

Contribution from the Department of Chemistry,
University of California, Riverside, California 92521

Polarographic and Spectroscopic Studies of the Manganese(II), -(III), and -(IV) Complexes Formed by Polyhydroxy Ligands

KEITH D. MAGERS, CECIL G. SMITH, and DONALD T. SAWYER*

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The complexes of manganese with aliphatic and aromatic polyhydroxy ligands in basic media have been studied by electrochemical, spectrophotometric, and magnetic methods. The results indicate that glucarate, glycerate, L-tartrate, and *meso*-tartrate stabilize the +2, +3, and +4 oxidation states of manganese in much the same manner as gluconate ion. Sorbitol, mannitol, inositol, *meso*-erythritol, glycerol, 2,3-butanediol, and ethylene glycol do not appreciably form soluble Mn(II) complexes but produce stable Mn(III) and Mn(IV) complexes. Diethanolamine, triethanolamine, tartronate, and glycolate also form stable Mn(II) and -(III) complexes as well as transiently stable Mn(IV) complexes. Catechol, 2,3-dihydroxybenzoate, 1,2-dihydroxybenzene-3,5-disulfonate (Tiron), 3,5-di-*tert*-butylcatechol (DTBC), tetrafluorocatechol, 4,5-dihydroxynaphthalene-2,7-disulfonate, and salicylate stabilize the +2 and +3 oxidation states of manganese. A tris(DTBC semiquinone)manganese(III) complex is produced by oxidation of the Mn(II)-DTBC complex. The redox chemistry and solution equilibria for this group of complexes have been evaluated.

Manganese is known to be an essential element in many biological systems, and its oxidation-reduction chemistry is especially important to the electron-transfer reactions of mitochondrial superoxide dismutase¹ and photosystem II in green-plant photosynthesis.²⁻⁵ The manganese +2, +3, and +4 oxidation states appear to be involved in the biological electron-transfer reactions,⁶⁻⁹ but there is little hard evidence to support this belief.

To understand the role of the manganese cofactor in biological electron-transfer reactions, studies of manganese complexes that mimic its reaction chemistry are needed. Unfortunately, there are relatively few manganese(III) and manganese(IV) complexes that are stable in aqueous solutions.¹⁰ This has resulted in a search for ligands that stabilize and solubilize the higher oxidation states of manganese. Because polyhydroxy ligands can stabilize the higher valent manganese ions,¹¹⁻³⁴ a detailed study of the oxidation-reduction chemistry and solution equilibria of their manganese complexes has been undertaken.

The present paper summarizes the results of electrochemical, spectrophotometric, and magnetic studies of the manganese(II), -(III), and -(IV) complexes that are formed by triethanolamine,¹¹⁻¹⁷ diethanolamine, glycolate ion,¹⁸ L-tartrate ion,¹⁹⁻²² *meso*-tartrate ion, glycerate ion, mannitol,²³⁻²⁵ sorbitol,²⁶ inositol (hexahydroxycyclohexane),²⁷ *meso*-erythritol, tartronate ion, ethylene glycol, glycerol, 2,3-butanediol, D-gluconate ion,²⁸⁻³⁰ D-glucarate ion, catechol,³¹ 1,2-dihydroxybenzene-3,5-disulfonate ion,^{32,33} 3,5-di-*tert*-butylcatechol, 2,3-dihydroxybenzoate ion, tetrafluorocatechol, 4,5-dihydroxynaphthalene-2,7-disulfonate ion, and salicylate ion.³⁴

Experimental Section

Equipment. Polarography was performed with a potentiostat based on the use of solid-state operational amplifiers.³⁵ The dropping mercury electrode and the polarographic cell employed for these experiments have been described previously.³⁶

The spectrophotometric measurements were made with a Cary 14 spectrophotometer and quartz cells.

Magnetic susceptibilities were measured by the NMR method developed by Evans³⁷ and modified by Rettig;³⁸ diamagnetic corrections were made.³⁹ The paramagnetic shift between the two 3-(trimethylsilyl)propanesulfonate (DSS) peaks was measured on a Varian A-60D spectrometer. The probe temperature was determined with an ethylene glycol standard.

Reagents. The source of manganese(II) was Mn(ClO₄)₂ (G. Frederick Smith Chemical Co.) except for the manganese gluconate complexes, which were prepared from manganese(II) gluconate salt (Chas. Pfizer and Co.). The Mn(II) complexes were formed by addition of Mn(II) salt to oxygen-free solutions that contained both the base and the ligand. The Mn(III) and Mn(IV) complexes were prepared by oxidation of the corresponding Mn(II) complex with stoichiometric amounts of K₃Fe(CN)₆ (Mallinckrodt). Molecular oxygen also was used to produce some of the Mn(III) and Mn(IV) complexes from Mn(II). Manganese(III) acetate⁴⁰ also was used to produce some of the Mn(III) complexes.

The following is a list of the polyhydroxy ligands (and their sources): D-glucono- δ -lactone (Chas. Pfizer and Co.), D-saccharic acid 1,4-lactone (glucarolactone, Sigma Chemical Co.), potassium hydrogen tartrate (L-tartrate, Baker and Adamson), *meso*-tartaric acid hydrate (99%, Aldrich Chemical Co.), sorbitol (Matheson Coleman and Bell), mannitol (Mallinckrodt), inositol (Matheson Coleman and Bell), *meso*-erythritol (Calbiochem), tartronic acid (Matheson Coleman and Bell), ethylene glycol (Mallinckrodt), 2,3-butanediol (Aldrich Chemical Co.), glycerol (Mallinckrodt), glycolic acid (Matheson Coleman and Bell), triethanolamine (Mallinckrodt), diethanolamine (Matheson Coleman and Bell), catechol (Matheson Coleman and Bell), 2,3-dihydroxybenzoic acid (Aldrich Chemical Co.), 3,5-di-*tert*-butylcatechol (Aldrich Chemical Co.), disodium 1,2-dihydroxybenzene-3,5-disulfonate (Tiron, Aldrich Chemical Co.), salicylic acid (Baker and Adamson), and disodium 4,5-dihydroxynaphthalene-2,7-disulfonate dihydrate (chromotropic acid, 98% Aldrich Chemical Co.). Tetrafluorocatechol was synthesized⁴¹ and sodium glycerate was prepared by an exchange reaction between Na₂CO₃ (Baker and Adamson) and calcium glycerate (99% Aldrich Chemical Co.). Molecular oxygen was removed from solutions by deaeration with high-purity argon.

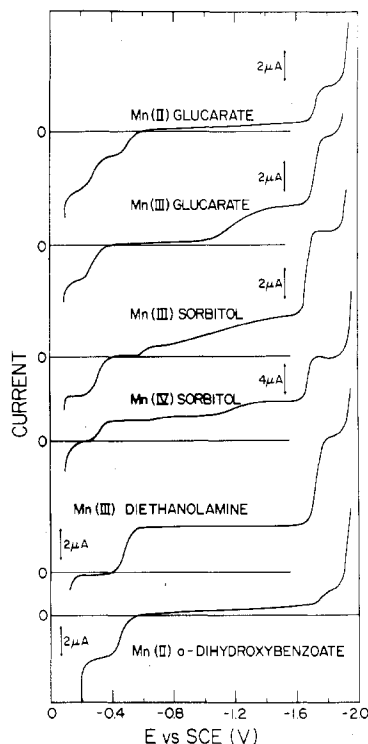


Figure 1. Polarograms of 1 mM $\text{Mn}^{\text{II}}(\text{ClO}_4)_2$ in solutions that contain 0.3 M NaOH and 0.1 M ligand. Mn(III) and Mn(IV) were produced from Mn(II) plus 1 and 2 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$, respectively.

Results

Aliphatic Polyhydroxy Complexes. Solutions of manganese(II) in the presence of alkaline glucarate ion (1,6-dicarboxylate derivative of D-glucose) result in a colorless complex that is stable when protected from oxygen. Polarograms for this complex exhibit a Mn(II)/Mn(IV) oxidation wave, a Mn(II)/Mn(III_B)⁴² oxidation wave, and a Mn(II)/Mn(0) reduction wave (Figure 1). The pink-orange manganese(III) glucarate complex is stable and gives three polarographic waves: a III_B/IV oxidation, a III_B/II reduction,⁴² and a II/0 reduction (Figure 1). The gold-orange Mn(IV) complex is stable for several hours before it eventually decomposes back to the Mn(III) complex. The three polarographic waves exhibited by this complex correspond to the IV/III_B, III_B/II, and II/0 reductions. The polarographic behavior of the manganese complexes that are formed by glucarate and the other polyhydroxy ligands is summarized in Table I. The Mn(III_B)/Mn(IV) oxidation and Mn(IV)/Mn(III_B) reduction occur at the same half-wave potential, which confirms that this is a reversible couple. Although a reduction wave for the Mn(III_A) polyhydroxy acid complexes is not observed, the value of $E_{3/4} - E_{1/4}$ for the Mn(II)/Mn(III_A) oxidation wave is 60 mV, which indicates that it meets one of the criteria for reversibility.⁴³ The Mn(III_B)/Mn(II) reduction wave is irreversible for this group of complexes and its half-wave potential is shifted negative by about 0.1 V for the Mn(IV) complexes.

When the glucarate concentration is lowered to 0.01 M (while maintaining all other conditions), a light yellow Mn(III) complex is formed. This complex exhibits the same polarographic behavior as the pink-orange complex; however, the half-wave potentials for the Mn(III_B) and Mn(II) reductions are shifted to -1.03 and -1.67 V vs. SCE, respectively.

Efforts to elucidate the electrode mechanisms for the redox reactions of the manganese complexes by use of cyclic voltammetry have been unsuccessful. The high background currents that result from the use of platinum, gold, or graphite

Table I. Polarographic Oxidation-Reduction Potentials for 1 mM Manganese Complexes in Solutions That Contain 0.1 M Ligand and 0.3 M NaOH

1. Aliphatic Polyhydroxy Complexes				
Ligand	Mn(III _B) ⇌ Mn(IV)	Mn(II) ⇌ Mn(III _A)	Mn(III _B) → Mn(II)	Mn(II) → Mn(0)
D-Gluconate	-0.28	-0.54	-1.07	-1.73
D-Glucarate	-0.28	-0.51	-1.19	-1.72
L-Tartrate	-0.22 ^a	-0.45	-0.95	-1.70
meso-Tartrate	-0.22 ^a	-0.46	-0.91	-1.73
Glycerate ^b	~0	-0.49	-0.87	-1.68
Sorbitol ^c	-0.32	-0.62	-1.11	-1.68
Mannitol ^c	-0.30	-0.61	-0.93	-1.67
Inositol ^c	-0.21	-0.62	-0.80	-1.66
meso-Erythritol ^c	-0.21	-0.53	-0.84	-1.66
Tartronate	~0	-0.39	-0.76	-1.69
Ethylene glycol ^{c,d}	~0	-0.52	-0.97	-1.66
Glycerol ^{b,c}	~0	-0.57	-0.86	-1.66
2,3-Butanediol ^{b,c}	~0	-0.59	-0.93	-1.66
Glycolate ^d	~0	-0.40		-1.69
2. Polyhydroxyamine Complexes				
Ligand	Mn(III) ⇌ Mn(IV)	Mn(III) ⇌ Mn(II)	Mn(II) → Mn(0)	
Triethanolamine	~0	-0.48	-1.72	
Diethanolamine	~0	-0.48	-1.72	
3. Aromatic Polyhydroxy Complexes				
Ligand	Mn(III) ⇌ Mn(II)	Mn(II) → Mn(0)		
Catechol	-0.52			
1,2-Dihydroxybenzene-3,5-disulfonate	-0.38			
3,5-Di- <i>tert</i> -butylcatechol	-0.61	-1.72		
2,3-Dihydroxybenzoate	-0.47	-1.74		
Tetrafluorocatechol	~-0.30			
4,5-Dihydroxynaphthalene-2,7-disulfonate ^{c,e}	-0.54	-1.67		
Salicylate ^b	-0.32	-1.74		

^a Irreversible. ^b 0.3 M ligand necessary for complex formation. ^c Mn(II) complex insoluble. ^d 1 M ligand necessary for complex stabilization. ^e 0.5 M NaOH.

electrodes in alkaline polyhydroxy media preclude meaningful measurements. With a mercury-film electrode the cyclic voltammetric data were not reproducible because of surface reactions by the product species. However, the faster electron-transfer kinetics that are imposed by this technique appear to result in the direct oxidation of the manganese(II) glucarate complex to its Mn(IV) form, without the intermediate formation of the Mn(III_A) complex.

Manganese complexes with L-tartrate and meso-tartrate are quite similar in chemical behavior. Solutions with the same base, ligand, and manganese concentrations as for the glucarate complexes result in colorless manganese(II) tartrate complexes which exhibit two oxidation waves and one reduction wave. These are similar to those observed for the manganese(II) glucarate complex, but with different half-wave potentials (Table I). Manganese(III) tartrate complexes differ from the corresponding glucarate complex in that they are light yellow in color and give three reduction waves but no oxidation wave. The Mn(III_A) reduction wave is small and occurs at a potential that corresponds to the Mn(II)/Mn(III_A) oxidation, which indicates that the couple is reversible. The Mn(III_B) reduction wave is much larger and irreversible. The manganese(IV) tartrate complex decomposes more rapidly than the manganese(IV) glucarate complex and exhibits a spontaneous IV/III_B reduction plus two reduction waves. The fact that

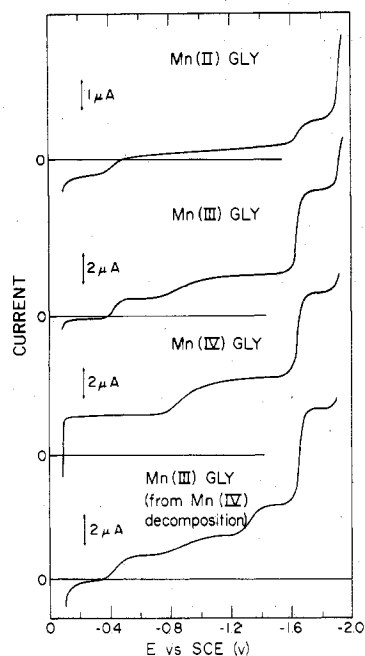


Figure 2. Polarograms of 1 mM $\text{Mn}^{\text{II}}(\text{ClO}_4)_2$ in solutions that contain 0.05 M NaOH and 0.3 M sodium glycerate.

a Mn(II)/Mn(IV) oxidation wave is observed for manganese(II) tartrate solutions, but not for Mn(III) solutions, while IV/III_B reduction is spontaneous, indicates a lack of reversibility. Manganese(IV) tartrate solutions only exhibit the Mn(III_B) reduction, which is shifted by about -0.05 V. As the Mn(IV) complex decomposes back to Mn(III_B), a polarographic reduction wave appears at about -1.3 V, which apparently is due to oxidized ligand.

Solutions that contain 1 mM Mn(II), 0.1 M tartronate, and 0.3 M NaOH result in a colorless complex that gives only one polarographic oxidation wave and one reduction wave (Table I). For analogous conditions the Mn(III) complex is yellow and exhibits three reduction waves that are similar to those for the manganese(III) tartrate complex. However, in the case of the tartronate complex, the reversible Mn(III_A) reduction wave is almost as large as the irreversible Mn(III_B) reduction wave. The manganese(IV) tartronate complex is orange and only momentarily stable before it decomposes to a brown precipitate. (The redox potential for this and other Mn(IV)/Mn(III) couples that have spontaneous polarographic reductions is estimated to be about 0.0 V because it lies between the cutoff potential for the dropping mercury electrode and the oxidation potential of the potassium ferricyanide that has been used to produce the Mn(IV).)

Figure 2 illustrates the polarographic behavior of the manganese glycerate complexes, which only are stable when the ligand concentration is 0.2 M or greater. The top curve is for the oxidation of the colorless Mn(II) complex to the Mn(III_A) complex and its reduction to the metal. The second curve is for the reversible Mn(III_A)/Mn(II), the irreversible Mn(III_B)/Mn(II), and the Mn(II)/Mn(0) reductions for the pink-orange Mn(III) species. As the base concentration is increased above 0.05 M, the Mn(III_B) reduction wave is enhanced at the expense of the Mn(III_A) reduction wave; at a base concentration of 0.5 M, the latter almost disappears. Decreases in the base concentration produce the opposite effect; at a base concentration of 0.01 M the Mn(III_B) reduction almost disappears. Increases in the ligand concentration also favor the Mn(III_B) species over the Mn(III_A) species.

The gold-orange manganese(IV) glycerate complex is spontaneously reduced and also exhibits III_B/II and II/0 reductions. At a base concentration of 0.03 M the manga-

nese(IV) glycerate complex exhibits a Mn(III_A) reduction which grows at the expense of the Mn(III_B) reduction as base concentration decreases. The Mn(IV) complex decomposes to Mn(III) in about 90 min, as illustrated by the bottom polarogram of Figure 2. This polarogram has the expected Mn(III) reduction waves plus an additional reduction wave at -1.3 V that is similar to the waves that are observed after the decomposition of manganese(IV) tartrates. These appear to be due to the reduction of oxidized ligand. This belief is supported by the observation that potassium ferricyanide slowly oxidizes a solution that contains 0.3 M glycerate and 0.05 M base to a product that exhibits a reduction wave at -1.3 V.

The oxidation and reduction waves for the glycerate complexes of the Mn(II)/Mn(III_A) couple have the same half-wave potentials. The Mn(II)/Mn(0) couple also appears to be reversible ($E_{3/4} - E_{1/4} = 30 \text{ mV}$). Because of the apparent reversibility of the two couples, a study of the dependence of the half-wave potential on hydroxide concentration has been made. For the Mn(II) reduction the relation⁴⁴

$$\Delta E_{1/2} = p(-0.0591/n)\Delta \log C_{\text{OH}^-} \quad (1)$$

has been used, where $E_{1/2}$ is the half-wave potential, C_{OH^-} the hydroxide concentration, n the number of electrons in the reduction step, and p the number of hydroxide equivalents incorporated into the complex. For the Mn(II)/Mn(III_A) oxidation the relation⁴⁵

$$\Delta E_{1/2} = (p - q)(-0.0591/n)\Delta \log C_{\text{OH}^-} \quad (2)$$

has been used, where p is the number of hydroxide equivalents per oxidized complex and q the number per reduced complex. For solutions that contain 1 mM Mn(II), 0.3 M sodium glycerate, and 0.01–0.5 M NaOH such a treatment of the polarographic data indicates that two hydroxides per Mn(II) are involved in the formation reaction for the complex and that two more are added when the Mn(III_A) complex is formed.

A meaningful determination of the glycerate stoichiometry has not been possible by use of the polarographic data because of the high ligand concentration that is required. However, increases in the glycerate concentration do not affect the half-wave potential for the Mn(II)/Mn(III_A) couple, but do shift the Mn(II)/Mn(0) wave to more negative potentials.

Visible spectroscopy has been used to characterize the manganese(III) glycerate complexes under conditions where the Mn(III_A) and Mn(III_B) species are favored. Solutions that contain 0.5 M sodium glycerate and 0.5 M NaOH lead to the predominant formation of the pink Mn(III_B) complex with absorption bands at 440 nm (ϵ 210) and 510 nm (ϵ 185). Solutions that contain 0.3 M sodium glycerate and 0.01 M NaOH result mainly in the light brown Mn(III_A) complex with an absorption band at 425 nm (ϵ 260).

Magnetic susceptibility studies also have been employed to distinguish between the Mn(III_A) and Mn(III_B) species. Reference to Table II indicates that the magnetic susceptibility value for the Mn(III_B) species is close to the spin-only value of 4.90 for this oxidation state. The value for the Mn(III_A) complex is somewhat lower. For a comparison, magnetic susceptibility measurements have been made for the two analogous manganese(III) gluconate species.²⁸ The manganese(III_B) gluconate complex also has a spin-only moment. In contrast, the manganese(III_A) gluconate complex has a magnetic susceptibility that is much lower than that for a complex with four unpaired electrons. The lower magnetic moments for the Mn(III_A) species probably result from the electron pairing that occurs upon formation of binuclear complexes.

Manganese glycolate complexes can be stabilized only in alkaline media that contain a large excess of ligand. The

Table II. Magnetic Susceptibilities for Manganese(III) Complexes^{a-d}

	μ, μ_B	
	Uncor	Cor
Manganese(III _A) glycerate, 0.05 M LiOH, 0.3 M sodium glycerate	4.68	4.71
Manganese(III _B) glycerate, 0.5 M LiOH, 0.5 M sodium glycerate	4.90	4.92
Manganese(III _A) gluconate, 0.05 M NaOH, 0.05 M sodium gluconate	3.92	4.04
Manganese(III _B) gluconate, 0.3 M LiOH, 1 M lithium gluconate	4.89	4.91
Manganese(III) triethanolamine, 0.3 M NaOH, 1 M TEA	4.72	4.74
Manganese(III) catechol, 0.15 M NaOH, 0.06 M catechol	4.96	4.98

^a All complexes are 20 mM. ^b Mn^{III} from Mn^{III}(OAc)₃. ^c All solutions are 0.1 M in DSS. ^d Reference solution for manganese(III_A) glycerate contains only 0.1 M DSS. In all other cases the reference solutions are identical with the sample solutions without manganese. ^e Theoretical magnetic moment for high-spin Mn(III) is 4.90 μ_B .

colorless Mn(II) complex exhibits an oxidation and a reduction wave, and the yellow Mn(III) complex yields two reduction waves (Table I). The Mn(IV) complex is orange and only momentarily stable.

The manganese complexes that are formed by six- and four-carbon polyols (sorbitol, mannitol, inositol, and meso-erythritol) have similar electrochemical and spectroscopic properties. In strongly alkaline solutions these ligands do not form soluble Mn(II) complexes but yield a silky, white precipitate. The light orange Mn(III) complexes that are formed by these ligands are soluble and exhibit a Mn(III_B)/Mn(IV) oxidation, two Mn(III)/Mn(II) reductions (with the exception of inositol), and a Mn(II)/Mn(0) reduction (Figure 1). The sorbitol and mannitol complexes only have a small Mn(III_A)/Mn(II) reduction wave, but the meso-erythritol complex has a III_A/II reduction wave that is almost as large as the Mn(III_B)/Mn(II) reduction wave. The manganese(III)-inositol complex only exhibits a III_A/II reduction wave.

The Mn(IV) complexes that are formed by these polyol ligands are gold-orange and stable for several hours before they decompose to Mn(III). The manganese(IV)-mannitol complex has three reduction waves, including one for the Mn(III_B)/Mn(II) reduction but not one for the Mn(III_A)/Mn(II) reduction. The other Mn(IV) complexes exhibit four reduction waves, including both a small Mn(III_A)/Mn(II) reduction and a larger Mn(III_B)/Mn(II) reduction. The Mn(III_A)/Mn(II) reduction for the manganese(IV) erythritol complex is shifted by -0.1 V.

Soluble Mn(II) complexes are not formed in alkaline solutions that contain short-chain polyols (ethylene glycol, 2,3-butanediol, and glycerol). Mn(III) complexes are formed by these ligands to give yellow to orange-yellow solutions. These complexes exhibit three reduction waves, including a Mn(III_A)/Mn(II) wave and a small Mn(III_B)/Mn(II) wave. The gold-orange Mn(IV) complexes give spontaneous polarographic reductions plus three reduction waves that correspond to those for the Mn(III) complexes. Both the Mn(III) and Mn(IV) solutions exhibit a slight degree of cloudiness.

Polyhydroxyamine Complexes. Triethanolamine (TEA) and diethanolamine (DEA) form colorless Mn(II) complexes in alkaline solutions. Both complexes display almost identical polarograms, with a reversible Mn(II)/Mn(III) oxidation and an apparently reversible Mn(II)/Mn(0) reduction wave ($E_{3/4} - E_{1/4} = 30$ mV). The green Mn(III)-TEA and -DEA complexes give polarograms with two reduction waves (Figure 1). The magnetic susceptibility for the Mn(III)-TEA

complex, which is somewhat lower than the spin-only value, is compared with the values for other Mn(III) complexes in Table II.

Addition of excess K₃Fe(CN)₆ to the Mn(III)-TEA and -DEA complexes yields red-orange Mn(IV) complexes which decompose to Mn(III) in about 15 min. These complexes give a spontaneous polarographic reduction current plus the two reduction waves that are observed for the Mn(III) complexes. The addition of excess hydrogen peroxide to Mn(III)-TEA solutions leads to the formation of a short-lived pink complex, quite different in appearance from the Mn(IV) species.

The dependence of the half-wave potentials for the Mn(III)/Mn(II) and Mn(II)/Mn(0) couples on TEA and hydroxide concentrations has been studied by use of the relations in eq 1 and 2.^{44,45} Such studies indicate that two TEA ligands are incorporated per metal in the Mn(II) and Mn(III) complexes. They also indicate that 3 equiv of hydroxide/equiv of metal is consumed in the formation of the Mn(II) and Mn(III) complexes when the hydroxide concentration is greater than 0.1 M. At lower concentrations there is some change in the hydroxide stoichiometry for the complexes.

Ethanolamine does not form stable Mn(II), -(III), or -(IV) complexes in alkaline media, which confirms that two or more hydroxy groups are necessary for complexation.

Aromatic Polyhydroxy Complexes. Catechol, 2,3-dihydroxybenzoate (DHBA), di-*tert*-butylcatechol (DTBC), tetrafluorocatechol (TFC), 1,2-dihydroxybenzene-3,5-disulfonate (Tiron), and salicylate form colorless Mn(II) complexes in alkaline solutions.⁴⁶ All of these complexes exhibit reversible Mn(II)/Mn(III) polarographic oxidation waves (Table I). The complexes formed by DTBC, DHBA, and salicylate also exhibit a Mn(II)/Mn(0) reduction wave, but the other complexes do not. For solutions that contain 0.1 M 4,5-dihydroxynaphthalene-2,7-disulfonate (DHNSA) and less than 0.2 M NaOH, a soluble Mn(II) complex is formed that exhibits an irreversible oxidation wave at -0.05 V and a Mn(II)/Mn(0) reduction wave at -1.54 V.

This same group of ligands also produces soluble, stable Mn(III) complexes under alkaline conditions.⁴⁶ Unfortunately, the oxidation of excess ligand by K₃Fe(CN)₆ often precludes complete oxidation of the Mn(II) complex to its Mn(III) form. This is especially true for the TFC complex, which is oxidized at a potential that is only 0.05 V less positive than that for the free ligand. For this reason, only a small amount of the Mn(III)-TFC complex can be produced by K₃Fe(CN)₆ addition. Manganese(III) acetate is a useful source of trivalent manganese for the formation of complexes with catechol, DHBA, Tiron, and DHNSA. Polarograms for the Mn(III) aromatic polyhydroxy complexes exhibit reversible Mn(III)/Mn(II) reductions and Mn(II)/Mn(0) reduction waves, which correspond to those observed for their Mn(II) complexes. Formation of Mn(IV) complexes by these ligands is not possible because the ligands are more easily oxidized than is Mn(III).

Mn(III) complexes that are formed by aromatic polyhydroxy ligands range in color from green for the catechol complex to yellow for the salicylate complex. The visible absorption spectra for the Mn(III) complexes with catechol, Tiron, DTBC, DHBA, and DHNSA are presented in Figure 3. All of the complexes exhibit apparent d-d absorption shoulders at wavelengths between 550 and 750 nm. The small variations in the spectra for the five complexes probably are due to aromatic substituent effects. Mole ratio studies conducted with manganese(III) acetate and catechol in alkaline media indicate that the complex contains three ligands per metal ion. The other aromatic polyhydroxy ligands do not form sufficiently stable Mn(III) complexes for meaningful mole ratio studies.

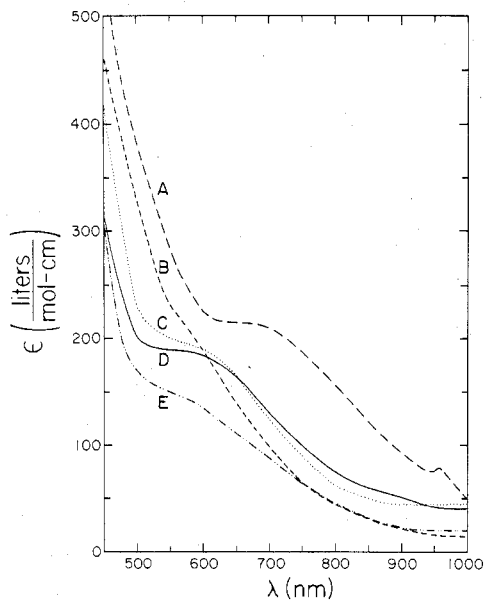


Figure 3. Visible absorption spectra for manganese(III) complexes with aromatic polyhydroxy ligands: (A) 0.4 mM $\text{Mn}^{\text{II}}(\text{ClO}_4)_2$, 0.4 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.3 M NaOH, 0.1 M DTBC; (B) 3 mM $\text{Mn}^{\text{III}}(\text{OAc})_3$, 0.5 M NaOH, 0.1 M DHNDSA; (C) 4 mM $\text{Mn}^{\text{III}}(\text{OAc})_3$, 0.3 M NaOH, 0.1 M Tiron; (D) 10 mM $\text{Mn}^{\text{III}}(\text{OAc})_3$, 0.3 M NaOH, 0.1 M catechol; (E) 2.5 mM $\text{Mn}^{\text{III}}(\text{OAc})_3$, 0.3 M NaOH, 0.1 M DHBA.

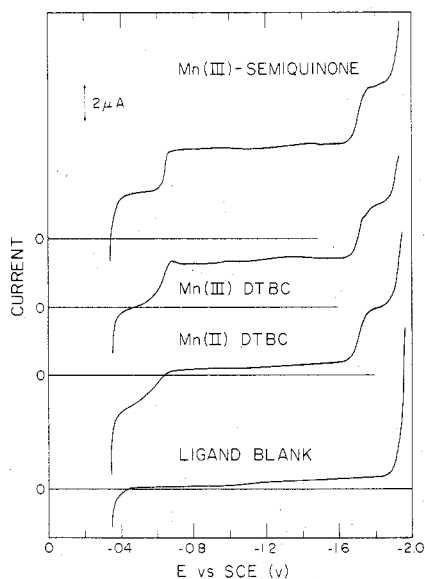


Figure 4. Polarograms of 1 mM $\text{Mn}^{\text{II}}(\text{ClO}_4)_2$ in solutions that contain 0.3 M NaOH and 0.1 M DTBC (ligand blank contains no manganese). $\text{Mn}(\text{III})$ and manganese(III) semiquinone were produced from $\text{Mn}(\text{II})$ plus 1 and 2 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$, respectively.

The tris(catechol)manganese(III) complex is oxidized by molecular oxygen or potassium ferricyanide to a short-lived, intensely blue complex, which appears to include the semiquinone of catechol. This complex decomposes to give a green-yellow solution.

The magnetic susceptibility of the manganese(III)-catechol complex also has been measured. Its value, along with those for other $\text{Mn}(\text{III})$ complexes, is summarized in Table II and is in close agreement with the spin-only value.

The manganese-DTBC system has some unique properties in addition to those of the other aromatic polyhydroxy complexes (Figure 4). The yellow-green $\text{Mn}(\text{III})$ complex that results from the addition of a stoichiometric equivalent of $\text{K}_3\text{Fe}(\text{CN})_6$ to the $\text{Mn}(\text{II})$ complex gives two reduction

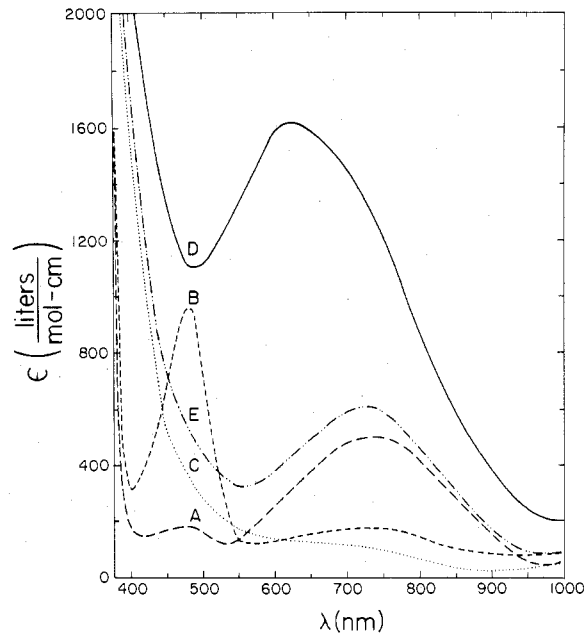


Figure 5. Visible absorption spectra for solutions that contain 0.3 M NaOH and 0.1 M DTBC plus: (A) 1 mM semiquinone from oxidation of ligand by 1 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$; (B) decomposition product from semiquinone of (A) after 24 h; (C) 1 mM $\text{Mn}^{\text{III}}\text{DTBC}$ from $\text{Mn}^{\text{II}}(\text{ClO}_4)_2$ plus 1 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$; (D) manganese(III) semiquinone from 1 mM $\text{Mn}^{\text{II}}(\text{ClO}_4)_2$ plus 2 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$; (E) summation of curves A and C.

waves (Table I). Addition of another equivalent of $\text{K}_3\text{Fe}(\text{CN})_6$ produces an intense blue $\text{Mn}(\text{III})$ -DTBC semiquinone complex, which exhibits a spontaneous reduction plus the two reduction waves that are observed for the $\text{Mn}(\text{III})$ -DTBC complex. The complex decomposes in about 24 h to give a green solution.

When 1 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$ is added to the DTBC ligand in alkaline media, a blue semiquinone species is produced which gives a spontaneous polarographic reduction current of about the same magnitude as that for the manganese(III)-semiquinone complex. Both polarography and spectroscopy indicate that the free DTBC semiquinone will oxidize an equivalent amount of $\text{Mn}(\text{II})$ to produce the $\text{Mn}(\text{III})$ -DTBC complex. The free semiquinone decomposes in about 24 h to give a yellow solution. The decomposition products from the manganese(III)-semiquinone complex and from free semiquinone obscure meaningful polarographic measurements.

The absorption spectrum for free DTBC semiquinone, which exhibits a strong band at 740 nm and a weak band at 480 nm, is illustrated by curve A of Figure 5; curve B is for the yellow DTBC semiquinone decomposition product. The 740-nm band appears to correspond to the semiquinone and the 480-nm band to the decomposition product that is present in both solutions. Curve C illustrates the comparatively low-intensity spectrum for the $\text{Mn}(\text{III})$ DTBC complex. The manganese(III) semiquinone complex has a strong band at 620 nm, which is illustrated by curve D. Curve E of Figure 5 represents the summation of the absorbances for curves A and C. Comparison of curve D and curve E establishes that the former represents a unique $\text{Mn}(\text{III})$ -DTBC semiquinone complex and not merely the combined spectra of the free DTBC semiquinone and the $\text{Mn}(\text{III})$ -DTBC complex. Spectroscopy also confirms that the decomposition product from the $\text{Mn}(\text{III})$ -DTBC semiquinone complex is the same as that from the free semiquinone.

The spectra of Figure 6 provide additional insight into the nature of the $\text{Mn}(\text{III})$ -DTBC semiquinone complex. Curve A represents the spectrum for the free DTBC semiquinone,

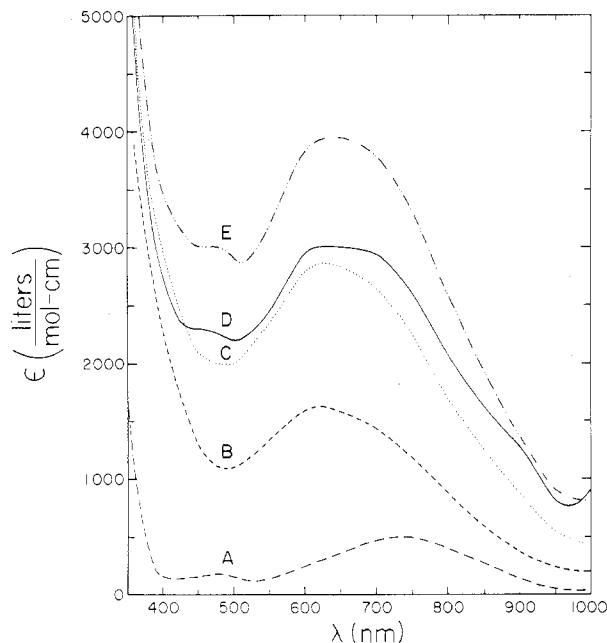


Figure 6. Visible absorption spectra for solutions that contain 0.3 M NaOH and 0.1 M DTBC plus: (A) 1 mM semiquinone from oxidation of ligand by 1 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$; (B), (C), (D), and (E) manganese(III) semiquinone from 1 mM $\text{Mn}^{\text{II}}(\text{ClO}_4)_2$ plus 2, 3, 4, and 5 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$, respectively.

and curve B the spectrum for the manganese(III)–semiquinone complex formed by the addition of 2 equiv of $\text{K}_3\text{Fe}(\text{CN})_6$ to the Mn(II)–DTBC complex. Addition of another equivalent of $\text{K}_3\text{Fe}(\text{CN})_6$ approximately doubles the intensity for the 620-nm band (curve C), which indicates the formation of a complex with two semiquinone ligands per manganese. Addition of a fourth equivalent of $\text{K}_3\text{Fe}(\text{CN})_6$ does not significantly increase the 620-nm band, but it does broaden it and also produces a band at 480 nm (curve D). This indicates that the formation of some free semiquinone and semiquinone decomposition product is favored over the formation of a third stoichiometric equivalent of manganese-bound DTBC semiquinone. Curve E illustrates that the addition of a fifth equivalent of $\text{K}_3\text{Fe}(\text{CN})_6$ slightly increases the 480-nm band and significantly increases the 620-nm band. The 2.5-fold increase in the 620-nm band in curve E over that in curve B indicates that the Mn(III)–DTBC complex can be oxidized to form a tris(DTBC semiquinone)manganese(III) complex.

Discussion and Conclusions

The data of Figure 1 and Table I establish that polyhydroxy ligands form stable complexes with Mn(II), -(III), and -(IV) ions in alkaline media. Such complexes appear to be the result of the expected strong interactions between the “hard acid” character of the metal ions and the “hard base” character of the oxo anions of the ligands. The complexes are stabilized further by the chelate effect that results from the formation of five- and six-membered rings. As a result, the ligands compete effectively with hydroxide ion for the metal-binding sites to give soluble complexes. The carboxylate and amine groups of some of the ligands also act as “hard bases” but do not effectively compete with the stronger oxo anion and hydroxide ion bases. In our view, the anions of the polyhydroxy ligands represent the equivalent of “polyhydroxide ions” that yield soluble complexes because of their associated organic functionality.

The Mn(II), -(III), and -(IV) complexes that are formed by glucarate ion (a dicarboxylate) appear to be representative of the aliphatic, polyhydroxy class of ligands and similar to those formed by the gluconate ion (a monocarboxylate).²⁸

However, the manganese(III_B) glucarate complex appears to be more stable relative to the Mn(II) complex than does the manganese(III_B) gluconate complex (see Table I), and a Mn(III_A)/Mn(II) reduction is not observed for the glucarate system. The electrochemical data indicate that the manganese(III) and -(IV) tartrate complexes are less stable than those formed by the glucarate and gluconate ligands. The L-tartrate configuration also appears to stabilize the Mn(III_B) species slightly better than *meso*-tartrate. The smaller polyhydroxy acid ligands (tartronate, glycerate, and glycolate) form even less stable manganese complexes. This may result because the smaller ligands must make use of the carboxylate groups to form chelate rings, and such groups do not bind manganese as strongly as oxo anion groups. These smaller ligands also may be less able to stabilize the negative charge that results from deprotonation of the hydroxy groups.

The aliphatic polyol ligands form stable, soluble complexes with both Mn(III) and -(IV). On the basis of the data in Table I the Mn(III_A) polyol complexes are more stable than their comparable Mn(III_A) polyhydroxy acid complexes. The polyol ligands do not form soluble Mn(II) complexes unless the hydroxide and ligand concentrations are increased beyond those employed for the polyhydroxy acid complexes.^{24,26,27} This indicates that the carboxylate group aids in the solubilization of the Mn(II) complexes. Again, there is a tendency for the stability of manganese complexes to decrease as the size of the polyol decreases. On the basis of the electrochemical results, the mannitol configuration produces a less stable Mn(III_B) species than does its epimer, sorbitol. The UV-visible spectra for the Mn(III) and -(IV) complexes with sorbitol and mannitol are almost identical.^{24,26} They also correspond well to the spectra for manganese(III) glycerate and the manganese(III) and -(IV) gluconate complexes.²⁸ The Mn(IV) complexes all decompose with time by oxidation of the ligand.

Almost all of the aliphatic polyhydroxy ligands form two different Mn(III) complexes. Polarography shows that a soluble Mn(II) complex is reversibly oxidized to the Mn(III_A) complex. This, in turn, rearranges to form the Mn(III_B) complex until an equilibrium is reached. Because the rate of equilibration is slow, polarograms of Mn(III) systems exhibit a reversible reduction wave for the Mn(III_A) complex, as well as an irreversible reduction wave at more negative potential for the Mn(III_B) complex. Studies with both glycerate and gluconate²⁸ indicate that the Mn(III_B) complex is favored as the ligand concentration is increased.⁴⁷ Polarographic and spectrophotometric data indicate that the Mn(II) and Mn(III_A) aliphatic polyhydroxy complexes have ligand-to-manganese stoichiometries of 2:1.^{23,24,26–28} Hence, because the formation of the Mn(III_B) complex is favored by increasing ligand concentration, it must have a ligand:metal stoichiometry that is greater than 2:1; a 3:1 stoichiometry appears reasonable. The fact that the Mn(IV) complexes tend to give only the Mn(III_B)/Mn(II) polarographic reduction implies that the Mn(IV) and Mn(III_B) complexes have similar stoichiometries and structures.

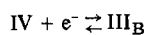
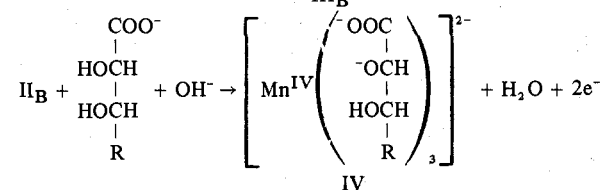
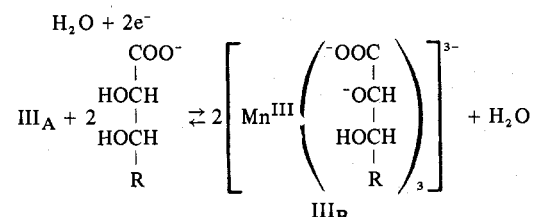
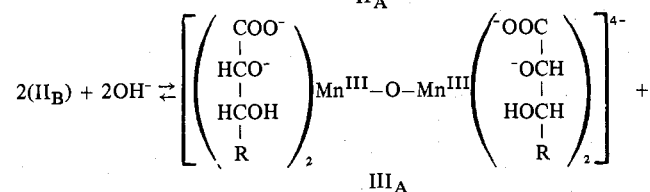
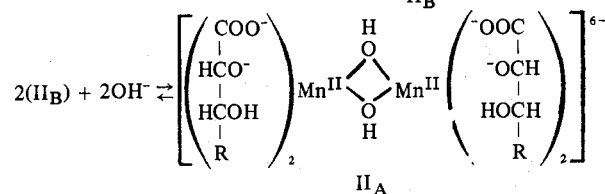
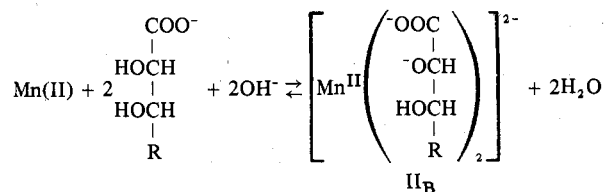
The circular dichroism (CD) spectra for the manganese(III_B) and manganese(IV) glucarate complexes are almost identical,⁴⁸ which is supportive of the conclusion that these two complexes have similar structures. In contrast, the manganese(III_A) glucarate complex exhibits a completely different CD spectrum.

The magnetic moments for the Mn(III_A) complexes formed by glycerate and gluconate are lower than those for the Mn(III_B) complexes (Table II); the latter are close to the spin-only value. The magnetic moment for the manganese(III_A) gluconate complex is especially low and indicates that some electron pairing occurs, probably through formation of

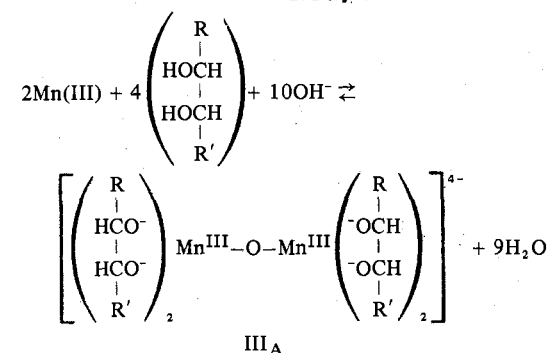
Table III. Proposed Formation Reactions for the Mn(II), -(III), and -(IV) Complexes with Polyhydroxy Ligands

A. Aliphatic Polyhydroxy Ligands

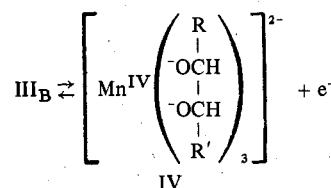
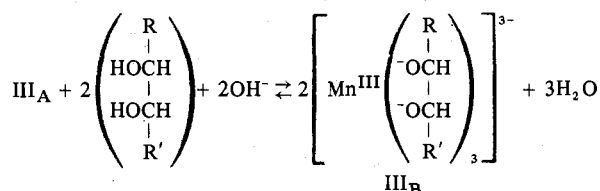
1. Hydroxy Acids



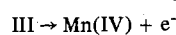
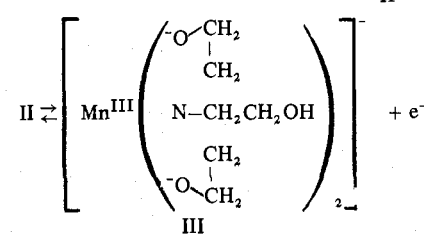
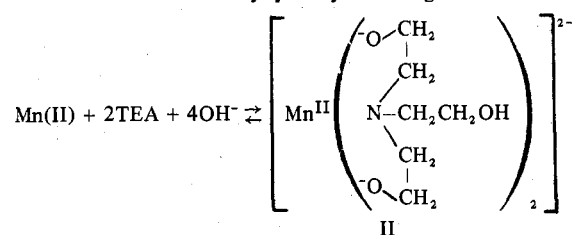
2. Polyols



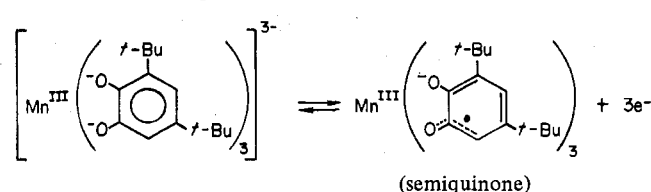
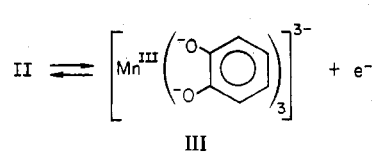
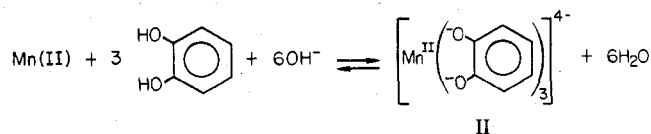
2. Polyols (Continued)



B. Polyhydroxyamine Ligands



C. Aromatic Polyhydroxy Ligands



a binuclear complex. The long-chain ligands appear to favor the formation of the Mn(III_B) complex and the short-chain ligands and inositol (hexahydroxycyclohexane) the formation of the Mn(III_A) species.

On the basis of the data and the preceding arguments, formation reactions for the manganese-polyhydroxy complexes are presented in Table III. We believe that the stoichiometries are supported by the spectrophotometric and polarographic data and that the proposed formation of binuclear systems is consistent with the magnetic susceptibility data.

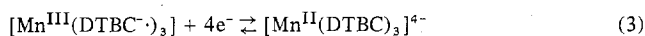
Both DEA and TEA form stable Mn(II) and Mn(III) complexes, and transiently stable Mn(IV) complexes which

decompose through oxidation of the ligand. Reference to Table I indicates that these manganese complexes have about the same stabilities as those for the corresponding aliphatic polyhydroxy complexes; however, they do not exhibit a Mn(III_B)/Mn(II) polarographic reduction. The fact that DEA and TEA appear to form almost identical complexes whereas ethanolamine does not complex manganese ions indicates that two hydroxy groups are necessary for ligand binding. Because electrochemical and spectroscopic studies¹³ indicate that the TEA-to-manganese stoichiometry for the Mn(II) and -(III) complexes is 2:1, each ligand probably binds through the nitrogen and two deprotonated oxygens to form an octahedral

complex (see Table III). There is some evidence that the Mn(III)-TEA complex is uncharged,¹⁷ which would require that only three deprotonated oxygens from the two TEA ligands be bound to the manganese. The remaining octahedral coordination site then must be occupied by an uncharged complexing agent. The somewhat depressed magnetic moment for the Mn(III)-TEA complex may indicate some intermetal binding by the ligands with attendant electron pairing.

The aromatic polyhydroxy ligands form stable Mn(II) and -(III) complexes. Manganese(IV) complexes are not formed because the ligands are more easily oxidized than the Mn(III) ion. The ability of the ligands to stabilize the Mn(III) complex relative to that for Mn(II) decreases in the order DTBC > DHNSA, catechol > DHBA > Tiron > salicylate, TFC (Table I). The order of stability for the *o*-dihydroxybenzene ligands appears to result from substituent effects. The relative instability of the manganese(III) salicylate complex indicates that two adjacent aromatic hydroxy groups bind Mn(III) more effectively than adjacent aromatic hydroxy and carboxylate groups. The fact that the Mn(III)-DHBA complex exhibits properties more like those for the catechol complex rather than the salicylate complex indicates that the DHBA ligand binds primarily through its two hydroxy groups and not through its carboxylate group. Comparison with other polyhydroxy ligands indicates that the Mn(II) and -(III) complexes are stabilized to about the same extent; however, why several aromatic polyhydroxy ligands do not exhibit Mn(II)/Mn(0) polarographic reductions is not known. This and other studies^{30,31,33} indicate that manganese tends to form tris complexes with catechol and other aromatic polyhydroxy ligands (see Table III).

The presence of *tert*-butyl blocking groups on the catechol aromatic ring makes it possible to oxidize DTBC reversibly to a stable semiquinone in basic media. Oxidation of the Mn(III)-DTBC complex leads to the formation of a stable manganese(III)-semiquinone complex (Figures 4-6). The ability of small amounts of the semiquinone to complex Mn(III) in the presence of much larger amounts of DTBC indicates that it is a much better ligand for Mn(III) than catechol. The semiquinone complex of Mn(III) appears to have a ligand-to-metal stoichiometry of 3:1 and to act as a four-electron oxidizing agent



where DTBC⁻ is the semiquinone. The tris(semiquinone)-manganese(III) complex cannot be obtained by stoichiometry oxidation because of competing equilibria that involve the formation of free semiquinone, Mn-DTBC complexes, and a decomposition product from the semiquinone.

Although the polyhydroxy ligands stabilize and solubilize the Mn(II), -(III), and -(IV) ions, these complexes do not appear to be realistic reaction models for the manganese cofactor in photosystem II. An ideal model complex should stabilize the higher oxidation states of manganese, resist ligand oxidation, and provide a four-electron oxidizing stoichiometry per complex. Such a model also should provide a redox couple with a potential of +0.2 V vs. SCE or more at pH 14³⁰ and a sterically and kinetically convenient pathway for the oxidation of water to molecular oxygen. A tetrameric Mn(III) complex is a possible model which would satisfy these requirements. A more likely model would be a binuclear Mn(IV) complex with di- μ -oxo bridging, such as has been reported for Mn(IV) complexes.^{49,50} Such systems may provide a mechanism by which the bridging oxygens are themselves oxidized to molecular oxygen and then re-formed by water to complete the cycle. Another possible model would involve a manganese complex with ligands that can be reversibly oxidized, much like the tris(DTBC semiquinone)manganese(III) complex. Such a complex could store oxidizing power in both

the manganese ion and the ligands.

Acknowledgment. This work was supported by the U.S. Public Health Service-NIH under Grant No. GM-22761.

Registry No. Mn, 7439-96-5; D-gluconic acid, 526-95-4; D-glucuronic acid, 87-73-0; L-tartaric acid, 87-69-4; *meso*-tartaric acid, 147-73-9; glyceric acid, 473-81-4; sorbitol, 50-70-4; mannitol, 69-65-8; inositol, 87-89-8; *meso*-erythritol, 149-32-6; tartronic acid, 80-69-3; ethylene glycol, 107-21-1; glycerol, 56-81-5; 2,3-butanediol, 513-85-9; glycolic acid, 79-14-1; triethanolamine, 102-71-6; diethanolamine, 929-06-6; 1,2-dihydroxybenzene-3,5-disulfonic acid, 149-46-2; 3,5-di-*tert*-butylcatechol, 1020-31-1; 2,3-dihydroxybenzoic acid, 303-38-8; tetrafluorocatechol, 1996-23-2; 4,5-dihydroxynaphthalene-2,7-disulfonic acid, 148-25-4; salicylic acid, 69-72-7; manganese(III_A) glycerate, 65120-29-8; manganese(III_B) glycerate, 65120-28-7; manganese(III_A) gluconate, 65149-40-8; manganese(III_B) gluconate, 65120-51-6; manganese(III) triethanolamine, 65120-50-5; manganese(III) catechol, 65120-49-2; catechol, 120-80-9.

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- The term manganese(III_A) refers to the manganese complex that is reversibly formed from the manganese(II) complex at less negative potentials. The term manganese(III_B) refers to the complex that is irreversibly reduced to the manganese(II) complex at more negative potentials.

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Contribution from the Departments of Inorganic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, Great Britain, and University of Oxford, Oxford, OX1 3QR, Great Britain

Characterization by Infrared and Raman Spectroscopy of Matrix-Isolated $M(\text{CO})_5\text{N}_2$ ($M = \text{Cr}, \text{Mo}, \text{or W}$) Produced by Photolysis of $M(\text{CO})_6$ ^{1a}

JEREMY K. BURDETT,^{*1b} ANTHONY J. DOWNS,^{*1c} GEOFFREY P. GASKILL,^{1c} MICHAEL A. GRAHAM,^{1b} JAMES J. TURNER,^{*1b} and ROBERT F. TURNER^{1b}

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Photolysis of matrix-isolated molybdenum hexacarbonyl in the presence of dinitrogen leads to the formation of the hitherto unknown molybdenum pentacarbonyl dinitrogen $\text{Mo}(\text{CO})_5\text{N}_2$; the product has been detected by its infrared and Raman spectra which, with the aid of polarization measurements and isotopic variations involving ¹⁵N and ¹³CO enrichment, serve to characterize its stoichiometry and geometry. The formation under similar conditions of the analogous species chromium and tungsten pentacarbonyl dinitrogen has been demonstrated unequivocally by monitoring the Raman spectra of matrices containing the corresponding hexacarbonyls in the presence of dinitrogen. Confirmation of the C_{4v} symmetry of the molybdenum pentacarbonyl dinitrogen molecule, with the linear $\text{Mo}-\text{N}\equiv\text{N}$ unit thus implied, is provided by an analysis using a frequency-factored force field of the infrared-active C—O stretching modes of the isotopic variants $\text{Mo}(\text{CO})_x(\text{C}^{13}\text{CO})_{5-x}\text{N}_2$ ($x = 0-5$), and an estimate of $90 \pm 4^\circ$ for the $\text{OC}_{\text{ax}}-\text{Mo}-\text{CO}_{\text{eq}}$ bond angle has been derived from the relative intensities of the bands due to $\text{Mo}(\text{CO})_5\text{N}_2$. Consideration is given, insofar as the results allow, to the likely contribution made by the N_2 oscillator to the force field of $\text{Mo}(\text{CO})_5\text{N}_2$; hence it is evident that some provision must be made for CO_2N_2 coupling if the finer details of the vibrational properties are to be interpreted. The species $M(\text{CO})_5\text{N}_2$ ($M = \text{Cr}, \text{Mo}, \text{or W}$), unlike $\text{X}\cdots\text{M}(\text{CO})_5$ ($\text{X} = \text{Ar}$ or CH_4), is stable with respect to irradiation in the green region of the visible spectrum, and a scheme has been devised for the photochemical interconversion of the three species $\text{Mo}(\text{CO})_6$, $\text{Mo}(\text{CO})_5\text{N}_2$, and $\text{X}\cdots\text{M}(\text{CO})_5$ in a mixed matrix composed of N_2 and X molecules.

1. Introduction

To the familiar binary carbonyls and the more recently described binary dinitrogen derivatives of transition metals, synthesized in low-temperature matrices,²⁻⁷ have been added mixed carbonyl dinitrogen species. For example, $\text{Ni}(\text{CO})_3\text{N}_2$ has been made⁸ by photolysis of nickel tetracarbonyl in a solid nitrogen matrix, and the complete series of molecules $\text{Ni}(\text{CO})_x(\text{N}_2)_{4-x}$ ($x = 1-3$) later identified⁹ in the products formed by cocondensing nickel atoms with nitrogen/carbon monoxide mixtures at 10 K. Such molecules are of interest not merely because of their novelty but also because of the light shed by their structures, vibrational properties, and photochemistry on the bonding and reactions of the moieties $\text{M}-\text{CO}$ and $\text{M}-\text{N}_2$ formed by a metal M. In this paper we describe the characterization in terms of its infrared and Raman spectra of the molecule $\text{Mo}(\text{CO})_5\text{N}_2$ prepared by photolysis of molybdenum hexacarbonyl in matrices composed of pure nitrogen or mixtures of nitrogen with either methane or argon. The use of ¹⁵N-enriched N_2 or ¹³CO-enriched $\text{Mo}(\text{CO})_6$ leaves no doubt about the stoichiometry of the product; less certain is the mode of coordination of the N_2 molecule although all the spectroscopic information available is compatible with a molecular model with C_{4v} symmetry and with a linear $\text{Mo}-\text{N}\equiv\text{N}$ moiety. We consider here the vibrational force field, structure, ultraviolet/visible spectrum, and photochemistry of the new species.

Similar both in mode of formation and in structure, it appears, are the molecules $\text{Cr}(\text{CO})_5\text{N}_2$ and $\text{W}(\text{CO})_5\text{N}_2$ identified by their Raman spectra following the photolysis of either a nitrogen matrix or a methane matrix doped with nitrogen incorporating the corresponding hexacarbonyl. Although the carbonyl dinitrogen systems of chromium, molybdenum, and tungsten are evidently closely related in the spectral patterns and photochemistry which they exhibit, the

present account is concerned preeminently with the molybdenum system for which there is maximum common ground between the infrared and Raman measurements carried out for the most part independently in our two laboratories.¹⁰ The formation and trapping in matrices of other mixed carbonyl dinitrogen derivatives of molybdenum, which have been characterized only by their infrared spectra, will be treated separately in a future paper;¹¹ elsewhere too will be found a more detailed account of the experiments exploring the suitability of the Raman effect for monitoring photochemical changes of matrix-isolated metal carbonyls.¹²

To the best of our knowledge, the only allusion hitherto made to a mixed carbonyl dinitrogen derivative of the group 6 elements concerns the chromium compound $\text{Cr}(\text{CO})_5\text{N}_2$ predicted to be thermodynamically stable on the grounds of a theoretical study.¹³ This compound has also been postulated by Nasielski and Wyart¹⁴ as an intermediate in the photochemical reactions of chromium hexacarbonyl contained in cyclohexane solution and with an overpressure of gaseous nitrogen. The results of flash photolysis experiments have shown an absorption at 370 nm which has been attributed to the transient $\text{Cr}(\text{CO})_5\text{N}_2$; the half-life of this species varies with the nitrogen pressure but is in the order of seconds at room temperature. A new band has also been observed to develop at ca. 1970 cm^{-1} in the infrared spectrum of a cyclohexane solution of the hexacarbonyl held at room temperature under an atmosphere of nitrogen, but only for as long as the solution is irradiated.

2. Raman Spectra of the Matrix-Isolated Molecules $M(\text{CO})_6$ and $M(\text{CO})_5$ ($M = \text{Cr}, \text{Mo}, \text{or W}$)

It has now been established beyond doubt that the photolysis of the hexacarbonyl $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{or W}$) in an argon or methane matrix generates the corresponding pentacarbonyl