Electrochemical and Spectroscopic Studies of Manganese(II), -(III), and -(IV) Gluconate Complexes. 2. Reactivity and Equilibria with Molecular Oxygen and Hydrogen Peroxide

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Abstract: Sodium gluconate (oxidation product of D-glucose) in alkaline media solubilizes and stabilizes the +2, +3, and +4 oxidation states of manganese. The redox chemistry of these complexes and of their reactions with molecular oxygen and hydrogen peroxide has been studied by polarography, spectrophotometry, an oxygen-membrane electrode, and stopped-flow techniques. Molecular oxygen oxidizes the binuclear manganese(II) gluconate complex (first order in each) to the manganese(III) complex plus peroxide ion. It also oxidizes the binuclear manganese(III) complex to the manganese(IV) complex plus peroxide ion. The latter reaction is reversed upon addition of acid. Hydrogen peroxide oxidizes the manganese(II) complex to the manganese(III) complex by a process which is first order in H_2O_2 and in Mn(II). Rate constants have been determined for the various reactions, and reaction mechanisms are proposed.

Manganese is involved catalytically in at least two biological oxidation–reduction processes: the dismutation of superoxide ion by the mitochondrial version of the superoxide dismutase (SOD) enzyme[1] and the oxidation of water in the oxygen-evolution process of photosystem II in green-plant photosynthesis.[2] Although manganese is known to be essential, there is no information either about the structure of the active site or the oxidation states involved in the oxidation–reduction reactions. In the case of SOD, there is still controversy as to whether the enzyme contains one or two manganese atoms per enzyme molecule.[3,4] A recent report[5] indicates that the SOD catalytic cycle can be represented by

$$E + O_2^- \rightarrow E^- + O_2$$

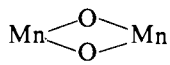
$$E^- + O_2^- \xrightarrow{H^+} E + H_2O_2$$

$$E^- + O_2^- \rightarrow E^{2-} + O_2$$

$$E^{2-} + O_2^- \xrightarrow{H^+} E^- + H_2O_2$$

Depending upon the number of manganese atoms in the active site, either two or three oxidation states are involved in the mechanism of the enzymic reaction.

The situation is analogous for photosystem II, where there is neither agreement as to the electron transfer mechanism nor to the manganese oxidation states and number of manganese atoms in the active group.[6] Joliot and co-workers[7] have proposed a two-quantum mechanism in which the primary electron donor and oxidized chlorophyll oscillate between the oxidation states. On the other hand, Kok and co-workers have proposed a four-step mechanism in which the electron donor group undergoes a four-electron oxidation before the release of an oxygen molecule.[8] Both mechanisms infer the presence of a dimeric or tetrameric unit at the active site. Recent studies of complexes of manganese(IV)[9,10] indicate that it has the tendency to dimerize to yield a μ-dioxo-bridged group



This behavior also has been observed for a binuclear mixed oxidation state complex of manganese(III) and −(IV).[11]

The presence of three equivalent manganese atoms per water-oxidizing unit has been proposed for photosystem II.[12] Because the oxidation of water to oxygen is a four-electron process that requires two water molecules, the electron-transfer mechanism for a three-manganese grouping is an intriguing and challenging question.

Although the reaction chemistry of the higher oxidation states of manganese is known to be complicated, its relevance to electrochemistry and probably to biological systems has prompted numerous investigations. Studies, both kinetic and synthetic, of the complexes of manganese(III) with oxalate and malonate confirm that it has a particularly strong affinity for oxygen-containing ligands[13-17] and that such manganese–oxygen bonds apparently promote electron transfer to the manganese atom.

In our search for ligands to stabilize the higher oxidation states of manganese in aqueous solution, we found that sodium gluconate ($NaC_6H_{10}O_7$), the salt of the fermentation product of D-glucose, complexes and solubilizes the +2, +3, and +4 oxidation states of manganese in strongly alkaline media.[18,19] These prior studies indicate that the gluconate complexes of manganese ions form dimeric groups. If the +3 and +4 oxidation states of manganese are involved in the mechanism for the water-oxidation reaction in photosynthesis and for the dismutation reaction of the superoxide dismutase enzyme, then gluconate may be representative of the kind of environment that is needed to stabilize such species. Likewise, the reactions of hydrogen peroxide and oxygen with the three stabilized oxidation states represent interesting chemistry that has direct relevance to the understanding of the biological mechanisms.

The present paper summarizes the results of a study of the reaction stoichiometry and kinetics of the gluconate complexes of manganese(II), manganese(III), and manganese(IV) with hydrogen peroxide and molecular oxygen.

Experimental Section

Polarography was performed by use of a three-electrode potentiostat that was constructed with solid-state operational amplifiers[20] and by use of a Sargent Polarograph (Model XV). When a three-electrode system was used, the electrochemical cell consisted of a 100-ml electrolytic beaker and a Leeds and Northrup polyethylene electrochemical cell top. The cell top supported the auxiliary compartment (a Pyrex tube with a fine porosity frit on the end), the Luggin capillary held the reference electrode, a bubbler deaerated the solutions with argon, and a short piece of glass tube flowed argon above the solution surface while the polarograms were recorded. When a two-electrode system was used, a conventional polarographic cell with a built-in reference electrode was employed.

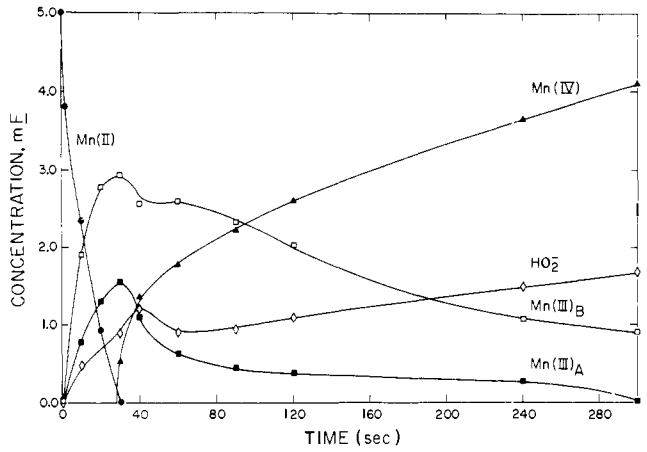


Figure 1. Concentrations of product species as a function of time for the reaction of 5 mM manganese(II) gluconate in 0.1 M $NaGH_4$ and 0.3 M NaOH with O_2 at 1 atm. A and B represent the binuclear bis- and monomeric trisgluconate complexes of manganese(III), respectively.

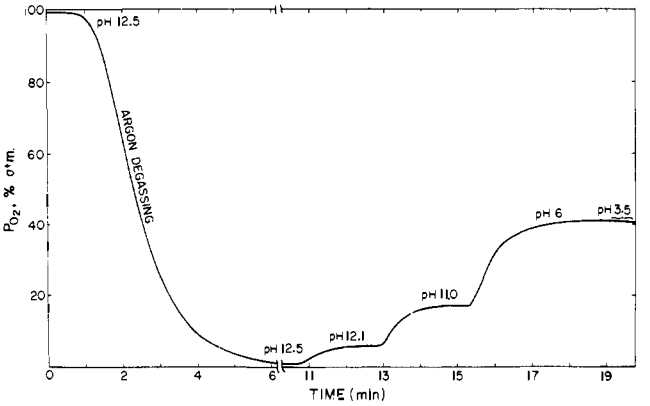


Figure 2. Partial pressure of O_2 for a solution that originally contained 5 mM Mn(II), 0.1 M $NaGH_4$, and 0.3 M NaOH and was oxygenated for 20 min with O_2 at 1 atm prior to purging with argon. pH lowered by addition of concentrated $HClO_4$ to a sealed cell. Partial pressures of O_2 measured with a Beckman membrane electrode system (Model 1008).

The spectrophotometric measurements were performed with a Perkin-Elmer Model 450 spectrophotometer equipped with quartz cells. The solutions in the reference cell contained concentrations of sodium hydroxide and sodium gluconate equimolar to those in the sample cell.

The magnetic susceptibilities were determined by the NMR method developed by Evans[21] and modified by Rettig.[22] The inner tube was made from 3-mm o.d. Pyrex tubing sealed with a nearly saturated solution of TMS (sodium 2,2-dimethyl-1,2-silipentane-5-sulfonate) inside. The outer tube was a standard NMR tube and was filled with a sample in a nitrogen atmosphere glove box. The shift between the two TMS peaks was measured with a Varian A-60 D NMR spectrometer at ambient temperature; the probe temperature was determined with an ethylene glycol standard. The magnetic susceptibilities were calculated by the method of Rettig with values for diamagnetic corrections from Figgis and Lewis.[23]

The measurements of the concentration of molecular oxygen in the solutions were accomplished with a Beckman Fieldlab Oxygen Analyzer (Model 1008) and Oxygen Sensor (Model 39553). For the study of the kinetics of the reaction between manganese(III) gluconate and oxygen, a solution that contained 0.3 M sodium hydroxide and 0.1 M sodium gluconate was saturated either with air or with pure oxygen and a layer of cyclohexane was placed on its surface. A small volume of a concentrated solution of manganese(III) gluconate then was injected with a syringe and the concentration of oxygen in the solution was followed with the Oxygen Sensor.

For the reaction between the manganese(II) gluconate complex and hydrogen peroxide, the kinetics were followed polarographically with the electrode potential set at −0.4 V vs. SCE. The observed current represented the concentration of manganese(II) in the solution after the peroxide was injected.

The reaction of the manganese(II) gluconate complex with oxygen was studied by use of a Durrum stopped-flow instrument (Model D-110) that was equipped with a signal averager (Fabritek Model 1074, Nicolet Instruments). The system was interfaced with a Hewlett-Packard Model HP 3000 computer.

Reagents. Manganese(II) gluconate was used for most of the experiments and was obtained from Chas. Pfizer and Co.; the stock solutions were standardized by titration with EDTA.[24] Solutions of gluconate ion were prepared from D-glucono-δ-lactone (Chas. Pfizer and Co.), which was recrystallized from ethylene glycol monomethyl ether.[25] Manganese(III) acetate was synthesized by the procedure of Brauer;[26] in some experiments it was used as the source of manganese(III). All the other chemicals were Reagent Grade.

Results

Electrochemistry and Spectroscopy. A previous paper[18] has discussed the oxidation-reduction chemistry of manganese(II) in the presece of sodium gluconate ($NaGH_4$) and base. The manganese(II) gluconate complex, $[Mn^{II}_2(GH_3)_4(H_2O)_2]^{4-}$, can be oxidized to the corresponding complexes of manganese(III) and manganese(IV), either by controlled potential electrolysis or by means of oxidizing agents such as potassium ferricyanide, oxygen, or hydrogen peroxide (GH_3^{2-} represents the dianion of gluconic acid which results from the removal of the carboxylate proton and one of the secondary alcoholic protons). Figure 1 illustrates the extent of the reaction between the Mn(II) complex and molecular oxygen at 1 atm, as well as the concentrations of the product species. The data for this figure have been obtained by quenching the reaction with argon after different times and then recording a polarogram of the solution. The data indicate that the oxidation of manganese(II) to manganese(III) is faster than the oxidation of manganese(III) to manganese(IV) and that hydrogen peroxide also is a product of the redox reactions. The presence of hydrogen peroxide is indicated by its oxidation wave at a half-wave potential of −0.18 V vs. SCE and its reduction wave at −1.2 V. After 300 s the concentration of hydrogen peroxide in the system is about half the concentration of the manganese(IV) gluconate complex.

Figure 1 also indicates the presence of two forms of the manganese(III) gluconate complex. The previous study[18] has established that these are in slow equilibrium with each other. One of these species corresponds to a bis gluconate complex that probably is binuclear in manganese (Mn^{III}_A) and formed preferentially at low concentrations of sodium gluconate. The other species (Mn^{III}_B) corresponds to a monomeric tris gluconate complex which is predominant at high concentrations of sodium gluconate. The apparent equilibrium constant for the conversion of the bis complex to the tris complex is 0.13[18] in a solution 0.3 M in NaOH and 0.1 M in sodium gluconate.

When a solution of the manganese(IV) gluconate complex is produced by oxidation of the manganese(II) complex with molecular oxygen and then is acidified with deaerated perchloric acid, evolution of oxygen is detected. Figure 2 illustrates the described process as a function of pH. When the solution of manganese(IV) is prepared by oxidizing manganese(II) gluconate with 2 equiv of potassium ferricyanide and then acidified, oxygen evolution is not observed and a bluish-gray precipitate is formed, presumably manganese(III) ferricyanide. The same negative result is obtained when the manganese(IV) species is prepared by controlled potential electrolysis. Also, a solution of hydrogen peroxide with gluconate ion and base, but without manganese(IV), does not evolve oxygen upon acidification. Consequently, the presence of peroxide and manganese(IV) is essential for this reaction to take place.

A solution of the manganese(IV) gluconate complex in the presence of peroxide is "cherry red" in color (as it is in the absence of peroxide). When it is titrated with deaerated perchloric acid, the solution changes color to dark brown at pH

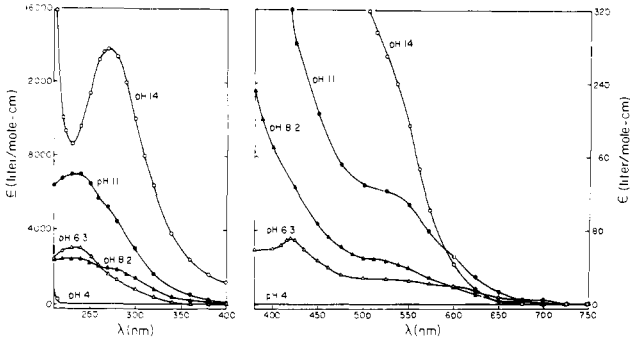


Figure 3. Spectra for solutions of 5 mM manganese(II) gluconate in 0.1 M $NaGH_4$ and O_2 at 1 atm as a function of pH.

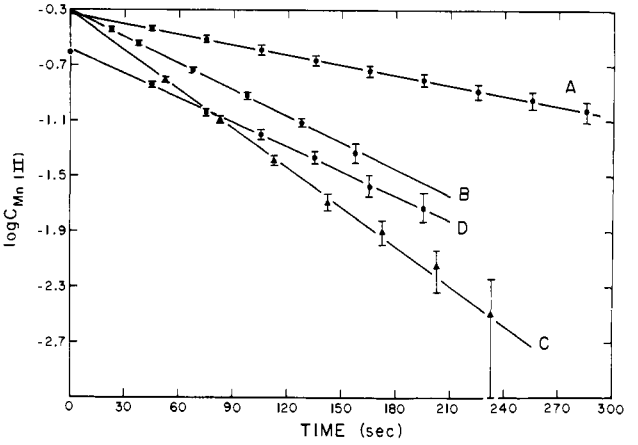


Figure 4. Logarithm of the concentration of manganese(II) gluconate (monitored by polarography) as a function of time. A, B, and C correspond to solutions with an initial Mn(II) concentration of 1 mM and initial H_2O_2 concentrations of 5, 10, and 20 mM, respectively. Curve D corresponds to an initial manganese(II) gluconate concentration of 0.5 mM and an initial H_2O_2 concentration of 10 mM. All solutions contained 0.1 M $NaGH_4$ and 0.3 M NaOH.

10, which indicates the reduction of manganese(IV) to manganese(III). If the solution is acidified further, a second color change, from brown to colorless, is observed at pH 2. A solution of manganese(III) prepared from manganic acetate in the presence of sodium gluconate and base does not evolve molecular oxygen upon acidification but exhibits the same color change from dark brown to colorless at pH 2.

These observations are consistent with the spectrophotometric results presented in Figure 3, which indicate that at pH 4 or lower the manganese(III) complex is not formed by bubbling with molecular oxygen. At pH 6.3 the oxidation of manganese(II) to manganese(III) becomes evident, with the binuclear manganese(III)$_A$ complex the dominant form. At pH 8.2 some of the manganese(IV) complex is produced as well as some of the monomeric manganese(III)$_B$ gluconate complex. As the pH is increased even further the amount of manganese(IV) produced increases; at pH 14 the conversion is practically quantitative.

Because the manganese(II) complex also is oxidized by hydrogen peroxide, the stoichiometry of this reaction has been established by allowing the reaction to go for 15 min before recording a polarogram to determine the amounts of manganese(II) and manganese(III) in the solutions. Table I summarizes the results of this study for solutions that initially contained 0.1 M sodium gluconate, 0.3 M sodium hydroxide, 5 mM manganese(II), and different initial concentrations of hydrogen peroxide. The molecular stoichiometry for the reaction is one Mn(II) oxidized per H_2O_2, which is intriguing because hydrogen peroxide is a two-electron oxidizing agent and should give 2:1 stoichiometry. When the concentration of sodium gluconate is varied and the same experiment is repeated with solutions 5 mM in manganese(II) gluconate complex and 2.5 mM in hydrogen peroxide, the analytical results in Table II indicate that the number of manganese atoms oxidized per molecule of peroxide decreases markedly as the concentration of gluconate is increased. This implies the presence of a competitive reaction between hydrogen peroxide and the ligand. Magnetic susceptibility measurements for different ratios of manganese(II) and hydrogen peroxide also confirm that the stoichiometry is about 1:1 in the presence of 0.1 M sodium gluconate.

A possible complexation reaction between manganese(III) gluconate and peroxide also has been considered. When solutions with different concentration ratios of these species are prepared and analyzed by polarography, the half-wave potentials are constant (and the same as for peroxide ion and manganese(III) gluconate in the absence of each other) and the diffusion currents are the same as those for peroxide ion and for the manganese(III) gluconate complex. These results indicate that peroxide ion does not complex or interact with the manganese(III) gluconate complexes.

Reaction Kinetics. The kinetics of the reaction between the manganese(II) gluconate complex and hydrogen peroxide in 0.3 M sodium hydroxide and 0.1 M sodium gluconate have been studied by monitoring the concentration of manganese(II) in the solution as a function of time. Figure 4 illustrates the results of this experiment. Curves A, B, and C correspond to an initial concentration of 1.0 mM manganese(II) gluconate and initial concentrations of hydrogen peroxide of 5, 10, and 20 mM, respectively. In each case linear semilogarithmic dependence is observed which indicates that the reaction is first order in the manganese(II) complex. The pseudo-first-order rate constants for the three peroxide concentrations are 2.5×10^{-3}, 6.7×10^{-3}, and 13×10^{-3} s^{-1}, respectively. Hence, the reaction also is first order in hydrogen peroxide. Curve D corresponds to a solution with initial concentrations of 0.5 mM manganese(II) complex and 10 mM hydrogen peroxide; the pseudo-first-order rate constant for the reaction is 5.9×10^{-3} s^{-1} at 25 °C. When the rate constants for the four curves are converted to second-order rate constants by dividing by the peroxide concentration, the average value of the rate constant is 6.0×10^{-1} l. mol^{-1} s^{-1}.

Table I. Concentrations of Manganese(II) and Manganese(III) Gluconate Complexes after Reaction with Hydrogen Peroxide for 15 min in the Presence of 0.1 M $NaGH_4$ and 0.3 M NaOH

	Concn after reaction	
Initial soln	Mn(II), mM	Mn(III), mM
5 mM Mn(II), 1 mM H_2O_2	4.21	0.79
5 mM Mn(II), 2.5 mM H_2O_2	2.35	2.75
5 mM Mn(II), 5 mM H_2O_2	0.98	4.02
5 mM Mn(II), 10 mM H_2O_2	0.00	5.00

Table II. Stoichiometries for the Redox Reaction between 5 mM Manganese(II) Gluconate and 2.5 mM Hydrogen Peroxide at Different Concentrations of Sodium Gluconate in the Presence of 0.3 M NaOH

Gluconate ion concn, M	Molecular stoichiometry, H_2O_2:Mn(II)
0.05	1.0:1.46
0.10	1.0:1.06
0.50	1.0:0.89
1.00	1.0:0.59

Table III. Initial Rates and Rate Constants for the Reaction between the Manganese(III) Gluconate Complex and Molecular Oxygen in the Presence of 0.1 M $NaGH_4$ and 0.3 M NaOH

Initial Mn(III) concn, mM		Initial rate with air,	Binuclear rate constant,	Initial rate with oxygen	Binuclear rate constant,
Total	Binuclear complex	mM/min	l. mol^{-1} s^{-1}	(1 atm), mM/min	l. mol^{-1} s^{-1}
0.5	0.09	0.075	5.8×10^4	0.33	5.4×10^4
1.0	0.23	0.145	4.2×10^4	0.60	3.7×10^4
2.0	0.57	0.30	3.5×10^4	1.25	3.0×10^4
5.0	1.75	0.90	3.4×10^4	3.0	2.4×10^4
			Av 4.2×10^4		Av 3.6×10^4

In the case of the reaction between the manganese(II) gluconate complex and molecular oxygen, the absorbance of the solution at 450 nm has been monitored as a function of time by use of the stopped-flow technique. The reaction is rapid and, as illustrated by Figure 5, corresponds to a process that is first order in molecular oxygen and first order in the dimer of the manganese(II) gluconate complex. The second-order rate constant for this reaction is 2.8×10^4 l. mol^{-1} s^{-1} at 25 °C. Spectroscopic analysis of the reaction media establishes that the binuclear form of the manganese(III) gluconate complex ($Mn^{III}{}_A$, which absorbs at 450 nm[18]) is the initial product of the redox reaction, which equilibrates to the second form of the manganese(III) gluconate complex ($Mn^{III}{}_B$) in a much slower process.

The two complexes of manganese(III) exhibit different reactivity in the presence of molecular oxygen. The monomeric tris gluconate complex ($Mn^{III}{}_B$) does not appear to react, whereas the binuclear bis gluconate complex ($Mn^{III}{}_A$) is oxidized at moderate rates to the manganese(IV) gluconate complex. However, because the potentials for the reduction of manganese(IV) and the oxidation of peroxide to oxygen are so close to each other, an equilibrium state is reached and the reaction does not go to completion. Therefore, the initial rate method has been applied by use of an oxygen-membrane electrode to monitor the concentration of oxygen in the solutions. Reference to Table III indicates that the ratio of the initial rates with air and with pure oxygen is about 1:5 and that the initial rate of the reaction doubles when the concentration of manganese is made twice as large. Consequently, this reaction is concluded to be first order in manganese(III) complex and first order in molecular oxygen. If the binuclear form of the Mn(III) complex is concluded to be the reactive component and its initial concentration is determined from the dimer-monomer equilibrium constant (0.13),[18] then the average value for the second-order rate constant (on the basis of data in Table III and the fact that the molecular oxygen concentration in 0.1 M $NaGH_4$ and 0.3 M NaOH is 1.2 mM at 1 atm) is 3.9×10^4 l. mol^{-1} s^{-1}.

Attempts have been made to study the kinetics of the oxygen evolution reaction upon acidification of a solution of manganese(IV) gluconate and peroxide. Unfortunately, the highly exothermic neutralization reaction precludes quantitative isothermal data and causes extensive formation of gas bubbles in the stopped flow cell. In addition, a photochemical decomposition reaction appears to occur when the manganese(IV) gluconate complex is in the presence of hydrogen peroxide.

Discussion and Conclusions

From the results described in the previous section the manganese(II) gluconate complex in basic media is oxidized by molecular oxygen in a fast reaction

$$Mn^{II}{}_2(GH_3)_4(H_2O)_2{}^{4-} + O_2 \xrightarrow[k_1 = 2.8 \times 10^4 \text{ l. mol}^{-1} \text{ s}^{-1}]{} Mn^{III}{}_2(GH_3)_4(OH)_2{}^{4-} + H_2O_2 \quad (1)$$

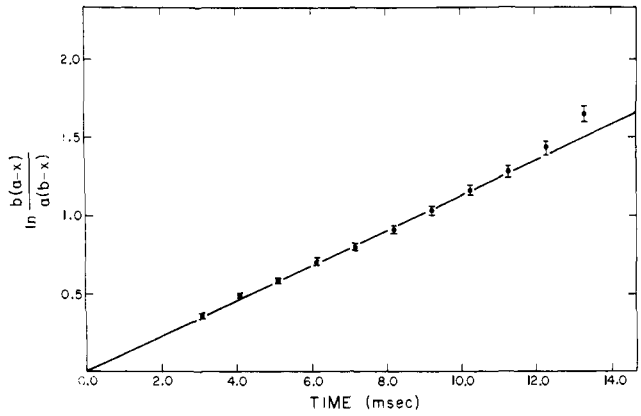


Figure 5. Plot of the logarithmic concentration function for a second-order reaction as a function of time. The solution was 0.3 M in NaOH and 0.1 M in $NaGH_4$, with an initial O_2 concentration of 0.5 mM (a) and an initial $Mn(II)_2$ dimer concentration of 0.25 mM (b).

The kinetic results are consistent with the presence of a binuclear form of the manganese(II) complex. Furthermore, this proposed structure is in accord with the stoichiometric formula determined in the prior electrochemical, spectroscopic, and magnetic study of these complexes.[18] The presence of peroxide as a product also is indicative of an interaction between one oxygen molecule and a unit containing two manganese atoms to yield an overall two-electron transfer. The experiments to study the kinetics of this reaction with the stopped-flow technique clearly establish that the first detectable product of the oxidation process is the binuclear bisgluconatomanganese(III) complex, which then slowly equilibrates with the monomeric trisgluconatomanganese(III) complex. In the presence of excess oxygen the yield of hydrogen peroxide from reaction with the manganese(II) complex is stoichiometric and in accord with eq 1.

The reactivity of the manganese(II) gluconate complex with molecular oxygen appears to follow a mechanism that is analogous to that for cobalt(II), iron(II), titanium(III), and vanadium(IV) complexes.[27-29] For each of these complexes reaction with oxygen yields a binuclear species after the initial formation of an adduct between oxygen and the mononuclear complex. In the case of manganese(II) gluconate the reactant already is binuclear, but the initial formation of an oxygen adduct prior to the electron-transfer reaction appears reasonable. The final product is a binuclear complex of manganese(III) plus peroxide ion.

When hydrogen peroxide is used as the oxidizing agent, the reaction is slower than with oxygen; the kinetic results indicate that the redox process can be represented by

$$Mn^{II}{}_2(GH_3)_4(H_2O)_2{}^{4-} + HO_2{}^- \xrightarrow[k_2 = 6.0 \times 10^{-1} \text{ l. mol}^{-1} \text{ s}^{-1}]{} Mn^{III}{}_2(GH_3)_4(OH)_2{}^{4-} + OH^- + H_2O \quad (2)$$

However, the overall stoichiometry of the reaction at completion does not correspond to two Mn(II) ions per peroxide, but instead it varies with the concentration of gluconate (see Table II); the number of manganese ions oxidized per peroxide decreases as the concentration of sodium gluconate is increased. The possibility of a catalytic decomposition of peroxide due to the presence of manganese(III) is ruled out because it would produce oxygen which in turn would react rapidly with the manganese(II) complex.

Because basic solutions of peroxide in the presence of gluconate are stable, we have to come to the conclusion that peroxide in the presence of the manganese(II) gluconate complex is catalytically activated, probably by a set of reactions analogous to those for Fenton's reagent.[30] Assuming the latter, the manganese(II) complex would react with hydrogen peroxide to yield manganese(III) and hydroxyl radicals. If, for simplicity, we consider the manganese complexes as monomeric groups and leave out the ligands, the reaction mechanism can be represented by

$$Mn^{II} + HO_2^- \rightarrow Mn^{III}(OH^-) + \cdot O^- \quad (3)$$

$$\cdot O^- + GH_4^- \rightarrow [GH_4\dot{C}HOH]^- + OH^- \quad (4)$$

$$\cdot O^- + Mn^{II} \xrightarrow{H_2O} Mn^{III}(OH^-) + OH^- \quad (5)$$

$$2[GH_4\dot{C}HOH]^- \rightarrow \left[\begin{array}{c} GH_4{-}CH{-}CH{-}GH_4 \\ \quad\;\; |\quad\; | \\ \quad OH\;\; OH \end{array}\right]^{2-} \quad (6)$$

$$[GH_4\dot{C}HOH]^- + Mn^{III} \xrightarrow{OH^-} Mn^{II} + [GH_4CHO]^- + H_2O \quad (7)$$

where $[GH_4\dot{C}HOH]^-$ represents the radical that results from hydrogen abstraction from the terminal primary alcoholic group of gluconate ion, and $[GH_4CHO]^-$ represents the anion of glucuronic acid (the oxidation product of gluconate). Additional research is in progress to confirm the exact nature of these reactions, but the proposed mechanism accounts for the variable stoichiometry that is observed for the overall reaction of the manganese(II) gluconate complex and hydrogen peroxide (Table II). The kinetic results (Figure 4) indicate a stoichiometry of two Mn(II) ions oxidized per peroxide because the experiments used a large excess of hydrogen peroxide and a moderate concentration of gluconate ion. This kind of mechanism, which involves the formation of hydroxyl radicals, also is observed for the reactions of vanadium(IV), chromium(II), titanium(III), and iron(II) with hydrogen peroxide.[27]

The oxidation of the manganese(III) gluconate complex to the manganese(IV) complex can be achieved with molecular oxygen only when the concentration of sodium gluconate is 0.1 M or less. This strongly supports the conclusion that the binuclear bisgluconatomanganese(III) complex is the only oxidizable species

$$Mn^{III}_2(GH_3)_4(OH)_2^{4-} + O_2 + 3OH^- \xrightarrow{k_3 = 3.9 \times 10^4\ l\ mol^{-1}\ s^{-1}} Mn^{IV}_2(GH_3)_4O_2(OH)_2^{6-} + HO_2^- + H_2O \quad (8)$$

This conclusion is consistent with the kinetic results and with the stoichiometric formulas and equilibria that are discussed in the previous paper.[18] Upon acidification, the equilibrium of eq 8 is shifted to the left with the evolution of molecular oxygen and the reduction of manganese(IV) to manganese(III) (see Figure 2). The forward process appears slow because of the slow equilibration from the monomeric form of the Mn(III) complex to the active binuclear form. Therefore, molecular oxygen at 1 atm must be bubbled through a basic solution of the manganese(III) gluconate complex for approximately 20 min to achieve complete conversion to the "cherry-red" manganese(IV) gluconate complex.

In contrast to some cobalt(II) and iron(II) systems,[30-33] the manganese gluconate complexes clearly do not have the characteristics of an oxygen carrier. Apparently, this is because manganese(II) gluconate is easily oxidized to the Mn(III) and Mn(IV) complexes by molecular oxygen, whereas cobalt(II) can remain unoxidized while associated in an oxygen-adduct complex.[31]

Although the present results do not explain the role of manganese in biological redox systems, a knowledge of the chemical characteristics and reactivity of this element in its higher oxidation states is an essential first step. The results establish that the manganese(IV) complex reacts with peroxide to produce molecular oxygen. However, the redox potential of the Mn(IV)/Mn(III) couple in basic gluconate solutions is not positive enough to oxidize water. If the pH of the system is lowered, the potentials are shifted to more positive values, but this results in the destruction of the complexes.

On the basis of the present results and the redox potentials for the H_2O/O_2 system,[32,33] an optimal model for the manganese unit in the chloroplast would be a complex with a ligand resistant to oxidation and able to stabilize both the manganese(III) and the manganese(IV) states in such a way that the redox potential for this couple would be at least +0.2 vs. SCE at pH 14.

The proposition of binuclear manganese complexes in photosystem II (as well as tetranuclear systems) is attractive because it would provide a favorable kinetic path for the formation of the (O-O) bond which is the mechanistically difficult step. Furthermore, such groupings would provide the means to accomplish the four-electron transfer that is required to oxidize water to molecular oxygen.

Acknowledgment. This work was supported by the U.S. Public Health Service-NIH under Grant No. GM 22761 and, in its initial phase, by the National Science Foundation under Grant No. CHE 73-05204. We are grateful for a Predoctoral Fellowship to M.E.B. from the Catholic University of Chile, and to Ms. Laurie A. Willis and Mr. Thomas L. Riechel for assistance in the spectroscopic and magnetic measurements.

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Observation of a Direct Interaction between the Carbonyl Oxygen, O(6), of a N(7)-Bonded 6-Oxopurine and a Metal Center. Preparation and Crystal and Molecular Structure of (*N*-3,4-Benzosalicylidene-*N'*,*N'*-dimethylethylenediamine)-(theophyllinato)copper(II) Monohydrate

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Abstract: The preparation and crystal and molecular structure of the complex (*N*-3,4-benzosalicylidene-*N'*,*N'*-dimethylethylenediamine)(theophyllinato)copper(II) are reported. The complex crystallizes, as the monohydrate, from the reaction mixture with 95% ethanol as the solvent. The crystals are monoclinic, space group *Pc*, with $a = 10.689$ (2), $b = 6.925$ (3), $c = 15.463$ (4) Å, $\beta = 100.27$ (2)°, $Z = 2$, $V = 1126.2$ Å^3, $d_{measd} = 1.50$ (2) g cm^{-3}, $d_{calcd} = 1.48$ g cm^{-3}. The 7359 reflections in the $+h$ hemisphere to $2\theta = 60°$ were collected by counter methods on an automated diffractometer, employing crystal-monochromated MoK$\bar{\alpha}$ radiation and the θ–2θ scan technique. The 7359 measured reflections were subsequently reduced to a symmetry independent set of 3138 intensities, which were used in the structural solution and refinement. Standard heavy-atom Patterson and Fourier methods were used to solve the structure, and refinement by full-matrix least squares, based on F, has led to a final R value of 0.037. The coordination geometry about the copper(II) is (4 + 1) with the equatorial positions occupied by the tridentate Schiff base chelate and N(7) of the theophylline monoanion, Cu–N(7) bond length = 1.956 (3) Å, and one of the axial positions is occupied by the carbonyl oxygen at C(6) of the purine ring system, Cu–O(6) distance = 2.919 (3) Å. This represents the first observation of a significant, direct interaction between the carbonyl oxygen of a 6-oxopurine and a metal center. The complexes are connected along the *a* axis by an O(10)(Schiff base)...H–O–H...O(2)(theophylline monoanion) hydrogen bond system involving translationally related complexes. Further crystal stability is obtained by a "pinning" of the naphthylidene rings of the Schiff base chelate by methyl groups from the ethylenediamine terminus and the theophylline monoanion ring.

Investigations into the binding of metal ions and metal complexes to nucleic acids and their constituents, both in solution[1] and in the solid state,[2] have recently been summarized. Activity in this area has been stimulated by both the importance of such interactions in living systems, and also the potential importance of metal binding in the functioning of platinum(II) cancer chemotherapeutics.

Chelation of metal centers by N(7) and either the 6-oxo or 6-amino exocyclic groups of purines has been widely suggested on the basis of a number of spectroscopic and physical criteria.[3] Such chelate formation has been a major theme in the early literature and has been continually suggested despite numerous recent solution[1] and x-ray structural[2] investigations, which have failed to provide direct evidence for such a mode of binding. Rather, it has become clear that whereas N(7) of the five-membered imidazole ring of purines forms a strong bond to the metal, the exocyclic oxo or amino groups engage in hydrogen bonding to other ligands attached to the metal.[2] No direct bond has been found between the common exocyclic groups of the purines and the metal center.

Some insight into the chelation mode of binding has been derived from structural studies on 6-thiopurines. In bis(6-mercapto-9-benzylpurine)palladium(II),[4,5] the palladium(II) is complexed to both N(7), Pd(II)–N(7) bond lengths of 2.05 (1) and 2.08 (1) Å for the two independent ligands, and S(6), Pd(II)–S(6) bond lengths of 2.305 (3) and 2.311 (3) Å. All these bond lengths are normal for Pd(II) chelate systems.[2,4,5] A second example of 6-thiopurine chelation has been found in the complex bis[dichloro(6-mercapto-9-methylpurine)copper(II)].[6] In this complex, however, the Cu(II)–N(7) bond length, 1.992 (4) Å, is normal, while the Cu(II)–S(6) bond length, 2.424 (1) Å, is about 0.2–0.4 Å longer than expected.[6]

The absence of chelation in 6-oxopurines, but the presence of such chelate formation in 6-thiopurines, has been rationalized on the basis of geometric[7] and coordination affinity grounds.[2]

We have investigated a metal–chelate ligand system which precludes interligand hydrogen bonding to the exocyclic oxo group, but nevertheless presents a vacant coordination site for direct binding between the exocyclic oxygen and the metal center. The system selected contans Cu(II) chelated by the mononegative, tridentate Schiff base ligand *N*-3,4-benzosalicylidene-*N'*,*N'*-dimethylethylenediamine. In this system, the