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Electrochemistry and Oxygenation Kinetics of Tridentate Schiff Base Manganese Complexes

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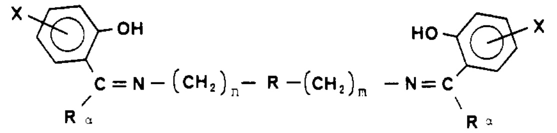
Manganese complexes containing tridentate ligands derived from substituted salicylaldehyde or pyridine-2-carboxaldehyde condensed with 2-(aminomethyl)pyridine and 2-(2-aminoethyl)pyridine have been prepared. High-spin Mn(II) and Mn(III) complexes have been characterized by elemental analyses, magnetic susceptibility, solution conductivity, and IR, UV–visible, and ESR spectra. Complexes with the neutral pyridine-2-carboxaldehyde derived ligands were found to be O_2 insensitive and electrochemically inactive. Salicylaldehyde-derived ligands promote O_2 reactivity with manganese(II), but only those formed with 2-(2-aminoethyl)pyridine are electrochemically active. The kinetics of the reaction with O_2 in dimethyl sulfoxide and pyridine have been studied, and a mechanism is proposed on the basis of the results.

Introduction

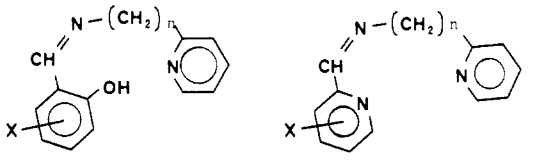
Certain manganese(II) complexes containing multidentate ligands have been shown to react and coordinate with O_2[2a] and NO.[2b] Ligands with four and five donor atoms have most often been successfully employed. In this regard we have described the reactivity patterns of Mn(II) and Mn(III) complexes comprised of dianionic tetradentate, pentadentate, and hexadentate ligands (structure I) with O_2, O_2^-, HO_2^-, and NO.[3-7]



I: X = NO_2, MeO, Cl, H, Me; R_α = H, Ph; R = NH, NR, O, S, CH_2, NH-$(CH_2)_x$-NH

The extent and rate of dioxygen and nitric oxide reactivity have been shown to be related to the aryl and R_α substituents, the presence of a donor atom in the bridging chain (R), and the length of the bridging chain. The reactivity of Mn(II) complexes with NO was reversible, whereas the dioxygen reactivity was irreversible. Manganese(III) complexes did not react with O_2. In addition, large differences in the electrochemical behavior of both Mn(II) and Mn(III) complexes have been correlated with these various ligand modifications.[8-11] Replacement of the salicylaldehyde moiety with pyridine-2-carboxaldehyde always yielded dioxygen-*insensitive* and electrochemically *inactive* Mn(II) complexes.

This report describes the preparation, characterization, O_2 reactivity and kinetics, and electrochemistry of a series of manganese(II)/manganese(III) complexes with the ligands shown in II. These ligands incorporate a number of features that as yet have not been examined such as monoanionic tridentate coordination and the combination of salicylaldehyde and pyridine functionalities. In addition, while manganese complexes employing tridentate ligands to date have contained O_2N, N_3, and O_3 donor sets,[12-16] we believe this to be the first report of manganese complexes containing an ON_2 ligand donor set.



II

$n = 1$ = SALAMP
$n = 2$ = SALAEP
X = NO_2, MeO, H, Cl

$n = 1$ = PYAMP
$n = 2$ = PYAEP
X = H, Me

Experimental Section

Materials. Salicylaldehyde (SAL), 3-methoxysalicylaldehyde (3-MeOSAL), 5-methoxysalicylaldehyde (5-MeOSAL), pyridine-2-carboxaldehyde (PY), 2-(aminomethyl)pyridine (AMP), and 2-(aminoethyl)pyridine (AEP) were obtained from Aldrich Chemical Co. and used without further purification. 6-Methylpyridine-2-carboxaldehyde was obtained from Aldrich but was distilled in vacuo prior to use. 5-Nitrosalicylaldehyde (5-NO_2SAL) and 5-chlorosalicylaldehyde (5-ClSAL) were obtained from Eastman Chemical Co. Potassium superoxide and $Mn(OAc)_2{\cdot}4H_2O$ were obtained from Alfa-Ventron Inorganics. All other materials were reagent grade or equivalent. Superoxide solutions in anhydrous Me_2SO were prepared according to a previously reported procedure.[17]

Preparation of $Mn(ZPYAMP)_2(NCS)_2$ and $Mn(ZPYAEP)(NCS)_2$. AMP or AEP (0.005 mol) dissolved in 20 mL of isopropyl alcohol was added to a stirring solution of the appropriate pyridine-2-carboxaldehyde (0.005 mol), also dissolved in 20 mL of isopropyl alcohol. Nitrogen was bubbled continuously through the resulting yellow solution maintained at room temperature. A deaerated solution of $Mn(OAc)_2{\cdot}4H_2O$ (0.0025 mol) in 10 mL of H_2O was added dropwise, followed by addition of solid NH_4NCS (0.03 mol), whereupon a yellow precipitate appeared. After removal of the N_2 blanket, the precipitate was isolated via filtration, washed with isopropyl alcohol/water and dried at 100 °C in vacuo.

Preparation of $Mn(ZSALAMP)_2$ and $Mn(ZSALAEP)_2$. AMP or AEP (0.01 mol) dissolved in 30 mL of isopropyl alcohol/*tert*-butyl alcohol was added to a solution of the appropriate salicylaldehyde (0.01 mol) also in 30 mL of isopropyl alcohol/*tert*-butyl alcohol. Solid KOH (0.01 mol) was added and the solution stirred until the base had dissolved. The solution was then refluxed under a flow of N_2 for 15 min to remove dissolved O_2. After the solution was allowed

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[2] (a) Coleman, W. M.; Taylor, L. T. *Coord. Chem. Rev.* **1980**, *32*, 1. (b) Coleman, W. M.; Taylor, L. T. *J. Am. Chem. Soc.* **1978**, *100*, 1705.
[3] Coleman, W. M.; Taylor, L. T. *Inorg. Chem.* **1977**, *16*, 1114.
[4] Coleman, W. M.; Taylor, L. T. *J. Inorg. Nucl. Chem.* **1979**, *41*, 95.
[5] Barr, W. M.; Titus, S. J. E.; Taylor, L. T. *Inorg. Chim. Acta* **1979**, *32*, 103.
[6] Coleman, W. M.; Taylor, L. T. *J. Inorg. Nucl. Chem.* **1980**, *42*, 683.
[7] Coleman, W. M.; Taylor, L. T. *Inorg. Chim. Acta* **1981**.
[8] Coleman, W. M.; Goehring, R. R.; Taylor, L. T.; Mason, J. G.; Boggess, R. K. *J. Am. Chem. Soc.* **1979**, *101*, 2311.
[9] Coleman, W. M.; Taylor, L. T.; Boggess, R. K.; Hughes, J. W. *Inorg. Chim. Acta* **1980**, *38*, 183.
[10] Coleman, W. M.; Boggess, R. K.; Hughes, J. W.; Taylor, L. T. *Inorg. Chem.* **1981**, *20*, 700.
[11] Coleman, W. M.; Boggess, R. K.; Hughes, J. W.; Taylor, L. T. *Inorg. Chem.* **1981**, *20*, 1253.
[12] Mukherjee, A. K.; Ray, P. *J. Indian Chem. Soc.* **1955**, *32*, 581.
[13] Butler, K. D.; Murray, K. S.; West, B. O. *Aust. J. Chem.* **1971**, *24*, 2249.
[14] Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1978**, *17*, 333.
[15] Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Gleria, M. *Science (Washington, D.C.)* **1975**, *189*, 852.
[16] Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1978**, *17*, 338.
[17] Valentine, J. S.; Curtis, A. B. *J. Am. Chem. Soc.* **1975**, *97*, 224.

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Table I. Analytical Data for Manganese Pyridine-Derived Tridentate Schiff Base Complexes

compd	Λ_m, mho cm^2/mol	% C		% H		% N		μ_{eff}, μ_B
		calcd	found	calcd	found	calcd	found	
$Mn(6\text{-}MePYAMP)_2(NCS)_2$	77.5[a]	55.80	56.01	4.53	4.33	18.60	18.23	6.11
$Mn(PYAEP)(NCS)_2$	73.0	47.12	47.87	3.43	3.63	18.31	18.07	5.83
$Mn(6\text{-}MePYAEP)_2(NCS)_2$	70.7	48.49	48.90	3.81	3.92	17.66	17.62	5.95

[a] Λ_m for $Ni(ClO_4)_2 \cdot 6H_2O$ is 74.2 mho cm^2/mol.

Table II. Analytical Data for Manganese Salicylaldehyde-Derived Schiff Base Complexes[a]

compd	Λ_m, mho cm^2/mol	% C		% H		% N		μ_{eff}, μ_B
		calcd	found	calcd	found	calcd	found	
$Mn(SALAMP)_2 \cdot C_3H_7OH$		64.80	63.37	5.64	5.18	10.42	10.55	c
$Mn(5\text{-}ClSALAMP)_2 \cdot H_2O$		55.35	55.34	3.93	3.95	9.93	9.90	6.1
$Mn(SALAEP)_2 \cdot 2H_2O$		62.11	61.12	5.60	5.60	10.34	10.20	6.11
$Mn(5\text{-}NO_2SALAEP)_2$		56.47	56.59	4.06	4.25	14.12	13.95	5.96
$Mn(5\text{-}ClSALAMP)_2(NCS)$	32.5[b]	53.65	53.32	3.34	3.03	11.59	11.74	4.91
$Mn(5\text{-}ClSALAEP)_2(NCS)$	34.3	55.08	54.80	3.83	3.90	11.07	10.97	4.95

[a] It will be noticed that a number of possible complexes are absent from this table. We have found that the complexes are hydrolyzable and thermally unstable, making some syntheses not practical. [b] Λ_m for $(C_2H_5)_4$ is 35.0. [c] Unable to measure due to rapid oxidation.

to cool to room temperature, $Mn(OAc)_2 \cdot 4H_2O$ (0.005 mol) in 25 mL of deaerated H_2O was added dropwise. The resulting yellow-orange suspension was stirred under N_2 for 1 h, after which it was sealed and transferred into a glovebox containing an Ar atmosphere. The precipitate was suction filtered, washed with 95% ethanol and heptane, and dried in vacuo over silica gel.

Preparation of $Mn(ZSALAMP)_2NCS$ and $Mn(ZSALAEP)_2NCS$. The previous preparation was followed up to the point at which the Mn(II) complex was taken into the glovebox. For preparation of the Mn(III) complexes, the suspension was instead oxidized by passing a stream of O_2 through it for 1 h. NH_4NCS (10 g) was then added and the resulting dark colored solution stirred for a further 15 min. H_2O (100 mL) was then added to precipitate the product, which was filtered, washed with 95% ethanol and H_2O, and dried in vacuo at 100 °C.

Physical Measurements. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. IR spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer. UV–visible spectra were obtained with use of an Aminco DW2 spectrophotometer, which was also used for kinetic studies. ESR spectra were obtained on a Varian Model 4500 spectrometer. Magnetic susceptibility measurements were performed on a Cahn electrobalance at 296 K by using the Faraday method. Conductivities were measured with a Beckman conductivity bridge. Electrochemical studies were performed with a Bioanalytical Systems CV-1A cyclic voltammetry instrument.

Kinetic Studies. The reaction of manganese(II) complexes with O_2 was studied by following the change in the UV spectrum of the complex as a function of time in an excess (>10:1) of O_2. The order of the reaction with respect to the complex, specific rate constants, and activation energies were determined by standard methods.[18]

Results and Discussion

Manganese(II) PYAM(E)P Complexes. Manganese(II) complexes containing neutral PY-derived ligands divide themselves into two groups depending on the amine used in the preparation. Complexes made from AMP have a 2:1 ligand to metal ratio, while those from AEP have a 1:1 ratio even though the ratio utilized in all syntheses was 2:1. Except for the difference in ligand to metal ratio, the complexes have similar properties. They are orange-yellow, high-spin, d^5 solids (Table I). ESR spectra were consistent with those of other high-spin Mn(II) complexes containing N donor atoms.[19] In Me_2SO a six-line pattern centered around 3350 G with a coupling constant of 90 G appears. No splitting due to ^{14}N coupling suggests that little or no electron delocalization from the Mn(II) center to the N donor atoms occurs. Conductivity measurements show that the compounds are 1:2 electrolytes in Me_2SO (Table I).

Infrared spectra of the complexes exhibit bands at 1600 and 1575 cm^{-1}, indicative of coordinated imine and pyridine nitrogens, respectively.[20] There is also absorption at 2000–2050 cm^{-1}, due to the thiocyanate ion.[21] The assignment of this peak is ambiguous, because both free and coordinated NCS^- absorb in this range. However, since molecular models show that both PYAMP and PYAEP can serve as tridentate ligands without undue bond strain, we have postulated that all octahedral sites are filled by the two tridentate ligands in the ZPYAMP complex, and the NCS^- is only present as a counterion. The ZPYAEP complexes, in light of their stoichiometry, may be highly associated, possibly with NCS^- in a coordination site.

Each of these complexes with neutral N_3 donor sets was found to be electrochemically inactive to manganese oxidation or reduction and O_2 insensitive. A similar situation was found to be the case with analogous neutral N_5 and N_6 donor sets.[22]

Manganese(II) SALAM(E)P Complexes. The manganese(II) SAL-derived complexes have a number of properties in common with the PY-based complexes. They are yellow-orange solids with no detectable d–d bands in their UV–visible spectra, they have magnetic moments indicative of a high-spin d^5 configuration, and they possess peaks in their IR spectra indicative of coordinated imine and pyridine groups (Table II). However, there are more differences than similarities, some of them quite significant. The SAL-based ligands are anionic; therefore, there is no counterion in the compounds. Conductivity measurements show that the complexes are nonelectrolytes in Me_2SO. The most important differences are in the reactivities of the complexes. SAL-derived complexes *are* both chemically and electrochemically oxidizable (vide infra) in agreement with earlier findings regarding higher denticity ligands.

Manganese(III) SALAM(E)P Complexes. These light brown complexes exhibit properties typical of a high-spin d^4 electron configuration (Table II). UV–visible spectra contain a shoulder at ~600 nm, $\epsilon \approx 200$ M^{-1} cm^{-1}, assignable to a d–d transition. Its high intensity and width ($\Delta\nu_{1/2} \approx 125$ nm), are commonly found in Jahn–Teller-distorted, ESR-silent, Mn(III) ($\mu_{eff} \approx 4.9$ μ_B) complexes. The IR spectra show coordinated imine and pyridine bands at 1600 and 1575 cm^{-1}

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(18) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, MA, 1974.

(19) Coleman, W. M.; Taylor, L. T., unpublished results.

(20) Spencer, C. T.; Taylor, L. T. *Inorg. Chem.* **1971**, *10*, 2407.

(21) Singh, P. P. *Coord. Chem. Rev.* **1980**, *32*, 33.

(22) Coleman, W. M.; Taylor, L. T. *J. Inorg. Nucl. Chem.* **1979**, *41*, 95.

Table III. Electrochemical Results for Manganese(III) Complexes

starting compd	redn potential, V (100 mV/s)
$Mn(5\text{-}NO_2SALAEP)_2$	-1.30^a
$Mn(5\text{-}ClSALAEP)_2(NCS)$	-0.14
$Mn(SALAEP)_2$	-0.21
$Mn(5\text{-}MeOSALAEP)_2(NCS)^b$	-0.33

[a] NO_2 reduction rather than Mn(III) reduction. [b] Analytically pure but $\mu = 5.40\mu_B$.

and an NCS^- band at ~2025 cm^{-1}. Conductivity measurements show the compounds to be 1:1 electrolytes in Me_2SO.

The reactions of these complexes with reducing agents, namely, NO and O_2^-, are similar to those of previously reported higher denticity complexes.[2b,6,7] Green solutions of the complexes in Me_2SO react with NO to produce yellow, ESR-active (six lines, $A = 90$ G) solutions with no detectable d–d transitions in their UV–visible spectra, interpretable as a reduction to a Mn(II) complex. The reaction in Me_2SO with crown ether solubilized KO_2 also suggests a reduction to Mn(II), with ESR and spectral results similar to those obtained with NO. It is significant that these results are in contrast with the observations made for reactions of analogous penta- and hexadentate complexes with O_2^-. Spectrally, titration of the tridentate complex yielded no isobestic points, while the reverse was true for the higher denticity complexes. Furthermore, no ESR signal was detected in earlier work after complete O_2^- reaction, whereas a six-line pattern is observable here. The absence of an ESR signal was attributed to spin coupling between Mn and O_2 in what was formally considered to be the formation of a manganese(II)–dioxygen adduct.

Electrochemical Studies. Of the complexes studied, only those containing the ZSALAEP ligands were electrochemically active. The inactivity of the PY-derived complexes is in agreement with our earlier work, but that of the ZSALAMP complexes is a surprise, since they only differ from the ZSALAEP complexes by a single methylene linkage. We have investigated the effects of chain length on O_2 reactivity,[5] but this is the first drastic effect on the electrochemical properties that we have seen.

Table III shows the potentials found by cyclic voltammetry for the reduction of the chemically or electrochemically generated Mn(III) complexes of ZSALAEP. The potentials found are in agreement with earlier findings in that the order of ease of reduction is Cl > H > MeO. An anodic sweep of $Mn(5\text{-}NO_2SALAEP)$ does not generate the Mn(III) complex. A reduction wave, however, does appear at −1.3 V, characteristic of reduction of the nitro group. The voltammograms differ from those of previous complexes in that the reductions are quasi-reversible. Figure 1 shows a typical CV of a ZSALAEP complex. Irreversibility is indicated by the absence of a single oxidation peak (Mn(II)/Mn(III)) on the anodic part of the scan and the extreme width of the reduction peak (Mn(III)/Mn(II)). Not visible from the figure is the shift of the peaks away from each other with an increase in scan rate, also an indication of irreversibility. Repetitive scans produce identical voltammograms, therefore, the overall electrode reactions *are* reversible. Three distinct reproducible oxidation waves are observed and can be assigned to the reactions

$$A:\quad Mn^{II}(ZSALAEP)_2(Me_2SO)_2 \rightarrow Mn^{III}(ZSALAEP)_2^+ + e^- + 2Me_2SO$$

$$B:\quad Mn^{II}(ZSALAEP)_2(Me_2SO) \rightarrow Mn^{III}(ZSALAEP)_2^+ + Me_2SO + e^-$$

$$C:\quad Mn^{II}(ZSALAEP)_2 \rightarrow Mn^{III}(ZSALAEP)_2^+ + e^-$$

This observation may be rationalized by assuming that the pyridine end of the tridentate ligand may be displaced by a solvent molecule in the Mn(II) complex as it is formed by reduction of the Mn(III) complex. The three Mn(II) species in solution are suggested to have slightly different oxidation potentials. The higher oxidation state should hold the tridentate ligands more tightly; therefore only one Mn(III) species exists. The anodic shift as Me_2SO replaces a pyridine functionality is not surprising because of our previous findings that a pyridine group in a ligand makes oxidation more difficult, if not impossible. Our previous work with pentadentate ligands has established that Mn(III) is coordinated more strongly than Mn(II) and that a ligand may change in denticity as the metal oxidation state changes.[11] The ratios of the anodic peak heights are a function of scan rate. Fast scans produce only peaks B and C, with C being the largest. As the scan rate is decreased, peak A grows at the expense of B and C, and at extremely slow scan rates, it is the largest of the three, with C being the smallest. The equilibrium between the three species is apparently in favor of the disolvated Mn(II) species, but the addition of solvent is relatively slow. Attempts to isolate these various solvated species have been unsuccessful to date.

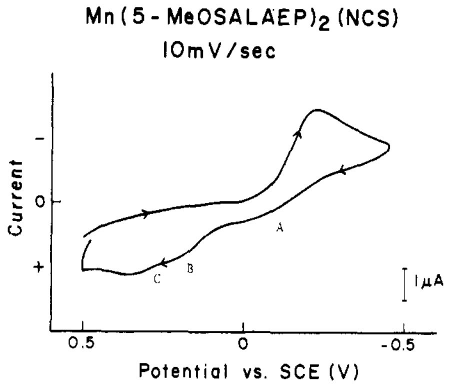

Figure 1. Cyclic voltammogram of $Mn(5\text{-}MeOSALAEP)_2(NCS)$.

Coulometric experiments were attempted with *n* values of 0.8 ± 0.1. The reduced solutions exhibited a yellow color characteristic of Mn(II). Direct comparison with a known spectrum was not possible because of our inability to prepare both Mn(II) and Mn(III) complexes of the same ligand.

It should be noted again that the results for the unsubstituted compound were obtained with use of the Mn(II) complex. We were unable to chemically prepare pure $Mn(SALAEP)_2(NCS)$, but electrochemical oxidation apparently cleanly produces the Mn(III) complex, since the CV features fall neatly between those of the MeO- and Cl-substituted complexes.

Oxygenation of Mn(II) Complexes. The reaction of the SAL-based complexes with O_2 possess similarities to, and differences from, the reactions of previously studied higher denticity ligands. The effect of various substituents on the salicylaldehyde ring are identical with those previously discovered; i.e., as one changes from electron-withdrawing to electron-donating groups (NO_2 to MeO substituted), the O_2 sensitivity increases. The NO_2 group actually inhibits the reaction with O_2 completely. Relative rates were determined by visual observation of the complexes in solution on exposure to air. Ease of oxygenation correlates with electrochemical activity in that the most negative reduction potential is found for the species whose reduced form oxidizes fastest.

The substituent effect operates in both solution and solid-state oxygenations, but in the solid state the effect of methylene chain length can also be seen. In earlier studies on tetradentate complexes, increasing the length of the chain between donor groups produced compounds that were more oxygen sensitive.[5] It was postulated that a change in coordination geometry from octahedral to tetrahedral occurred, which made it easier for

Table IV. Rate Constants for Oxygenation of $Mn(SALAEP)_2$[a]

solvent	T, °C	K, M^{-1} min^{-1}
Me_2SO	22.5	12.6 (9.43)
	28.2	33.8
	36.3	80.0
pyridine	23.1	1.84 (1.30)

[a] Activation energy 24.1 kcal/mol (Me_2SO).

Table V. Rate Constants for Oxygenation of $Mn(SALAMP)_2$[a]

solvent	T, °C	K, M^{-1} min^{-1}	solvent	T, °C	K, M^{-1} min^{-1}
pyridine	17.5	0.92	Me_2SO	22.2	9.43
	28.0	1.80		31.1	14.2

[a] Activation energy 11.1 (pyridine) and 8.16 kcal/mol (Me_2SO).

O_2 to reach the Mn center. For the tridentates, however, the situation is reversed; solid $Mn(SALAEP)_2$ is not air sensitive, but $Mn(SALAMP)_2$ is. We believe that the SALAEP ligand, being more flexible, coordinates the Mn center more tightly, thus inhibiting entry of the O_2 molecule.

Solid-state oxygenation of $Mn(SALAMP)_2$ produces a compound whose IR spectrum contains a doublet at ~620 cm^{-1}, assignable as an Mn–O stretch. Apparently the ligands cannot force the O_2 out of the coordination sphere, and the O_2 remains bound to Mn after electron transfer occurs. This of course implies that, just as in solution, a dangling coordinated group (probably the pyridine unit) exists in the oxygenated product. On the basis of a manometric study and a measured magnetic moment of 4.8 μ_B/Mn, the solid-state product is most likely a μ-peroxo manganese(III) species.

The products of solution oxygenation are the Mn(III) species with no coordination by the O_2 reduction products. The UV–visible spectra of isolated Mn(III) species are identical with those of oxidation products with only the Mn(II) complex and O_2 in solution. The tridentates are thus similar to hexadentate complexes, which undergo only electron transfer in the overall reaction,[6] and different from the tetra-[5] and pentadentate[3] complexes, which incorporate oxygen into their coordination sphere. The manometric study of the reaction gives an overall $Mn:O_2$ ratio of 2:1, making the tridentates similar to the tetradentates in this respect.

Oxygenation Kinetics of Mn(II) Complexes. We have performed a kinetic study on the solution reaction of several of these Mn(II) complexes with O_2. The reaction was followed by observing the changes in the near-UV spectrum of the complex during oxidation. Figure 2 is a typical repetitive scan of an oxygenation reaction. The reaction was initiated by dissolving ~0.1 mg of the complex in 10 mL of solvent that had been saturated with O_2. The solution was filtered to remove any undissolved complex and an aliquot placed in a thermostated spectrophotometer cell. The amount of complex used was small enough to ensure at least a 10:1 ratio of O_2 to complex, i.e., pseudo-order conditions.[23]

Tables IV and V show the calculated rate constants and activation energies for the unsubstituted complexes reacting with O_2. A number of points should be noted from these tables. First, as with the tetradentate ligands,[24a] the activation energy for a given complex is higher in pyridine than in Me_2SO, since pyridine is a better donor solvent. Second, the SALAEP complex is seen to have a much higher E_a than the SALAMP complex. This can be explained, as was previously done for the solid-state oxygenations, by the increased flexibility and better fit of SALAEP around the manganese. The activation energies that we have calculated are similar to those found for the oxidation of O_2-sensitive Co complexes, 4–17 kcal/mol.[24b]

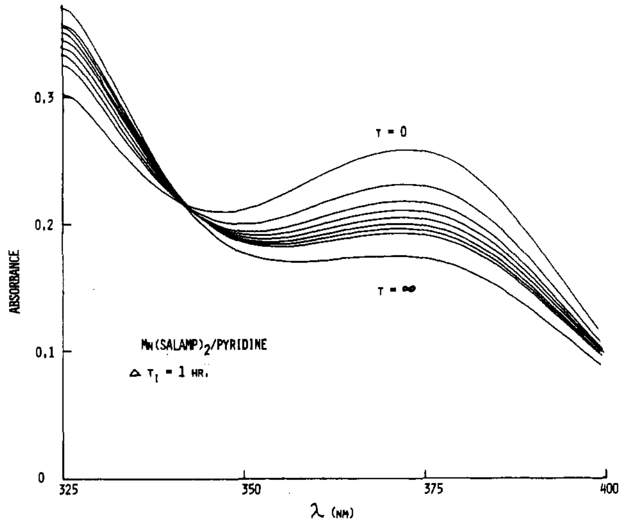

Figure 2. Repetitive scan for the oxygenation of $Mn(SALAMP)_2$ in pyridine.

The reaction was found to be first order in the complex. On the basis of this and all other data we have gathered, we postulate the mechanism given in eq 1–3 for solution oxygenation.

$$Mn^{II}L_2S_2 + O_2 \xrightarrow{\text{slow}} Mn^{III}L_2(O_2^-) + 2S \quad (1)$$

$$Mn^{III}L_2(O_2^-) + Mn^{II}L_2S_2 \rightarrow Mn^{III}L_2(O_2^{2-})Mn^{III}L_2 + 2S \quad (2)$$

$$Mn^{III}L_2(O_2^{2-})Mn^{III}L_2 \rightarrow 2Mn^{III}L_2 + O_2^{2-} \quad (3)$$

The peroxide anion would go on to react with the solvent or disproportionate. Other formulations for the various manganese oxygenated species can be envisioned. Our choices are based on familiar Mn, Fe, and Co species in the literature. Since the rate is first order in Mn there should be no buildup of these species to enable our isolation of them. The incorporation of a solvent molecule in the coordination sphere of the species being oxidized is required to explain the ~1.4× increase in E_a on going from Me_2SO to pyridine, i.e., increasing the donor strength of the solvent. For the tetradentate ligands, an increase of ~2× was found for the same solvent change,[24a] which we believe is due to initial displacement of coordinated solvent by O_2. This correlates with the electrochemical results in that the disolvated species is the easiest to oxidize.

In conclusion, we have prepared a number of Mn(II) and Mn(III) complexes with tridentate Schiff base ligands. Ligand modifications have been shown to have a substantial effect on the electrochemistry and O_2 sensitivity of the complexes.

Acknowledgment. This research was supported by NIH Research Grant No. 21844-01. We wish to thank Steve Coleman for preparing many of the complexes used in this study.

Registry No. $Mn(6\text{-}MePYAMP)_2(NCS)_2$, 84279-64-1; $Mn(PYAEP)(NCS)_2$, 84279-65-2; $Mn(6\text{-}MePYAEP)(NCS)_2$, 84279-66-3; $Mn(SALAMP)_2$, 84279-67-4; $Mn(5\text{-}ClSALAMP)_2$, 84279-68-5; $Mn(SALAEP)_2$, 84279-69-6; $Mn(5\text{-}NO_2SALAEP)_2$, 84279-70-9; $Mn(5\text{-}ClSALAMP)_2(NCS)$, 84279-72-1; $Mn(5\text{-}ClSALAEP)_2(NCS)$, 84279-74-3; $Mn(5\text{-}MeOSALAEP)_2(NCS)$, 84279-76-5.

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(23) The reaction was not monitored with an excess of complex because of lack of a suitable technique for measuring the O_2 concentration as a function of time. However, in the mathematical treatment of the data, we have assumed that the reaction is first order in O_2. We feel justified in this assumption because of the previously mentioned manometric study. It is difficult to envision how a second molecule of O_2 could become involved in the mechanism without appearing in the overall reaction.

(24) (a) Frederick, F. C.; Taylor, L. T., unpublished results. (b) Miller, F.; Simplicio, J.; Wilkins, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 1962.