path with confidence. No conclusion can be drawn as to the nature of the k_0 path, but the strongly basic nature of the sulfur suggests the possibility of the "tautomeric" mechanism[7] in which the leaving group is a protonated ligand, the proton coming from an intermolecular transfer instead of a simple aquation. The activation parameters of the k_0' path may elucidate the mechanism present.[3] Also at higher excesses of Cr(II) a "tautomeric" path of the form $k_3[Cr^{2+}]$ may well be observed.

Acknowledgment. R.W.C. is grateful for a Non-Service Fellowship supported by the University of Tennessee.

Registry No. I, 50639-78-6; II, 50639-79-7; IV, 54642-85-2; Cr^{2+}, 22541-79-3; Br^-, 24959-67-9; $[(NH_3)_5Ru(C_6H_6N_2S)](ClO_4)_2$, 54566-87-9; $[(NH_3)_5Ru(C_6H_6N_2S)](ClO_4)_3$, 54566-89-1.

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Manganese–Schiff Base Complexes. VI. Synthesis and Spectroscopy of Aquo[*N*,*N*'-ethylenebis(4-*sec*-butylsalicylaldiminato)]manganese(III) Perchlorate and μ-Dioxo-bis[*N*,*N*'-ethylenebis(4-*sec*-butylsalicylaldiminato)]dimanganese(IV) and the Related *N*,*N*'-Trimethylenebis(4-*sec*-butylsalicylaldimine) Complexes

L. J. BOUCHER* and C. G. COE

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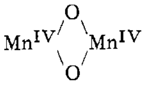
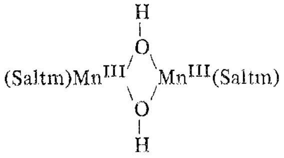
The new five-coordinate cationic complexes of Mn(III), $[Mn(SB)H_2O]ClO_4$, where SB is the dianion of the tetradentate Schiff base *N*,*N*'-ethylenebis(4-*sec*-butylsalicylaldimine) (BuSalen) and *N*,*N*'-trimethylenebis(4-*sec*-butylsalicylaldimine) (BuSaltm) have been synthesized and characterized. Mild base hydrolysis of chloroform solutions of these complexes in air yielded the new six-coordinate species $[Mn_2(BuSalen)_2O_2]\cdot H_2O$ and $[Mn_2(BuSaltm)O_2]\cdot 2H_2O$. The Mn(IV) complexes are dimeric in chloroform solution and show reduced room-temperature magnetic moments, $\mu = 2.5$ BM. Ir and visible spectral properties are also consistent with the presence of the ring

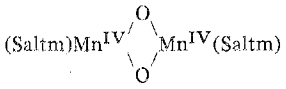


in these complexes.

Rapid progress has been made toward a detailed understanding of the important reaction of oxygen with metal ions in biological systems. Work on naturally occurring iron complexes and model compounds has revealed the complexities of the processes.[1] In order to assess the unique role of the metal atom, comparisons have been made between the behavior of the iron complexes and that of the complexes of the similar metals like cobalt and manganese. The bulk of the work to date has been carried out with cobalt[2] while the manganese system has been the subject of scattered reports. The reaction of a divalent metal complex with oxygen can lead to reversible oxygen binding or irreversible oxidation of the metal. In general, the latter process ultimately leads to the formation of tri- and tetravalent metal complexes which occur as dimeric and polymeric materials with oxo, peroxo, or hydroxo bridges between the metal ions. For manganese(II) complexes, the reaction with oxygen appears to lead to oxidation of the metal. For example, the reaction of oxygen with phthalocyaninemanganese(II) yields a dimeric complex with the linear unit $Mn^{III}–O–Mn^{III}$.[3] It should be pointed out that the reactant is a rare example of an intermediate-spin manganese complex.

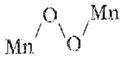
A number of manganese complexes of the tetradentate Schiff bases *N*,*N*'-ethylenebis(salicylaldimine), H_2Salen, and *N*,*N*'-trimethylenebis(salicylaldimine), H_2Saltm, have been prepared. Recent reports indicate that the high-spin Mn(II) complexes react with oxygen irreversibly to yield various oxidation products. The crystal structure of the major reaction product for $Mn(Saltm)H_2O$ is a dimer with bridging oxygen atoms (Mn–Mn distance 2.7 Å).[4] Unfortunately the reported X-ray data[4] do not allow an unambiguous choice between the two possibilities



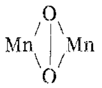


The MnO2Mn ring gives rise to a prominent and characteristic ir absorption in the 650–600-cm^{-1} region.[5] The dimer also shows a reduced magnetic moment of μ = 2.15 BM at room temperature which is consistent with antiferromagnetic coupling of either high-spin Mn(III) or high-spin Mn(IV) atoms. Reaction of oxygen with the related chelate Mn(Salen) yields a sparingly soluble product $Mn_2(Salen)_2O_2$ which displays similar properties, i.e., ir absorptions at 645 and 631 cm^{-1} and μ = 1.96 BM.[6] The reaction of excess oxygen with Mn(Saltm) and Mn(Salen) in benzene or DMSO yields a second insoluble product. This has properties similar to but not identical with those of the sparingly soluble dimer. The complex has been formulated as a polymeric μ-oxomanganese(IV) complex, $[Mn(Salen)O]_n$.

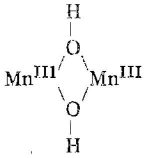
In summary, the only fully authenticated product of air oxidation of manganese(II)–Schiff base complexes appears to be a dimer. The nature of this dimer is the subject of some discussion since the X-ray structure suggests a μ-dihydroxo-dimanganese(III) unit.[4] Other workers formulate analogous complexes as μ-peroxo dimers with an intermediate-spin Mn(III). One piece of circumstantial evidence however argues against the latter formulation, since the existence of intermediate-spin complexes has not been previously shown for any other Mn(III) complex. In fact only extremely strong ligand field complexes give rise to spin pairing; i.e., all complexes with oxygen–nitrogen donors are always high spin. Thus, the reported low magnetic moment, ~2.0 BM, for these materials must arise as a consequence of antiferromagnetic coupling of the two manganese atoms in the dimer. However the presence of a peroxo bridge

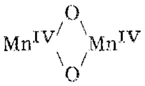


in the dimer does not appear to allow a close enough approach of the manganese atoms (4.4 Å from a $Co^{III}–O_2^{2-}–Co^{III}$ complex).[7] The same argument applies to the structure



which should give a Mn–Mn distance of 3.7 Å, based on standard bond length data, again too long, to give efficient antiferromagnetic coupling. Thus the only allowable structures are ones that contain the units





Much of the previous work on the characterization of the oxidation products has been hampered by the limited solubility of both the reactants and the products. The use of alkyl-substituted Schiff bases should give complexes with improved solubility which will allow purification and detailed characterization of the various products.[8] If the oxygenation of Mn(SB) yields the dihydroxo dimer, it then should be possible to prepare it by an alternate route which eliminates the possibility of deleterious side reactions, e.g., the reaction of manganese(III)–Schiff base (SB) complexes with aqueous base. The initial product would be the Mn(SB)OH which then would dimerize to form the desired product. Preliminary experiments show that this reaction with strong base, pH >12, in water leads to decomposition while at lower pH no appreciable hydrolysis occurs. In order to produce the various base hydrolysis products for manganese(III)–Schiff base complexes using mild conditions we have synthesized new five-coordinate cationic manganese(III) complexes that contain a coordinated water, $[Mn(BuSalen)H_2O]ClO_4$ and $[Mn(BuSaltm)H_2O]ClO_4$. The coordinated water molecule in these complexes is expected to be acidic. Thus chloroform solutions of the complexes react with mild aqueous base to give good yields of what we now formulate as $Mn_2(BuSalen)_2O_2$ and $Mn_2(BuSalen)_2O_2$ (see Figure 1). We wish to report here the synthesis and chemical and physical characterization of these new complexes.

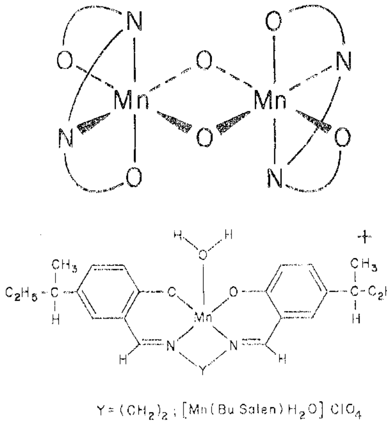


Figure 1. Structural representations for $[Mn(SB)H_2O]ClO_4$ (bottom) and $Mn_2(SB)_2O_2$ (top).

Experimental Section

Materials. The ligands were prepared as previously described.[8] All other materials were reagent grade and were used without further purification.

Preparation of Complexes. $[Mn(BuSalen)H_2O]ClO_4$. The ligand H_2-*s*-BuSalen, 8.2 g (0.022 mol), was dissolved in 200 ml of methanol and 4 ml of 4 *M* NaOH (0.016 mol) was added. Immediately upon dissolution of 16 g of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.044 mol) the orange solution turned dark brown. The resulting reaction mixture was stirred for 5 days at room temperature with no attempt to exclude air or light. After stripping off of the methanol, the reaction residue was extracted with 150 ml of acetone. The acetone solution was filtered, leaving a residue of unreacted $Mn(ClO_4)_2 \cdot 6H_2O$, and then dried and reduced in volume to 50 ml. A brown crystalline product was crystallized from the acetone solution by the addition of 500 ml of diethyl ether with cooling at 4°, overnight; yield 8.2 g (70% based on weight of ligand used); R_f 0.54; μ(solid, 298°) = 4.86 BM. Anal. Calcd for $C_{24}H_{32}O_7N_2MnCl$: C, 52.27; H, 5.81; N, 5.08. Found: C, 52.00; H, 5.62; N, 5.26. Elemental analyses were by Chemalytics, Tempe, Ariz.

$[Mn(BuSaltm)H_2O]ClO_4$. The ligand H_2-*s*-BuSaltm, 10 g (0.0026 mol), was dissolved in 300 ml of methanol and 4 ml of 4 *M* NaOH (0.016 mol) was added. Dissolution of 15 g of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.041 mol) caused immediate darkening of the solution. The reaction mixture was stirred at room temperature for 5 days in air. After stripping off of the methanol, the residue was extracted with 100 ml of benzene to remove some of the unreacted ligand. The remaining residue was extracted into 150 ml of acetone. The filtered acetone solution was dried over Drierite and reduced in volume to 50 ml. Addition of 500 ml of diethyl ether to the acetone solution yielded a gummy solid which, after washing with three 50-ml portions of diethyl ether and air-drying, yielded 7.8 g of an olive green solid. The impure product was washed with 50 ml of water to remove unreacted starting materials. The green solid was then crystallized from 50 ml of acetone by the addition of 500 ml of diethyl ether with overnight cooling. The pure product was collected on a filter, washed with ether, and air-dried; yield 6.7 g (44% based on the weight of ligand used); *Rf* 0.60; μ(solid) = 4.96 BM. Anal. Calcd for $C_{25}H_{34}O_7N_2MnCl$: C, 53.25; H, 6.02; N, 4.96. Found: C, 52.63; H, 5.96; N, 4.76.

[Mn$_2$(BuSalen)$_2$O$_2$]·H$_2$O. A slurry of 3.0 g of [Mn(BuSalen)-H_2O]ClO_4 (0.0054 mol) in 500 ml of chloroform was shaken with ten separate 300-ml washes of aqueous 0.005 *M* NaOH (0.015 mol). The resulting cherry red chloroform solution was separated, dried over Drierite, and filtered, and the volume was reduced to 50 ml. Addition of 500 ml of petroleum ether followed by cooling yielded 1.5 g of a red-brown solid. The pure solid was crystallized from 50 ml of methylene chloride–500 ml of petroleum ether with cooling. The resulting solid was isolated on a filter, washed with petroleum ether (bp 30–60°), and air-dried; yield 1.0 g (42% based on the weight of manganese salt used); *Rf* 0.70; μ(solid) = 2.47 BM, μ(solution) = 2.56 BM. Anal. Calcd for $(C_{24}H_{30}O_3N_2Mn)_2 \cdot H_2O$: C, 63.08; H, 6.79; N, 6.13. Found: C, 62.94; H, 6.94; N, 6.03. Molecular weight: calcd, 916; found, 930 ± 15.

[Mn$_2$(BuSaltm)$_2$O$_2$]·2H$_2$O. A solution of 1.0 g (0.0017 mol) of [Mn(BuSaltm)H_2O]ClO_4 in 150 ml of chloroform was shaken with eight washes of 150 ml each of aqueous 0.005 *M* NaOH (0.006 mol). The deep cherry red chloroform solution was separated, filtered, and dried over Drierite. After reduction of the chloroform solution volume to 50 ml, 500 ml of petroleum ether was added and the crude product precipitated out. The pure product was crystallized from 50 ml of chloroform–500 ml of petroleum ether with cooling. The red-brown solid was isolated on a filter, washed with petroleum ether, and air-dried; yield 0.52 g (66% based on Mn(III) salt used); *Rf* 0.67; μ(solid) = 2.59 BM, μ(solution) = 2.50 BM. Anal. Calcd for $(C_{25}H_{32}O_3N_2Mn)_2 \cdot 2H_2O$: C, 62.25; H, 7.07; N, 6.05. Found: C, 61.88; H, 6.73; H, 5.82. Molecular weight: calcd, 962; found, 1014 ± 25.

Measurements. Magnetic moments of the solids were determined by the Faraday method at 25°. The susceptibilities of the complexes were found to be independent of field strengths and the value for different measurements agreed to ±2% (0.1 BM). Hg[Co(NCS)$_4$] was used as a calibrant. Diamagnetic corrections were calculated from the relevant Pascal constants.[8] Solution magnetic moments were determined by the NMR method[9] using 10% TMS–$CHCl_3$ solutions of the complex, 2 mg/ml (~0.002 *M*) with a 250-MHz spectrometer at ambient temperature, ~25°. Electronic spectra of the complexes in chloroform and pyridine were measured with a Cary 14 spectrophotometer. Ir spectra were determined with materials in KBr disks and Fluorolube mulls with a PE 337-B grating spectrophotometer. Molecular weights of the complex were determined with a Mechrolab Model 301 A vapor pressure osmometer. Measurements at room temperature were made on chloroform solutions of the complexes, 0.002 *M*. An Industrial Instruments Model RC 16B2 conductivity bridge was used for the conductivity measurements which were made on nitromethane solutions, 10^{-3} *M*, at room temperature. *Rf* values were determined by one development (15 cm) on a 50 μ thick silica gel G plate (Analtech) with 25% methanol–benzene elution.

Results and Discussion

Mn(III) Complexes. The formation of the complex [Mn(SB)H_2O]ClO_4 (SB = BuSalen, BuSaltm) occurs via the slow air oxidation of Mn(SB) in methanol. The Mn(II) complex is formed upon mixing of the ligand and metal ion. In order to achieve good yields of the Mn(III) complex, the oxidation is allowed to proceed for several days at room temperature. Vigorous aeration and/or refluxing of the methanol solution does not substantially decrease the time needed for the reaction. Removal of the solvent, methanol, leads to the crystallization of the perchlorate salt. Under similar conditions and in the presence of a good coordinating anion, like Cl^- or $C_2H_3O_2^-$, the five-coordinate inner complex Mn(SB)X forms. Thus in the absence of any such anion the aquo complex will form. The complex [Mn(BuSalen)-H_2O]ClO_4 is a brown-red crystalline solid and has limited solubility in water, chloroform, and benzene but good solubility in methanol, pyridine, acetone, and nitromethane. On the other hand the complex [Mn(BuSaltm)H_2O]ClO_4 is an olive green solid which has improved solubility in chloroform but reduced solubility in water. Both materials are stable in the solid state, and solutions in methanol, water, and pyridine can be refluxed for more than 12 hr and the materials can be recovered unchanged. It is interesting to note that crystallization of the salts from pyridine does not lead to the formation of a solid pyridinate complex; i.e., the material crystallizes as the aquo complex and the pyridine does not displace the coordinate water molecules. However the formation of complexes of other Lewis base donors, of the type [Mn(SB)B]ClO_4, has not been attempted.

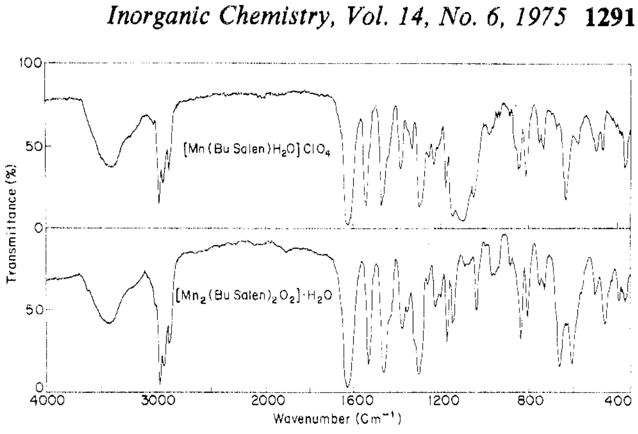


Figure 2. Infrared spectra (KBr disk) for [Mn(BuSalen)H_2O]-ClO_4 (top) and [Mn_2(BuSalen)$_2O_2$]·H_2O (bottom).

The salts [Mn(SB)H_2O]ClO_4 (SB = BuSalen, BuSaltm) show solid-state magnetic moments of 4.86 and 4.96 BM, respectively. This is consistent with the presence of monomeric Mn(III) high-spin d^4 complexes. Conductivity measurements on nitromethane solutions at 25° give equivalent conductances of 118 and 90 ohm^{-1} cm^2 mol^{-1}, respectively. These values are consistent with the presence of a 1:1 electrolyte, in the noncoordinating solvent.[10] The anion complexes Mn(BuSalen)X are nonelectrolytes under the same conditions. The infrared spectra of the salts in the solid state also support the notion that ClO_4^- species is not coordinated to the manganese ion;[11] i.e., a strong single Cl–O stretching absorption appears at 1085 cm^{-1}. The Fluorolube mull spectra of the complexes also show a medium-intensity broad band at 3350 cm^{-1} which can be assigned to the ν(O–H) of the coordinated water. Thus the materials can be formulated as cationic five-coordinate complexes, presumably square pyramidal with axially coordinated water molecules.

The infrared spectra of [Mn(SB)H_2O]ClO_4 show prominent absorptions at 3020, 2960, 2920, and 2870 cm^{-1} due to ν(C–H) of the aromatic and alkyl groups, at 1615 and 1540 cm^{-1} due to C=N and C=C stretching vibrations, at 1460 and 1380 cm^{-1} for alkyl C–H deformation modes, at 1290 and 1130 cm^{-1} due to ν(C–N) and ν(C–O), at 840, 810, and 735 cm^{-1} for out-of-plane aromatic C–H bends, and at 630 and 575 cm^{-1} due to chelate ring deformations. The BuSalen complex shows prominent chelate ring deformation bands at 492, 466, and 362 cm^{-1} while the BuSaltm complex shows bands at 458 and 370 cm^{-1}. The spectra of the perchlorate salts except for the H_2O and ClO_4^- absorptions are almost superimposable on those of the five-coordinate anion complexes Mn(BuSalen)X[8] (see Figure 2).

The electronic spectra of [Mn(SB)H_2O]ClO_4 were determined with chloroform and pyridine solutions. Typical spectra are shown in Figures 3 and 4 and the frequencies of the absorption maxima are collected in Table I. The general shape and intensity of the spectral display are similar to those of other manganese(III)–Schiff base complexes.[8] Typically the spectra show several broad bands and poorly resolved shoulders and therefore are difficult to analyze accurately. Nonetheless a ligand field band d_{xy}, $d_{yz} \rightarrow d_{x^2-y^2}$ for pseudo

Table I. Absorption Maxima (cm^{-1} × 1000) of Complexes in Chloroform and Pyridine

Solvent	$[\mathrm{Mn(BuSalen)H_2O]ClO_4}$	$[\mathrm{Mn_2(BuSaltm)H_2O]ClO_4}$	$[\mathrm{Mn_2(BuSalen)_2O_2}]\cdot\mathrm{H_2O}$	$[\mathrm{Mn_2(BuSaltm)_2O_2}]\cdot 2\mathrm{H_2O}$
Chloroform	~20	~20	~20.6	~20.2
	~24	26.0 (3.95)[a]	~24	~24
	~28	~28		
	~31	~32	~30	~31
	34.7 (4.16)	35.1 (4.23)		
Pyridine	~19	~19	~21	~21
	23.7 (3.61)	25.6 (3.93)	~23.7	~24.5
	~28	~28		
	~31	~31		~30

[a] log $\epsilon_{\max}$ in parentheses.

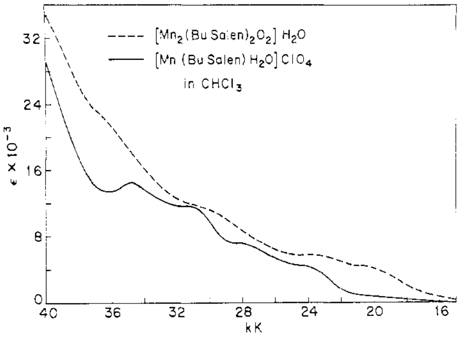


Figure 3. Electronic absorption spectra in chloroform of $[\mathrm{Mn_2(BuSalen)_2O_2}]\cdot\mathrm{H_2O}$ (- - - -) and $[\mathrm{Mn(BuSalen)H_2O]ClO_4}$ (——).

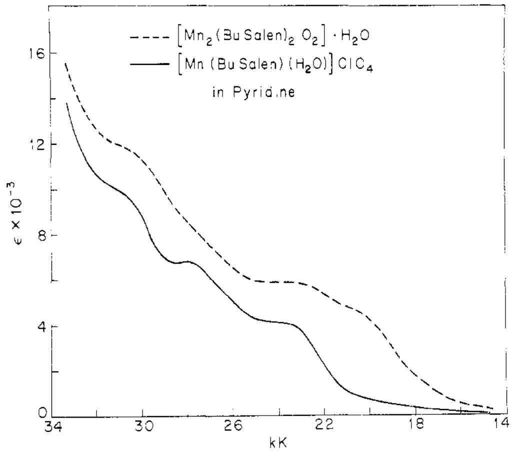
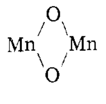


Figure 4. Electronic absorption spectra in pyridine of $[\mathrm{Mn_2(BuSalen)_2O_2}]\cdot\mathrm{H_2O}$ (- - - -) and $[\mathrm{Mn(BuSalen)H_2O]ClO_4}$ (——).

C_{4v} symmetry[8] is seen as a broad weak shoulder at ~20 kK. This band is not sensitive to the axial ligand and it appears in the chloroform solution spectra at the same frequency as for the anion complex Mn(BuSalen)X.[8] Similarly, charge-transfer bands d → π^*(C=N) are seen at ~24,000 and ~28,000 cm^{-1} while the ligand band $\pi \rightarrow \pi^*$(C=N) is seen at ~31,000 cm^{-1}. Finally, a high-energy charge-transfer band n → π^*(phenolic oxygen) appears at ~35,000 cm^{-1}. The absorption maxima are shifted slightly in going from chloroform solution to pyridine solution and are identical with those for pyridine solutions of the anion complexes.

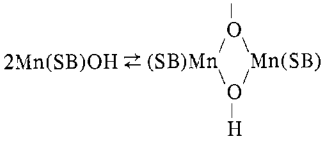
Mn(IV) Complexes. A two-phase reaction of the perchlorate salts in chloroform with mild threefold excess aqueous base yields the dimer $\mathrm{Mn_2(SB)_2O_2}$. Present evidence (vide infra) supports the formulation of the salt as a Mn(IV) complex containing the ring



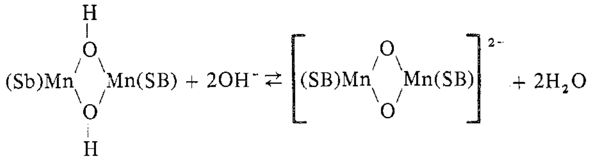
$$\mathrm{Mn}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}\mathrm{Mn}$$

This means that the addition of base has led to a redox reaction, i.e., the oxidation of Mn(III) to Mn(IV). The oxidant involved is oxygen of air. A reaction scheme can be proposed for the interfacial reaction (eq 1–4).

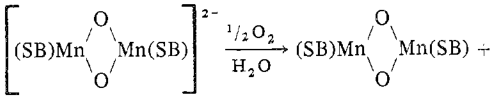
$$[\mathrm{Mn(SB)H_2O}]^+ + \mathrm{OH}^- \rightleftarrows \mathrm{Mn(SB)OH} + \mathrm{H_2O} \qquad (1)$$



$$2\mathrm{Mn(SB)OH} \rightleftarrows \mathrm{(SB)Mn}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}}}\mathrm{Mn(SB)} \qquad (2)$$



$$\mathrm{(Sb)Mn}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}}}\mathrm{Mn(SB)} + 2\mathrm{OH}^- \rightleftarrows \left[\mathrm{(SB)Mn}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}\mathrm{Mn(SB)}\right]^{2-} + 2\mathrm{H_2O} \qquad (3)$$

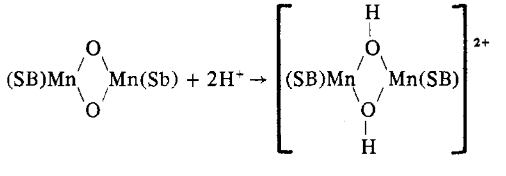


$$\left[\mathrm{(SB)Mn}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}\mathrm{Mn(SB)}\right]^{2-} \xrightarrow[\mathrm{H_2O}]{1/2\,\mathrm{O_2}} \mathrm{(SB)Mn}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}\mathrm{Mn(SB)} + 2\mathrm{OH}^- \qquad (4)$$

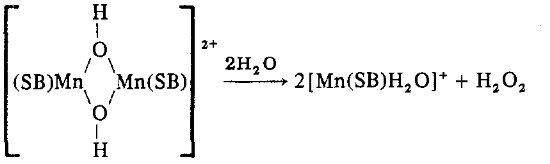
Reactions 1 and 3, proton transfers, should be rapid and the formation of product favored by the expected increased acidity of hydrogen of the coordinated water molecule. Reaction 2 would require an increase in coordination number (5 to 6) for the manganese and a rearrangement of the SB ligand from a "coplanar" array of the three chelate rings to one in which two rings remain coplanar and the end one is disposed 90° to the plane of the other two (see Figure 1). Thus reaction 2, while most likely rapid, like all reactions of Mn(III) a high-spin d^4 case, should not be thermodynamically favored. The third reaction is undoubtedly a complicated one. A sensitive test for $\mathrm{H_2O_2}$[12] in the reaction mixture during the reaction was negative. Addition of stoichiometric amounts of a powerful oxidizing agent, like $\mathrm{S_2O_8}^{2-}$ or $\mathrm{H_2O_2}$, to the reaction mixture does not give the dimer unless dilute base is added. Further the combination of $\mathrm{S_2O_8}^{2-}$ and OH$^-$ does not lead to a substantially improved yield of the dimer. These results indicate that the hydroxy precursor, presumably a dimer, is necessary for the oxidation to occur and that the nature of the oxidizing agent needed subsequent to this is not important. Dichlorocarbene, generated by the reaction of OH$^-$ with solvent $\mathrm{CHCl_3}$, can be ruled out as the oxidizing agent since the reactions proceed equally well in $\mathrm{CH_2Cl_2}$. Further, the role of oxygen from air as the oxidizing agent was confirmed by carrying out the base hydrolysis under a $\mathrm{N_2}$ blanket. No dimer formed with the exclusion of oxygen when equal volumes of aqueous base and chloroform solution of $[\mathrm{Mn(BuSalen)H_2O]ClO_4}$, in a 2:1 ratio, were agitated by rapid passage of $\mathrm{N_2}$ gas for 30 min at room temperature. In a parallel experiment, air was bubbled through a similar mixture and substantial amounts of the dimer were formed (~50% yield). Although much more reactive the corresponding reaction with $[\mathrm{Mn(Saltm)H_2O]ClO_4}$ qualitatively gave the same result. The only material isolated from the attempted base hydrolysis, at low concentration, was the perchlorate salt starting material. Evidently the various equilibria shown in reactions 1–4 favor the reactants rather than products. Further, the irreversible reaction with oxygen to form the dimer, which is the thermodynamically stable product in the system, must pull all the rapid preequilibria to the right.

Alternate routes to the synthesis of the dimers proved by and large to be unsuccessful. For example, direct reaction of Mn(BuSalen)X ($X^- = Cl^-, N_3^-$, etc.) in aqueous base always leads to the decomposition of the complex into brown insoluble manganese(III) oxide and free ligand, and only traces of the dimers are formed. Similarily use of other bases such as pyridine or triethylamine in ethanol or silver oxide slurry in ethanol gives only small yields, <5%, of the dimer. Finally the two-phase reaction of a chloroform solution of Mn(BuSalen)X and dilute aqueous base does not lead to any product. The synthetic utility of $[Mn(BuSaltm)H_2O]ClO_4$ rests on the fact that it is sufficiently soluble in chloroform and also contains an acidic water molecule in its coordination sphere. Treatment with dilute aqueous base removes the ionizable proton without unduly exposing the complex to the deleterious effect of the hydrolytic solvent. Apparently axial anions like Cl^- or N_3^- cannot be displaced in chloroform by dilute aqueous OH^- at the interface.

The dimers are cherry red solids that do not lose oxygen or decompose with heating to 110° in vacuo for 7 days. However, work by previous workers shows that heating of analogous compounds to ~200° does lead to the loss of oxygen and in some cases subsequent decomposition.[6] The dimers show limited solubility in benzene, chloroform, CH_2Cl_2, acetone, and methanol but are insoluble in water. The dimers are stable in chloroform, benzene, methanol, and pyridine solution at room temperature for days and can be recovered from the solvents unchanged. Thus even coordinating solvents do not lead to the breakdown of the dimer. Further, bubbling CO_2 through chloroform or methanol solution does not lead to any reaction, i.e., the formation of HCO_3^- or CO_3^{2-} complexes which might be expected if these were dihydroxy complexes. While refluxing solutions of the dimer in CH_2Cl_2 does not lead to any reaction, refluxing a chloroform solution of $Mn_2(BuSalen)_2O_2$ for 16 hr leads to the formation of <25% of several other chloroform-soluble materials. To this date we have not been able to separate and purify these minor components. Similar treatment of $Mn_2(BuSaltm)_2O_2$ in $CHCl_3$ and methanol does not lead to any apparent reaction. The enhanced stability of the latter compound may be related to the presence of a six-member chelate ring which more readily allows the tetradentate ring system to adopt a folded configuration in the dimer. Further, refluxing the dimer $Mn_2(BuSalen)_2O_2$ in methanol for 8 hr leads to decomposition of the dimer with the formation of free ligand, manganese(III) oxide, and a new compound tentatively assigned as an impure manganese(III) methoxide complex (50% yield).


(5)

$$(SB)Mn(\mu\text{-}O)_2Mn(Sb) + 2H^+ \rightarrow [(SB)Mn(\mu\text{-}OH)_2Mn(SB)]^{2+} \quad (5)$$


(6)

$$[(SB)Mn(\mu\text{-}OH)_2Mn(SB)]^{2+} \xrightarrow{2H_2O} 2[Mn(SB)H_2O]^+ + H_2O_2 \quad (6)$$

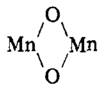
Addition of a stoichiometric amount of dilute $HClO_4$ to an acetone solution of the dimers at ice-bath temperature yields hydrogen peroxide and $[Mn(BuSalen)H_2O]ClO_4$. The formation of insoluble manganese(III) oxide is also a minor product so the reaction is not clean. H_2O_2 can be detected in the solution.[12] The reaction sequence envisioned is shown by eq 5 and 6. Semiquantitative volumetric measurements on a closed system show that 2.5×10^{-4} mol of dimer does not yield oxygen. Evolution of oxygen was monitored by sweeping the solution with a N_2 stream which was then bubbled through pyrogallol.[12] The yield of recrystallized $[Mn(BuSalen)H_2O]ClO_4$ is 62% based on the amount of manganese in the dimer. Thus, reactions 1–6 can be thought of as a catalytic cycle for reaction 7. Presumably oxygen can be

$$2H^+ + 2OH^- + {}^1\!/_2O_2 \xrightarrow{Mn(III)} H_2O_2 + H_2O \qquad (7)$$

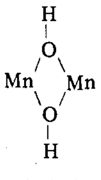
replaced by a generalized oxidizing agent, perhaps even by a photosensitized one. The details of this interesting process are currently being studied.

The dimers show solid-state magnetic moments of 2.47 and 2.59 BM (per Mn atom), respectively, while similar low values of 2.56 and 2.50 BM are observed for chloroform solutions at room temperature. Further, chloroform solution molecular weight measurements are consistent with the dimer formulation given here. The room-temperature magnetic moment, ~2.5 BM, is consistent with antiferromagnetically coupled high-spin complexes for either Mn(III) d^4 or Mn(IV) d^3. Since the low-spin Mn(III) complexes are restricted to very strong-field ligand complexes, we can rule out this possibility here. Variable-temperature magnetic susceptibility measurements are needed to sort out conclusively the details of this system.

In general the ir spectra of the dimers show SB ligand absorptions at the same frequencies as the perchlorate salts. Exceptions are the ν(C–N) and a medium-weak aromatic ring absorption which appear at 1300 and 1350 cm^{-1} for the dimers, which are shifted to 1290 and 1328 cm^{-1} for the perchlorate salt. The sharp, medium-intensity ligand and chelate ring deformation absorption seen at 630 cm^{-1} for the Mn(III) complexes is seen at 600 cm^{-1} for the dimer. Other low-frequency ligand absorptions in the dimer are seen at 580, 490, 453, 385, and 362 cm^{-1}. The major difference between the low-frequency spectra of the dimers and the perchlorate salts is the dramatic gain in intensity of the 460-cm^{-1} band and loss in intensity of the 360-cm^{-1} band. The changes in ligand and chelate ring deformation absorptions may be related to the difference between the planar conformation of the Schiff base ligand for the perchlorate salt and the cis-folded conformation for the Schiff base ligand in the dimer.[13] A new medium-intensity band is seen in the dimer at 655 cm^{-1} in BuSalen and 642 cm^{-1} in the BuSaltm. This band is absent in the ligand and in the five-coordinate Mn(III) complexes and can be associated with a ring vibration of the



system. Similar bands have been seen in the spectra of other dimers of this type. No band attributable to the presence of the unit



in the complexes is seen in their ir spectra;[14] i.e., no ν(O–H) is seen at 3500–3600 cm^{-1} and no Mn–OH bending vibration band is seen at ~1100 cm^{-1}. However, lattice water absorptions are seen in the 3300–3400-cm^{-1} region.

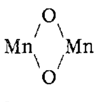
The electronic spectra were measured with chloroform and pyridine solutions of the dimer. Typical spectra are shown in Figures 3 and 4 and the frequencies of the maxima are collected in Table I. The absorption spectra of the dimers are difficult to analyze because of the lack of well-resolved bands; i.e., only broad, poorly resolved shoulders are seen. Nonetheless the ligand $\pi \rightarrow \pi^*$ ($\sim$31,000 cm^{-1}) and $d\pi \rightarrow \pi^*$ ($\sim$24,000 and $\sim$28,000 cm^{-1}) bands can be identified if not accurately placed.

The fact that both the ir spectra and the uv spectra are qualitatively similar to those of the Mn(III) complexes supports the notion that the Schiff base ligand is not altered (oxidized) in the formation of the dimer.

The major difference between the spectra of the manganese(III)–Schiff base complexes and those of the dimer is the presence of a moderate-intensity ($\epsilon \sim 4000$) band at $\sim$21,000 cm^{-1}. The intensity is such that the band cannot be assigned to a ligand field transition but it is consistent with a charge-transfer transition. The band can most likely be associated with a charge transfer from the bridging O^{2-} ligand to the metal $d\pi$ orbital. A similar assignment has been made for dimeric Fe(III) complexes.[15] The question now arises as to whether the electronic spectra of the dimer can be used to distinguish among the two possible oxidation states, Mn(III) or Mn(IV). A Mn(IV) complex would be a spin-free d^3 system, $d_{xy}{}^1$, $(d_{xz}, d_{yz})^2$ in a pseudooctahedral field. The actual symmetry is lower and considering only the ligand donor atoms of *cis*-N_2O_4, the effective symmetry would be C_{2v}. Under low symmetry, the two octahedral bands $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ should be split into two components which may or may not be resolved in the spectra. In fact the visible spectra of the Cr(III), d^3, complex $[Cr(Salen)(H_2O)_2]^+$ show a poorly resolved band at $\sim$20,000 cm^{-1} of low intensity which has been assigned to the first ligand field band.[16] Since the Mn(IV) d-orbital splitting is expected to be greater than for Cr(III), the corresponding ligand field band would be expected to be at >20,000 cm^{-1}. Thus, this type of absorption is most likely masked by the high-intensity charge-transfer bands for $Mn_2(SB)_2O_2$.

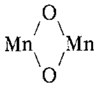
At this point it is of interest to link the results presented here with the work on the characterization of oxygenation products of manganese(II)–Schiff base complexes. The oxygenation of $Mn(Saltm)H_2O$ in benzene or pyridine leads to a sparingly soluble product variously formulated as $Mn^{III}{}_2(Saltm)_2O_2$, $Mn^{III}{}_2(Saltm)_2(OH)_2$, or $Mn^{IV}(Saltm)O$. The reported low magnetic moments, ir spectra in the 600–700-cm^{-1} region, and empirical formulas are similar to those reported here for $Mn_2(BuSaltm)_2O_2$. It seems likely that all of these materials belong to the same class of compounds. A similar conclusion can be drawn with respect to the Mn(Salen) oxygenation products. Ultimately an accurate X-ray crystal structure will settle this point of contention. On the basis of the results detailed here we prefer to describe the dimers as formally μ-dioxo-manganese(IV) complexes. The structure in Figure 1, which shows one of the five possible geometrical isomers, depicts the Schiff base arrangement for the oxygenation product of $Mn(Saltm)H_2O$.[4] However, it must be pointed out that none of the data accumulated here allows a definitive assignment of this type of structure to the dimer $Mn_2(BuSalen)_2O_2$ or $Mn_2(BuSaltm)_2O_2$.

Additional corrobatory evidence for the formulation are the reports of manganese(IV) complexes with nitrogen and nitrogen–oxygen ligand donors with the

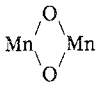


unit, e.g., phenanthroline[18] and picolinic acid[19] anion. In the latter case spectroscopic evidence supports the $Mn^{IV}O^{2-}$ formulation.[19] For example, X-ray photoelectron spectroscopy gives the $2P_{1/2}$ and $2P_{3/2}$ binding energies of manganese (with reference to carbon 1S binding energy of graphite) of $Mn_2(pic)_2O_2$ as 653.9 ± 0.2 and 642.7 ± 0.2 eV. These values are significantly higher, $\sim$1 eV, than the reported value for an analogous Mn(II) complex $Mn(pic)_2{\cdot}2H_2O$ and thus they are consistent with Mn(IV). Furthermore, the X-ray photoelectron spectrum of $Mn_2(Salen)_2O_2$ shows a similar shift of the Mn binding energies in going to it from Mn^{II}Salen.[20]

The presence of a strong oxygen to metal charge-transfer transition in the visible region presents the possibility of a photoactivated liberation of oxygen from this type of complex, as suggested by Calvin.[17] The chemical properties of the dimers are thus particularly relevant to the suggested role of manganese in green plant photosynthesis and in particular to the nature of the manganese photocatalyst that mediates the formation of oxygen from water in the chloroplast. Another interesting point about the dimeric materials is that they maintain their integrity in donor solvents like pyridine and methanol. This is shown by the observation that the charge-transfer band at 20,000 cm^{-1} is seen in the spectra of the dimer in these solvents. Further, the compounds can be recovered unchanged from these solvents. The marked stability of the dimers may be related to the presence of strong $Mn(d\pi) \leftarrow O^{2-}(p\pi)$ mixing in the



unit. This is consistent with the observation of a strong charge-transfer transition in the visible region and also with the expected strong π-acceptor properties of the high oxidation state of the metal, Mn(IV). If π mixing is as strong as suggested, it is probably somewhat simplistic to think of integral values of oxidation states, such as Mn(IV) and O^{2-}. It is probably more reasonable to consider the electronic charge as being distributed in a localized molecular orbital which encompasses the whole



unit.

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Registry No. $[Mn(BuSalen)H_2O]ClO_4$, 54657-53-3; $[Mn(BuSaltm)H_2O]ClO_4$, 54657-55-5; $[Mn_2(BuSalen)_2O_2]$, 54657-56-6; $[Mn_2(BuSaltm)_2O_2]$, 54657-57-7.

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