Further, the similarities of the first reductive wave under these conditions for all of the iron and noniron porphyrins studied herein suggest that the π system of the porphyrin ring is a viable pathway for electron transfer.

Conclusion

The Fe^{III}TMPyP compound undergoes a fast one-electron reduction with an $E_{0.85}$ of +0.18 ($\pm$0.01) V at a highly polished, glassy carbon electrode with a k_s value of 5.8 ($\pm$0.9) $\times$ 10^{-3} cm^{-1} in acidic solutions. Except for a dimeric species in borate solutions, there was no evidence for surface adsorption by either Fe^{III}- or Fe^{II}TMPyP. Optically coupled electrochemical experiments as a function of pH indicate that four major ferriporphyrin species and two ferroporphyrin species are sufficient to explain the electrochemical results. The ferriporphyrin species are a five-coordinate monomer, a monohydroxyl monomer, a dihydroxyl monomer, and a bridged dimer. All are reduced to a monomeric ferroporphyrin species with $n = 1$ per iron stoichiometry. Unfortunately, the present data do not provide for any additional evidence to distinguish whether the dimer formed in basic solutions exists as a μ-oxo- or a μ-hydroxyl-bridged species.

Proton equilibria exist between the three ferriporphyrin monomers with pK_a values of ca. 4.7 and 6.5. Proton equilibria also exist between the two ferroporphyrin species with a pK_a of ca. 7. A value of 2 $\times$ 10^3 M^{-1} was evaluated for the dimerization constant. Both oxidation states of FeTMPyP appear to be stable as evidenced by the repetitive cycling between redox states by coulometry. Although the noniron porphyrins, TMPyP and TPyP, undergo reduction at potentials similar to those of Fe^{III}TMPyP, the number of electrons involved is more than 1, the waves are irreversible, and a second reduction wave appears at more negative potential.

Recent MCD results[22] have suggested that the ferroporphyrin species at pH 4.7 is a five-coordinate high-spin iron(II) porphyrin. Preliminary stopped-flow kinetic experiments between the water-soluble tetrakis(*N*-methyl-4-pyridyl)ferroporphyrin and molecular oxygen have indicated that the removal rate of the ferroporphyrin was independent of pH (pH range 1–9).[27]

Experiments are under way to determine the mechanistic pathway for the electrocatalytic reduction of oxygen to hydrogen peroxide and/or water via the water-soluble or surface-bound iron and cobalt porphyrins. The results of these experiments will be reported in a subsequent paper.

(27) Shu-Weng, D. Leussing, and T. Kuwana, unpublished results.

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Electrochemical Studies of Manganese(II) Complexes Containing Pentadentate Ligands with O₂N₃, O₃N₂, and O₂SN₂ Donor Sets

W. M. COLEMAN,[1a] R. K. BOGGESS,[1b] J. W. HUGHES,[1b] and L. T. TAYLOR*[1c]

Manganese(II) complexes of linear, potentially pentadentate ligands with donor sets of O₂N₃, O₃N₂, and O₂SN₂ derived from substituted aldehydes and polyamines have been synthesized. Characterization via elemental analysis, infrared spectra, and magnetic susceptibility has been accomplished. Differences in reactivity with dioxygen and nitric oxide both in solution and in the solid state suggest that some subtle effects exist between complexes. Dioxygen reactivity leads to initial oxidation of manganese(II) followed by irreversible oxidation of the coordinated ligand. Reaction with nitric oxide produces manganese(I) nitrosyls. Cyclic voltammetry has been performed on the manganese(II) precursors in dimethyl sulfoxide. A donor atom as well as aromatic ring substituent effect was noted for each quasi-reversible redox couple. Complexes with C₂H₄ units between potential donor groups exhibited additional electrochemical activity, some of which was sweep-rate dependent.

Introduction

Manganese, cobalt, nickel, and copper complexes of the ligand system derived from substituted salicylaldehydes and bis(3-aminopropyl)amine (structure I) have received much study in this laboratory.[2-6] These studies have revolved around synthesis, characterization, and, most importantly, the reactivity of manganese and cobalt complexes with dioxygen and nitric oxide. With cobalt(II) the dioxygen results are reasonably straightforward as μ-peroxo species (Co–O₂–Co) are the predominant products. The rate of dioxygenation appears to be a function of the aromatic substituent on the salicylaldehyde moiety (e.g., greater dioxygen reactivity with electron-donating groups).[8] A similar pattern was found with

I
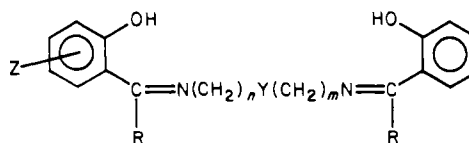
R	n	m	Y	name
H	1	1	not present	SALEN (Ia)
H	2	2	N–H	ZSALDIEN (Ib)
H	2	2	–S–	ZSALDAES (Ic)
H	2	3	N–H	ZSALEPT (Id)
H	3	3	N–H	ZSALDPT (Ie)
H	3	4	N–H	ZSALBPT (If)
H	3	3	–O–	ZSALDAPE (Ig)
C₆H₅	3	3	N–H	HBPDPT (Ih)

manganese(II) complexes of these ligands;[2a] however, isolation of a dioxygen adduct was hampered by irreversible ligand

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oxidation. With incorporation of a nitro substituent into the salicylaldehyde function, ligand oxidation was inhibited sufficiently so that a μ-peroxo manganese(III) species could be isolated.[9] Extension of this study to other polydentate ligands derived from salicylaldehyde has led to different results. Tetradentate ligands where the amine component is ethylenediamine or 1,3-diaminopropane yielded di-μ-oxo manganese(IV) materials.[10] Linear hexadentate ligands embodying tetraamines mimicked their pentadentate analogues for the unsubstituted derivatives whereas nitro groups, in contrast, totally inhibited reaction with dioxygen in solution or in the solid state.[11]

In an effort to explain these phenomena, cyclic voltammetry studies on manganese(III) complexes of selected salicylaldehyde-derived pentadentate ligands were conducted.[12] For those cases investigated, electron-donating groups stabilized manganese(III) while electron-withdrawing stabilized manganese(II). Several ligands that were suspected to be four-coordinate wherein one donor group was dangling because of either restricted chelate ring size (SALEPT) or inadequate donor ability (SALDAPE) yielded more positive Mn(III)/Mn(II) reduction potentials for comparable degrees of substitution.[13] Since dioxygen reactivity concerns oxidative addition to manganese(II), we have now conducted a cyclic voltammetry study on a series of manganese(II) chelates and correlated their oxidation potential with dioxygen reactivity. Linear, potentially pentadentate ligands (I) provide the donor set in most cases. A limited series of pentadentate ligands derived from pyridine-2-carboxaldehyde (II) in place of sal-

n	m	name
2	3	PYEPT (IIa)
3	3	PYDPT (IIb)
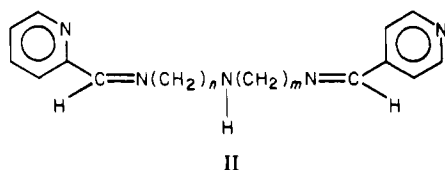
icylaldehyde is also reported. A number of the complexes dealt with in this study have never been reported; therefore, a brief description of their properties is also provided.

Experimental Section

Materials. Bis(3-aminopropyl) ether was prepared by a catalytic hydrogenation method similar to that of Modest et al.[14] N-(2-Aminoethyl)-1,3-propanediamine, N-(3-aminopropyl)-1,4-butanediamine, and diethylenetriamine were obtained from Aldrich Chemical Co. Manganese acetate and salicylaldehyde were obtained from Fisher Scientific Co. 5-Nitrosalicylaldehyde, 3-nitrosalicylaldehyde, 2-

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hydroxy-1-naphthaldehyde, and 2-hydroxybenzophenone were obtained from Eastman Chemical Co. Bis(2-aminoethyl) thioether was kindly provided by the Dow Chemical Co. All other chemicals were reagent grade or equivalent.

Synthesis of New Complexes. Mn(ZSALDIEN). Due to the instability of solutions of these manganese(II) complexes in air, all operations were carried out under nitrogen. The general method of preparation was as follows. To a stirring solution of the appropriate aldehyde (0.02 mol) in 40 mL of absolute ethanol was added 0.01 mol of diethylenetriamine (DIEN) dissolved in 40 mL of absolute ethanol. The solution was refluxed for 1 h and then cooled to room temperature. Then 0.02 mol of KOH in 30 mL of oxygen-free methanol was added, followed by the slow dropwise addition of an oxygen-free methanol solution containing 0.01 mol of Mn(OAc)$_2$·4H$_2$O. Usually a bright yellow precipitate formed halfway through the Mn(II) addition, which was stirred for 1 h, isolated via filtration in an argon-filled drybox, washed with dry methanol, and then dried overnight in vacuo over CaCl$_2$.

Mn(ZSALEPT). The above procedure was followed except that *tert*-butyl alcohol was used in place of absolute ethanol and N-(2-aminoethyl)-1,3-propanediamine (EPT) was substituted for DIEN. Water was used to dissolve the Mn(OAc)$_2$·4H$_2$O.

Mn(SALDAES). The procedure employed for Mn(SALDIEN) was followed, substituting bis(2-aminoethyl) thioether (DAES) for DIEN.

Mn(ZSALBPT). To a solution prepared by dissolving 0.02 mol of salicylaldehyde in 40 mL of *tert*-butyl alcohol was added 0.01 mol of N-(3-aminopropyl)-1,4-butanediamine (BPT) dissolved in 40 mL of *tert*-butyl alcohol. The yellow solution was brought to reflux under nitrogen for 1 h and then cooled to room temperature. Next 0.02 mol of KOH in 40 mL of oxygen-free methanol was added followed by the slow dropwise addition of 0.01 mol of Mn(OAc)$_2$·4H$_2$O in 40 mL of oxygen-free methanol. No precipitate formed. The solution volume was reduced to approximately 50 mL with a stream of nitrogen and gentle heat. Heat was removed, and when room temperature was reached, a bright yellow precipitate formed. The material was isolated via filtration, washed with methanol, and dried overnight in vacuo over CaCl$_2$. The isolated yellow product rapidly discolored upon exposure to air.

Mn(ZSALDAPE). The procedure for the preparation of these complexes was similar to that followed for the preparation of Mn-(ZSALDIEN), the only difference being that bis(3-aminopropyl) ether (DAPE) was used instead of DIEN and 10 mL of oxygen-free H$_2$O was used to dissolve the KOH instead of methanol.

Mn(NAPDPT). This complex was prepared in the manner described for Mn(ZSALDIEN) substituting 2-hydroxy-1-naphthaldehyde (NAP) for salicylaldehyde.

Mn(HBPDPT). To a refluxing solution of 0.02 mol of 2-hydroxybenzophenone(HBP) in 20 mL of methanol was added 0.01 mol of bis(3-aminopropyl)amine (DPT) in 30 mL of methanol. To this yellow solution was added 0.02 mol of KOH dissolved in 20 mL of methanol. The solution was cooled to room temperature and degassed with nitrogen for 1/4 h. This oxygen-free solution was then added dropwise to an oxygen-free solution containing 0.01 mol of Mn(OAc)$_2$·4H$_2$O in 30 mL of methanol, all under a nitrogen stream. A precipitate formed about 1/4 h after the ligand addition was complete. The material was isolated via filtration, washed with methanol, and dried overnight in vacuo over CaCl$_2$.

Mn(SALDAES)NCS. The preformed ligand H$_2$SALDAES (1.6 g; 0.005 mol) was dissolved in 25 mL of CHCl$_3$. To this solution was added NH$_4$NCS (7.1 g) dissolved in 20 mL of absolute ethanol. The solution was deoxygenated, after which powdered Mn(OAc)$_3$·2H$_2$O (1.3 g; 0.005 mol) was slowly added over a period of 1 h. Stirring of the solution was continued for another 2 h, during which time the color changed from brown to dark green. The resulting solution was filtered, the filtrate was chilled, and the green precipitate which formed was isolated by filtration. The precipitate was washed with ethanol and dried in vacuo at 50 °C.

Mn(5-NO$_2$SALDIEN)NCS. This compound was prepared as described above except that H$_2$-5-NO$_2$SALDIEN was substituted for H$_2$SALDAES. A brown solid was isolated and dried in vacuo at room temperature.

Physical Measurements. All of the measurement techniques and apparatus used have been described in detail previously.[2b,3,12] All electrochemical measurements were done at 10^{-3} M in dimethyl sulfoxide (Me$_2$SO) with use of tetraethylammonium perchlorate as

the supporting electrolyte. The working electrode was a Beckman platinum-button electrode and the auxiliary electrode was a coil of Pt wire. An SCE which was separated from the Me_2SO solution by a NaCl–agar salt bridge served as the reference electrode. Other experimental conditions have been previously reported.[12]

Results and Discussion

Characterization of New Complexes. A number of new manganese(II) complexes have been synthesized by the reaction of alcoholic solutions of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ and the preformed deprotonated ligand under a nitrogen atmosphere. The ligands employed (SALDIEN, SALDAES, SALDAPE, SALEPT, SALBPT, NAPDPT, and HBPDPT) are modifications of the parent SALDPT ligand which has been previously reported.[2a] Specific ligand modifications include a different central donor group (SALDAES and SALDAPE), a different chelate ring size (SALDIEN, SALEPT, and SALBPT), and a different α-carbon substituent (HBPDPT). The resulting manganese(II) complexes with these ligands are yellow to orange and on the basis of elemental analysis data (Table I) have the general formula $MnL \cdot xH_2O$. Several of the complexes (SALDAPE and SALBPT) were so dioxygen sensitive that reliable elemental analysis and magnetic moment data were not obtainable. Dioxygen sensitivity was readily noted by the immediate discoloration of the complex on exposure to air. For those solid materials which were stable in air, magnetic moments in the range indicative of high-spin manganese(II) were obtained.

From infrared spectral measurements and data obtained on similar ligands with other first-row transition metals, certain structural implications can be ascertained for these complexes. For the ligands employing the O_2N_3 donor set, the infrared data seem to divide the complexes into two groups (e.g., DIEN set and EPT/BPT set). The N–H stretching frequency of 3300–3330 cm^{-1} for the DIEN set is between 40 and 140 cm^{-1} higher than that for the other set, hence suggesting a different degree of N–H coordination in Mn(SALDIEN) or a difference in structure. A recent X-ray crystal structure determination was performed on a like complex, $Cu^{II}(SALDIEN)$. The Cu(II) complex was shown to be a dimer with each Cu(II) being five-coordinate, using three donor atoms from one ligand and two from the other.[15] The formation of a dimer no doubt was caused in part by the inability of the two-carbon aliphatic chain to effectively bridge the points of a monomeric trigonal-bipyramid or square-pyramid structure. The nickel(II) complex of SALDIEN has been clearly shown[16] to be square planar wherein one donor group is dangling, on the basis of visible spectral and magnetic data. It, therefore, seems reasonable to expect Mn(SALDIEN) to have one of these structures wherein the secondary amine is loosely bound. The N–H stretching frequencies of EPT and BPT complexes more closely parallel those of complexes already shown to be fully five-coordinate.[2,6,17] It, therefore, seems reasonable to suggest that EPT is long enough and BPT is not too long to bridge the coordination sites of a five-coordinate structure, much in the same manner as DPT.[2,6,17]

Infrared data also provide structural information with regard to the SALDAPE series. In addition to coordination of azomethine nitrogen, the C–O stretching frequency (ca. 1080 cm^{-1}) suggests coordination of the ether oxygen. This is in contrast to the reported C–O stretching frequency (1110 cm^{-1}) for the comparable Co^{II} (SALDAPE) complex[5] which has been shown to be tetrahedral. Ether oxygen coordination, however, was observed with cobalt(II) when electron-withdrawing groups were present on the SAL moiety (i.e., a shift to 1079 cm^{-1} was observed for 5-ClSAL).[5] The structure of

Table I. Analytical Data and Magnetic Moments for New Manganese Complexes

complex	calcd			found			μ, μ_B
	% C	% H	% N	% C	% H	% N	
Mn(SALDIEN)	59.4	5.3	11.5	59.4	4.9	10.9	5.70
Mn(5-NO$_2$SALDIEN)·H$_2$O	45.8	4.0	14.8	45.9	3.6	14.7	5.67
Mn(SALDAES)·H$_2$O	54.1	5.0	7.0	53.9	4.7	7.1	5.58
Mn(3-NO$_2$SALDAPE)·H$_2$O	47.9	4.0	11.2	48.1	3.8	10.9	4.57
Mn(SALEPT)	60.3	5.6	11.1	60.5	5.5	10.9	5.80
Mn(5-NO$_2$SALEPT)	48.7	4.1	14.9	48.3	4.2	14.6	5.91
Mn(5-NO$_2$SALBPT)	50.8	4.6	14.1	50.5	4.4	14.3	5.83
Mn(NAPDPT)	68.3	5.5	8.5	68.3	5.5	8.4	5.58
Mn(HBPDPT)·½H$_2$O	69.4	5.8	7.6	69.5	5.6	7.6	5.89
Mn(SALDAES)NCS	51.7	4.6	9.5	51.7	4.6	9.5	
Mn(5-NO$_2$SALDIEN)NCS	44.5	3.3	16.4	44.2	3.6	15.5	

Mn(SALDAES) can only be conjectured on the basis of what is known about the analogous Ni(SALDAES) complex. The visible spectrum, magnetic moment, and molecular weight of Ni(SALDAES) suggest a five-coordinate dimeric structure in which the thioether group is coordinated.[18,19] A structure similar to that of Cu(SALDIEN) may be envisioned for Ni(SALDAES), and extension of these findings to Mn(SALDAES) is possible.

With regard to each complex's dioxygen reactivity, the following observations have been made. The complexes Mn(SALDIEN) and Mn(5-NO$_2$SALDIEN), Mn(SALEPT) and Mn(5-NO$_2$SALEPT), and Mn(HBPDPT) and Mn(SALDAES) react with oxygen in a manner similar to that observed for Mn(ZSALDPT).[2a] Oxygenation is continuous for unsubstituted complexes with no break or pause at $n_{O_2}/n_{Mn} = 0.5$, suggesting that both manganese and ligand are undergoing oxidation. For the nitro derivatives, dioxygen is consumed at a slower rate in a manner similar to that of Mn(5-NO$_2$SALDPT).[9] The n_{O_2}/n_{Mn} ratio of 0.5 for the latter is suggestive of a μ-peroxo manganese(III) product. Similar preliminary findings have been noted for Mn(ZSALDAPE). Unlike the other complexes, Mn(SALBPT) reacts with dioxygen in the solid state; however, the stoichiometry is not well-defined.

With regard to nitric oxide reactivity, Mn(ZSALDIEN), Mn(SALDAES), and Mn(ZSALDAPE) complexes do not react with NO in solution or in the solid state. Mn(ZSALEPT), Mn(ZSALBPT), and Mn(HBPDPT) react with NO in a manner similar to that of the Mn(ZSALDPT) series.[2b] That is, upon exposure to nitric oxide, the slight orange-yellow solution of the Mn(II) complex immediately turned dark blood red, followed by precipitation of a fluffy, red-purple material which no doubt is a $Mn^I(NO^+)L$ species.

Electrochemical Studies. The purpose of the electrochemical measurements was to see if a correlation between dioxygen reactivity and ease of oxidation of the Mn(II) complexes could be established. Each of the SAL complexes studied is electrochemically active in dimethyl sulfoxide (Me$_2$SO) and undergoes an apparent one-electron oxidation and subsequent reduction in the +0.3 to –0.3 V range. The electrochemical properties of the complexes are those of a quasi-reversible redox couple (Table II) as indicated by (1) E_{pa} and subsequent E_{pc} sweep-rate dependence, (2) ΔE values greater than 58 mV which increases with sweep rate, (3) a current ratio generally greater than 1, and (4) current vs. the square root of sweep-rate plots (Figure 1), which were linear over a tenfold range of 20

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Table II. Cyclic Voltammetry Mn(II)/Mn(III) for the Manganese(II) Complexes

complex	v, mV/s	E_{pa}, V	E_{pc}, V	ΔE, mV	i_{pa}, μA	i_{pa}/i_{pc}
Mn(SALEN)	2	−0.214	−0.277	63	3.1	1.17
	5	−0.218	−0.280	62	5.1	1.08
	10	−0.217	−0.280	63	7.4	1.03
	20	−0.215	−0.285	70	9.7	1.01
Mn(SALDIEN)	2	+0.002	−0.081	83	3.3	1.03
(1st wave)	5	+0.001	−0.074	75	5.0	1.09
	10	+0.002	−0.070	72	6.9	1.13
Mn(SALDIEN)	10	+0.742			5.1	
(2nd wave)	20	+0.742			7.1	
	50	+0.744	+0.630	114	12.0	
	100	+0.752	+0.635	117	17.0	
Mn(SALDAPE)	2	−0.113	−0.189	76	a	1.01
	5	−0.113	−0.186	73		1.04
	10	−0.112	−0.186	74		1.06
	20	−0.109	−0.189	80		1.08
Mn(SALEPT)	5	−0.081	−0.150	69	5.2	1.03
(1st wave)	10	−0.080	−0.151	71	7.3	1.01
	20	−0.078	−0.152	74	10.4	1.00
	50	−0.072	−0.158	86	15.6	0.98
Mn(SALEPT)	10	+0.703	+0.563	140	6.4	
(2nd wave)	20	+0.706	+0.560	146	8.9	
	50	+0.715	+0.552	163	14.9	
Mn(5-NO₂SALEPT)	2	+0.223	+0.154	69	2.9	1.03
	5	+0.225	+0.153	72	4.6	1.00
	10	+0.228	+0.151	77	6.5	0.98
	20	+0.232	+0.148	84	9.0	0.97
Mn(SALBPT)	2	−0.145	−0.222	77	a	0.98
	5	−0.142	−0.228	86		1.01
	10	−0.137	−0.237	100		1.00
	20	−0.128	−0.244	116		0.98
Mn(NAPDPT)	2	−0.241	−0.310	69	3.3	0.97
	5	−0.240	−0.310	70	5.1	1.00
	10	−0.238	−0.314	76	7.0	1.01
	20	−0.235	−0.318	83	9.6	0.99
Mn(HBPDPT)·¹⁄₂H₂O	2	−0.268	−0.340	72	a	0.97
	5	−0.266	−0.345	79		1.00
	10	−0.262	−0.347	85		1.00
	20	−0.258	−0.351	93		1.00
Mn(SALDPT)·³⁄₂H₂O	2	−0.178	−0.244	66	3.4	0.99
	5	−0.178	−0.246	68	5.3	0.99
	10	−0.177	−0.247	70	7.6	0.99
	20	−0.174	−0.251	77	10.3	0.98
Mn(5-NO₂SALDPT)	2	+0.187	+0.120	67	3.2	1.02
	5	+6.188	+0.120	68	5.0	1.04
	10	+0.190	+0.120	70	7.0	1.02
	20	+0.192	+0.118	74	9.9	1.62
Mn(3-NO₂SALMeDPT)	2	+0.112	+0.033	79	3.2	0.97
	5	+0.117	+0.028	89	5.1	1.00
	10	+0.123	+0.023	100	6.9	1.00
	20	+0.131	+0.016	125	9.4	1.00

a Solution concentrations are unknown due to the potential reaction of the complex with O_2 in the solid state.

sweep rates. The cyclic voltammogram (CV) for Mn(SALDPT) (Figure 2) illustrates the nature of this Mn(II)/Mn(III) redox wave. All nitro compounds have additional electrochemical activity at potentials more negative than −1.0 V, and this is attributed to the reduction of the NO_2 group. Several complexes also exhibit other electrochemical activity, and they are individually discussed below. The oxidation peak potentials (E_{pa}) in the +0.30 to −0.30 V range for each graphically represented in Figure 3. A substituent effect similar to that described previously for Mn(III) complexes[12] is observed (i.e., E_{pa} values are more positive for those complexes containing the electron-withdrawing NO_2 group compared to the unsubstituted ligand). There are also differences attributable to the central donor atom. For coordinated secondary amine compared to etheral oxygen, the oxidation occurs
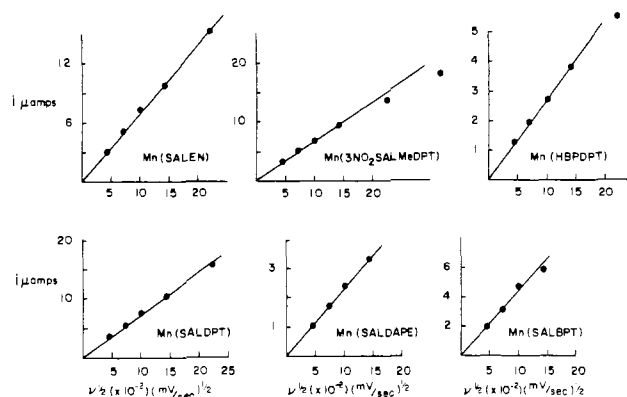
Figure 1. Oxidative current vs. the square root of sweep rate for selected manganese(II) complexes in dimethyl sulfoxide.
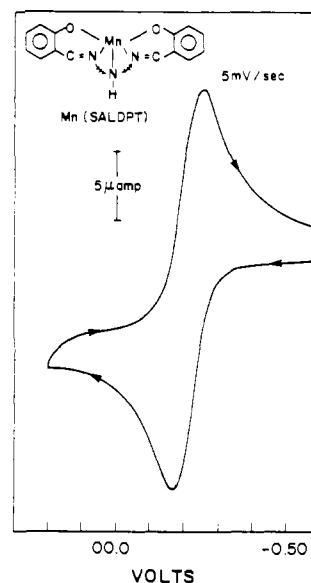
Figure 2. Cyclic voltammogram of Mn(SALDPT) in dimethyl sulfoxide. Scan rate = 5 mV/s.
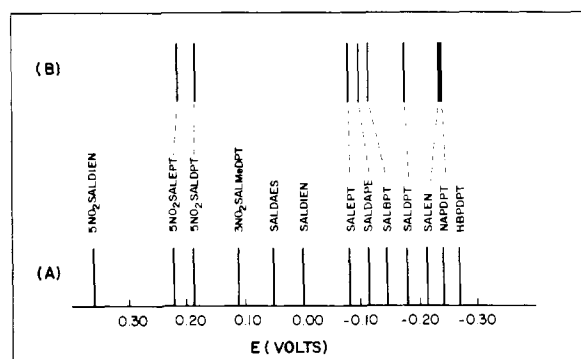
Figure 3. Manganese(II) oxidation potential (E_{pa}) data from cyclic voltammetry for various ligand environments starting with either (A) [Mn^{II}L] or (B) [Mn^{III}L(NCS)]. See structure I for ligand abbreviations.

at a more negative (less positive) potential consistent with the fact that nitrogen is a better σ donor than oxygen and thereby is more effective at stabilizing the higher oxidation state.

Those complexes which proved to be most easily oxidized include Mn(NAPDPT) and Mn(HBPDPT). The former complex embodies naphthaldehyde in place of salicylaldehyde. Fusion of a six-membered ring to the salicylaldehyde moiety results in added electron donation compared to the simple "4,5-HSAL" thereby stabilizing the more highly charged metal ion. The HBPDPT ligand has a phenyl group on the imino

carbon compared to a hydrogen atom in SALDPT. The phenyl group is also electron donating compared to hydrogen, and it is reasonable that this complex displays the most negative E_{pa}. In other words these two ligands are best able to stabilize the higher oxidation state.

The E_{pa} value for Mn(SALEN) is between those of Mn-(NAPDPT) and Mn(SALDPT). Considering only the potential donor sets (N_2O_2 for SALEN and N_3O_2 for NAPDPT and SALDPT), this value for Mn(SALEN) would appear to be too negative. Evidently factors other than the potential donor set are important. Several SALEN complexes are known to be dimeric,[21] and it is likely that the Mn(II) complex is also.

Also illustrated in Figure 3 are the Mn(II) E_{pa} values obtained after the cathodic scan of the cyclic voltammograms of manganese(III) complexes[12,13] which incorporate the same pentadentate ligand. These data enable a comparison to be made between the E_{pa} values for authentic Mn(II) complexes and the E_{pa} values for the Mn(II) electrochemically generated from original Mn(III) complexes.[12,13] The nearness of the E_{pa} values strongly suggests that the coordination geometry of both the Mn(II) and MN(III) complexes are similar. In general, the ease of electrochemical oxidation follows the rate of chemical oxidation of the complexes, and in lieu of other complications, correlations between dioxygen reactivity and either Mn(II) E_{pa} values or the position of the Mn(III)/Mn(II) redox couple are probably valid.

Referring again to Figure 3, other interesting features are evident. Mn(SALEPT) and Mn(SALDIEN) contain the same potential donor set as Mn(SALDPT) and Mn-(SALBPT). The fact that the E_{pa} values for the latter two complexes are within 35 mV of one another suggests a similar ligand environment around each Mn(II). On the other hand, the significantly more positive E_{pa} values for Mn(SALEPT) and particularly Mn(SALDIEN) compared to Mn(SALDPT) suggest a different ligand environment or structure for the former two complexes. SALEPT and SALDIEN ligands contain ethylene carbon (C_2H_4) bridges between nitrogen donor atoms, and the obvious rationalization would be that the central ligand donor atom cannot coordinate. The crystal structures, however, of Fe(SAL-1,4,7,10)X, where X = Cl·2H$_2$O and NO$_3$·H$_2$O[22] and wherein the ligand has three C_2H_4 bridges (III), show unequivocally that this ligand can function
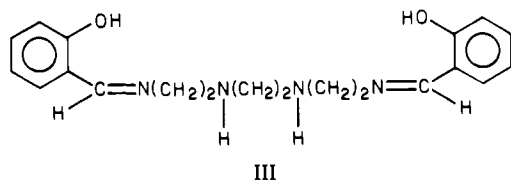
as a full six-coordinate ligand with little steric strain. It thus appears possible that all three donor atoms of EPT and DIEN can coordinate, and if so, other more subtle reasons for these differences must be sought. On the other hand, the size differential between Fe(III) and Mn(II) may preclude secondary amine–manganese interaction.

A second interesting feature of Mn(SALEPT) and Mn-(SALDIEN) complexes is the appearance of a second quasi-reversible oxidation near +0.70 V (Figure 4). The origin of this second oxidation is unknown, but several possibilities are discussed. First, the second wave could be a formal Mn(III) → Mn(IV) oxidation. This seems totally out of line since SALDPT and HBPDPT complexes do not exhibit this second wave. That is to say, if the original Mn(II) complexes

(21) R. H. Holm, G. W. Everett, and A. Charkavorty, *Prog. Inorg. Chem.*, **7**, 82 (1966); D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).
(22) E. Sinn, G. Sim, E. V. Dose, M. F. Tweedle, and L. J. Wilson, *J. Am. Chem. Soc.*, **100**, 3375 (1978).

Figure 4. Cyclic voltammograms of Mn(SALEPT) in dimethyl sulfoxide. Scan rate = 50 mV/s.

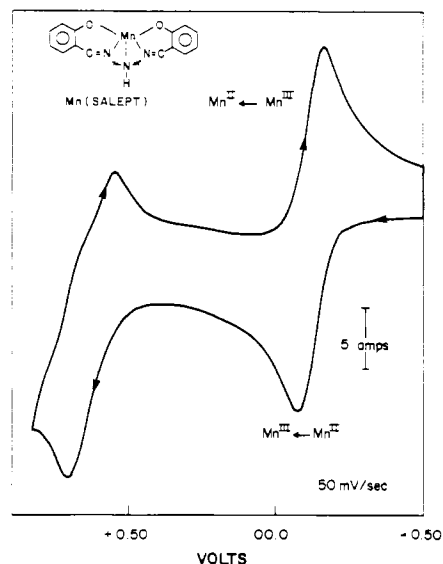of SALEPT and SALDIEN are postulated to contain only tetradentate ligands, it seems unlikely that this poorer donor set would then stabilize an even higher oxidation state. It is possible that a chemical rearrangement to yield a pentadentate ligand after the Mn(II) → Mn(III) oxidation could occur, but we see no evidence of this from our electrochemical studies. In addition, if a simple pentadentate Mn(III) is the product of the first oxidation, then there is no logical reason that the Mn(SALDPT)$^+$ and Mn(SALBPT)$^+$ complexes, which already contain pentadentate ligands, should not exhibit further oxidation.

A second suggestion is that if the secondary amine is not coordinated, then it may be a site of oxidation. Although we cannot rule this out, earlier experiments[13] with Mn(SA-LEPT)NCS and Mn(SAL-1,4,7,10)NCS reveals little change in cyclic voltammetry on addition of CH$_3$I. If one assumes that CH$_3$I methylates the noncoordinated secondary amine, then the second oxidation should disappear or at least be shifted substantially. With Mn(SALEPT) or Mn(SALDIEN) and CH$_3$I, this did not happen.

A third suggestion is that the complexes containing ligands with one or more C_2H_4 units may be dimeric in solution. Although the two Fe(III) complexes with SAL-1,4,7,10 cited previously are monomeric, this does not rule out a dimeric solution structure. As previously discussed, SALDIEN is known to form a dimer with Cu(II)[15] and to coordinate as a tetradentate with Ni(II).[16] We can present no definitive physical evidence to support the dimer formulation[24] for Mn(II) at present; however, the formation of a dimer may explain the two oxidation waves. The first oxidation would yield a Mn^{II}L$_2$Mn^{III} species followed by the second oxidation to yield a Mn^{III}L$_2$Mn^{III} species. An investigation of the electronic spectrum and the EPR signal after the first and second oxidations is in progress and should greatly aid in clarifying the nature of both oxidations.

Two other complexes have yielded interesting electrochemical data, namely, Mn(5-NO$_2$SALDIEN) and Mn(SAL-DAES) (Table III). Both complexes contain a ligand with two C_2H_4 bridges, but each gives only one fully developed oxidation wave. In view of the E_{pa} value for the first wave, this is not surprising as the second oxidation may simply be beyond the range available in Me$_2$SO. The interesting feature of their electrochemistry is the sweep-rate dependence of the Mn(III)/Mn(II) reduction.

For Mn(5-NO$_2$SALDIEN), at fairly fast sweep rates (500 mV/s) (Figure 5), the CV appears as a simple redox couple

Figure 5. Cyclic voltammograms of Mn(5-NO$_2$SALDIEN) in dimethyl sulfoxide at various scan rates.

Figure 6. Cyclic voltammograms of Mn(5-NO$_2$SALDIEN)NCS in dimethyl sulfoxide. Scan rates = 10 and 100 mV/s.

Figure 7. Cyclic voltammograms of Mn(5-NO$_2$SALDIEN)NCS at different voltage sweeps in dimethyl sulfoxide. Scan rate = 100 mV/s.

with a current ratio near 1.0. However, as the sweep rate is decreased, the peak height of the first reduction near +0.285 V decreases, and a second reduction near +0.160 V appears. A sequence of events consistent with these data is

$$[Mn^{II}L] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Mn^{III}L]$$

$$+e^- \searrow \qquad \nearrow\!\!\!\nearrow$$

$$"[Mn^{II}L]"$$

If the sweep rate is relatively fast, only the reduction of [Mn^{III}L] is seen. Given sufficient time, however, a second manganese geometry "[Mn^{III}L]" is preferred. At slow sweep rates both reductions are observed. On subsequent reoxidation, there appears to be no change in the oxidation process, and thus both [Mn^{III}L] and "[Mn^{III}L]" are reduced to the same Mn(II) complex. The nature and hence differences between the two Mn(III) complexes are not known but two possibilities are suggested below.

It has been shown previously that electron-withdrawing groups on the SAL ring enhance the coordination of the central ligand atom, at least in the case of SALDAPE.[5] If a monomeric complex containing a tetradentate ligand (noncoordinated NH or S) is present, the oxidation to Mn(III) with the resulting higher charge may enhance the coordination of the central NH or S. Thus, [Mn^{II}L] may contain a tetradentate ligand as would its immediate oxidation product, [Mn^{III}L]. Given sufficient time, however, the more "acidic" Mn(III) would force coordination of the central ligand atom to give "[Mn^{III}L]" with a fully coordinated pentadentate ligand.

A second suggestion to explain the sweep-rate dependence of the Mn(5-NO$_2$SALDIEN) and Mn(SALDAES) involves a monomer–dimer equilibrium. Since we have suggested the possibility of a dimer for Mn(SALDIEN), the same may be the preferred form for Mn(5-NO$_2$SALDIEN) and Mn(SAL-

DAES). The two Mn(III) products therefore could be a dimeric, mixed-valence product (A) or a mixture of monomeric Mn(III) and Mn(II) products (B). The latter suggestion does

$$[Mn^{II}L_2Mn^{II}] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Mn^{III}L_2Mn^{II}]$$

$$+e^- \searrow \qquad \nearrow\!\!\!\nearrow \quad A$$

$$[Mn^{III}L + Mn^{II}L]$$

$$B$$

not appear to be valid, however, as we have prepared authentic Mn(III) samples of both complexes (Table I). Initial reductions of Mn(5-NO$_2$SALDIEN)NCS and Mn(SALDAES)NCS show clearly that two different Mn(III) complexes are present and that both are reduced to a common Mn(II) species as evidenced by the fact that only a single oxidation wave is observed (Figure 6). There are differences, however, in the electrochemistry of the Mn(II) and Mn(III) complexes. In Mn(5-NO$_2$SALDIEN)NCS, the values of the oxidation peak potential and the first reduction peak potential are close to those of Mn(5-NO$_2$SALDIEN). The peak potential of the second reduction is less positive in the Mn(III) complex compared to the Mn(II) complex. Secondly, the relative ratio of the currents for the two reductions appears to be independent of sweep rate for the Mn(III) complex.

Table III. Cyclic Voltammetry Mn(II)/Mn(III) Data for Mn(5-NO$_2$SALDIEN) and Mn(SALDAES)

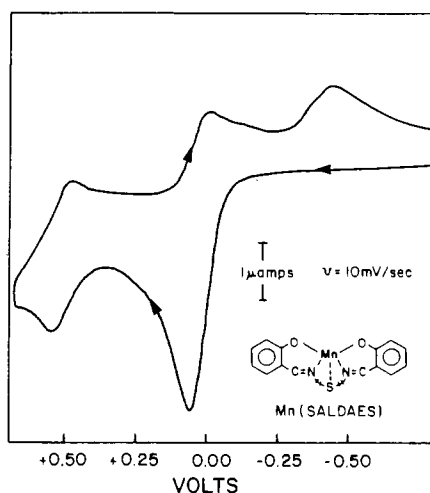| complex	v, mV/s	E_{pa}, V	$E_{pc(1)}$, V	ΔE, mV	i_{pa}, μA	i_{pa}/i_{pc}	$E_{pc(2)}$, V
Mn(5-NO$_2$SALDIEN)	2	+0.352			3.0		+0.223
	5	+0.360			4.7		+0.200
	10	+0.364	~+0.31		6.5		+0.187
	20	+0.369	~+0.30		9.4		+0.175
	50	+0.370	~+0.29		15.0		+0.160
	100	+0.378	+0.294	84	21.3	1.5	~+0.16
	200	+0.385	+0.285	100	29.3	1.2	
	500	+0.393	+0.282	111	44.1	1.1	
Mn(SALDAES)	5	+0.050			4.7		-0.412
(1st oxidn)	10	+0.056	-0.009	65	6.8	2.73	-0.433
	20	+0.060	-0.006	66	10.0	2.07	-0.457
	50	+0.069	-0.010	79	16.3	1.63	-0.475
	100	+0.075	-0.015	90	23.3	1.39	-0.475
	200	+0.080	-0.020	100	32.8	1.25	
	500	+0.095	-0.035	130	48.3	1.17	
Mn(SALDAES)	5	+0.543	+0.468	75	1.6	~1	
(2nd oxidn)	10	+0.548	+0.473	75	1.7	~1	
	20	+0.548	+0.473	75	1.9	~1	
	50	+0.553	+0.445	108	2.4	~1	

Figure 8. Cyclic voltammogram of Mn(SALDAES) in dimethyl sulfoxide. Scan rate = 10 mV/s.

Finally, the size of the oxidation wave is dependent upon whether both reductions were carried out (Figure 7). Except for the differences in the peak potential of the second reduction, the data are consistent with similar structures for the Mn(II) and Mn(III) complexes regardless of how they are formed. The Mn(5-NO$_2$SALDIEN)NCS complex may exist in both forms, and thus the relative concentrations of each Mn(III) species should not be sweep-rate dependent; therefore, the size of the oxidation wave should depend upon whether both Mn(III) complexes have been reduced.

The electrochemistry of Mn(SALDAES) compared to that of Mn(SALDAES)NCS is similar to that of the 5-NO$_2$SALDIEN complexes; i.e., the oxidation peak potentials are nearly the same in both complexes but there are differences in the position of the reduction waves and there is absence of sweep-rate dependence on each reduction wave current.

The Mn(SALDAES) electrochemistry is further complicated by the appearance of a second oxidation near +0.55 V (Figure 8). The current for this wave is less than half that of the first oxidation, but it is clearly quasi-reversible and has none of the sweep-rate dependent properties common to Mn(5-NO$_2$SALDIEN) or the first oxidation of Mn(SALDAES). It is also present in the authentic Mn(III)

complex. The electrochemical properties of the first oxidation are not dependent to any large extent on the second oxidation.

The electrochemistry of two similar ligands, formed by replacing the SAL ring with a pyridine (PY) ring to give an N$_5$ donor set (IIa and IIb), has also been investigated. Unlike their SAL counterparts, these Mn(II) complexes exhibit no activity toward dioxygen or nitric oxide.[23] Their electrochemistry is also devoid of any activity in the +0.30 to –0.30 V region where the SAL-ligand complexes exhibit the Mn(II)/Mn(III) oxidation. Both Mn(PYEPT)(NCS)$_2$ and Mn(PYDPT)(NCS$_2$) show a large oxidation near +0.80 V, which is probably associated with the SCN$^-$ moiety. Also present in both complexes is a reduction near –1.30 V which, on subsequent oxidation, yields two oxidation waves, the first near –1.20 V and the second near –0.55 V. Although the reduction may be formally assigned to a Mn(II)/Mn(I) couple, in view of the lack of reactivity with NO which would produce a formal Mn(I) species, the reduction is probably the ligand itself. Further characterization has not been carried out.

(23) W. M. Coleman and L. T. Taylor, *J. Inorg. Nucl. Chem.*, **41**, 95 (1979).
(24) A molecular weight determination for Mn(SALDAES) (see later Discussion) was performed and a value near that of a monomer obtained (theoretical 381, found 457). However, experimental conditions required the use of *N*,*N*-dimethylformamide and a temperature of 90 °C. Thus, these data are not reliable for answering the question of whether a dimer in Me$_2$SO temperature is present.