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Electrochemical and Spectroscopic Studies of Manganese(II), -(III), and -(IV) Gluconate Complexes. 1. Formulas and Oxidation–Reduction Stoichiometry

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The complexes of manganese with D-gluconate ion in aqueous alkaline solution have been studied by polarographic, voltammetric, amperometric, magnetic, and spectrophotometric methods. The results establish that stable complexes of manganese(II), manganese(III), and manganese(IV) are formed and that their apparent formulas are $[Mn^{II}(GH_3)_2]^{2-}$, $[Mn^{III}(GH_3)_2(OH)]^{2-}$, and $[Mn^{IV}(GH_3)_2(OH)_3]^{3-}$ with GH_3^{2-} representing the dianion of D-gluconic acid. Manganese(III) also forms a second complex; a possible formula is $[Mn^{III}(GH_3)_3]^{3-}$. Some evidence has been obtained (electrochemical and magnetic) that the Mn(II) complex dimerizes at higher concentrations; possible structures for the complexes are proposed on the basis of the data. Oxidation of manganese(II) gluconate with stoichiometric amounts of $K_3Fe(CN)_6$ produces stable solutions of the manganese(III) complex (brown) and of the manganese(IV) complex ("cherry red"); combination of the manganese(II) gluconate complex with oxygen also yields the manganese(IV) complex. The half-wave potentials for the reductions of Mn(IV) to Mn(III), Mn(III) to Mn(II), and Mn(II) to Mn(0) are −0.29, −0.54 and −1.10, and −1.75 V vs. SCE, respectively.

Manganese is an essential component of several biological systems that are associated with electron-transfer reactions. One of these is the mitochondrial version of the superoxide dismutase enzyme.[1] Another is photosystem II in green-plant photosynthesis.[2,3] In both cases the oxidation states +2, +3, and +4 are believed to be involved[4,5] but there are few data to confirm this assumption.

Because of the current interest in the oxidation–reduction chemistry of manganese in biological systems and the limited number of complexes of manganese(III) and manganese(IV) that are stable in aqueous solution,[6] a systematic search for complexing agents to stabilize the higher oxidation states of this element has been initiated. Previous experience has established that sodium gluconate, the salt of the carboxylic acid derivative of D-glucose, is especially effective for the stabilization of strongly acidic ions in alkaline media, e.g., Fe(III), Bi(III), Sb(III), Ce(IV), and Os(VI),[7] and is more resistant to oxidation than most other sugar acids.

A preliminary communication[8] has discussed the stabilization of the higher oxidation states of manganese by alkaline gluconate solutions as well as their interaction with hydrogen peroxide and with oxygen. The evolution of oxygen from solutions of the manganese(IV) gluconate complex also is described in the preceding report. The present paper summarizes the results of a detailed study of the gluconate complexes of manganese(II), manganese(III), and manganese(IV) in alkaline media. Electrochemical, spectrophotometric, and magnetic susceptibility measurements have been used to establish the formulas, oxidation–reduction stoichiometry, and chemical characteristics of the complexes. These have been determined to provide a basis for understanding the mechanism of the water-oxidation reaction in future studies of the oxygen-evolution process associated with photosystem II.

Experimental Section

Polarography and cyclic voltammetry were performed with a three-electrode potentiostat based on the use of solid-state operational amplifiers.[9] Controlled-potential electrolyses were accomplished by use of a Wenking Model 61-RH potentiostat; the current–time curves were recorded with a Sargent Model SR strip-chart recorder and their areas determined with a K and E planimeter.

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 to hold the reference electrode, a bubbler for degassing the solution with argon, and a short piece of glass tubing to flow argon above the solution surface while the polarograms were recorded. The top also had an opening to introduce either the dropping mercury electrode or the mercury working electrode in the case of cyclic voltammetry. The latter consisted of a Beckman platinum-inlay electrode whose surface had been abraded under mercury.

For controlled-potential electrolysis, a nickel wire was sealed in the wall close to the bottom of the cell to provide an electrical connection with the mercury-pool working electrode.

The auxiliary electrode was a small piece of platinum mesh. The reference electrode consisted of a silver wire coated with AgCl in a Pyrex tube closed with a small soft-glass cracked-bead tip. The electrode was filled with a solution of aqueous tetramethylammonium chloride (Matheson Coleman and Bell) with the concentration adjusted such that the electrode potential was 0.000 V vs. SCE. The reference electrode was placed inside a Luggin capillary in the cell assembly.

The spectrophotometric measurements were performed with a Cary Model 14 and a Perkin-Elmer Model 450 spectrophotometer using quartz cells. All of the spectra were recorded with equimolar concentrations of sodium hydroxide and sodium gluconate in the reference cell and in the sample cell.

ESR spectra were obtained with a Varian Model V-4500 spectrophotometer by use of a standard flat-faced quartz cell. When work was done with air-sensitive solutions, the cell was filled in an inert-atmosphere glovebox.

The magnetic susceptibilities were determined by the NMR method developed by Evans[10] and modified by Rettig.[11] The inner tube was made from 3-mm o.d. Pyrex tubing, sealed with a nearly saturated solution of TMS* (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) inside. The outer tube was a standard NMR tube and was filled with the sample in a nitrogen-atmosphere glovebox. The shift between the two TMS* peaks was measured on a Varian A-60D spectrometer at ambient temperature; the probe temperature was determined with an ethylene glycol standard. The magnetic susceptibilities were calculated by the method of Rettig,[11] with values for diamagnetic corrections from Figgis and Lewis.[12]

Reagents. The source of manganese ion was manganese(II) gluconate from Chas. Pfizer and Co.; the stock solutions were standardized by titration with EDTA.[13] The source of gluconate ion was D-glucono-δ-lactone (Chas. Pfizer and Co.), which was recrystallized from ethylene glycol monomethyl ether.[14] The stock solution of sodium gluconate was prepared by neutralization of the D-glucono-δ-lactone with sodium hydroxide. Manganese(III) acetate was synthesized by the procedure of Christensen;[15] in some experiments it was used as the source of manganese(III). Triply distilled mercury was used both for the dropping mercury electrode and for the pool in controlled-potential electrolysis. All the other chemicals were reagent grade.

Results

Electrochemistry. The polarogram for a solution of manganese(II) gluconate in 0.3 M NaOH and 0.1 M sodium gluconate ($NaGH_4$) exhibits two oxidation waves and a reduction wave with half-wave potentials of −0.29, −0.54 and −1.75 vs. SCE, respectively (curve A of Figure 1). Analysis of the current–voltage curves for the polarographic waves

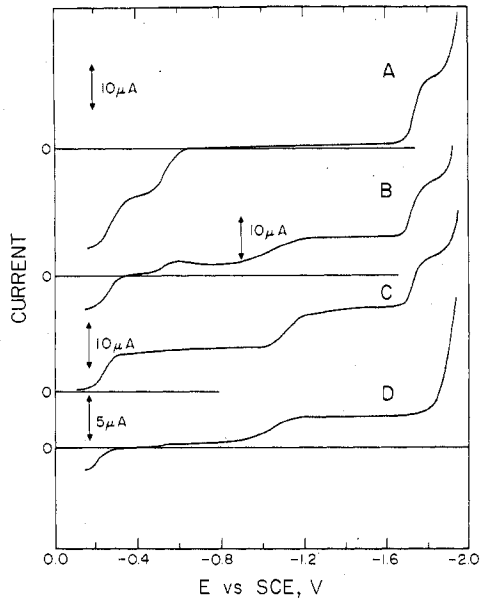


Figure 1. Polarograms of manganese in 0.1 M sodium gluconate and 0.3 M NaOH: A, 4 mM Mn^{II}; B, 5 mM $Mn^{III}(OAc)_3$; C, 5 mM Mn^{II} plus 10 mM $K_3Fe(CN)_6$; D, 5 mM $Mn^{III}(OAc)_3$ plus 0.5 M sodium gluconate. Solutions were degassed with argon prior to recording their polarograms; voltage scan rate 0.3 V min^{-1}; DME drop time 4.0 s. Curves represent the envelope of the maxima of the DME current oscillations.

Table I. Characteristics of the Polarographic Waves of the Manganese(II), -(III), and -(IV) Gluconate Complexes[a]

Oxidn state	Change in oxidn state	$E_{3/4} - E_{1/4}$, mV	$E_{1/2}$, V vs. SCE	I^b
Mn(II)	II → IV		−0.29	−2.12
Mn(II)	II → III	60	−0.54	−1.02
Mn(II)	II → 0	30	−1.75	1.71
Mn(III)	III → IV	55	−0.27	−1.02
Mn(III)	III → II	55	−0.53	−0.36
Mn(III)	III → II	135	−1.04	−0.69
Mn(III)	III → 0		−1.73	2.80
Mn(IV)	IV → III	55	−0.27	1.16
Mn(IV)	IV → II		−1.10	2.21
Mn(IV)	IV → 0		−1.73	4.30

[a] 0.3 M NaOH and 0.1 M sodium gluconate; 1 mM manganese. [b] $I = 706nD^{1/2} = i_d/Cm^{2/3}t^{1/6}$, with i_d in μA (maxima of the current oscillations), C in mM, m in mg/s, and t in s; n represents the number of electrons in the electrochemical process and D the diffusion coefficient of the electroactive species.

(Table I) indicates that they meet one of the criteria for reversibility[16] [$E_{3/4} - E_{1/4} = 56$ mV/n], with both oxidations corresponding to one-electron processes and the reduction to a two-electron process. Reference to Table I also confirms that the forward and reverse electrolysis reactions for the II–III and III–IV couples have essentially the same half-wave potentials, which is the ultimate criterion for reversibility.

Attempts to perform cyclic voltammetry at a mercury-film electrode are complicated by the limited solubility of manganese metal in mercury and by formation of insoluble, nonconductive surface films. However, rapid-scan reductions (0.5 V/s) of manganese(II) gluconate yield half-wave potentials that are essentially the same as those for the polarographic measurements of Table I. This is persuasive evidence that the II–0 reduction process obeys the Nernst equation.

Reference to Figure 2 indicates that the diffusion currents for the anodic processes increase linearly with the concentration of manganese up to 10 mM. For the cathodic process the diffusion current is linear with concentration up to 1 mM manganese(II). Apparently the manganese metal from the

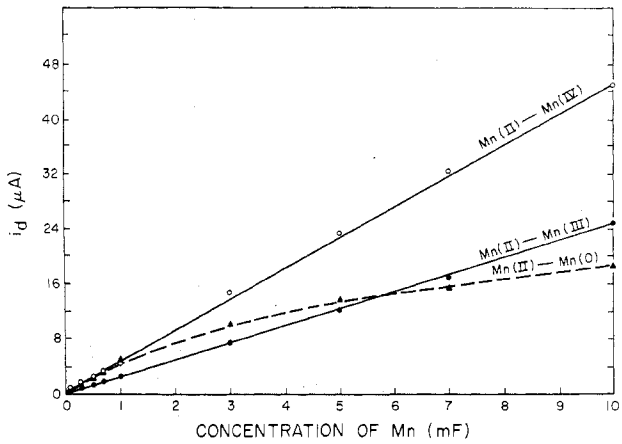


Figure 2. Polarographic diffusion currents for the reduction and oxidation of manganese(II) gluconate as a function of metal complex concentration; solutions contain 0.1 M sodium gluconate and 0.3 M NaOH.

reduction process forms an amalgam up to this concentration; the half-wave potential is −1.70 V vs. SCE. For the higher concentrations the mercury drops become saturated and a nonconductive unreactive film is formed on their surface. This suppresses the available surface area for the reduction process and causes the current to cease to be diffusion controlled and to become dependent on electrode area.

Further support for the conclusion that the polarographic half-wave potentials obey the Nernst equation is the fact that they are independent of manganese concentration and of the drop time.[16]

The polarographic characteristics of the three manganese(II) waves are summarized in Table I, as are those for the manganese(III) and -(IV) complexes. The diffusion currents for the three waves increase linearly with the square root of the height of the mercury column for the dropping mercury electrode,[17] which indicates that these are diffusion-controlled processes. In the case of the reduction wave at −1.75 V its current becomes independent of the square root of the height of the mercury column when the concentration of manganese is 5 mM or higher. This is further evidence for formation of a nonconductive film on the mercury drops.

The presence of nitrate ion in the solutions interferes with the manganese(II) reduction wave because of its catalytic reduction at the same potential. Therefore, manganese(II) gluconate has been used as the source of manganese ion in these studies. Some attempts have been made to use lithium hydroxide and lithium gluconate to avoid the interference from the reduction of sodium ion. Unfortunately, the presence of lithium ion seems to affect the behavior of the system and causes surface interactions with the electrode. Consequently, sodium hydroxide and sodium gluconate have been used, although the Mn(II) half-wave potential cannot be measured accurately at high concentrations of base or gluconate ion. Another problem at high concentrations of ligand is that the manganese(II) reduction wave begins to appear as a double wave, probably due to the presence of two different hydrolytic forms of the complex. Some electrostatic interaction with the surface of the electrode is assumed to be responsible for the difference in potential of the two waves.

As a result of the apparent reversibility of the redox processes, a study of the dependence of the half-wave potentials on the concentration of gluconate ion and of hydroxide ion has been made. In the case of the reduction of manganese(II) to the metal, the relation[17]

$$\Delta E_{1/2} = -p\frac{0.0591}{n}\Delta \log C_X$$

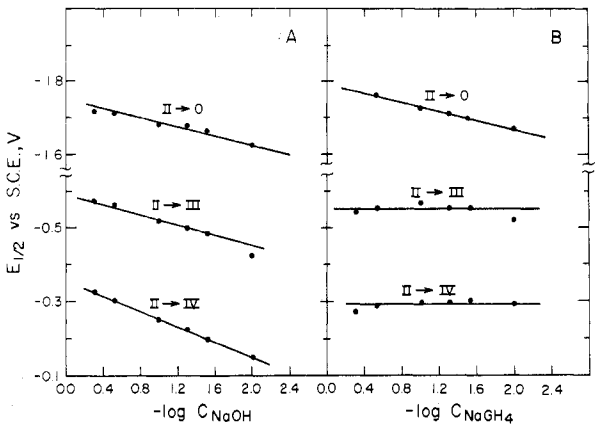


Figure 3. Polarographic half-wave potentials as a function of hydroxide ion and gluconate ion concentration for the indicated changes in oxidation state; manganese concentration 5 mM: A, solutions 0.05 M in sodium gluconate ($NaGH_4$); B, solutions 0.1 M in NaOH.

is applicable, where C_X is the concentration of the ligand, p the number of ligands per metal atom in the complexed species, and n the number of electrons in the reduction step. Reference to Figure 3 indicates that the manganese(II) complex has two gluconate ions and two OH^- ions per manganese ion. In the case of the Mn(II) oxidation waves the corresponding relation is[18]

$$\Delta E_{1/2} = -(p - q)\frac{0.0591}{n}\Delta \log C_X$$

where C_X is the concentration of the ligand, p the number of ligands per metal ion in the oxidized species, and q the number of ligands per metal atom in the reduced species. The curves of Figure 3 indicate that the number of gluconate molecules per manganese does not change in going from manganese(II) to manganese(III) or to manganese(IV). In the case of hydroxide ion, the data indicate that three OH^- ions are added in the formation of the manganese(III) complex and that five OH^- ions are required to form the manganese(IV) complex. The same results are obtained when this study is made for the reduction waves of the manganese(III) and -(IV) complexes.

The effect of pH on the diffusion current for the reduction of Mn(II) to Mn(0) is illustrated by Figure 4; the current reaches a minimum value at about pH 12. As the pH is made more acidic, a remarkable increase in the diffusion current is observed, which probably is indicative of the presence of uncomplexed manganese(II). For solutions above pH 12.0 the diffusion current also increases to a constant value. Above pH 13.5 this wave cannot be observed because of the interference from the reduction of sodium ion.

The manganese(III) gluconate complex has been prepared in solution by three different methods. Manganese(III) acetate can be added to an excess of an alkaline gluconate solution to give a stable and reproducible complex. Another method is to add 1 equiv of potassium ferricyanide/mol of manganese in an alkaline solution of manganese(II) gluconate. The third method is to electrolyze an alkaline solution of manganese(II) gluconate at −0.4 V vs. SCE by means of a mercury-pool working electrode. The initial current in the electrolytic process is strongly dependent on the stirring rate; the highest possible speed with a magnetic stirrer has been used to increase the efficiency of the electrolysis process. Integration of the current–time curve confirms that the electrolysis is a one-electron oxidation at this potential. Regardless of the method of preparation, the same dark brown solution of the manganese(III) gluconate complex is obtained whose polarograms are identical. The action of hydrogen peroxide on a solution of manganese(II) gluconate also leads to the formation of the

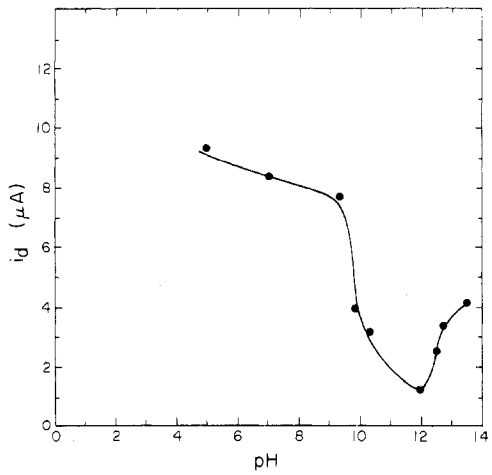


Figure 4. Polarographic diffusion current for the reduction of 1 mM manganese(II) gluconate as a function of solution pH in 0.1 M sodium gluconate solutions (NaOH and $HClO_4$ used to adjust solution conditions).

brown solution and the polarograms indicate the presence of manganese(III). Preparation of the manganese(III) complex also has been attempted by use of $KMnO_4$ as the oxidizing agent. Unfortunately, under these conditions permanganate oxidizes the gluconate ion.

Curve B of Figure 1 illustrates the polarogram for a manganese(III) gluconate solution. A reduction wave with a half-wave potential of −1.06 V vs. SCE is observed in addition to the expected reduction at −0.54 V, which indicates the presence of a new species in the system. This wave is totally irreversible and the ratio of diffusion current for the reduction wave at −0.54 V and for this new wave at −1.06 V is dependent on the concentration of gluconate in the solution. This dependence can be seen if curves B and D are compared in Figure 1. The concentration of base also has some influence on the half-wave potential of these waves. Hence, as the concentration of NaOH in the solution is increased, the half-wave potential of the reduction at −0.54 V shifts to more negative potentials and its diffusion current decreases. Exactly the opposite effect is observed for the wave at −1.06 V, which moves toward more positive potentials and its diffusion current increases.

When a solution of manganese(III) gluconate is reduced by controlled-potential electrolysis at −0.7 V vs. SCE, manganese(II) is produced after a long period of time (5 h). However, electrolysis at −1.4 V vs. SCE also yields manganese(II), but the reduction is complete in 15 min. Integration of the current–time curves confirms that the electron stoichiometry in each reduction is one electron per manganese-(III).

The manganese(IV)–gluconate complex, which has a "cherry red" appearance, has been prepared by three different procedures. The most direct is to bubble pure oxygen through an alkaline solution of manganese(II) gluconate for 20 min. A somewhat more complete oxidation is achieved by adding 2 equiv of potassium ferricyanide/mol of the manganese(II) complex in basic media. The third method of preparation is by means of controlled-potential electrolysis of a basic manganese(II) gluconate solution at −0.2 V vs. SCE. Integration of the current–time curve of the electrolysis confirms that the oxidation is a two-electron process.

Reference to curve C of Figure 1 indicates that the manganese(IV) gluconate complex yields a polarogram with reduction waves at −0.27, −1.11, and −1.75 V vs. SCE. A reduction wave is not observed at −0.54 V. Table I summarizes the polarographic characteristics of the manganese(III) and -(IV) gluconate complexes.

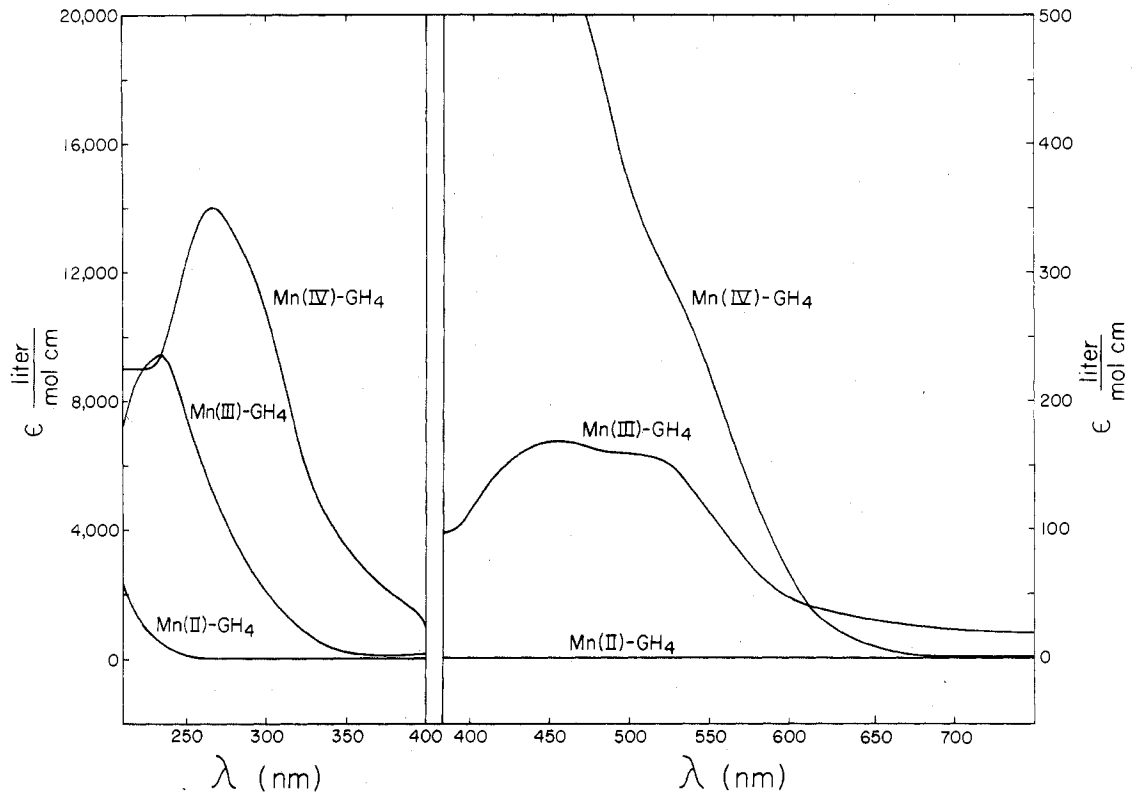


Figure 5. Absorption spectra for manganese complexes in 0.1 M sodium gluconate and 0.3 M NaOH; Mn^{III} is from $Mn^{III}(OAc)_3$ and Mn^{IV} is from $Mn^{II}(GH_4)_2$ plus 2 equiv of $K_3Fe(CN)_6$.

Table II. Experimental n Values and $K_3Fe(CN)_6$ Titration Stoichiometry

A. Controlled Potential Electrolysis

Electrode reaction	Controlled potential, V vs. SCE	n Value
II → III	−0.4	0.70
II → IV	−0.2	2.15
IV → III	−0.4	1.03
III → II	−0.7	1.02
III → II	−1.4	1.20

B. Redox Stoichiometry with $K_3Fe(CN)_6$ as Titrant

Reaction	Mol of $K_3Fe(CN)_6$/mole of Mn Ion
II → III	1.0
II → IV	2.0

Table II summarizes the results of a number of controlled-potential electrolyses for the various manganese gluconate complexes as well as the redox stoichiometry for amperometric titrations of the manganese(II) gluconate complex in basic media with potassium ferricyanide.

Spectroscopy. Figure 5 illustrates the uv–visible spectra for the manganese(II), manganese(III), and manganese(IV) gluconate complexes in 0.3 M NaOH and 0.1 M sodium gluconate. The manganese(II) gluconate complex solution does not exhibit any significant absorption band, except for an increased absorbance in the uv spectrum. The manganese(III) complex has two absorption bands in the visible region, 450 nm (ϵ 170 M^{-1} cm^{-1}) and 510 nm (ϵ 150), and a much more intense band in the uv region, 235 nm (ϵ 9500). In the case of the manganese(IV) complex, an absorption spectrum with shoulders at 510 nm (ϵ 310) and at 385 nm (ϵ 1500) and an intense band at 265 nm (ϵ 14000) is observed.

Mole ratio studies at 265 nm for the absorbance of the manganese(IV) gluconate system (Mn(II) plus increasing ratios of GH_4^- with oxidation by oxygen for 20 min) establish that the major species has two ligands per metal ion. This confirms the interpretations based on the electrochemical data of Figure 3. The half-wave potentials of the III–IV and III–II couples are independent of gluconate concentration, which indicates that the manganese(III) and -(II) gluconate complexes have the same ligand-to-metal mole ratio as the manganese(IV) complex. (Any concern with the Nerstian behavior of the II–0 couple and the associated interpretations is obviated by this alternative analytical approach.)

The effect of gluconate concentration upon the absorption spectra for manganese(III) is illustrated by Figure 6. An isosbestic point is evident, which confirms the presence of two forms of the manganese(III) gluconate complex. At high gluconate concentrations the species with an absorption maximum at 510 nm predominates; the species at 450 nm is dominant at low ligand concentrations. Reference to Figure 6 indicates that the two species are equimolar when the gluconate concentration is approximately 0.2 M.

The ESR spectrum of a 5 mM aqueous solution of manganese(II) gluconate consists of six lines of nearly identical intensities, as expected for a nuclear spin of $^5/_2$. The spectrum is about 650 G wide overall and has a g value of approximately 2. The spectrum of $MnSO_4$, obtained for comparison, is essentially identical. When excess ligand is added to a manganese(II) gluconate solution, no change in the spectrum is observed. However, when base is added to a solution which contains 8 mM manganese(II) and 120 mM gluconate ion in the absence of air, both qualitative and quantitative changes are observed in the ESR spectrum. The initial spectrum (prior to addition of base) is the same as that for a 1:1 neutral manganese(II) gluconate solution. When the solution is 4 or 8 mM in base, the signal intensity of the spectrum is lower but qualitatively the same. For the condition when the solution is 12 mM in base, the signal intensity is much lower and the six lines form the envelope of a broad derivative curve. When the base concentration is increased to 16 mM (one OH^- ion per coordinated ligand), the spectrum is one broad derivative curve, almost 1500 G wide, with a g value of about 2 and a

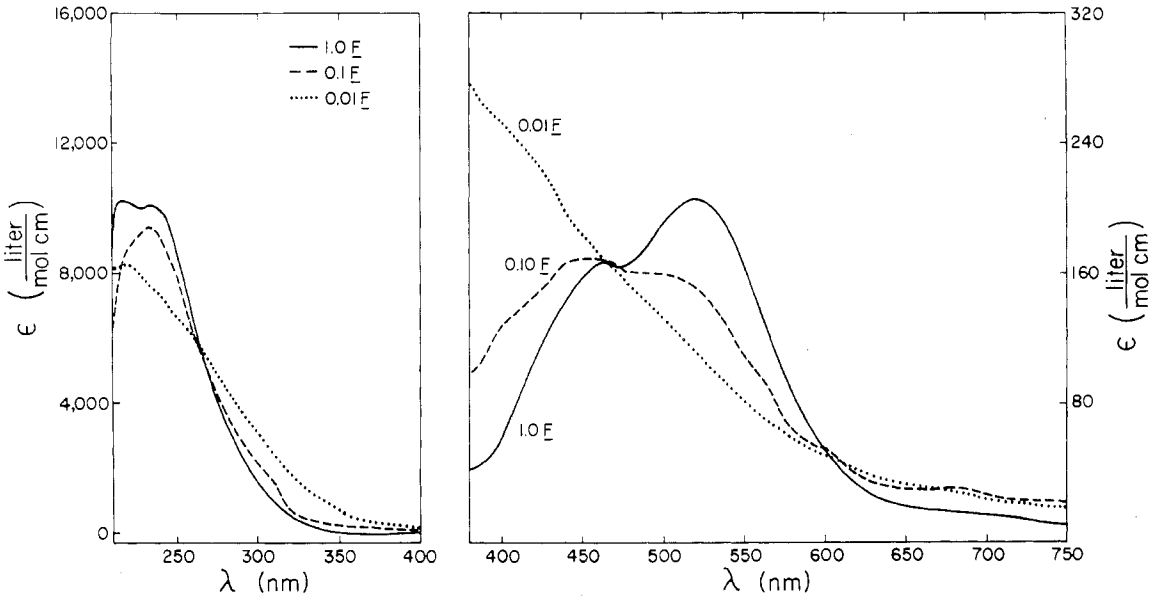


Figure 6. Absorption spectra for 5 mM manganese(III) in 0.3 M NaOH as a function of sodium gluconate concentration; Mn^{III} is from $Mn^{III}(OAc)_3$.

Table III. Magnetic Susceptibilities for the Manganese Gluconate Complexes (40 mM) in 0.1 M Sodium Gluconate

	μ, μ_B		
	Uncor	Cor	Theoretical for (n) electrons
$Mn^{II}GH_4$	5.81	5.85	5.92 (5)
$Mn^{II}GH_4$, 0.3 M NaOH	5.24	5.37	5.92 (5)
$Mn^{III}GH_4$, 0.3 M NaOH (from $Mn^{III}(OAc)_3$)	4.51	4.64	4.90 (4)
$Mn^{III}GH_4$, 0.3 M NaOH (from Mn^{II} + $K_3Fe(CN)_6$)	4.79	4.98	4.90 (4)
$Mn^{IV}GH_4$, 0.3 M NaOH (from Mn^{II} + $2K_3Fe(CN)_6$)	3.78	4.06	3.82 (3)
$Mn^{IV}GH_4$, 0.3 M NaOH (from Mn^{II} + O_2 at 1 atm for 20 min)	3.89	4.08	3.82 (3)

signal intensity about 50 times smaller than that of the original signal. When the solution is 24 mM in base, the spectrum is essentially the same as that for 16 mM base.

Table III summarizes the magnetic moments for the manganese(II), manganese(III), and manganese(IV) gluconate complexes. The corrected magnetic moments are close to the theoretical values for the five, four, and three unpaired electrons that correspond to the three different oxidation states of manganese, respectively. The value for manganese(II) gluconate in basic media is low, which may indicate some degree of electron pairing in the complex molecule. The low value for the manganese(III) gluconate complex that is derived from manganese(III) acetate may be accounted for in terms of some oxidation to the manganese(IV) complex. The two manganese(IV) solutions yield values which are in remarkable agreement with each other and are close to the theoretical value of the magnetic moment for three unpaired electrons.

Discussion and Conclusions

The electrochemical and magnetic measurements establish that stable complexes of manganese(II), manganese(III), and manganese(IV) are formed with gluconate ion in basic aqueous solutions. This is especially significant in the case of the manganese(IV) species because stable, water-soluble complexes of this oxidation state have been virtually unknown.

On the basis of the ESR and magnetic susceptibility data some dimerization of the manganese(II) gluconate complex appears to occur in basic media. That is, the number of unpaired electrons decreases as the solution of manganese(II) gluconate is made more basic. This conclusion also is supported by the decrease in the diffusion current–pH curve (Figure 4) for the reduction of manganese(II) gluconate. Such a dimerization can be represented by

$$2[Mn^{II}(GH_3)_2(H_2O)_2]^{2-} \rightleftarrows \left[(GH_3)_2Mn^{II}\begin{matrix}H_2O\\ \diagup\ \diagdown\\ O\quad O\\ \diagdown\ \diagup\\ H_2O\end{matrix}Mn^{II}(GH_3)_2\right]^{4-} + 2H_2O \qquad (1)$$

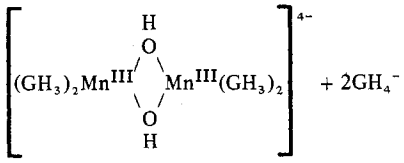
where GH_3^{2-} represents the dianion of gluconic acid that results from ionization of the carboxylic acid and α-hydroxyl protons.

The electrochemical data indicate that oxidation of the manganese(II) gluconate complex yields two forms of the manganese(III) gluconate complex that are in slow kinetic equilibrium with each other. This conclusion is supported by the fact that alkaline manganese(III) gluconate solutions exhibit two reduction waves whose total diffusion current corresponds to a one-electron process. Further evidence for the presence of two species in slow equilibrium results from the controlled-potential electrolysis rates and stoichiometries.

The oxidation of the manganese(II) gluconate complex at −0.54 V can be expressed by

$$\left[(GH_3)_2Mn^{II}\begin{matrix}H_2O\\ \diagup\ \diagdown\\ O\quad O\\ \diagdown\ \diagup\\ H_2O\end{matrix}Mn^{II}(GH_3)_2\right]^{4-} + 2OH^- \rightarrow 2H_2O + \left[(GH_3)_2Mn^{III}\begin{matrix}H_2O\\ \diagup\ \diagdown\\ O\quad O\\ \diagdown\ \diagup\\ H\end{matrix}Mn^{III}(GH_3)_2\right]^{4-} + 2e^- \qquad (2)$$

At higher gluconate concentrations the electron-transfer reaction apparently is followed by a rearrangement to a new form of the Mn(III) complex

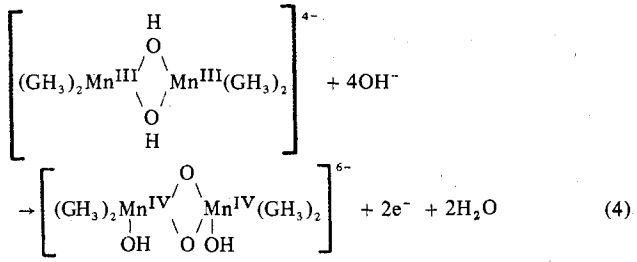


$$\rightleftharpoons^{\text{slow}} 2Mn(GH_3)_3^{3-} + 2H_2O \qquad (3)$$

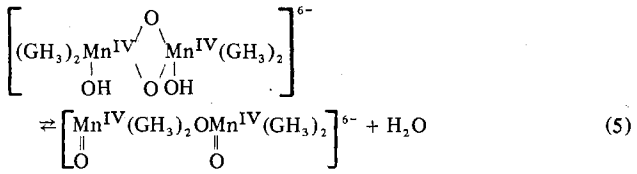
which is responsible for the reduction wave at −1.04 V. Such a wave is observed for alkaline solutions of manganese(III) and manganese(IV) gluconate (see Figure 1). The data of Figure 6 also confirm that an equilibrium exists; as expressed by eq 3 the apparent equilibrium constant is approximately 0.13.

The formula of the manganese(III) complex that is expressed in eq 2 is consistent with the results for the dependence of the half-wave potentials upon the concentration of both NaOH and sodium gluconate (see Figure 3). The conclusion that a tris(gluconate) complex of manganese(III) is formed (eq 3) is supported by the observed increase in the diffusion current for the reduction wave at −1.04 V with increasing concentrations of gluconate ion (curve D, Figure 1) and by Figure 6.

From the stoichiometry indicated by the polarographic studies, the oxidation of Mn(III) to Mn(IV) involves the addition of two hydroxides per manganese atom. A reasonable anodic reaction is

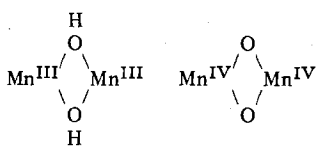


The oxidation product (formulated with seven-coordinate Mn(IV)) may rearrange to a six-coordinate form with terminal oxo groups



Further spectroscopic experiments are planned to confirm the formulas and determine the solution structures of these and other members of this series of manganese gluconate complexes.

Studies of manganese–Schiff base complexes[19] indicate that the only fully authenticated product of air oxidation of the manganese(III) species is a dimer, and the spectroscopy of these compounds is consistent with the presence of oxo-bridged binuclear groups[20]



The manganese(IV)–Schiff base dimer, which has been described[20] as "cherry red", has an electronic spectrum with the same general features as that for the manganese(IV) gluconate species (Figure 6). Another piece of evidence in support of the proposition that oxo-bridged binuclear (or higher) manganese(III) and manganese(IV) gluconate are formed is the crystal structure for the binuclear manganese(III)–manganese(IV)–bipyridyl complex, which has a dioxo bridge.[21]

The sharp decrease in the diffusion current for the reduction of the manganese(II) gluconate complex at pH 12 (see Figure 4) indicates a high degree of association and the possible formation of a tetranuclear Mn(II) group. This may result because the isoelectronic condition for the complex occurs at this pH.

The manganese gluconate complexes, in basic media, represent a system that undergoes oxidation–reduction chemistry that parallels much that is observed for the manganese group in photosystem II.[22] The existence of a tetranuclear manganese(IV) group is an interesting proposition, because it could provide the 4 equiv that are required for the oxidation of water to an oxygen molecule. This kind of oxidation center fits well into the schematic mechanisms for oxygen evolution that have been proposed by Joliot[23] and Kok.[24] We currently are investigating the interactions of the three manganese gluconate complexes with oxygen, hydrogen peroxide, and water and the oxygen-evolution process that is observed under certain conditions for the manganese(IV) gluconate complex.[8]

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Registry No. $[(GH_3)_2Mn^{II}(\mu\text{-}OH_2)_2Mn^{II}(GH_3)_2]^{4-}$, 59043-29-7; $[(GH_3)_2Mn^{III}(\mu\text{-}OH)_2Mn^{III}(GH_3)_2]^{4-}$, 59043-30-0; $[Mn^{IV}O(GH_3)_2(\mu\text{-}O)Mn^{IV}O(GH_3)_2]^{6-}$, 59043-31-1; gluconic acid, 133-42-6; Mn, 7439-96-5.

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