## PREPARATION AND CHARACTERIZATION OF DICHLOROBIS(N-ALKYL-SUBSTITUTED SALICYLIDENEAMINATO)MANGANESE(IV) COMPLEXES

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Abstract—A series of dichlorobis(N-alkyl-substituted salicylideneaminato)manganese(IV) complexes, Mn(N-R-Xsal)<sub>2</sub>Cl<sub>2</sub>, was prepared by the reaction of Mn(N-R-Xsal)<sub>2</sub>Cl complexes with hydrogen chloride, where R can be  $n-C_8H_{17}$  (Oct),  $n-C_{12}H_{25}$  (Dod),  $n-C_{18}H_{37}$  (Octd), and CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (Bz) and X can be 5-bromo, 5-nitro, and 5,6-benzo groups. These complexes were characterized by the magnetic susceptibilities, IR and electronic spectra, and cyclic voltammograms.

Manganese(III) and -(IV) complexes are of interest in relation to the biological redox systems catalyzed by include disions. which the manganese proportionation of superoxide ion  $(O_2^-)$  by the manganese-containing superoxide dismutases and the photosynthetic oxygen evolution by water oxidation in green plants.<sup>1,2</sup> Although a number of manganese(III) complexes with various ligands have been investigated, very few manganese(IV) complexes have been isolated and characterized so far. The reason seems to be that manganese(IV) ion is a strong oxidizing agent and its complexes are unstable toward moisture.3,4

Previously we have found that a series of chloromanganese(III) complexes with the bidentate and tetradentate Schiff base ligands reacts with hydrogen chloride to give the corresponding dichloromanganese(IV) complexes as deep green crystals.<sup>5</sup> These complexes, however, are not stable toward water even in the solid state and decompose gradually to their reduced manganese(III) complexes. In an earlier paper we have shown that the dichloromanganese(IV) complexes with the bidenatae Schiff bases which were derived from salicylaldehyde and long-chain aliphatic monoamines such as  $n-C_{12}H_{25}NH_2$  and  $n-C_{18}H_{37}NH_2$ are more stable toward water than those derived from  $n-C_{3}H_7NH_2$  and  $n-C_4H_9NH_2$ .<sup>6</sup>

Present paper describes the preparation and characterization of new dichloromanganese(IV) complexes as shown in Fig. 1.

## **EXPERIMENTAL**

Preparation of Mn(III) Schiff Base Complexes, Mn(N-R-Xsal)<sub>2</sub>Cl. Chlorobis(N - dodecyl - 5 - bromosalicylideneaminato)manganese(III), Mn(N - Dod - 5 -Brsal)<sub>2</sub>Cl. N - Dodecyl - 5 - bromosalicylideneamine (N -Dod - 5 - BrsalH) was prepared by the condensation of 5-bromosalicylaldehyde and equimolar dodecylamine in tetrahydrofuran. This was recrystallized from ether. The other bidentate Schiff bases were prepared in a similar manner. Their melting points and analytical data are listed in Table 1.

To an ethanol solution  $(100 \text{ cm}^3)$  of N-Dod-5-BrsalH (7.37 g, 0.02 mol), Mn(III)  $(CH_3CO_2)_3$ ·2H<sub>2</sub>O (2.68 g, 0.01 mol) and LiCl (0.84 g, 0.02 mol) were added. The mixture was warmed at 60°C for 1 hr with stirring and then

evaporated to remove the solvent under reduced pressure. The resulting brown solids were collected on a glass filter, washed with small amounts of ethanol, and dried *in vacuo*. They were extracted with dichloromethane  $(150 \text{ cm}^3)$ , and the solution was evaporated to give brown solids. They were recrystallized from acetonitrile.

The other manganese(III) complexes were prepared in a similar manner. The solvents employed for recrystallization were acetonitrile for  $Mn(N-Oct-5-Brsal)_2CI$ ,  $Mn(N-Oct-5,6-Benzosal)_2CI$ ,  $Mn(N-Oct-5,6-Benzosal)_2CI$ ,  $Mn(N-Oct-5-NO_2sal)_2CI$ , and  $Mn(N-Octd-5-Brsal)_2CI$ , acetone for  $Mn(N-Octd-5-Brsal)_2CI$  and  $Mn(N-Octd-5,6-Benzosal)_2CI$ , dichloromethane for  $Mn(N-Bz-5Brsal)_2CI$  and  $Mn(N-Octd-5-NO_2sal)_2CI$ , methanol for  $Mn(N-Bz-5-Brsal)_2CI$ , and N,N-dimethylformamide for  $Mn(N-Bz-5-NO_2sal)_2CI$ . These complexes are soluble in dichloromethane, methanol, and acetonitrile, slightly soluble in ether, and insoluble in water. The analytical data for these complexes are given in Table 2.

Preparation of Mn(IV) Schiff Base Complexes, Mn(N-R-Xsal)<sub>2</sub>Cl<sub>2</sub>. Dichlorobis(N - dodecyl - 5 - bromosalicylideneaminato)manganese(IV), Mn(N-Dod-5-To a 2-propanol (70 cm<sup>3</sup>) containing Brsal)<sub>2</sub>Cl<sub>2</sub>. Mn(N-Dod-5-Brsal)<sub>2</sub>Cl (1.0 g) was added a 2-propanol solution of hydrogen chloride (1.5 molar folds over the complex) at room temperature. The mixture was stirred for 1 hr to give deep green precipitates. They were collected on a glass filter, washed with 2-propanol, and dried in vacuo. They were recrystallized from benzene to give deep green crystals. The yield was ca. 0.2 g. This complex is soluble in dichloromethane, benzene, and acetone to give deep green colour. These solutions show no measurable change in colour allowing to stand for 1 hr in an aerial atmosphere. This complex

	o-Q H=C H
Mn(N-R-X so	al)2 <sup>C1</sup> 2
	X
n-C8H17 (Oct)	5-Br
n-C <sub>12</sub> H <sub>25</sub> (Dod)	5,6-Benzo
n-C <sub>18</sub> H <sub>37</sub> (Octd)	5-N02
CH2C6H5 (Bz)	-

Fig. 1. Mn(IV) complexes.

	М.Р.	Found (Calcd) (%)			
Ligand	°C	С	<u>н</u>	<u>N</u>	
N-Dod-5-BrsaiH	24 - 25	61.51(61.95)	8.30( 8.21)	3.83(3.80)	
N-Octd-5-BrsalH	50.5 - 51	65.98(66.36)	9.39( 9.36)	3.07(3.10)	
N-Dod-5,6-Benzosa <b>i</b> H	64.5	81.07(81.61)	9.80( 9.53)	4.20(4.14)	
N-Octd-5,6-BenzosaiH	82 - 82.5	82.25(82.41)	10.84(10.49)	3.37(3.31)	
N-Dod-5-NO <sub>2</sub> saiH	93 - 93.5	67.97(68.23)	9.05( 9.04)	8.31(8.38)	
N-Octd-5-NO <sub>2</sub> saiH	99.5 - 100	71.69(71.73)	10.18(10.11)	6.78(6.69)	

Table 1. Melting points and analytical data for Schiff base ligands

Table 2. Analytical data for manganese(III) Schiff base complexes

Mn(N-R-Xsai) <sub>2</sub> C1			Found	(Calcd) (%)	
R	х	С	Н	N	Mn
Oct	5-Br	50.88(50.54)	6.08(5.94)	3.96(3.93)	7.62(7.71)
Dod	5-Br	55.33(55.32)	7.12(7.09)	3.32(3.40)	6.74(6.66)
Octd	5-Br	60.06(60.45)	8.30(8.32)	2.84(2.82)	5.59(5.53)
Βz	5-Br	50.30(50.29)	3.40(3.32)	4.07(4.19)	8.32(8.22)
Oct	5,6-Benzo	69.52(69.66)	7.44(7.38)	4.19(4.28)	8.46(8.38)
Dod	5,6-Benzo	72.31(72.00)	8.56(8.41)	3.71(3.65)	7.13(7.16)
Octd	5,6-Benzo	74.19(74.45)	9.40(9.48)	2.96(2.99)	6.02(5.87)
Bz	5,6-Benzo	70.61(70.77)	4.69(4.62)	4.54(4.58)	9.02(8.99)
Oct	5-NO <sub>2</sub>	55.50(55.86)	8,60(8.69)	6.63(6.56)	8.45(8.52)
Dod	5 - NO <sub>2</sub>	59.79(60.27)	7.77(7.72)	7.38(7.40)	7.11(7.25)
Octd	5-NO <sub>2</sub>	64.80(64.88)	9.07(8.93)	5.95(6.05)	5.92(5.94)
Bz	5-NO <sub>2</sub> a)	57.96(57.64)	4.06(3.97)	9.54(9.60)	9.38(9.42)

a) Values for Mn(N-Bz-5-NO<sub>2</sub>sai)<sub>2</sub>OH.

also is soluble in pyridine and methanol but these solutions change in colour from green to brown gradually.

The other dichloromanganese(IV) Schiff base complexes were prepared in a similar manner. The analytical data for the manganese(IV) complexes are given in Table 3.

Measurements. The melting points were determined by means of a Yanagimoto MP-1 melting point apparatus and uncorrected. The UV and VIS spectra were obtained by a Hitachi 340 spectrophotometer. The IR spectra were recorded on a Hitachi EPI-215 grating spectrophotometer in the 650-4000 cm<sup>-1</sup> regions and on a Hitachi EPI-L grating spectrophotometer in the 200-700 cm<sup>-1</sup> regions. The magnetic susceptibilities were measured by the Gouy method at room temperature. The cyclic voltammetry was performed with a Yanagimoto P-8 polarograph connected with a Yanagimoto P8-PT potentiostat. The working electrode was a platinum-inlay electrode, while the auxiliary electrode was a platinum wire. The reference electrode was a saturated calomel electrode which was inserted in an aqueous solution of 1 M KCl in a 100 cm<sup>3</sup> beaker connected with a conventional brown H-Type cell by means of a 4% agar-KCl gel bridge. Tetrabutylammonium saturated perchlorate, Bu<sub>4</sub>NClO<sub>4</sub>, was used as the supporting electrolyte (0.1 M). The dissolved oxygen was removed by passing  $N_2$  gas through a sample solution for 20 min. The cyclic voltammograms were recorded under the following conditions: concentration of the complexes was  $5 \times 10^{-4}$  M, the scan rate was 0.06 V/s, and temperature was kept at 25°C.

*Materials.* All reagents were of reagent grade. The solvents were purified by a usual manner. Acetonitrile was distilled twice over diphosphorus pentaoxide prior to use. Benzene was distilled over sodium.

## **RESULTS AND DISCUSSION**

Preparation. We reported previously the preparation and characterization of dichlorobis (N-butylsubstituted salicylideneaminato)manganese(IV) complexes, Mn(N-Bu-Xsal)<sub>2</sub>Cl<sub>2</sub>, where X can be H, 5-Br, 5-NO<sub>2</sub>, and 5,6-Benzo groups.<sup>5</sup> These complexes were decomposed gradually to the reduced manganese(III) complexes by moisture allowing to stand in an aerial condition even in the solid state. Thus in order to obtain pure manganese (IV) complexes much care should be taken to remove trace amounts of water in the solvents used. In an earlier paper<sup>6</sup> we have reported that the manganese(IV) complexes incorporating long-chain alkyl groups such as  $n-C_{12}H_{25}$  and  $n-C_{18}H_{37}$  can be protected from attack of water. These

Mn(N-R-Xsai) <sub>2</sub> C1 <sub>2</sub>		F	ound (Calcd)	(\$)	
R X	С	Н	N	C1	Mn
Oct 5-Br	48.28(48.15)	5.82(5.66)	3.74(3.74)	30.55(30.84) <sup>a</sup>	7.33(7.34)
Dod 5-Br	53.12(53.04)	6.90(6.79)	3.28(3.26)	26.56(26.81) <sup>a</sup>	)6.52(6.38)
Octd 5-Br	57.92(58.37)	8.18(8.03)	2.81(2.72)	22.91(22.53) <sup>a</sup>	)5.31(5.34)
Bz 5-Br	47.96(47.76)	3.26(3.15)	3.95(3.98)	32.62(32.77) <sup>a</sup>	)7.80(7.80)
Oct 5,6-Benzo	66.39(66.08)	7.11(7.01)	4.42(4.06)	10.75(10.27)	8.11(7.95)
Dod 5,6-Benzo	68.58(68.82)	8.09(8.03)	3.50(3.49)	8.67( 8.83)	7.05(6.84)
Octd 5,6-Benzo	71.44(71.73)	9.21(9.13)	2.91(2.88)	7.52( 7.30)	5.70(5.66)
Bz 5,6-Benzo	66.69(66.89)	4.41(4.37)	4.45(4.33)	11.10(10.97)	8.54(8.50)
Oct 5-NO <sub>2</sub>	52.74(52.95)	6.23(6.22)	8.39(8.24)	10.00(10.42)	8.10(8.07)
Dod 5-NO <sub>2</sub>	57.74(57.57)	7.53(7.37)	7.05(7.07)	9.05( 8.94)	6.93(6.93)
Octd 5-NO <sub>2</sub>	62.24(62.49)	8.78(8.50)	5.92(5.83)	8.34(7.34)	5.69(5.72)
Bz 5-NO <sub>2</sub> b)	50.19(50.42)	3.53(3.42)	8.22(8.25)	16.33(15.67)	8.56(8.09)

Table 3. Analytical data for manganese(IV) Schiff base complexes

a) C1 + Br. b) Inclusion of  $(CH_2Cl_2)_{0.5}$  as a crystalline solvent.

findings led us to prepare a series of dichloromanganese(IV) Schiff base complexes having longchain alkyl groups. All the manganese(III) complexes which were prepared have a composition of  $Mn(N-R-Xsal)_2Cl$ , with the exception of  $Mn(N-Bz-5-NO_2sal)_2OH$  (Table 2). All the manganese(IV) complexes which were obtained have a composition of  $Mn(N-R-Xsal)_2Cl_2$  (Table 3). The properties for the manganese(III) and manganese(IV) complexes are summarized in Tables 4 and 5, respectively.

Melting points. The manganese(III) complexes having the long-chain alkyl groups showed low melting points without decomposition. As seen in Table 4, the longer the alkyl groups the lower melting points are obtained in the order of Bz > Oct > Dod > Octd. As to the substituents on the aromatic ring the melting

R-Xsai) <sub>2</sub> C1	М.Р.	a) <sup>µ</sup> eff	$v_{max}$ (107 c)	ν (Mn - C1	) <sup>c)</sup> E <sub>p/2</sub> vs. SCE <sup>d)</sup>
x	°c	ВМ	$10^3 \text{ cm}^{-1}$	cm <sup>-1</sup>	V Mn(III)→Mn(II)
5-Br	141 - 145	4.95	14.97 (2.72)	306	0.08
5 - Br	122 - 123	4.92	14.93 (2.75)	305	0.08
5-Br	104 - 105	4.83	14.97 (2.75)	306	0.07
5-Br	229 - 230 <sup>f</sup> )	4.91	14.86 (2.77)	330	0.08
5,6-Benzo	136 - 137	4.91	15.11 (2.70)	306	-0.09
5,6-Benzo	109 - 110	4.83	15.15 (2.72)	305	-0.08
5,6-Benzo	94 - 95	4.82	15.13 (2.71)	305	-0.06
5,6-Benzo	208 - 209 <sup>t</sup> )	3.25	15.08 (2.70)	313	-0.07
5-N0 <sub>2</sub>	197 - 198	3.89	15.92 (2.84)	293	0.28
5 - NO 2	181 - 182	3.79	15.67 (2.70)	294	0.25
5 - NO <sub>2</sub>	179 - 180	3.53	15.72 (2.72)	293	0.30
5-N0 <sub>2</sub>	220 - 222 <sup>f</sup> )	4.20	15.82 (2.65)	293	0.28
H e)	154 - 155	4.93	15.20 (2.60)	317	-0.16
	$R-Xsail)_{2}Cl$ $X$ $S-Br$ $S-Br$ $S-Br$ $S-Br$ $S, 6-Benzo$ $S, 8-Benzo$ $S, 8-B$	$\begin{array}{c cccc} R-Xsai)_2C1 & \underline{M.P.} \\ X & & \underline{O_C} \\ \hline \\ \hline S-Br & 141 & -145 \\ \hline S-Br & 122 & -123 \\ \hline S-Br & 104 & -105 \\ \hline S-Br & 229 & -230^{f} \\ \hline S,6-Benzo & 136 & -137 \\ \hline S,6-Benzo & 109 & -110 \\ \hline S,6-Benzo & 94 & -95 \\ \hline S,6-Benzo & 208 & -209^{f} \\ \hline S-NO_2 & 197 & -198 \\ \hline S-NO_2 & 181 & -182 \\ \hline S-NO_2 & 179 & -180 \\ \hline S-NO_2 & 220 & -222^{f} \\ \hline H & e^{} & 154 & -155 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 4. Properties of manganese(III) Schiff base complexes

a) Measured at room temperature. b) Measured in dichloromethane. c) Measured in Nujol mulls. d) Measured in acetonitrile containing  $(Bu)_4 NC10_4$  (0.1 mol dm<sup>-3</sup>) at 25 °C. e) In a previous work.<sup>6</sup> f) With decomposition.

Mn (N -	R-Xsaí) <sub>2</sub> C1 <sub>2</sub>	M.P.	a) <sup>µ</sup> eff	$v_{max}$ (log s)	c) √(Mn-Cl)	d) E <sub>p/2</sub> vs. SCE	
R	x	°c	ВМ	$10^3 \text{ cm}^{-1}$	cm <sup>-1</sup>	V In(IV)→Mn(III)→Mn(	11)
Oct	5-Br	123 - 124	4.07	15.72 (3.72)	329	0.87 -0.12	
Dod	5-Br	115 - 116	4.02	15.72 (3.73)	326	0.85 -0.10 <sup>f</sup> )	
Octd	5-Br	111 - 112	4.07	15.67 (3.66)	337	0.85 -0.10 <sup>f)</sup>	
Βz	5-Br	184 - 185	3.87	15.77 (3.55)	337	0.90 -0.03	
Oct	5,6-Benzo	94 - 95	4.02	14.84 (3.68)	336	0.40 -0.13	
Dod	5,6-Benzo	86 - 87	4.04	14.75 (3.77)	327	0.39 -0.13 <sup>f)</sup>	
Octd	5,6-Benzo	83 - 84	3.91	14.75 (3.75)	326	0.40 -0.07 <sup>f)</sup>	
Bz	5,6-Benzo	148 - 149	3.90	14.83 (3.77)	326	0.41 -0.07	
Oct	5 - NO <sub>2</sub>	190 - 193	3.93	16.98 (3.72)	358	0.93 0.06	
Dod	5 - NO <sub>2</sub>	185 - 190	4.06	17.01 (3.77)	354	0.92 0.06	
Octd	5-N0 <sub>2</sub>	180 - 184	4.10	16.85 (3.74)	358	0.93 0.12 <sup>f)</sup>	
Βz	5-NO <sub>2</sub>	>280	3.94	17.12 (3.74)	355	1.00 0.21	
0ct	H <sup>e)</sup>	106 - 107	3.92	16.00 (3.62)	348	0.83 -0.12	

Table 5. Properties of manganese(IV) Schiff base complexes

a) Measured at room temperature. b) Measured in dichloromethane. c) Measured in Nujol mulls. d) Measured in acetonitrile containing  $(Bu)_4 NClO_4$  (0.1 mol dm<sup>-3</sup>) at 25 °C. e) In a previous work.<sup>6</sup> f) Measured in a mixture of acetonitrile and dichloromethane (1/1 volume ratio). All the melting points were observed with decomposition.

are lowered points in the order of  $5-NO_2 > H > 5-Br > 5,6-Benzo$  groups. The melting points for Mn(N-R-sal)<sub>2</sub>Cl which were prepared in a preceding work are 154-155, 129-130, 119.5-120, and 205–206°C for R = Oct, Dod, Octd and Bz, respectively. On the other hand, the melting points of the manganese(IV) complexes are lower than those of the corresponding manganese(III) complexes, and they decompose at near melting points, showing colour changes from green to brown (Table 5). As to the alkyl groups the melting points are lowered in the same order as that for the manganese(III) complexes, and as to the substituents on the aromatic ring they are lowered in the order of  $5-NO_2 > 5-Br > H >$ 5,6-Benzo groups, with the exception of Mn(N-Bzsal)<sub>2</sub>Cl<sub>2</sub>. The melting points of Mn(N-R-sal)<sub>2</sub>Cl<sub>2</sub> which were prepared in a preceding work are 106-107, 97.5-98.5, 94-95, and 112-113°C for R = Oct, Dod, Octd and Bz, respectively.

Magnetic properties. The magnetic moments for the manganese(III) complexes fall within the range of 4.82-4.95 BM, with the exception of Mn(N-Bz-5,6-Benzosal)<sub>2</sub>Cl and all the 5-nitro derivatives (Table 4). These values are consistent with the spin-only value expected for a complex having a  $d^4$  high-spin electron configuration. The lower values observed for the above complexes may be caused by antiferromagnetic interaction between manganese atoms due to a binuclear structure in which they are bridged by two phenolic oxygen atoms. No further investigation on magnetic properties for these complexes has been made.

The magnetic moments for the manganese(IV) complexes fall within the range of 3.87-4.10 BM

(Table 5). These values are consistent with the spinonly value expected for a complex having a  $d^3$  electron configuration.

Electronic spectra. The electronic spectra of the manganese(III) complexes measured in dichloromethane show the absorption bands (log  $\epsilon = 2.7$ ) around  $15000 \text{ cm}^{-1}$ . These complexes may have a five-coordinate configuration around the central manganese atom in such a noncoordinating solvent.<sup>7</sup> Therefore, these bands can be assigned to a ligand field transition due to  $d_{xy} \rightarrow d_{x^2-y^2}$ . The absorption maxima are affected by the aromatic ring substituents and are shifted to higher energies in the order of 5- $NO_2 > H > 5,6$ -Benzo > 5-Br groups (Table 4). The alkyl groups attached to the nitrogen atoms have little effect on the absorption maxima. On the other hand, the electronic spectra of the manganese(IV) complexes in dichloromethane show the more intense absorption bands (log  $\epsilon = 3.7$ ) in the range of 14700–17100 cm<sup>-1</sup> compared with those for the manganese(III) complexes. These bands can be assigned charge-transfer transition to а due to  $Cl(p\pi) \rightarrow Mn(d\pi)$  from their intensities as discussed in the previous papers.<sup>5,6</sup> These absorption maxima are also affected by the aromatic ring substituents and are shifted to higher energies in the order of  $5-NO_2 > H > 5-Br > 5,6-Benzo groups$  (Table 5). The alkyl groups have little effect on the absorption maxima as well as the manganese(III) complexes.

*IR spectra*. The IR spectra of the manganese(IV) complexes show almost the same pattern as those of the manganese(III) complexes in the region from 500 to 4000 cm<sup>-1</sup>, but both spectra are significantly different in the region from 200 to 500 cm<sup>-1</sup>. In this

region the absorption bands due to Mn-Cl stretching vibrations should be observed.<sup>8</sup> Both manganese(III) and manganese(IV) complexes showed one absorption band assignable to v(Mn-Cl) (Tables 4 and 5). The frequencies for the manganese(IV) complexes are observed in higher energies compared with those for the corresponding manganese(III) complexes. This may be caused by the change in the oxidation state of the central manganese atom from Mn(III) to Mn(IV). The results that one absorption band due to v(Mn-Cl) is observed for the manganese(IV) complexes imply that two chlorine atoms coordinate to the manganese atom as a trans-configuration. Thus we propose a trans-octahedral configuration for the manganese(IV) complexes investigated here as shown above.

Electrochemical properties. The cyclic voltammograms of the manganese(III) and manganese(IV) complexes were measured in acetonitrile. Some of the manganese(IV) complexes were measured in a mixtute of acetonitrile and dichloromethane (1:1) owing to their poor solubility in acetonitrile. The current-potential curves for the manganese(III) complexes showed the one cathodic wave around 0.0 V (vs SCE) in the +1.2 to -0.8 V range. This can be assigned to the one-electron reduction from Mn(III) to Mn(II).9 On the other hand, the current-potential curves for the manganese(IV) complexes showed the two-step cathodic waves around +0.9 and 0.0 V with similar wave heights. These waves can be assigned to the oneelectron reductions from Mn(IV) to Mn(III) and from Mn(III) to Mn(II), respectively. The separations of the peak potentials between the cathodic wave and the corresponding anodic wave for both redox waves are larger than the 57 mV expected for a reversible one-electron redox wave, so these electrode reactions may be irreversible. Thus the half-peak potentials  $(E_{p/2})$  of the cathodic waves for the manganese(III) and manganese(IV) complexes are summarized in Tables 4 and 5, respectively. The reduction potentials for the manganese(III) complexes are affected by the aromatic ring substituents and are shifted to more positive potentials in the order of  $5-NO_2 > 5-Br > 5,6-Benzo groups$ . And they are little affected by the alkyl groups. On the other hand, the reduction potentials for the manganese(IV) complexes are significantly affected by the aromatic ring substituents and are shifted to more positive potentials in the order of  $5-NO_2 > 5-Br > 5,6-Benzo$ groups. These potential shifts can be explained by the electron-withdrawing ability of the substituent groups. And also the alkyl groups have little effect on the reduction potentials. These results are not inconsistent with those obtained in the electronic and IR spectra.

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