THE SYNTHESIS AND CHARACTERIZATION OF SOME MANGANESE(II) SCHIFF BASE COMPLEXES AND THEIR OXYGENATION PRODUCTS

by

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To my Parents and Chris
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INTRODUCTION

For manganese (1), the divalent oxidation state is the most stable. The most common geometry is octahedral, however, tetrahedral and square planar complexes also exist. Mn(II) is readily oxidized in alkaline solution to Mn(III) or Mn(IV). It has no ligand field stabilization energy in the high-spin state, whereas in the low-spin electron configuration is has 20 Dq units of crystal field stabilization energy.

Mn(III), $d^4$, forms few simple compounds (1), in contrast to Mn(II). It is fairly stable in complexes, which tend to be either anionic or neutral. It's most common geometry in the high-spin state is expected to be distorted octahedral arising from Jahn Teller distortion (1). Mn(IV) is most stable in anionic complexes, but even these are not extremely stable, being subject to hydrolysis and reduction. However, when manganese combines with certain polydentate ligands such as Schiff bases, these trends may not always be followed.

Manganese is an essential element in the oxygen-evolving step of photosynthesis (2). It has been suggested that the Mn(II)-Mn(III)-Mn(IV) redox system takes part in the electron transfer chain from an electron donor (usually water) to an electron acceptor (CO$_2$). The manganese ion binding sites, the ligands coordinated to the manganese and the coordination geometry are not known. Porphyrin-like ligands (3) were initially suggested as models, however, other ligand systems are now believed to
be involved. These systems involve $\text{N}_2\text{O}_2$ donor ligands such as may be found in biological systems. Manganese and oxygen together have also been implicated in certain forms of superoxide dismutase isolated from E. coli (4). In this system manganese catalyzes the disproportionation of superoxide to molecular oxygen and hydrogen peroxide.

The purpose of this thesis is to examine a potential Mn(II) complex model system and its corresponding oxygenated products. The Schiff base ligands chosen for this study (Figure 3) were of the type believed to be in the environment of manganese as it exists in the photosynthetic process. The ligand systems employed will be derived from salicylaldehyde and a series of straight-chain diamines and 3,3'-bis(aminopropyl)-amine.
HISTORICAL

Photosynthesis (2) can be described by the following equation,

\[ nH_2O + nCO_2 \xrightarrow{\text{light}} (CH_2O)_n + nO_2 \]

All photosynthetic organisms except bacteria use water as an electron or hydrogen donor to reduce \( CO_2 \) or some other electron acceptor. As a consequence, photosynthetic organisms evolve molecular \( O_2 \). It has been determined that the \( O_2 \) comes from \( H_2O \), not \( CO_2 \) (2). In fact, experiments by Robert Hill in 1937 have shown that for \( O_2 \) evolution, \( CO_2 \) is not required, and, therefore, the \( O_2 \) evolution and \( CO_2 \) reduction processes can be dissociated.

It is known that manganese deficiency (loss of two of three Mn ions) in plants will cause loss of up to three-fourths of the plants' photosynthetic capacity (5). Studies on manganese deficient plants showed reduced ability to evolve \( O_2 \) and to fix \( CO_2 \) (6). These experiments were supplemented by studies (7) of manganese addition to deficient plants. It was found that through a light dependent reactivation, photosynthesis is restored in these manganese deficient plants when manganese is added.

Manganese deficiency, as mentioned earlier, reduces photosynthetic ability. However, photoreduction (reduction of an electron acceptor, such as \( CO_2 \)) (5) is not affected. Since oxygen evolution is the only process of photosynthesis not needed for photoreduction (as shown in experiments by Robert Hill), it appears manganese is involved in
oxygen evolution. In another (8) experiment using Rps. sherdos, it was shown that this organism had no photosynthetic need for manganese. Since this bacteria is known to be a non-oxygen-evolving species, this evidence further supports the role of manganese in oxygen evolution.

Photosystem II (PSII) is the oxygen-evolving system of photosynthesis. Experiments (9,10) show that a reagent which can remove all manganese from plant chloroplasts can also inhibit electron transport between $H_2O$ and PSII. This inhibition in electron transport could then be due to removal of manganese. The inability of manganese deficient cells to evolve oxygen (PSII) while still reducing NADP+* (PSI) further links manganese to PSII.

Manganese is then, currently believed to be involved in PSII and, therefore, oxygen evolution. An extensive study by Chenniae and Martin (11) led to a proposed site of manganese activity. Some of the important points from their results were:

1. Each PSII trapping and $O_2$-evolving center contains three manganese ions;
2. $O_2$-evolving capacity is abolished when two of the three manganese ions are removed;
3. Of the three manganese ions associated with each center, one is linked more closely to the center than the other two; and
4. Manganese functions solely on the oxidant side of PSII.

These observations led to the following postulated sites of manganese in PSII:

* Nicotinamide adenine dinucleotide phosphate
As shown in the scheme above, two equivalent Mn atoms are closely associated with the $O_2$-evolution, while the third is associated with the photochemical center. The accepted view is that light energy is used in the first phase of photosynthesis (2).
Calvin (12) has also proposed a mechanism for the oxygen evolution system involving manganese. Four electrons are involved in the process of converting two molecules of water into a molecule of oxygen and four hydrogen ions. Manganese, being involved in this process, must be able to remove these four electrons from the water molecules. As a model for studying the role of manganese in PSII, Calvin has proposed a binuclear manganese complex, di-μ-oxotetrakis(2,2'-bipyridine)dimanganese(III,IV) perchlorate, (Structure I)

![Structure I](image)

which upon irradiation in aqueous solution, evolves oxygen. With no irradiation, no reaction occurs. So far, only the first step of the proposed mechanism has been experimentally tested. The reduced catalyst has been produced; however, its structure is not known. Recent work by
Calvin (13) has, however, placed doubt as to the oxygen evolving ability of this complex.

The proposed scheme, with manganese as the catalyst, is:

\[
\begin{align*}
\frac{1}{2}H_2O \quad \text{hv} \quad [\text{cat}]_{\text{ox}} \quad \rightarrow \quad \frac{1}{2}O_2^+ + [H][\text{cat}]_{\text{red}} \\
[H][\text{cat}]_{\text{red}} + Fd^{+3} \quad \text{hv} \quad \rightarrow Fd^{+2} + [\text{cat}]_{\text{ox}} \\
2Fd^{+2} + 2H^+ \quad \begin{array}{c}
\text{(i)nitrogenase} \\
\text{(ii)hydrogenase}
\end{array} \quad \rightarrow \quad H_2^+ + 2Fd^{+3}
\end{align*}
\]  

where: Fd - ferredoxin  
ox - oxidized  
red - reduced

Another proposed mechanism (14) has Mn\(^{+2}\) photooxidized to Mn\(^{+3}\) in PSII first, then:

\[2Mn^{+3} + H_2O \rightarrow \frac{1}{2}O_2 + 2Mn^{+2} + 2H^+\]

Mn\(^{+3}\) oxidizes H\(_2\)O by the dark reaction.

A few other mechanisms can be found in the literature (15). However, they all involve photochemical reactions leading to the oxidation of water.

The exact environment of manganese in the photosynthetic organism remains unknown. It is probably not present as the aquated manganese ion (3), but most likely bound to an organic ligand of some kind. Calvin initially suggested that the ligand may be a porphyrin derivative.
Chlorophyll $\alpha$ has a modified porphyrin structure, as do many compounds found in living cells.

The manganese porphyrin complex Calvin (3) studied was Mn(II) Hematoporphyrin IX:

![Structure II]

Although the structure depicts this complex with manganese in the $+2$ oxidation state, the Mn(III) complex seems to be the more stable. The Mn(IV) complex can also be isolated (3), but with considerable difficulty. If this is indeed the manganese environment in the chloroplasts, the Mn(IV) state would be a strong enough oxidizing agent to liberate oxygen, and the Mn(II) will be a strong enough reducing agent to reduce most cofactors involved in biological reductions. However, Calvin did
not study any reactions of the complex with oxygen.

There have been other studies of manganese porphyrins (16,17). It is no longer generally believed (18), however, that a porphyrin derivative is the ligand environment of manganese in the photosynthetic organism.

Another $N_4$ donor ligand and its complexes with manganese has been studied concurrently with porphyrins as a model for the photosynthetic manganese-containing system. Phthalocyanine is similar in structure to the porphyrins and has often been used as a model for the porphyrins.

Manganese(II) Phthalocyanine

Structure III

Lever and Elvidge (19) found manganese(II) phthalocyanine (MnPc) to be a reversible oxygen carrier. The olive green pyridine solution of MnPc absorbs oxygen in the cold, turning dark blue. On boiling, the
solution is again green and capable of reabsorbing oxygen. Pyridine was initially believed to be essential; however, subsequent work (20) has shown that other bases can also be used as solvents (i.e. n-methyl imidazole, 3-picoline and piperidine). Oxygen uptake was one molecule of $O_2$ per two molecules of manganese phthalocyanine. The isolated product was suggested to have the formula $\text{PcMn(IV)OPy}$. This material had infrared absorption bands at 3000 and 1200 cm$^{-1}$, characteristic of pyridine, and a band at 1096 cm$^{-1}$ which Lever and Elvidge assigned to a Mn=O linkage. A new compound, postulated as $\text{PcMn(IV)O}$ can be isolated after heating $\text{PcMn(IV)OPy}$ at 180°C. This new substance has a magnetic moment of 3.77 B. M. and an infrared absorption at 820 cm$^{-1}$ indicating the presence of a Mn-O-Mn linkage. Attempts by Calvin (3), however, to observe the oxygen released on heating of $\text{PcMnOPy}$ have failed.

Further work by Lever (21) has shown that manganese phthalocyanine complexes can be formed in oxidation states from 0 to 4 inclusive. The stable oxidation state in an alcoholic alkaline media is, however, pH dependent. The oxidation of Mn(III) to Mn(IV) is easier at higher pH. Engelsma et al. (22), in further investigations of Lever's original work, found that the oxidation proceeds from +2 to +3 to +4 in successive steps.

The isolated product, believed earlier to be $\text{PcMn(IV)O}$ containing a Mn=O bond, has been shown by Vogt et al. (23) to be $(\text{MnPcPy})_2O$. An X-ray diffraction study showed the phthalocyanine rings to be flat and parallel to each other, joined by an oxygen atom midway between the manganese atoms. The Mn-O bond length is 1.71 Å. Magnetic moments for this compound vary with preparation, but due to the short Mn-O bond
length, it is proposed that the manganese atoms are spin-coupled and, therefore, diamagnetic with varying amounts of impurities causing the observed paramagnetism (24). This elucidation of the structure of the final product led Yamamoto et al. (25) to propose the following mechanism for the oxidation and reduction reactions of MnPc in pyridine:

Structure IV

Recently, Canham and Lever (20), in a further investigation, prepared the corresponding N-methylimidazole adduct. The analytical and spectroscopic data were consistent with a formulation of (N-methylimidazole MnPc)\(_2\)O. Similarly, adducts of 3-picoline [(3-picoline MnPc)\(_2\)O] and piperidine [(piperidine MnPc)\(_2\)\cdot H\(_2\)O] have also been prepared. These compounds, found to be weakly paramagnetic, are, however, considered to be diamagnetic, with trace amounts of high-spin manganese ions present.
The position of the asymmetric Mn-O-Mn stretching frequency in the compounds mentioned above and related complexes is a matter of controversy. In related oxo-bridged Fe(III) and Mn(III) porphyrin complexes, it is observed as a strong band at 850 cm\(^{-1}\). This band, for the iron complex, shifts to higher energy on cooling. No shift is observed for the corresponding band of the manganese complexes. However, due to the weak paramagnetism (or diamagnetism) which parallels the behavior of (Mn(III)PcPy)\(_2\)O, coupled with visible spectral evidence, Canham and Lever (20) nevertheless believe they have a Mn-O-Mn species.

Ligands which are N\(_2\)O\(_2\) donors have also been studied as possible models for the environment of manganese in the photosynthetic process. Complexes of manganese with tetradeutate Schiff base ligands are widely known and studied. The Schiff base made from the condensation of salicylaldehyde and ethylenediamine \([N,N'\text{-ethylenebis(salicylideneimine)}, (\text{SALEN})]\) has been extensively investigated (26).

Mn(SALEN) was first isolated by Pfeiffer in 1933 (26). The complex was found to be stable to air in the solid state, but extremely oxidizable in solution. Numerous studies (27,28) of the magnetic properties of Mn(SALEN) have shown the room temperature magnetic moment to be 5.2 B. M., well below the spin-only value of 5.90 B. M., accompanied by considerable deviation from Curie-Weiss behavior at lower temperatures. This behavior indicates the presence of antiferromagnetic exchange interaction. This magnetic behavior can be explained by assuming Mn(SALEN) has a binuclear structure with interaction between the spins of the metal ions. The significant lowering of the magnetic moment thus indicates the manganese ions are in rather close proximity, as
would be in a binuclear structure. Further evidence for the binuclear complex comes from the comparison of X-ray diffraction powder data of Cu(SALEN) and Mn(SALEN). Cu(SALEN) (29) was found to be dimeric, with mutual sharing of one oxygen atom of each ligand by the copper atoms. The X-ray diffraction powder pattern of Mn(SALEN) was similar to that of Cu(SALEN), which suggests the binuclear structure. However, if Mn(SALEN) is binuclear as suspected, it would contain manganese ions with a coordination number of five (28), which is rare for spin-free Mn(II).

The Mn(II) Schiff base complex of SALEN discussed above reacts very slowly with oxygen when dry. However, when wet with organic solvents, it is readily oxidizable, often irreversibly, to what is most likely higher oxidation states of manganese. The isolated complexes have been postulated (30,31) to occur as dimers or polymeric materials with \textit{oxo}, peroxo, dioxo, or hydroxo bridges.

Lewis \textit{et al}. (28) reported that in pyridine and N,N'-dimethylformamide solution, Mn(SALEN) was readily oxidized to form an insoluble brown product. Magnetic moments of isolated products ranged from 1.9 to 2.0 B. M., with analyses which correspond to Mn(SALEN)(OH). The magnetic moments of these samples, however, decreased markedly with temperature, indicating antiferromagnetic interaction. This suggests perhaps \[\text{Mn (SALEN)}\textsubscript{2}O\] is a better formulation, even though elemental analysis would not be consistent with this formulation. The variation in the magnetic susceptibility with temperature best fits a spin-paired binuclear model. Molecular weight determinations were not possible due to the sample's insolubility in suitable solvents. The infrared spectrum does not suggest the oxy-bridged dimer, due to the lack of a band near 820 cm\textsuperscript{-1}. 
as in the similar Fe(III) complex (32).

Later, Matsushita et al. (30) also studied complexes obtained from oxygenated solutions of Mn(SALEN) in organic solvents such as DMSO and pyridine. The compound obtained from DMSO was slightly soluble. The elemental analysis agreed with the formula Mn(SALEN)(O). Oxygen uptake experiments show that Mn(SALEN) in solution absorbs 0.5 mole of O₂ per mole of Mn, and TGA data on Mn(SALEN)(O) shows the loss of 0.5 mole of O₂ per mole of Mn. The magnetic moment at room temperature is 1.96 B. M. with significant deviation from the Curie-Weiss law temperature. They explain the deviation by considering the existence of a thermal equilibrium between spin-free and spin-paired configurations in the complex. The IR spectrum of this compound is comparable with the spectrum of Mn(SALEN) in the 700-4000 cm⁻¹ region. In the 600-700 cm⁻¹ region, however, the oxidized complex gives rise to two intense bands at 645 and 631 cm⁻¹, attributable to the Mn-O bond. Thus, with the above data and a visible spectrum resembling that of a penta-coordinate Mn(III) complex, the structure assigned to this complex can be represented as

![Structure V](image)
This structure, containing a μ-peroxo bond, has penta-coordinate Mn(III) in a square pyramidal environment. The magnetic moment is low compared to what is expected for this structure. In addition to the thermal equilibrium, the authors also suggest antiferromagnetism via a superexchange mechanism through the μ-peroxo bridge to account for the low moment.

A second compound (30), this one isolated from pyridine, was found to be insoluble in water and common organic solvents. The elemental analysis for this compound corresponded to the formula Mn(SALEN)(O). Mn(SALEN) here again showed the uptake of 0.5 mole of O₂ per mole of Mn, with the loss of the TGA curve of Mn(SALEN)(O) corresponding to the same ratio. The magnetic moment at room temperature is 1.99 B. M. The IR spectrum has bands at 662 and 602 cm⁻¹ attributable to Mn-O bonds. Visible spectra were not possible due to insolubility in suitable solvents. The structure proposed for this compound, poly catena-oxoN,N'-ethylenebis(salicylideneiminato)manganese(IV) is

Structure VI
The magnetic moment (1.9 B. M.) is lower than expected for this octahedral Mn(IV) structure. Antiferromagnetic interaction between manganese atoms bridged by an oxygen atom could account for this.

Another compound (30) isolated from pyridine was \([-\text{Mn}(3-\text{MeO-} \text{SALEN})\text{-O-}]_n\). Its oxygen uptake and TGA loss correspond to 0.5 mole of \(O_2\) per mole of Mn. The magnetic moment is 1.58 B. M. This compound was also assigned the polymeric structure shown in Structure VI.

The last compound isolated by Matsushita et al. (30) has a magnetic moment of 3.81 B. M. TGA data shows the loss of two molecules of methanol per mole of manganese. The IR spectrum shows a new band at 840 cm\(^{-1}\), attributable to the Mn=O bond; however, there are no bands in the 600-660 cm\(^{-1}\) region. This, along with a visible spectrum consistent with spin-free octahedral Mn(IV), led to the proposed structure of the compound, oxo-N,N'-ethylenbis(3-MeO-salicylideneiminato)manganese(IV) (Structure VII):

![Structure VII](image)
This structure, as proposed by Matsushita et al. (30), indicates the second methanol is a methanol of solution.

Another complex (31) of manganese and SALEN which has oxygen bound directly to manganese is postulated to be di-\(\mu\)-oxobis[\(N,N'\)-ethylenbis(5-secbutylsalicylideneiminato)]dimanganese(IV), \([\text{Mn}_2(\text{BuSALEN})_2\text{O}_2]\cdot\text{H}_2\text{O}\). This compound was prepared by shaking a chloroform solution of \([\text{Mn}(\text{BuSALEN})\text{H}_2\text{O}]\text{ClO}_4\) with NaOH, and was then crystallized from methylene chloride and petroleum ether. The magnetic moment is 2.47 B. M., indicative of antiferromagnetic coupling of either high-spin Mn(III) or Mn(IV). The IR spectrum shows a band at 655 cm\(^{-1}\), which is similar in position to those in the complexes isolated by Matsushita (30). The structure proposed to account for the experimental data involves a di-\(\mu\)-oxo bridge,

![Structure VIII](image-url)

Structure VIII

Anion complexes of Mn(SALEN) and its derivatives have also been studied. Complexes of \([\text{Mn}(\text{SALEN})\text{X}]\), where \(\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{and C}_2\text{H}_3\text{O}_2^-\) have been isolated (27,33). \([\text{Mn}(4\text{-secbutylSALEN})\text{X}]\), where \(\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{N}_3^-, \text{NCS}^-, \text{OCN}^-, \text{NO}_2^-, \text{and C}_2\text{H}_3\text{O}_2^-\) have been extensively studied by Boucher et al. (34). Boucher (35) has also studied the chloro-
complexes of several Mn(SALEN) derivatives. The compounds do not bind oxygen or react with oxygen in any way, so they will not be discussed further.

Manganese complexes of the Schiff base made from 1,3-diamino-propane and salicyaldehyde [N,N'-propylenebis(salicylideneimine), SALTM] have also been studied. Johnson and Beveridge (36) isolated Mn(SALTM) (H₂O). The yellow complex reacts slowly with air, and by its magnetic moment of 5.93 B. M. is a high-spin Mn(II) complex. Using mass spectra and molecular weight determinations as their basis, Miller and Oliver (37) believe that complexes of manganese and SALTM⁻² are polymeric, with the flexible ligands bridging neighboring manganese atoms. An anhydrous form of Mn(SALTM) could also be isolated (38). This complex was suggested to be more air sensitive than the water adduct.

Dey (39) has isolated a Mn(II) complex made from 1,3-diaminopropane-2-ol and salicylaldehyde [Mn(SB)]. The complex is stable in air when dry; when wet, however, it is readily oxidized. The low magnetic moment of 5.40 B. M. is in accordance with the low moments of other Mn(II) compounds reported above. This could be due again to antiferromagnetic exchange interaction between ions in the solid state, however, more studies are needed here.

Johnson and Beveridge (36) reported that Mn(SALTM)(H₂O) in benzene solution will form a 1:1 adduct with molecular oxygen. The oxygen uptake was reported to be reversible. The IR bands attributable to Mn–O were found at 859 and 560 cm⁻¹, but no structure was proposed. The oxygen uptake has been confirmed (38); however, its reversibility was questioned.
Miller and Oliver (37) also reacted Mn(SALTM)(H₂O) with O₂ in benzene. The ratio of O₂ to Mn varied from 1:1 to 0.25:1. The product obtained when the ratio was 1:1 is thought to be Mn(SALTM)-(O₂)(H₂O). The room temperature magnetic moment is 2.88 B. M., and TGA data shows a loss of one molecule of oxygen per Mn. The product obtained when the ratio was 0.5:1 is formulated as [Mn(SALTM)(O)·2(C₆H₆)]. This complex has a room temperature magnetic moment of 2.15 B. M. Both of these complexes have the expected broad IR band in the 600-650 cm⁻¹ region which is absent in the parent compound. Neither of these compounds will release oxygen upon refluxing in benzene or chloroform. A molecular weight determination of [Mn(SALTM)(O)·2(C₆H₆)], performed in anhydrous pyridine using a vapor pressure osmometer, showed this product to be polymeric. The authors believe these products are non-monomeric, containing low-spin Mn(III) atoms bridged by both the Schiff base ligands and by peroxyde groups. Water or benzene molecules can be retained within the lattice.

Mn(SALTM) (37), when reacted with oxygen in a pyridine solution, gave an O₂ to Mn ratio of 1:2. This compound is formulated as [Mn(SALTM)(OH)]₂·4Py. This compound has been the subject of an X-ray study (40). It was found to be dimeric, with each manganese ion bonding octahedrally to two bridging hydroxy groups and to the quadridentate ligand system. The pyridine is not directly bonded to the complex. The manganese-manganese distance of 2.72 Å is quite close. Since the manganese ions are in close proximity, there is the possibility of interaction between them. This can help explain the antiferromagnetic nature of this compound and other analogous compounds. The compound is,
therefore, di-μ-hydroxobis[N,N'-propylenebis(salicylideneiminato)Mn(III)]
tetrapyridine.

A similar structure, one containing a di-μ-oxo bridge rather than
the di-μ-hydroxo bridge discussed above, has been proposed for a complex
made from 5-secbutylsalicylaldehyde and 1,3-diaminopropane (31). This compound, [Mn₂(Bu SALTM)₂O₂]·2H₂O, was made by shaking a chloroform
solution of [Mn(BuSALTM)H₂O]C₁₀₄ with NaOH. The crude product was
crystallized from chloroform and petroleum ether. The complex has a low
magnetic moment of 2.59 B. M., which points to the antiferromagnetic
interaction of either high-spin Mn(III) or Mn(IV) ions present in this
structure. Molecular weight determinations in chloroform show the complex
to be a dimer. Boucher suggests the band at 642 cm⁻¹ in the IR spectrum
can be attributed to the ring vibration of the Mn₄O₉-Mn system.

A similar bridging unit has been suggested for a Mn(IV) complex (41)
of pyridine-2-carboxylic acid, [Mn(pic)₂O]ₙ. This complex is formed by
extended refluxing of pyridine-2-carboxylic acid, potassium peroxydi-
sulfate and Mn(II) carbonate in water. The compound has a magnetic
moment of 1.94 B. M., which changes with temperature. The IR spectrum
shows an intense doublet centered at 660 cm⁻¹. The spectrum also
shows the absence of -OH groups. The low magnetic moment and IR
spectrum led the authors to propose the di-μ-oxo structure for this
compound.

Another complex (42), di-μ-oxo-tetrakis(2,2'-bipyridine)dimangan-
ese(III,IV), with magnetic moment of 1.79 B. M., has shown through X-ray
analysis to contain the di-μ-oxo bridge. The manganese-manganese
distance is 2.72 Å, as in the [Mn(SALTM)(O)] complex mentioned earlier.
(40), which places the manganese ions in close proximity and could account for the low magnetic ions in close proximity and could account for the low magnetic moment. Calvin (12) has found that upon irradiation of this compound in aqueous solution, oxygen was evolved.

As has been shown, many of the oxygen complexes mentioned above display reduced magnetic moments, most probably caused by antiferromagnetic interaction, and similar IR spectra in the 600-700 cm$^{-1}$ region. These compounds have empirical formulas showing one O to one Mn. Two of these compounds have been shown via X-ray analysis to contain the di-μ-oxo bridge. It is not unlikely that some, if not all, of these compounds belong to this same class. One proposed structure (30) contains a manganese-manganese distance of 4.4 Å (31), too long to account for the degree of antiferromagnetic coupling seen. Further investigation and X-ray studies are needed to determine the exact structure of these complexes.

The purpose of the work described herein is to study Mn(II) complexes and their oxygenation products with ligands analogous to those mentioned above, but with the additional feature that the carbon chain joining azomethine linkages would be varied in length (see Figure 3). These increases could cause different properties and structures in these complexes due to increased flexibility of the ligand system. Vacant cis positions would be more readily available to an oxygen molecule. Although it is not known whether oxygen is ever actually bound to manganese in the photosynthetic process this study was begun to determine whether these manganese complexes could reversibly bind
oxygen. If so, it is possible they could prove to be a good model system for the role of manganese in the photosynthetic system.
EXPERIMENTAL

MATERIALS

The compounds 1,3-diaminopropane, 1,5-diaminopentane, 1,7-diaminoheptane, and 3,3'-bis(aminopropyl)amine were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Salicylaldehyde, acetylacetone, dimethylsulfoxide, and ethylenediamine were obtained from Fisher Scientific Company, Fairlawn, New Jersey. All other chemicals were of reagent grade or equivalent.

PREPARATION OF LIGANDS

Preparation of \( \text{H}_2\text{BAE} \) [N,N'-ethylenebis(acetylacetimine)]

To a stirred solution of 100 g (1 mol) of acetylacetone dissolved in 150 ml of absolute ethanol, was added dropwise 30 g (0.50 mol) of anhydrous ethylenediamine diluted with 30 ml of absolute ethanol. The solution was kept in an ice bath during the addition, which was complete when the crystals of unknown composition were gone. The volume was reduced, and upon cooling, white crystals were formed. These were suction filtered and recrystallized twice from toluene, using decoloring charcoal, after which they were dried at room temperature in vacuo, mp 110° [Lit. (43) mp 111-113°].
Preparation of $\text{H}_2\text{TFACACEN}$ [$\text{N},\text{N}^{\prime}\text{-ethylenebis(1,1,1-trifluoroacetylacetonimine)}$]

To a stirred, cold (0°C) solution of 7.70 g (0.50 mol) of 1,1,1-trifluoro-2,4-pentanedione in 50 ml of absolute ethanol, was added 1.60 g (0.026 mol, excess) of ethylenediamine in 40 ml of absolute ethanol. The crystals of unknown composition dissolved rapidly with stirring in the orange solution. The volume was reduced, and small white crystals were separated by filtration and recrystallized from toluene, mp 149-151°. Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_{2}\text{N}_{2}\text{F}_{6}$: C, 43.37; H, 4.22; N, 8.43. Found: C, 43.16; H, 4.23; N, 8.33

Preparation of $\text{H}_2\text{SALTM}$ [$\text{N},\text{N}^{\prime}\text{-propylenebis(salicylideneimine)}$]

To a stirred, refluxing solution of 30.53 g (0.25 mol) of salicylaldehyde in 250 ml of absolute ethanol was added 9.25 g (0.125 mol) of 1,3-diaminopropane. The reaction occurred immediately, as evidenced by the yellow color produced. The yellow crystals obtained after cooling the solution were filtered by suction and recrystallized from absolute ethanol, and dried at room temperature in vacuo, mp 53-54° [Lit. (44) mp 51°]. Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_{2}\text{O}_{2}$: C, 72.32; H, 6.43; N, 9.93. Found: C, 72.29; H, 6.22; N, 9.89

Preparation of $\text{H}_2\text{SALPTDA}$ [$\text{N},\text{N}^{\prime}\text{-pentamethylenebis(salicylideneimine)}$]

To a heated, refluxing solution of 24.40 g (0.20 mol) of salicylaldehyde in 100 ml of methanol was added 10.22 g (0.10 mol) of 1,5-diaminopentane dissolved in 100 ml of methanol. The yellow solution was refluxed for 15 min. The volume of the solution was reduced, whereupon yellow crystals were formed with cooling and were filtered by suction.
The ligand was recrystallized from methanol and dried at room temperature \textit{in vacuo}, mp 62-63° [Lit. (45) mp 64°]. Anal. Calcd. for C_{19}H_{22}N_{2}O_{2}: C, 73.52; H, 7.15; N, 9.03. Found: C, 73.71; H, 7.19; N, 9.29.

Preparation of H_{2}SALHTDA [N,N'-heptamethylenebis(salicylideneimine)]

To a stirred, refluxing solution of 24.40 g (0.20 mol) of salicylaldehyde in 100 ml of methanol, was added 13.02 g (0.10 mol) of 1,7-diaminoheptane in 100 ml of methanol. The orange solution was refluxed for 15 min, after which the volume was reduced, and the solution was cooled. Yellow crystals were formed, filtered by suction and recrystallized from methanol. These were dried at room temperature \textit{in vacuo}, mp 51°. Anal. Calcd. for C_{21}H_{26}N_{2}O_{2}: C, 74.53; H, 7.74; N, 8.28. Found: C, 74.57; H, 7.82; N, 8.36.

PREPARATION OF MANGANESE(II) COMPLEXES

Preparation of Mn(SALDPT) [N,N'-(3,3'-bis[propyl]amine)bis(salicylideneiminato)manganese(II)]

Under nitrogen, 13.12 g (0.10 mol) of 3,3'-bis(aminopropyl)-amine was dissolved in 175 ml of 95% ethanol. In one addition, 24.42 g (0.20 mol) of salicylaldehyde in 100 ml of 95% ethanol was added. The solution was refluxed for 10 min, after which 8 g (0.20 mol) of NaOH dissolved in 30 ml of H_{2}O was added dropwise. Next, 24.42 g (0.10 mol) of Mn(C_{2}H_{3}O_{2})_{2}\cdot4H_{2}O in 175 ml of warm H_{2}O was added dropwise. A yellow precipitate appeared before addition was complete. The dark orange solution was refluxed for 2 hrs. The flask was sealed and taken into the inert atmosphere box, where the solution was filtered by suction. The isolated light yellow precipitate was dried for several days \textit{in vacuo}. Extended drying was needed to remove water from the compound.
Preparation of Mn(SALDPT)(H$_2$O) and Mn(SALDPT)(H$_2$O)$_2$ [N,N'-(3,3'-bis
[propyl]amine)bis(salicylideneiminato)aquoaquo and diaquomanganese(II)]

Under nitrogen, 1.13 g (0.01 mol) of 3,3'-bis(aminopropyl)amine
was dissolved in 30 ml of methanol. Next, 2.44 g (0.02 mol) of sali­
cylaldehyde dissolved in 30 ml of methanol was added in one addition.
The solution was allowed to reflux 10 min with stirring. KOH (1.12 g, 0.02 mol) dissolved in 15 ml of methanol was added dropwise to the
orange solution, causing it to become yellow. Upon dropwise addition of
2.45 g (0.01 mol) of Mn(C$_2$H$_3$O$_2$)$_2$·6H$_2$O in 30 ml of hot methanol, the
solution turned orange. The solution was refluxed 45 min, with no pre­
cipitate formation. In the inert atmosphere box, the solution was
separated into two portions. To the first aliquot, water was added until
the precipitate first formed. An oil also formed at this point.
Methanol was then added until the precipitate redissolved. The solution
was then allowed to stand in the box for several days. Water was also
added to the second aliquot. When all precipitation seemed to have
occurred, the oil was removed from the solution. The filtrate was also
allowed to stand for several days. Small orange crystals of the
dihydrate (vide infra) were isolated from the first solution, large red­
orange crystals of the monohydrate (vide infra) were isolated from the
second solution. The crystals were dried at room temperature in vacuo.

Preparation of Mn(SALTM) [N,N'-propylenebis(salicylideneiminato)­
manganese(II)]

This preparation followed that used by Johnson and Beveridge (36).
Under nitrogen, 7.0 g (0.025 mol) of H$_2$SALTM was dissolved in 190 ml of
70% ethanol with slight heating. When the ligand was completely
dissolved, the solution was allowed to cool to room temperature. 
Next, 8.94 g (0.025 mol) of manganese(II) nitrate (50% H₂O solution) in 
100 ml of 70% ethanol was added dropwise to the solution. The addition 
took 30 min with stirring. The precipitate formed slowly. The mixture 
was then sealed and filtered in an inert atmosphere box. A yellow- 
orange powder was obtained, and dried overnight at room temperature in 
vacuo.

Preparation of Mn(SALPTDA) [N,N'-pentamethylenebis(salicylideneiminato) 
manganese(II)]

A stirred solution of 9.32 g (0.03 mol) of H₂SALPTDA in 500 ml of 
absolute ethanol was refluxed for 10 min under nitrogen. Solid NaOH 
(2.4 g, 0.06 mol) was added. When the base had dissolved, 7.26 g (0.03 
 mol) of crushed Mn(C₂H₃O₂)₂·4H₂O was added along with 200 ml of hot 
absolute ethanol. The pale yellow solution thickened immediately, and 
was then stirred and refluxed for 30 min, during which the mixture 
turned orange-yellow. The orange-yellow powder was isolated and dried 
as described above.

Preparation of Mn(SALHTDA) [N,N'-heptamethylenebis(salicylideneiminato) 
manganese(II)]

A solution of 1.69 g (0.005 mol) of H₂SALHTDA in 500 ml of 95% 
ethanol was refluxed under nitrogen for 10 min. NaOH (0.4g, 0.01 mol) 
was dissolved in 15 ml of H₂O and added dropwise. Next, 1.22 g (0.005 
 mol) of Mn(C₂H₃O₂)₂·4H₂O was dissolved in 50 ml of hot H₂O and slowly 
added dropwise. The yellow precipitate formed immediately. The 
orange-yellow solution was refluxed for 45 min, after which the sample 
was isolated and dried as described above.
Oxygenation of Mn(SALTM)

Lab air was bubbled through a stirred solution of 14.11 g (0.05 mol) of $\text{H}_2\text{SALTM}$ in 400 ml of 95% ethanol. The solution was refluxed for 10 min. To this yellow solution, 4 g (0.10 mol) of NaOH dissolved in 15 ml of $\text{H}_2\text{O}$ was added dropwise. Next, 12.21 g (0.05 mol) of Mn($\text{C}_2\text{H}_3\text{O}_2$)$_2\cdot4\text{H}_2\text{O}$ dissolved in 100 ml of warm $\text{H}_2\text{O}$ was added dropwise. An immediate color change from yellow to dark green accompanied by precipitate formation occurred. After refluxing the solution for 1.5 hrs, the dark greenish-gray precipitate was filtered by suction and then dried at room temperature in vacuo. This material was continuously extracted in a Soxhlet apparatus (8.0 g to 500 ml) for 48 hrs in absolute ethanol. Upon reduction of the volume, small, dark brown crystals were obtained. These were found to be hydrated. The water could be driven off at elevated temperatures (120°C for 24 hrs) in vacuo. However, the compound quickly absorbed water from the atmosphere on standing.

Alternate Method for Oxygenation of Mn(SALTM)

In an inert atmosphere box, 0.506 g (0.00151 mol) of Mn(SALTM) was placed in a reaction flask and sealed. It was removed and quickly attached to an oxygen-uptake apparatus (Figure 2). The DMSO used was degassed by placing it under vacuum for 1.5 hrs or by the freeze-thaw method. The system was placed under a positive oxygen pressure (approximately 1.08 atm of pressure) and closed. Over a one day period, the volume of oxygen at constant pressure taken up by the compound was measured in milliliters. Using the ideal gas law, $PV = nRT$, the number of moles of oxygen consumed could then be calculated. The solution
was filtered and a brown powder was isolated and dried at room temperature in vacuo. The compound was purified by extraction for 24 hrs in methylene chloride.

**Oxygenation of Mn(SALPTDA)**

In an inert atmosphere box, 0.540 g (0.00149 mol) of Mn(SALPTDA) was placed in 150 ml of DMSO. The compound did not completely dissolve. Oxygen was passed over the stirred suspension for 22 hrs. On filtering, a dark brown compound was obtained along with a near colorless filtrate. The product was found to be hydrated, even after being dried at room temperature in vacuo.

**Oxygenation of Mn(SALPTDA) under 1.08 atm pressure**

The same method used for Mn(SALTM) was employed with Mn(SALPTDA). The sample sizes were in the same range (0.0015 mol). Complete uptake occurs in one day. The solution was filtered and the isolated brown product was dried at room temperature in vacuo.

**Oxygenation of Mn(SALHTDA) in the Solid State**

Dry, solid Mn(SALHTDA), on exposure to oxygen, was oxidized. The orange-yellow compound changed to dark red-brown in a week. This change occurs on standing in air or in oxygen. Using the oxygen uptake apparatus shown in Figure 2, 0.437 g (0.0011 mol) of Mn(SALHTDA) was oxygenated under 1.08 atm oxygen pressure. The same red-brown product was obtained. Under pressure, the oxygenation was complete in less than four days.

**Oxygenation of Mn(SALHTDA) in DMSO**

The same procedure followed for Mn(SALPTDA) was used for Mn(SALHTDA). The oxygenations, as with Mn(SALPTDA), were carried out both under 1.08
atm of oxygen, and with oxygen passing through the solution at atmospheric pressure (0.93 atm). The solutions were filtered, and in both cases, a dark brown, anhydrous powder was obtained. These products were dried at room temperature in vacuo.

UNSUCCESSFUL PREPARATIONS

**Attempted Preparations of Mn(BAE) [N,N'-ethylenebis(acetylacetoniminate) manganese(II)]**

The preparation of Mn(BAE) was attempted using numerous methods. None of these methods, which are outlined below, proved successful in the isolation of this compound.

The first procedure followed the Morgan and Smith (46) preparation of Co(BAE). To a stirred, heated solution of 4.90 g (0.02 mol) of Mn(C$_2$H$_3$O$_2$)$_2$·4H$_2$O in 20 ml of hot H$_2$O, was added 4.5 g (0.02 mol) of H$_2$BAE in 25 ml of hot H$_2$O followed by 1.6 g (0.04 mol) of NaOH in 8 ml of H$_2$O. The cream colored solution was heated for 20 min with no color change. The precipitate was difficult to filter, and exposure to the laboratory atmosphere caused the mixture to turn dark brown. It was soluble only in acid, pointing to the formation of some manganese oxide or similar species.

A second procedure followed the method of Lewis, Mabbs, and Weigold (28) for the preparation of Mn(SALEN). A solution of 1.23 g (0.005 mol) of Mn(C$_2$H$_3$O$_2$)$_2$·4H$_2$O in a mixture of 20 ml of hot absolute ethanol and 5 ml of hot H$_2$O was prepared. A second solution of 0.3 g (0.0075 mol) of NaOH and 0.96 g (0.005 mol) of H$_2$BAE in 20 ml of hot absolute ethanol was prepared. Under nitrogen, the two solutions were mixed with no further heating. After 1 hr, a similar light brown sludge was
obtained and discarded.

A third procedure involved adding 0.3 g (0.0075 mol) of solid NaOH to a stirred, refluxing solution of 0.96 g (0.005 mol) of H₂BAE in 100 ml of absolute ethanol. After a steady flow of nitrogen was begun, 1.23 (0.005 mol) of Mn(C₂H₃O₂)₂·4H₂O dissolved in 50 ml of hot absolute ethanol was added dropwise. The pale yellow solution was refluxed under a nitrogen flow for 2.5 hrs, and then cooled to room temperature. The flask was stoppered and placed in an inert atmosphere box. A cream colored precipitate was obtained by suction filtering. This precipitate was soluble in acid but insoluble in most common organic solvents. Elemental and infrared analyses showed that this material was not the desired product, but more likely a manganese oxide.

As in the procedure outlined above, 0.3 g (0.0075 mol) of solid NaOH was added to a refluxing solution of 0.96 g (0.005 mol) of H₂BAE. The metal source was MnCl₂·4H₂O (0.005 mol). The solution was refluxed for 2 hrs. The solution was filtered and a cream colored precipitate was isolated. Elemental analyses suggest that the products from the third procedure and this preparation were similar.

Under nitrogen, 9.61 g (0.05 mol) of H₂BAE was dissolved in 140 ml of 95% ethanol. The solution was refluxed for 10 min, after which 4 g (0.10 mol) of NaOH dissolved in 15 ml of H₂O was added dropwise. Next, 12.25 g (0.05 mol) of Mn(C₂H₃O₂)₂·4H₂O dissolved in 80 ml of warm H₂O was added dropwise with stirring. The solution was refluxed for 1 hr and transferred to the inert atmosphere box. A light brown sludge was obtained as in the initial two reactions.
To a stirred, refluxing solution of 9.61 g (0.05 mol) of $\text{H}_2\text{BAE}$ in 300 ml of absolute ethanol was added 12.21 g (0.05 mol) of $\text{Mn(C}_2\text{H}_3\text{O}_2)_2\cdot4\text{H}_2\text{O}$ dissolved in 300 ml of hot absolute ethanol. The yellow solution was refluxed 1 hr and then filtered. A white precipitate was obtained. The addition of four equivalents of triethylamine produced no noticeable change in the solution when heated. Next, two equivalents of sodium methoxide were added, which caused the solution to darken. A similar dark brown sludge was obtained when the liquid was filtered.

**Attempted Preparations of Mn(BAE)$_X$**

The preparation of Mn(BAE)$_X$ was also attempted without success by blowing air through a stirred, refluxing solution of 19.21 g (0.10 mol) of $\text{H}_2\text{BAE}$ in 350 ml of 95% ethanol to which had been added dropwise 8 g (0.2 mol) of NaOH in 30 ml of H$_2$O. Next, 24.43 g (0.10 mol) of $\text{Mn(C}_2\text{H}_3\text{O}_2)_2\cdot4\text{H}_2\text{O}$ in 225 ml of warm H$_2$O was added dropwise. The solution was refluxed for 2 hrs and then allowed to cool. The dark brown precipitate which had formed was hard to filter. This dried material was extracted continuously for 24 hrs in chloroform but no material appeared to be soluble in the chloroform.

This procedure was followed again using smaller amounts of materials and allowing 6 hrs for refluxing. Again, a dark brown sludge was obtained which could not be dissolved in common organic solvents.

A third preparation of a manganese(III) complex of BAE$^{-2}$ involved adding dropwise to a stirred solution of 0.96 g (0.005 mol) of $\text{H}_2\text{BAE}$ in 100 ml of absolute ethanol, 1.33 g (0.005 mol) of $\text{Mn(C}_2\text{H}_3\text{O}_2)_2\cdot4\text{H}_2\text{O}$ in 100 ml of warm absolute ethanol. The solution was refluxed 1.5 hrs, filtered hot and allowed to stand for 48 hrs. No precipitate appeared.
The solution was again brought to reflux, whereupon 90 ml of a hot, saturated solution of ammonium hexafluorophosphate was added. The solution was refluxed for 1 hr. The volume was reduced by passing air through the solution for 12 hrs. A small amount of a light brown powder appeared.

These products had elemental and infrared characteristics and solubility properties consistent with manganese(III or IV) oxides or hydroxides rather than to Mn(BAE) or Mn(BAE)X.

**Attempted Preparation of Mn(TFACACEN) [N,N'-ethylenebis(1,1,1-trifluoroacetylacetoinminato)manganese(II)]**

Under nitrogen, 0.08 g (0.002 mol) of NaOH in 5 ml of H₂O was added dropwise to a refluxing solution of 0.33 g (0.001 mol) of H₂TFACACEN in 50 ml of 95% ethanol. Next, 0.245 g (0.001 mol) of Mn(C₂H₃O₂)₂·4H₂O in 30 ml of warm H₂O was added dropwise. The solution turned a light brown color and was cloudy in appearance. No precipitate was isolated.

In another attempt, 0.332 g (0.001 mol) of H₂TFACACEN was dissolved with heat in 50 ml of absolute ethanol. After refluxing for 10 min, one pellet of NaOH was added. When it had dissolved, the clear solution turned yellow. Next, 0.198 g (0.001 mol) of MnCl₂·4H₂O dissolved in 30 ml of warm absolute ethanol was added dropwise. The solution darkened immediately, but no precipitate was isolated.
PHYSICAL MEASUREMENTS

Carbon, hydrogen, and nitrogen analyses were performed using a Perkin-Elmer Model 240 Elemental Analyzer.

Infrared spectra were obtained using a Beckman IR 20A-X spectrometer over the range of 4000-300 cm\(^{-1}\). The solid samples were prepared as Nujol mulls between potassium bromide windows.

Magnetic susceptibility data on solid samples were obtained by the Faraday method using a Varian V2900 electromagnetic power supply and a Cahn RG Electro-balance with a capacity of 2.5 grams and a sensitivity of 0.1 microgram. Susceptibilities, which were measured at room temperature, were obtained at four different field strengths. The system was calibrated using Hg\([\text{Co(NCS)}_4]\), mercury tetraisothiocyanato-cobalt(II) and \([\text{Ni(en)}_3\]S\(_2\)O\(_3\)), tris(ethylenediamine)nickel(II) thiosulfate. Molar diamagnetic susceptibilities were calculated using Pascal's constants (47).

Thermal gravimetric analyses (TGA) were performed using a Cahn RG Electro-balance with a Stone S-101 Programmer, S-601 Amplifier, and LD-202 Recorder-controller. Samples weighing 15 mg were heated in vacuo from 20° to 270°C, using a 2°C/min heating rate. The system was tested using copper(II) sulfate pentahydrate.

Oxygen-sensitive compounds were filtered and stored in a Vacuum Atmospheres Company inert atmosphere box, Model He 43-2 Dri-Lab,
in an $O_2$-free argon atmosphere.

Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7 double focusing mass spectrometer. Solid samples were placed on a solid inlet probe and heated to a temperature where vaporization but not decomposition would occur. The chamber and the sources were kept at approximately the same temperature. Pressure was maintained at $10^{-6}$ Torr. Ionizing electron energy was 70 eV.
ABBREVIATIONS FOR MANGANESE(II) COMPLEXES

![Diagram of a manganese(II) complex]

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
</tr>
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<tbody>
<tr>
<td>Mn(SALTM)</td>
<td>$(\text{CH}_2)_3$</td>
</tr>
<tr>
<td>Mn(SALPTDA)</td>
<td>$(\text{CH}_2)_5$</td>
</tr>
<tr>
<td>Mn(SALHTDA)</td>
<td>$(\text{CH}_2)_7$</td>
</tr>
<tr>
<td>Mn(SALDPT)</td>
<td>$-(\text{CH}_2)_3\text{H}-(\text{CH}_2)_3^-$</td>
</tr>
</tbody>
</table>

Figure 3
RESULTS AND DISCUSSION OF MANGANESE(II) COMPLEXES

The Mn(II) complexes under consideration were isolated by one of the following methods: (1) addition of Mn(C$_2$H$_3$O$_2$)$_2$·4H$_2$O in water to a hot or cold 70-95% ethanol solution of the previously isolated ligand and base; (2) addition of solid Mn(C$_2$H$_3$O$_2$)$_2$·4H$_2$O to a refluxing absolute ethanol solution of the previously isolated ligand and base; or (3) addition of Mn(C$_2$H$_3$O$_2$)$_2$·4H$_2$O in methanol to a refluxing solution of the ligand and base, followed by precipitation with water. All complexes were prepared and isolated in an inert atmosphere to prevent the possibility of oxidation of Mn(II) to Mn(III) or Mn(IV).

The neutral anhydrous complexes Mn(SALTN), Mn(SALPTDA), Mn(SALHTDA), and Mn(SALDPT) are powders and range in color from pale to bright yellow. The compounds, exclusive of Mn(SALHTDA), are stable in air when dry; however, when wet all the compounds rapidly turn dark brown, indicating oxidation. They are insoluble in most common organic solvents. Upon heating to 100°C at approximately 10^{-2} torr, Mn(SALTm) and Mn(SALPTDA) remain yellow, while Mn(SALHTDA) and Mn(SALDPT) turn brown, suggesting oxidation or decomposition has occurred.

The hydrated complexes of Mn(SALDPT) are also stable in air when dry. The compounds are crystalline and slightly soluble in organic solvents, showing no color change which indicated the absence of oxidation. The compounds, when heated in vacuo at 100°C for 24 hours,
remain crystalline but change from orange to black in color. The black crystals are insoluble in all common organic solvents and water.

Analytical data in support of the proposed compositions of these compounds are listed in Table 1. Carbon analyses are usually low and often not reproducible. Numerous preparations of Mn(SALTM) resulted in the same low carbon analysis. The analysis of Mn(SALHTDA) must be performed rapidly to prevent oxidation from occurring. Recrystallization was not possible to purify the compounds due to insolubilities and sensitivities to oxygen in solution.

Several of the complexes reported above [Mn(SALDPT) and Mn(SALTM)] have been reported elsewhere (37,48). However, when the reported preparations were followed, either no products were isolated, or the properties of the isolated compounds differed from those of the previously reported compounds.

Mn(SALDPT) was made following the method of Sacconi and Bertini (48), by adding Mn(C$_2$H$_3$O$_2$)$_2$·4H$_2$O to an ethanol solution of salicylaldehyde and 3,3'-bis(aminopropyl)amine. The solution was refluxed for 30 minutes, and water was added to facilitate precipitation.

This procedure was followed several times, varying the amount of water added and the time it was added. No precipitate was ever isolated, due to the formation of an oil in the reaction mixture. When water was added at the start of the reaction, as part of the solvent, a yellow powder precipitates before addition of the metal is complete. The product is hydrated, but with continued drying at room temperature, the anhydrous complex is formed. This complex is readily oxidized in solution as is the complex reported by Sacconi and
Table 1

ELEMENTAL ANALYSIS DATA FOR MANGANESE(II) COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analysis(%)</th>
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<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td><strong>Mn(SALTM)</strong></td>
<td>Calcd.</td>
<td>60.90</td>
<td>4.81</td>
<td>8.36</td>
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<tr>
<td></td>
<td>Found</td>
<td>57.74</td>
<td>4.78</td>
<td>7.94</td>
</tr>
<tr>
<td><strong>Mn(SALPTDA)</strong></td>
<td>Calcd.</td>
<td>62.81</td>
<td>5.54</td>
<td>7.71</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>62.53</td>
<td>5.64</td>
<td>8.21</td>
</tr>
<tr>
<td><strong>Mn(SALHTDA)</strong></td>
<td>Calcd.</td>
<td>64.45</td>
<td>6.18</td>
<td>7.16</td>
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<tr>
<td></td>
<td>Found</td>
<td>63.93</td>
<td>6.51</td>
<td>7.42</td>
</tr>
<tr>
<td><strong>Mn(SALDPT)</strong></td>
<td>Calcd.</td>
<td>61.23</td>
<td>5.91</td>
<td>10.71</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>60.37</td>
<td>5.89</td>
<td>10.51</td>
</tr>
<tr>
<td><strong>Mn(SALDPT)(H₂O)</strong></td>
<td>Calcd.</td>
<td>58.54</td>
<td>6.14</td>
<td>10.24</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>57.88</td>
<td>6.27</td>
<td>10.28</td>
</tr>
<tr>
<td><strong>Mn(SALDPT)(H₂O)₂</strong></td>
<td>Calcd.</td>
<td>56.07</td>
<td>6.30</td>
<td>9.48</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>56.30</td>
<td>6.52</td>
<td>9.81</td>
</tr>
</tbody>
</table>
Bertini (48), however, it is stable in air when dry, in contrast to their compound.

The hydrated crystals of Mn(SALDPT) reported above were prepared in methanol rather than in ethanol, as in the previously reported method. These two compounds are also precipitated with water. Mn(SALDPT)(H₂O)₂ was allowed to precipitate slowly after adding water to begin precipitation and next adding methanol until all compound disappears. Mn(SALDPT)(H₂O) is prepared by adding water to the methanol solution until precipitation appeared to be complete. This compound was also allowed to precipitate slowly. These compounds, formed in a procedure which differs only in solvent to that reported previously, are different from the compound reported by Sacconi and Bertini (48). These compounds are hydrated, and are stable in air when dry and when in solution, in contrast to the compound previously isolated.

Mn(SALT₅)(H₂O) (36) is reported to be prepared at room temperature by dissolving the Schiff base ligand in 70% ethanol and adding to this a solution of manganese(II) nitrate in 70% ethanol. The hydrated complex (37) reportedly reacts slowly with air when dry, and quickly when in solution. When the above procedure was repeated in this study, an anhydrous compound was formed which had the same characteristics as the hydrated complex (i.e. being slow to air oxidize in the solid state). An anhydrous Mn(SALT₅) complex had previously been prepared and isolated by Calderazzo et al. (38) by reacting H₂SALT₅ with [Mn(CO)₅]₂. The compound is stated to be extremely air sensitive when dry as well as when dissolved in organic solvents. The compound which we have prepared is anhydrous; however, in the solid state
it is reasonably air stable.

Elemental analyses, magnetic moments, and infrared spectra are similar for all the anhydrous compounds. The reasons for their differing properties could possibly be due to the subtle differences in preparative procedures which result in compounds which differ in crystal form. Differences in crystal packing could cause a compound to have varying degrees of sensitivity to oxygen as has been observed with certain cobalt complexes (35,49).

Infrared spectra of the manganese(II) complexes were obtained as Nujol mulls. The mulls were prepared under an inert atmosphere to prevent the possibility of oxidation. The band assignments for the free ligands and the complexes appear in Tables 2-5. The C=N stretching frequency can be of use in determining whether the nitrogens of the ligand are coordinated to the metal. The C=N stretch normally occurs near 1640 cm\(^{-1}\) (50). Coordination of the imine nitrogen to the metal should weaken the C=N bond strength, thus causing a shift in the stretching frequency. In the free ligand, this band occurs between 1640-1630 cm\(^{-1}\). The manganese complexes show shifts of 10-22 cm\(^{-1}\), the bands appearing at 1628-1618 cm\(^{-1}\). These shifts indicate that coordination of the imine nitrogen to the metal has occurred. The C-O stretching vibration for a phenolic species, as the free ligands are, appears at 1230 cm\(^{-1}\) (50). Upon coordination to the metal, the oxygen is no longer of the free phenolic type, but is bound to a carbon atom and the metal. The strength of the C-O bond should, therefore, be weakened, causing a shift to lower frequencies. A shift of 5-25 cm\(^{-1}\) is observed on going from the free ligand to the metal complex.
Table 2

INFRARED DATA ON Mn(SALTM) AND ITS OXYGENATION PRODUCTS*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Assignments (cm$^{-1}$)</th>
<th>O-H str</th>
<th>C=N str</th>
<th>C-O str</th>
<th>C-N rock</th>
<th>Mn-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{SALTM}$</td>
<td>3610m 1640, 1620s 1285s</td>
<td>1150m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Mn(SALTM)</td>
<td>--</td>
<td>1620s</td>
<td>1275s</td>
<td>1155m</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Mn(SALTM) (OH) ($\text{H}_2\text{O}$)$^a$</td>
<td>3620w 1627s 1300s</td>
<td>1155m</td>
<td>640m, 615s</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$[\text{Mn(SALTM)}]_2\text{O}^b$</td>
<td>--</td>
<td>1625s</td>
<td>1300s</td>
<td>1150m</td>
<td>640m, 615s</td>
<td>--</td>
</tr>
<tr>
<td>Mn(SALTM) (O)$^c$</td>
<td>--</td>
<td>1623s</td>
<td>1300m</td>
<td>1155m</td>
<td>655m, 620s</td>
<td>--</td>
</tr>
</tbody>
</table>

* abbreviations used: w - weak; m - medium, s - strong; sh - shoulder

$^a$ethanol, air preparation
$^b$ethanol, air preparation, dried
$^c$DMSO, oxygen pressure preparation
Table 3

INFRARED DATA ON Mn(SALPTDA) AND ITS OXYGENATION PRODUCTS*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Assignments (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-H str</td>
</tr>
<tr>
<td>H₂SALPTDA</td>
<td>3600m</td>
</tr>
<tr>
<td>Mn(SALPTDA)</td>
<td>--</td>
</tr>
<tr>
<td>Mn(SALPTDA)(O)(H₂O)a</td>
<td>3400m</td>
</tr>
<tr>
<td>Mn(SALPTDA)(O)b</td>
<td>--</td>
</tr>
</tbody>
</table>

*abbreviations used: m - medium; s - strong; sh - shoulder

aDMSO, air preparation

bDMSO, oxygen pressure preparation
<table>
<thead>
<tr>
<th>Compound</th>
<th>O-H str</th>
<th>C=N str</th>
<th>C-O str</th>
<th>C-N rock</th>
<th>Mn-O str</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{SALHTDA} )</td>
<td>3600m</td>
<td>1635m</td>
<td>1280m</td>
<td>1150m</td>
<td>--</td>
</tr>
<tr>
<td>Mn(SALHTDA)</td>
<td>--</td>
<td>1620s</td>
<td>1290s</td>
<td>1150m</td>
<td>--</td>
</tr>
<tr>
<td>Mn(SALHTDA(O))\text{a}</td>
<td>--</td>
<td>1625s</td>
<td>1290s</td>
<td>1150m</td>
<td>625s, 600s</td>
</tr>
<tr>
<td>Mn(SALHTDA(O))\text{b}</td>
<td>--</td>
<td>1620s</td>
<td>1320s</td>
<td>1150m</td>
<td>630s, 600s</td>
</tr>
<tr>
<td>Mn(SALHTDA(O))\text{c}</td>
<td>--</td>
<td>1620s</td>
<td>1295m</td>
<td>1145m</td>
<td>625m, 595m</td>
</tr>
<tr>
<td>Mn(SALHTDA(O))\text{d}</td>
<td>--</td>
<td>1625s</td>
<td>1320s</td>
<td>1155m</td>
<td>630s, 605s</td>
</tr>
</tbody>
</table>

*abbreviations used: m - medium; s - strong; sh - shoulder
\( \text{a} \) solid state, air preparation
\( \text{b} \) solid state, oxygen pressure preparation
\( \text{c} \) DMSO, air preparation
\( \text{d} \) DMSO, oxygen pressure preparation
Table 5

INFRARED DATA ON Mn(SALDPT) COMPLEXES*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Assignments (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-H str</td>
</tr>
<tr>
<td>Mn(SALDPT)</td>
<td>--</td>
</tr>
<tr>
<td>Mn(SALDPT)(H(_2)O)</td>
<td>3400m</td>
</tr>
<tr>
<td>Mn(SALDPT)(H(_2)O)(_2)</td>
<td>3420m</td>
</tr>
</tbody>
</table>

*abbreviations used: m - medium; s - strong; sh - shoulder
Mn(SALTM), Mn(SALPTDA), and Mn(SALHTDA) show no absorption above 3050 cm\(^{-1}\) whereas Mn(SALDPT)(H\(_2\)O) and Mn(SALDPT)(H\(_2\)O\(_2\)) both show a broad band at 3400 cm\(^{-1}\) due to water. All three SALDPT complexes should show a band near 3450-3310 cm\(^{-1}\) due to a secondary N-H stretch, and at 1580-1490 cm\(^{-1}\) due to the N-H bending frequency \((50)\). Both of these bands are weak, and the latter may be obscured by aromatic ring bands. These compounds all contain a weak band in the region 3280-3190 cm\(^{-1}\) assignable to a secondary N-H stretch. Strong bands in the region 1580-1490 cm\(^{-1}\) due to the aromatic rings do indeed obscure any weak bands due to the N-H vibrational mode. The shift to lower frequency relative to the free ligand of the N-H stretching mode tends to support the coordination of the amine nitrogen to the metal, thus making the ligand pentacoordinate. Sacconi and Bertini came to similar conclusions for the analogous Co(II), Ni(II), Cu(II), and Zn(II) complexes \((48)\).

To determine that the ligand has not been modified in the reaction with the metal, the infrared spectra were inspected for bands characteristic of the ligand. Besides the bands mentioned above to indicate coordination, several bands characteristic of the aromatic system are present. Bands between 770-735 cm\(^{-1}\) are characteristic of the C-H out-of-plane bending in 1,2-disubstituted benzene \((50)\). The aromatic ring out-of-plane bend occurs between 875-670 cm\(^{-1}\) \((50)\). In this range, these complexes have several bands. The most intense set of bands appears at approximately 770, 760, and 740 cm\(^{-1}\) for all compounds, with variations of \(+10\) cm\(^{-1}\). Several bands also occur between 860-800 cm\(^{-1}\).
Bands for the CH$_2$ scissor vibration should also be present. These bands occur between 1475-1350 cm$^{-1}$ (50). The compounds have bands at approximately 1450, 1405, and 1350 cm$^{-1}$, with variations of $\pm 5$ cm$^{-1}$.

The bands listed above are also present in the ligands. It is reasonable to assume that the ligands remained intact upon complexation with the metal.

Positive ion mass spectra were obtained on the manganese(II) complexes. The complexes gave parent ion isotopic clusters as shown in Table 6, which support the suggested composition in the gas phase. Mass spectra of all compounds were scanned above the parent ion mass to charge ratio to determine the presence of any dimeric species. No dimeric species were detected at the appropriate mass to charge ratio. However, Mn(SALPTDA), Mn(SALHTDA), and Mn(SALDPT) did show fragments at higher masses than the parent peaks. These fragments were no more than 100 mass units above the parent peak. The hydrated complexes of Mn(SALDPT) lose water easily, so the parent ion clusters correspond to the anhydrous compound.

The magnetic susceptibilities of the manganese(II) complexes were measured in air at room temperature and atmospheric pressure. The magnetic moments of these compounds, as shown on Table 7, range from 5.65 to 6.01 B. M. This is within the experimental range expected for a d$^5$ high-spin manganese(II) complex (5.92 B. M.). These values have been corrected for the diamagnetic contribution of the ligands. The values listed are averages of measurements taken at four different field strengths.
Table 6

MASS SPECTRAL DATA ON THE MANGANESE(II) COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample Temp., °C</th>
<th>Parent Ion Cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(SALTM)</td>
<td>200</td>
<td>335*, 336**, 337</td>
</tr>
<tr>
<td>Mn(SALPTDA)</td>
<td>185</td>
<td>363*, 364**, 365</td>
</tr>
<tr>
<td>Mn(SALHTDA)</td>
<td>260</td>
<td>391*, 392**, 393</td>
</tr>
<tr>
<td>Mn(SALDPT)</td>
<td>200</td>
<td>392*, 393**, 394</td>
</tr>
<tr>
<td>Mn(SALDPT)(H₂O)</td>
<td>200</td>
<td>392^a, 393**, 394</td>
</tr>
<tr>
<td>Mn(SALDPT)(H₂O)₂</td>
<td>190</td>
<td>392^b, 393**, 394</td>
</tr>
</tbody>
</table>

* corresponds to the calculated molecular weight
** corresponds to C¹³ contribution

^a this compound, MW = 410, loses one H₂O, parent ion is for anhydrous complex

^b this compound, MW = 428, loses two H₂O, parent ion is for anhydrous complex
Table 7

SOLID STATE MAGNETIC PROPERTIES OF MANGANESE(II) COMPLEXES*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp., °C</th>
<th>$X_m \times 10^{-6}$</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>Lit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(SALTM)</td>
<td>20</td>
<td>13,568.3</td>
<td>5.66</td>
<td>5.93&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mn(SALPTDA)</td>
<td>20</td>
<td>13,257.1</td>
<td>5.63</td>
<td></td>
</tr>
<tr>
<td>Mn(SALHTDA)</td>
<td>20</td>
<td>13,040.2</td>
<td>5.76</td>
<td></td>
</tr>
<tr>
<td>Mn(SALDPT)</td>
<td>23</td>
<td>13,772.7</td>
<td>5.79</td>
<td>5.90&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mn(SALDPT)(H&lt;sub&gt;2&lt;/sub&gt;O)</td>
<td>21</td>
<td>14,563.4</td>
<td>5.88</td>
<td></td>
</tr>
<tr>
<td>Mn(SALDPT)(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>23</td>
<td>15,159.3</td>
<td>6.01</td>
<td></td>
</tr>
</tbody>
</table>

* $X_m$ and $\mu_{\text{eff}}$ are averages of replicative measurements at four different field strengths

<sup>a</sup>(48)  
<sup>b</sup>(37)
These magnetic moments are in agreement with several other previously reported manganese(II) complexes. Sacconi and Bertini (48) report 5.90 B. M. for Mn(SALDPT). Mn(SALTm) has a magnetic moment of 5.93 B. M. (37). Mn(SALEN), on the other hand, has a magnetic moment of 5.24 B. M. (27). The lower magnetic moment is caused by the interaction of two manganese ions resulting in antiferromagnetic coupling, which is present because Mn(SALEN) has been shown to be a dimer (28).

As shown on the Table, the anhydrous complexes studied here all exhibit slightly low magnetic moments. The mass spectra of Mn(SALTm) does not appear to be due to a dimeric species. The compound is, however, slightly impure as indicated by the elemental analysis. This impurity could be the cause of the slightly lower magnetic moment. The mass spectra of Mn(SALPTDA), Mn(SALHTDA), and Mn(SALDPT) do show fragments at higher mass than the parent peaks. It is possible that these compounds contain a small amount of polymeric impurity which lowered the moment but was too unstable to appear as a true dimeric species on the mass spectra. These magnetic moments are not low enough to indicate that these compounds are present only in the dimeric state. The hydrated complexes, with the expected magnetic moments, are considered to be monomeric.

Thermal gravimetric analysis (TGA) data was obtained on the two hydrated Mn(SALDPT) complexes. Mn(SALDPT)(H_2O) loses one molecule of water at 90°C (calcd. loss of one H_2O: 4.41%; found: 4.26%), with decomposition occurring near 130°C. The weight loss observed for Mn(SALDPT)(H_2O)_2 corresponds to approximately 1.5 molecules of water.
(calcd. loss of two $\text{H}_2\text{O}$: 8.41%; found: 5.73%), with decomposition occurring before all water can be lost.

Visible spectra would be useful in determining the structures of these compounds. However, visible spectra were not possible for these compounds due to their insolubility in common organic solvents, and their sensitivity to air when in solution.

The manganese(II) complexes studied above have been shown to contain the desired ligands. Their magnetic moments are within the range expected for a $d^5$ high-spin complex. Elemental analyses also correspond to the proposed composition. As previously mentioned, some of these compounds may have polymeric impurities. These impurities may also account in part for the insolubilities of these compounds. The complexes may, however, be monomeric. The magnetic moments are not low enough to indicate the interaction present in a dimeric species.

Mn(SALDPT) is monomeric and has an X-ray powder pattern (48) similar to that of Ni(II)(SALMeDPT). This compound, like Mn(SALDPT), is five coordinate, and has a structure which is intermediate between trigonal bipyramid and square pyramid. It appears, therefore, that Mn(SALDPT) has this same intermediate structure.
The hydrated manganese complexes, which should be six coordinate, are probably octahedral in geometry.

In Mn(SALTM), the ligand probably does not have enough flexibility to allow the complex to exist in an essentially tetrahedral geometry. The ligands with longer methylene chains are more flexible, allowing the complex to approach a tetrahedral geometry more closely. Harihan and Urbach (51), in a series of analogous Co(II) complexes, found that increasing the length of the methylene chain relaxed the structural requirements of the ligands, and a tetrahedral geometry was assumed. As in the Co(II) complexes, distortion toward a tetrahedral geometry is expected in Mn(SALPTDA) and Mn(SALHTDA). Mn(SALTM), on the other hand, probably assumes a highly flattened tetrahedron due to structural limitations.
RESULTS AND DISCUSSION OF OXYGENATED MANGANESE COMPLEXES

The oxygenated complexes (hereafter referred to by the simplest formula) were prepared using various methods, including: (1) bubbling air through a heated ethanol-water solution of the appropriate previously isolated ligand, base and metal ion followed by continuous extraction of the product with absolute ethanol; (2) oxygenation in the solid state with air at atmospheric pressure (0.93 atm) and/or with oxygen at approximately 1.08 atmospheres pressure; (3) oxygenation in DMSO with air at atmospheric pressure (0.93) and/or with oxygen at approximately 1.08 atmosphere pressure. Purification of the product from method 3 by continuous extraction using a Soxhlet apparatus with methylene chloride was necessary in several instances.

All the oxygenated manganese complexes are neutral and range in color from dark brown to dark red-brown. Several compounds which were continuously extracted are crystalline while the remainder are powders. Mn(SALTM)(OH)(H₂O) is slightly soluble or soluble in many organic solvents; however, the other complexes are insoluble in most common organic solvents. Upon prolonged heating at 165–200°C in vacuo, the compounds lighten in color, and their magnetic moments increase toward that expected for a manganese(II) complex. Upon re-exposure to air, the compounds show a decrease in magnetic moment, however, it does not decrease to the former value. When these compounds are
placed under vacuum, no oxygen is lost. The compounds show the loss (by TGA) of water and oxygen in the range 100-180°C. Anhydrous complexes are thermally stable until approximately 150°C.

Elemental analysis data supporting the simplest formula for the compounds are listed in Table 8. The carbon analyses for Mn(SALHTDA)-(O) made from three methods (see Table 8) were consistently low. Repeated analyses always gave the same values. These compounds appeared to be homogeneous. A possible explanation for these low values is incomplete oxygenation. In the solid state, oxygen pressure may have caused surface oxygenation to occur. Oxygen uptake results (Table 11) show that complete oxygenation did not occur. The compounds prepared in DMSO were not soluble in DMSO. It is believed that since Mn(SALHTDA) is slightly soluble in DMSO, the compound in solution is oxygenated and comes out of solution. As this oxygenated product precipitated, it is possible that some unoxygenated compound is trapped, thus causing the low analyses.

Oxygenated forms of Mn(SALTM) have been reported previously (37). Suspensions of Mn(SALTM)(H₂O) in benzene, when exposed to differing amounts of oxygen, are reported to yield products designated as [Mn(SALTM)(O₂)(H₂O)] and [Mn(SALTM)(O)·½(C₆H₆)]. Solutions in pyridine yield [Mn(SALTM)(OH)]₂·4Py on exposure to oxygen, which can be converted to Mn(SALTM)(O) on drying in vacuo. Anhydrous Mn(SALTM) yields [Mn(SALTM)(O)·½(C₆H₆)] from benzene. Mn(SALTM)(O) is formed when Mn(SALTM) is heated at 80°C in oxygen. All of these complexes are only slightly soluble in common organic solvents such as DMF, pyridine, and chloroform.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Analysis (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(SALTM)(OH)(H₂O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Calcd.</td>
<td>55.29</td>
<td>4.91</td>
<td>7.59</td>
<td></td>
</tr>
<tr>
<td>Found a</td>
<td>55.13</td>
<td>4.92</td>
<td>7.76</td>
<td></td>
</tr>
<tr>
<td>Mn(SALTM)(0)</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Calcd.</td>
<td>58.13</td>
<td>4.59</td>
<td>7.98</td>
<td></td>
</tr>
<tr>
<td>Found c</td>
<td>57.49</td>
<td>4.75</td>
<td>7.91</td>
<td></td>
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<tr>
<td>[Mn(SALTM)]₂O</td>
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<tr>
<td>Calcd.</td>
<td>59.48</td>
<td>4.66</td>
<td>8.16</td>
<td></td>
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<tr>
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<td>57.62</td>
<td>4.71</td>
<td>7.98</td>
<td></td>
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<tr>
<td>Mn(SALPTDA)(0)(H₂O)</td>
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<td></td>
<td></td>
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<tr>
<td>Calcd.</td>
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<td>5.03</td>
<td>7.04</td>
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<tr>
<td>Found d</td>
<td>57.28</td>
<td>5.44</td>
<td>6.92</td>
<td></td>
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<tr>
<td>Mn(SALPTDA)(0)</td>
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<td></td>
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<tr>
<td>Calcd.</td>
<td>60.16</td>
<td>5.31</td>
<td>7.39</td>
<td></td>
</tr>
<tr>
<td>Found c</td>
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<td>5.30</td>
<td>7.44</td>
<td></td>
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<tr>
<td>Mn(SALHTDA)(0)</td>
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<td></td>
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<tr>
<td>Calcd.</td>
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<td>5.94</td>
<td>6.88</td>
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<tr>
<td>Found e</td>
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<td>6.05</td>
<td>7.10</td>
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<tr>
<td>Found f</td>
<td>58.74</td>
<td>5.76</td>
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<td>Found d</td>
<td>58.33</td>
<td>5.45</td>
<td>6.64</td>
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<tr>
<td>Found c</td>
<td>58.42</td>
<td>5.83</td>
<td>6.78</td>
<td></td>
</tr>
</tbody>
</table>

* a. ethanol, air preparation
* b. ethanol, air preparation, dried
* c. DMSO, oxygen pressure preparation
* d. DMSO, air preparation
* e. solid state, air preparation
* f. solid state, oxygen pressure preparation
The oxygenated Mn(SALTM) complexes isolated in this study were produced either by in situ oxidation of Mn(SALTM) in ethanol or by oxidation of a suspension of the previously prepared and isolated Mn(SALTM) in DMSO. The products obtained both give similar magnetic moments, which are in turn lower than those for Mn(SALTM) oxidized complexes originally reported by Miller and Oliver (37). Mn(SALTM)(OH)-(H₂O), produced by the in situ method, is soluble in acetone, DMF, DMSO, dioxane, and ethanol, whereas Mn(SALTM)(O) is only slightly soluble in acetone, methanol, and chloroform. The preparation in pyridine (37) previously reported was not attempted in this study. Attempts to reproduce the results reported for benzene suspensions failed to yield either of the reported products. The compounds obtained are, however, similar in composition to the products reported except that they are not solvent adducts.

OXYGENATED COMPLEXES OF Mn(SALTM)

Oxygenation of Mn(SALTM) produced three complexes: Mn(SALTM)(OH)-(H₂O) formed in the in situ reaction; [Mn(SALTM)]₂O, formed after heating Mn(SALTM)(OH)(H₂O) at 100°C in vacuo; and Mn(SALTM)(O), formed from oxygenation of Mn(SALTM) in DMSO. These compounds exhibit some differing properties. The hydrated species is soluble in acetone, DMF, DMSO, dioxane, and ethanol. The anhydrous compounds are only slightly soluble in acetone, methanol, and chloroform. The magnetic moments of these compounds also differ.

It has been suggested (30,31) that certain structures have characteristic infrared bands. The use of these bands, plus other information, will hopefully lead to assignment of the correct structures.
for these compounds. Mn(SALTM)(OH)(H₂O) has a sharp infrared band at 3620 cm⁻¹ (Table 4) corresponding to an -OH stretching frequency, and a broad band at 3300 cm⁻¹ due to water, both of which are absent in [Mn-(SALTM)]₂O. A strong band resolved into peaks at 640 and 616 cm⁻¹ due to Mn-O stretching mode (Figure 4) appears which is not present in the precursor.

The complexes designated as Mn(SALTM)(O) and [Mn(SALTM)]₂O have a broad band with resolved peaks at 640, 615 cm⁻¹ and 655, 620 cm⁻¹ respectively. Miller and Oliver (37) found a single, intense broad band in the 600-650 cm⁻¹ region for their oxygenated products of Mn-(SALTM). One of their products ([Mn(SALTM)(OH)]·4Py) has been shown to be a dimer with a di-µ-hydroxo bridge (40). Bands in this region then, can be associated with a di-µ-hydroxo bridge. Further, Boucher (31) has suggested that a band at 642 cm⁻¹ for [Mn(BuSALTM)₂-O₂]·2H₂O, and at 655 cm⁻¹ for [Mn(BuSALEN)₂-O₂]H₂O, is characteristic of a di-µ-oxo bridge (Structure VIII), although he has no X-ray data to confirm this. Matsushita et al. (30) propose three possible structures to account for their 1:1 Mn:O complexes. A band at 840 cm⁻¹ is attributed to the complex with the oxo-bond as shown in Structure VII. This structure can be eliminated for the complexes studied here, since none of them show this band. A second structure, containing a µ-peroxo bond as shown in Structure V, is assigned characteristic Mn-O stretching modes at 645 and 631 cm⁻¹. This structure is a possibility for the compounds under study. The third structure, shown in Structure VI, contains a µ-catenaxo bond. The characteristic bands for this structure appear at 662 and 602 cm⁻¹. Another compound containing the catena-oxo bond,
INFRARED SPECTRUM OF Mn(SALTM) AND OXYGENATION PRODUCTS

Mn(SALTM)

Mn(SALTM) (OH) (H₂O)

[Mn(SALTM)]₂O

Mn(SALTM) (0) from DMSO

Figure 4
\([-\text{Mn(3-MeOSALEN)-O-}]_n\), has bands at 655 and 609 cm\(^{-1}\). From these experimental results, the compounds studied here, with a Mn-O stretching mode appearing between 600 and 655 cm\(^{-1}\), could theoretically contain di-\(\mu\)-hydroxo, di-\(\mu\)-oxo, \(\mu\)-peroxo, catena-oxo bridges, or some as yet undiscovered manganese-oxygen linkage. The spectra of Mn(SALTM)(O) and [Mn(SALTM)]\(_2\)O are not identical, and neither contain evidence of an \(\cdot\text{OH}\) stretching frequency. It is possible then that these three compounds have differing structures. The final assignment will have to be made with other data in mind.

Mn(SALTM) in the solid state does not react with oxygen when dry, therefore, no experiments were performed in this manner. As can be seen by the information in Table 9, oxygen uptake by Mn(SALTM) suspended in DMSO is rapid, being complete in one day. The \(N_{O_2}/N_{Mn}\) mole ratio average is 0.53, which is consistent with the proposed formula. Matsushita et al. (30) performed oxygen uptake experiments on Mn(SALEN) in DMSO, DMF, and methanol. They also obtained a mole ratio of approximately 0.5. Miller and Oliver (37), however, in their experiments with Mn(SALTM)(H\(_2\)O) in benzene, found complete oxygen uptake to take several days. They also observed varying degrees of uptake. The \(O_2:\text{Mn}\) ratio varied from 1:1 to 0.25:1. Also, different ratios gave different products. This is in marked contrast to the experiments disclosed herein where oxygen uptake is rapid, the same ratio is always achieved, and only one product is isolated. The difference may be due to solvent effects, or to the differences in a hydrated complex (used by Miller and Oliver) and an anhydrous one (used in this study).
Table 9
OXYGEN UPTAKE RESULTS

<table>
<thead>
<tr>
<th>Oxygenated Compound</th>
<th>Moles Mn</th>
<th>T, °C</th>
<th>Time (days)</th>
<th>$O_2$ Pres (atm)</th>
<th>$N_{O_2}/N_{Mn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(SALTM)(O)$^a$</td>
<td>1.49</td>
<td>31</td>
<td>1</td>
<td>1.08</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>1.60</td>
<td>28</td>
<td>1</td>
<td>1.08</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>1.51</td>
<td>27</td>
<td>1</td>
<td>1.07</td>
<td>0.48</td>
</tr>
<tr>
<td>Mn(SALPTDA)(O)$^a$</td>
<td>1.54</td>
<td>25</td>
<td>2</td>
<td>1.07</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>1.29</td>
<td>27</td>
<td>4</td>
<td>1.08</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>1.37</td>
<td>25</td>
<td>3</td>
<td>1.09</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>1.52</td>
<td>25</td>
<td>5</td>
<td>1.08</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>1.42</td>
<td>29</td>
<td>2</td>
<td>1.06</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>1.34</td>
<td>24</td>
<td>3</td>
<td>1.07</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>1.38</td>
<td>26</td>
<td>3/4</td>
<td>1.08</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>1.36</td>
<td>24</td>
<td>3/4</td>
<td>1.07</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>1.36</td>
<td>24</td>
<td>4</td>
<td>1.07</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>1.39</td>
<td>28</td>
<td>3/4</td>
<td>1.07</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>1.39</td>
<td>28</td>
<td>5</td>
<td>1.07</td>
<td>0.81</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)$^b$</td>
<td>1.10</td>
<td>21</td>
<td>4</td>
<td>1.04</td>
<td>0.42</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)$^a$</td>
<td>1.31</td>
<td>26</td>
<td>3</td>
<td>1.08</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>1.36</td>
<td>29</td>
<td>3</td>
<td>1.08</td>
<td>0.47</td>
</tr>
</tbody>
</table>

$^a$DMSO method
$^b$solid state method
Thermal gravimetric analysis (TGA) (Table 10) was used to help determine the stability of these complexes, as well as to confirm the loss of oxygen or a water molecule suspected to be present in the compound. Mn(SALTM)(OH)(H₂O) loses weight corresponding to 18 a.m.u., assumed to be water, with decomposition occurring near 180°C, before the oxygen is released (See Figure 5). [Mn(SALTM)]₂O made from drying the hydrated complex loses more weight than expected for this formulation which is believed to be the extremely hydroscopic nature of the compound. Decomposition occurs near 180°C. Repeated attempts using Mn(SALTM)(O) made in DMSO failed to show the loss of a complete 16 a.m.u. per Mn. Decomposition occurs near 210°C, which suggests the oxygen is very tightly bound and decomposition occurs before all oxygen can be released. This also suggests a structure differing from that of Mn(SALTM)(O) (made from drying the hydrated complex), which loses its oxygen atom more completely.

The magnetic moments of these compounds are listed in Table 11. As can be seen, the hydrated complex and Mn(SALTM)(O) isolated from DMSO have similar magnetic moments of approximately 2.1 B. M., whereas Mn(SALTM)(O), obtained after driving the water off the hydrated complex, has a moment of 4.08 B. M. This suggests that there are at least two different forms of these complexes involved even though they have the same empirical formula. The spin-only magnetic moment expected for a d⁴ high-spin Mn(III) system is between 4.75 to 4.90 B. M. For a d⁴ low-spin Mn(III) system, the expected moment is 2.83 B. M. A d³Mn(IV) system has a magnetic moment of 3.80 to 4.00 B. M. (47).
TGA of Mn(SALTM)(OH)(H₂O)

Figure 5
Table 10

TGA DATA FOR OXYGENATED MANGANESE COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fragment</th>
<th>% Calcd.</th>
<th>% Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(SALTM)(OH)(H₂O)ᵃ</td>
<td>H₂O</td>
<td>4.88</td>
<td>4.94</td>
</tr>
<tr>
<td>[Mn(SALTM)]₂Oᵇ</td>
<td>0</td>
<td>2.33</td>
<td>4.28</td>
</tr>
<tr>
<td>Mn(SALTM)(O)ᶜ</td>
<td>0</td>
<td>4.55</td>
<td>3.29</td>
</tr>
<tr>
<td>Mn(SALPTDA)(O)(H₂O)ᵈ</td>
<td>H₂O, O</td>
<td>8.56</td>
<td>8.56</td>
</tr>
<tr>
<td>Mn(SALPTDA)(O)ᶜ</td>
<td>0</td>
<td>2.34*</td>
<td>2.34</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)ᵉ</td>
<td>0</td>
<td>3.93</td>
<td>4.37</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)ᶠ</td>
<td>0</td>
<td>3.29*</td>
<td>3.06</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)ᵈ</td>
<td>0</td>
<td>3.93</td>
<td>3.98</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)ᶜ</td>
<td>0</td>
<td>3.51*</td>
<td>3.37</td>
</tr>
</tbody>
</table>

ᵃ ethanol, air preparation
ᵇ ethanol, air preparation, dried
ᶜ DMSO, oxygen pressure preparation
ᵈ DMSO, air preparation
ᵉ solid state, air preparation
ᶠ solid state, oxygen pressure preparation
* calculated values are calculated for percent gain in oxygen uptake experiments, assuming the amount gained will be lost
### Table 11

**SOLID STATE MAGNETIC PROPERTIES OF OXYGENATED MANGANESE COMPLEXES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp, °C</th>
<th>$\chi_m \times 10^{-6}$</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(SALTM)(OH)(H₂O)⁹</td>
<td>23</td>
<td>1,939.1</td>
<td>2.15</td>
</tr>
<tr>
<td>[Mn(SALTM)]₂⁹</td>
<td>20</td>
<td>6,917.0</td>
<td>4.05</td>
</tr>
<tr>
<td>Mn(SALTM)(O)³</td>
<td>21</td>
<td>1,861.3</td>
<td>2.10</td>
</tr>
<tr>
<td>Mn(SALPTDA)(O)(H₂O)⁴</td>
<td>20</td>
<td>6,493.5</td>
<td>3.92</td>
</tr>
<tr>
<td>Mn(SALPTDA)(O)⁵</td>
<td>23</td>
<td>8,558.2</td>
<td>3.69-4.61</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)²</td>
<td>20</td>
<td>4,695.8</td>
<td>3.33</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)⁶</td>
<td>23</td>
<td>4,893.9</td>
<td>3.42</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)⁸</td>
<td>20</td>
<td>4,689.3</td>
<td>3.33</td>
</tr>
<tr>
<td>Mn(SALHTDA)(O)⁷</td>
<td>23</td>
<td>5,616.6</td>
<td>3.53</td>
</tr>
</tbody>
</table>

* $\chi_m$ and $\mu_{\text{eff}}$ are averages of measurements at four different field strengths

a. ethanol, air preparation  
b. ethanol, air preparation, dried  
c. DMSO, oxygen pressure preparation  
d. DMSO, air preparation  
e. solid state, air preparation  
f. solid state, oxygen pressure preparation
Antiferromagnetic interaction between two manganese ions would cause a lowering in the value of the observed magnetic moment (52). The degree of this interaction depends upon the proximity of the manganese ions or the covalency of the Mn-O linkage if the complexes are polymeric with alternating Mn and O linkages. The observed magnetic moments of 2.1 B. M. would indicate that these compounds do involve antiferromagnetic interaction, and, therefore, their structure must be such that the manganese ions are in close proximity. A low-spin complex can be ruled out, since very few low-spin complexes of manganese are known, and these involve strong field ligands such as CN\(^-\). The complex with a magnetic moment of 4.08 B. M. is either a Mn(III) complex with some interaction of the manganese ions or a Mn(IV) system with no interaction involved. Proposed structures for all compounds will be discussed in a later section.

**OXYGENATED COMPLEXES OF Mn(SALPTDA)**

Mn(SALPTDA) has been oxygenated to form two complexes, referred to a Mn(SALPTDA)(O)(H\(_2\)O) and Mn(SALPTDA)(O). These compounds are both prepared in DMSO, the first in air (0.92 atm), the second under positive oxygen pressure (1.08 atm). Oxygenation in the solid state was not possible due to the stability of the complex in air. Both of the dark brown compounds are slightly soluble in DMSO, methylene chloride, DMF, and chloroform. Elemental analyses for Mn(SALPTDA)(O) varied considerably. The major variable in the method by which this compound was prepared was the amount of time the reaction was allowed to proceed. Repeated trials using identical times produced compounds which gave
varying analyses. Trials which showed widely varying amounts of oxygen uptake (see Table 9) produced products with similar analyses. Possible reasons for these discrepancies will be discussed later.

As mentioned earlier, information as to the correct structural assignment for these compounds is believed to be present in certain infrared bands (30,31). Mn(SALPTDA)(O)(H₂O) has an infrared band at 3400 cm⁻¹ due to water which is not present in Mn(SALPTDA)(O). Neither Mn(SALPTDA)(O)(H₂O) nor Mn(SALPTDA)(O) has a band near 3600 cm⁻¹ confirming the absence of an -OH. This suggests that these compounds are not like Mn(SALTM)(OH)(H₂O) in structure. Further evidence that the compounds are not similar is found in the solubilities. Mn(SALTM)(OH)-(H₂O) is much more soluble than the oxygenated complexes of Mn(SALPTDA).

The bands are due to Mn-O stretching modes for Mn(SALPTDA)(O)(H₂O) appear at 670 and 640 cm⁻¹ (Figure 6), the latter being the strongest band. No bands appear at 1096 cm⁻¹ (19) or at 840 cm⁻¹ (30) which can be attributed to the Mn=O bond. The IR spectrum of Mn(SALPTDA)(O) shows the appearance of new bands at 660 and 630 cm⁻¹, assigned again to the Mn-O stretching mode. No band appears which can be correlated with an Mn=O bond. So again, as in the case of the oxygenated compounds of Mn(SALTM), the characteristic infrared bands appear between 600 and 660 cm⁻¹. This suggests that complexes with di-μ-oxo, μ-peroxo, or catena-oxo bridges are possibilities. Final assignments must be made in conjunction with other experimental data.

Oxygen uptake experiments were not performed on solid Mn(SALPTDA) due to its stability to air. The uptake experiments performed in DMSO solution, as seen in Table 9, varied considerably. As can be seen in
INFRARED SPECTRA OF Mn(SALPTDA) AND OXYGENATION PRODUCTS

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6}
\caption{Figure 6}
\end{figure}

the first six attempts (Series 1), there was no correlation of time to ratio observed. In the second series, improved techniques helped to give more reproducible results. To achieve the proposed formula, Mn(SALPTDA)(O), the desired ratio, $N_{O_2}/N_{Mn}$, is 0.50. Values near this ratio are achieved after 18 hours. After five days, a maximum ratio of 0.81 is observed. Products isolated after 18 hours and after five days gave similar elemental analyses. The compounds isolated here are anhydrous, unlike the product isolated from the DMSO in air reaction. The anhydrous products are prepared under an oxygen pressure, so the compound is exposed only to the small amount of water which may be in solution. The hydrated complex was exposed to the atmosphere while being prepared, and it therefore came into contact with more moisture. While in solution, Mn(SALPTDA)(O) may be susceptible to hydration if exposed to water. This would explain the formation of two different compounds. The anhydrous products isolated, irregardless of the time of the reaction, gave identical infrared spectra. This spectrum differs from that of Mn(SALPTDA)(C)(H$_2$O). These compounds gave varying magnetic moments, which will be discussed further in a later section.

As mentioned earlier, the desired ratio is achieved after 18 hours; however, all isolated products gave similar analyses. It is, therefore, suggested that the insoluble, desired product is produced within 24 hours, and any new product formed from further oxygen uptake is apparently soluble. This soluble product has not been isolated or identified. Manganese is known to catalyze the oxidation of certain organic molecules, such as mandelic acid, ethylene glycol, and dithion-
ite (53,54). The manganese present in solution could cause the oxidation of the ligands present, thus being reduced. The reoxidation of manganese would account for the further oxygen uptake observed.

Thermal gravimetric analysis (Table 10) suggests the presence of oxygen in these complexes. Mn(SALPTDA)(O)(H₂O) shows the loss of 18 a.m.u. per Mn, assumed to be water at 90°C and of 16 a.m.u. per Mn at 150°C, assumed to be oxygen. Decomposition occurs near 210°C. The TGA of Mn(SALPTDA)(O) shows a weight loss at 150°C which corresponds to the loss of 16 a.m.u. per Mn, assumed to be oxygen. Decomposition occurs near 180°C. One oxygen uptake experiment yielded a ratio of 0.28. A TGA was performed of the product isolated from this experiment. The weight loss by the compound coincides with the percent oxygen (56%) gained in the oxygen uptake experiment.

The magnetic moments of the compounds are listed in Table 11. Mn(SALPTDA)(O)(H₂O) has a moment of 3.92 B. M., which suggests a d³ Mn(IV) system or a d⁴ Mn(III) system involving antiferromagnetic interaction. Mn(SALPTDA)(O) has a magnetic moment that ranges from 3.69 to 4.61 B. M. This indicated either a d³ Mn(IV) or a d⁴ Mn(III) system. The value of the magnetic moment has no correlation with the amount of oxygen taken up by the compound, or with the time involved, the temperature or exact pressure used. Two compounds with similar elemental analyses, and reaction times (three days) gave magnetic moments of 3.96 and 4.52 B. M. The highest magnetic moment (4.61 B. M.) was observed for a compound isolated after only 18 hours. A possible explanation could be the formation of a mixture of structures, which as they vary in total percentage, would cause a variation in the observed
magnetic moments.

**OXYGENATED COMPLEXES OF Mn(SALHTDA)**

Mn(SALHTDA) can be oxygenated in the solid state and in DMSO solution, with air and with pure oxygen at positive pressure. The four isolated products are red-brown in color, and insoluble in most common organic solvents. It is highly likely that these four complexes are very similar or in fact identical in structure.

The IR spectra of the four isolated complexes made by the oxygenation of Mn(SALHTDA) are very similar in all respects. Each contains a set of peaks of equal intensity (Figure 7) which are attributable to Mn-O stretching modes and occur at approximately 600 and 630 cm⁻¹ (See Table 6). The separation is 25-30 cm⁻¹ in all cases. These bands are much more intense than the Mn-O stretching modes seen in the other compounds studied here. The band positions are similar; however, in the other complexes, one band is far more intense. No other bands are present to indicate a structure containing an oxo bond. These compounds do not show an infrared band at 3600 cm⁻¹ indicative of an -OH stretching frequency, or at 3400 cm⁻¹ indicative of the presence of water. This suggests these compounds are not similar to Mn(SALTM)(OH)(H₂O).

Oxygen uptake experiments were performed on Mn(SALHTDA) in the solid state and in DMSO solution. Results are shown in Table 9. Oxygen uptake proceeds faster for the suspensions than for the solid state. The products isolated from DMSO and the solid state products are red-brown in color, and are homogeneous. No yellow compound is detected, even with crushing. If Mn(SALHTDA) is isolated as an ethanol adduct,
INFRARED SPECTRA OF Mn(SALHTDA) AND OXYGENATED PRODUCTS

Mn(SALHTDA)

Mn(SALHTDA)(O)

solid state methods and DMSO methods

Figure 7
exposure to oxygen in the solid state results in oxygenation which proceeds at a rate faster than Mn(SALHTDA). In all cases, the desired ratio of 0.50 is approached, supporting the proposed formula.

Thermal gravimetric analyses of the four compounds (Table 10) show a weight loss occurring at 150°C (See Figure 8). The four compounds also show decomposition near 190°C. Within reasonable experimental range, the weight losses coincide with the loss of 16 a.m.u. per Mn assumed to be oxygen. The similarities in the TGA's support the suggestion that these compounds are similar or identical.

Magnetic moments are shown in Table 11. The magnetic moments of all four compounds are in the range of 3.33 to 3.53 B. M., suggesting either a d⁴ high-spin Mn(III) system or a d³ Mn(IV) system, each involving some degree of antiferromagnetic coupling. A low-spin d⁴ Mn(III) system (2.83 B. M.) can be ruled out because the observed magnetic moments are too high, and also because the ligand is probably not strong enough to cause a low-spin configuration. Other methods must be used to determine the exact oxidation state and the appropriate structure.

**ATTEMPTED OXYGENATION OF Mn(SALDPT)**

Oxygen uptake experiments in DMSO were attempted using Mn(SALDPT). Due to its stability in air when dry, no solid state experiments were attempted. Conditions similar to those used in experiments on other compounds were used (50 ml solvent, 1.5 mmoles compound, 1.08 atm oxygen pressure). This experiment was repeated numerous times. Each time, within 24 hours, all available oxygen had been consumed. No
product could be isolated from the dark brown solution. Repeated experiments with smaller sample sizes produced the same result. Since manganese is known to catalyze the oxidation of certain organic substances (53,54), it is suggested that manganese is oxidizing the ligand present, and reoxidation of the manganese causes the consumption of all available oxygen. It is known that the oxygenation of Co(SALDPT) in solution results in a 1:2 oxygen-cobalt adduct (35). Calderazzo et al. (35) found that depending upon the solvent used, variable amounts of oxygen uptake were observed. In certain solvents, oxygen uptake exceeded that necessary for the formation of the 1:2 adduct. They have suggested that a partial oxidative dehydrogenation of the \(-(CH_2)_3-NH-(CH_2)_3\) bridge occurs:

![Structure X](image-url)
In these solvents, no product was isolated. This dehydrogenation of the ligand could conceivably be the case in this study.

POSTULATED STRUCTURES OF OXYGENATED PRODUCTS

Possible structures can be assigned to the compounds based upon experimental data. Oxygen uptake in solution and in the solid state for Mn(SALTM) and Mn(SALHTDA), as well as elemental analyses, confirms the formulas proposed in Table 1. These compounds, in the anhydrous form isolated, all show the uptake of one mole of oxygen per one mole of manganese. The formulas for Mn(SALTM)(OH)(H₂O), Mn(SALTM)(O) made from drying the hydrated form, and Mn(SALPTDA)(O)(H₂O) are based on elemental analyses, infrared spectra and TGA data showing the loss of water and oxygen. Mn(SALPTDA)(O) gave varying results in oxygen uptake experiments. The formula is based on elemental analyses and TGA data.

Mn(SALTM)(OH)(H₂O) has a low magnetic moment, indicative of anti-ferromagnetic coupling of manganese ions. For this coupling to occur, the ions must be in close proximity. A low magnetic moment is also observed in \([\text{Mn(SALTM)(OH)}]_2 \cdot 4\text{Py}\). An X-ray study of this compound revealed a manganese-manganese distance of 2.7 Å, close enough for considerable reaction. Both these compounds have Mn-O stretching modes in the 600-650 cm⁻¹ region, and both are quite soluble in organic solvents. Mn(SALTM)(OH)(H₂O) also shows a band at 3620 cm⁻¹, verifying the presence of the -OH group. \([\text{Mn(SALTM)(OH)}]_2 \cdot 4\text{Py}\) was shown through the X-ray study to contain a di-µ-hydroxo bridge. The structure we propose for Mn(SALTM)(OH)(H₂O) is believed to be similar where the water molecules are not coordinated.
Mn(SALTM)(O), isolated from DMSO, also has a low magnetic moment, and shows the infrared bands in the region of 600–650 cm\(^{-1}\). It does not, however, show the \(-\text{OH}\) stretching frequency. The oxygen is lost with difficulty, which may suggest a binuclear structure. The proposed structure for this compound is similar to that proposed above:

\[
\text{H}_2\text{O} \cdot (\text{SALTM})_{\text{II}}\text{Mn} \overset{\text{O}}{\rightarrow} \text{Mn}_{\text{II}}(\text{SALTM}) \cdot \text{H}_2\text{O}
\]

Structure XI

\[
(\text{SALTM})_{\text{IV}}\text{Mn} \overset{\text{O}}{\rightarrow} \text{Mn}_{\text{IV}}(\text{SALTM})
\]

Structure XII

\[
[\text{Mn(SALTM)}]_2\text{O} \text{isolated after drying Mn(SALTM)(OH)(H}_2\text{O)} \text{has a magnetic moment of 4.1 B. M., which could indicate a d}^3 \text{ or d}^4 \text{ high-spin manganese system. The magnetic moment is not lowered enough to indicate a great deal of interaction between manganese ions. The infrared spectrum shows}
\]
a broad peak at 620 cm\textsuperscript{-1}, but no peak to indicate a Mn=O bond. The compound is not extremely soluble in common organic solvents, as compared with the starting compound, which would tend to suggest a structure of dimeric or polymeric nature. The compound rapidly picks up water on standing, with the result that the magnetic moment drops to 2.00 B. M. as in the starting compound. The proposed structure must take into consideration the suspected dimeric character, and manganese ions which are not in extremely close proximity, and can reasonably be formed from the structure of the parent compound (Structure XI). It is possible then that the following occurs:

\[
\begin{align*}
\text{(H}_2\text{O)}(\text{SALTM})\text{Mn} & \text{O} \text{Mn(SALTM)(H}_2\text{O)} - 3\text{H}_2\text{O} \\
\text{(SALTM)(II)}\text{Mn—O—Mn(III)(SALTM)}
\end{align*}
\]

Structure XIII

This structure, with a Mn—O—Mn linkage, was also suggested by Yamamoto et al. (25) for (MnPcPy)\textsubscript{2}O. They do not, however, list a magnetic moment or characteristic infrared absorptions for reference purposes. The structure of the oxygenation products of Mn(SALPTDA) are not easily assigned either. Mn(SALPTDA)(O)(H\textsubscript{2}O) has a magnetic moment of
3.92 B. M., which could indicate a $d^3$ Mn(IV) high-spin system, or a $d^4$ Mn(III) high-spin system involving a small degree of interaction between the manganese ions. The IR spectrum shows a band at 3400 cm$^{-1}$ due to water, but no band near 3600 cm$^{-1}$ indicative of the $-\text{OH}$. There is a broad band at 640 cm$^{-1}$, but no bands to indicate a Mn=O bond. However, to account for the presence of H$_2$O and the magnetic moment, the oxo-bond structure appears to be the best choice. Complete insolubility would suggest a polymeric structure; however, this compound is slightly soluble in several organic solvents. In order for the structure to be assigned with more accuracy, X-ray analysis is needed to help determine the exact coordination of the oxygen to the manganese.

Mn(SALPTDA)(O) also possesses slight degree of solubility in organic solvents. However, values for the magnetic moment range from 3.69 to 4.61 B. M. There is no correlation between amounts of oxygen uptake (Table 9) and the magnetic moments. Compounds with similar elemental analyses give varying moments. The formula is based mostly on elemental analyses. The IR spectrum shows the characteristic Mn-O band at 630 cm$^{-1}$. The variation in the magnetic moments makes it difficult to determine whether the manganese is present in the +3 or +4 oxidation state. No one structure will account for all the experimental data, therefore, we propose a mixture of structures. One proposed structure is polymeric to account for the Mn(IV) magnetic moments and one structure is dimeric to account for the Mn(III) moments and slight solubility. The structures are:
Extraction in methylene chloride indicated that only part of this compound was soluble, further evidence supporting a mixture.

Matsushita et al. (30) assigned Structures XIV and XV to two of the compounds they isolated. The compounds had characteristic bands in the 600–660 cm\(^{-1}\) region and magnetic moments of 1.96 and 1.99 B. M. These structures do not appear to bring the manganese ions close enough to allow for the interaction of the magnitude needed to cause the large drop in the observed magnetic moments. X-ray studies (40) have shown that a 2.7 Å metal-metal distance will cause a large drop in the magnetic moments. The metal-metal distance of a Co(III) complex with the \(\mu\)-peroxo
structure is 4.4 Å (31). This is a large separation, and would account for only a small drop in the observed magnetic moments. This suggests that this structure could be one of the possible structures for this compound, since the observed magnetic moments only show a small drop from the expected.

The four complexes isolated from the oxygenation of Mn(SALHTDA) are believed to be similar in structure. The infrared spectra of the four compounds are almost identical. The complexes are all formulated as Mn(SALHTDA)(O). The compounds are extremely insoluble in organic solvents. The magnetic moments range from 3.33 to 3.53 B. M. If the proposed structure contains manganese in the +4 oxidation state, there must be some interaction between manganese ions to cause the drop in the moment. The proposed structure is polymeric, with a catena-oxo bridge:

\[
\begin{array}{c}
\text{L(SALHTDA)(IV)Mn} \\
\text{O-Mn(IV)(SALHTDA)-O} \\
\text{Structure XVI}
\end{array}
\]

This structure also accounts for the insolubility of the compound.

These structures are not suggested as absolute. Measurement of solid state visible spectra was attempted, however, charge transfer
bands obscured the d-d transitions needed for geometrical studies. Solution spectra were not possible due to the insolubility of most of the compounds in suitable solvents. X-ray analyses would be the best way of determining the true structures. The structures proposed for these compounds are assigned to best fit the experimental data.
In the preparation of Mn(BAE), the first step is the deprotenation of the ligand, H$_2$BAE. A base is needed for this deprotenation and it is believed that the presence of this base in the reaction mixture destroys the complex. Manganese(II), a high-spin d$^5$ system, has no crystal field stabilization energy. The complex would be unstable, and quite susceptible to attack by a strong base. Complexes of BAE with other metals are known (28,46). These metals supply the stabilization necessary for the formation of the complexes.

Protection of the complex would require the presence of a weaker base. For deprotenation by a weaker base, a more acidic ligand was needed. Trifluoroacetylacetone was substituted for the original acetylacetone in the hopes of accomplishing this. However, even the weaker bases used were strong enough to destroy the complex. In light of these findings, no further reactions were attempted.

Preparation of Mn(III)(BAE) has been attempted by other workers without success. Boucher (55) has attempted the preparation using Mn(III) acetate and H$_2$BAE under a variety of conditions. However, a crystal structure study of the isolated products showed that the ligand had been oxidized in the course of the reaction.
BIBLIOGRAPHY


55. Private communication, L. J. Boucher.
VITA

Sara Jane Ebbs was born in Petersburg, Virginia on May 13, 1949. Her father, being an officer in the Army, was frequently transferred. She has lived in Alaska, Japan, Colorado, Indiana, Illinois, and Pennsylvania. She was graduated from Yorktown High School, Arlington, Virginia in June, 1967. In June, 1971, she received the Bachelor of Arts Degree in chemistry from Radford College, Radford, Virginia. She was enrolled as a graduate student in chemistry at Virginia Polytechnic Institute and State University in September, 1972.

Sara Jane Ebbs
Manganese(II) complexes formed by the reaction of salicylaldehyde and 3,3'-iminobispropylamine (SALDPT), 1,3-diaminopropane (SALTM), 1,5-diaminopentane (SALPTDA), or 1,7-diaminoheptane (SALHTDA) have been isolated. All complexes except Mn(SALHTDA) are stable in air when dry. When wet, however, all complexes react with oxygen to form Mn(III) or Mn(IV) complexes.

Oxygenation of Mn(SALTM) in situ produced Mn(SALTM)(OH)(H₂O), which has a magnetic moment of 2.0 B.M., which upon heating yielded [Mn(SALTM)]₂O, which has a magnetic moment of 4.05 B.M. Oxygenation of the previously isolated Mn(SALTM) in DMSO produced a third compound Mn(SALTM)(O), which has a magnetic moment of 2.0 B.M. The structure of Mn(SALTM)(OH)(H₂O) is suggested to contain a di-μ-hydroxo bridge. [Mn(SALTM)]₂O and Mn(SALTM)(O) are believed to contain Mn-O-Mn linkage and a di-μ-oxo bridge respectively.

The oxygenation of Mn(SALPTDA) produced two compounds. Mn(SALPTDA)-(O)(H₂O), which has a magnetic moment of 3.92 B.M., was not assigned a
structure. Mn(SALPTDA)(O), with a magnetic moment which varies from 3.69 to 4.61 B. M., is suggested to contain a mixture of structures, one a dimer with a \(\mu\)-peroxo bridge, the other a polymer with a catena-oxo bridge.

Mn(SALHTDA), formed in both the solid state and in solution, has a magnetic moment of 3.33 to 3.53 B. M. and a structure believed to be polymeric with a catena-oxo bridge.

Oxygenation of Mn(SALDPT) was attempted; however, more than stoichiometric amounts of oxygen were consumed indicating the occurrence of a reaction with the ligand. No product could be isolated.

Attempts to prepare manganese(II) and (III) complexes with ligands formed from ethylenediamine and several \(\beta\)-diketones was unsuccessful.