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Oxygenation Studies of Manganese(II) Complexes Employing Tetradentate Ligands Derived from Salicylaldehyde and Long Chain Diamines

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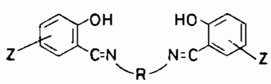
Manganese(II) complexes formed by the reaction of either salicylaldehyde or 5-chlorosalicylaldehyde and polymethylenediamines have been isolated. The complexes Mn(SALC$_6$), Mn(SALC$_8$), and Mn(SALC$_{10}$) rapidly darken upon exposure to air. Mn(SALC$_4$) and the chloro derivatives are stable in air when dry. When suspended in DMSO all complexes, with the exception of Mn(SALC$_4$), react with oxygen to form manganese(IV) complexes. All of the complexes react with oxygen in solution. The rates of oxygenation of the complexes in the solid state, as DMSO suspensions, and in pyridine solution suggest a two step oxygenation. A manganese(III) intermediate is isolated for the Mn(SALC$_8$) case. These results are correlated with previous oxygenation studies of Mn(SALC$_2$) and Mn(SALC$_3$). The structure of the fully oxygenated complexes is proposed to be polymeric with μ-dioxo bridges between pairs of manganese atoms.

Introduction

Schiff base N_2O_2 donor ligands have been extensively studied as oxygen-carriers with cobalt [1]. More recently manganese complexes employing some of these ligands have also been explored. A complex of the Schiff base derived from salicylaldehyde and ethylenediamine (H_2SALC_2) (Structure I, R = C_2H_4) has received the most attention. Several conflicting reports regarding the reaction of Mn(SALC$_2$) with O_2 have been reported. Pfeiffer and coworkers [2] described the preparation of [Mn(SALC$_2$)(OH)] by the air oxidation of a Mn(SALC$_2$) solution. Lewis, *et al.* [3] observed that the products of air oxidation depended upon the solvent employed. Magnetic susceptibilities of samples prepared in pyridine or DMF were found to decrease markedly with temperature; therefore, a formulation of [Mn(SALC$_2$)]$_2$O or [Mn(SALC$_2$)O$_{0.5}$]$_n$ was proposed. Recently these oxygenation products have been reexamined again [4, 5]. Three types of complexes involving Mn^{III}-O_2-Mn^{III}, Mn^{IV}-O and [Mn^{IV}-O]$_n$ were postulated to be obtainable upon reacting either Mn(SALC$_2$), Mn(3-CH_3OSALC$_2$) or Mn(5-NO_2SALC$_2$) with molecular oxygen in organic solvents. X-ray analysis on these interesting materials is currently lacking. An X-ray photoelectron spectroscopic study [6] indicated a positive chemical shift in going from Mn(SALC$_2$) to the postulated Mn^{III}-O_2-Mn^{III} species; however, a near zero shift was observed on comparing Mn(II) with the Mn(IV) complexes. A report of the interaction of oxygen with pyridine solutions of related ethylene-chain substituted manganese(II) complexes has also appeared [7]. In boiling pyridine as well as pyridine solutions at –15 °C complexes of stoichiometry [Mn(Ligand)(OH)] are believed to be the major reaction product.



Structure I

Considerable attention has been devoted to a closely related compount, Mn(SALC$_3$) (Structure I, R = C_3H_6), which also has yielded a number of contradictory results. Johnson and Beveridge [8] reported that [Mn(SALC$_3$)(H_2O)] reacts reversibly with O_2, N_2 and CO forming 1:1 gas adducts as evidenced by gas-uptake experiments and infrared band assignments. Several years later the precursor suspended in benzene and exposed to air was postulated [9] to yield materials of formula [Mn(SALC$_3$)(O_2)(H_2O)] and [Mn(SALC$_3$)(O)(C_6H_6)$_{0.5}$]. When suspended in pyridine the parent complex was believed to yield Mn(SALC$_3$)(O)(py)]. A re-examination [10] of this compound via X-ray analysis revealed it to be dimeric with each manganese atom octahedrally coordinated to the non-planar SALC$_3$ tetradentate ligand and to two bridging hydroxy groups. Four molecules of pyridine were associated with each dimeric unit; however, they were not directly bonded to the manganese atom. While the authors prefer two formally Mn(III) species bridged to hydroxy groups, the X-ray data could have been interpreted as two Mn(IV) centers bridged by two oxide ions.

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In a related study [11] manganese(II) complexes incorporating a linear pentadentate N_3O_2 ligand ($H_2SALDPT$) (Structure I, R = $(CH_2)_3$-NH-$(CH_2)_3$) have been shown to undergo irreversible oxidation to Mn(III) along with oxidation of the ligand. Nitro substituents on the aromatic portion of the ligand inhibited ligand oxidation so that a material of formula, Mn(5-NO_2SALDPT)(OH), was isolable. Electron donating groups were found to enhance ligand oxidation.

A preliminary report [12] on N_2O_2 donor ligands similar to H_2SALC_2 has revealed that the extent and rate of reaction with oxygen may be a function of the carbon chain joining nitrogen donor linkages. In an effort to more completely characterize the materials described therein and to extend the study to carbon chains of different length we wish to outline the oxygen reactivity of Mn(SALR) in solution and in the solid state where R = C_2H_4-$C_{10}H_{20}$.

Experimental

Materials

Diamines were obtained from Aldrich Chemical Co., Milwaukee, Wis. Salicylaldehyde and 5-chloro-salicylaldehyde were obtained from Fisher Scientific Co., Fairlawn, N. J. and Eastman Kodak Co., Rochester, N.Y. Mn($SALC_2$) and Mn($SALC_3$) were prepared via published procedures [5, 8]. All other chemicals were of reagent grade or equivalent.

General Preparation of Ligands

To a stirred refluxing solution of the appropriate salicylaldehyde (0.25 mol) dissolved in 150 ml of methanol was added the diamine (0.125 mol) dissolved in 25 ml of methanol. The resulting yellow solution was refluxed for 30 min. The volume of the solution was then reduced whereupon yellow crystals formed on cooling which were filtered by suction and washed with ice-cold absolute ethanol. The yellow product was recrystallized from methanol and dried at room temperature *in vacuo*. Elemental analyses (CHN), infrared spectra and melting points from the literature [13] where available indicated formation of the tetradentate ligand in each case.

General Preparation of Unsubstituted Manganese(II) Complexes

A stirred solution of tetradentate ligand (0.01 mol) in 150 ml of methanol was refluxed for 10 min under N_2. Solid NaOH (0.02 mol) was added to the refluxing solution. When the base had dissolved, $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ (0.01 mol) dissolved in 50 ml of cold deoxygenated water was added dropwise to the refluxing ligand solution. An orange-yellow precipitate formed after approximately one-half of the manganese solution was added. The mixture was refluxed with stirring for 2 hours under N_2 after which the flask was sealed and transferred to an inert atmosphere box. The microcrystalline product was filtered by suction, washed with methanol and dried 12 hours at room temperature *in vacuo.*

General Preparation of 5-Chloro-substituted Manganese(II) Complexes

To the appropriate tetradentate ligand (0.01 mol) suspended in 150 ml of tert-butanol under N_2 was added KOH (0.02 mol) dissolved in 20 ml of water. The suspension was heated with stirring to reflux whereupon a red-orange solution was produced. After refluxing the solution for 30 min and allowing it to come to room temperature, $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ (0.01 mol) dissolved in 50 ml of cold, deoxygenated water was added. The resulting mixture was stirred an additional 2 hours, sealed and transferred to an inert atmosphere box. The orange-yellow precipitate which formed was isolated, washed and dried as described above.

Preparation of Oxygenated Manganese Complexes

Small amounts (0.001 mol) of each manganese(II) complex were exposed to various oxygen pressures: (a) air, (b) pure O_2, P_{O_2} = 800 Torr, and (c) pure O_2, P_{O_2} = 400 Torr. The complexes were exposed as dry powders, suspended or dissolved in DMSO and as pyridine solutions. The red brown products which formed during oxygenations in solution were filtered by suction, washed with methanol and dried at 100 °C *in vacuo* for 2 days. The filtrates, except those of Mn($SALC_2$) and Mn($SALC_3$), were colorless.

Physical Measurements

Manipulation of oxygen-sensitive compounds was carried out in a Vacuum Atmosphere Corporation inert atmosphere box (Model He 43-2-Dri-Lab) in a O_2-free argon or nitrogen atmosphere. Oxygen uptake measurements were obtained with a modified Warburg apparatus which has been described previously [11]. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240 Elemental Analyser. Infrared spectra were obtained using a Beckman IR 20A-X spectrophotometer over the range 4000–300 cm^{-1}. The solid samples were prepared as Nujol mulls between KBr plates. Electron spin resonance spectra were obtained with a Varian E-12 electron paramagnetic resonance spectrometer. Samples were run as powders or as dilute solutions in quartz capillary tubes. The field and frequency calibrations were made using Varian Weak Pitch and a Fluke frequency meter, Model 1953-A. Thermogravimetric analysis (TGA) data were obtained on a Tracor TGA-5 system. Samples in the range of 12–20 mg were heated *in vacuo* from 20° to 270 °C using a 2 °C per min heating rate. Magnetic susceptibility measurements were made by the Faraday method.

Susceptibilities were measured at room temperature at field strengths of approximately 6.8, 9.3, 10.8, and 11.6 kilogauss produced by a Varian V2900 power supply to a Varian V4005 electromagnet. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7 double focusing mass spectrometer. Pressure was maintained at 10^{-6} Torr. The ionizing electron energy was in the range of 50 to 70 eV. All spectra were calibrated wiht perfluorokerosene.

Results and Discussion

Manganese(II) Complexes

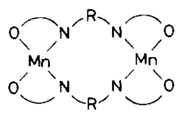
Manganese(II) complexes employing tetradentate ligands formed by the reaction of salicylaldehyde and various linear diamines which differ in the number of carbon atoms joining amino groups have been isolated. More specifically new powdery compounds have been prepared with 1,4-diaminobutane(C_4), 1,5-diaminopentane(C_5), 1,6-diaminohexane(C_6), 1,7-diaminoheptane(C_7), 1,8-diaminooctane(C_8) and 1,10-diaminodecane(C_{10}) which range in color from bright yellow to orange. Similar looking materials were prepared using the 5-chloro derivative of the C_{6-8} tetradentate ligand. Analytical data in support of the one manganese: one tetradentate ligand empirical formulation are listed in Table I. In several cases rapid analyses were required because the compounds oxygenate readily in the solid state. Purification of the compounds via recrystallization was not possible due to their insolubility in an appropriate solvent.

Infrared spectra of the compounds prepared in an inert atmosphere are consistent with incorporation of the deprotonated tetradentate ligand and the anhydrous formulation. Positive ion mass spectra were obtained and each complex gave an isotopic cluster corresponding to a monomeric parent ion.

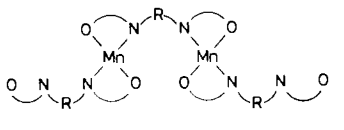
Magnetic moments for the complexes are shown in Table I and the values range from 5.63 to 5.88 B.M. The moments are in agreement with previously reported manganese(II) complexes [14]. Mn(SALC$_3$) has been reported to have μ_{eff} = 5.93 B.M. Mn(SALC$_2$) is believed [15] to exist as a dimer in the solid state with μ_{eff} = 5.24 B.M. This lower magnetic moment is suggested to be caused by antiferromagnetic coupling between manganese centers. While these new compounds may be polymeric in the solid state, magnetic measurements suggest that little or no spin–spin interaction exists. Certainly with increasing length of the polymethylene chain the possibility for the tetradentate ligand to bind two metal ions improves considerably. This may result in a binuclear complex similar to those reported by Pfeiffer [16] (Structure II) or a more extensive polymeric species (Structure III). Additional polymeric structures can be envisioned wherein the coordination number of manganese is expanded. The progressively lower complex solubility in going from C_2 to C_{10} lends credance to this argument. Molecular weight measurements in any solvent are precluded because of poor solubility.

TABLE I. Analytical Data for Manganese(II) Complexes.

Compound		Analysis (%)			
		C	H	N	μ_{eff} (B.M.)
Mn(SALC$_4$)	Calcd.	61.89	5.15	8.02	5.74
	Found	61.78	5.17	7.99	
Mn(SALC$_5$)	Calcd.	62.81	5.54	7.71	5.63
	Found	62.53	5.64	8.21	
Mn(SALC$_6$)	Calcd.	63.66	5.84	7.43	5.64
	Found	63.24	5.59	7.29	
Mn(5-ClSALC$_6$)	Calcd.	53.81	4.48	6.28	5.63
	Found	53.48	4.50	6.18	
Mn(SALC$_7$)	Calcd.	64.45	6.18	7.16	5.76
	Found	63.93	6.51	7.42	
Mn(5-ClSALC$_7$)	Calcd.	54.79	4.78	6.09	5.88
	Found	54.39	5.13	6.26	
Mn(SALC$_8$)	Calcd.	65.18	6.42	6.91	5.63
	Found	64.90	6.57	7.07	
Mn(5-ClSALC$_8$)	Calcd.	55.81	5.06	5.91	5.76
	Found	55.69	5.20	5.55	
Mn(SALC$_{10}$)	Calcd.	66.51	6.93	6.45	5.71
	Found	66.47	6.85	6.58	



Structure II



Structure III

Electron spin resonance spectra have been measured for all the complexes in the solid state in an effort to obtain structural information. Several rules have been published [17] which attempt to correlate ESR spectra and manganese(II) geometry. Pseudotetrahedral monomeric complexes of manganese(II) are stated [18] to give rise to intense absorption at $g_{eff} \cong 4.27$, while compounds with a *trans*-octahedral geometry exhibit strong absorption [19] around $g_{eff} \cong 6.0$. Spectra of $Mn(SALC_n)$ where n = 4–10 do not match-up with previously published spectra of compounds of any known structure [20–21]. Closest agreement is found with a *trans*-octahedral or a "polymeric" structure. It is important to note, as will be alluded to later, that there are apparently structural changes in going from C_3 to C_{10} as a comparison of esr spectra in Figures 1 and 2 will attest. For a series of analogous cobalt(II) complexes [22, 23] a change in geometry from square planar (C_{2-3}) to tetrahedral (C_{4-10}) was observed based on a comparison of visible spectra. A similar progression could be envisioned for manganese(II) with the added feature that the tetrahedral manganese ions are part of a polymeric array.

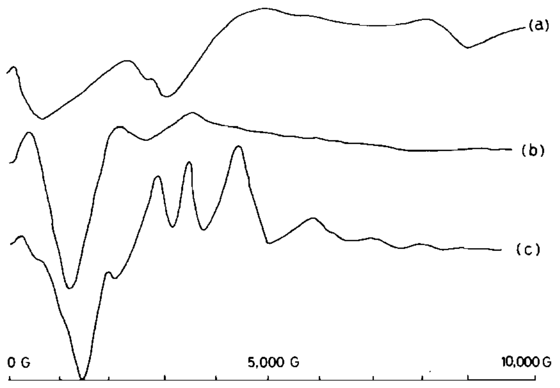


Figure 1. Solid state e.s.r. spectra of (a) $Mn(SALC_3)$, (b) $Mn(SALC_4)$ and (c) $Mn(SALC_5)$ at room temperature.

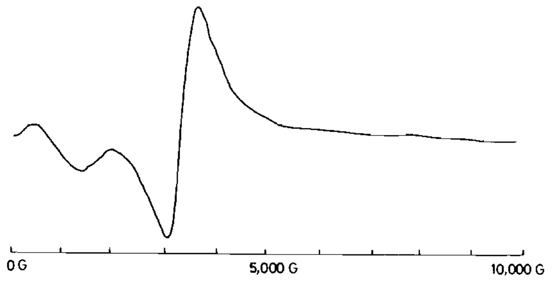


Figure 2. Solid state e.s.r. spectrum of $Mn(SALC_7)$ at room temperature.

Oxygenated Manganese Complexes

$Mn(SALC_{2-5})$ complexes are reasonably stable when dry and in the solid state. When moist, suspended in DMSO or dissolved in pyridine each compound readily turns brown on exposure to dioxygen. $Mn(SALC_{6-10})$ complexes rapidly react with dioxygen regardless of the physical state. In some preparations of $Mn(SALC_6)$ and $Mn(SALC_7)$ an ethanol of solvation was associated with these complexes which appeared to enhance reactivity towards oxygen. Oxygenation in the solid state consumed several days whereas in solution or suspension the major oxygen uptake is accomplished in 24 hours. The reactivity toward oxygen of the 5-chloro derivatives is considerably reduced in comparison to their unsubstituted analogs. It is not clear whether this behavior is due to the ligand not being able to stabilize as readily a higher manganese oxidation state or a different solid state structure for the chloro and unsubstituted materials. Solid state esr data suggest that different structures are probable. The amount of oxygen consumed by $Mn(SALC_{4-10})$ regardless of the physical state and derivative corresponds to approximately 0.5 mol of O_2 per mol of Mn. For $Mn(SALC_8)$, an intermediate oxygenation product could be isolated ($n_{O_2}/n_{Mn} \cong 0.25$) in addition to the fully oxidized product.

Red brown powdery materials are isolable from oxygenations of $Mn(SALC_{5-10})$ in the solid state and/or suspended in DMSO. A similar looking material is produced in pyridine when $Mn(SALC_4)$ is exposed to oxygen. All complexes were found to be insoluble in the following organic solvents: $CHCl_3$, methanol, ethanol, tetrahydrofuran, DMSO, benzene, toluene, CH_2Cl_2, glyme, nitromethane, ether, and CCl_4. Averaged duplicate elemental analyses in support of the proposed empirical formulations are listed in Table II in addition to the results of triplicate O_2 uptake experiments. Upon prolonged heating at 150–180 °C *in vacuo* most of the compounds lighten somewhat in color but do not return to the orange-yellow color of their precursors. The compound, $Mn(SALC_8)(O)_{0.5}$, however, does return to the color of its precursor, $Mn(SALC_8)$, and its magnetic moment increases to that of freshly prepared $Mn(SALC_8)$. Upon re-exposure to air, this deoxygenated compound rapidly changes to a red-brown color and its magnetic moment decreases to ~3.0 B.M.

Thermal gravimetric analysis data on these materials in the stated temperature range support the incorporation of oxygen into the sample and the proposed elemental formulation (Table II). An interesting observation in the TGA experiment is that weight loss is a two step process. The first step is evidenced by a small change in slope at a weight loss equal to 0.25 mol of O_2 per Mn followed by a further weight loss prior to sample decomposition. The step loss in oxygen is most pronounced in the TGA of

TABLE II. Analytical Data on Oxygenated Manganese Compounds.

Compound		C	H	N	n_{O_2}/n_{Mn}	TGA (%)
Mn(SALC$_4$)(O)	calcd.	59.12	4.93	7.67		4.37^{d}
	found^{c}	59.22	4.95	7.94	0.50	4.25
Mn(SALC$_5$)(O)	calcd.	60.16	5.31	7.39		2.34^{f}
	found^{b}	60.16	5.30	7.44	0.47	2.34
Mn(SALC$_6$)(O)	calcd.	61.07	5.60	7.12		4.07^{d}
	found^{a}	61.27	6.02	7.07	0.47	4.13
	found^{b}	61.07	5.76	7.12	0.44	3.90
Mn(5-ClSALC$_6$)(O)	calcd.	51.95	4.34	6.06		3.46
	found^{b}	52.09	4.65	5.12	0.50	3.35^{d}
Mn(SALC$_7$)(O)	calcd.	61.97	5.94	6.87		3.93
	found^{a}	61.29	5.81	6.90	0.42	3.92
Mn(5-ClSALC$_7$)(O)	calcd.	52.94	4.62	5.88		3.36
	found^{b}	53.00	4.75	5.92	0.49	3.30^{d}
Mn(SALC$_8$)(O)$_{0.5}$	calcd.	63.92	6.30	5.78		1.90^{e}
	found^{a}	63.99	6.29	6.58	0.23	1.94
	found^{b}	63.65	5.96	6.60	0.22	1.96
Mn(SALC$_8$)(O)	calcd.	62.71	6.17	6.65		3.80^{d}
	found^{a}	62.85	6.48	6.33	0.50	3.64
	found^{b}	62.50	6.03	6.53	0.49	3.76
Mn(5-ClSALC$_8$)(O)	calcd.	53.88	4.90	5.71		3.26
	found^{b}	53.53	5.00	5.58	0.49	3.17^{d}
Mn(SALC$_{10}$)(O)	calcd.	64.14	6.68	6.24		3.56^{d}
	found^{a}	63.88	6.88	6.18	0.48	3.47
	found^{b}	64.10	6.63	6.21	0.49	3.51

[a] Solid state, pure O_2, 1.08 atm pressure. [b] DMSO, pure O_2, 1.08 atm pressure. [c] Pyridine, pure O_2, 1.08 atm pressure. [d] Calculated for loss weight equivalent to 16 a.m.u. per formula unit. [e] Calculated for loss of weight equivalent to 8 a.m.u. per formula unit. [f] Calculated from percent gain in oxygen uptake experiments assuming the amount gained will be the amount lost.

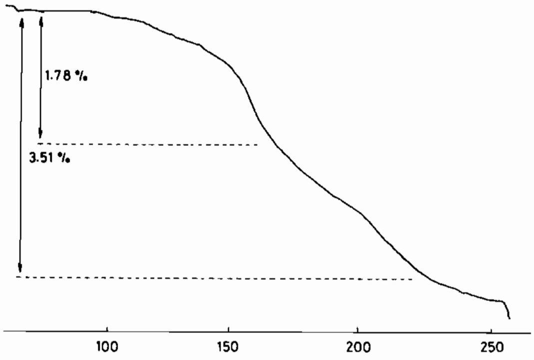


Figure 3. TGA profile of Mn(SALC$_{10}$)(O).

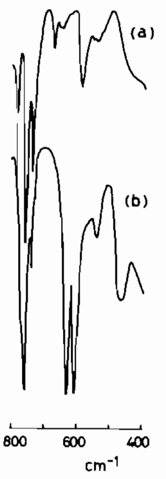


Figure 4. Nujol mull infrared spectra of (a) Mn(SALC$_7$) and (b) Mn(SALC$_7$)(O).

Mn(SALC$_{10}$)(O) from DMSO shown in Figure 3. To further corroborate that only the oxygen incorporated into the sample was being removed by heating, several oxygenations were stopped prior to completion and subjected to thermal analysis. In each case the percent weight lost on heating corresponded to the percent weight gained upon oxygenation.

A comparison of the infrared spectrum of precursor and oxygenated product offers some clue as to the nature of this reaction with oxygen. Of particular interest are the new bands between 650 and 600 cm^{-1} assignable to Mn–O stretching modes which are not present in the manganese(II) precursors

(Figure 4). All of the complexes with the exception of $Mn(SALC_4)(O)$ show a broad band resolved into peaks near 640 and 600 cm^{-1} with ± 5 cm^{-1} variations. $Mn(SALC_4)(O)$ exhibits a broad band resolved into three peaks at 630, 620, and 610 cm^{-1}. All other bands are superimposeable on the infrared spectrum of the precursor. No oxidation of the ligands is apparent from this analysis.

Similar IR activity in the 600 cm^{-1} region has been reported [9] for the oxygenated complexes of $Mn(SALC_3)$. These bands have also been assigned to Mn–O stretching modes. The oxygenated product of $Mn(SALC_3)$ was interpreted from an X-ray analysis to have μ-hydroxo bridges although no OH stretching mode was seen in the IR. A compound formed upon shaking in air a chloroform solution of $[Mn(5\text{-}BuSALC_2)(H_2O)]ClO_4$ with NaOH also exhibits a strong band at 655 cm^{-1}. This material is postulated [24] to be di-μ-oxobis[N,N'-ethylenebis(5-secbutylsalicylideneiminato)] dimanganese(IV), $[Mn_2(5\text{-}BuSALEN)_2O_2]\cdot H_2O$. The soluble fraction of the $Mn(SALC_2)$ oxygenated product from DMSO which has been proposed to be a μ-peroxo species [5] features characteristic Mn–O stretching frequencies at 645 and 631 cm^{-1}. The insoluble fraction is proposed to be a polymeric material with μ-catena-oxo bridges and contains Mn–O stretching modes at 662 and 602 cm^{-1}. This assignment is not consistent with previous studies which have suggested [25, 26] that a polymeric structure of the $[Mn\text{-}O]_n$ type should have absorption bands in the 900–750 cm^{-1} region. The di-μ-oxo bridged dinuclear manganese complex tetrakis(2,2'-bipyridyl)di-μ-oxodimanganese-(III, IV) perchlorate, $[Mn_2(bipy)_4O_2](ClO_4)_3$, exhibits bands at 686 cm^{-1}, 652 cm^{-1} and 580 cm^{-1} [27, 28]. The crystal structure of this mixed valence material reveals two distinct manganese-oxygen bond lengths [29]. Infrared absorption in this region has been claimed [30] to be diagnostic for double oxygen bridges with a symmetry other than D_{2h}. It therefore appears clear that oxygen has reacted with $Mn(SALC_n)$ and is bonded to manganese. While the compounds discussed herein could contain di-μ-oxo, μ-peroxo, catena-oxo bridge or some new type of manganese oxygen grouping, IR evidence seems to more strongly support a double oxygen bridge between pairs of manganese atoms.

Magnetic moments in the solid state for the oxygenated compounds are listed in Table III. The magnetic moments of fully oxygenated complexes isolated from oxygenations in the solid-state and DMSO suspensions are in the range 3.2–3.6 B.M. The magnetic moment of the only new compound isolated from solution (pyridine), $Mn(SALC_4)(O)$, is considerably lower, 2.3–2.2 B.M., even though oxygen-uptake measurements and TGA data are identical. This observation that oxygenation in the solid-state and in suspension yields magnetic moments near 3.5 B.M. and oxygenation in solution yields a product with magnetic moments near 2.0 B.M. is consistent with previous work on oxygenated $Mn(SALC_2)$ and $Mn(SALC_3)$. In solution (DMSO and pyridine) $Mn(SALC_2)$ is reported to react with oxygen to yield solids with magnetic moments *ca.* 2.0 B.M. We have confirmed these observations (Table III). $Mn(SALC_3)$ partially dissolved in DMSO has also been observed (Table III) to give a magnetic moment of 2.10 B.M. No solvent except pyridine has been found to solubilize $Mn(SALC_{5-10})$. Oxygenation readily occurs in these cases but the precipitates isolated from pyridine appear as black powders of indeterminable formula. The highly colored filtrate yields a pale brown precipitate of also uncertain composition.

TABLE III. Solid State Magnetic Properties of Oxygenated Manganese Compounds.

Compound	μ_{eff} (B.M.)
$Mn(SALC_2)(O)$	1.96[b,c] 1.99[c,d]
$Mn(SALC_3)(O)$	2.1[b]
$Mn(SALC_4)(O)$	2.3[c]
$Mn(SALC_5)(O)$	3.7[b]
$Mn(SALC_6)(O)$	3.6[a] 3.6[b]
$Mn(5\text{-}ClSALC_6)(O)$	3.4[b]
$Mn(SALC_7)(O)$	3.4[a] 3.5[b]
$Mn(5\text{-}ClSALC_7)(O)$	3.2[b]
$Mn(SALC_8)(O)_{0.5}$	4.8[a] 4.8[b]
$Mn(SALC_8)(O)$	3.3[a] 3.3[b]
$Mn(5\text{-}ClSALC_8)(O)$	3.3[b]
$Mn(SALC_{10})(O)$	3.2[a] 3.3[b]

[a] Solid state, pure O_2, 1.08 atm pressure. [b] DMSO, pure O_2, 1.08 atm pressure. [c] Pyridine, pure O_2, 1.08 atm pressure. [d] Reference [5].

Magnetic moments from solid state oxygenations are suggestive of three unpaired electrons which may arise from high spin Mn(IV) or spin coupled Mn(III) species. Products isolated from solution yield magnetic moments typical of one unpaired electron attributable to low spin Mn(IV) or spin coupled Mn(III) and/or Mn(IV) species. A magnetic moment *versus* temperature study for $Mn(SALC_7)(O)$ (Fig. 5) shows a rapid decrease in magnetic moment with temperature from 3.4 B.M. to 1.8 B.M. at 4.2 °K. This suggests appreciable antiferromagnetism between

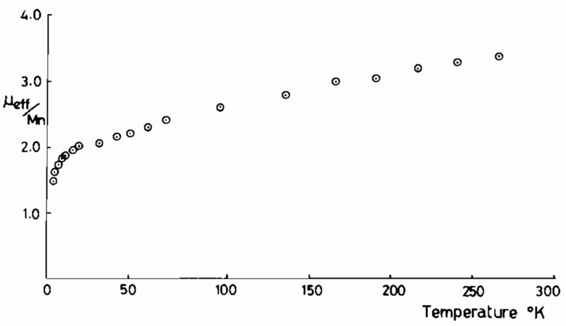


Figure 5. Magnetic moment per manganese as a function of temperature for Mn(SALC$_7$)(O).

manganese centers or a high to low spin conversion. Such information, however, does not preclude either Mn^{+3} or Mn^{+4} or a combination of the two.

$[Mn_2^{III,IV}(bipy)_4O_2](ClO_4)_3$ which contains a μ-dioxo bridge as verified by X-ray analysis and discussed previously has μ_{eff} = 2.53 B.M. [29] and 2.56 B.M. [31] in the solid state and solution respectively. Exchange interaction between manganese centers has been demonstrated via low temperature magnetic measurements [38]. $[Mn_2^{III,III}(phen)_4O_2](ClO_4)_4$ and $[Mn_2^{IV,IV}(phen)_4O_2](ClO_4)_2$ have also been observed [31] to yield magnetic moments *ca.* 2.0 B.M. In a recent study [32] of $[Mn_2(5\text{-}BuSALC_2)_2O_2]$ and $[Mn_2(Pic)_4O_2]$, both of which are believed to contain μ-dioxo bridges, a decrease in magnetic moment was observed in going to 4.2 °K from 2.2 and 2.0 B.M. to 1.5 and 0.8 B.M. respectively (Pic = 2-picolinic acid). Two suggestions have been put forward to explain this data: (1) a mixed valence Mn(III)–Mn(IV) or (2) two low spin weakly coupled Mn(IV).

Superficially it appears that at low temperature μ_{eff} for solid state oxygenation products approaches μ_{eff} for room temperature solution oxygenation products. A conclusion which could follow from these observations is that antiferromagnetic interactions are more pronounced in the solution product where more optimum orbital overlap can be achieved between manganese centers or between manganese centers and bridging oxygen atoms. Alternatively solid state and solution products may be high and low spin Mn(IV) respectively wherein the solid state materials undergo a spin state change at low temperature. Solution oxidized products, on the other hand, of Mn(SALC$_2$) over the temperature range 100°–300 °K have been reported [5] to have a large antiferromagnetic interaction (μ_{eff} at 100 °K = 0.8 B.M.).

All oxygenated complexes are ESR active. The spectra of powdered complexes from solid-state/DMSO suspension and solution oxygenations give strikingly similar room temperature ESR spectra even though their magnetic moments are different. The spectrum of Mn(SALC$_8$)(O) is shown in Figure 6. Under these measurement conditions no hyperfine interaction was apparent. The great insolubility of these materials in any suitable ESR solvent prevented measurement in solution. It is, therefore, reasonable to assume that all of the compounds have very similar electronic and structural characteristics. Manganese(III) solely is apparently ruled out because the oxygen complexes give active ESR spectra. All solid-state/DMSO suspension oxidation products are powders. The few compounds isolated from solution oxidation are crystalline and X-ray structural analysis has been performed on the Mn(SALC$_3$) oxidized products from pyridine. The complex is reported to contain

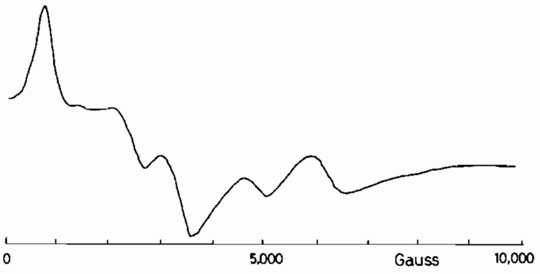
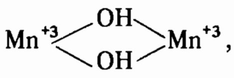
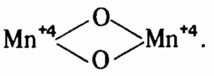


Figure 6. Solid state e.s.r. spectrum of Mn(SALC$_8$)(O) from oxygenation of Mn(SALC$_8$) in the solid state or suspended in DMSO.



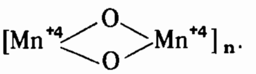
$$Mn^{+3}\overset{OH}{\underset{OH}{\diamond}}Mn^{+3},$$

however, in light of its ESR activity, one can suppose the structure to really be



$$Mn^{+4}\overset{O}{\underset{O}{\diamond}}Mn^{+4}.$$

Therefore, we suggest all fully oxygenated complexes in this series have a di-μ-oxo linkage since all ESR's are similar. The great insolubility of the solid-state and DMSO oxygenation products, however, suggests that the di-μ-oxo linkage is part of a polymeric array (*e.g.*



$$[Mn^{+4}\overset{O}{\underset{O}{\diamond}}Mn^{+4}]_n.$$

The complexes isolated from solution oxygenation in this and earlier studies (*e.g.* $[Mn_2(SALC_2)_2O_2]$, [Mn(SALC$_3$)(O)] and [Mn(SALC$_4$)(O)]) are probably dimeric di-μ-oxo materials rather than μ-peroxo or di-μ-hydroxo species as previously suggested. It should be noted, however, that a Mn(III)–Mn(IV) dimer would be ESR active and possibly could exhibit antiferromagnetic coupling.

The mechanism whereby these complexes are formed is of interest. No doubt the solid-state/DMSO suspension oxygenation proceeds by a common pathway while solution oxidations may proceed via some different path. Several points must be kept in mind prior to postulation of a mechanism. With the exception of magnetic and solubility data all oxygenated materials appear to possess the same properties from $Mn(SALC_2)$ to $Mn(SALC_{10})$. Many of these oxygenations occur in the solid state which is unusual insofar as Mn(II) chelates are concerned. Precursors and products are in most cases very insoluble. A poorly defined two-step weight loss is observed upon analysis via thermogravimetric measurement. One partially oxidized product has been isolated, $Mn(SALC_8)(O)_{0.5}$, whose solid-state ESR spectrum is silent. Coupled with $\mu_{eff} = 4.8$ B.M. this compound is no doubt a manganese(III) intermediate. A Mn^{III}-O-Mn^{III} linkage is envisioned. In support of this observation all compounds were observed to absorb oxygen in two steps (Figures 7, 8). An initial absorption of oxygen to a molecular oxygen to manganese ratio (n_{O_2}/n_{Mn}) of 0.25 was followed by a period of no measurable oxygen absorption then a slow oxygen absorption to a n_{O_2}/n_{Mn} equal to approximately 0.50 occurred. Upon prolonged exposure to oxygen, no further color change or oxygen-uptake was observed. As is seen in Figures 7–8 oxygen-uptake in the solid state is quite slow taking several days whereas suspension and solution oxygenations require less time.

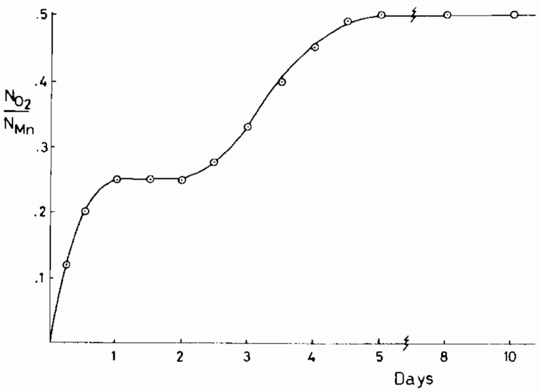


Figure 7. Oxygen uptake as a function of time for $Mn(SALC_6)$ in the solid state at room temperature.

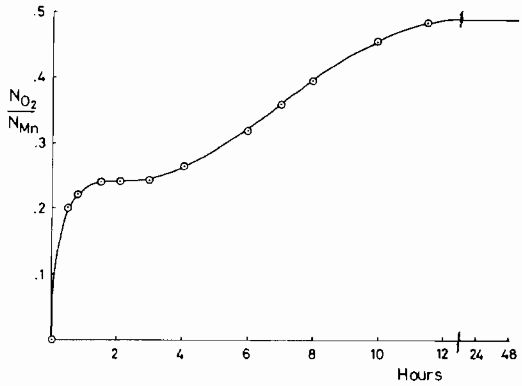


Figure 8. Oxygen uptake as a function of time ror $Mn(SALC_2)$ dissolved in DMSO at room temperature.

In light of these experimental facts a four-step mechanism for solid-state/suspension oxygen uptake is proposed in Figure 9: (1) diffusion of oxygen into the polymer lattice; (2) formation of manganese(III) ions with μ-oxo bridges, (3) slow diffusion of additional oxygen into the polymer, and (4) reaction to form manganese(IV) with di-μ-oxy bridges between manganese. The reaction of the manganese(II) complexes in solution may proceed via the same

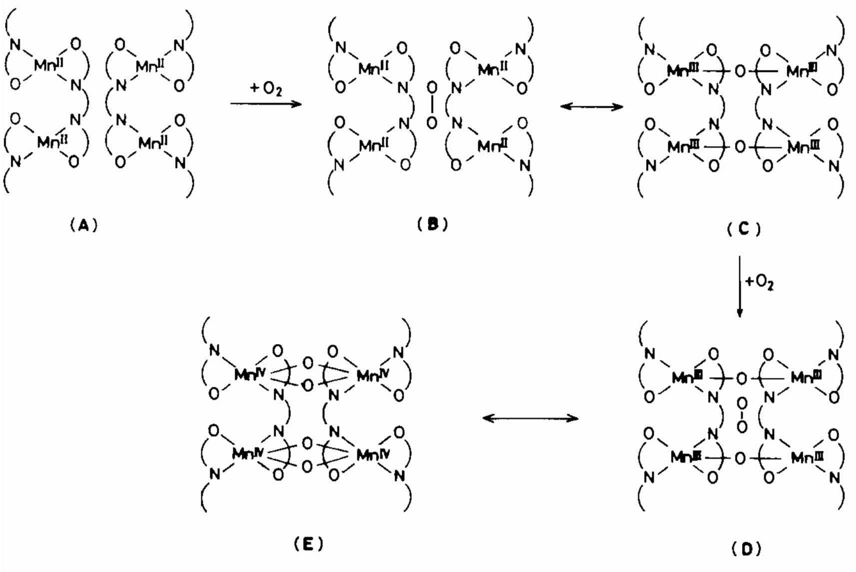


Figure 9. Proposed mechanism for oxygenation of $Mn(SALC_n)$ in the solid state and/or DMSO suspension.

mechanism except that smaller portions of the polymer exist in solution. Further study in this area is underway to test this hypothesis.

In conclusion we have observed that manganese(II) compounds employing a tetradentate ligand derived from salicylaldehyde and various diamines readily reacts with oxygen. Increasing the length of the methylene chain joining imine donors increases in general the reactivity of these complexes with oxygen. An electron withdrawing group on the salicylaldehyde ring tends to deactivate reactivity toward oxygen. The products produced via these reactions are believed to be di-μ-oxo species.

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