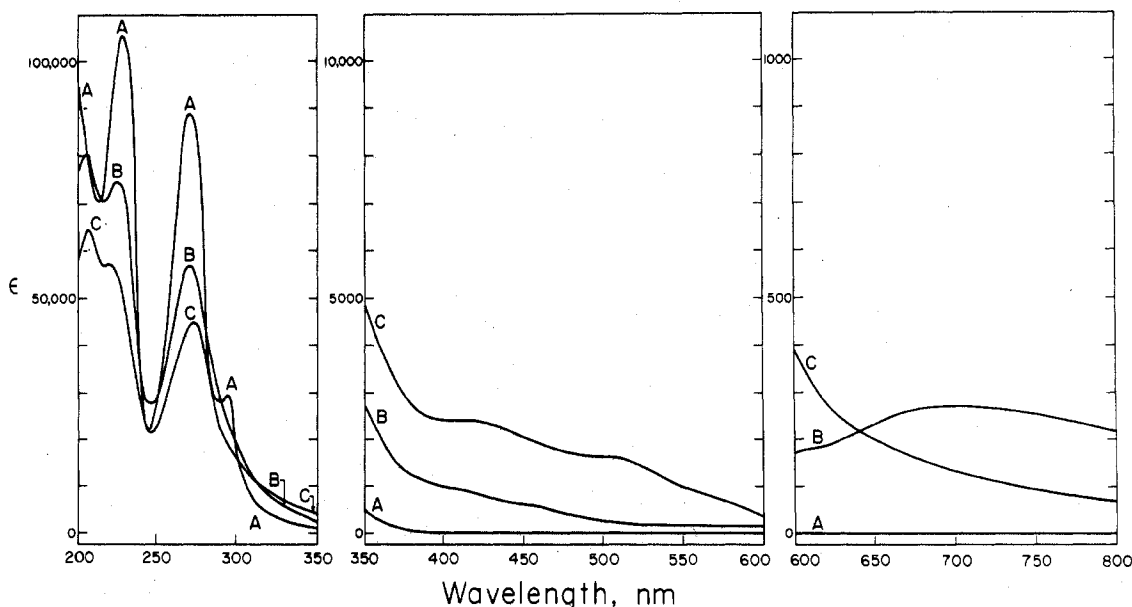


Figure 4. Ultraviolet, visible, and near-infrared absorption spectra of Mn(phen)₃(ClO₄)₂ in acetonitrile, 0.1 M TPAP: A, before electrolysis; B, after exhaustive electrolysis at +1.50 V followed by reductive electrolysis at +0.50 V; C, after exhaustive electrolysis at +1.50 V. Molar absorptivity, ε, relative to manganese content.

oxidized complex at +0.80 V adds 0.50 electron per manganese. Half-wave potentials for the reduction of these di- μ -oxo-dimanganese(IV,IV) complexes to di- μ -oxo-dimanganese(III,IV) complexes and the cathodic peak potentials for the reduction of di- μ -oxo-dimanganese(III,IV) complexes are summarized in Table I.

The cyclic voltammetry for the isolated Mn₂O₂L₄(ClO₄)₃ complexes (where L is a bpy- or phen-type ligand) differs slightly from that for the comparable complexes that have been formed in situ by electrosynthesis. The potentials and currents for the Mn₂(III,IV) \rightleftharpoons Mn₂(IV,IV) + e⁻ process are identical, and the peak currents for reduction of the isolated complexes are approximately equal to those for the Mn₂(III,IV) \rightleftharpoons Mn₂(IV,IV) + e⁻ process (in contrast to the data of Figure 1b). In addition, some component of a reverse wave is observed for the reduction of the isolated complexes. For electro-generated complexes the peak currents for the reduction process are much larger than for the Mn₂(III,IV) \rightleftharpoons Mn₂(IV,IV) + e⁻ process. Controlled-potential reduction of the binuclear III and IV complexes at -0.50 V results in the addition of three electrons per dimeric complex.

The cyclic voltammogram of Mn^{II}(terpy)₂(ClO₄)₂ is illustrated by Figure 2a. Electrolysis at +1.60 V yields a nonstoichiometric value (greater than 2) for the number of electrons transferred per manganese. The measured value increases as the time for the electrolysis is extended. In contrast to the Mn(II)-bpy and -phen complexes, the oxidation of the Mn(II)-terpy complex does not appear to occur by a single straightforward rearrangement during electrolysis (see Figure 2b).

Spectroscopy. Controlled-potential electrolysis of the manganese-polyimine complexes changes their UV-visible, near-IR, and EPR spectra. Figure 3 illustrates the near-IR spectra for the manganese(II) phenanthroline complex as a function of the extent of electrolysis. The presence of a stable intermediate from the electrolysis, with an absorption maxima at 690 nm, is apparent. The UV-visible-near-IR spectra for Mn(phen)₃(ClO₄)₂ before electrolysis, after electrolysis at +1.60 V, and after rereduction at +0.80 V, are illustrated by Figure 4. Spectra B and C of Figure 4 are superimposable with those observed for Mn₂O₂(phen)₄(ClO₄)₄ and Mn₂O₂(phen)₄(ClO₄)₃, respectively, which have been prepared by chemical synthesis. Figure 5 demonstrates similar changes

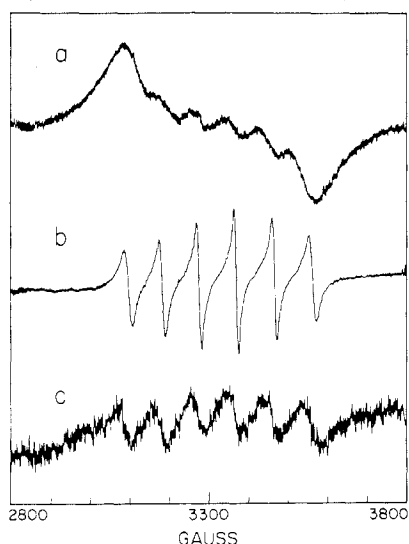


Figure 5. X-band electron paramagnetic resonance spectra of 0.73 mM tris(4,4'-diphenyl-2,2'-bipyridyl)manganese(II) perchlorate in acetonitrile, 0.1 M TPAP, as a function of the extent of electrolysis: (a) before electrolysis; (b) after complete electrolysis at +1.60 V vs. SCE; (c) as (b) followed by reductive electrolysis at +0.50 V.

Table II. EPR Data for Various Manganese Species in Acetonitrile, 0.1 M TPAP

L	$\text{MnL}_3(\text{ClO}_4)_2$		$\text{Mn}_2\text{O}_2\text{L}_4(\text{ClO}_4)_4$		$\text{Mn}_2\text{O}_2\text{L}_4(\text{ClO}_4)_3$	
	g value	A, G	g value	A, G	g value	A, G
bpy	2.01	83	2.03	83	2.01	79
terpy	2.03	<i>a</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Me ₂ bpy	2.01	85	2.01	77	2.01	78
Ph ₂ bpy	2.01	<i>a</i>	2.01	79	2.01	77
phen	2.01	86	2.01		2.01	78
Ph ₂ phen	2.01	<i>a</i>	2.01	78		

^a Unresolved. ^b Structure of species uncertain (see text).

in the EPR for $\text{Mn}(\text{Ph}_2\text{bpy})_3(\text{ClO}_4)_2$ during electrolysis. Spectra b and c of Figure 5 are virtually identical with those obtained from synthetic samples of the di- μ -oxo-dimanganese(IV,IV) and di- μ -oxo-dimanganese(III,IV) complexes. EPR data for the three different manganese species with various ligands are summarized in Table II.

Reactions. The reactions of the tetrakis(1,10-phenanthroline)di- μ -oxo-dimanganese(III,IV) and -(IV,IV) complexes have been monitored by potentiometry and cyclic voltammetry. $\text{Mn}_2\text{O}_2(\text{phen})_4(\text{ClO}_4)_4$ is reduced by a variety of substrates, including hydroxide ion, chloride ion, and catechols. The red $\text{Mn}_2\text{O}_2(\text{phen})_4^{4+}$ redox center is reduced to the green $\text{Mn}_2\text{O}_2(\text{phen})_4^{3+}$ species by 1 equiv of chloride ion or hydroxide ion on the basis of the changes in the rest potentials and the cyclic voltammogram of the solution after substrate additions. Further addition of either chloride ion or hydroxide ion beyond a one-to-one stoichiometry causes decomposition of the di- μ -oxo bridge. This conclusion is based on the disappearance of the $\text{Mn}_2\text{O}_2(\text{phen})_4^{3+/4+}$ redox couple from the cyclic voltammogram and an increase in the solution magnetic moment.⁵⁹ Reaction of $\text{Mn}_2\text{O}_2(\text{phen})_4^{4+}$ with catechols results in the formation of quinones and a Mn(II) species; as observed by the change in color of the solution to yellow. These reactions do not appear to generate "free" molecular oxygen from water on the basis of measurements with an oxygen-membrane electrode.

Discussion and Conclusions

Previous electrochemical studies of divalent manganese polyimine complexes have been limited to reduction processes⁶⁰⁻⁶⁶ with one exception.⁶⁷ Although similar reduction

behavior has been observed for these complexes,⁶⁸ our interest has been directed to the oxidation-reduction chemistry of higher valent manganese species.

The oxidation of $\text{Mn}(\text{terpy})_2(\text{ClO}_4)_2$ in acetonitrile has been studied by dc and ac linear-sweep voltammetry at a rotating platinum electrode⁶⁷ and interpreted as a reversible one-electron process on the basis of peak shape. Although the $E_{1/2}$ value that we have determined for this process (Table I) is in accord with their results, we do not observe the electrochemical reversibility for the oxidation of divalent manganese bpy and phen complexes which they report for the $\text{Mn}(\text{terpy})_2^{2+}$ complex. Furthermore, the one-electron oxidation of $\text{MnL}_3(\text{ClO}_4)_2$ is followed by a chemical reaction which forms the di- μ -oxo-dimanganese(III,IV) complex. A reasonable reaction mechanism for the formation of the dimeric species involves disproportionation of Mn(III) to Mn(II) and Mn(IV). The Mn(IV) that is formed probably reacts with another Mn(III) to form the di- μ -oxo-dimanganese(III,IV) species. The formation of the dimeric structure at the expense of the monomeric species undoubtedly is favored because of the charge neutralization by the bridging oxo groups. The manganese(II) terpyridyl complex appears to be more resistant to dimerization, perhaps due to steric considerations. However, the results that are presented in Figure 2 indicate that follow-up chemical reactions take place to some extent.

The oxidation of the Mn(II) complexes and the subsequent dimerization of the product species require release of four protons to yield the di- μ -oxo-dimanganese(III,IV) complexes

$$2\text{MnL}_3^{2+} + 2\text{H}_2\text{O} = \text{Mn}_2\text{O}_2\text{L}_4^{3+} + 4\text{H}^+ + 3\text{e}^- + 2\text{L} \quad (2)$$

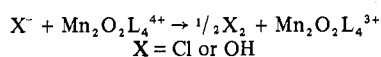
In acetonitrile solution the probable fate of the generated protons is protonation of the free ligands that are released in the oxidation reaction. Reduction of $\text{Mn}_2\text{O}_2\text{L}_4^{3+}$ back to MnL_3^{2+} (Figure 1b) is possible due to the availability of protons to form water from the oxo bridges and the availability of excess ligand to displace oxo ligands. In their absence the reduction to divalent manganese apparently is not possible.⁵⁰ This accounts for the slight dissimilarity between the electrochemistry of chemically generated and electrogenerated solutions of the $\text{Mn}_2\text{O}_2\text{L}_4^{3+}$ species.

For the oxidation of the Mn(II) complexes to Mn(III) the bipyridyl-type complexes have more positive potentials than the corresponding phenanthroline complexes. This trend is reversed for the redox reactions that involve the di- μ -oxo-dimanganese groups. The shift in potentials does not follow a linear free energy relationship. Hence, the shifts in half-wave potential probably are associated with steric effects that stabilize one oxidation state over another.

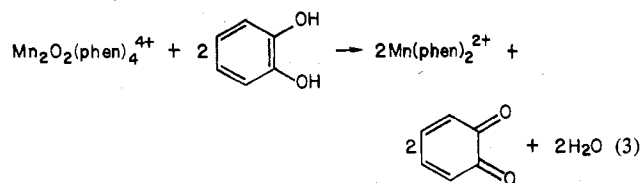
The EPR spectra are distinctly different for the three manganese species. The narrow line widths for the Mn(IV) complexes relative to those for Mn(II) systems probably are due to the less efficient electron spin relaxation for the Mn(IV) ion. The EPR spectra for the $\text{Mn}_2\text{O}_2\text{L}_4^{4+}$ complexes confirm that the two Mn(IV) ions are equivalent and that there is not significant electronic pairing between them. In the case of the $\text{Mn}_2\text{O}_2\text{L}_4^{3+}$ complexes, the EPR spectra are broadened due to superexchange with the oxo ligands and electron exchange between the two metal centers.⁵⁹

While complete assignments of the optical spectra for the three classes of complexes are not possible because of the lack of an octahedral ligand field, their spectra differ significantly in the visible-near-IR region. The near-IR band for the $\text{Mn}_2\text{O}_2\text{L}_4^{3+}$ complexes appears to be due to a metal-metal charge-transfer band, based on similar bands for mixed-oxidation-state dimers.⁶⁹ Similar spectra have been obtained by Boucher and Coe for the μ -hydroxo- μ -oxo-dimanganese(III,IV) Schiff base complexes.^{29,30}

The reactions of $\text{Mn}_2\text{O}_2(\text{phen})_4(\text{ClO}_4)_4$ with Cl^- or OH^- are consistent with a strong one-electron oxidizing agent.

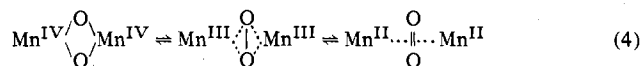


In contrast, the reaction of the $\text{Mn}_2\text{O}_2\text{L}_4^{4+}$ complexes with catechols involves a four-electron process



Catechol serves as a useful model substrate for water oxidation because it can be oxidized in a two-electron step to form quinone with the release of two protons.

In conclusion, these di- μ -oxo-dimanganese(IV,IV) complexes appear to lie at a potential energy minimum relative to monomeric species in terms of the stabilization of the Mn(IV) oxidation state. Although the di- μ -oxo-bridged structure is a conceptually and mechanistically attractive structure to achieve the net oxidation of water to molecular oxygen, the experimental evidence indicates that the process is not kinetically favored under our solution conditions. Kinetic and isotope studies by Shafirovich and co-workers^{44,45} indicate that a dimeric Mn(IV) group does produce dioxygen in 6–15 M sulfuric acid at 60–100 °C. Such solution conditions differ from those believed to prevail in plant photosynthesis. The relatively mild conditions of the present study may preclude significant oxidation of water. Additional investigations are in progress to bring about a shift to the right of the postulated tautomerism for the $\text{Mn}_2\text{O}_2\text{L}_4^{4+}$ complexes.



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